AN INVESTIGATION, USING SYNCHROTRON RADIATION AND OTHER TECHNIQUES, OF THE COMPOSITION OF SAN ROCK ART PAINTS AND EXCAVATED PIGMENTS FROM MAQONQO SHELTER, AND COMPARATIVE PAINT DATA FROM THREE OTHER SITES IN KWAZULU-NATAL, SOUTH AFRICA.

by

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ABSTRACT

This study aimed to: 1) characterise the individual San parietal art rock art paint colours; 2) relate paint compositions to erosion susceptibility; 3) determine if paint pigments can be related to pigment samples excavated from a Shelter deposit, and/or a variety of field samples; and 4) determine if paint samples from geographically distinct sites can be distinguished on their composition. A combination of mineralogical (X-ray diffraction (XRD), synchrotron micro-XRD (μ-XRD)) and chemical (energy dispersive X-ray micro-analysis (EDX), X-ray fluorescence spectrometry (XRF), and synchrotron micro-XRF (μ-XRF)) analytical techniques were used.

Maqonqo Shelter (MQ), 35 km south-east of Dundee, KwaZulu-Natal, South Africa, was the primary study site chosen as it contained both a large number of paintings, as well as a large deposit. Thirty paint (of various colours) and 3 blank wall samples were collected using Silver Mylar tape and analysed using a combination of EDX, μ-XRD and μ-XRF techniques. Sixty two large (> 2.5 g) 'ochre' pieces were selected from the upper three layers of the deposit and analysed using XRD, XRF and EDX. A further 63 small pieces (< 2.5 g) were analysed using μ-XRD and μ-XRF techniques.

To compare the MQ paint samples with potential source materials, three distinct sample sets were collected. The first included samples of the Shelter wall and surface rocks located near the painted panel (analysed by XRD, XRF and EDX). A second sample set of 17 samples was collected from the surrounding landscape (± 3 km radius of MQ; analysed by XRD and XRF). Their selection was based on ease of accessibility, degree of pulverulence, and perceived Fe content i.e., red and/or yellow colouration. No white sources were found. A third set of 11 samples (obtained from six sites, analysed using XRD and XRF) was collected within ± 50 km distance of the Shelter. Their selection was based on old mining survey reports that detailed the location of Fe ore outcrops.

Paint samples from three additional shelters i.e., Fergies Cave (FC), Giants Castle Game Reserve, central Drakensberg; Sheltered Vale (SV), Mount Currie District, south-western KwaZulu-Natal; and Twagwa Shelter (TW), Izingolweni District, southern KwaZulu-Natal, were collected to compare paint composition over distance. Site selection was determined according to the following criteria: 1) the shelters had to reside a significant distance away from the primary site so as to minimise any possible interaction that might have existed between the authors of the respective artworks (each site is at least 100 km distant from the other); 2) each had to be located upon a distinct geological formation so that external influences from different regions, and their possible affects on the paint samples, could be noted; and 3) the climatic regimes of each of the shelters should be relatively distinct. Fifteen paint and nine blank wall samples were collected from the three shelters (three each of red, white and blank samples; analysed using EDX, μ-XRD and μ-XRF), with the exception that no white samples were collected from FC.

In total, 673 EDX, 212 μ-XRD, 378 μ-XRF, 98 XRD, 98 XRF and 6 ICP-MS traces were produced and analysed. Due to the extremely heterogeneous nature of the paint samples at the micro-

scale, the more generalised EDX reduced window scans were used as the basis of the paint samples' characterisation, with the data obtained from the more precise μ-XRD and μ-XRF techniques providing additional supportive information. Irrespective of colour, almost all of the MQ paint samples had elevated Ca contents that tended to increase in the order of black < orange ≤ red and yellow < pink < white. The predominant Ca-based mineral was gypsum, although Ca-oxalates, whewellite and weddellite, were also present. The blank samples collected from MQ also had high gypsum content, but no Ca-oxalate. It is thus proposed that the Ca-oxalates formed after the painting event and were derived from the original paint constituents.

The white pigments consisted of gypsum (dominant), anhydrite, bassanite and whewellite, or a combination thereof. Whewellite increased within increasing paint depth, while gypsum showed the reverse trend. This indicates that, whilst both gypsum and whewellite were originally present within the original paint pigment, additional gypsum has been added via secondary evaporite deposition. Although initially considered to be sourced along with the gypsum, another potential whewellite source is organic additives. The most likely source for the white pigments would be precipitates found on sandstone walls of shelters near MQ. Of more immediate importance, however, is that the pigments, being gypsum based, are water-soluble and thus susceptible to erosion.

Most of the orange paints had an elevated Al content and contained gibbsite, suggesting bauxitic material associated with locally sourced dolerite within the Ecca Series within KwaZulu-Natal (as evidenced by their respective Ti levels). Two samples were so similar that it is likely that the same pigment was utilised in the creation of both images. Two samples did not contain high Al contents, however, indicating that they were probably sourced from the soft, ochreous material found within local Fe nodules.

A consistent combination of goethite and haematite, together with a low Al and elevated Ti content, indicate that the yellow and red samples were probably sourced from Fe nodules found locally, the red samples differing from the yellow pigments primarily in their higher haematite content. A low Si and relatively low Fe content discounts red sands/clays and Fe-ores as sources of the red pigments. The red samples were 'thinner' than the other samples with quartz contents comparable to those of the blank samples. The thin nature of the red paints, the erratic distribution of whewellite upon the paint surfaces, the dominance of gypsum and, to a certain extent quartz, all strongly suggest that the red paints are at least partly absorbed into the surface of the Shelter wall. This, together with the strong staining ability of haematite, is probably the most important reason that the red pigments have outlasted images painted in other colours. It may also account for the high degree of variability found within the red paint dataset, though age differences between the sampled images could also be a contributing factor.

The single dark red paint sample, except for an elevated Mn content, was very similar in many ways to the red paint samples analysed. The only readily available pigment source identified that had both low Al and high Fe and Mn contents, was plinthite. The pink samples represented the 'middle-ground' between the red and white paints, suggesting that this colour was the result of a blending of the two. The black paint sample had the highest recorded Fe content of the entire paint dataset. A high Mn and relatively low Al content suggest that a soft inner core of an Fe nodule was used in its manufacture. The presence of maghemite and a dark colouration strongly suggest that the manufacture also involved calcination.

The initial distinction between the paint and excavated samples was that the former all exhibited elevated Ca and S values due to the deposition of secondary evaporite minerals. Even when taking these additional deposits into account, however, the two datasets still remained distinct indicating that the excavated materials sampled were not utilised in the manufacture of the MQ paints. A potential exception concerned the orange paint samples, which were similar in composition to both doleritic samples from deeper excavated layers and the local (weathered doleritic samples) and distant (bauxite samples) field samples. Whilst weathered dolerite/bauxitic material was clearly the source of the orange pigments, a more detailed investigation is needed to find a precise location. No other relationships between the paint pigments and the excavated pigments and field samples were established.

A comparison of the blank samples from all four study sites showed that the techniques used could distinguish between different sites despite sampling the smallest and, relatively speaking, poorest quality samples. The FC blank samples had elevated C and Ca contents (associated with Ca-oxalates). The conditions within this Shelter favour the formation of weddellite and whewellite, the former not typically found at the other three sites. In addition, low K, Si and Al contents (often associated with sandstone matrix minerals) indicate that the surface of the relatively dense, compact Cave sandstone is more resistant to physical erosion compared to the other sites, and/or FC shelter experiences a high amount of secondary deposition, with the result that a majority of the samples are composed of evaporite minerals. The SV samples were composed primarily of the evaporite-type minerals, with only minor sandstone 'contamination' indicated by quartz and kaolinite. The quartz content, whilst not always high, was present in most of the samples analysed, possibly indicating a greater amount of more uniform surface erosion (relative to the other sites). The TW blank samples were distinct from the other shelters' as they contained no Ca-based minerals but did contain the very rare mineral schlossmacherite.

A comparison of the paint colours also revealed differences between the different shelters. Whilst the white samples from SV and MQ are dominated by whewellite and gypsum (minerals probably present within the pigments when they were applied), the presence of quartz, sanidine and apatite in the SV samples indicated a degree of shelter wall 'contamination', with anhydrite, bassanite and glushinskite suggesting climatic variations that favoured various evaporite depositional regimes. The TW white paint contained minimal secondary deposited minerals common in the other shelters. The one mineral that is dominant within the TW samples is minamiite. As this mineral was not identified in any of the blank samples, it is likely that this mineral originates from the original pigment source.

The TW white paints also contained 10 to 40 times more Zn than those recorded for any of the other paint samples. This was possibly present within the structure of greigite.

The red SV samples could be distinguished from MQ red samples by the presence of wall ‘contaminants’ in a manner similar to that described for the white samples. The TW samples indicate a change in pigment source and/or manner of paint manufacturing technique, for these red samples contained minamiite. This mineral is white and thus its selection could not have been based on colour but rather it must represent a paint additive. With the exception of only one sample from TW, no goethite was found within any of the red samples collected from the three additional sites indicating a different haematite source to that of MQ.

An interesting facet of this study, although not directly addressed, concerns what the results do *not* show with respect to the compositional nature of the pigments analysed. Most texts available today list a number of pigment sources stated to have been utilised in the manufacture of the San parietal rock art. This study has shown that very few of these potential sources were utilised within the four shelters investigated. In addition, this study has also highlighted the presence of minerals about which little is known, yet which appear to be commonly associated with parietal rock art.

DECLARATION OF ORIGINALITY

I, Boyd John Escott, declare that

1. The research reported in this thesis, except where otherwise indicated, is my original research.

2. This thesis has not been submitted for any degree or examination at any other university.

3. This thesis does not contain other persons' data, pictures, graphs or other information, unless specifically acknowledged as being sourced from other persons.

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As the candidate's supervisor I have/have not approved this thesis/dissertation for submission.

Signed: ________________ Name: ________________ Date: __________________

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PROJECT TERMINOLOGY

Group, band or camp?

Although the term ‘band’ has frequently been used in the literature to characterise San groupings, it can be associated with the idea of a closely-knit group related to the male line that resides within a clearly defined territory. From the ethnographic records, it is known that not only were members of the groups free to come and go as they pleased, but San group territories were a lot more ‘variable’. Also, their societies were essentially egalitarian. As a result, I prefer to use the collective term ‘camp’ as was first proposed by Richard Lee (1979), as this term has none of the previously mentioned connotations. Thus, a San tribe (e.g. /Xam) was comprised of a number of smaller camps.

Bushman vs. San

The use of the terms ‘Hottentot’ and ‘Bushmen’ have been subject to much debate over the last 30 years, as they are considered by many as derogatory terms that should be abandoned. Both are collective terms that refer to specific groups, or camps, of indigenous peoples which share similar linguistic characteristics, social structures, customs, traditions and beliefs, as opposed to representing specific cultural groupings (Rudner, 1982). These distinctions are not always clear-cut, however, with a blending or overlapping of these characteristics frequently occurring (Wright, 1971; Rudner, 1982). As a result, these terms have frequently been used interchangeably, often incorrectly.

The names themselves have different origins, with the term ‘Hottentot’ being a name given to the pastoralists living in the South Western Cape by the early Dutch settlers in the 1650's (Willcox, 1976). The Bushmen, or Bosjesmans, were also named by the Dutch, the difference in name recognising a difference in lifestyle (hunter-gatherers as opposed to pastoralists) between the two peoples (Willcox, 1976). The term San, or Sonquas, was given to the Bushmen by the Hottentots (Willcox, 1976; 1984; Rudner, 1982), the literal definition being ‘vagabond’ (Lewis-Williams and Dowson, 1992).

Due to the negative connotations frequently associated with the above terms, there is a general tendency today to use the terms ‘Khoi’ or ‘Khoikhoi’ (or more recently ‘KhoeKhoe’) for the Hottentots and ‘San’ for the Bushmen (Willcox, 1976; Rudner, 1982). The term ‘Khoisan’ was created to recognise the similarities between both the Khoi and the San as opposed to the other peoples located in southern Africa. These are merely generic names, however, and are generally not accepted by the people they represent. The Hottentots as a group no longer exist, with the remnants of this people now referring to themselves either by their old tribal names or generally as ‘Nama’ (Rudner, 1982). They do not refer to themselves as Khoi.

No general name that the Bushmen might have had for themselves is known (Willcox, 1984). In Namibia, some of the remaining Bushmen refer to themselves as ‘Boesmans’ (the name of a political party), whilst an individual clan in the same area is known to refer to itself as ‘Baster’ (Rudner, 1982). In South Africa, the term ‘San’ is widely recognized by formal bodies and governmental organisations as representing the Bushmen peoples. As a result, and in keeping with modern convention, the term ‘San’ will be used throughout this study as a collective name for the hunter-gatherer people who lived and painted within southern Africa, and in particular the KwaZulu-Natal region.

Ochre and pigmentaceous material

Most of the archaeological literature refers to the term ‘ochre’ as a general descriptor for both the material utilised as the primary source of paint pigment production, as well as for the material recovered from excavations exhibiting distinctive colouration. Archaeologically, ochre is defined as “…a natural earth containing ferric oxide and silica [that is] used as a pigment” (Hall, 1996). According to the *Glossary of Geology* (Gary *et al.*, 1973), ochre is described as being “…an earthy, usually impure, pulverulent, red, yellow, or brown oxide that is extensively used as a pigment.” Thus, as a descriptor, the term ‘ochre’ places limitations on the nature of possible sources of material that might have been utilised in both parietal and body paint manufacture. Based on both of these definitions, it can be seen that most of the excavated material currently recorded as ‘ochre’ is, in fact, incorrectly classified, for the majority of this material is neither pulverulent nor an impure iron oxide; but is instead generally comprised of hard iron-enriched shale, weathered sandstone or iron ore. Consequently, although ochreous material is a strong possible source, a term that is capable of correctly classifying and encompassing all possible sources of pigment is required. I thus propose that the terms *pigment* or *pigmentaceous material* be used instead of ochre.

This clarification has to be made because ochre, as a high quality pigment source, is typically not common in the South African landscape (Coetzee, 1976). As the composition of the San paint has not yet been quantitatively established, all possible pigment sources have to be considered, including iron ore (red, brown and black pigment), ferruginous shale (yellow and red pigment), marine and fresh water shells (white pigment and/or bulking agent), and bone (white pigment and/or bulking agent), to name just a few (see Rudner (1982) for a comprehensive list of suspected pigment materials, and their sources). The suggested term *pigmentaceous material* enables the author to refer to all these materials collectively, with a possible distinction being made regarding the pigment’s organic or inorganic origin.

ACRONYMS

AMS	Accelerator Mass Spectrometry
CA	Correspondence Analysis
BRG	Bioresource Group
EDX	Energy Dispersive X-ray Micro-analysis
ESEM	Environmental Scanning Electron Microscope
FC	Fergies Cave
FTIR	Fourier Transform Infrared Spectroscopy
ICP-MS	Inductively Couple Plasma Mass Spectrometry
LAM-ICP-MS	Laser Ablation Microprobe-Inductively Coupled Plasma-Mass Spectrometry
LIA	Late Iron Age
L.O.I.	Loss on Ignition
LSA	Late Stone Age
MQ	Maqonqo Shelter
MSA	Middle Stone Age
PCA	Principal Components Analysis
PIXE	Particle Induced X-ray Emission
ppm	parts per million
RARRU	Rock Art Recording and Research Unit
SEM	Scanning Electron Microscope
SV	Sheltered Vale Shelter
µ-XRF	Synchrotron micro X-ray Fluorescence (micro-XRF)
µ-XRD	Synchrotron micro X-ray Diffraction (micro-XRD)
TW	Twagwa Shelter
WT%	Weight Percentage
XRD	X-ray Diffraction
XRF	X-ray Fluorescence Spectrometry

GLOSSARY OF GEOLOGICAL TERMS
(according to Gary *et al*., 1973 unless otherwise stated)

Adamellite	A term originally used for orthoclase-bearing tonalite of the Adamello massif, but later used for granites with about equal amounts of alkali feldspar and plagioclase, which do not occur in the Adamello. The term should normally be avoided because of ambiguity and it is recommended that such rocks be called monzogranite (Le Maitre (Ed.), 1989).
Amygdaloidal	Rocks that contain amygdales, which are gas cavities or vesicles within igneous rocks that have in-filled with secondary minerals such as quartz, zeolite and calcite.
Augen	Large, lenticular [lens shaped] mineral grains or mineral aggregates having the shape of an eye in cross-section, in contrast to the shapes of the other minerals in the rocks. Commonly formed by feldspar, quartz and garnet.
Complex	A large-scale association or assemblage of different rocks of any age or origin, having structural relations that are so intrinsically involved or otherwise complicated that the rocks cannot be differentiated in mapping.
Felsic	Applied to an igneous rock containing light-coloured minerals of quartz and feldspar. Opposite of mafic.
Ferromagnesian	Containing iron and magnesium. A term often applied to mafic minerals such as amphibole, biotite and olivine.
Foliation	A general term referring to the planar arrangement of textural or structural features in any type of rock. This is typically associated with slate, schist and gneiss. Foliated (adj.)
Formation	The basic or fundamental rock stratigraphic unit in geological classification. It consists of a body of rock generally characterised by some degree of internal lithologic homogeneity.
Granoblastic	Harker (1939) defined granoblastic as a type of texture in a non-schistose, metamorphic rock within which essentially equidimensional crystals formed with normal well-structured boundaries on re-crystallisation.
Granodiorite	A coarse-grained, plutonic rock intermediate in composition between quartz diorite and quartz monzonite. It contains quartz, plagioclase and orthoclase, with biotite and hornblende as its major mafic components.
Leucocratic	A light coloured igneous rock relatively poor (< 30 – 35%) in mafic minerals. Compare felsic.

Mafic	An igneous rock when composed primarily of one or more ferromagnesian, dark-coloured minerals is said to be mafic. Refers also to those ferromagnesian minerals themselves. Opposite of felsic.
Megacrystic	An igneous or metamorphic rock that contains any crystals or grains that are significantly larger than the surrounding groundmass or matrix.
Member	A clearly defined stratigraphic unit within a Formation.
Monzonite	A group of plutonic rocks containing approximately equal amounts of plagioclase and orthoclase, with little to no quartz.
Phenocryst	A relatively large, conspicuous crystal in a porphyritic rock.
Plinthite	A highly weathered material consisting of a mixture of clay and quartz that is rich is sesquioxides and poor in humus Repeated wetting and drying changes the plinthite into ironstone hardpan or irregular aggregates (von M Harmse, 1984).
Pluton	An igneous intrusion.
Poikilitic	The texture of an igneous rock in which small crystals of one mineral are irregularly scattered without common orientation in a larger crystal of another mineral. Also refers to the enclosed crystal.
Porphyritic	The texture of an igneous rock in which the larger crystals (phenocrysts) are set in a finer matrix which may be crystalline or glassy, or both.
Schist	A strongly foliated crystalline rock formed by dynamic metamorphism with sub-parallel orientation of the micaceous minerals that dominate its composition (Soil Classification Working Group, 1991).
Suite	A suite comprises (1) two or more related, named intrusive igneous rock units or metamorphic units which have significantly lithological features in common, or (2) an igneous or metamorphic unit which consists of several (related) rock types and which cannot therefore be satisfactorily named using a single lithological designation (Johnson, 1996).

MINERAL NOTATIONS

Mineral	Chemical notation	Mineral Colour
Albite	See Feldspar Group	
Alunite	$(K,Na)Al_3(SO_4)_2(OH)_6$	White; greyish; yellowish; reddish; brownish
Anatase	TiO_2	Brown, dark-blue, black
Anhydrite	$CaSO_4$	White or slightly coloured
Anorthite	See Feldspar Group	
Apatite	$Ca_5(PO_4)_3(OH)$	White, Yellow, Green, Red, Blue
Aragonite	$CaCO_3$	White, yellowish, grey
Arfvedsonite	$Na_3(Fe,Mg)_4FeSi_8O_{22}(OH)_2$	Black
Augite	$(Ca,Na)(Mg,Fe^{+2},Al)(Si,Al)_2O_6$	Black, greenish-black, dark-green
Azurite	$Cu_3(CO_3)_2(OH)_2$	Deep-blue to violetish-blue
Barite (Baryte)	$BaSO_4$	White, yellow or colourless
Bassanite	$2CaSO_4.H_2O$ or $CaSO_4.½H_2O$	White
Biotite	See Mica Group	
Boehmite or Böhmite	γ-AlOOH or AlO(OH)	Greyish, brownish, reddish, white, light yellow, yellowish green
Brushite	$CaHPO_4.2H_2O$	Nearly colourless
Buserite	$Na_4Mn_{14}O_{27}.21H_2O$	Black
Calcite	$CaCO_3$	White, colourless, or pale shades of grey, yellow and blue
Celadonite	$KMgAlSi_4O_{10}(OH)_2$	Green, grey-green
Cinnabar	HgS	Red crystals, or red, brownish or greyish in veins or alluvial deposits
Clinochlore	$Mg_5Al(Si_3Al)O_{10}(OH)_8$	Greenish
Corundum	Al_2O_3	Various
Crandallite	$(Ca,Sr,Pb)_2Al_7(PO_4)_3(OH)_{16}.3H_2O$	White to light-greyish
Cristobalite	SiO_2 (at 500 °C)	White
Cuprorivaite	$CaCuSi_4O_{10}$	Blue, sky-blue
Dumortierite	$(Al_9Fe)_7BSi_3O_{18}$	Bright to greenish-blue
Feldspar Group	General formula = $MAl(Al,Si)_3O_8$ where M = K, Na, Ca, Ba, Rb, Sr, and Fe	Alkali series = Microcline, Sanidine, Orthoclase Plagioclase = Albite, Oligoclase, Anorthite.
Albite	$NaAlSi_3O_8$	Colourless or milky white
Anorthite	$CaAl_2Si_2O_8$	Colourless or milky white
Labradorite (plagioclase)	Ranges from An50Ab50 to An30Ab70 Where An = Anorthite and Ab = Albite	Dark (grey, blue, green or brown)
Microcline	$KAlSi_3O_8$	Colourless, white to light-grey, pale-yellow, brick-red, green
Orthoclase	$KAlSi_3O_8$	Colourless, white, cream-yellow, flesh-reddish, greyish
Sanidine	$KAlSi_3O_8$	Colourless
Ferrihydrite	$Fe_5O_7(OH).4H_2O$	Brown, yellow
Gibbsite	$A-Al(OH)_3$	White
Glushinskite	$MgC_2O_4.2H_2O$	Cream white; colourless; brownish white
Goethite	A-FeOOH	Yellowish, reddish, brownish-black
Goyazite	$SrAl_3(PO_4)_2(OH)_5.H_2O$	Yellowish-white
Graphite	C	Iron-black to steel-grey
Greigite	Fe_3S_4	Blue, Blue black, Bronze, Pink.
Gypsum	$CaSO_4.2H_2O$	White, colourless when pure, but can be tinted greyish, reddish, yellowish, brownish and bluish
Haematite	$\alpha-Fe_2O_3$	Steel-grey, iron-black or deep-red, red-brown
Specularite	Fe_2O_3	Black, grey or silvery
Halloysite	$Al_2Si_2O_5(OH)_4.2H_2O$	White
Hollandite	$BaFeMn_7O_{16}$	Silver-grey to black

Mineral	Chemical notation	Mineral Colour
Huntite	$CaMg_3(CO_3)_4$	White
Ilmenite	$FeTiO_3$	Iron-black
Jarosite	$KFe_3(SO_4)_2(OH)_6$	Ochre-yellow or brown
Kaolinite	$Al_2Si_2O_5(OH)_4$	White to greyish or yellowish
Labradorite (plagioclase)	See Feldspar Group	
Lepidocrocite	γ-FeOOH or $Fe_2O_3.xH_2O$	Blood-red to reddish brown
Leucophosphite	$KFe_2(PO_4)_2OH.2H_2O$	White
Lime	CaO	White
Limonite	$Fe_2O_3.3H_2O$	Dark-brown, yellowish-brown, yellow, red or nearly black
Lithiophorite	$(Li,Al)MnO_2.(OH)_2$	Bluish black to black
Lonecreekite	$NH_4Fe(SO_4)_2.12H_2O$	Colourless
Lusungite	$(Sr,Pb)Fe_3(PO_4)_2(OH)_{16}.3H_2O$	Translucent yellow-brown
Maghemite	$\gamma - Fe_2O_3$	Red
Magnetite	Fe_3O_4	Black
Mica Group	$(K,Na,Ca)(Mg,Fe,Li,Al)_{2-3}$ $(Al,Si)_4O_{10}(OH,F)_2$	Colourless, silvery-white, pale brown, or yellow to green or black
Biotite	$K(Mg,Fe^{+2})_3(Al,Fe^{+3})Si_{3-}O_{10}(OH)_2$	Black, dark-brown or dark-green
Muscovite	$KAl_2Si_3AlO_{10}(OH)_2$	Colourless, whitish, pale brown
Sericite	A fine-grained mica.	White
Microcline	See Feldspar Group	
Minamiite	$(Na,Ca)_1$-$xAl_3(SO_4)_2(OH)_6$	Colourless, white
Minium	Pb_3O_4	Bright-red, scarlet, orange-red
Muscovite	See Mica Group	
Natrolite	$Na_2Al_2Si_3O_{10}.2H_2O$	Colourless, white, grey, bluish, yellowish, pink
Orpheite	$H_6Pb_{10}Al_{20}(PO_4)_{12}(SO_4)_5(OH)_{40}.$ $11H_2O$	Colourless; grey; pale blue; pale green; yellow-green; green-yellow; green-blue; bluish; grey-blue
Orthoclase	See Feldspar Group	
Osarizwaite	$Pb(Cu,Al)_3(SO_4)_2(OH)_6$	Yellow
Perthite	Intergrowth orthoclase and plagioclase	Colourless, white, cream-yellow, flesh-reddish, bluish-green, greyish
Plumbogummite	$Pb_{0.93}Al_{3.07}H_{1.57}(P_{1.48}C_{0.40}Al_{0.12})O_8$ $(OH)_6.0.38H_2O$	Greyish-white; yellowish-grey; brown; reddish-brown; yellow; greenish; bluish; greenish-blue; grey-white
Psilomelane	$(Ba.H_2O)Mn_5O_{10}$	Iron black, bluish black, steel grey
Pyrite	FeS_2	Pale-bronze, brass-yellow
Pyrolusite	MnO_2	Iron-black or dark steel-grey
Quartz	SiO_2	Colourless (tinted yellow, brown, purple, red, green, blue, or black)
Rutile	TiO_2	Reddish-brown (sometimes yellowish, deep-red or black)
Sanidine	See Feldspar Group	
Schlossmacherite	$(H_3O,Ca)Al_3(SO_4,AsO_4)_2(OH)_6$	Pale to greyish green; white streak
Sepiolite	$Mg_2Si_3O_8.2H_2O$	White to light-grey or light yellow
Sericite	See Mica Group	
Siderite	$FeCO_3$	Yellowish-brown, brownish-red or brownish-black, sometimes white or grey
Specularite	See Haematite	
Strontianite	$SrCO_3$	Pale-green, white, grey or yellowish
Talc	$Mg_3Si_4O_{10}(OH)_2$	Whitish, greenish or greyish
Tinsleyite	$KAl_2(PO_4)_2(OH).2H_2O$	Dark red
Tschermigite	$NH_4Al(SO_4)_2.12H_2O$	White or colourless
Weddellite	$CaC_2O_4.2H_2O$ or $Ca(COO)_2.2H_2O$	White or colourless
Whewellite	$CaC_2O_4.H_2O$ or $Ca(COO)_2.H_2O$	White or colourless

The primary study site - Maqonqo Shelter, near Dundee, KwaZulu-Natal

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CHAPTER ONE

INTRODUCTION

San rock art is widely distributed across southern Africa with the characteristic red, white and yellow paintings found in various states of preservation in most rock shelters. For many years archaeologists have studied these images in order to try to understand their role within the ancient San communities (e.g. Lewis-Williams, 1980; 2003; Lewis-Williams and Dowson, 1989; 1994; Solomon, 1997; 1999). Surprisingly, however, little scientific investigation into their composition has been conducted, with studies by Wilson *et al*. (1990), Mazel and Watchman (1997; 2003), Escott (2000) and Hughes and Solomon (2000) being notable exceptions. Though iron-containing materials (in particular ochre) have for a long time been considered to be the primary source of the pigments, very few studies have been conducted either to analyse or to try to source these pigments (e.g. Hughes and Solomon, 2000).

Ochre is typically not common within a landscape, and thus had to be sought from specific sources. At the present time, no known ochre deposits (in KwaZulu-Natal) that were specifically utilised by the San have been identified or alluded to in archaeological or historical literature.

A complicating factor is that it is thought that the San practised seasonal migration, following herds of game, which were in turn following good grazing (Carter, 1970; 1977). The implication is that ochre used for painting could have been sourced from areas far removed from that of the painting site. Furthermore, it is strongly suspected by archaeologists that the peoples living within the KwaZulu-Natal region traded internally and externally. An extreme example of the distance over which trading is known to have occurred is illustrated at Andriesgrond Cave in the Cederberg Mountains, south-western Cape. The cave deposit contained two species of marine shell (*Conus sp.* and *Glycermeris sp.*) both of which live in warm water, and are typically found along the south and east coast of South Africa (Anderson, 1991).

Many shelter deposits throughout southern Africa have revealed the presence of objects that could only have arrived there if the camp of people covered extraordinarily large distances, or if there was trade (Mazel, 1993; G. Anderson, pers. comm., 2000). The Maqonqo site studied in this project indicates the latter. Some of the artefacts recovered during the excavation included ostrich egg shell (OES) beads and fragments. It has been found by Dean (1989) that the nearest location capable of supporting ostriches under natural conditions lies approximately 150 km west of the Thukela Basin on the Harrismith plains. During the colonial period, ostriches were introduced to the area, but the young were not suited to the wet climate. As a result, few successful breeding populations were established. Little is known about the climate of the study area over the last 4 000 years, and as a result it cannot as yet be conclusively proven that ostriches did not occur locally. The possibility does, however, exist that they did not (Mazel, 1996a). Other examples of long distance movement and/or interaction include the presence of OES in shell middens along the KwaZulu-Natal south coast (Schoute-

Vanneck and Walsh, 1959), and the depiction in paintings of ‘exotic’ faunal species that are known not to have existed locally (e.g. a seal at Makhetas, northern Lesotho (Willcox, 1963); elephant, giraffe and mormyrid fish at Rose Cottage Cave in the Free State (Ouzman and Wadley, 1997)).

The implications of findings such as these are that the ingredients for the paint could, theoretically, have been sourced across the whole of southern Africa. This therefore makes the sourcing of such pigments very difficult. A further difficulty, and probably a more important factor to consider, is the fact that the manner in which the paints were made is not known. There are many accounts from sources describing the manufacture of these paints, but none has yet been conclusively proven to be the actual method(s) (for more information see Rudner, 1982). Furthermore, historical accounts alluding to the nature of the manufacturing process as well as the ingredients utilised tend to vary depending on the geographical region from which they were obtained e.g. the eastern vs. western seaboard areas of South Africa.

Finally, the ages of the images cannot, as yet, be accurately determined. As a result, the sequence of pigment introduction/painting style cannot be determined. Consequently, this has led to the inability of researchers to determine the relative susceptibilities of each of the pigments/paintings to weathering processes. This, together with the fact that the weathering agency or agencies that are primarily responsible for this erosion are also yet to be determined, has severely limited the development and implementation of appropriate conservation and site management techniques.

The main focus of the research to date attempts to answer the question ‘why was it painted?’ As can be seen, very little empirically based information about the paints has been determined relating to how and when were they made, where the composite materials used within their creation were obtained, or nature (and possible succession) of the techniques used within their manufacture. This study aimed to establish a reliable methodology that will be used in future to help resolve some of these important, yet hitherto neglected, facets within the field of San rock art research, with special emphasis on conservation.

CHAPTER TWO

AIMS AND OBJECTIVES

2.1 INTRODUCTION

Due to the interdisciplinary nature of this study, it is inevitable that a wide variety of objectives will be investigated, the aims being dependent upon which facet of the project is currently being discussed i.e., the methodology developed and employed within the investigation, the technical aspects of the techniques used, and the possible impacts of the results of this study on our current understanding of our archaeological heritage. In order to better clarify these different aspects, these objectives will be independently addressed within separate Chapters, as these aims often fall within either the ‘archaeological’ or ‘pure-science’ realms of the study. The purpose of this Chapter is to concisely outline all of the aims and objectives followed within this study as a whole, thus eliminating the introduction of new aims and objectives with each successive chapter.

2.2 THE PRIMARY STUDY OBJECTIVES

Although this study had several objectives, the primary one is the characterisation of San rock art paints. In order for this to be achieved, however, a number of different focal areas had to be addressed. These can be more readily described as follows:

2.2.1 The composition of the Maqonqo Shelter paint pigments (the primary study site)

This initial area of focus will lead to an indication as to the specificity of the selection process for the pigments, be it localized to one source point or rock type, or of a more random and haphazard nature. The findings could have a major impact on the current understanding with regards to the purpose of the paintings. Should the findings indicate a ‘specific’ selection process, this would tend to support the current philosophy that the paintings were created for spiritual purposes (this assumption is based on the idea that only specific pigments would have been seen as being of a quality worthy of the spiritual act). This latter point does have some ethnographical support, with a number of accounts claiming that only specific sources were utilised (e.g. How, 1970; Jolly, 1986; Butler, 2001).

The individual tests conducted in order to achieve these objectives are listed as follows:

- The paint sample datasets obtained using energy dispersive X-ray microanalysis (EDX) and synchrotron micro X-ray fluorescence spectrometry (μ-XRF) were analysed separately to determine the differences, if any, which exist within and between the various paint colours.

- The paint elemental data obtained from the repeat samples collected were compared to determine if any changes occur within the paint samples with increasing depth (EDX and µ-XRF analysed separately).
- Elemental data from an excavated paint fragment and the suspected fragmentation point located on the wall were analysed to investigate if any similarities between the two could be determined (EDX and µ-XRF data analysed separately).
- The elemental data derived from the blank wall samples were analysed in order to determine possible influences of the shelter wall on the paint sample compositions (EDX and µ-XRF data analysed separately).
- Using the synchrotron micro X-ray diffraction (µ-XRD) data only, mineral compositions were compared in order to determine the differences, if any, that exist within and between the various paint colours.

2.2.2 The analysis of the excavated pigmentaceous material from Maqonqo Shelter

This was conducted in order to determine if any changes in pigmentaceous material composition occurred with increasing depth (≈ time). This might have important implications for the development of an indirect relative dating method, and might be able to aid in the determination of 'true' pigment vs. waste material. The techniques used were as follows:

- The large (> 3.0 g) excavated pigments originally collected from the first three layers of the deposit were compared in order to determine the degree of similarity that might exist between them (using XRF and XRD data).
- The small (< 0.5 g) excavated pigments originally collected from the first eleven layers of the deposit were compared in order to determine the degree of similarity that might exist between them (using µ-XRF and µ-XRD data).
- Using the mineralogical (µ-XRD) and elemental (EDX, XRF and µ-XRF) datasets, a comparison between all of the excavated pigmentaceous material was conducted in order to determine the degree of similarity of these pieces throughout the deposit.

2.2.3 A comparison between the Maqonqo Shelter paint samples and excavated pigmentaceous materials

Though the excavated pigments were analysed in the same manner as the paints, the question being asked is quite different. In a previous study, it was shown that little to no similarity existed between the large excavated pigments in the first three layers of the deposit and the paint samples obtained from Maqonqo Shelter (MQ) (Escott, 2000). The lack of similarity between the paints and these excavated pigments leads one to question their original purpose.

There are three possible reasons for this lack in similarity. Firstly, the samples analysed were never utilised for paint pigment manufacture, but rather for some other unrelated purpose; secondly, the pieces analysed were not used in the manufacture of the pigments used in the paintings sampled, but were used in some of the other, as yet, unanalysed images located within the same shelter (unlikely); and finally, the pieces sampled represented waste material removed from the actual pigment used. Apart from the study mentioned above, no scientific research has been conducted to specifically look into this anomaly.

In order to address this question, additional samples (from a variety of layers within the deposit) were selected and analysed. Whether or not a 'match' is found, an understanding of the excavated pigments could be just as valuable to the archaeologist as that of the paints, as it would provide greater insights into the San way of life. Currently, these materials are classified as 'waste lithic material', and as a result, with the possible exception of Watts (2002), little scientific research on this resource has been conducted.

The individual tests conducted in order to achieve these objectives are listed as follows:

- Using the major element data only, the paint pigments were compared to the large excavated pigment dataset (EDX and XRF datasets, respectively).
- The µ-XRF and µ-XRD datasets recorded for both the paint samples and the small excavated pigmentaceous materials were also compared.

2.2.4 The provenance of potential paint pigments from the field (MQ only)

This was investigated in order to gain a greater understanding of the problem of sourcing pigmentaceous materials for future studies. For this project to be as comprehensive as possible, this database needs to be as detailed as possible. Currently, no database detailing the variability of possible pigment sources is available. Unfortunately, not only are there no references in the ethnographic record to any specific pigment sources, there are also a large variety of conflicting accounts as to what the possible source materials might be. Thus, with no initial guide, it was decided to analyse as many materials with high iron content as could be discovered, no matter the source from which they were derived. This database was then used to determine both variation in iron content over distance (within similar geologies), as well as to try and 'match' any of these source points with both the excavated pigments and the paints themselves. This investigation can thus be considered as a pilot study upon which future studies can be based (see Chapter 8).

In order to achieve these objectives, the following individual tests were conducted:

- Using the major element data only, the paint and field pigments (EDX and XRF, respectively) were compared to determine if any similarity existed between them.
- Using both major and minor element data (XRF), the large excavated pigment and local field sample sets were compared to determine if any similarity existed between them.
- The elemental datasets for the small excavated pigments and the field samples were also compared.

2.2.5 The variability of paint composition with geographical distance

This was to determine the composition of paint samples gathered from different localities and from different geological substrates. This was done in order to highlight influences on the recorded paint compositions that could be attributed to either natural deposition, different sources of similar pigments, or, potentially, the discovery of previously undocumented pigmentaceous materials. Any information regarding changes in paint composition associated with either location or substrate will be of great importance for the development and implementation of proper conservation techniques.

The following individual tests were conducted in order to meet these objectives:

- The paint sample datasets, obtained using EDX and µ-XRF, were analysed separately to determine the differences, if any, which exist within and between the various paint colours obtained from all of the shelters.
- The elemental data derived from the blank wall samples were analysed to determine possible differences that exist both within and between the different shelters (EDX and µ-XRF/µ-XRD data analysed separately).
- Using the µ-XRD data only, mineral compositions were compared in order to determine the differences, if any, that exist within and between the various paint colours obtained from the four shelters sampled.
- The red and white paint samples collected from all four shelters were compared (EDX and µ-XRF/µ-XRD data analysed separately).

2.2.6 Conclusion

The primary object of this study was therefore to determine the nature of the inorganic constituents of the paints collected from MQ, and the three other sites sampled from around KwaZulu-Natal, with the latter three sites being sampled for comparative purposes only. As part of this investigation, additional experiments were conducted in order to determine the presence (if any) of secondary deposited materials that might now reside on the shelter wall surfaces (their presence would directly influence the interpretation of the paint pigment compositional data). An attempt was also made to ascertain the origin of these materials. As a result, three different sample sets were collected, namely (a) a paint sample set consisting of paint pigments collected from MQ, Twagwa Shelter (TW), Fergies Cave (FC) and Sheltered Vale Shelter (SV); (b) a set of blank samples (collected in the same manner as the paint pigments but from unpainted sections of the different shelter walls); and (c) a collection of water samples from each of four sample sites.

The secondary objective, although no less important, was to try and determine if any significant relationships might exist between either the paint or the excavated samples from MQ, and any of the known pigmentaceous ores that exist within a 50 km radius of the site (the distance was chosen on an arbitrary basis). As a result, two additional sample sets were collected in addition to the paint sample data already collected from MQ, namely the analysis of pigmentaceous samples selected from the previously excavated layers from the site, and various possible sources/materials gathered from the surrounding area.

The overall aspects of the paint samples to be investigated are as follows:

- To determine what influence, if any, the rock face (and rock surface deposits) and the paint samples have on one another.
- To determine the mineralogical forms of both the sulphur (S) and calcium (Ca) (both found in high concentrations in the paint samples analysed in previous studies), in order to determine the possible implications for both preservation and sourcing (see Chapter 2).
- To see if it is possible to ‘match’ a painting located on the rock face with an exfoliated fragment recovered from the MQ deposit. This could provide an alternative method of indirectly dating the paintings.
- To gain high quality elemental and mineralogical data from the paint pigments.
- To determine the relationship (if any) between the paint and excavated pigments.
- To determine if the paint components change with distance, geology, and possibly time (indirectly determined via over-painting and style).

2.3 TECHNICAL CONSIDERATIONS

Due to the differences in both precision and accuracy expressed by the individual techniques used within this study, special consideration has to be given to the relative compatibility of each technique’s resultant dataset relative to one another, especially when inter-technique comparisons are to be considered.

In order to test the ability of these datasets to relate to one another, the following tests were conducted:

- To compare the degree of accuracy (and precision) that exists between the different experimental procedures, elemental data for five 'standard' excavated pigment samples (MQ) were obtained by each of the techniques. These were then compared and statistically analysed against one another[1].
- The spot and reduced window results obtained from EDX were analysed separately in order to determine the most accurate/precise dataset that should be used. These data were then compared with the major elemental data obtained from XRF. In both cases, the XRF data were reworked to reflect a wet percentage for each element in order to allow for comparison.
- The µ-XRF data were compared against the XRF data. The XRF data were reworked to reflect a wet percentage for each element to allow for comparison.
- The relative trends regarding the elemental data from each of the three datasets (EDX, XRF and µ-XRF) were compared in order to highlight the sensitivity of each technique relative to one another, thus highlighting the feasibility of inter-technique dataset comparisons.

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[1] In an ideal situation, a comparative study would have been conducted using a larger sample size. Unfortunately, only a minimum acceptable number samples could be utilised for this comparison because of a two primary contributing factors: a) the limited number of excavated material of the size large enough to supply enough sample material required by the techniques being compared; and b) the cultural sensitivity of the site and the irreplaceable nature of the samples in question placed a limit the number of samples that could be utilised for this purpose.

CHAPTER THREE

THE HISTORY OF SAN PAINT CHARACTERISATION AND ANALYSIS (WITH COMPARABLE EXAMPLES FROM OVERSEAS STUDIES)

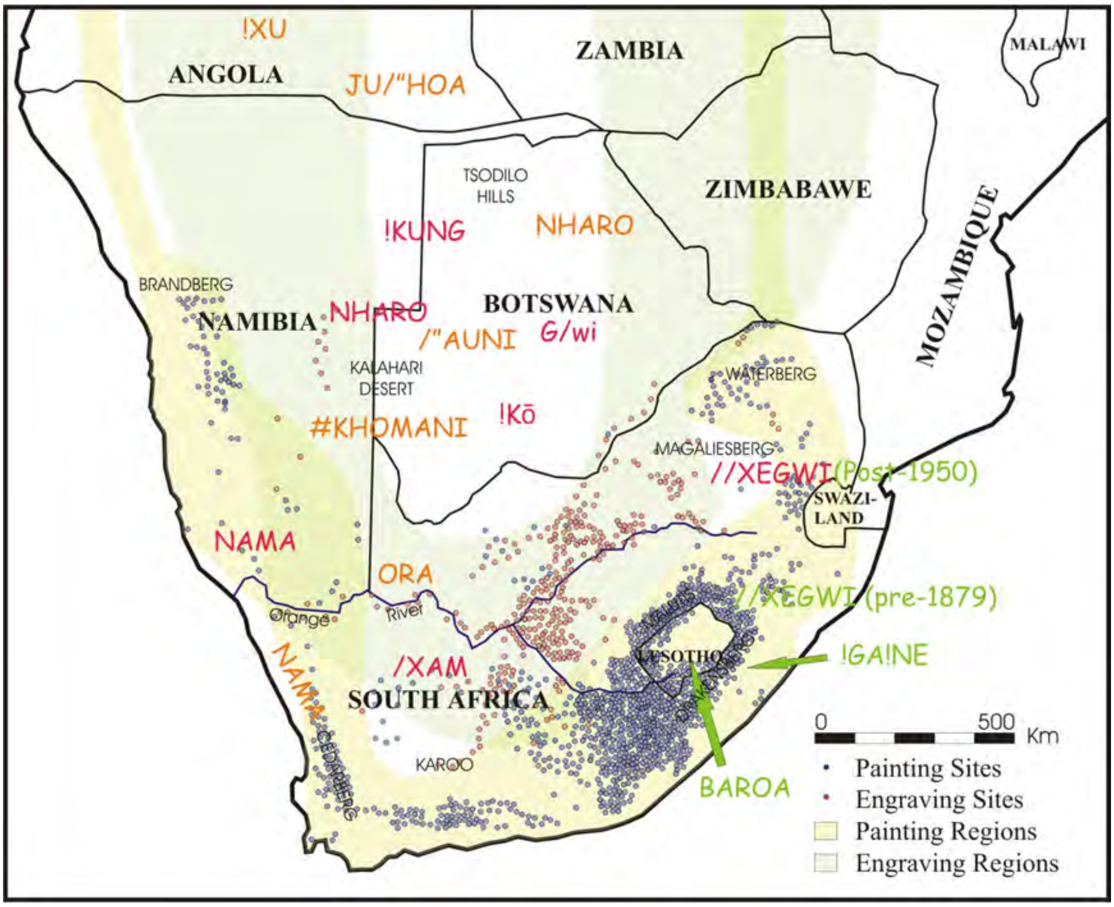
3.1 INTRODUCTION

Archaeology has long been posing questions and proposing hypotheses about the history of given areas and their inhabitants. In areas where an historical account of one form or another is present, these theories can often be substantiated or ‘proved’, but in areas where no such records exist (as is generally the case in southern Africa), these theories can remain unsubstantiated. Evidence gained from the excavation of Late Stone Age (LSA) sites allows for an understanding of certain features of the day-to-day existence of the San, such as what they ate, where they slept, and so on, but can only provide qualitative information on other aspects of San life (such as their social networks, spiritual beliefs and customs). Quantitative information (e.g. actual material sourcing) has to be obtained from other sources.

A majority of our knowledge of San religious beliefs has been gained from the transcripts of the /Xam San collected by W.H.I. Bleek and L.C. Lloyd between 1870 and 1884 (Deacon and Dowson, 1996). These records are supported to a much lesser extent by the information collected by Orpen in 1874 from one San informant in the Drakensberg region, and by the more contemporary records obtained from modern day San (in particular the !Kung and Nharo) in the Kalahari (Deacon, 1994). These records represent the oral histories and traditions of a very small number of the more than 20 ethnic groups, with the majority of the information related specifically to the /Xam, and were collected from informants originating from a specific area and over a relatively limited period of time (Lewis-Williams and Dowson, 1989; Deacon, 1994; Deacon and Dowson, 1996; F. Prins, pers. comm., 2005).

As a result, questions arise about just how much of this historical resource can be ascribed to the San peoples in general, and how much is specifically group related. Schmidt (1996) found that although similarities do exist in the folklores of different ethnic groups, notable differences are also apparent; there were changes in emphasis within individual stories, while certain groups had certain tales and characters that others did not. Thus, with differences in language and folklore being established, it is reasonable to assume that certain traditions e.g. those relating to painting, could also vary from region to region, group to group, and within a single band over time (Prins, 1994).

A further complicating factor relates to the location of the /XAM and !Kung groups from which the majority of the ethnographic record was obtained. Map 3.1 shows that both of these groups are located within regions not generally associated with a painting tradition in a region far removed from KwaZulu-Natal, the province within which this study is being conducted.



Map 3.1: Southern Africa depicting the distribution of painting and rock engraving regions, together with the well known San ethnic groups. The painting and engraving regions are modified from Lewis-Williams and Dowson (1989), the positions of recorded painting and engraving sites have been adapted from van Riet Lowe (1952)[1], and the San tribal locations were determined according to Lewis-Williams and Dowson (1989), Deacon and Dowson (1996) (and references within) and Prins (pers. comm., 2005); represented in red, orange and green text, respectively.[2]

These two factors further bring into question the applicability of this ethnographic record when trying to describe and understand the KwaZulu-Natal San communities. While the available ethnographic record must not be discounted, one must take care not to overemphasise its relevance to the KwaZulu-Natal region.

For a long time, it was generally accepted that the original San peoples of KwaZulu-Natal had long since disappeared as a direct result of colonialism, genocide, ethnocide, tribal conflicts and a general loss of hunting land (Wright, 1971; Vinnicombe, 1976). Frans Prins has, during the course of

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[1] These data show the distribution of the 1 592 known rock painting sites and 340 known rock engraving sites as collated by van Riet Lowe (1952).

[2] The !Kung and the !XU are related to one another - !XU is the correct name, but the term !Kung is more commonly used in the literature (Rudner, 1982). The distinction between the two groups is based on their spatial locality, their ecological adaptation (the !XU were woodland dwellers, and practised some cultivation in historic times, whilst the !Kung were desert dwellers, and have no history of cultivation). The latter are also known as the Jul//wasi (Prins, pers. comm., 2005).

his work, located over 400 descendants of the San within the eastern seaboard regions, most of whom have been assimilated into the Bantu speaking society. Unfortunately, whilst the people have not died out, their culture (including their painting tradition) has, with only five individuals alive today who are known to be able to provide second or third hand knowledge about the traditional San way of life that used to exist within this region (Prins, pers. comm., 2005). It is for this reason that the conservation of the rock art is of great importance – it represents one of the most visible, easily accessible, and irreplaceable records of this now lost cultural era.

The wide distribution of the art, its variability of subject matter and aesthetics, and its origins have long fascinated archaeologists and laymen alike. What makes these images all the more intriguing is that, though they have been studied for a long time, very little is known about them scientifically. Most of this academic interest has, until recently, focused on the dating (e.g. Mazel and Watchman, 1997; 2003) and the cultural meanings (e.g. Lewis-Williams, 1980; Solomon, 1997; 1999; Lewis-Williams and Pearce, 2004) of the paintings, as opposed to the more technical aspects relating to how the pigments were made, their composition, and their places of origin. An exception to this is the publication by Rudner (1982), who provided the most detailed review of all information to that date dealing specifically with paint pigment composition and manufacture, and comparing information of both an historical and scientific nature. Her conclusions showed that, whilst a number of sources are indicated within the literature to be the 'true' sources of the pigments, further scientific investigation is required in order to determine the validity of these suggestions/accounts.

The implications of the determination of the paint pigment compositions are potentially enormous. By gaining a greater understanding as to how these pigments were manufactured, ways in which to best protect and conserve this ancient heritage can be pursued. Furthermore, by studying a number of painted sites, it might be shown that the 'recipes' changed over time, as was shown to have occurred in France (Menu and Walter, 1992; Clottes, 1993; 1997), and/or from region to region. If the 'recipes' changed over time, the change may allow 'relative dating'. The results could then be used to compare with other relative dating methods, such as the Harris matrix (e.g. Russell, 2000; Pearce, 2001, 2002). If it can be determined that the paint recipes or pigment compositions changed regionally and/or over time, social networks and interrelationships between camps might be established.

Finally, the question of authenticity of paintings could be addressed. An example in which this direction of research is applicable relates to the study conducted on the Coldstream Stone (Section 3.5.4). In this case, the authenticity of the burial stone was brought into question, for, whilst the stone had been buried for a protracted period of time, the images upon it were bright and clear. An investigation into the paint constituents on the stone, and comparisons with paint pigments obtained both within and from surrounding shelters, would lead to a greater degree of certainty in the authenticity of the find. A further example involves the individual characterisation of Bantu and San paint compositions and/or pigment sources, thus allowing for the easier distinction between the two for images of uncertain origin.

Archaeology, by its very nature, has always been characterised by inter-disciplinary approaches. Scientifically derived empirical data may resolve hypotheses originally based, for the most part, on historical, semi-quantitative and generally fragmented evidence. As much of the remaining evidence in rock art is inorganic in nature, the methods sought have had to take this into account. It is only since the 1970s that any type of analysis has been undertaken with the aim of either sourcing and/or highlighting similarities between samples of Palaeolithic rock art, utilised ochre materials and ochre-stained objects (Clottes, 1997). One of the methods used, and the one used within this study, is that of statistically comparing major and trace element data obtained from the paint, excavated pigment samples (also referred to as 'waste lithic material'), and field pigmentaceous materials in order to determine their degree of similarity, with the possible determination of specific source characteristics.

The use of trace element analysis as a technique to aid in the sourcing of materials has been used with great success in a variety of studies, ranging from the sourcing of Aboriginal ochres in Australia (Jercher *et al.*, 1998) and the compositional determination of paint pigments in King Herod's palaces in Israel (Porat and Ilani, 1998), to porcelain sourcing and authentication in China (Yu and Miao, 1998) and potato sourcing in the USA (Anderson *et al.*, 1999). Within these studies, many different experimental techniques have been used to determine the trace element data required. Although the selection of each of these experimental techniques is determined primarily by ease of access to the respective technologies and the related costs per sample, other important factors that are considered relate to their relative degrees of reliability, the amount and nature of sample required, and the level of element detection. The basic methodology behind their use is the same throughout, however, as is illustrated by the examples discussed in Sections 3.5 and 3.6.

The determination of data alone does not aid in the solving of problems. All of the above-mentioned case studies, as well as the scientific studies that will be examined more closely below, have had to undergo statistical manipulation in order to determine if any trends or groupings between the studied samples do in fact exist. The statistical techniques employed are just as varied as the techniques used to obtain the elemental data, the choice being determined by the nature of the dataset(s), as well as the objectives of the study concerned. Some of the statistical measures that have been used include principal component analysis (PCA), correspondence analysis (CA), discriminant analysis (DA) and quantitative fabric analysis (QFA). All of these techniques share the same objective i.e., to group samples of similar characteristics (possibly indicating the same source), whilst separating the various groupings sufficiently to allow for an accurate assessment to be made regarding their 'individuality'. The ideal situation would result in the distinct separation of the individual groups, but this is seldom achieved.

The one factor that all these case studies have in common, and which sets the present study apart, is that all of the above examples had reference sources against which they could compare their sample sets. At the time of submission, no information indicating possible sources of pigmentaceous materials known to have been utilised by the San in KwaZulu-Natal had been found. Furthermore, very little work using this scientific approach has been conducted in South Africa, with studies by Wilson *et al*. (1990), Mazel and Watchman (1997; 2003) and Hughes and Solomon (2000) being notable exceptions. The nine southern African examples discussed in Section 3.5 were the most relevant to the topic with respect to the methodologies employed, as well as the quantitative and qualitative data produced. However, before one can discuss these analytical studies, three less definitive methods of paint composition characterisation must be recognised, namely: 1) determination via ethnographic information; 2) speculative experimentation; and 3) early analytical experimentation. It must be noted that mineral notations have only been used if they were in the original text. So that no suppositions as to the identity of the mineral(s) based on their crystallographic structure could be made, the original identifiers have been used, e.g. $CaCO_3$, which could refer to either calcite, aragonite or vaterite, will remain $CaCO_3$ in the text. Similarly, the term ‘iron oxides’ also remains un-clarified.

3.2 ETHNOGRAPHIC INFORMATION

As mentioned previously, much of the historical information available is often fragmented, contradictory, or just plain speculation. The earliest reference (known to the author) to the composition of the paints was given by Somerville (1799 – 1802), who, on his journeys along the eastern Cape frontier, commented that the black pigments were derived from charcoal, red pigments from Fe ore, and white pigments from the dried excrement of water fowl. Whilst a number of accounts referring to paint pigments followed this report, very few of these anecdotes ever mentioned the original sources of the pigments, and even fewer were authenticated or verified. As a result, very little reliable information about the composition of the San paints has been collected, and the little that has cannot be totally relied upon. A few of the pigmentaceous materials that have been purported to represent the ‘true’ paint pigment components are listed below (summarised from Rudner, 1982):

Red: Blood; Fe oxide; Mushroom powder; Haematite; Specularite; Siderite; Cinnibar; Ferruginous shale; Burnt ochre.
White: Clay; Kaolin; Bird droppings; Gypsum; Lime; Plant sap; Burnt bone; Chalk; Zn oxide; Quartzite; Calcite; Talc; Ash; Marl[1]; Natrolite; Tuff[2]; China clay[3].
Yellow: Clay; Goethite; Limonite; Un-burnt ochre; Dolerite; Sulphur; Fe pyrites[4].
Black: Charcoal; ‘Black stone’; ‘Coal’; Soot; Burnt bone; Magnetite; Lampblack; Manganese; Graphite; Shale; Hyrax excrement.

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[1] Marl is defined by Hamilton and Cooke (1939) as a clay ‘…in which a fair quantity of calcareous material is present, giving rise to a peculiar granular texture.’ It is an old term no longer used.

[2] Gary *et al.* (1973) define Tuff as “…a compacted pyroclastic deposit of volcanic ash and dust...”

[3] “A commercial term for kaolin obtained from china-clay rock…” Gary *et al.* (1973).

[4] Probably weathered with some goethite.

Just as numerous and varied are the binders (the additives to the paints that are supposed to lend greater resistance to weathering) and/or media (added to the pigments in order to facilitate easy application to the rock surface) that are purported to have been mixed with the pigments to produce the San paint. Some are listed below (summarised from Rudner, 1982):

Binders: Fat; Brains; Bone marrow; Honey; Gum; Plant sap; Animal glues.
Media: Saliva; Water; Urine; Blood; Milk; Egg tempera; Gum; Bile; Wax; Resin; Beeswax; Gelatine; Stomach liquid; Plant sap.

Although a large range of materials has been suggested within the literature, not all of the accounts are in agreement with one another about which were used, and contradictions between different authors occur. In order to try and gain an unbiased and fair assessment of this ethnographic record, only first-, second- and third-hand accounts have been considered. Table 3.1 gives a summarised list of San paint components as recorded from these accounts (adapted from Rudner, 1982). These accounts have been ranked according to the approximate area from which each anecdote was obtained, as well as by the date of the publication within which they were recorded.

As can be seen, the long lists of both pigments and binders/media mentioned previously have now been greatly reduced. This does not mean that the omitted materials were not employed in the manufacture of the San paints, but rather that the chances of their usage can be considered to be less likely when compared with those that are repeatedly mentioned on Table 3.1.

In general, red pigments were described as ochreous in nature, and identified as clay, Fe oxide, ochre, ‘fatty stone’ or ‘earth’. On two occasions, plant ingredients were indicated as providing the red pigment. The use of haematite was mentioned only twice. Yellow pigments were almost exclusively derived from an ochreous source, also being referred to as clay, marl, or earth. The white pigments were derived from clays, with only one account claiming that the pigment was composed of the milky sap extracted from the kernel of *Chrysophyllum magalismontanum*, and one stating that lime was the source. The black pigments were obtained from an organic source: charcoal, coal, burnt sticks or hyrax excrement. A ‘black stone’ was the only recorded inorganic source of black pigment. Fat was the predominant paint medium mentioned, with honey and blood each being mentioned in three separate accounts.

When one compares all of these accounts in relation to their areas of origin, two distinct painting regions seem to emerge. The only accounts that mention the use of blood, and specifically eland blood, in the manufacture of the paints come from the Lesotho-KwaZulu-Natal region; a finding supported by the Hemastix tests conducted by Williamson (2000). In addition, it is only in this area that the accounts relating to specific sources for red pigment and the use of plant saps/juices as paint media were collected. The only two accounts of mixing the paint pigments with boiling fat or brains, and the single account in which honey is used, were collected from the Botswana-Namibia-northern

Table 3.1: First-, second- and third-hand ethnographic information describing paint pigment composition.

SOURCE	INFORMANT	AREA/ REGION	PREPARATION TECHNIQUES	MEDIA	RED	YELLOW	WHITE	BLACK	OTHER	REFERENCE
2	Old farmer	Northern Kalahari	Made paste of boiled brain of antelope and red ochre (‘rooiklip’) which was reheated to paint on rocks	Boiled brains	Ochre	--	-	-	-	Buys (pers. comm., 1969)*(pg65)
1? or 2?	‘Bushmen’	Southern Namibia	-	Fat, honey and gum Arabic – proportions not known	Fatty stone	Marl	Lime	‘Coal’	-	Hahn (1879)*
1? or 2?	‘Khoikhoi women’	Southern Namibia	-	-	Ochre	-	-	-	-	Hahn (1881)*
3?	Various ‘natives’	-	-	-	-	-	-	Hyrax excrement	-	Moszeik (1910)*
1? or 2?	-	Sansokwe river, Botswana	Sometimes mixed with fat and allowed to dry =- crayon	Fat; If a dry crayon, moistened with water and/or saliva	Clay	-	-	Burnt stick for outline	Blue = clay	Dornan (1917)*
1? or 2?	-	Sansokwe river, Botswana	Mixed with boiling fat, allowed to cool = crayon; Also applied warm liquid paint to surface	Boiled fat	Haematite	Blue clay	White clay	Burnt stick for outline	-	Dornan (1925) (probably from the same informant as above)
2? or 3?	-	Tsolido Hills, Botswana	Haematite roasted, quicklime mixed with urine and applied to the walls. When it comes off the walls, a red stain remains.	Urine	Haematite or from a reaction of certain sandstone walls with quicklime made from certain plants	-	-	-	-	Yelland (pers. comm., 2006)
2	Farmer	Namaqualand, Western Cape	-	Ostrich fat	Mushroom powder called *ajous*	-	-	-	-	Currlé (1913)

Source – 1, 2, 3 represent first-, second- and third-hand information, respectively.
\- – Not mentioned in text.
* – Obtained from quoted extracts listed in Rudner (1982:pg 50 - 67).

Table 3.1 (Cont.): First-, second- and third-hand ethnographic information describing paint pigment composition.

SOURCE	INFORMANT	AREA/ REGION	PREPARATION TECHNIQUES	MEDIA	RED	YELLOW	WHITE	BLACK	OTHER	REFERENCE
3	Andries – a 'Hottentot'	Baviaans River, Eastern Cape	-	Fat	Clay	Clay	Clay	Charcoal; black stone	-	Baines (1842 – 53)*
3	Tembus	Dordrecht, Eastern Cape	Not mixed. Honey applied to the rock surface, and the rock used as a crayon	Honey	Clay stone	Clay stone	-	-	-	Péringuey (1913)*(pg54)
3	'Old Bantu'	Dordrecht, Eastern Cape	-	Honey	-	-	-	-	-	Hey (1954)
2	Hlatine Nikwe	Eastern Cape	Rubbed wall with stones in preparation for painting	-	Mudstone obtained along river banks	-	-	-	-	Prins (pers. comm., 2004)
3	Lindiso (half San) and Poponi (a relative of Lindiso)	Tsolo District, Transkei	-	Water and fat	Clay	Clay	Clay	Charcoal from wood of *Erythrina caffra*	-	Apthorp (1913)*(pg54)
3	-	Transkei	-	Fat	Ochre	Ochre	-	-	-	Péringuey (1914)*(pg55)
2	'M' (first generation San descendant), real name Manqindi or Maqoqa Dyantyi	Tsolo District, Transkei	Blood and fat mixed with pigments	Eland blood and Eland fat	-	-	-	-	-	Jolly (1986); Blundell (2004)
2	Sister Mariya	Tsolo District, Transkei	-	Chicken or bird droppings, not egg whites; When blood used, it was mixed with plant juice that stops clotting	Clay – from specific dongas	Clay – from specific dongas	-	-	-	Butler (2001)

Source – 1, 2, 3 represent first-, second- and third-hand information, respectively.
- – Not mentioned in text.
* – Obtained from quoted extracts listed in Rudner (1982:pg 50 - 67).

Table 3.1 (Cont.): First-, second- and third-hand ethnographic information describing paint pigment composition.

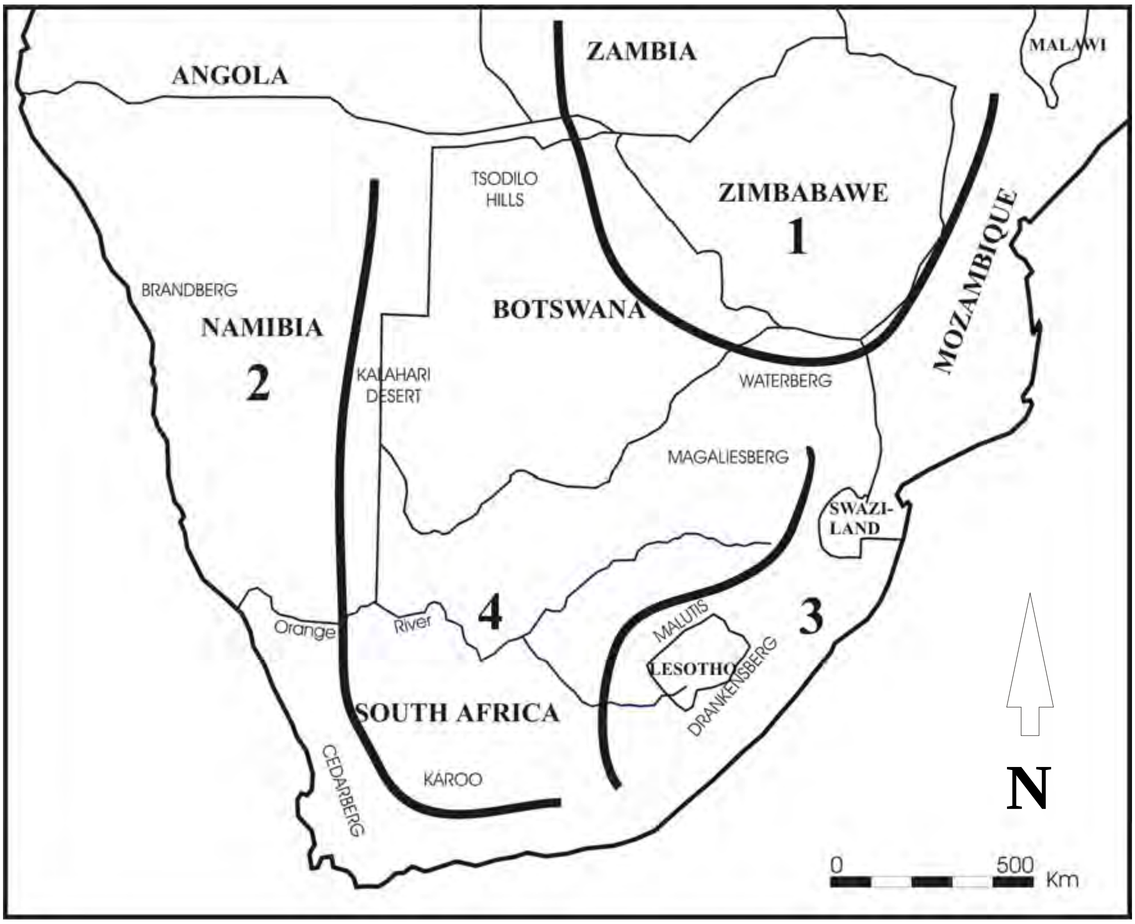
SOURCE	INFORMANT	AREA/ REGION	PREPARATION TECHNIQUES	MEDIA	RED	YELLOW	WHITE	BLACK	OTHER	REFERENCE
3	Old San descendant	KwaZulu-Natal	-	-	Plant pigment?	Plant pigment?	Plant pigment – milky kernel of *Chrysophyllum magalismontanum*	-	-	Roberts (1916)
2	75 year old Scottish Farmer	Near Umzinkulu, KwaZulu-Natal	-	Juice of a bulb	-	-	-	-	-	Lebzelter (1930)*
2? or 3?	Diamond, a middle-aged black man	Cathkin Park, KwaZulu-Natal	Ground up and mixed with animal fats	Animal fat	Coloured minerals?	Coloured minerals?	Coloured minerals?	Coloured minerals?	-	Wells (1933)
2	Kerik	Drakensberg, KwaZulu-Natal	Rubbed wall with stones in preparation for painting; sometimes also heated samples	-	Ferrugenous sandstone; nodules from within sandstone; weathered dolerite; in Lesotho – weathered dolerite with micaceous flecks	Ferrugenous sandstone	Sap of *Euphorbia clavarioides*	-	-	Prins (pers. comm., 2004)

Source – 1, 2, 3 represent first-, second- and third-hand information, respectively.
- – Not mentioned in text.
* – Obtained from quoted extracts listed in Rudner (1982:pg 50 - 67).

Table 3.1 (Cont.): First-, second- and third-hand ethnographic information describing paint pigment composition.

SOURCE	INFORMANT	AREA/ REGION	PREPARATION TECHNIQUES	MEDIA	RED	YELLOW	WHITE	BLACK	OTHER	REFERENCE
2?	Silayi (not San, but lived with them)	Drakensberg, Lesotho	‘Taken out of the ground’; Some prepared by fire	-	Earth?	Earth?	Earth?	-	-	Stanford (1910)
2	Old Basuto woman called Elisabeth ‘Malėkėtanyanė Môhanoė’	Lesotho	Used Black Wildebeest and later horse tail hair for paint brushes; Mixed with melted fat; stated that ochre was not used	Animal Fat	Not ochre; didn’t say what was used	Not ochre; didn’t say what was used	Not ochre; didn’t say what was used	Not ochre; didn’t say what was used	-	Ellenberger (1953)*(pg60); also translated by Dr. Peter Mitchell
2	Mapote	Lesotho	Red ochre (*quang quang*) heated and then ground up	Red = eland blood; white = plant sap from stem of *Ascepia gibba*	Fe-oxides; glistens and sparkles = *quang quang*	-	Clay called *phepha*	Charcoal; burnt sticks	-	How (1970)

Source – 1, 2, 3 represent first-, second- and third-hand information, respectively.
\- – Not mentioned in text.
* – Obtained from quoted extracts listed in Rudner (1982:pg 50 - 67).



Map 3.2: The proposed rock art regions of southern Africa (adapted from Lewis-Williams (1983)).

Cape region, although one account from Lesotho suggests that the pigments were mixed with melted fat. Also, the only account in which a red mushroom pigment was used was recorded in Namaqualand.

As intriguing as this observation is, it must be noted that these trends are based on limited information of variable reliability. However, when this trend is compared with the regions of San rock art as proposed by Burkitt (1928), certain similarities emerge (Map 3.2): the Namaqualand region corresponds with Region 2, the Lesotho-KwaZulu-Natal region corresponds with Region 3, and the Botswana-Namibia-northern Cape region corresponds with Region 4.

These rock art regions represent geographical areas within which imagery/content, style and technique are relatively distinct. Region 1 is characterised by naturalistic depictions of animals (although with characteristically fewer eland than in the other regions) and humans in mono-, bi- and polychrome painting styles (Lewis-Williams, 1983). Plant imagery, rarely depicted in the other regions, is also depicted here e.g. trees, grass and fruit.

Region 2, although similar to Region 1 in many ways (Willcox, 1963; Lewis-Williams, 1983), is also characterised by the presence of handprints. Two forms of handprint are found, namely full and stylised. The full handprint involved the painting of the hand and placement of it on the wall, whilst the stylised print involved the painting of a single line from the thumb, around the base of the palm to the end of the little finger. A second line was painted from the first finger to the third, with a third line painted within that (Lewis-Williams, 1983). The resultant image on the wall was very distinctive. Although measurements of the handprints showed that the painter's hands were of a similar size to that of the modern day San, the restriction of this imagery to the western part of southern Africa suggests that the images were the work of the KhoiKhoi (Hottentots), a pastoral people known to have originally lived within this area (Rudner, 1982; Lewis-Williams, 1983; Anderson, 1994; Van Rijssen, 1994; Yates *et. al.*, 1994). The large number of sheep imagery within the paintings further supports this theory.

Region 3 is characterised by complex and finely painted imagery. Shaded polychromes are common – a technique not found in Region 2 (Lewis-Williams, 1983). In addition, handprints are rarely found (Willcox, 1963). Region 4 is possibly the most distinctive of the four regions. Although some animals are depicted, a majority of the images are monochromatic geometric designs i.e., circles, grids, crosses and dots (Lewis-Williams, 1983).

While it must be clearly pointed out that these regions are based on subjective criteria and in no way represent definitive and discrete regions, the similarities in the delineation of regions based on two separate criteria ('components' vs. 'style') does serve to highlight the point previously alluded to i.e., the possibility that paint composition/recipe(s) differ between different geographical regions, and possibly even San communities.

3.3 SPECULATIVE EXPERIMENTATION

Numerous experiments have been carried out over the last 100 years in an attempt to either validate certain assumptions with regards to San paint manufacture, and/or to recreate the colours and durability found within 'original' San rock art. Most of these accounts are found as notes within publications, seeming to have been conducted for curiosity reasons as opposed to constructive investigations to understand the nature of the paints. Only a few papers have attempted to scientifically evaluate the interactions of the proposed pigments, media and preparation techniques (see Section 3.2) and relate their findings to the 'original' painted images based on their durability and longevity (e.g. Moszeik, 1910; Johnson, 1957; Huwiler, 1972; Bassett, 2001).

Table 3.2 gives a brief summary of some of the findings as determined by the various authors using their own choice of pigments, media and preparation techniques. As can be seen, a wide variety of combinations of pigment sources and media have been investigated. Two points are immediately apparent: 1) almost all of these studies focussed almost exclusively on the nature of the medium employed, and not the pigment used; and 2) similar combinations of pigment and media, when analysed by different authors, usually produced contradictory results (e.g. the use of marrow as a medium: Johnson (1957) showed a positive result, whilst Huwiler's (1972) tests confirmed the opposite). One finding common to all the texts studied, however, is that the use of water as a medium never produced paints capable of longevity.

Apart from the limited work conducted by two authors (Dr. E. Denninger and Ms. B.S. Williamson: see Section 3.5), very little work into the determination of the organic constituents of San paints has been conducted, with the studies mentioned effectively representing 'presence/absence' tests. The nature of any binder/media has still to be determined. Should organic constituents be adequately characterised, the next scientific question to answer would be 'Are binders/media ubiquitous throughout all San art?'

Work into the analysis of any possible organic components within San paints is thus in its infancy. The experiments summarised in Table 3.2 are thus all pre-emptive – all trying to determine the nature of the paint without knowledge of the constituents. Some of the 'recipes' might work, but until analysis is conducted on 'original' San paints, the results obtained are effectively redundant. As a consequence, the results obtained from these experiments (with regards to which pigmentaceous materials and binders/media were best suited to paint manufacture) had no influence on the approach adopted within this study concerning paint pigment composition determination.

3.4 EARLY ANALYTICAL EXPERIMENTATION

These early investigations (carried out between 1910 and 1962) were quite crude and rudimentary by modern standards, for obvious reasons. As a result, they are, in general, not very detailed in their conclusions. They are mentioned, however, as they represent the first analytical endeavours into the characterisation, and eventually sourcing, of the San paint pigments.

The antiquity of the investigations, and the fact that no sources were supplied within the secondary texts that were identified resulted in my inability to obtain copies of the original reports for the experiments mentioned below. As a result, I had to rely solely on these secondary sources for the information presented here. It is because of this that the information presented below is not complete regarding the technical aspects of the studies.

Due to the scarcity of information given (relating to the original locality of the samples, precise numerical data obtained from the analysis, etc.), the information discussed within these accounts could not help in any substantial manner the findings obtained in the present study i.e., the data obtained could not be utilised as an independent paint composition source against which the findings of the current study could be compared. The results do, however, form part of a basic database of known inorganic paint constituents against which the current findings can be compared.

Table 3.2: Speculative investigations into the nature of paint composition.

COLOUR	PIGMENT	MEDIA	TECHNIQUE/COMMENT	TEST EMPLOYED	FINDING	REFERENCE
Red	Earth pigment	Sheep marrow	Mixed to thin 'gruel' then painted on rock and allowed to dry	Under running water for three weeks	Not noticeably affected	Moszeik (1910)*
Yellow						
White					Washed off	
Red		Water			Almost no trace left	
Yellow						
White						
Red	Haematite	None	Finely ground with a mortar and pestle	Applied to different bits of porcelain and stone	Redder colour produced when oil or fat used than when just pigment. Fat or oil would have oxidised on the rock, thus disappearing with time, hence not being present today	J. Muller to Pérenguey (1914)*(pg55)
		Vegetable oil				
		Animal oil				
Various	Red Fe ore, limonite, etc.	Solution (water?)	Mixed with pigment	Painted on rock	The solution did not penetrate well and washed off	De Laporte to Pérenguey (1914)*(pg55)
Red	Root of *Elephantorrhiza burchelli*			Strong solution painted on rock	At first was faint but grew darker with time. Did not wash off	
Red	Red pigment	Fat	Mixed together	Rubbed on to stones	'…tenacity beyond question'	W.B. Magennis to Pérenguey (1915)*(pg55)
Red	Root of *Elephantorrhiza burchelli*	Solution (water?)	Mixed together	Painted on rock	Leaves a dark stain difficult to remove, similar to San paintings	Stevenson-Hamilton (1929)
Various, dependent on the degree of heating	Earthy limonite from within nodules	-	Pigment heated carefully to varying temperatures	-	Dependent on the temperature used, different colours from the original yellow, through yellowish reds, brownish-reds, dark-reds to black were achieved. The reds were dull due to the low Fe content in the original	Segal (1935)
	Siderite	Tallow and water	Pigment heated, crushed, and then mixed with the media	10 months of exposure to normal atmospheric conditions	The colours were unaffected	

* – Quoted extracts listed in Rudner (1982:pg 50 - 67).

Table 3.2 (Cont.): Speculative investigations into the nature of paint composition.

COLOUR	PIGMENT	MEDIA	TECHNIQUE/COMMENT	TEST EMPLOYED	FINDING	REFERENCE
Red	Ochre	Wax resin	Heated pigment to 100 ^{o}C, then ground the pigment and mixed it with the media	A quill and a brush of bristle were used to apply the paint to a sandstone	The most difficult to use. The palette had to be kept heated; the ochre dried quickly and had to be applied as a paste. Fine lines were impossible. Easily peeled off	Johnson (1957)
		Marrow fat			Mixed well into a thick paste. A lot of marrow required for limited surface coverage. Relatively successful method	
		Hyrax urine			Failure	
		Fat			Fine lines difficult.	
		Juice of an *Euphorbia*			Great quantity required. Only a light image was produced	
		Juice of botterboom (*Tylecodon paniculatus*)			Gave a 'tacky' effect. Fine lines impossible	
		Juice of *Euryops laxus*				
		Gall-bladder juice			Mild success, but a large quantity is required. Although is easy to apply, a lot of time would be required to obtain this medium	
		Honey			Very sticky. Washed off immediately	
		Tempera			Unquestionably the best method. Can only make fine lines with this media	
Yellow	Yellow ochre	Blood	-	Treated with water and brushes over a six month period	No Damage. Easily applied. Fine lines possible	Denninger (1966a)
Red	Haematite	Blood				

Table 3.2 (Cont.): Speculative investigations into the nature of paint composition.

COLOUR	PIGMENT	MEDIA	TECHNIQUE/COMMENT	TEST EMPLOYED	FINDING	REFERENCE
Black	Charcoal or graphite	Water	-	Each media was subject to tests of stability (sealed and unsealed), and then mixed with the pigments mentioned. Changes in colour were noted, and then the paints were applied to slabs of granite in both vertical and overhead positions, the degree of and time taken to harden being noted. Examples which passed all of these tests were then subjected to repeated washing, heating in the sun, being chilled in a refrigerator, rubbed, scratched, and finally subjected to the test of time	Negative	Huwiler (1972)
Grey	Calcite	Honey	Came off after some time		Negative	
Dark grey	Talc	Hyrax urine	Poor availability. Didn't harden. Washed off		Negative	
White	Quartzite	Resin	Not easy to mix when cold or heated		Negative	
Green	Quartz with mica and calcite	Berry juices	Mixed well but discoloured pigment. Couldn't paint overhead. When dries, paint returns to powder		Negative	
Grey/Black	Shale	Cactus juice	Same as above		Negative	
Dark yellow	Ferruginous shale	Animal fat	Easy to paint with, except overhead more difficult. Darkened colour. When exposed to the sun, paint ran freely. After weeks of drying, could be wiped off		Negative	
Light red	Phyllite[Φ] (sericite, mica) haematite, quartz	Beeswax	Required heating. Application difficult		Negative	
Dark red	Phyllite (with haematite bands)	Bone marrow	Not easy to mix when cold or heated		Negative	
Light yellow	Sulphur	Blood	As a paint, easy to paint with. Stains rock after time. Can only be removed with hard rubbing or washing		Acceptable	
White	Bird droppings	Blood mixed with pigment	Easily mixed. Darkens colour. When dry, easily rubbed off		Acceptable	
White	Ash	Blood plasma	Similar to 'Blood'. Slightly harder		Acceptable	

Φ – Phyllite is a general term referring to minerals with a layered crystal structure (Gary *et al.*, 1973).

Table 3.2 (Cont.): Speculative investigations into the nature of paint composition.

COLOUR	PIGMENT	MEDIA	TECHNIQUE/COMMENT	TEST EMPLOYED	FINDING	REFERENCE
Only the pigments that met the following criteria were listed: readily available; easily crushed and prepared with simple equipment; give true and long lasting colour. All were used with each media to evaluate the media's applicability		Egg white	Easy to paint with, except overhead more difficult. Darkened colour. When exposed to the sun, paint ran freely. After weeks of drying, could be wiped off	Each media was subject to tests of stability (sealed and unsealed), and then mixed with the pigments mentioned. Changes in colour were noted, and then the paints were applied to slabs of granite in both vertical and overhead positions, the degree of and time taken to harden being noted. Examples which passed all of these tests were then subjected to repeated washing, heating in the sun, being chilled in a refrigerator, rubbed, scratched, and finally subjected to the test of time	Acceptable	Huwiler (1972) Cont.
		Tree latex	Did not mix well. Application difficult. Can't be rubbed or washed off		Acceptable	
		Vegetable albumen	Difficult to extract.		Good	
		Gelatine	Laborious extraction (have to boil bones and tissue in water). Mixes very well. Easy to apply. Takes 12 to 15 hours to dry. Colour lightens. Good resistance to water and weather. Needs to be heated to keep it liquid enough to mix with the pigments		Good	
		Candelabra sap (*Euphorbiaceae*)	With the exception of charcoal, easy to mix and paint. Dries in 3 to 4 hours. Can't be rubbed, scratched or washed off. Heat and cold have no effect. If in a sealed container, will stay liquid for weeks. Colour stays clear after a period of time. Gelatine and Candelabra were the only media to pass all the tests		Good	

Table 3.2 (Cont.): Speculative investigations into the nature of paint composition.

COLOUR	PIGMENT	MEDIA	TECHNIQUE/COMMENT	TEST EMPLOYED	FINDING	REFERENCE
Red	Blood	None	Congealed whole blood used	Applied to coarse-grained quartzitic sandstone that was kept out of direct sunlight and rain. A Pelikan paint colour chart was used to identify the colours. Colours were recorded at 18 March 1980 (A) and 18 May 1982 (B)	(A) Blotchy deep madder [red]; (B) Blotchy brown. Did not mix or adhere well	Rudner (1983)
			Whisked blood (less fibrin)		(A) Bengal red; (B) Transparent brown. Did not mix or adhere well	
			Shaken blood (broken fibrin)		(A) Bengal red; (B) Transparent brown. Did not mix or adhere well	
	Blood	Beef fat	Congealed whole blood used		(A) Blotchy deep madder; (B) Spotty brown	
			Whisked blood (less fibrin)		(A) Blotchy Bengal red; (B) Spotty brown	
			Shaken blood (broken fibrin)		(A) Blotchy Bengal red; (B) Spotty brown	
	Blood	Ostrich oil	Congealed whole blood used		(A) Blotchy deep madder; (B) Spotty brown	
			Whisked blood (less fibrin)		(A) Blotchy Bengal red; (B) Spotty brown	
			Shaken blood (broken fibrin)		(A) Blotchy Bengal red; (B) Spotty brown	
	Red ochre	Blood	Congealed whole blood used		(A) Indian red; (B) Dark Indian red	
			Serum		(A) Lighter Indian red; (B) Light Indian red	
			Whisked blood (less fibrin)		(A) Indian red; (B) Dark Indian red	
			Shaken blood (broken fibrin)		(A) Indian red; (B) Dark Indian red	
	Red ochre	Blood and fat	Congealed whole blood used		(A) Slightly darker Indian red; (B) Darker Indian red	
			Serum		(A) Light Indian red; (B) Light Indian red	
			Whisked blood (less fibrin)		(A) Slightly darker Indian red; (B) Dark Indian red	
			Shaken blood (broken fibrin)		(A) Slightly darker Indian red; (B) Dark Indian red	

Table 3.2 (Cont.): Speculative investigations into the nature of paint composition.

COLOUR	PIGMENT	MEDIA	TECHNIQUE/COMMENT	TEST EMPLOYED	FINDING	REFERENCE
Red	Red Ochre	Water	-	Applied to coarse-grained quartzitic sandstone that was kept out of direct sunlight and rain. A Pelikan paint colour chart was used to identify the colours. Colours were recorded at 18 March 1980 (A) and 18 May 1982 (B)	(A) Light Indian red; (B) Very pale red stain	Rudner (1983) Cont.
		Fat	Applied well		(A) Dark burnt sienna; (B) Darker Indian red	
		Water and fat	Applied well		(A) Burnt sienna; (B) Indian red	
Yellow	Yellow ochre	Water	-		(A) Light yellow ochre; (B) Almost invisible yellowish stain	
		Fat	Applied well		(A) Dark yellow ochre; (B) Dark yellow ochre	
		Water and fat	Applied well		(A) Yellow ochre; (B) Yellow ochre	
Black	Coarse specularite	Water	-		(A) Light grey; (B) Almost invisible reddish stain	
		Fat	Applied well		(A) Charcoal; (B) Charcoal	
		Water and fat	Applied well		(A) Light charcoal; (B) Charcoal	
	Fine specularite	Water	-		(A) Light grey; (B) Almost invisible reddish stain	
		Fat	Applied well		(A) Charcoal; (B) Charcoal	
		Water and fat	Applied well		(A) Light charcoal; (B) Blotchy transparent charcoal	
Red	Red ochre	Blood emulsified fat	Painted onto a stable sandstone surface	Three tests were performed: (1) Covered throughout (Blank); (2) Water abraded for 5 seconds; (3) Water abraded for a further 10 seconds and allowed to dry. This was then sand abraded for 3 seconds.	Deteriorated badly with abrasion	Basset (2001)
		Egg emulsified fat			Most resilient	
		Water			Had quickest and greatest rate of deterioration	
		Egg and blood			Rapid deterioration during second wetting. Seems the egg softened after first wetting	
		Gall emulsified fat			Most resilient	
		Blood + gall emulsified fat			Showed small signs of decay during second wetting	

The accounts in which the results of these early experiments are discussed are given below:

Moszeik, (1910: cited in Rudner, 1982):

A chemist made tests on scrapings from badly preserved paintings from various sites. It was determined that all the colours, with the exception of black, originated from earth pigments. Red and brown were from ‘Bolus’ (coloured clay containing Fe oxides) and haematite; yellow was ‘Fe ochre’; white was Zn oxide; black was charcoal. Thus Moszeik believed that, in the areas of sampling at least, only inorganic pigments were utilised in the San paint manufacture (also see Table 3.2).

Pérenguey to Daily Dispatch, 18 May 1913, South African Museum Correspondence (cited in Rudner, 1982):

‘An analysis of the red material of some of our paintings at the Museum has shown that oxide of iron and not blood was utilised for the red paint.’

J. Muller to Pérenguey, 24 January 1914, South African Museum Correspondence (cited in Rudner, 1982):

J. Muller was the Assistant Government Analyst at the Government Chemical Laboratory in Cape Town. He submitted to Pérenguey an ‘…analysis of a certain native paint adhering to a slab of slate and also pieces of haematite’. The slab of slate (No. 33) had a red coating of variable thickness of Fe oxide. ‘Some of the paint was removed and carefully examined for the presence of oil or resin with the result that although a fairly considerable proportion of organic matter was found to be present, it is quite impossible to determine its exact origin.’ The mineral pieces were crystalline haematite (also see Table 3.2).

Willcox (1956):

‘…and an analysis done at the University of the Witwatersrand shows a high nitrogen content, consistent with urine having been the medium of the sample.’

How (1970) (originally conducted in 1962):

Samples of the red pigment *Quang Quang* were sent to Mr B. Uranovsky at the South African Council for Scientific and Industrial Research (CSIR) in Pretoria. He found that the sample contained haematite, and mixed hydrated Fe oxides e.g., limonite and goethite. The presence of hydrated Fe oxides was determined using differential thermal analysis.

A sample of the white clay (*phepha*) was also sent and analysed, and it was found to contain: SiO_2, plus insolubles (large); Fe_2O_3 (possibly including some Al_2O_3) (slight to fair); CaO (slight); MgO (nil); and sulphate (slight) (the brackets indicate the percentage presence of each mineral). Mr Uranovsky stated that this white pigment '…is clearly largely silica (a fine sand with clay material). I am frankly doubtful whether it could form a good white pigment as the covering power of such material is very limited. It is also difficult to grind such material very finely. If, therefore, it has been used by the bushmen as a white pigment, it may explain some of the poor results that have been observed with white as far as clarity and durability are concerned.'

3.5 ARTEFACT SOURCING STUDIES WITHIN SOUTHERN AFRICA

The accounts reviewed below represent the only intensive scientific investigations (of which the author is aware at the time of submission) to have been conducted within southern Africa specifically investigating the composition of San rock art paints and pigments. A majority of these accounts are focussed primarily on the characterisation of the paints (either exclusively the organic or inorganic fractions), with only one paper (Hughes and Solomon, 2000) attempting to source the inorganic pigments suspected of being used. With only three reports (one of which is from Namibia) and seven papers having been produced (again, one from Namibia), it is clear to see that this avenue of research is still in its infancy within southern Africa.

In addition, one paper looking at the sourcing of pottery sherds has also been reviewed. Although the topic discussed is far removed from San paint analysis, it does represent an example of the successful use of the methodology adopted within this study, and highlights its applicability for archaeological studies in general within South Africa.

3.5.1 Investigations of rock paintings within southern Africa using chromatographic analysis of albuminous binding media (Denninger, 1962; 1966a; 1966b; 1971)

Dr. E. Denninger conducted a series of analyses on paint samples gathered from throughout southern Africa between the years 1962 and 1966. The aim of these studies was to identify both the media with which the paints were painted and the dates thereof. A fundamental premise of this research was that all prehistoric rock art paintings were originally created with paints containing both pigments and binding media, and that these media would contain albuminous proteins (Denninger, 1962). A second premise was that 10 specific amino acids would be present within a fresh albuminous fraction, and that these would decay at a steady, predetermined rate (Table 3.3).

Table 3.3: Relative ages based on amino acid content (Denninger, 1962; 1971).

NUMBER OF AMINO ACIDS	APPROXIMATE AGE (YEARS)		APPROXIMATE TOLERANCES (± VALUES)	
	1962	1971	1962	1971
10	-	10	-	5
9	-	-	-	-
8	-	20	-	10
7	-	40	-	10
6	50	60	25	20
5	100	100	50	20
4	200	200	75	50
3	350	400	100	100
2	600	800	300	200
1	1500	1500	500	300
0	> 2000	> 2000	-	-

With the use of chromatographic analysis, the number of these amino acids within a paint sample would be determined, and this in turn would provide a date estimate for the painting (up to a maximum of 2 000 years). This assumption was based on the trend derived from the results obtained from the analyses of a large number of fixatives of known ages (Denninger, 1962). Should no amino acids be found, then the paint sample either did not contain amino acids originally, or the paintings were older than 2 000 years. Denninger (1962) believed the latter to be the case.

Unfortunately, the technique is not specific enough to allow the accurate identification of the albuminous media. These could be sourced from a number of products including milk, casein (as calcium casein or casein distemper), animal glue (as calcium glue compounds), egg proteins (either as egg white or egg distemper), blood and blood serum (fibrin) (Denninger, 1962), and vegetable albumen (e.g. the sap of *Euphorbiaceae*) (Denninger, 1966a). The classification of the binding media was determined via a process of elimination based on the differences in the composition of these albuminous products. For example, if no lime was found within the paintings, then media that contain lime such as calcium casein or animal glues containing calcium glue compounds would be eliminated from the list of possible albuminous compounds (Denninger, 1962). Denninger (1962) also automatically discounted egg whites as a possible source of albumen, stating "…their binding media is not resistant to solution by water to the degree required for the preservation of paintings on outdoor sites". By following this process of elimination and assumption, Denninger (1962; 1966b) concluded that the only albuminous media that would be present within prehistoric rock art would be either blood or blood serum, although in one case in KwaZulu-Natal, amino acids not present within blood were found (Denninger, 1966a).

In order for the rate of amino acid decay to be constant, no strong external influences, either climatological or biological, should have interfered with the 'natural' rate of degeneration of the amino acids present within the paints (Denninger, 1966a; 1971). Any deviance would result in the ‘premature’ loss of the amino acids, resulting in older dates being determined, and subsequently would result in the faster deterioration of the painted image. It is known, however, that each site, and indeed each painting within each site, may be subject to variable climatological and biological influences (e.g. some are exposed to sunlight, others are not; some receive more surface moisture than others, etc.), and so this assumption cannot be guaranteed. As additional influencing factors, fire events, which are relatively frequent in most of the regions within which the painted shelters are located, could also have a detrimental effect on the rate of amino acid decay. Furthermore, many accounts exist of early explorers and archaeologists wetting the images in order to see them better or to photograph them. It is this latter practice that has been blamed in part for the loss/fading of previously bright images, and it is for this reason that this practice is no longer condoned. No allowance for these potential influences was made.

Denninger (1966a; 1971) found that most paintings within Namibia and South Africa are covered with sintered layers that consisted exclusively of silica or hydrated silica (see Sections 3.5.3 and 3.5.8). He claimed that these sintered films protected the paintings, resulting in the rate of amino acid decay not being overly influenced in almost all cases (Denninger, 1971). Unfortunately, in earlier reports, he mentioned that a majority of these protective films are composed of $CaCO_3$ (Denninger, 1962). This material is more soluble than a pure silica skin, and thus the level of protection afforded the paintings would be greatly reduced.

In order to justify the method, comparisons of the chromatographic dates obtained from images of ‘known’ age were conducted, examples of which include imagery of Voortrekker troops (± 1 850 A.D. - western Cape) and a three-masted galleon (between 1 600 and 1 800 A.D. - western Cape). As a majority of the results produced dates of similar antiquity to the accepted time periods associated with the sampled images, the method’s accuracy was accepted (see results summary in Appendix 3.1).

Two problems with this approach are apparent. Firstly, as all the colonial imagery found in southern Africa can only be dated back as far as 450 years, these tests effectively reflect the precision of the method as opposed to its applicability for dating older imagery. As can be seen in Table 3.3, the dates derived from the first six amino acids are relatively close to one another. When one takes into consideration the error values associated with each date, a certain degree of overlap can occur e.g., seven amino acids give an associated date of 40 ± 10 years whilst six amino acids infer a date of 60 ± 20 years. In addition, as the amino acid numbers decrease (counts of four and lower), the associated error increases, yet certain dates are not included at all e.g. two amino acids reflect a date of 800 ± 200 years, whilst one amino acid infers a date of 1 500 ± 300 years. When taking the high and low error factors into account for these two dates, respectively, the 200 years between 1 000 to 1 200 A.D. remain unaccounted for. A reliable dating technique should not have ‘time gaps’ associated with it.

Secondly, the paintings of ‘known’ age are actually just estimates with a predetermined age limit i.e., just because horses were introduced into KwaZulu-Natal 200 years ago does not mean that the paintings were executed then. The possibly does exist that the images were created within only the last 100 years. Without the support of dates using another technique (such as ^{14}C dating), the accuracy of the method cannot be adequately determined.

3.5.2 The feasibility of dating rock paintings from Brandberg, Namibia, with ^{14}C (Conard *et al*., 1988)

As the title of the paper implies, this study looked into the feasibility of ^{14}C rock painting dating by photo-electron spectroscopy analysis. The project was initiated in an attempt to address the question of ‘how old are the paintings?’, a subject about which very little was known. The project approach was formulated on, and supported by, the information obtained from both ethnographic sources and the Denninger reports (Sections 3.2 and 3.5.1, respectively). Five samples of red, pink and yellow paint were analysed (H. Pager collected the samples from the Brandberg in 1983). The selection of the samples was considered to be ideal for two reasons: a) all of the paints were on granite (no C present), and b) the paintings selected were particularly significant to the development of a chronological sequence in the area.

The technique is destructive, involving the sputtering away of successive layers of material. It is estimated that, after half an hour of sputtering, approximately 50 nm of surface material will be removed. The approach does have certain advantages, however, the main one being that changes in paint composition with depth can be noted. In the case of the five samples tested, all showed a significant decrease in C content with increasing depth, quickly reaching background levels i.e., no noticeable C presence. The surface C levels were in agreement with normal surface C contamination levels.

In order to validate the results obtained, the red and yellow samples, and an additional black sample (also obtained from the Brandberg), were analysed using gas chromatography for the presence of amino acids and fatty acids. The amino acid tests for all three samples were negative at the microgram level. The fatty acid tests showed that little to no fatty acids were present within the three samples tested: the red sample came back negative, whilst the yellow and black samples contained minute quantities of materials that reacted like fatty acids (although the detectable presence was so small as to be negligible).

The end conclusion was that the paintings of the Brandberg do not contain an organic component. It was suggested that if proteinaceous substances or lipids had been used in the preparation of the paints, they would still have been present, for the arid climate, within which the paintings are located, is not conducive to the rapid degeneration of these products. ^{14}C dating was thus not considered feasible.

This paper adequately highlights some very important problems with our current understanding of rock art pigment composition today. The ‘knowledge’ of today is very subjective and contradictory, as Sections 3.2 and 3.3 have shown, but most accounts are in agreement with the fact that organic binders/media were used in the manufacture of the paints. The results of this paper suggest otherwise. However, to view these results as definitive proof that organic components were never used in the manufacture of rock art paints would be equally problematic – B. Williamson has subsequently detected the presence of blood within paints collected from Rose Cottage (see Section 3.5.8). The logical assumption, therefore, is that different 'recipes' were used in different areas, with the recipes being determined by a combination of factors, including material availability and cultural practice.

Some important information was not declared within this paper, the most notable being the location of the paint samples analysed. A comparison between these samples, their locality and composition, versus those analysed by Denninger in the 1960's could have produced some interesting information, and could have supported or refuted the Denninger reports (see Section 3.5.1). Changes in paint recipes over short distances are not impossible, and could represent changes in painting periods and/or cultures (see Sections 3.6.1, 3.6.2 and 3.6.3). It is only with more sampling (associated with a comprehensive methodology and advanced techniques) that this question can ever be addressed in any meaningful manner.

3.5.3 Analysis of rock art pigments using X-ray fluorescence spectrometry (Van Rijssen, 1990)

The aim of this study was to determine the elemental composition of South African rock art paints and raw pigmentaceous materials. A scanning electron microscope (SEM) was used to analyse a total of 35 samples that originated from a variety of locations in the south-western Cape and Eastern Cape Provinces and Lesotho[1]. The technique allows for the detection of all the elements with atomic numbers greater than 11, with the restriction that they constitute a weight percentage greater than the minimum detection limit (0.1 %). In order to reduce the amount of inherent error associated with the elemental recording (the relative errors were increased as the samples were neither homogeneous nor flat), several analyses were conducted, with the results being averaged.

The elements were given in the form of weight percentages. The results for each sample were then compared with one another, with reference being given to the original recorded colour. Conclusions were drawn solely by visual comparisons between the results. The conclusions as to the composition of the different coloured paint pigments were that red and yellow were sourced from clays coloured with iron oxides; black was derived from manganese oxides and not from charcoal; and white was from clays. It is interesting to note the relatively high Ca and P content present in about

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[1] The two 'Lesotho' samples are from paintings now residing in the South African Museum, Cape Town, and originate from the Maclear District in the Eastern Cape. All the western Cape paint samples were collected from sites in the Cedarberg region, as well as from south of Vanrhynsdorp. The exact locations of each paint sample could not, however, be determined (Van Rijssen, via Wilson, pers. comm., 2004).

a third of the samples analysed (this trend was also noted within the current study). Gypsum was observed under high magnification in some of the paints analysed.

Several criticisms against this paper can be raised, the primary one being that most of the conclusions were based on a visual assessment of the results. No statistical techniques were used to highlight the inherent differences in composition that could be expected to occur between the paint samples. Instead, the author chose to look first at the recorded colours and then proceeded to look for ‘visual’ differences between the respective results. Statistical tests could also have been used to show if paint pigment composition varied between different regions (see Section 6.2.6 for the results of the PCA analysis of this data).

Although the possibility of geological and/or biological ‘contamination’ of the samples was discussed, no blank analyses were studied in order to either confirm or refute this as a possible influence on the paint sample readings. Also, presence/absence of certain elements could have resulted from the geological substrate specific to each sample.

Unfortunately, without any analyses detailing the full mineralogical and elemental composition of these paints, the suggestions made within this study with regards to the sources of the colours remain hypothetical (compare with the findings in Section 3.5.5). No set method for paint manufacture has been defined, although several possible methods have been indicated (Rudner, 1982). As no precise source can be determined (particularly with respect to both the white and black pigments), it is suggested that no hypotheses about their sources can be definitively put forward.

3.5.4 An investigation into the Coldstream Stone (Wilson *et al*., 1990)

This study aimed to authenticate an unusually well preserved, polychrome painted stone, recovered from a cave in the south-western Cape Province, using EDX. The experimental design that was employed in the previous example was also used within this study, as the same restrictions applied.

It was suggested that the white pigment was sourced from a marine shell (due to its relatively high Ca content). Comparative tests were conducted between the white pigments and a single marine shell, with the results strongly indicating the use of this resource in the pigment manufacture. Though possible sources of the black pigments were not indicated by the results, it was shown that the pigments were not derived from Mn-based compounds. It is interesting to note that the black pigment also showed a high Ca content. These data were compared with that of a black paint sample taken from the Cederberg. The latter contained almost no Ca, thus showing that either the two pigments were clearly from different sources, the recipe for their manufacture differed with distance, or the coastal site experienced secondary Ca deposition whilst the Cederberg did not. The black samples were also compared with data obtained from burnt mammal bone, but this too proved to be distinctly different in composition and was thus not considered to be the source of the pigment.

The red hue was determined to be related to Fe content. It is interesting to note that the four red samples contained almost no Ca. The authors could not explain the variability in Ca concentration within and between the paint samples. Two possible explanations can, however, be postulated: a) different paint recipes were used for each image; and b) the various Ca concentrations reflect variable deposition. Further investigations are required in order to clarify this phenomenon.

Two ochre samples excavated from the cave were also analysed so that a comparison between the possible red ochre sources and the red paint pigments could be achieved. The ochre samples were selected after visually comparing the sample's colour to that of the red pigment. Both samples were found to vary distinctly from the paints in most respects. A possible reason for this might lie in the manner in which the samples were initially selected. Had the 'crushed' colour of the samples been used to compare the samples with the pigments, as opposed to the 'solid' colour, a closer match might have been found.

Though a limited database of elements was created with this technique, this study did show the usefulness of using elemental compositions of artefacts as a means of either confirming or disputing the authenticity thereof. A statistical analysis of the results would have highlighted the degree to which the samples were related to one another, however.

3.5.5 A nuclear analytical study of rock paintings (Peisach *et al*., 1991a)

This paper determined the nature of an exfoliated fragment of rock painting (gathered from Ha Khotso Shelter in Lesotho) in order to gain insights on how to conserve the rock art. Differentiated backscatter spectrometry was used to determine the paint thickness, and the elemental composition of the sample was determined by particle induced X-ray emission (PIXE). It was found that the paint sample contained very high concentrations of Fe and Ca, both of which affected the other readings. An absorber was used in order to reduce these counts, as well as to eliminate the low energy X-rays (e.g. from Si, a major matrix component).

Correspondence analysis was then conducted on the results obtained, and three distinct groups distinguished, namely Fe, Ca, and Mn. The points located near the Mn group represented all the sites on the substrate that did not contain any paint. Those points located near the Ca group represented the paint areas of lighter colour, whilst those near the Fe group contained the darkest coloured paint.

Suggestions as to the sources for the different colours were as follows: red was Fe-rich, probably obtained from iron ores; the white was Ca-rich, indicating that it was probably composed of an admixture of ground sea shells; the black pigment was either Mn-rich, indicating its source as being manganese ores, or Ca-rich, indicating its origin as being from burnt bones or sea shells (compare with Sections 3.5.3 and 3.5.4). It was further suggested that the relatively high Ca content within the paints was of archaeological importance from a conservation point of view, for Ca is a potentially mobile element, and as such is at high risk especially in the presence of acid rain.

A singular criticism is that no data were presented indicating which elements were present, nor were their associated relative percentage compositions given. Also only one paint sample was analysed, thus allowing for no comparisons. If this paper's aim was to evaluate the use of PIXE as a technique to determine the elemental composition of rock art pigments, this could be justified. The stated aim of the paper was, however, to determine the elemental composition of the sample so that possible focus areas for the conservation of rock art might be discovered. The analysis of a single paint sample cannot form the basis for an approach to conservation of all rock art paintings. As had been indicated in the previous paper, paint samples can differ in composition not only between colours, but also between locations. There are therefore not enough data to draw any positive conclusions on either topic.

It was mentioned that the high Fe (and Ca) content affected the ability of the technique to analyse the sample. It is widely accepted that most rock art paintings contain relatively high Fe contents with the red hue being due to the presence of haematite. Though no indication is given as to how great an effect either the absorber or the high Fe and Ca contents had on the determination of the remaining elements, the fact that an absorber had to be used in order for elemental readings to be captured indicates that further work dealing with the technical aspects of this technique is required in order to confirm its appropriateness for the study and analysis of rock art (or pigment) elemental compositions.

Finally, it is not known in what mineralogical form the Ca is contained within the pigment. Furthermore, no data showing that this element was present exclusively within the lighter colours were given (it might have been present across the rock surface, but at lower concentrations). Until these facts are known, no accurate predictions as to how this element will react can be stated. Acid rain is not a man-made phenomena (though its frequency/strength has increased markedly since industrialisation), thus the painting would have been subjected to this form of weathering for the total period of time since its completion (via acids such as carbonic acid). If the Ca was very mobile, theoretically the values recorded should not be high. Before it can be stated that a focus on Ca should be instigated in order to preserve South African rock art, further comprehensive studies into the composition, both mineralogical and elemental, of various pigments should be undertaken. It must be remembered that the Ca could be present due to deposition on the rock surface via natural weathering processes subsequent to the painting event (see Appendix 3.2).

3.5.6 Analytical study of pottery from Soutpansberg (Peisach *et al.*, 1991b)

This paper aimed to try and understand the interaction(s) that might have existed between the historical communities that were located in the greater Soutpansberg area. It is known that the communities did indeed interact, as is evidenced by the sharing of certain linguistic traits and oral customs, but the extent of this interaction is unknown. In order to achieve this, this study looked at the style and geochemical composition of potsherds found on both sides of the Soutpansberg range, to determine if the interaction was in the form of either physical trade or the exchanging of ideas (represented in pottery style), or both.

Seven different pottery styles have been identified from the Soutpansberg region: three from the north and two from the south of the mountain range, whilst two were found to be regional. Occasionally, examples of both the northern and southern pottery were ‘transposed’, indicating some form of cultural exchange. By analysing the potsherds’ individual geochemistry, as well as a few ‘standards’ obtained from the areas concerned, it was possible to differentiate between pottery manufactured north and south of the Soutpansberg range, with the mean values of K, Ca and Zr higher in the northern samples, and Cr and Ni higher in the southern samples.

When comparing these findings with knowledge of the stylistic origins of the pottery, a four-phase model for ‘trade’ patterns was established (Table 3.4). This paper showed how a detailed knowledge of artefact geochemistry is invaluable in their sourcing. It also highlighted how this knowledge can be manipulated in order to understand abstract concepts such as trade, inter-population interactions and knowledge/idea movements. The methodology employed thus represents a very powerful tool for archaeologists.

Table 3.4: Model for ‘trade’ patterns (Peisach *et al.*, 1991b).

Case	Site of Manufacture	Site of Discovery	Regional Style	Comment
I	A	A	A	No interactional movement
II	A	B	A	Movement of artefact A ⇒ B
III	A	A	B	Movement of idea B ⇒ A
IV	A	B	B	Complex movement, Idea B ⇒ A then artefact A ⇒ B

3.5.7 A preliminary study of ochres and pigmentaceous materials from KwaZulu-Natal, South Africa: towards an understanding of San pigment and paint use (Hughes and Solomon, 2000)

In this paper, a variety of samples from geographically diverse locations were physically, mineralogically and chemically compared in order to determine the degree of diversity that they might exhibit. In order to do this, a large number of techniques were employed, namely: physical (colour, hardness, streak), chemical (organic carbon, extractable iron, aluminium, and manganese; total major and minor elements using XRF; major elemental analysis using EDX), and mineralogical ((XRD) and transmission and scanning electron microscopy (TEM and SEM, respectively)). With the exception of the physical descriptors, the data were analysed using PCA.

The results can be summarized briefly as follows:

Physical data: Most of the samples, despite their spatial variability, tended to display similar characteristics with respect to their physical descriptions, and as a result these data were no longer considered within the study.

Mineralogical data: Sample morphology was studied using TEM. The angular and platy nature of many of the particles in all the samples was noticeable, as was the extremely small size of most of the individual particles. Only one sample was found to be morphologically unique (yellow infilling from a snuffbox shale[1] sample). This sample was found to contain a large quantity of tubular material.

Chemical data: The elemental composition of the samples was determined by both EDX and XRF. Using EDX, the tubular material found in the snuffbox shale was determined to be halloysite (consisted only of Si and Al). It was further noted that the infilling also contained the rare earth, holmium. The other samples were shown to be comprised of a combination of all or some of the following: haematite, mica, feldspar, or kaolinite.

Statistical interpretation The major and minor elemental data (from XRF) were analysed separately with the separation based on the nature of the data (weight percentage and parts per million (ppm), respectively). The analysis of the major elements showed that PCA axis 1 (50 %) and 2 (17 %) represented 67 % of the total variance. PCA1 was strongly related to rock type, whilst PCA2 was related to both silica and clay content.

The minor elemental analyses showed that PCA1 (32 %) and PCA2 (21 %) represented 53 % of the total variance. PCA1 was related positively to copper, nickel, and cobalt, and negatively to fluorine. PCA2 was strongly related to niobium, and less strongly with zirconium, thorium, and cerium. Though it can be seen that rock type still plays a dominant role in PCA1, it is less clear as to what specific characteristic is driving the separation of PCA2.

On the whole, the results obtained show that each of the samples is relatively distinct. Even samples obtained from the same basic rock type (e.g. dolerite) were shown to be similar in some ways and different in others, thus highlighting the applicability of this methodology to separate out samples according to their original geographical position. Essential to this process is, however, the use of a number of techniques in conjunction with one another in order to analyse the data holistically. Not all the techniques used were shown to be applicable, however. The key characteristics for the

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[1] Originally a typical shale, Fe deposits, initially in the form of pyrite, are deposited along the fracture and bedding planes within the shale body. Over time, this forms a solid ‘wall’ or ‘box’ of iron oxides and hydroxides around the remaining shale material. This latter material continues to weather *in situ* within the solid confines of the iron boundary, often forming a core of fine, brightly coloured powder, generally red, yellow or orange in colour, although white powders have been noted.

identification of separate sources of samples are mineralogical and, especially, chemical in nature. Information as to the physical nature of the samples only became important when the data were to be analysed using PCA.

Though the methodology established within this paper has been shown to be viable, the extent of this viability has yet to be determined. The analysis of several samples from the same rock type at one geographical point would have shown the degree of variability within individual rock sources. This would have great implications for the reliability of any future findings. This paper seems to have assumed that individual rock sources display relatively uniform mineralogical and chemical characteristics throughout their matrices. Though this assumption can be considered to be valid for primary rock materials such as lava flows (see Section 3.6.6), less is known about the variation within deposited secondary rock/ochre sources. This requires further investigation.

3.5.8 Direct testing of rock painting pigments for traces of haemoglobin at Rose Cottage Cave, South Africa (Williamson, 2000)

The purpose of this investigation was to test for the presence of haemoglobin in rock art pigments; specifically those from Rose Cottage Cave, South Africa. The Hemastix® test[1], a colorimetric test used successfully for the determination of the presence of blood in a variety of disciplines such as medicine and archaeology (blood residue detection on stone tools), and which has a sensitivity of 0.15 – 0.62 ng/µl, was used. In addition to these factors, this test was chosen because it is easy to use, can be carried out on site, and requires a minute sample upon which a determination can be made, the latter resulting in very little damage to the painted surface.

The Hemastix® test strips specifically react with the heme units of both the haemoglobin and myoglobin molecules within blood residue, a positive reading indicated by a changing of colour. Unfortunately, the reagents also react with positively charged metal ions (e.g. Mn, Cu, Mg), as well as the Mg porphyrin ring in chlorophyll and its breakdown products (common sources of which include lichens, cyanobacteria, and short lived vegetable and bacterial peroxidases). These 'false-positives' can, however, be corrected for with a minor adjustment to the pre-treatment of the sample prior to a second round of testing. As a consequence, samples that show positive readings in both the initial and the subsequent 'false-positive' correction tests are considered to contain the heme unit (called 'true positives'). Conversely, a positive then negative result would indicate the presence of either soluble cations or chlorophyll and short-lived peroxidases. In either case, the samples must be closely examined for the presence of biological growths prior to testing. The Rose Cottage samples were determined to be 'uncontaminated'.

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[1] Also known as "Labstix", is available from Bayer Diagnostics, South Africa.

Two methods of sampling were employed. The ‘Direct test’ involved the application of 10 – 20 µl of ultra-pure deionised water directly on to a 1 cm^2 area of the pigment. This was agitated with a pipette tip, and the sample (in the water) was then extracted and applied to the Hemastix® test strip. The reaction time of 60 seconds was allowed, after which a score was taken (negative; trace - ~ 150 ng/µl; positive-range of between +1 and +5 (up to ~ 620 ng/µl). In cases in which the rock surface was too porous to allow for the sample extraction, a second sampling method was employed.

The ‘Scraping and Hydration test’ involved the use of a sterilised scalpel to scrape a few mg of sample into a vial. The sample was then hydrated with 10 µl ultra-pure deionised water for one hour, after which a 5 µl aliquot was applied to the Hemastix® test strip. The remaining 5µl was kept for future analyses.

In total, 11 samples (eight red, one yellow and two black) gave negative results. Four samples (all yellow) received ratings as follows: trace, +1, +2 and +5. The latter two samples were confirmed as true positives after re-testing for ‘false positive’ results. These samples were submitted for further analysis in order to determine from which species the blood originated. The former two samples did not pass both tests. Two possible reasons exist: 1) biological contaminants were present within the sample, or 2) not enough detectable heme was present within the second (diluted) test. These results do, however, highlight the efficiency of this two-phase testing regime in the screening of samples for further analysis that is both more time consuming and costly.

At the outset, it was stated that this was merely an investigation into the validity of this form of scientific approach. It was not meant to represent a comprehensive analysis of the composition of rock art pigments. The findings do, however, lead to many additional questions. The only pigments that showed a strongly positive reaction were yellow. All previous references to blood being used as an additive/fixative have generally involved red pigments (see Sections 3.2 and 3.3). Although no answers could be given as to why the results reflected this finding, several hypotheses were suggested. These included (square brackets indicate my comments):

- different recipes were used with differing amounts of blood;
- different images may have been imbued with additional “power” through the addition of blood to the paint;
- yellow paint may have needed the addition of blood because it lacked the appearance of blood natural to red pigment [heat modification could have been more practical];
- there may have been regional variability due to ethnic/language group variations and different beliefs;
- practically – the binding properties of the blood might have been required for the yellow pigments and not for the other pigments; and
- [the heme units were not detected within the other samples as they have decayed away i.e., the images are too old].

The findings of this study highlight a new avenue of research (looked at only once before - see Section 3.5.1) with a technique that is easy to use, can be used on site, and requires minimal sample in order to work (virtually no impact on the painted image). Follow-up studies, looking at additional sites both within the vicinity of Rose Cottage Cave and in regions further away, as well as a more comprehensive look at the provenancing of the DNA of the true positive samples is required i.e., the determination from which species the blood originated. Further work looking at the stability of heme units in exposed environments (especially the effects of fire, water, biological interaction, etc.) is also required. It is interesting to note that Rose Cottage Cave is located in Region 3 (see Map 3.2), the region in which all ethnological accounts of the use of blood as a paint medium have been collected (see Section 3.2).

3.5.9 Dating rock paintings in the uKhahlamba-Drakensberg and the Biggarsberg, KwaZulu-Natal, South Africa (Mazel and Watchman, 2003)

The aim of this paper was to determine ^{14}C dates for selected San rock art pigments, and thus improve our chronological knowledge of San rock art. As previous attempts at dating San paintings using conventional ^{14}C dating techniques have proved less than satisfactory, this paper proposed the new approach of dating the Ca-oxalate crusts, whewellite and/or weddellite, which are associated with a majority of the prehistoric paintings. Ideally, an over- and underlying Ca-oxalate layer would be dated, thus providing a minimum/maximum date range for the painting. Unfortunately, the majority of images only displayed a surface layer, and thus only minimum dates could be determined (of the 32 samples collected, only six contained underlying crusts).

Fifteen paint samples[1] were collected from Main Caves North, Blesbok Paddock, Highmoor 1 and White Elephant Shelters in the uKhahlamba-Drakensberg region, with an additional four samples collected from MQ in the eastern Biggarsberg. The selection of samples, which consisted of partly detached flakes of encrusted sandstone, was on the basis of motif and "…on appropriateness for sample removal." The samples were analysed using a range of techniques, including petrographic analysis, SEM fitted with EDX (for major elemental determination), and XRD (GADDS, to determine mineralogy).

Sub-samples were placed in rapidly curing epoxy resin, and then cut and polished as a cross-section. The mineralogy, inorganic chemistry and thickness of the faded paintings, mineral coating and rock type were then determined. For ^{14}C dating, a large flake of the sample was selected and cut into slices (not in resin) to expose the layers of paint and crust minerals. The carbon within the crust layers was then removed using both chemical oxidation and focussed laser extraction techniques

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[1] In fact, 32 samples were collected from all of the shelters mentioned, 19 of these were sent for ^{14}C dating, but only eight were actually dated. Six of these dates were obtained for the only six samples displaying underlying Ca-oxalate crusts (according to Table 1 in the original text).

(FLECS). The carbon produced was then dated using accelerator mass spectroscopy (AMS). Both of these methods produced ^{14}C dates, which were then averaged to provide a mean date for the formation of the Ca-oxalate salts.

All of the samples were analysed mineralogically, although the results obtained were not discussed. Minerals common to almost all of the samples were gypsum, quartz, whewellite, and to a lesser extent albite and haematite. Quartz and albite probably originate from the underlying rock substrate, whilst gypsum is a natural, depositional mineral in caves (Mazel and Watchman, 2003). As haematite was only detected in samples that were either dark-red to maroon in colour, it probably originates from the paint. What is interesting to note is that of the six instances in which haematite was detected, only one of these samples contained whewellite, indicating either that this mineral was not part of the original paint and/or that the whewellite had not begun to form on, or has been lost from, these samples. None of these samples was dated.

Two minimum dates were obtained for Barnes and White Elephant Shelters (1 060 ± 65 years b.p.[1] and 1 930 ± 65 years b.p., respectively). As no date for an underlying layer was determined, there is no way to tell just when these images were painted.

Two maximum dates were collected from Highmoor 1 Shelter, namely 2 310 ± 70 and 2 770 ± 75 years b.p. Maqonqo Shelter produced a maximum date of 3 720 ± 100 years b.p. Three maximum dates were obtained from Main Caves North, namely 2 360 ± 70, 2 900 ± 80 and 2760 ± 75 years b.p., the latter two being derived from different parts of the same image. The relative similarity in the latter two dates (a difference of only ± 240 years) was used to support the use of this technique as a viable method of indirect rock art dating.

As the time lapse between Ca-oxalate formation and painting is unknown, it is impossible to know just when these images were painted. In order to answer this question, the origin of the Ca-oxalate salts needs to be known, for this will affect both depositional rates and periods of deposition i.e., is this a continuous process, or can it be linked to specific events (changes in temperature and/or humidity)? In studies in Australia, it has been determined that the stable carbon isotope values for Ca-oxalates averaged –15 %o for micro-organic processes related to fungal and bacterial growth (Mazel and Watchman, 2003). Ca-oxalate salts formed from solutions permeating through the rock substrate generally display stable isotopic values that are more positive. The authors state that the stable C isotope values determined within this study indicate the former process and thus supports their claim that the Ca-oxalates are derived via microbial action and not, as is in the case of other studies (e.g. Russ *et al.*, 1995; 1996), via lichen action. The data to support this contention were not provided, however. To the best of my knowledge, no work on the formation of Ca-oxalates on rock walls has

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[1] b.p. refers to 'before present', with 'present' being set at 1950. This was to ensure that all historical dates mentioned within a paper have a fixed 'starting' date. In this way, dates presented in a paper can be correctly interpreted even if the paper is read several years after initial publication. Conventionally, B.P. is used to represent calibrated radiocarbon dates, whilst b.p. represents uncalibrated dates.

been conducted in South Africa. It is therefore possible that the factors controlling Ca-oxalate production could be different than those documented in other countries/continents. Only with further studies in this field will the pathways involved be fully understood.

This said, the authors concluded that the Ca-oxalate salts detected in the South African environment were produced via microbial action. A further inferred assumption made by the authors was that the process of Ca-oxalate formation (within the shelters investigated) is an ongoing one, with the Ca-oxalates forming within the shelters both with or without the presence of the painted images; this deduction is based on the fact that the authors expected/hoped to find Ca-oxalate layers both above and below the painted figures. If this assumption is accepted and the process of Ca-oxalate formation is continuous (at a depositional rate of ± 5 μm per human lifetime [assumed by the author to represent between 80 and 100 years]), then theoretically the thinner the depositional layer of Ca-oxalate, the more closely the painting event and the date of the extracted Ca-oxalate are correlated i.e., one can assume that the paintings were created within a couple of hundred years of the Ca-oxalate formation.

This assumption has three associated problems, however. Firstly, if the formation of the Ca-oxalate salts is a continuous and natural event, why is it that most prehistoric images are noted as having been painted directly onto the rock substrate and not upon Ca-oxalate crusts? The most obvious answer would be that these crusts were not there. If this were so, then the next question to ask would be ‘why were underlying paint surface crusts found, but not in all cases?’ Possible explanations for this phenomenon are as follows:

- the rock was originally pre-treated. It has been suggested by a couple of informants that the rock was first prepared for painting by rubbing down the surface with a stone (F. Prins, pers. comm., 2005). It is, however, unlikely that this process would have effectively removed all of the Ca-oxalate on the rock surface, especially to the scale at which the samples were analysed;
- the Ca-oxalate crusts found might represent the remnants of much older, and highly eroded, painted images that are no longer visible i.e., the underlying crusts might actually be ‘surface crusts’ of much older, no longer identifiable, imagery; and
- different pathways result in the formation of Ca-oxalate including the micro-organic processes of cyanobacteria and fungi mentioned here. Other pathways deriving from ‘natural’ sources include natural chemical deposition (reactions of natural organic compounds in rainwater and aerosols at the rock surface), reactions of natural dissolved organic acids originating from groundwater/leaching, and micro-organic processes related to lichens. These pathways would result in the ‘selective’ deposition of Ca-oxalates within a shelter, based on micro-climate and/or water movement within the sandstone. This, however, suggests an

alternate pathway to that proposed by Mazel and Watchman (2003). Stable isotopic values for C from these surface deposits are required in order to determine if this is an accurate interpretation. The 'worst case scenario' would be that several Ca-oxalate forming pathways are found to be operating concurrently within the same shelter.

A second problem lies in the assumption that, in the few cases in which underlying crusts are present, the paintings were applied to the rock surface within a couple of hundred years of the crust formation. Following the assumption that the Ca-oxalate formation is an ongoing process, it would be reasonable to assume that surface crusts would have had an extended period of time to form prior to the painting event resulting in both a relatively 'thick' surface deposit, as well as recording very old dates. This was not noted in the samples analysed.

One could argue that successive depositional layers of Ca-oxalate were formed, but this would have a detrimental effect on the resultant ^{14}C dates – if 'old' and 'young' ^{14}C Ca-oxalate containing minerals were analysed simultaneously, one would obtain a 'blended' date[1]. Sample selection (from perceived depositional layers) and the subsequent C extraction would therefore have to be highly accurate, with a range of dates needing to be determined from a number of points within a single Ca-oxalate sample. As natural depositional events are seldom uniform or ubiquitous across a surface, the selection of representative samples could prove to be highly problematic. An example of this is the one quoted earlier within this text (it is also the one used by the authors to validate this method as a means of dating rock art). The two dates collected (2 900 ± 80 and 2 760 ± 75 years b.p., respectively), show a difference of between 0 and 295 years (taking the respective errors into account). It would be interesting to see what a third analysis would have produced.

A third problem is highlighted if one builds further upon the assumptions outlined above. To illustrate this point, I will use the ^{14}C date (2 360 ± 70 years b.p.) obtained for ANDRA 17 as an example. Assuming that the minimum age limit of 2 290 years b.p. is the actual age of the underlying oxalate crust (taking the error into account), and assuming that the painting was applied 200 years post this depositional event, then it can be determined that there is a minimum time period of about 2 000 years within which additional Ca-oxalate salts could have been deposited. At the suggested rate of 5 µm every ± 100 years, a crust layer of ± 100 µm (or 0.1 mm) should be present, more than enough sample for the techniques employed to detect. As no Ca-oxalate was detected at all, one (or both) of the assumptions must be incorrect i.e., either a) that the Ca-oxalate deposition is not continuous; or b) that the paintings were not painted that long ago.

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[1] The result would more than likely not represent an average between the two ^{14}C dates, but rather a 'blended date' dependant on the relative proportions of the ^{14}C containing minerals and their associated respective dates. The dates could therefore be highly distorted if individual phases of Ca-oxalate production are formed as opposed to a continuous Ca-oxalate deposition.

It is important to note that there was some difficultly in clearly identifying the location of some of the Ca-oxalate samples. Samples ANDRA 15 and 16 are particular cases in point, with both being stated to represent crusts extracted either beneath or above an image, dependent upon which section of the text one consults. It is therefore difficult to correctly ascertain which of these statements is correct. It has, however, been assumed that these dates represent underlying dates i.e., maximum dates.

In either respect, the predominant question to ask is 'why are Ca-oxalates predominantly found upon the paints, but not beneath them?' as was noted by the authors[1]. Two possibilities exist, either the Ca-oxalates were present within the paints (i.e., introduced within a binder and/or as a component of the source pigment) or they formed upon the paints subsequent to their completion. As the cross-sections provided within the paper strongly indicate the deposition of Ca-oxalate, the latter scenario is most likely.

The Ca-oxalate formation could be derived from the degeneration of organic constituents originally within the paint. Experimentation has shown that Ca-oxalate salts can be formed as a result of the oxidation of a wide variety of organic compounds such as gum Arabic, egg albumen, milk, and egg yolk (Cariati *et al*., 2000), most of which have been suggested in the historical records as having been used by the San (see Section 3.2). An analysis of the composition of the painted layers within the samples could have determined the presence/absence of Ca-oxalate salts, effectively addressing this possibility. In addition, the analysis of these paints would have either confirmed or denied the presence of C, thus either substantiating or refuting the authors' claim that San rock art paints do not contain organic constituents. Unfortunately these data were not determined within this paper.

In conclusion, several unsubstantiated assumptions were made during the course of this investigation. These include the following:

- painted images within a shelter are related to the excavated deposit, with the dates obtained from the excavations being used to collaborate the dates obtained from the Ca-oxalate dating results. Whilst this is a possibility, many examples exist where shelters with deposits have no paintings (e.g. Umhlatuzana Shelter[2], Mzinyashana Shelters 1 and 2[3]) and *vice versa* (e.g. Ladder Cave[4] and Esikholweni Shelter[5]). No studies clearly linking deposit material with the painted images have been produced to my knowledge, and thus, using the one dataset to substantiate the other is misleading;

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[1] A majority of the samples collected showed a Ca-oxalate presence upon the paint sample, but none beneath. However, it was only in a majority of the samples within which the Ca-oxalate was located beneath the paint sample that there was sufficient ^{14}C present to allow for a date determination.

[2] Umhlatuzana Shelter – the deposit dates back over 100 000 years, and produced tens of thousands of artefacts (Kaplan, 1989; 1990).

[3] Mzinyashana Shelters 1 and 2 – the deposit dates back about 4 200 years, and produced thousands of artefacts (Mazel, 1997).

[4] Ladder Cave, near Cathedral Peak, contains 317 paintings (Pager, 1971).

[5] Esikholweni Shelter, near Cathedral Peak, contains 542 paintings (Pager, 1971).

- it is clearly stated (with no references) that San paintings do not contain organic binders. Two studies reviewed earlier suggest otherwise (see Sections 3.5.1 and 3.5.8);
- it is inferred that all of the paintings occurred within a similar time period. In this paper, the minimum date of Ca-oxalate formation in White Elephant Shelter was used to substantiate the assumption that the paint samples obtained from Main Caves North and Highmoor 1 (maximum dates of between 2 300 and 2 900 years) predate 2 000 years. As there was no minimum date determined for these latter two shelters, this cannot be claimed; and
- it is assumed that all of the Ca-oxalate deposits are derived from the same mechanism. It is also assumed that the Ca-oxalate production pathway in South Africa is the same as that determined in Australia. Many studies (e.g. Watchman, 1990; Verrecchia *et al*., 1993; Russ *et al*., 2000) have shown that many pathways involved in Ca-oxalate production can be very specific to each area, and have been found to differ within the same site (e.g. Watchman *et al*., 2001). The only reliable manner in which the pathways can be determined is to analyse the stable isotope values for the C present within the individual oxalate salts (these data were not supplied by the authors). As no such studies have been conducted within South Africa (to the best of my knowledge), trends obtained from field data collected in Australia were used. No investigations into the nature of the shelter walls, the atmospheric moisture and elemental contents, or groundwater compositions were conducted. As a result, all assumptions relating to depositional rates and continuity of deposition, as well as the pathway(s) of Ca-oxalate formation, have to be questioned.

It may be noted that all of the maximum Ca-oxalate dates obtained within the Ukhahlamba-Drakensberg region fall within a narrow range of between 2 300 and 2 900 years. The question could be asked: Could these dates be indicative of minor climatic changes that resulted in microbiological ‘flushes’. It is interesting to note that the dates can be separated out into three periods: Period 1) 2 900 ± 80 years b.p.; Period 2) 2 770 ± 75 and 2 760 ± 75 years b.p.; and Period 3) 2 360 ± 70 and 2 310 ± 70 years b.p. Furthermore, Periods 2 and 3 are obtained from two different shelters (Main Caves North Shelter and High Moor Shelter). As all of these sites are located in close proximity to one another, climatic changes within a 15 km radius of Barnes Shelter would have affected all of the Drakensberg shelters in a similar manner. This trend, real or not, must be investigated for it has important implications for the assumption that the Ca-oxalate salts are deposited on a continuous basis – a basic premise of this paper.

Maqonqo Shelter gave a much older maximum date of 3 720 ± 100 years b.p. This shelter, however, is about 150 km from the Drakensberg shelters. As a consequence, both the geological and climatological conditions experienced are vastly different to those of the other sites studied within this paper. None of these factors were taken into account. Being at a lower altitude, located on only a very minor watershed, and far removed from the controlling effect of the maritime climate, this site is probably the most susceptible to dynamic climate changes including drought conditions; determined to be the predominant controlling factor for fungal growth, and hence Ca-oxalate production derived therefrom. Using a variety of different indicators, Partridge ***et al***. (1990) determined that the eastern region of South Africa experienced a brief period of higher temperatures and associated drier conditions about 4 000 years ago. Since this period, the temperatures have dropped to coincide with current temperature ranges, whilst the moisture regime, whilst it has been variable, has consistently maintained higher moisture levels. As this period corresponds quite closely with the date determined for MQ, this would support the theory that climatic conditions control the bloom periods for micro-organisms, and, in turn, the periods of maximum Ca-oxalate production. This is, however, just a theory, and more substantial evidence is required in order to validate/refute its conclusions.

For a more comprehensive discussion on Ca-oxalates, see Appendix 3.2.

3.6 ARTEFACT SOURCING STUDIES OUTSIDE SOUTH AFRICA

3.6.1a) Physical and chemical analysis of prehistoric paints in Cougnac Cave (Labeau, 1990)

This paper used SEM, EDX and XRD to analyse paint samples from, as well as local natural ochres associated with, the Cougnac Cave in France. It was shown that the black pigment was composed of charcoal, whilst the red pigments were composed of mixtures of quartz, haematite, calcite, minor phase kaolinite, minor element P, Ti traces and, for some paints, Mn traces.

Although this paper could not conclusively show that the locally occurring ochres and the paint pigments were one and the same, it was shown that the elemental and mineralogical compositions of both tended to occur in similar ratios. The paints seem to have had some additives mixed with them during their manufacture. Until the nature of these additives can be determined, an accurate comparison and identification of the sources of the pigments used cannot be conducted. Of interest from the perspective of the present study was the fact that P was found to be present in the paint in relatively large amounts (> 1 %).

3.6.1b) Comments on the analyses of the ochres from Cougnac (Fitte, 1990)

A continuation of the above paper, this study concentrated primarily on the nature of the locally occurring ochres that were found in the general region of the Cougnac Cave site. After characterizing the ochres, it was determined that the specific samples in question could not have been the source of the pigments used in the Cougnac Cave. This conclusion was based on several reasons, namely a) the samples were gathered from sites far removed from the cave itself; b) the geological formation from which they were derived is very hard to locate (rare) in the vicinity of the cave site; and c) the minerals revealed as traces during the analyses of the pigments belong essentially to the detrital materials of Limousin (a geological formation not locally present).

Although this study did not source the paint material, the fact that researchers can now start limiting areas from which the pigments were originally collected still provides great insight into the movements and habits of these prehistoric painters. The methodology of the study has been shown to be valid. The only 'drawbacks' to the study were the limited field sample database, and the fact that none of the data were statistically analysed.

3.6.2 Prehistoric cave painting PIXE analysis for the identification of paint "pots" (Menu and Walter, 1992)

This investigation used PIXE to analyse over 300 paint samples collected from a range of different prehistoric sites throughout the French Pyrenees. In this study, the results obtained from three of the most important sites (namely Niaux, Gargus (French Pyrenees) and Lascaux (Perigord, France)) are compared and analysed in an attempt to characterise the prehistoric rock art in relation to the early and late Magdalenian Periods. It was hoped that, by identifying the different pigments within the paintings, different pigment sources could be established. This would in turn aid in the development of a scientifically based painting chronology that could be compared with the current chronology that is based exclusively on stylistic criteria.

In order to determine the applicability of the methodology and technique to be used, an independent test was conducted using NBS standard river sediment as a test sample. Two independent samples (of the same size as the paint samples) were prepared. The first sample was stuck on scintillator foil with glue; the second was placed on Kapton foil using carbon glue. A third sample was pressed into a pellet in order to evaluate the dispersion effects of the small samples on the results. Following analysis, the results obtained from the three samples were found to be roughly consistent, proving that PIXE is sensitive enough to characterise samples of small size accurately enough to allow for accurate comparisons. The results obtained from the three sites are discussed separately below.

- <u>Niaux Cave:</u>

The samples were collected from the best-known chamber (called Salon Noir), where most of the paintings within the cave are concentrated. The initial findings indicated that the paint compositions were complex, with the pigments being mixed with mineral extenders and binders according to well-defined recipes. The analysis of the paints highlighted two principal recipes, which differed in relation to the extenders (K-feldspar or the same with excess of biotite), but associated with different kinds of pigments. The red pigments were determined to be haematite, whilst the black pigment consisted of either Mn oxides or finely ground charcoal.

In order to verify that the minute samples of paint collected did indeed represent the painting as a whole, different minute samples from the same image were collected and analysed. Consistent results between different samples verified the accuracy of the individual sample results, as well as the determination that different paint recipes were utilised.

Furthermore, it was determined that these recipes occurred in chronological order. The analysis of 10 painted artefacts from another cave (La Vache Cave) located about 150 m from Niaux Cave, revealed that only the same extender containing biotite was used with haematite for the red and Mn oxide for the black pigments. These pigments were dated from 12 850 to 11 650 years B.P. (Upper Magdalenian Period). Additional painted artefacts from two neighbouring sites (Enlène and Mas-d'Azil Caves) showed that the extenders consisted of K-feldspar alone, and were dated from 13 940 to 12 900 years B.P. (Middle Magdalenian Period). The data therefore suggest that these two periods can be identified within the paint based on extender composition.

- Lascaux Cave:

The use of quartz as a pigment extender had been suggested in a past study, but is discounted here as rather representing the contamination of the paint pigments during the grinding process. Although the use of other extenders is suggested, none are mentioned.

Instead of analysing the paintings, this study focussed mainly on the artefacts that were located in front of the painted panels, namely six black ochre pencils. The XRD analysis revealed that all of the pigments were Mn oxides of varying origin, namely pyrolusite, hollandite and psilomelane. Two of the 'pencils' were determined to be of similar origin, whilst the other four were from different sources.

- Gargas Cave:

The analysis of 35 samples from four red and black paintings led to the conclusion that the paintings were composed of pigments alone, without any extenders or binders. Furthermore, characteristic minerals were detected that might lead to the identification of the original mineral sources. Although all four paintings belong to the same panel located close to the entrance of the cave, two of the images were shown to have similar trace elemental compositions, the third image is particularly rich in clay (indicated by a high Al and Si content), whilst the fourth has less impurities and lacks Ba and aluminosilicates. Thus, three very different pigment sources are represented within only four images.

The implications of these findings are that the images were created over a much longer period of time than previously thought, with each different recipe representing a different, separate painting event.

Several differences exist between the prehistoric sites mentioned in this paper and those common to South Africa, the most obvious of which is that the French paintings are true cave paintings, whilst the San imagery is found in rock overhangs and shelters. This difference in location has important implications for both image preservation and chemical weathering. The methodology behind the characterisation of the prehistoric pigments is, however, the same for both regions, only the possible contaminants and conditions of paint preservation will differ. The methodology employed within the current investigation is identical to that used by Menu and Walter (1992), only the techniques employed differ.

3.6.3 Paint analyses from several Magdalenian Caves in the Ariège Region of France (Clottes, 1993)

This paper is based in part upon the work and data described in the investigation by Menu and Walter (1992) (Section 3.6.2). Unlike the previous investigation, however, this paper discusses the merits of both the techniques employed, together with the potential value of this form of scientific investigation in increasing our understanding of the Magdalenian artists way-of-life.

Essentially, the technical approach to paint characterisation is no different from the original method of painting classification based on a stylistic point of view. The fundamental aims of both approaches are the same, with both trying to characterise well-defined cultural and geographic groups and, more importantly, what differences exist between such groups and what those differences mean. As such, the technical approach to paint characterisation should be seen to run parallel with already established stylistic concepts, the only difference being that it would yield more precise results.

The advantage of the stylistic approach is that all images can be, and indeed have to be, analysed in order for a comprehensive interpretation of the meaning of the art to be determined. Effectively, the entire painting record can be regarded as this approach’s ‘database.’ The technical approach, on the other hand, demands that a database be created via sampling of the paint pigments. Although it is technically possible to sample and analyse pigments from a majority of the paintings, the practical limitations of both time and money, together with the knowledge that sampling causes damage to the painted image, precludes this as a viable option. As a consequence, methodological approaches have to be amended in order to attain the correct balance between minimising sampling requirements, whilst maximising information realisation.

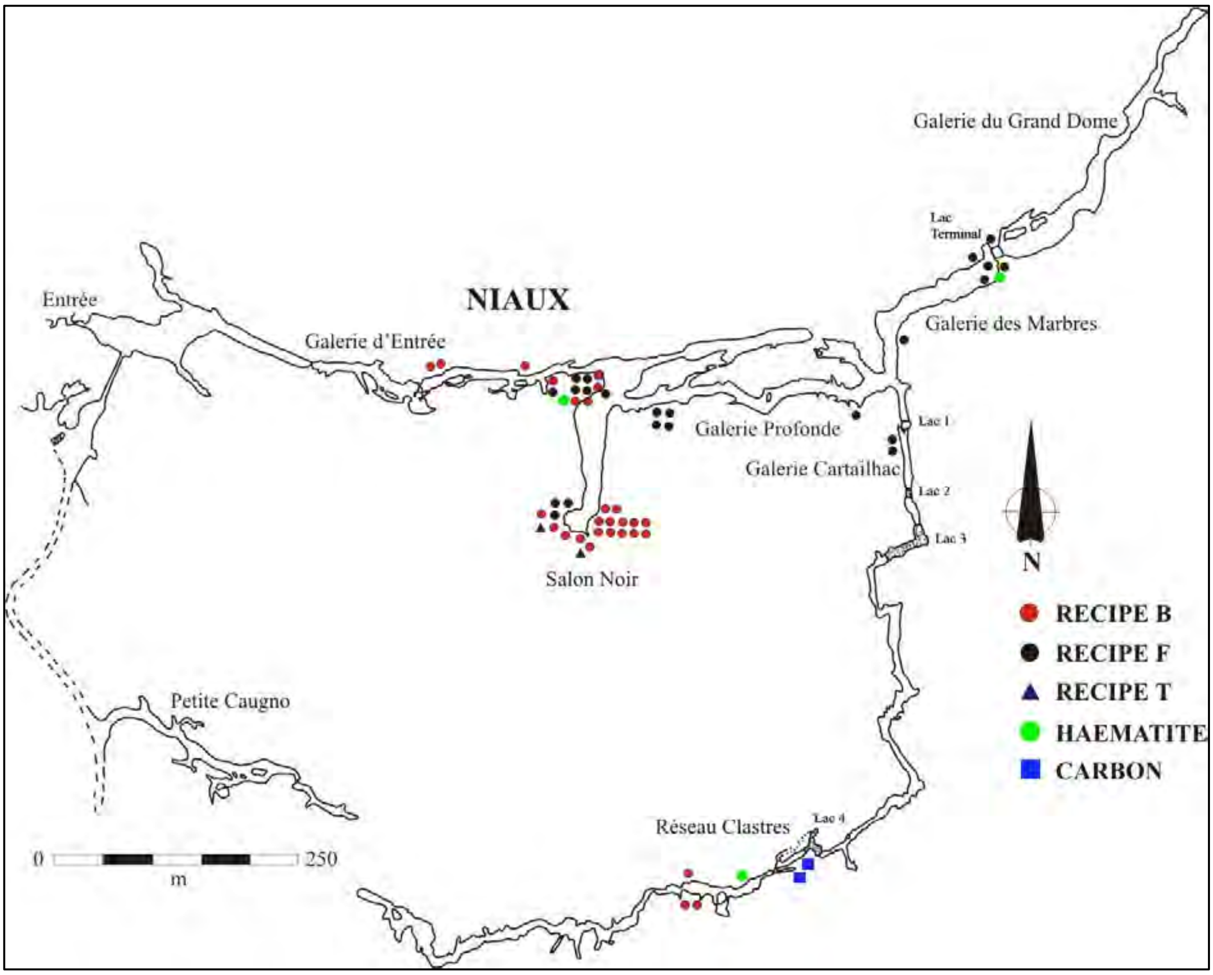
The methodology of the technical approach is thus often adapted to answer some (or all) of the following questions (square brackets indicate my comments):

- are the paintings within a cave contemporaneous (near the entrance vs. those deeper into the tunnel network) and are they made from the same materials? [Niaux Cave, on which this paper is focussed, is over 2 km long. Several paint galleries are present at different ‘depths’ within the cave.];
- were the pigments used in an image of ‘importance’ the same as those for another ‘less important’ image?;
- are the images within a panel contemporaneous (currently assumed to have been painted with similar/the same paint(s) based on their close proximity and similar colours, textures and/or means of execution), or were they ‘built-up’ over time?;
- can a chronology based on paint recipes be determined? [This requires a large cave with many painted images, and the sampling and analysis of many samples]; and
- can the relationships between different caves be established?

Guided by these questions, 75 paint samples were collected for analysis – 69 from the main gallery of Niaux Cave, and six in the Réseau Clastres (another ‘chamber’ within the Niaux Cave network), both located within the Ariège Pyrenees (Figure 3.1). In addition, a study of roughly contemporaneous caves within the same region was conducted in order to establish both what they have in common, and how they differ. Once completed, two additional comparisons were to be conducted i.e., geographical differences/similarities within painting styles/pigment sources, and secondly, comparisons between paintings generally considered to belong to an early time period.

Three general categories of technical approach were followed: 1) macrophotography and direct examination; 2) paint constituent analysis; and 3) binders/extender analysis. The first approach is considered to represent the pre-sampling stage of an investigation. It involves the visual assessment of the images, and looks specifically at the manner in which the paintings were applied and the number of pigments used in their execution. If it were determined, for example, that an image consisted of a uniform application of a single pigment, then the sampling regime would require the collection of only one sample for that specific image (possibly two to make sure that the results are representative). By adopting this approach, only the minimum required number of samples are collected.

The second category involves the physical examination of paint samples. A range of techniques are available to aid in the determination of the paint constituents. In this paper, the samples were analysed using an SEM linked with an X-ray detector, thus allowing for determination of the samples’ visible morphology and the identification of the samples’ elemental composition. XRD Analysis provided mineralogical information whilst the elemental composition was determined using PIXE.



<u>Figure 3.1: The Niaux Cave network depicting the localities of the Salon Noir and Réseau Clastres, as well as the locality of the different paint recipes and positions of the red and black images (from Clottes, 1993).</u>

The third category involved the classification of the organic binders existing within the paint samples using gas chromatography, which in turn was verified by mass spectroscopy and fragmentometry. The conditions for sampling were highly restrictive. The samples had to be free of any form of contamination. The sampling method also had to ensure no physical contact of the samples with the skin (to prevent contamination). These conditions precluded large-scale sampling, as only a few sites and painted images were considered to be 'contamination-free'. The presence and character of lipids (the main constituents of oil or grease) and sterols (that indicate either an animal or vegetable origin) were determined.

The findings of this research are as follows:

- <u>Macrophotography and direct examination:</u>

Some of the images found in the main gallery of Niaux Cave were found to have been applied using fingers, with fingerprints still being visible on a few. In the Réseau Clastres paintbrushes had been used, whilst in the Salon Noir, evidence of a preliminary sketch in charcoal being drawn prior to the painting event was found (substantiated by the laboratory analyses). These sketches were only found under paintings created using recipe B (characteristic of the Late Magdalenian Period).

- Paint constituent analysis:

The pigments used were haematite for the red images, and Mn oxide with or without charcoal for the black images.

- Binders/extender analysis:

Two predominant paint recipes were determined; namely B and F. In addition, it was found that two different extenders had been used; either K-feldspar alone (Recipe F – 22 cases), or K-feldspar mixed with a large amount of biotite (Recipe B – 15 cases). A third Recipe (T) used talc as an extender (only two cases). It is theorised that extenders were used to ‘bulk out’ paint pigments thus saving on pigment usage. The use of extenders would also help produce a more homogeneous mixture that could be more easily applied to the walls, as well as allowing for better paint adhesion.

As no binders were found present within the Réseau Clastres samples, it is suspected that water was the medium with which the paints were applied. Organic fatty elements were identified in paint samples obtained from Fontanet, Enlène and Les Trois-Frères Caves, however. In the last two caves, the fatty elements were identical and determined to be of plant origin. The first site’s fatty elements were of animal origin.

These findings have important archaeological implications, with the most important relating to the identification of different recipes. This finding could have two possible implications. Firstly, different recipes indicate that a chronological shift in pigment usage and evolution occurred; or secondly, the recipes represent different social uses. The latter point can again be broken down into three additional possibilities: a) different images were composed of different recipes based on their relative importance; b) different recipes were used by people of different social stations, genders, ages, etc.; or c) different recipes were dependent on seasonal shifts. The former seems unlikely for the recipes were not restricted to specific imagery or symbols (thus lending special significance to those images). The latter two points are much harder to resolve. Several facts tend to support the theory of chronological change as opposed to social usage, however.

Nine artefacts analysed from La Vache Cave, and dated to the Late Magdalenian Period, were all found to be painted with Recipe B. Furthermore, the analysis of seven artefacts obtained from Le Mas d’Azil, Enlène and Les Trois-Frères Caves, all dated to the Middle Magdalenian Period, were found to be painted with Recipe F. Although it is recognised that these samples represent a very small sample set against which chronological dating can be compared, on the evidence currently available, it appears that the change in paint recipe is directly related to chronological change.

Certain considerations have to be taken into account, however. It must be remembered that these findings are representative of a small area only, and that they are related to a very small time span (the Middle to Late Magdalenian). It is not known how widespread the usage of these recipes is, nor at which point one recipe superseded the other. Stylistic changes might occur independently of recipe change, and could reflect either a change in painting style or improved methods of paint manufacture (dependent on which changed first).

In addition, the deposit might not always reflect chronological changes in paint composition. The change over from one mindset or culture (be it stone industry, painting style or recipe) is never clearly defined. As a consequence, a cave might reflect only one painting style, yet the images are composed of a mixture of the two recipes, thereby indicating a point of recipe interchange. Similarly, certain Late Magdalenian imagery/recipes might be associated with Middle Magdalenian artefacts. This is to be expected, for it would be highly unusual for a change in painting style, paint recipe and the development and adoption of new stone tools to all occur at the same, clearly defined time.

What this paper clearly highlights is the need for the development of a well-planned methodology, together with a well-orchestrated sampling regime. For their analyses, 75 samples were collected (more than double the number in this study) from some of the best-known and best-preserved sites in France. To get conclusive results, one needs good quality samples i.e., sufficient sample that will provide high quality data. The project aims and manner of execution are, however, the same as laid out in the present study.

3.6.4 Rietveld X-ray diffraction and X-ray fluorescence analysis of Australian aboriginal ochres (Jercher *et al*., 1998)

The subject matter and methodology contained within this paper have a similar contextual basis to that of the present study, only that the sourcing of ‘ochre’, and not its characterisation, is the primary objective.

The Aboriginal peoples, like the San of southern Africa, have a very long historical association with ochres, particularly red ochre, with its significance founded in its symbolic status within the Aboriginal belief system. One of the earliest uses was dated to 30 000 years, when red ochre was buried with a corpse, and subsequently stained the skeleton (Bowler and Thorpe, 1976).

Not all ochre sources held the same value, however, with certain sources being actively sought out in preference to others. ‘Pilgrimages’ covering several hundred kilometres have been recorded, often passing many other sources of ochre on the way (Jones, 1984). Knowledge that specific sources were used in preference to others allows for the possibility of determining sources of ochre found in burial sites. This would in turn allow for an increased understanding of the patterns of movement, and interactions between the different Aboriginal groupings of the past.

The ochres themselves were determined to vary considerably, ranging from almost 'pure' samples of either haematite or goethite, to samples of mixed mineralogical composition. It was further determined that the composition of these minerals was also highly variable. Based on this high degree of variability, it was hypothesised that by studying both the phase and the bulk compositions (major and trace elements), it would be possible to distinguish between different ochre sources.

To test this hypothesis, a group of ochre samples extracted from six different sites known to have been utilised by Aboriginal peoples were studied. The aim was to determine the degree of reliability of the XRD and XRF methods for fingerprinting ochres, as well as to create a database containing the chemical and mineralogical characteristics of ochre sources from anthropologically important sites.

A standard XRD technique was used to record the mineralogical composition of the different samples. The data obtained for each sample were then subjected to a profile analysis method (Rietveld refinement), which 'fits' a profile to the pattern to allow for the relatively easy identification of the mineralogical composition of the sample. However, in a sample containing a mixture of minerals, there is frequent overlap between the diffraction patterns. This usually disallows any possible quantitative determination of the relative percentages of the mineralogical components. A complete refinement of the pattern by the programme can allow for the quantitative determination of the proportions of each mineral component, by using a scale factor (in this case the Rietveld scale factor) of each phase (Bish and Post, 1988). The elemental analysis was conducted using standard XRF procedures. The morphology and the colour (using the Royal Horticultural Society Colour Chart - RHSCC) were also recorded for each of the samples.

It was determined that the combined use of both XRD and XRF analyses in order to determine ochre provenance was justified. On an individual basis, however, XRF was shown to be the more appropriate technique. The use of the Rietveld XRD technique was shown to be problematic for several reasons, namely a) the samples were not totally crystalline, thus making quantification of the minerals difficult; b) the amorphous phases constituted up to 38% of the total sample. This latter fraction's composition is unknown, thus making correlation between the bulk chemical analysis and the phase analysis impossible; and c) the uncertainties associated with the phases calculated (using quantitative phase analysis) to represent 1 % or less of the total sample percentage were found to be high. Fingerprinting methods based on the presence or absence of 'trace' phases is therefore suspect.

The main problem with this study is that no statistical comparisons of the data obtained were carried out. Only a physical description (to the elemental level) was given, with the comparisons being made on this basis. Should this approach be used in future, statistical analysis would have to be used in order to show a relationship between the artefact and the potential ochre source. Knowledge as to how closely the sources are related (both mineralogically and chemically) to one another would also aid in the matching of the artefacts to individual source points.

It was stated that the choice of XRF as a method for elemental determination was determined primarily by ease of use and availability. This would typically not be the primary method of choice, due to the need for relatively large sample sizes. Most archaeological excavations produce artefacts that are usually small in size. Other micro-analytical techniques would be preferred over this technique if sample sizes were restrictive; two examples being neutron activation analysis (NAA) and laser ablation microprobe inductively coupled plasma mass spectroscopy (LAM-ICP-MS).

3.6.5 The composition of paint pigments in King Herod's palaces (Porat and Ilani, 1998)

The mineralogical and chemical composition of paint pigments used to decorate the walls of King Herod's palaces in Jericho and Massada were investigated. The nine samples collected were analysed using XRD and SEM, the latter fitted with EDX.

The colours were determined to be sourced from the following ingredients i.e., red from cinnabar; orange from minium*; green from celadonite; black from soot*; white from chalk; pink from kaolinite^{*1}; brick red from haematite; yellow from goethite; and blue from cuprorivaite* (where * = man-made or modified).

The data obtained were then compared against geological data on raw materials and ore minerals from Israel and the surrounding vicinity, as well as from the Near East and the Mediterranean regions in order to determine the origins of the studied pigments. Ancient and modern literature was also consulted. It was determined that the red, green and orange pigments were imported, for their constituents did not occur locally. The determination of their exact source was unsuccessful, however. Due to standardisation of the techniques used in the preparation of the paints within the Roman Empire, and the use of specific commissioned painters throughout the Empire, great similarities in paints and painting techniques between various frescoes have been noted. It was suggested that the trace elements within each of the pigments should be determined and used to aid in the sourcing of their inherent components.

The determination of these sample's compositions was aided by the fact that almost all the colours were found in a pure form. There was also sufficient material available to allow for mineralogical analysis - very rare in the field of archaeology. A combination of the two analytical techniques allowed for the accurate determination of the constituents contained within each paint hue. Historical records, which relate how each pigment was manufactured, further substantiated these findings.

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[1] Tests were conducted which showed that natural kaolinite (white), when heated to 850 ^{o}C for two hours, produced a deep pink colour. The colour change was due to the presence of trace Fe-oxides and hydroxides which when heated, transform into haematite that imparts the pink colour.

3.6.6 The fingerprinting of ancient Egyptian quarries (Mallory-Greenough *et al*., 1999)

The aim of this study was to evaluate the use of a laser probe as a discriminating tool for material sourcing. To test its ability, it was used to source basalt artefacts to specific quarries excavated during the Pharaonic period of Egyptian history. Based on the assumption that rare minerals would be easier to source than those that are common, pyroxene (augite), plagioclase (labradorite) and Fe-Ti oxides (magnetite-ilmenite) found within the basalts were examined. As it was shown in previous studies (Nisbet and Pearce, 1977) that the examination of the minor elements (< 4 % m/m) in pyroxenes (e.g. augite) were more useful in the discrimination of basaltic sources than were the major elements (> 4 % m/m), the main focus was directed at their determination. Furthermore, it was suggested that trace elements (< 0.1 % m/m) would be even more successful for fingerprinting purposes.

To determine the trace element compositions of samples taken from the seven known Pharaonic Egyptian basalt quarries LAM-ICP-MS was used. Nine New Kingdom pottery sherds were also examined. The results were compared using CA, with the findings being reproduced in the form of a dendrogram. The data were further statistically analysed using univariant F-tests (to indicate degree of correlation between both the major and trace elements with the lava flow source) and multivariate tests (to demonstrate the effectiveness of the selected elements, representing different geological groups, for flow analysis), that showed a highly significant relationship to be present ($p < 0.01$). Discriminant analysis was conducted on seven elements representing different geological groups. Using these techniques, it was determined that the use of only a few trace elements was required to identify the origin of each sample. The use of the additional elements would aid in this identification, but there would only be a minimal increase in the successful classification of the source areas.

In this investigation, elemental compositions of rare minerals were used to aid in the sourcing of the rocks, as opposed to the more commonly used bulk elemental compositions. The use of this approach is based on the fact that basalts are igneous rocks that have undergone no secondary modification (neither metamorphic nor sedimentary). The samples are thus still in their ‘pure’ form. It has also been shown by Abdel Aal (1988) that the degree of variability present within trace element analyses, taken from widely spaced samples along the Haddadin lava flow, were within analytical error. This extreme homogeneity within lava flows further supports this line of analytical study.

Ochres on the other hand are typically sedimentary in nature. The nature of the mineral compositions within different ochre samples within one site would thus not be expected to show the same degree of homogeneity as was found within the lava flows. The use of bulk elemental analysis to determine sourcing is thus more applicable to this scenario than to the sourcing of igneous rocks. The use of LAM-ICP-MS is generally more attractive than that of XRF for artefact studies, as only very small sample sizes are required. The problem associated with this technique is, however, the fact that the researcher must first know what elements to test for prior to analysis (since the technique is destructive), and the smaller the sample size, the fewer the number of elements that can be determined accurately.

There could potentially be a second problem associated with this approach. Should a more reliable analytical technique be used in the future which would require the input of elements not tested for using LAM-ICP-MS, these experiments would either have to be repeated or discounted. The bulk composition techniques (e.g. XRF) would provide all data associated with a given sample, allowing for the creation of a comprehensive database, sections of which could be utilised in future research.

3.6.7 Identification of minerals in pigments from aboriginal rock art in the Laura and Kimberley regions, Australia (Ward *et al.*, 2001)

In order to determine why LSA painters chose certain paint ingredients over others, the mineralogy of a number of pigments were analysed, with the results being compared to highlight any regional patterns in pigment composition that might exist. It was clearly stated, however, that the aim of this study was neither to try and source these pigments, nor to look at the material quality as a means of explaining the selective use of particular ochre pigments.

The mineralogical analysis was conducted using smear samples run on an XRD. The analyses were run through a trace-match program (‘Search’) to identify the major mineral phases. Geochemical analyses were conducted to help identify and confirm the mineral phases. This was achieved by mounting the samples on aluminium stubs (using carbon tape), and using an SEM fitted with EDX.

The study showed that the technique was capable, to a degree, of characterising some of the paint samples from the Laura and Kimberley regions. The analyses showed that mulberry paints contained jarosite, yellows contained jarosite and goethite, the reds contained haematite, and most of the whites were composed of kaolinite or huntite (the latter finding was rare). This clearly showed a variation in paint component selection, and that it was not just a case of simply heating goethite to form the various shades of red required for the paintings.

Although the study was conducted in Australia, several important features of general applicability must be noted, namely a) the use of chemical and mineralogical analyses can aid in the characterisation of the various paints analysed; b) the procedure of manufacturing paints was much more complex than was generally accepted, despite the antiquity of this skill; and c) a suite of complimentary techniques are required in order to truly understand paint pigment analyses, and the reasons behind and for their manufacture.

3.7 CONCLUSIONS OF LITERATURE SURVEY

Only a few of the papers mentioned in this Chapter (Van Rijssen, 1990; Wilson *et al.*, 1990; Peisach *et al.*, 1991a) are directly related to the content of this thesis. The reason for this is quite simple – the papers listed here represent the sum total of the readily available scientific work conducted in order to determine the chemistry and mineralogy of southern African rock art. Unfortunately, the results of these papers are often contradictory, which further adds to the confusion surrounding the subject of paint composition. I will not, however, compare the findings of these particular papers in this section, but will rather discuss them in Chapter 6 along with the findings of this particular study. I would, instead, like to discuss the methodologies as described in the papers outlined above.

The methodology employed, the techniques utilised, and the reasons behind the scientific investigation of prehistoric rock art are the same the world over. Only the location of the images within the landscape changes, together with the composition and sourcing of the paint pigments. The French sites (Labeau, 1990; Menu and Walter, 1992; Clottes, 1993) offer several obvious ‘scientific’ advantages over those found in South Africa, the primary one being that their art has been ‘buried’ below the Earth’s surface in a proverbial “time capsule” far removed from most destructive influences, groundwater being a notable exception.

Besides being protected from the natural elements and pollution (and hence contamination), a number of the images are also composed of charcoal. Several of these images have now been ^{14}C dated, thus providing a chronological framework against which the stylistic interpretations can be related. In addition, this also allows for the determination of the chronological evolution of both painting styles and compositions (the latter in the form of recipes).

San art is very difficult to date as very little to no organic carbon has been found. In addition, due to its exposed position, it is also far more susceptible to degradation via natural weathering processes brought about through significant changes in temperature and humidity regimes (both seasonal and random – fire, wetting via a human agency, unique storm events, etc.), as well as through biological agencies (lichen, cyanobacteria, large animals rubbing against the painted surfaces, etc.). As a consequence, the chronology of painting development has been based on stylistic criteria and pigment colour[1]. So far, there is very little evidence available that adequately supports the various chronologies that have been proposed (e.g. Pager, 1971; Vinnicombe, 1976; Russell, 2000) (see Section 6.2.1). The only meaningful way in which the question of painting chronology can be addressed, therefore, is to characterise the paint pigments in order to identify potential differences/similarities that might exist in pigment sources and/or paint recipes, both within and between different shelters. By comparing these components against the few ^{14}C dates available, then relating the findings to the current stylistic chronology, a more precise and informed chronology could be established.

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[1] See Appendix 3.3 for notes on problems associated with the accurate quantification of pigment colour.

Although the topics in the papers reviewed are sometimes quite divergent from the one presently under investigation, the methodologies followed and the statistical analyses employed are relevant to the study at hand. In almost all of the papers, a combination of both mineralogical and chemical techniques was used in an attempt to characterise the samples. The use of mineralogy has a) led to some important insights into the creation of paint pigments; b) aided in the determination of possible weathering rates; and c) given an indication as to the nature of possible pigment sources.

As has been shown in the above papers, mineralogy can give an important insight into the nature of the pigment, but it cannot necessarily be used as the primary means of sourcing the pigment material. For example, it might be determined that a large amount of haematite is present within a sample, thus suggesting an iron ore source. The KwaZulu-Natal landscape, and in particular the Ecca Group, contains numerous Fe ore outcrops. Only by determining the chemical 'fingerprint' of the sample under study, and matching this with a source point, can the provenancing of an artefact become a reality. Only if the XRD technique is sensitive enough to detect changes within the individual mineral crystal structure (brought about by elemental 'impurities') may the technique be used to distinguish between different sources of the same mineral.

It has been shown that knowledge of the mineralogical component of a sample can be an important factor in the sourcing of the material in cases where areas of widely divergent geological deposits are being investigated (e.g. Jercher *et al.*, 1998). This is not a prerequisite for the sourcing of material, however, for with changing geological material one could also expect a corresponding change in elemental composition (as illustrated in Peisach *et al.*, 1991b).

Once the chemical data have been captured, a statistical means for analysing the data must be determined. A wide variety of statistical techniques have been employed, including PCA (e.g. Hughes and Solomon, 2000), CA (e.g. Peisach *et al.*, 1991b) and ANOVA (e.g. Jercher *et al.*, 1998). In some cases, no statistical analyses were conducted, with comments being made purely on a visual comparison of the raw data (Fitte, 1990; Labeau, 1990; Porat and Ilani, 1998; Ward *et al.*, 2001). It is my opinion that, without some form of statistical support for the findings, any assertion made stating that a geological formation is or is not the source of a pigment cannot be completely accepted.

Due to the nature of the dataset created during the course of this investigation, a large number of samples, each with an equally large number of variables, had to be analysed. A multivariate technique was therefore employed. The two most common techniques used in the field of artefact provenancing are PCA and CA. As each technique has advantages and disadvantages, careful consideration was given as to which technique would be best suited to this particular investigation.

There are many algorithms for CA, with no generally accepted 'best' method. Unfortunately, not all of the algorithms produce the same results on a given dataset, and as a result, the assessment of the results can be problematic (Manly, 1994). Another problem with the technique is noticed when there is considerable overlap between the initial data (as is the case with the current excavated deposit and local field data i.e., all have high Fe contents). From CA, a solution might be produced that is quite different from the true situation (Manly, 1994).

On the other hand, PCA is a much simpler multivariate technique, working best when the original variables are highly correlated, positively or negatively (Manly, 1994). During the course of this investigation it will be shown that this is indeed the case with these datasets. As a result, based on the above determinations, it was decided to use PCA rather than CA.

The papers discussed above show that it is possible to characterise and even provenance, with relatively high degrees of certainty, the artefacts under examination. Careful consideration as to technique(s) and statistical methods can and should be given in order to gain the most information pertaining to each particular study. Given that this form of analysis has been conducted in an archaeological context since the 1970s, it is surprising that the origins of San rock art have yet to be fully explored, with only a few exploratory attempts having been made (e.g. Van Rijssen, 1990; Hughes and Solomon, 2000).

CHAPTER FOUR

THE GEOGRAPHICAL AND ARCHAEOLOGICAL CONTEXT OF THE FOUR SAMPLE SITES

4.1 INTRODUCTION

The sampling regime employed within this study was carried out in two phases. The primary site (MQ) was sampled thoroughly, with paint, excavated pigment, and local and distant field samples being analysed. Phase two involved the collection of paint samples from three additional sites in order to provide a paint sample set against which to compare the MQ paint data. Unlike MQ, however, these three additional sites were selected primarily on their geographical and geological relationship, or more precisely ‘non-relationship’, to the primary site, and not on archaeological information related to each site in particular (Map 4.1).

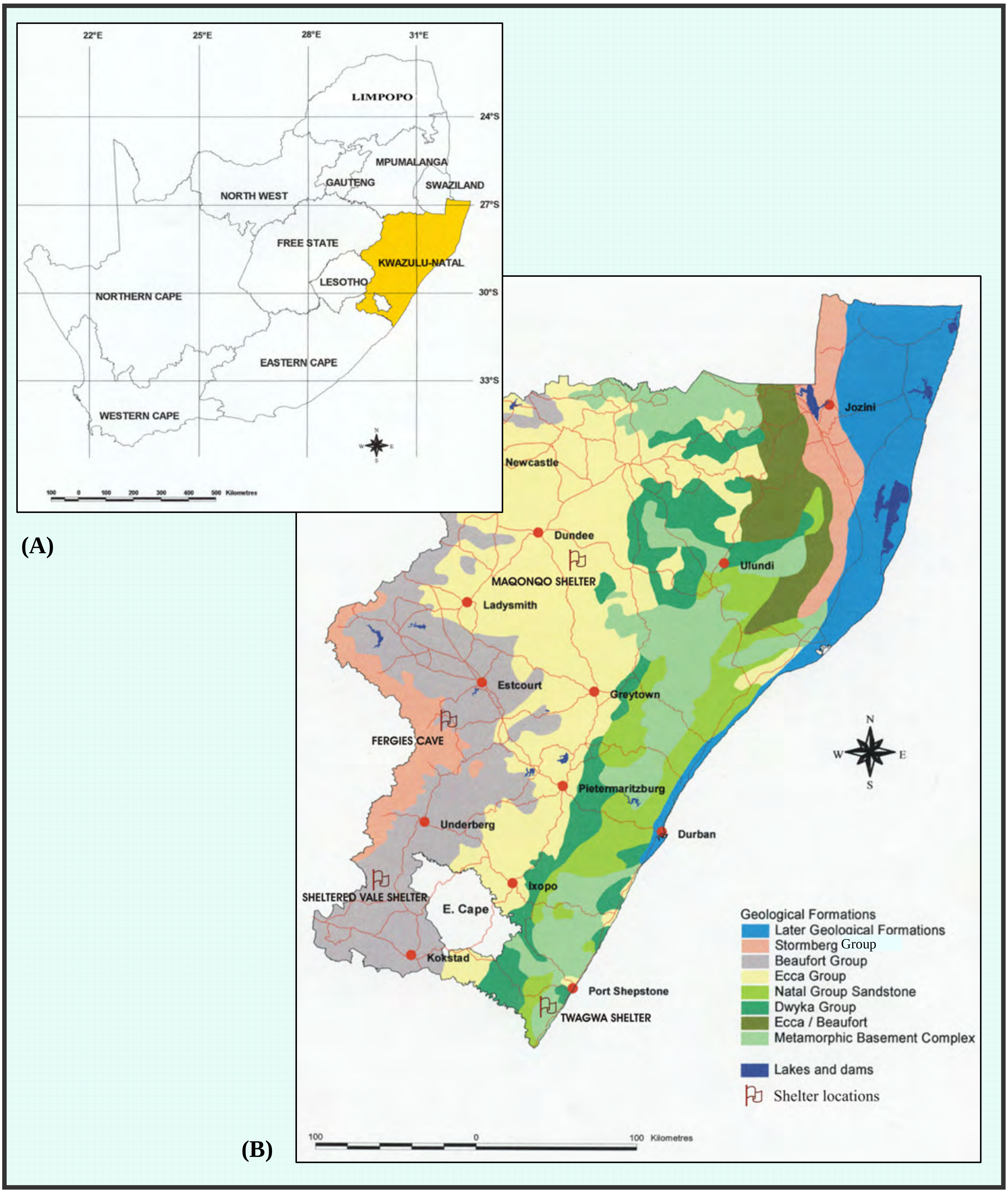
As a consequence, each site can be considered to be distinct from one another in terms of geology, and to a lesser degree, climate and vegetation. Each site will thus be discussed individually. For more information on the sampling regime employed, the reader is referred to Sections 5.2.1 and 5.2.2. For further information on the geology associated with each shelter see Appendix 4.1. A short glossary of geological terms is provided at the beginning of this thesis. Unless otherwise stated, all co-ordinates are presented using CAPE 1880 datum.

4.2 A DESCRIPTION OF THE HELPMEKAAR DISTRICT SURROUNDING MAQONQO SHELTER (PRIMARY SITE)

4.2.1 Introduction

The Shelter (see Frontispiece) is located on Vaalkop Farm situated in the Helpmekaar District (28^{o} 20' 37" S; 30^{o} 25' 28" E), approximately 35 km south-east of Dundee (Map 4.1). The dominant land-use within this District is farming, with both grazing and cultivation (predominantly ***Pennisetum purpureum*** fodder) being practised. Some hunting reserves have also been created within the area, and MQ is located on one of these.

The area experiences a strongly seasonal climate with winter drought and summer rainfall. The mean annual temperature ranges between 16 and 18 ^{0}C, the average rainfall is between 700 and 800 mm p.a. and the average evapotranspiration is between 1 700 and 1 800 mm p.a. (Eksteen *et al.*, 1990). All of these factors are a result of the controlling influence of the eastern seaboard’s warm Indian Ocean, and its effect on the inland weather systems.



Map 4.1: (A) Location of KwaZulu-Natal within South Africa and (B) Location of the four sample sites in relation to the geological formations within KwaZulu-Natal (King, 1982).

In order to better understand the parameters within which this study was conducted, three broad features of the study site, namely the general setting, geology and human history, are discussed. As well as situating the study within its correct context, these features also strongly influenced the research approach adopted.

4.2.2 General geographical setting

The landscape around this north-east facing Shelter is characterised by minor escarpments surrounded by undulating lowland. Many highly eroded river channels, formed between extensive, gently sloping plains located within the watershed, feed the perennial Mzinyathi River. Sandstone outcrops occur along almost all the steeper slopes of the mountains, with one such outcrop forming the ‘roof’ and rear ‘wall’ of MQ. Further outcrops form some of the crests of the hills within the watershed. Dolerite outcrops predominantly occur along the slopes of the steeper, higher hills, but are of limited extent.

The soils located within the area are, in general, yellow-brown in colour, coarse in texture and friable. These yellow-brown apedal materials typically overlay soft or hard plinthic soil horizons of soils located within the general landscape, whilst E horizons’ typically overlay G and plinthic horizons in soils located near the river channels (e.g. Avalon, Glencoe, Longlands and Kroonstad soil forms – the latter two typically associated with the river channels)[1]. Shallow soils (Glenrosa and Mispah) are also common within the valley. Red soils are uncommon. The dominant grasses associated with these soils consist of components of the ***Themeda-Hyparrhenia*** and ***Tristachya-Digitaria*** grasslands, typical of the Interior Basin Vegetation (Edwards, 1967), or Dry Lowland Tall Grassveld (Bioresource Group[2] or BRG 16) (Camp, 1999).

4.2.3 Geology

Twelve different geological Formations can be identified within ~ 12 km of MQ. The shelter itself is located on the Vryheid Formation (approximately 250 million years old), which is dominated by medium- to coarse-grained sandstones and grey micaceous shales (Linstrőm, 1987; Geological Survey, 1988a). This Formation, together with the Volksrust and Pietermaritzburg Formations, comprise the Ecca Group which, as a collective, are composed of sediments that were deposited in extensive, but shallow bodies of brackish water during a cold temperate period (Du Toit, 1954; Linstrőm, 1987). As such, the Ecca sandstones generally display a coarser grain size than do

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[1] All of the soil forms are named in accordance with the South African taxonomic soil classification system as outlined by the Soil Classification Working Group (1991).

[2] A Bioresource Group is defined by Camp (1999) as “…a specific vegetation type controlled by an interplay of climatic and biotic factors such as soil and altitude.”

sandstones found within other geological Groups and, as a result, are relatively more susceptible to weathering.

A variety of ore bodies, all potential pigment sources, have been known for many years to exist in the surrounding geological Formations. Whilst, in many cases, their limited area and quality have prevented them from being commercially mined, they do represent a good resource for small-scale pigment production. For example, iron deposits in the form of haematite, siderite, magnetite, and limonite[1] or, more commonly, as a mixture of these, occur throughout the region; bauxitic material is known to occur as isolated outcrops on the crests of some of the higher hills in the area, phosphate nodules are a characteristic feature of the Volksrust Formation (Linstrőm, 1987), coal seams are particularly common within the greater Dundee region (Geological Survey, 1988a; Camp, 1999), and a limestone deposit is known to be located approximately 38 km from MQ (Gray, 1906). Interestingly, no deposits of the one component most commonly said to be the main constituent of the white pigments (kaolin), are known to occur within the greater Dundee-Helpmekaar-Vryheid area.

4.2.4 Human history

The San are the earliest known inhabitants of this region. These nomadic hunter-gatherers relied exclusively on the veld for their subsistence, both via hunting or harvesting bulbs, roots and insects, and for the raw materials from which they made their equipment and tools. Although it is impossible to be certain, it is thought that they lived in small camps consisting of no more than about 20 individuals, the size of the camp dictated predominantly by the availability of food (Tobias, 1978). Although they did not own the land through which they passed, each camp laid claim to a specific territory within which they would travel looking for food. The boundaries of these territories were determined by a number of means, including conflict with other camps (A. C. Solomon, pers. comm., 2001). For shelter, the San either built temporary grass huts, or used rocky overhangs (these are relatively common within the area), of which MQ is an example. These shelters give the best insight into the lives of the San, and in many cases they provide the only evidence of their existence. The concentration of their artefacts in small areas, and in deposits (which can be dated) has been the primary source of information for archaeologists. The exceptional abundance of artefacts was one of the main reasons for the selection of MQ by Dr A. C. Solomon as the primary study site for this investigation.

Mazel (1996a) found that, although MQ was first occupied by peoples of the Middle Stone Age (MSA = > 25 000 years b.p.) who were later superseded by the LSA culture, the site was unoccupied for the period from 20 000 to 8 000 years. With further study of stratigraphic Layers 2 to 13, it was

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[1] The term limonite is generally used as a field term by geologists, and is used to denote a mixture of goethite (α-FeOOH), subordinate lepidocrocite (γ-FeOOH) and adsorbed water (Coetzee, 1976). It is, however, no longer an acceptable mineral term (Schwertmann and Taylor, 1977).

suggested that the site was again occupied for 4 500 years (between 8 000 and 3 500 years b.p.) by the hunter-gatherer peoples of the LSA, before being abandoned again. It must, however, be noted that the area surrounding MQ continued to be occupied by the hunter-gatherers throughout this second abandonment (Mazel, 1996a), as is evidenced by deposits in the nearby Mzinyashana Shelters 1 and 2 (Mazel, 1997). The reason for this desertion is not understood, but it has been suggested by Mazel (1989a; 1989b; 1993; 1996a; 1997) that changes in the social structure within the Thukela Basin as a whole were responsible.

Depositional evidence shows that the Shelter was again used from 1 500 AD to present. It is unclear if this usage was due to occupation by hunter-gatherers (LSA), or ephemeral usage by agriculturists (LIA) who had by this time settled within the area, or both. Several stone circles associated with agricultural communities who occupied the area within the last 500 years, are located in close proximity to the Shelter. The uppermost stratigraphic Layer 1 exclusively represents this last period of utilisation.

Though there are three distinct periods of occupation, it is strongly suggested by Mazel (1996a) that the majority of the paintings in MQ are associated with the second occupation (from 8 000 to 3 500 years b.p.). There is as yet little conclusive evidence to support this theory. However, Mazel and Watchman (2003) suggest that the 3 720 ± 100 b.p. date obtained from a Ca-oxalate crust underlying an indeterminate red figure supports this theory, despite the fact that no evidence yet exists to show a link between pigments within a deposit and those within the painted images (see Section 3.5.9).

Evidence does exist which shows that the practice of painting on rocks existed as far back as 26 000 years ago (Wendt, 1976). This evidence is, however, based solely on the finding of painted burial stones (mainly rounded river pebbles) and art mobilier that have been dated according to the stratigraphic layer in which they were found. An example of one of these artefacts is the Coldstream Stone found in 1911 on the south coast of the Cape Province, South Africa (Wilson *et al.*, 1990). Of the few parietal paintings that have been dated in southern Africa, the oldest have been shown to range from between 3 500 years b.p. (Jerardino and Yates, 1996) and 3 600 years b.p. (Jerardino and Swanepoel, 1999). Both of these dates were obtained from parietal painting fragments located within stratigraphic layers in the Steenbokfontein Cave, southwestern Cape. The maximum date of 3 720 ± 100 b.p. obtained by Mazel and Watchmen (2003) from MQ is, however, the oldest yet determined.

4.3 A DESCRIPTION OF THE GIANTS CASTLE AREA SURROUNDING FERGIES CAVE

4.3.1 Introduction

The Shelter (Figure 4.1) is N.N.W. facing and is located within the Giants Castle Game Reserve, which is itself located along the border of Lesotho in the central Drakensberg Mountains (29^{o} 09' 49.5" S; 29^{o} 25' 19.3" E) (Map 4.1). Conservation management practices represent the only land-use type to be found within this area, with path and tourism management, together with controlled fire management programmes representing the main human influences within the Ukhahlamba-Drakensberg Nature Reserve.

The area experiences a strongly seasonal climate, with dry, cold winters (often accompanied by snow on the mountain tops) and wet summers with high temperatures. The mean annual minimum and maximum temperatures are 9 and 26 ^{0}C, respectively, and the average annual rainfall is between 1 000 and 1 200 mm p.a. (Eksteen *et al.*, 1990). The climate is a result of the controlling influence of the Drakensberg Mountains (with the associated orographic uplift), together with the seasonal influences of cold fronts that migrate northwards during the winter.

4.3.2 General geographical setting

The landscape surrounding FC is characterised by long, deep river valleys dissected by ridges displaying exposed horizontal sedimentary strata. These valleys eventually lead up to and pinch out at the sandstone zone, often referred to as the '*little*' or '*small 'berg*.' Above this zone, the landscape is relatively flat, rolling country that leads up to the buttresses, scree slopes and fall faces of the main escarpment. Dolerite dykes occur sporadically throughout the landscape, evidence of past magma intrusions that occurred along fault planes in the sedimentary strata.

As a direct result of both altitudinal and geological influences, very definite ecological zones can be seen as one moves up the river valleys towards the main escarpment. At lower altitudes (below ± 1 800 m above sea level), below the sandstone zone, there exists a great variety of both plant and animal species, a majority of the former indicative of the Montane Veld, or BRG 10 (Camp, 1999), although elements of Moist Highveld Sourveld (BRG 8) are also present (Eksteen *et al.*, 1990). On the south-facing slopes and within the deeply incised ravines, Montane forests containing species such as *Scolopia mundtii*, *Cussonia spicata* and *Podocarpus* spp. can be found, whilst on the drier north-facing slopes, *Protea* spp. woodlands grow (Carter, 1977). In wetter areas near watercourses, tree ferns and mosses become abundant. *Alloteropsis semialata*, *Festuca costata*, *Themeda triandra* and

Figure 4.1: View of Fergies Cave. The central image depicts the fallen rocks upon which the paintings can be found.

Monocymbium ceresiiforme are some of the grassland indicator species that are typically found within this ecotope (Camp, 1999). It is within this zone that FC is situated.

As would be expected, the prominent soil forms found within this ecotope include Mispah and Glenrosa (on the steeper slopes), with red and colluvial soils such as Hutton, Shortlands, Valsrivier and Oakleaf being found further down-slope (Eksteen *et al.*, 1990). Soft plinthic soil forms are also common (Carter, 1977).

The landscape between the '*little 'berg*' and the escarpment is dominated by grassland of the Sub-alpine ecotype (GeoMap, 2001). As at the lower altitudes, aspect plays an important role in the species composition, with *Festuca costata* being prominent on the wetter south-facing slopes, whilst *Themeda triandra* is predominant on the scree slopes and valley plains. There is very little woody vegetation. Most of this is confined to sheltered slopes and valleys, and consists predominantly of *Leucosidea sericea* scrub, or sub-alpine fynbos (GeoMap, 2001). Closer to the sandstone and in amongst the sandstone outcrops, open woodlands of *Protea caffra* exist. Again the dominant soil forms include Mispah and Glenrosa, although soft plinthic soil forms do occur in low-lying areas near to streams (Carter, 1977).

Finally, the Alpine Belt ecotype of the escarpment is characterised by low heath-type vegetation dominated by *Erica* and *Helichrysum* spp. (GeoMap, 2001). In keeping with the harsh environment and steep slopes, Mispah and Glenrosa soil forms dominate.

4.3.3 Geology

It is in the Clarens Formation, or as it is more commonly known, the Cave Sandstone, that FC is located. This Formation is comprised of fine-grained, massive sandstone that is derived from aeolian deposition that occurred mainly under desert conditions (Linstrőm, 1981). Together with the Molteno and Elliot Formations, this Formation forms part of the Stormberg Group. This Group, ranging in age from between 250 and 180 million years old, represents a climatic change from a wet to dry environment, culminating in a volcanic period associated with the break-up of Gondwanaland.

Other geologies in the area include the Estcourt Formation and Tarkastad Subgroup (both members of the Beaufort Group), as well as the Masotcheni Formation (formed in the Quaternary period and which is comprised of semi-consolidated colluvial and alluvial deposits).

Within all of these geologies, however, there are no economically viable mineral deposits known (Coetzee, 1976; Linstrőm, 1981), although small coal deposits are known to occur. Also, due to the large number of dolerite dykes found throughout the landscape, Fe ore (in the form of nodules and veins) and bauxite (highly weathered dolerite) can also be found in isolated pockets.

4.3.4 Human history

Apart from documentation of the images present within the Shelter, no extensive archaeological investigation specific to FC has been conducted. A number of sites within the central and northern Drakensberg have, however, been investigated, and it is from this cumulative information that a reasonable idea of the human dynamics that once existed within the area has been established (e.g. Mazel, 1989b).

Unlike the rest of KwaZulu-Natal, there is as yet no evidence (in either tools or ^{14}C dates) that people of the MSA ever occupied the higher lying areas of the Drakensberg (Willcox, 1975; Mazel, 1989a; 1989b). One of the main reasons proposed for this is the climate, and its influence on the local vegetation. There is evidence that a colder and wetter climate existed in the Drakensberg region during the MSA and early LSA periods (Partridge *et al.*, 1990). This would have facilitated the establishment of large forests at higher altitudes in the Drakensberg Mountains, which in turn would have resulted in limited hunting opportunities (Willcox, 1975; Opperman, 1987). At lower altitudes, grassy plains would have flourished favouring the development, and sustaining, of large herds of game. The better living conditions and greater access to food sources would have ensured the occupation of the lower altitudes by the MSA peoples. It was only when the climate became drier, and the subsequent decrease in rainfall and increase in veld fires led to the retreat of the forest margins, that LSA peoples began to populate the higher altitudes of the Drakensberg region.

The evidence available seems to support this theory, for while sites in the central and coastal areas of KwaZulu-Natal have delivered ‘starting’ occupation dates from 7 000 years b.p. and older, the oldest known site within the elevated regions of the central and northern Drakensberg is between 4 000 and 5 000 years b.p. Most of the sites are younger, however, exhibiting ‘beginning’ occupational dates of between 2 000 and 4 000 years b.p. (Mazel, 1989b; Mazel and Watchman, 2003).

Based on the above evidence, the lack of deposit, and the general style of the images present within FC, the site was probably only used on an ephemeral basis within the last 2 000 years.

4.4 A DESCRIPTION OF THE MOUNT CURRIE DISTRICT SURROUNDING SHELTERED VALE SHELTER

4.4.1 Introduction

The Shelter (Figure 4.2), faces south-east, and is located on Sheltered Vale Farm situated in the Mount Currie District (30° 05' 08.1" S; 29° 07' 23.2" E) approximately 45 km north-west of Kokstad (Map 4.1). The dominant land-use within this district is farming, with both grazing and forestry (predominantly *Pinus* spp.) being practised.

Figure 4.2: View of Sheltered Vale Shelter. (Photograph courtesy of the Natal Museum).

The area experiences a strongly seasonal climate with winter drought and summer rainfall. The mean annual temperature ranges between 13 and 15 ^{0}C, and the average rainfall between 600 and 750 mm p.a. (Eksteen *et al.*, 1990; Camp, 1999). The warm Indian Ocean exerts a strong controlling influence over the weather conditions in the summer months, but in winter, the anti-cyclones of the southern latitudes migrate northwards, bringing with them cold fronts that move in from the west. These fronts often bring with them severe frosts, and sometimes snow, to the higher lying regions.

4.4.2 General geographical setting

The Shelter is surrounded by hilly terrain consisting of minor escarpments and incised valleys. The many streams that arise as a result of (and are the cause of) this undulating terrain, feed the perennial Mngeni River – a tributary of the Mzimvubu River. Sandstone outcrops occur along the steeper slopes of the higher mountains, with one such forming the ‘roof’ and rear ‘wall’ of SV. Dolerite outcrops generally ‘cap’ the mountains within the area.

The combination of sandstone, dolerite, and strongly seasonal climate, has resulted in a number of soil forms being found within the landscape. On the gentler slopes (toe-slopes and crests), a wide spectrum of soils has formed upon the underlying sandstone (e.g. Clovelly and Hutton). Duplex soil forms are common in the drier areas (e.g. Swartland, Valsrivier and Estcourt), with the Longlands soil form also present in the moister upland areas (Eksteen *et al.*, 1990; Camp, 1999). Where dolerite dykes have intruded into the sandstones, however, heavier textured soils are common (e.g. Shortlands, Bonheim, Arcadia and Rensburg) (Camp, 1999). Mispah and Glenrosa soil forms are common on the exposed shales and sandstones found along the valley sides, where slope is a dominating factor in soil formation. In the valley bottoms, duplex, plinthic and margalitic soils are common.

The combination of altitude, low rainfall and geology, has resulted in the following dominant grass species in the area: ***Digitaria tricholaenoides***, ***Harpochloa falx***, ***Hyparrhenia hirta*** and ***Trachypogon spicatus***. ***Acacia dealbata*** trees are also common in areas that have not been farmed. These are all indicator species of BRG 9, or Dry Highland Sourveld (Camp, 1999).

4.4.3 Geology

Being located in the foothills of the southern Drakensberg, it is not surprising that the geology found here is similar to that described for the central Drakensberg region (see Section 4.3.3). Essentially the same geological sequence is evident here, but with a few exceptions. From oldest to youngest, the geological Formations and Subgroups found are: Adelaide, Tarkastad, Molteno, Elliot, Clarens, and Drakensberg. Dolerite intrusions and alluvium are also present.

The only differences that exist between this site and FC are that the Estcourt Formation has been 'replaced' by the Adelaide Subgroup, and that the Masotcheni Formation is absent. Unlike FC, however, SV is located in the Tarkastad Subgroup. The sandstone associated with this Formation is massively bedded, but does contain small intrusions of purple mudstone in places (de Decker, 1981). It is important to note that a calcareous, clay-pellet, conglomerate can be found at the base of some of these sandstones. This conglomerate is characteristically full of lumps of limestone, with occasional fragments of reptilian bone also being found (de Decker, 1981).

4.4.4 Human history

Unlike the central and northern regions of the Drakensberg, the period in which the southern Drakensberg region was first occupied is not as clear. A large number of sites, both in the foothills of the southern Drakensberg and eastern Lesotho regions, have shown MSA occupations dating back as early as 20 200 years ± 200 B.P. (date from Sehonghong: Mitchell, 1995). In Lesotho, a large number of MSA sites are, however, 'open' i.e., exposed sites not located within shelters (Carter, 1977; Bousman, 1988). It has thus been proposed that these sites represent temporary summer hunting stations or butchery sites (Bousman, 1988), the ephemeral use again being dictated by the climate. During this period, the Drakensberg escarpment and valleys were left unoccupied – it is thought that the lower temperatures associated with the last glacial period resulted in a marked increase in precipitation within these regions. It was not until about 13 000 years ago, when temperatures began to rise, that the LSA peoples began to populate the Drakensberg escarpment (Carter, 1977; Opperman, 1987).

Sheltered Vale Shelter was excavated ca. 1966 by Major T. H. Farnden, and although the deposit only reached a maximum depth of between 2 and 10 inches (between 5 and 25 cm), three clearly defined spits were identified. Unfortunately, I have been unable to locate the original records of this excavation, but according to the limited information in the site record, the only material recovered was either LSA (Layers 1 and 3) or LIA (Layer 1) in origin. Layer 2 was devoid of artefacts.

These findings, together with the general trends described previously, indicate that this shelter was not occupied for long periods of time, and probably not before 13 000 years b.p. Furthermore, the fact that the majority of artefacts found were within the upper 7 cm of the deposit, and were found in conjunction with pottery sherds and OES beads, indicates that the occupants either were, or traded with, LIA peoples. It is not unreasonable to assume that this shelter was only occupied temporarily over the last 4 000 to 5 000 years, but for longer periods of time within the last 2 000 years.

This shelter is interesting in that it contains many painted images, a large number of which exist within one large panel dominated by superimposed imagery. This panel was recorded by Patricia Vinnicombe, and formed part of her work into stylistic interpretation as a means of determining relative ages for the rock art (Vinnicombe, 1976). According to criteria that she established, she deduced the images present within the panel represent relatively recent additions to the rock art record of South Africa.

Unfortunately, the shelter has been irreversibly damaged with some of the ‘single’ images from the remainder of the shelter having been physically removed.

4.5 A DESCRIPTION OF THE IZINGOLWENI DISTRICT SURROUNDING TWAGWA SHELTER

4.5.1 Introduction

Twagwa Shelter (Figure 4.3) is west facing, and is located in tribal land within the Izingolweni District (30° 51' 38.3" S; 30° 11' 26.1" E). The site is approximately 21 km south-west of Port Shepstone, and 13 km from the sea as the crow flies (Map 4.1). The dominant land-use within this district is subsistence farming, with small, cultivated plots in close proximity to most houses/settlements, whilst the larger open areas are used for communal grazing. Some commercial forestry plantations are encountered to the south of this site.

Unlike the previous sites, this area experiences relatively mild seasonal climatic change owing to its close proximity to the coast and its associated maritime climate. The mean annual temperature ranges between 18 and 20 ^{0}C, with the average rainfall being between 850 and 1 100 mm p.a. (Eksteen *et al.*, 1990; Camp, 1999). Frosts are known to occur during winter, during the passage of the cold fronts.

Figure 4.3: View of Twagwa Shelter. The trees in the middle distance are growing on the material originally excavated from the floor of the shelter.

4.5.2 General geographical setting

The landscape within which TW is located consists of a large undulating upland (known as the Maringo Flats), with deeply incised valleys cutting through it. The uplands have, for the most part, gentle slopes that end abruptly at either fall faces, or very steep slopes that then descend between 80 to 120 m to the valley bottom. Sandstone outcrops occur along almost all the steeper slopes of these valleys, and it is within one such outcrop that TW is located, overlooking the Mbizane River.

The landscape typically displays two different BRGs, the position of each being solely dependent on slope aspect. Due to the steepness of the slopes, the north-facing slopes are shielded from the rain-bearing winds, thus creating a rain shadow effect in the valleys that is more apparent here than in any other BRG in KwaZulu-Natal (Camp, 1999). The two BRGs found in the area are Moist Ngongoni Veld (BRG 3) and Dry Ngongoni Veld (BRG 4), their names clearly defining the positions within which they can be found within the landscape. The Ngongoni Veld type typically contains the following plant indicator species: *Aristida junctiformis*, *Digitaria eriantha* (tall form), *Lantana camara*, *Rauvolfia caffra*, *Syzygium cordatum* and *Acacia karoo* (Camp, 1999). The distribution of these and other species lead to the distinction between the two BRGs with, for example, the *Acacia* species being commonly found on the north-facing, drier slopes, but they are absent from the wetter south-facing slopes.

The changes in BRG accurately reflect differences that exist between the soil toposequences found on the respective slopes. On the drier north-facing slopes, duplex soils are common (e.g. Valsrivier, Swartland), whilst on the wetter south-facing slopes deep, well-drained apedal soils are typical (e.g. Hutton) (Camp, 1999). Shallow Cartref and Glenrosa soil forms are also common on the slopes, but these are as a result of slope angle as opposed to climatic influences. Humic (e.g. Inanda, Nomanci) soils are commonly found in the valley bottoms (Camp, 1999).

4.5.3 Geology

Geologically, this area is the oldest of the four sites discussed, its low elevation placing it at the oldest end of the Natal Monocline geological sequence (King, 1982). In addition, the geology within this area is a lot more complex than that at the other sites. Five geological periods (the oldest dating back to approximately 570 millions years old) are represented, namely Namibian, Ordovician/Silurian, Permian, Cretaceous, and Quaternary Periods.

Twagwa Shelter is located in the Natal Group Sandstone (formerly known as the Table Mountain Sandstone (Loxton *et al.*, 1971; King, 1982)), the exclusive representative of the Ordovician/Silurian period within this area (Thomas, 1988). This Group is highly resistant to weathering, resulting in the formation of the spectacular cliffs and associated deep ravines.

It is important to note that this group has been sub-divided into two distinct facies, each with its own characteristics. The Hibberdene facies is composed of red-brown, cross-bedded and micaceous arkoses and grits at the base, succeeded by a sequence of feldspathic, quartzitic and micaceous sandstones with minor siltstone and red mudstone lenses (Thomas, 1988). The Margate facies, in which TW is located, represents the entire Natal Group in the erst while Transkei region. The rocks, generally light grey in colour, are composed of a quartz-arenite association of grey quartzitic sandstones, and conglomerates with minor feldspathic grits (Kingsley, 1975).

Although there are a number of mineral occurrences within the greater Port Shepstone area, the deposits are generally small and of little economic potential (Thomas, 1988). The only two economic minerals mentioned that could represent potential pigment sources are limestone and graphite. Kaolin is also accessible from localised weathering deposits of the Margate facies. Iron pigments could be obtained from the dolerite dykes.

4.5.4 Human history

When compared with what is known of the LSA people of the Drakensberg and Thukela River regions, relatively little is known about the occupational habits of the LSA peoples in the south-eastern parts of KwaZulu-Natal. On the archaeological evidence available, however, the coastal lowland regions typically show the earliest LSA occupation dates (Mazel, 1989b). Sites around Pietermaritzburg and Durban have been found to have ‘beginning’ occupation dates of > 10 000 years b.p. (Mazel, 1989b). The Umhlatuzana Rock Shelter shows a gradual change from MSA to LSA between 35 000 and 20 000 B.P. (Kaplan, 1989; 1990), whilst at Shongweni Cave, this transition occurs between 21 000 and 10 000 years b.p. (Davies, 1975).

Very few dates are available from sites more closely associated with TW, mainly because most of these sites were excavated prior to the introduction of the ^{14}C dating techniques. However, inferences about the length of occupation, and by whom, can be made by judging both the number and composition of the artefact assemblages found at each of these sites. What is apparent is that a majority of the sites underwent prolonged use, with large numbers of artefacts generally being found (Cable, 1984).

The limited plant assemblages present also give an insight as to when these sites were occupied. As an example, *Sclerocarya caffra* (marula) fruit remains found at Shongweni Cave (dated to 4 060 ± 55 years B.P.) show that LSA peoples were present there between autumn and winter (the fruits become available during March and May) (Davies, 1975). Following a similar methodological approach, it has been found that shelters further inland tend to indicate spring and summer usage patterns. Based on these trends, Cable (1984) thus proposed that the LSA peoples migrated with the seasons, wintering in the coastal regions where the most predictable and abundant food resources would be at that time of year.

The notion of seasonal migration is further supported by the presence of ostrich eggshell beads at Borcher’s Cave in Oribi Gorge (Cable, 1984), within shell middens at the Ingane River mouth along the Natal south coast (Schoute-Vanneck and Walsh, 1959), and at Umbeli Belli Shelter located about 7 km inland from Scottburgh (Cable, 1984). As ostriches never naturally occurred within KwaZulu-Natal (Dean, 1989), the presence of the ostrich eggshell beads can only be inferred as being a result of either trading and/or population movement. The Umbeli Belli site is interesting for the evidence available suggests that the beads were manufactured on site, thus strongly suggesting people movement as opposed to ornament trading (Cable, 1984).

Other indicators of population movement include the depiction of animals in the rock art that are not found within the coastal regions, but are common within the Drakensberg (Vinnicombe, 1976; Cable, 1984). These include grassland species such as eland and rhebuck.

Although TW has been excavated, the records available are vague about the date of the excavation, as well as by whom the excavation was conducted (the site record suggests either Niddrie or Bazley). Based on Cable’s (1984) description of Bazley’s 1905 excavation, however, I do not think TW is the shelter that he excavated. This is based mainly on his description of the deposit being excavated to a depth of 5 m, a physical impossibility at the TW site. Unfortunately, I have not been able to locate Niddrie’s notes, and as such, I cannot confirm or deny his involvement, nor use his notes as a reference. What is certain is that the entire deposit was removed and deposited in front of the Shelter.

Judging by the size of the spoil-heap, the deposit must have been quite large. In addition, if the number of artefacts found in the drip line is an indication, the deposit was also rich in stone tools and pigmentaceous material (Figure 4.4). The presence of both of these artefacts in large numbers could possibly indicate that the Shelter was occupied for an extended period(s) of time (Mazel, 1989b). Unfortunately, without an accurate and detailed description of artefact succession within the deposit, no insights into the period(s) of occupation, and by whom (MSA, LSA or LIA), can be inferred.

This site is significant for two reasons. Firstly, although there are other shelters with paintings close to the sea, none has as many images as TW. Secondly, the Shelter lies in close proximity to tribal land officially named ‘Patwa’s Location’ (Batwa is isiZulu for Bushman). Both of these facts lend weight to the idea that this site was of some importance to the San that originally lived within the area.

Figure 4.4: Artefacts in the drip-line at Twagwa Shelter.

CHAPTER FIVE

RESEARCH METHODOLOGY

5.1 INTRODUCTION

As discussed in Chapter 3, the use of elemental analysis to determine the origin of archaeological materials is not a new concept, and has in fact been used with varying degrees of success in, amongst others, Australia, Italy, France, Japan and the USA. The three main differences between this study and earlier ones can be summarised as follows: (a) there are no known or suspected pigment sources that were specifically used by the San in KwaZulu-Natal; (b) paint pigment manufacture, including the constituents used and the method by which they were combined, is still debatable; and (c) it is considered by archaeologists that a comprehensive trade network between the communities existed at that time (e.g. Clarke, 1959). Although there is no evidence, either for or against a trade in pigmentaceous material, the possibility exists that the source(s) could be distant from the site of eventual pigment use.

The only way to shed some light (be it supportive or not) on any of these aspects would be to conduct a detailed investigation of all possible pigment sources found within a very extensive area. This is obviously not practical due to the limitation of resources. Thus, in order to simplify the sampling programme, an accurate knowledge of the actual paint constituents must be determined. This will lead to a refinement of the sampling regime employed, with only sources of known components being analysed. In addition, comparisons with the excavated pigmentaceous materials would also be undertaken in order to determine if any of these materials are in any way related to the paintings, and/or if these materials also have variable sources.

5.2 SAMPLE COLLECTION

5.2.1 Painting site selection

Four different rock art sites were visited during the course of this study. Maqonqo Shelter was selected (by Dr A. C. Solomon, then at the Natal Museum, Pietermaritzburg) as the primary site as it contained both a large number of poorly preserved paintings together with a large number of excavated pigments (5 931 pieces of unmodified “ochre”) from a deposit covering a period of approximately 9 000 years.

The selection of the three additional sites (TW, SV and FC) was based on the following criteria:

- their geographical distance from the primary site. The potential therefore existed that paints would differ from one site to the next;
- each of the sandstone formations on which the paintings are found were formed at different times and under different climatic conditions (see Appendix 4.1). As geology varies from site to site, the rock matrix and any potential differences in the composition of secondary surface deposits could be investigated;
- a difference in geological and geographical localities could potentially result in changes in paint component sourcing (either different pigments were used, or the same geological material was used but was sourced from different locations). The methods used are thus investigated to examine their viability to recognise such changes; and
- climatic effects on the nature of any surface depositional features could be investigated.

5.2.2 Paint samples

Before any paint samples are collected, the rationale behind their collection must be understood. This is particularly important in this study as the samples not only represent part of our national heritage, but are also irreplaceable. Both of these factors place limitations on the sampling regime to be adopted, with limited sample size and numbers, together with minimal impact on the rock art, being of primary importance. This, of course, has to be counter-balanced with scientific norms with regards to statistically valid sample numbers and viable minimum sample sizes. It is for these reasons that a two-stage paint sampling regime was adopted: 1) 30 paint samples (some of mixed colour) were collected from MQ with the aim of obtaining the maximum amount of information from the minimum number of samples; and 2) a maximum of six samples were collected from each of the three comparative sites; the aim being to see what influences geographical, geological and climatological factors may have on paint composition.

5.2.2.1 Primary site: Maqonqo Shelter

The 30 paint samples from MQ were carefully selected and collected by Dr A. C. Solomon, with the author in attendance. In accordance with stipulations contained within a permit issued by AMAFA (the KwaZulu-Natal cultural heritage organisation), care was taken to note the location of the sampled paintings on the shelter wall, as well as the nature (colour, size etc.) and subject matter depicted (see Appendix 5.1). These data were not required for the purposes of this project, and thus are not included.

The criteria used in selection of the samples were as follows:

- as small a sample as possible was collected, so as to leave the painting in as original a state as possible;
- in three instances, paintings were sampled twice at exactly the same spot. This was done to allow for a comparison to be made between the 'upper', more exposed surface of the paint, and the 'lower' underlying paint that has been, theoretically, less directly affected by surface weathering;
- whilst most of the samples were collected from different localities within the shelter so as to maximise any variability that might occur between the different images, some samples were collected from different spots on individual images. This was done in order to determine possible variations in pigment composition that might occur across the surface of an individual painting;
- areas of relatively thick paint were selected so that enough sample would be obtained for analysis;
- several samples of each colour were collected for comparative purposes;
- in order to see if it is possible to 'match' a painting located on rock face with an exfoliated paint fragment, samples were collected from a paint fragment recovered from the deposit together with the suspected point of detachment on the rock wall; and
- in addition to the paint samples collected, five sandstone samples from the shelter wall were also collected and analysed for comparative purposes.

It is important to note that most of the paintings found in MQ are in a very poor state of preservation, with many having faded and/or weathered away. In many cases, it was difficult to identify the images depicted. The sandstone on which the paintings are found is very coarse textured (Section 4.2.3), and this has probably hastened weathering. The Shelter also seems to lie along a seepage line, with watermarks and minor deposits on the wall being noted.

5.2.2.2 Comparative sites: Twagwa, Sheltered Vale and Fergies Cave

The author, under the supervision of an AMAFA representative, collected the paint samples from TW, SV and FC in accordance with stipulations contained within a permit issued by AMAFA. These sites were chosen primarily on their locality and geological character, and secondly on the 'value' of the sites. The imagery within these sites is, to a large extent, faded and has undergone physical degradation.

As these samples were only to be used for comparison, only a small number of samples were taken. These samples therefore do not represent a comprehensive study of each of the respective sites. The criteria used in selection of the samples were as follows:

- as small a sample as possible was collected, so as to leave the painting in as original a state as possible;
- where possible, paint was collected from the edges of the painted images, so as to minimise any visible damage to the painting as a whole;
- only ‘pure’ colours were sampled, so as to minimise possible ‘contamination’ effects of multiple colours on the analyses; and
- where possible, three red and three white paint samples were collected.

The choice of the two colours was decided for the following reasons:

- red colours are common in rock art throughout KZN, and are generally considered to be the most persistent of all of the paint colours utilised by the San;
- the nature of the white pigments is particularly interesting, with pigment sources being reported to be anything from clay (kaolin) and marine shells, to bird droppings and plant sap (see Chapter 3). It is also considered to be the first pigment to be lost via weathering (Vinnicombe, 1976; Jerardino and Swanepoel, 1999); and
- the elevated presence of Ca has been noted in a number of studies (e.g. Peisach *et al.*, 1991a; Mazel and Watchman, 1997; Escott, 2000). The relative concentration does, however, tend to increase from the reds, through the yellows and pinks to the whites (Escott, 2000). By choosing these two colours, the ‘opposite’ ends of the Ca range were sampled.

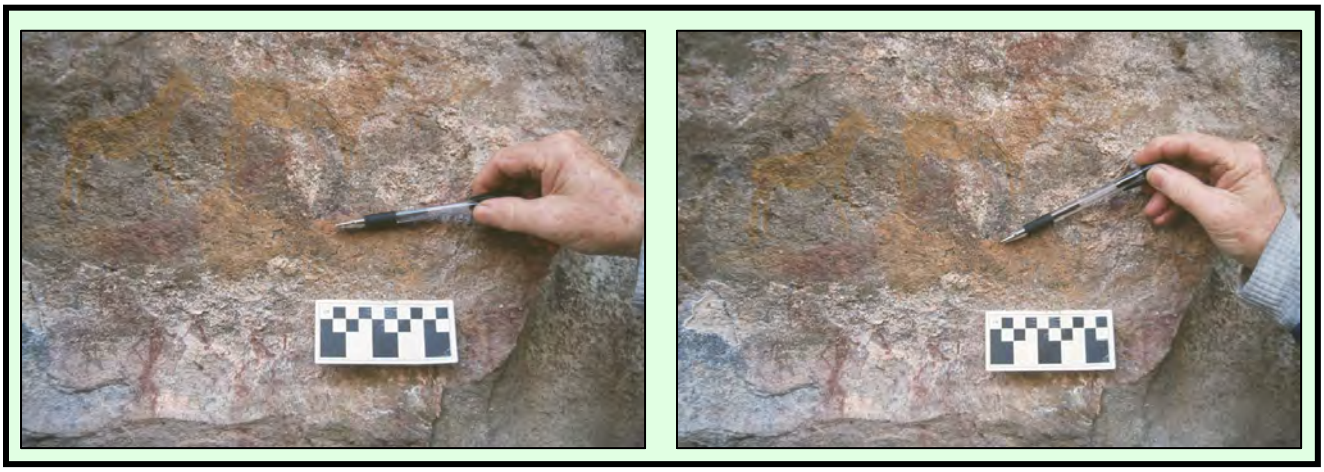
These areas of investigation are of great interest as differences in paint composition between sites might indicate that sites should be managed on a region-by-region basis.

5.2.2.3 Paint sampling method

The samples were collected following the method of Van Rijssen (1990). The adhesive side of silver mylar tape was placed onto the surface of the painting. After applying firm pressure to the tape for about 30 seconds, the tape was carefully removed from the painted surface. The area of collection was then evaluated to determine the amount of damage caused to the painting. This technique resulted in little or no visible damage to the paintings (Figure 5.1). Moreover, it ensured that the surface of the paint sample, which may be contaminated, was adjacent to the mylar tape and thus would not dominate the results of the subsequent analyses. Figure 5.2 shows the size and colour variation within two of the samples (a mixture of flakes and thin layers of paint) that were used in this investigation.

5.2.2.4 Additional shelter sampling

In addition to the paint samples mentioned above, five ‘blank’ samples of the rock surface were collected from all four shelters. The locations of these samples were carefully examined prior to sampling to ensure that no paint was present.



(A) **(B)**

Figure 5.1: (A) Painting before and (B) after sampling - paint sample 6 collected from Maqonqo Shelter.

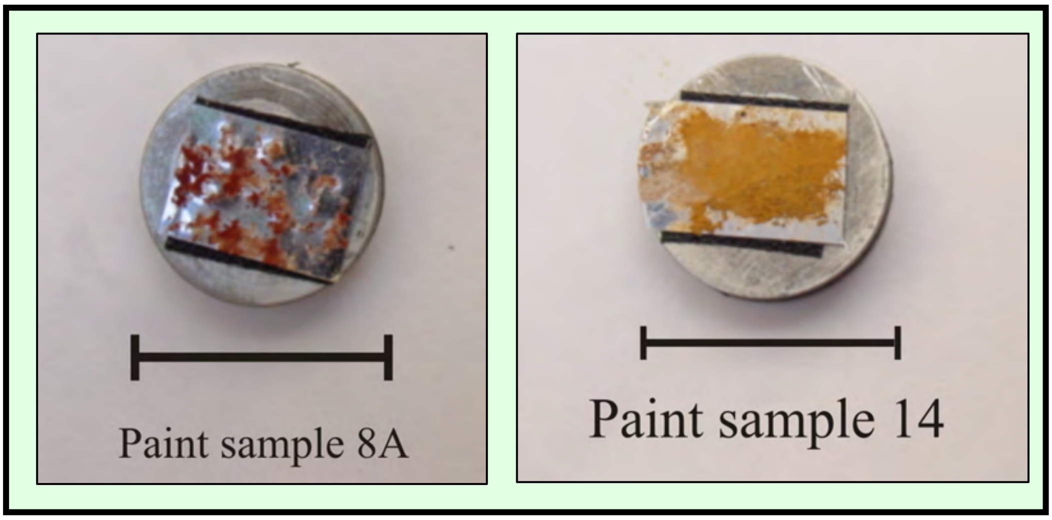


Figure 5.2: Two of the paint samples collected from Maqonqo Shelter. Scale bar = 10 mm.

Sampled in the same manner as the paint pigments, these samples were collected to detect and determine the nature of any surface deposits on the rock wall. Surface water samples (located along seepage lines) were also collected from each of the shelters: three from MQ, and one each from the remaining three shelters.

5.2.3 Shelter deposits

Maqonqo Shelter was excavated by A. D. Mazel during two, three-week fieldwork sessions from 28 January to 18 February 1992, and from 12 January to 2 February 1993. For a full account of the excavation, the reader is referred to Mazel (1996a). Most of the following information has been summarised directly from that paper.

Nine square metres were excavated on the east side of the shelter (Figure 5.2). Within these squares, 51 stratigraphic units were identified and grouped into 14 different layers. Unmodified ‘ochre’ was found within all of these layers, with just under a third of all the pigmentaceous material recovered located within the first three layers (Table 5.1). This material varied in size from relatively large stones weighing between 2.0 and 5.0 g, to very small fragments of material weighing less than 0.1 g. This range in pigment size led to the development of a two-phase sampling regime. The first one focussed on the larger samples that could be analysed using standard XRF and XRD. The second concerned the smaller, but generally more “ochreous” samples, which were analysed by µ-XRF and µ-XRD.

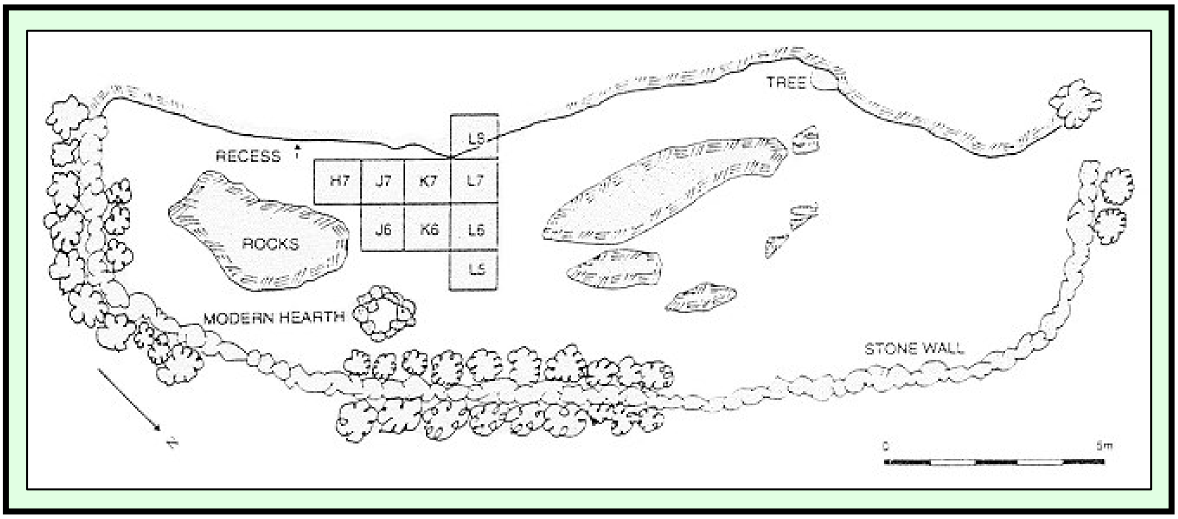


Figure 5.3: Maqonqo Shelter site plan (Mazel, 1996a).

Due to the amount of sample needed for standard XRF major and minor elemental analyses, the initial selection criteria was weight-based, with all samples being equal to or above about 2.5 g in weight, to allow for possible losses incurred during sample preparation.

Even with a 2.5 g minimum mass limit, there were too many pigment samples to analyse. In order to simplify this sampling regime, it was thus decided to focus on the first three layers only, for the following reasons:

- just under a third of all the pigmentaceous material recovered from this site was located within these first three layers (1 918 of a total of 5 931 pieces);

- the first three layers represent a time span of approximately 4 000 years. Changes in pigment usage over this period would highlight possible differences in pigment usage between the original inhabitants (the San) and the Bantu peoples, the latter having arrived in the KwaZulu-Natal region about 1 600 years B.P. (Willcox, 1976; Mazel, 1993; 1996a; A. Solomon, pers. comm., 2000; G. Whitelaw, pers. comm., 2000); and
- these layers coincide with the assumed period of painting. This time period also corresponds with the two oldest known dates in South Africa (3 600 years (Jerardino and Swanepoel, 1999) and 3 720 ± 100 (Mazel and Watchman, 2003).

Table 5.1: A description of the layers used in this investigation (Mazel, 1996a) and number of samples analysed.

Layer	Stratigraphic units	Volume of deposit (m^3)	^{14}C dates b.p.	No. of samples analysed	Total unmodified ochre	
					No. of pieces	% Total
1	Top Brown Sand; Top Hearth; Brown Sand 1; Brown Sand 1 (bedding); Top Dark Brown Sand; Lower Top Dark Brown Sand; Brown Sand 2; Pit Deposit	1.08	#	Large = 26; Small = 11 (1)*	1 013	17.08
2	Top Ashy Brown Sand; Crusty Ashy Brown Sand; Ash 1	0.31	3 560± 60	Large = 9; Small = 12 (4)*	323	5.45
3	Mottled Brown Sand; Mottled Brown Sand (front); Dark Brown Sand; Ash 1 Lower; Ash Hump	0.51	4 080 ± 25	Large = 27; Small = 11	582	9.81
5	Mottled Brown Sand 3; Dark Brown Sand 3	0.44	4 960 ± 70	Small = 1	502	8.46
6	Mottled Brown Sand 4; Dark Brown Sand 4	0.40	4 140 ± 60	Small = 2	480	8.09
7	Mottled Brown Sand 5; Dark Brown Sand 5	0.40	4 790 ± 60	Small = 11	303	5.11
9	Mottled Brown Sand 7; Mottled Brown Sand 7 (Orange); Mottled Brown Sand 7 (Grey); Dark Brown Sand 7	0.39	n.d.	Small = 3	280	4.72
11	Mottled Brown Sand 9; Mottled Brown Sand 9 (Orange); Mottled Brown Sand 9 (Grey); Lower Ashy Brown Sand	0.39	6 300 ± 80	Small = 12	394	6.64

- Though much of the material within this layer dates to around 3 500 years ago, the presence of glass beads, pottery and sheep bones (Plug, 1996) indicates a more modern time period. This is thus a disturbed layer, and hence no date can be assigned to it.

* - The second number indicates the number of 'duplicate' samples present i.e., the sample was analysed by both standard XRF and XRD, and µ-XRF and µ–XRD techniques.

n.d. - No date given.

This sample set was then classified into being of shale, dolerite, micaceous schist or sandstone origin (R. Maud, pers. comm., 2000). In addition, the physical characteristics of each piece were noted, with similar pieces being grouped together. After the pieces had been classified, 62 samples were chosen. The choice of these samples was determined in such a manner that each layer was represented, along with each sub-group within each layer. In all, 26 samples were selected from Layer 1, 9 from Layer 2, and 27 from Layer 3 (see Appendix 5.2 for images of these excavated samples).

The second set of pigment samples (< 2.5 g) were selected from all 14 layers. A large number of samples were selected, photographed and labelled, and then 63 of these (from 8 layers) were analysed using µ-XRF and µ-XRD. The number of samples analysed was limited by the beam-time available on the synchrotron (see Table 5.1; Appendix 5.3).

When selecting the samples (both large and small), no consideration was given to where in the deposit the samples originated. The samples were selected on the basis of size, colour, pulverulence, or a combination of the three. It is therefore interesting to note that a majority of the samples were obtained from the quadrats located towards the rear of the shelter (Appendix 5.4).

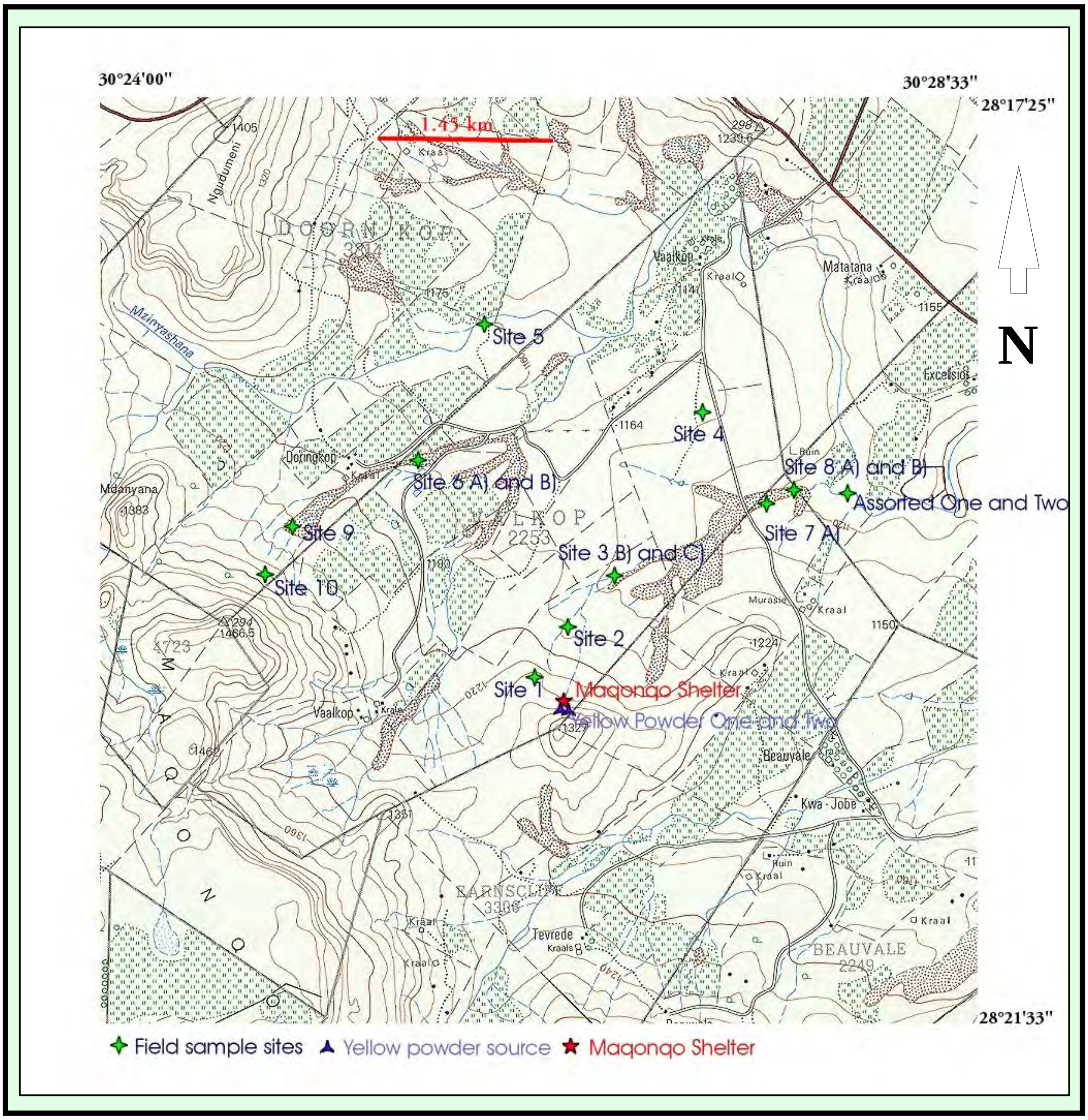
It is important to note that there is a chronological inversion within the stratigraphy between Layers 5 and 7 (Table 5.1). Due to the similarity in the ages of Layers 5 and 7, Mazel (1996a) concluded that these deposits formed during the same chronological period, and by default, so did Layer 6. This anomalous date for Layer 6 was attributed to contamination of the dated sample by younger carbon introduced from an overlying layer.

5.2.4 Field samples

As previously mentioned, there are no known sources of pigment that were specifically used in the manufacture of paints in this area. Furthermore, there is also a possibility that pigmentaceous material could have been imported from a distant locality. The sampling strategy was therefore highly flexible. In order to gain as much information as possible with a limited number of samples, it was decided that there would be three phases of field sample collection i.e., shelter, local and distant field samples.

The shelter sample collection included rocks found within MQ, both from the floor (three samples) and the wall (five samples with no paint pigments present). Four of the wall samples (samples A to D) were collected in order to investigate surface deposits found upon them, whilst the fifth sample, sample E, was to be used as a standard against which the paint samples could be compared (no surface deposition of any kind was noted). The floor samples were collected from the weathered surfaces of three dolerite rocks located on the Shelter floor. They were selected as they displayed both a pulverulent nature and a distinct red or yellow hue (samples F, G and H).

The collection of the local field samples involved searching for distinct red or yellow pulverulent rocks. They were collected within 3 km of MQ, in an area covering the most prominent river systems/dongas (Map 5.1). All the samples were collected in a north to north-easterly direction from



Map 5.1: Location of field sample sites in relation to the Maqonqo Shelter (adapted from 2830 AD HELPMEKAAR, Surveyor General, 1981).

the shelter from the lower areas of the local watershed; as only sandstone and dolerite outcrops were found on the hills in the southerly and south-westerly directions, these areas were not sampled.

As there is no reference as to where pigment sources might be located, the sampling strategy was based on the following assumptions:

- if no specific source was used, the channels would represent a natural gathering point (for the valley and/or the entire watershed) for highly weathered rock material, that could both be easily seen and gathered (no mining required);
- highly weathered rock tends to be pulverulent, thus fulfilling one of the criteria for ochre;
- the collecting of water would have necessitated constant travelling to and from the river. The possibility of a brightly coloured rock being discovered and carried back to the shelter was therefore quite high; and
- many rock strata may be exposed along these channels. The weathering action of the water would also facilitate the easy extraction of rocks associated with these strata.

The gathering of the local field samples thus involved the searching of the river channels located in close proximity to MQ. Samples of differing origins were collected e.g. highly weathered dolerite, pink/red shale, bauxite, and highly weathered plinthic material. Though yellow samples were collected, the search for red samples was given preference, as most of the paintings within the shelter were red in colour. However, very few red coloured samples were found. Suggestions have been put forward that the San increased the range of pigment colours by ‘burning’ the pigments in fires (Segal, 1935; Willcox, 1984)[1]. For the purposes of this study, however, it was assumed that unmodified rock was used in the paint manufacture.

Not all the samples collected in the field were used in this investigation. As many of the samples were similar in nature, it was decided that analysis of all the samples would add no further variance to the sample set, but merely increase the amount of repetition. A total of 26 local field samples were collected, but of these, only 17 were analysed. Map 5.1 indicates the location of the sampling points in relation to MQ. The yellow powder symbol highlights the positions of the ferrihydrite samples that were included in the local field sample dataset.

Distant samples of pigmentaceous material were selected primarily on their expected Fe content. The sites used in this survey were located using both old mining reports, as well as observations from the local community, and are generally found in a north to north-easterly direction from MQ. The 50 km distance restriction was arbitrarily chosen, based on the number of sample points and their localities. In total, six sites were sampled and 11 samples collected. The co-ordinates for both the

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[1] It has been shown by, *inter alia,* Pomiès *et al.* (1999) that heating goethite (yellow; α - FeOOH) at temperatures between 250 ^{o}C and 300 ^{o}C, transforms it to haematite (red; α - Fe_2O_3). This technique has been shown to have been used by Palaeolithic people in the northern hemisphere to gain a greater degree of colour variation or purity (Minzoni-Déroche *et al.*, 1995; Porat and Ilani, 1998).

local and distant field sample sites are listed in Appendix 5.5, whilst images of all the field samples collected are shown in Appendix 5.6.

5.3 SAMPLE PREPARATION

5.3.1 Paint sample preparation

The samples (still on the silver mylar tape), were mounted, using adhesive double-sided carbon tape, to aluminium stubs and analysed using an EDAX® detector attached to an environmental scanning electron microscope (ESEM)[1]. The samples were then removed from the stubs (still on the silver mylar tape) and mounted in slide holders using Kapton Tape[2] to hold them in place. They were then placed directly into the sample chamber and analysed by XRF and XRD using synchrotron radiation (µ-XRF and µ–XRD).

It must be noted that the samples were not polished prior to analysis. The samples therefore still display an irregular surface and an undefined thickness, both of which are factors which make the quantitative determination of both the samples' elemental and mineralogical composition impossible.

5.3.2 Large pigment preparation

The pigment samples were crushed using an agate mortar and pestle. A small fraction of the resultant powder was smeared onto double-sided carbon tape. This was done to ensure that as flat a surface as possible would be available - an irregular surface decreases the accuracy of the EDAX® detector[3]. This tape was in turn placed onto an aluminium stub to be used for Energy Dispersive X-ray (EDX) analysis and major element determination.

In order to determine the mineralogical composition of these same samples, the crushed sample was packed into a sample holder, ensuring random orientation, and analysed using XRD. The sample was then recovered and used for XRF analysis.

In order to conduct the XRF analysis, two sub-samples were prepared, one for elemental analysis, the other to determine the Loss on Ignition (L.O.I.). For the elemental analysis sample, fusion beads,

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[1] The primary advantage of the ESEM over a standard SEM is that samples can be analysed without the introduction of sample coatings. Charging and the interference of sample coatings are thus removed as factors in sample analysis.

[2] Kapton Tape®, is a polymide material with a heat resistant silicon adhesive (500 ^{o}C) (www.kaptontape.com).

[3] An EDAX detector works by detecting X-rays emitted from the sample. If the surface of the sample is directly facing the detector, the X-rays will be unobstructed and a reading can be determined. Should a samples' surface be highly irregular, the incidence of partial to complete obstruction of the generated X-rays from reaching the detector by another portion of the sample, increases thus influencing the overall X-ray counts. The degree to which this phenomenon can affect the results is also dependant on the atomic number of the sample being analysed, together with the beam voltage being used (Krüsemann, 2000).

composed of 2 g of Spectroflux 105 and 2 g of sample, were heated over an oxy-propane flame at a temperature of 1 000 °C, then poured into a 32 mm diameter mold that had been pre-heated to a similar temperature. The sample was then cooled by air jets to form a fused disk (R. Seyambu, pers. comm., 2000). The L.O.I. was established by calculating the weight of a 0.5 g sample at 110 °C, then again determining the weight of the sample after it had been subjected to 1 000 °C for an hour, thus allowing for the calculation of the percent water and other volatile gases present within the sample.

For minor element analysis 0.3 g of sample was placed in the bottom of a stainless steel die, with pure quartz being added on top when necessary in order to bring the sample to the required sample mass. A polysynthetic binding agent was also added, and this mixture was then compressed into a pellet under a force of 10 tonne (R. Seyambu, pers. comm., 2000).

5.3.3 Small pigment preparation

These samples were not crushed. Tiny fragments of the samples (< 1 mm diameter) were removed and placed onto Kapton Tape securely fitted within slide holders. They were then placed directly into the sample chamber and analysed using µ-XRF and µ–XRD.

5.4 ANALYTICAL TECHNIQUES

5.4.1 X-ray diffraction (XRD)

The ability to analyse a sample for its mineralogical composition replies heavily on the fact that minerals are crystalline in structure. X-ray Diffraction Spectrometry takes advantage of this phenomenon and the fact that that all planes within a crystal lattice will diffract a proportion of X-rays directed at it. By slowly changing the angle of incidence of the X-ray beam relative to sample and measuring the resultant combined diffraction patterns, the spectrometer takes advantage of a law first formulated by W. H. Braggs in 1913 (now known as ***Bragg's Law***). This law simply states that diffracted X-ray beams that are out of phase will produce no detectable diffraction pattern (the incident beams are represented in Figure 5.4 as lines 1 and 2). However, when the distance ABC (Figure 5.4) is the exact distance required to allow for the diffraction beams to become synchronous (see 'D' in Figure 5.4), reinforcement occurs and a diffraction maximum is recorded as a peak.

As different mineral have different lattice or crystal plane spacings (otherwise known as 'd – spacings), each will produce a unique diffraction pattern, effectively providing each mineral with its own distinct 'finger-print' and thus allowing for their identification. Furthermore, the relative strength of the pattern can give an indication as to the proportional contribution to the sample of that particular mineral.

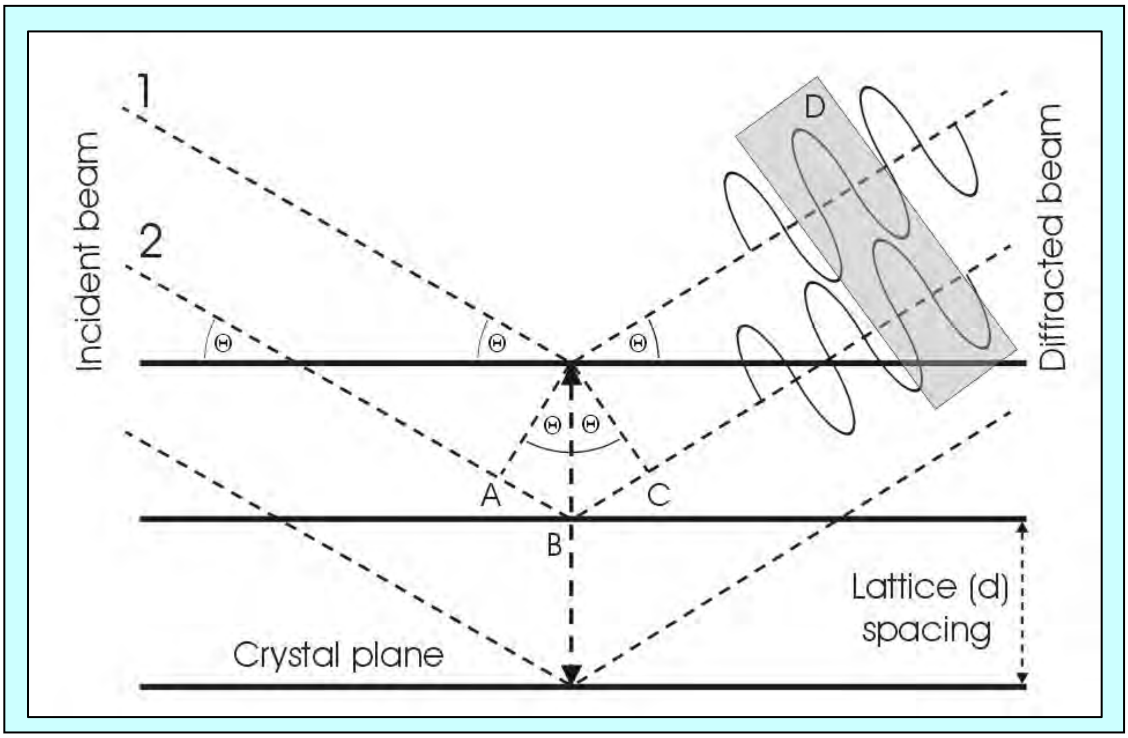

Figure 5.4: Diffraction maximum from crystal planes following Bragg's Law, $n\lambda = 2d \sin\theta$. When the distance ABC = $n\lambda$, then the diffracted X-rays will be in phase resulting in reinforcement and a diffraction maximum being recorded.

These principles hold true for both the standard XRD analytical techniques as well as the micro–XRD analyses generated using synchrotron radiation. The key difference between the two techniques lies in the manner in which the X-rays are originally generated. The Philips PW1050 diffractometer uses a vacuum-sealed X-ray tube to generate X-rays. It achieves this by initially accelerating electrons to a high speed by creating a large potential difference between its filament (cathode) and target (anode), in this case 40 kV. The X-rays are greeted when these electrons rapidly decelerate when they strike the target. The Synchrotron, on the other hand, generates X-rays when charged particles (electrons or positrons), travelling around the speed of light, pass through the magnetic field of the bending magnets as they are steered around a storage ring (Schulze and Bertsch, 1995). The difference between the two X-ray generation methods is that the latter technique allows for the generation of X-rays of a much higher intensity than those produced in the conventional vacuum-tubes, thus allowing for more precise and accurate results from much smaller samples over a much shorter analysis periods.

As previously mentioned, the conventional XRD analyses were carried out using a Philips PW1050 diffractometer. Fitted with a Philips PW1170 automatic sample changer, this was used to analyse the powdered samples (large excavated pigments, shelter samples, and local field samples). All samples were analysed at 40 kV and 40 mA using monochromated CoKα radiation at a scan speed of 1 ^{o}/min with a scanning step of 0.02^{o} from 3^{o} to 75^{o} 2θ. A Sietronics SIE122D automated interface unit running Sietronics X-ray analytical software© V2.6[1] was used to capture the X-ray data, whilst Sietronics XRD Traces processing software© V2.0[2] was used to analyse the traces captured. The raw data obtained have not been included due to the large quantity collected. It was, however, interpreted and analysed in the manner described for the µ-XRD patterns (see Appendix 5.9), and the qualitative data so obtained are listed in Appendix 5.10.

5.4.2 X-ray fluorescence spectrometry (XRF)

More correctly known as 'wavelength dispersive X-ray spectrometry', or XRFS, this analytical technique utilises X-rays to cause elements present within a sample to emit secondary (fluorescent) x-radiation (Karathanasis and Hajek, 2001). These secondary emissions are unique to each element allowing for their identification. In addition, the intensity of the readings is roughly proportional to the amount of the element present within the sample, thus allowing for quantitative determination of the amount of the element within the sample.

Both major and minor element analysis was conducted on all the samples, excluding the paint samples. All of the samples were analysed using a Philips PW 1410 wavelength dispersive X-ray fluorescence spectrometer utilising a vacuum-sealed X-ray tube set at 50 kV and 50 mA. Certified reference materials were used as calibration standards throughout all analyses (Govindaraju, 1994). For a list of the detection limits and accuracies associated with the detection of each element, the reader is referred to Appendix 5.7.

The data obtained give the elements in the form of their oxides. In order to allow comparisons to be made with the EDX data, these values were converted to the wet percentage[3] of each element. The formulae used in this conversion process and the data obtained are listed in Appendix 5.8.

5.4.3 Energy dispersive X-ray analysis (EDX)

Unlike the afore mentioned techniques which rely on X-rays to generate the required results, Energy Dispersive X-ray analysis relies on the interaction of an electron beam and the sample. When a high velocity electron impacts with an atom within a sample, a bound electron is removed from the atom's energy shell leaving that shell energetically unstable (see Figure 5.5). To counter this instability, an electron from a higher energy shell drops into this unstable shell, with the difference in potential energy being emitted in the form of an X-ray proton that can be detected by an appropriate detector.

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[1] Copyright Sietronics Pty Ltd 1994.

[2] Copyright Sietronics Pty Ltd 1991 – 1993.

[3] The Loss on Ignition for each sample was re-incorporated back into the percentage values of each element in order to allow for a more representative comparison between the two datasets – the EDX data were analysed in an unaltered state.

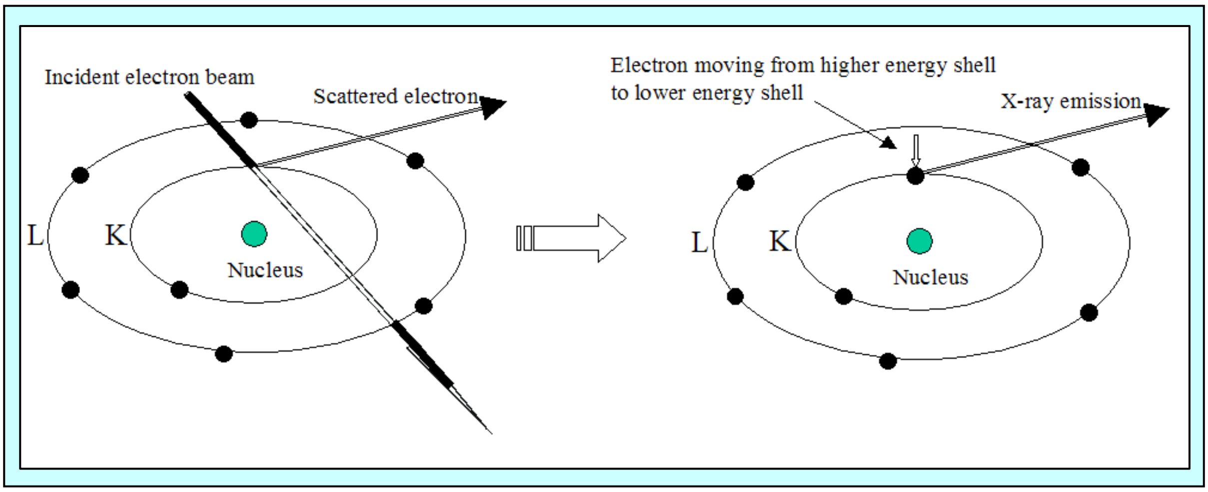

Figure 5.5: A diagrammatic representation of how X-rays are generated when an electron beam interacts with atoms within a study sample.

As each element has a unique number of energy shells and electrons, the X-ray photon produced will be characteristic of that element and thus allows for that elements identification.

All the samples (except the small excavated pigment samples[1]) were analysed using a Philips XL Series (XL30) ESEM fitted with an EDAX® detector. Recording of the spectra was conducted using Phoenix EDX® software, whilst Microsoft Windows® NT v4.7 software was employed to operate both the microscope and all additional operational software such as the EDX and image analysis programmes.

All the paint, blank rock wall and large excavated samples were placed under a high vacuum and analysed at 20 keV at a working distance of 10 mm. To increase the accuracy of the study, the dead time (DT) for each of the samples was maintained at approximately 30 %. In order to maintain both the DT and the working distance at constant values, the spot size was manipulated for each of the analyses (set between 3 and 5[2]). For all recordings, a tungsten thermionic emitter was used as the electron source. All the samples were subject to the same experimental conditions.

Fourteen spectra were recorded for each of the MQ paint and large excavated pigment samples, with nine spectra being obtained from spot analyses, and the remaining five from larger 'reduced window' scans[3]. Only nine 'reduced window' scans were collected from the remaining paint and blank rock wall samples. As the spot data tended to display high degrees of variability relative to the raster data, it was decided to use the raster data only (see Appendix 5.11). These semi-quantitative

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[1] This was due to limitations in both time and money.

[2] Although the typical spot size for the ESEM is ~ 8 nm, in actual fact the final spot size is dependant on competing factors; the magnification being used and the accelerator voltage being employed. The spot size indicated here doesn't refer to the actual spot size, but rather the factor at which the spot has been increased i.e., increasing the spot size by one step (3 to 4) will increase the diameter of the beam by a factor of 2, but also the beam current by a factor of 4. One manipulates this factor as a means of obtaining the best sample spatial resolution.

[3] A rectangular area or scanning extent pre-defined upon the surface of the sample by the operator. The extent of these scan areas always assumed the maximum sample surface area.

values (in the form of weight percentages) were then averaged in order to obtain an elemental composition for each sample. The resultant dataset is given in Appendices A5.12.1 and A5.12.2.

As previously mentioned, all the samples, with the exception of the small excavated pigments samples, were mounted onto aluminium stubs. The large excavated samples were pressed onto double-sided carbon tape and measured directly. The paint and blank samples, collected on silver mylar tape, were mounted (still present on the tape) using double-sided carbon tape to hold the silver mylar tape in place. The control sample (E) collected from the shelter wall (no paint present) was used to see how the sample would react under the electron beam generated by the ESEM. Silver mylar and double-sided carbon tape blanks were also examined. These results were considered with respect to the degree of influence that these had on the sample's overall elemental weight percentage. None of the elements present, with the exception of C, were found to be significant contributors within the pigment analyses. Their effect on the results was thus considered negligible.

5.4.4 Micro-XRF and micro–XRD using synchrotron radiation

The paint and blank wall samples from all four sites, together with the 63 small excavated pigment pieces, were analysed using synchrotron radiation on beam-line X26A at the National Synchrotron Light Source at Brookhaven Laboratory, Long Island, New York. The samples, mounted as described in Sections 5.3.1 and 5.3.3, were placed into the sample chamber. The samples were analysed using a focussed spot analysis on specific sections of the sample for a period of 120 seconds. A y-spot size of 6 µm and an x-spot size of 12 µm were used throughout all analyses. A wavelength of 0.72084 Å was used, produced at 17.2 KeV. Both the µ-XRF and µ-XRD analyses were collected simultaneously from the same sampling point.

The paint samples were analysed in two separate batches, with the second batch also containing the blank wall samples and the small pigment samples. An average of six scans per paint and blank wall sample were collected, with only three scans being recorded for the small pigment samples (the latter were found to be more homogeneous thus requiring fewer scans).

The small pigments were analysed under the same environmental conditions, except that a 5 nm diameter aperture was fitted to counteract the tendency of large crystals present within the sample producing a 'burning' effect during µ-XRD pattern analysis causing 'streaks' on the resultant XRD pattern.

Once all of the data had been captured they were transferred to CD, and taken to Purdue University, West Lafayette, Indiana for analysis. Before the µ-XRD data could be analysed however, corrections to the data had to be effected. The corrections relate specifically to the slight tilting in the beam angle as it hits the sample. Although the angle involved is small, it does lead to distortions in the data that impact on the ability of the software to correctly identify the minerals present. In order to identify and correct for these errors, a standard (corundum, $\alpha - Al_2O_3$) was analysed before, during and after the sample run. Figure 5.6 shows the various possible scenarios that have to be corrected for. The standard data were analysed first using FIT2D© software[1]. By comparing the uncorrected μ-XRD data with known data, the correction factors (in the x, y and z axes) were determined. The values were then applied (using a macro function within the FIT2D software) to most of the paint and all of the small pigment data.

As not all of the samples produced very good patterns, a system of categories was developed to allow comparisons between information of similar quality (for more information, see Appendix 5.13). Once corrected, the μ-XRD data obtained were analysed, and the minerals present identified, using JADE 3.1 software[2]. The results obtained are listed in Appendices 5.14, 5.15 and DIGITAL 1.

The μ-XRF data were analysed using an Inductively Coupled Plasma Multi-Component Analysis (or ICP MCA) Display Program[3] designed for IDL VIRTUAL MACHINE 6.0©[4]. In these data, the individual element peaks had to be identified and labelled, and then fitted to a standard background. Once fitted, the area beneath each K-α peak was determined, with these values then being converted into elemental percentage values for the sample by means of a standard comparison. This provided qualitative data for the samples analysed. Quantitative data can only be determined if the sample volume is known. Due to the nature of the samples studied, and their manner of preparation, this could not be achieved. A primary limitation was the fact that scales of a sufficient sensitivity were not available that would enable the accurate determination of the samples weight during the analytical procedure. It is important to note, however, that quantitative determinations are possible using this technique. The results of the μ-XRF analysis are listed in Appendixes 5.16, DIGITAL 2 and DIGITAL 3.

5.4.5 Inductively coupled plasma mass spectrometry (ICP-MS)

The water samples collected from each of the four sites, together with the five 'standard' excavated pigment samples were analysed on a Perkin Elmer Elan 6100 ICP-MS RF power 110W nebuliser (gas flow = 0.9 L/min) at the University of KwaZulu-Natal, Howard College Campus (Geological Sciences). Before analysis, 50 mg of each rock sample were digested in a 3:2 v/v HF and HNO_3 acid combination in a microwave oven at 200 ^{o}C and 700 p.s.i. These samples were then dried at a temperature of 80 ^{o}C. The samples were then treated twice with of 2 ml nitric acid, being dried out

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[1] FIT2D v10.132, copyright 1987-2001, Andy Hammersley, European Synchrotron Research Facility beam-lines (ESRF) (www.esrf.fr/computing/expg/subgroups/data_analysis/FIT2D/).

[2] JADE 3.1, from Materials Data Inc. (MDI), 1284 Concannon Boulevard, Livermore, California 94550, United States of America (www.materialsdata.com).

[3] ICP MCA Display Program v4.3.17, written in Nov 2001 by Mark Rivers, Centre for Advanced Radiation Sources, University of Chicago.

[4] IDL VIRTUAL MACHINE 6.0, copyright 2003, produced by Research Systems Inc. (RSI). For more information (www.rsinc.com/IDL/).

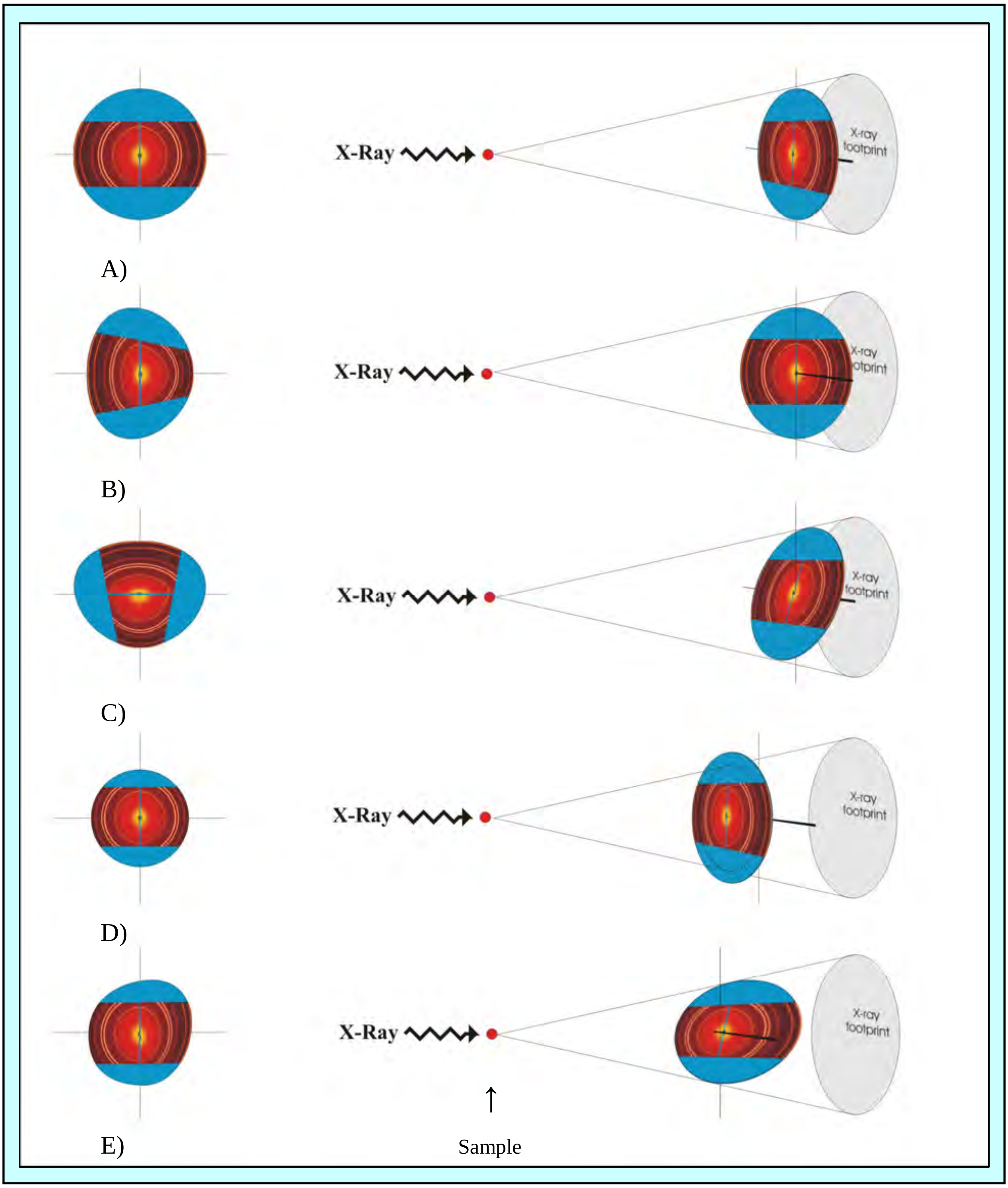

Figure 5.6: Micro-XRD Debye-Scherrer ring distortion: A) Perfect pattern; B) Non-alignment along the x-axis; C) Non-alignment along the y-axis; D) Variations in sample position (z-axis); E) A combination of all three – typical scenario.

(The first image indicates what the pattern looks like; the second image indicates how the first image forms)

after each treatment as before. Just prior to analysis, all of the samples were made up to 50 ml with 5 % HNO_3 solution containing Rh, Re, In and Bi as internal standards. Multi-element standards of 10, 20, 30, 50 and 100 ppb were used to plot calibration curves, from which the final sample concentrations were determined (see Appendix 5.17 for the results).

5.4.6 Statistical analysis

It was determined that the use of Principal Components Analysis (PCA) for the analysis of the data would prove to be the most relevant to this study (H. Dicks, pers. comm., 2000). This statistical technique has also been used in other studies that used trace elements to source materials (e.g. Yu and Miao, 1998; Adan-Bayewitz *et al*., 1999; Hughes and Solomon, 2000). Appendix 5.18 gives a brief description of this statistical technique, and highlights why this statistical approach was selected to analyse the data. The present study has made use of CANOCO FOR WINDOWS® (Braak and Smilauer, 1999) software to perform the PCA and to create the diagrams. In all cases, the datasets were first standardized and then centred. They were not post-transformed.

CHAPTER SIX

PRIMARY DATA ANALYSIS

6.1 INTRODUCTION

The sampling procedure adopted (Chapter 4) resulted in a very large and varied dataset being compiled, with just over 570 individual EDX analyses being collected for the paint and blank samples alone. With the additional XRF analyses (32 elements measured per sample) for the large excavated pigments (62 samples), ICP-MS analyses for the water samples (six samples), μ-XRF and μ-XRD analyses for the paint samples and small excavated pigments (43 and 62 samples, respectively) and combined field datasets (a total of 36 samples), it is clearly not possible to give a detailed discussion for each of the individual results within this database, and to do so would also detract from the inherent nature of this study, which is to look at the trends that the data display. That said, there are aspects that warrant mentioning and these will be discussed in detail together with the analyses with which they are most closely associated.

As mentioned in Chapter 1, there are five main focus areas that are considered within this study. For ease of discussion, each of these will be examined separately with the exception of the comparison of techniques, which is given in Chapter 8 and Appendix 5.15. As mentioned above, most of the data will not be illustrated; only the notable results will be highlighted. The reader is, however, referred to the relevant appendices if more information is required. A summary of the main findings of this study, together with a critical discussion will be given in Section 6.4.

6.2 PAINT ANALYSIS RESULTS AND DISCUSSION

6.2.1 Possible age implications on paint pigment composition

In most of the literature studied, it has generally been assumed that the white, pink and orange colours were all painted within a similar time period. This assumption is based, in part, on the determinations of several relative dating techniques employed by archaeologists who have attempted to describe the evolution of San painting technique over time (see Appendix 6.1).

It is important to note, however, that these dating techniques do not assume the same starting point. Mason (1933), in his comparison to L'Breuil's work (1930), states that the monochromatic stylistic form of rock art lasted for a much shorter period in the Cathkin Peak area (KwaZulu-Natal Drakensberg) than in the eastern Free State, with the opposite trend being apparent for the polychromatic stylistic form. These findings also suggest that the colour orange was only introduced late along the evolutionary scale of painting development.

All of these techniques fail to take into account the natural processes of weathering and their possible influence on the durability of the images as a whole, and that of the individual pigments. In order to answer the question “When were the individual colours first utilised for paintings?” one should first look at imagery of known ages that have been exceptionally preserved. In the main, only burial stones and/or *art mobilier* satisfy this requirement (see Appendix 6.2), primarily because these artefacts, being buried within shelter deposits, were not exposed to excessive erosional forces (either chemically by atmospheric or biological sources, or mechanically e.g. rubbing, scraping etc.). Appendix 6.1 thus gives an indication as to the assumed durability of the colours in question and Appendix 6.2 indicates the minimum known ages for colour (and pigment) introduction. If a particular colour has been used for a long period of time, yet is considered to be fugitive, certain assumptions about its durability and compositional components can be made.

In addition, it is also widely accepted (and can be extrapolated from the trends described below) that white and black pigments are the most fugitive (Rudner, 1982; Loubser, 1992), with, for example, estimates of < 15 % of the eland on ‘hook-head’ bichromes retaining their white/yellow portions (Yates *et al.*, 1985). One reason given for this is that the white pigments consist of larger, less dense particles that either do not mix well with binders or do not penetrate sandstone surfaces (Loubser, 1992). Dr. L. Péringuey (1917) (the then director of the South African Museum) wrote, “…the black pigment on the painted stones came off at the slightest touch. The black and white pigments were not as adhesive as the red and yellow ones”.

It may thus be inferred that most white, and, to a lesser degree, black pigments (which seem to be slightly more resistant to weathering), can be considered to be relatively young, with exceptions only occurring in areas that favour exceptional preservation. Similarly, if the pink colour was a mixture of red and white pigments, it too would also be considered young based on the same reasoning. If all of these pigments are considered as being young (i.e., painted in a similar era), the recipe for their creation may be assumed to be relatively constant assuming that the residents within the area of study were relatively sedentary. This assumption is substantiated (for MQ at least) by the fact that these three colour sub-sets indicate greater compositional similarity than do the remaining colours analysed (see Section 6.2.4).

Employing the same reasoning regarding paint composition similarity, together with the period of usage of the colours within San rock art in general, the opposite trend should be expected for the red and yellow colour sub-sets. This assumption is partly validated by the fact that these two sub-sets, and in particular the red sub-set, display the highest level of variability of all the paint colours analysed by all three of the techniques used. The variability is driven primarily by their Fe and Si contents, with the red sub-set also displaying a highly variable C content (as determined using EDX). This latter finding is due to the presence of only two samples with C contents above 34 % (Paint 3 and Paint 21); the remaining samples exhibit C contents similar to those of the rest of the paint dataset. Whilst the reason for these elevated C contents could be ascribed to the size of the original samples (both were very small, and it is therefore probable that the carbon tape was detected during analysis), the elevated O levels recorded in conjunction with these high C content would tend to indicate that these samples contained elevated Ca-oxalate contents instead (especially if the samples also showed elevated Ca contents as well). Nonetheless, the red paint sub-set appears to be the most variable relative to the rest of the paint dataset.

As the red and yellow paint sample sets display similar degrees of variability, and are also considered to display similar degrees of resistance to weathering, two assumptions regarding these two pigments have been made i.e., a) that the red and yellow pigments were utilised concurrently; and b) that they were utilised over similar time spans.

If it is accepted that the yellow and red samples may be older than the white, pink and orange samples, careful consideration must be given as to whether these data can be compared in a manner similar to that employed for the latter three paint colours. Their high variability could be a result of compositional changes over time, and thus ascribable to variations in source material, paint manufacture, and/or weathering.

It has been suggested by Mazel (1996a) that many, if not all, of the paintings present within MQ predate 4 000 b.p. He later supports this theory with a ‘maximum’ date obtained from a Ca-oxalate crust originally underlying a red paint sample collected from the same shelter (see Section 3.5.9). In addition, suspected paint fragments collected from excavated deposits from this Shelter have been dated to between 4 000 and 5 000 years b.p. (Mazel and Watchman, 2003).

The exact ages of the paintings, no matter what their colour, have not yet been established. However, based on the reasoning outlined earlier within this section, it seems unlikely that all of the images sampled were created over a similar time period i.e., imagery containing white colours could only have been created over a relatively restricted, and therefore relatively recent, time span. The red and yellow containing images, on the other hand, could have been created over a much longer period, and thus their individual ages and individual compositions, could vary considerably. This has important implications regarding possible pigment sources for both the yellow and red paints, and possibly introduces additional problems with regards to imagery interpretation. Possible solutions to these problems are highlighted in the discussion of the individual paint colours.

6.2.2 Paint heterogeneity

One of the assumptions of the methodology employed in this study is that the data being compared display a relatively high degree of precision i.e., there is not much variation within the analyses of individual sample points. In order to meet this requirement and thus ensure the validity of the present study, the samples must be relatively homogeneous, thus allowing for the reproducibility of the results. In the case of the field samples and pigmentaceous materials, evidence suggests that individual rock formations are chemically and mineralogically distinct, although it must be noted that the best results have been obtained from igneous geological formations. Unfortunately, no previous studies have been conducted on San paint samples specifically to determine their degree of homogeneity, even though the degree of which would shed some insight into the paint manufacturing technique.

The findings within this study have shown that the paint samples are heterogeneous at the micro-level (see Appendices DIGITAL 1, DIGITAL 2 and DIGITAL 4) with significant variations being recorded along transects a few nanometres in length. This should not be surprising, however, when one considers the diameters of the beam footprints utilised within each of these techniques to analyse the samples (either X-ray, electron or photon/laser sourced). When investigating a material at the nanometre scale, the presence of any material unique to a beam footprint will have a dramatic effect on that single reading. The reader is referred to Appendix 5.11 for a more comprehensive discussion of this phenomenon.

The degree of heterogeneity was also found to vary with regard to paint colour, with the least variable colour being pink and the highest variability being noted for the red colours. This high degree of variability can be attributed primarily to three of the elements analysed, namely Fe (except in the case of the white and pink colours), Ca and C. Explanations as to why these elements varied will be discussed in the following section.

The only way to account for these additional influences is by sampling ‘bare’ rock surfaces, and determining if the elemental variations noted within the paint samples are also present. The µ-XRD technique was invaluable in aiding in the determination of the minerals within which these elements reside.

As was discussed in Chapter 4, the historic, and hence invaluable, nature of the paintings inevitably restricts the maximum allowable sample size that, in turn, restricts the number and type of techniques that can be used. Precise techniques are required, but, as has been highlighted above, certain techniques can be considered to be too precise (e.g. LAM-ICP-MS). What is ideally required is a technique that is accurate enough to analyse small samples, while not being so precise as to over-emphasise the samples micro-heterogeneity. Of the three techniques used, the EDX technique was the least precise. Incongruously, its lack of specificity made this technique the most valuable in establishing the initial trends within the data. The other two techniques (µ-XRF and µ-XRD) were then employed to augment these initial data, facilitating a greater understanding of the samples as a whole. It is for this reason that the data obtained using EDX form the initial focus of this investigation, with the remaining data being used to support the interpretations and conclusions obtained.

6.2.3 External influences on the paint composition

The effects of external processes on the composition of parietal rock art are hard to quantify, with each image, and possibly even each part of an image, being subjected to a differing range and intensity of external influences. Common processes include climatic (moisture and temperature fluctuations), chemical (deposition or removal of chemical species to/from the painted image) and bio-chemical effects (e.g. fungi and/or bacteria derived chemical influences), as well as mechanical impacts (e.g. rubbing, scraping etc.). Furthermore, it is highly probable that an image is subject to a combination of these factors, and that both the combination and intensity of these processes have changed with time.

Although it might never be possible to determine the exact processes that had an impact on the paintings sampled, by analysing blank samples collected at random throughout the shelters, the products of these influences can be determined. It is then theoretically possible to ‘remove’ these products from the paint data and thus determine the current composition of the paint component under study.

Figure 6.1 shows the EDX data obtained for the blank samples from all four sites. This PCA (87.4%)[1] displays some features that are easily apparent. Firstly, there is the linear gradient between Si, Al and K at one extreme, and Ca on the other. Three of the sites separate out along this gradient; TW associating with the higher Si values; MQ aligning with the elevated Ca values; and SV lying between the two. Secondly, the FC samples are closely aligned with the elevated C values, the opposite extreme being elevated S and O contents. Finally, whilst TW and FC separate out clearly, the separation of MQ and SV is less distinct, though Ca seems to exert a higher influence of the MQ samples than the SV samples.

The sample distribution seen in Figure 6.1 is repeated in Figure 6.2, which highlights the averaged µ-XRF blank data (79.9 % variability). This similarity in sample distribution is interesting as the second dataset contains few of the elements found within the former EDX test. The one common element, Ca, also dominates the sample distribution in the µ-XRF data. Unlike Figure 6.1, however, three other distinct elements display an overriding influence on the dataset as a whole, namely Cu, Sr and Fe, with the degree of influence of these respective elements increasing in this same order.

The only distinct gradient lies between Cu and Sr, with the latter element dominating PCA2 variability (24.3 %). With the exception of SV, all of the sites tend to aggregate to a higher degree in this analysis. Generally, as one moves along the Ca - Fe gradient from the Fe end, the sites aggregate as follows: TW, SV, MQ and then FC. These sites are located in the same order, although less distinctly, following from Sr along the Sr – Cu gradient.

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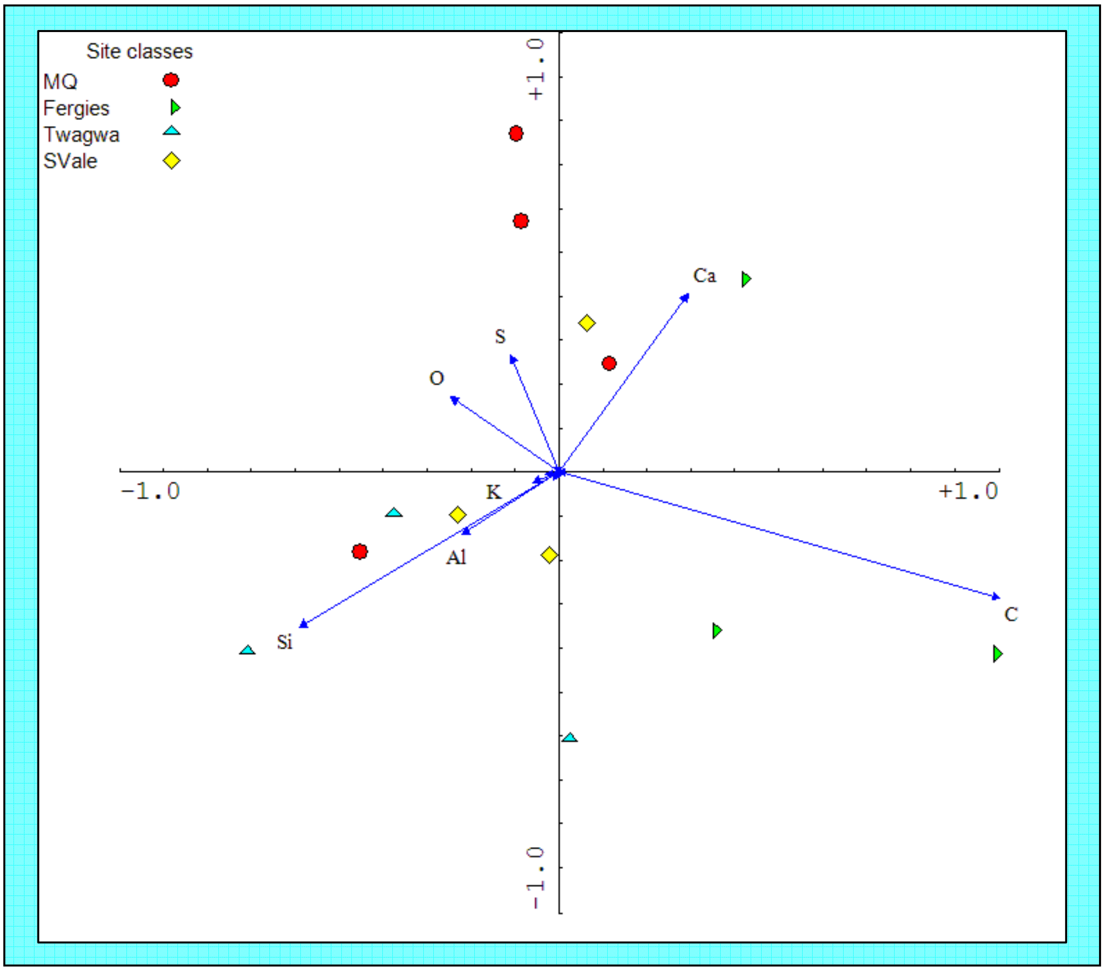
[1] This refers to the amount of the variability accounted for by the first two dimensions within the PCA diagram. It gives a measure of how relevant the trends displayed with the PCA are as compared to the dataset as a whole.



<u>Figure 6.1: Average reduced window EDX data of the blank samples from all four sites.</u>
Eigenvalues: PCA1 – 66.5; PCA2 – 20.9; PCA3 – 6.0
Scaling = -2

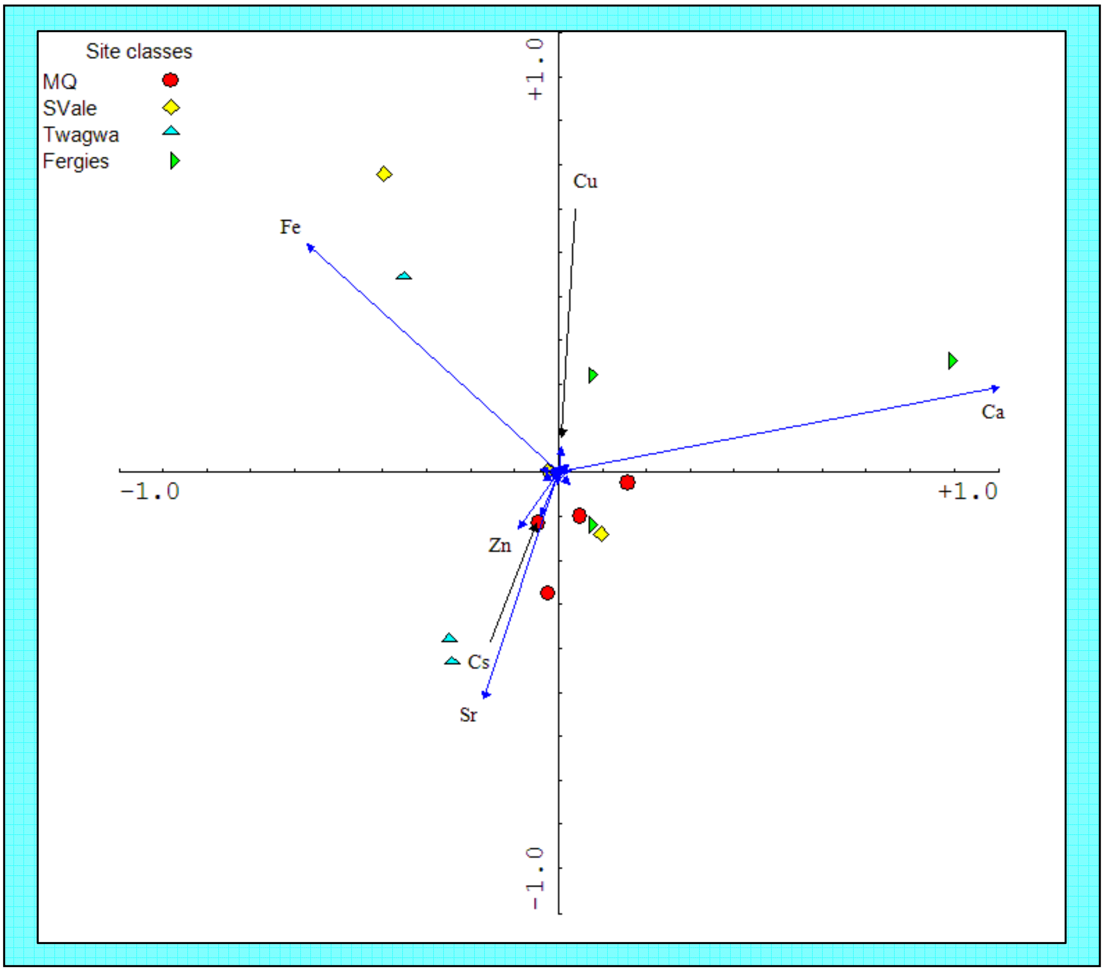


Figure 6.2: Average micro-XRF blank data for all four sites.
Eigenvalues: PCA1 – 55.6; PCA2 – 24.3; PCA3 – 12.9
Scaling = -2

Figure 6.3, representing the µ-XRD blank dataset (54.7 %), also shows a separation of the four sites, though, with the exception of the SV samples, the separation is subtle. One of the primary reasons for this is the 'crude' classification originally employed to classify the data (Appendix 5.9). It is likely that, with more quantitative data, the trends would be more distinct. Nonetheless, it is apparent that the samples separate out into three groups, these being derived by influential differences attributed to specific combinations of controlling minerals, namely 1) whewellite and kaolinite (mainly SV); 2) gypsum, quartz and weddellite (predominately FC and MQ samples); and 3) greigite, haematite, schlossmacherite and buserite (mainly TW).

Two linear gradients can be noted. The first lies between haematite and gypsum, and probably denotes a change from sandstone matrix components to secondarily deposited gypsum. This assumption is supported by the close association of feldspar, muscovite, greigite and buserite with the haematite vertex, all of which are minerals more commonly associated with geological formations than chemical deposition. The one exception is schlossmacherite, a secondarily deposited mineral identified only at TW. Twagwa Shelter displayed no gypsum presence, however, thus explaining its position at the opposite extreme along the sandstone: gypsum gradient being described. None-the-less, this effectively indicates the influence of geological locality and climatic influences on the degree, nature and extent of deposition that occurs within each of the respective shelters.

The other linear gradient represented exists between weddellite and calcite. To understand this dynamic, one must first explore the nature of these minerals. Although some evidence does exist that indicates that the diagenesis of weddellite can result in the production of calcite (Verrecchia *et al.*, 1993), the predominance of this mineral to the complete exclusion of weddellite (and whewellite) is indicative of a geological, and not biological, source (Appendix DIGITAL 1). A high calcite content can therefore be interpreted as a sandstone surface that has a limited surface depositional layer.

Weddellite, when it is found upon rock surfaces, is generally present as a depositional by-product that has had a biological influence in its formation via the addition of oxalic acid (Hofmann and Bernasconi, 1998). Whether this influence is direct (i.e., the mineral is produced *in situ* biologically as a by-product of, for example, epilithic and endolithic cyanobacteria (Del Monte and Sabbioni, 1988), bacteria (Mawk and Rowe, 1998), lichen (Russ *et al.*, 1995; Russ *et al.*, 2000) or fungi (Verrecchia *et al.*, 1993)) or indirect (i.e., the oxalic acid is produced elsewhere and transported to the wall surface via groundwater or rainwater (Ford *et al.*, 1994)) is, for this particular point, immaterial. What is important is that its presence is indicative of an environment suitable to its formation i.e., it is present without the aid of a human agency. The weddellite – calcite gradient therefore indicates a change in environmental conditions that governs the production of weddellite, with the calcite dominant end representing the least favourable end of the gradient (predominantly represented by TW). For more information on Ca-oxalates, see Appendix 3.2.

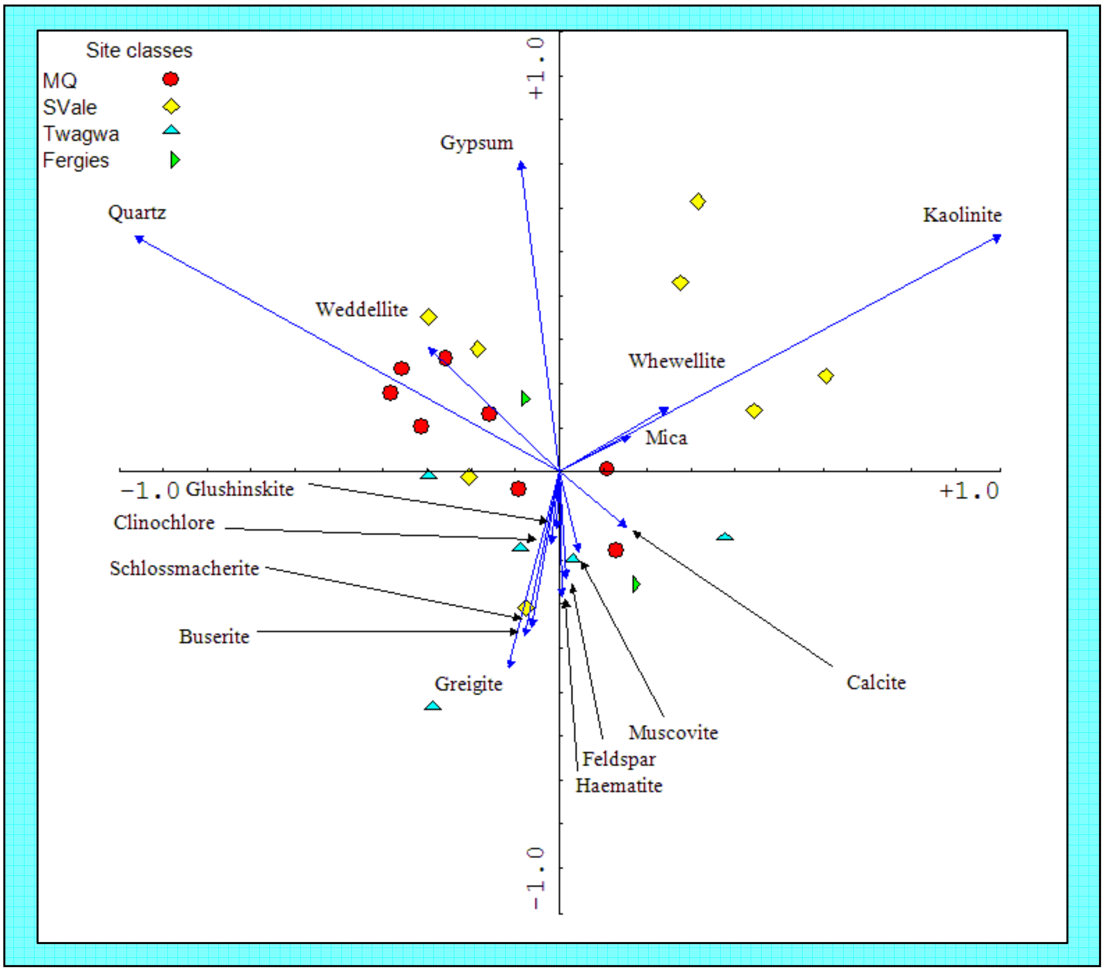


Figure 6.3: Micro-XRD blank data for all four sites.
Eigenvalues: PCA1 – 29.3; PCA2 – 25.4; PCA3 – 17.5
Scaling = -2

The complete lack of any Ca-oxalate formation within TW (even within the paint samples) could possibly be explained by the lack of physical protection afforded to the painted shelter wall. It has been found in other studies that direct rain and intense sunlight can limit crust formation, together with limited quantities of oxalate minerals (Watchman *et al.*, 2001). This phenomenon might be present within this Shelter, for it is the most exposed of the four sites studied. Another possible reason for a lack of Ca-based minerals might be that Ca is limited within the system. The relatively high Ca content within local river water samples would initially tend to contradict this, however (Table 6.1).

A simple explanation for this anomaly is as follows: TW is located near the top of the hill slope. As a result of its exposed position, 'leaching' processes dominate the weathering regime operating within the Shelter, resulting in a net loss of material and elements from the system (as opposed to 'accretion' processes in which additions to the Shelter of material originally eroded from further upslope would occur - in this case, there is virtually no 'up-slope'). It is therefore possible, due to its elevated position within the landscape, that there is no Ca within the vicinity of TW. Additional samples from the nearby surrounds will have to be ascertained in order to confirm this, however.

Sheltered Vale is the only site that shows a marked separation from the rest of the shelters, this distinctiveness is driven primarily by the presence of kaolinite and whewellite. The former mineral probably originates from the sandstone, the eventual weathering product of feldspars and micas. The relatively large amounts of quartz recorded in these samples would further indicate a dominating presence of sandstone particulates (Appendix DIGITAL 1). The presence of the whewellite phase instead of weddellite is, however, interesting.

Evidence suggests that the ratio of weddellite: whewellite is temperature dependent, with weddellite being preferentially formed below standard room temperature (21 ^{o}C), and whewellite showing the opposite trend (Ford *et al.*, 1994). As all three Ca-oxalate containing sites displayed mean annual temperatures below room temperature, it would be expected that all would contain the weddellite phase. Studies, however, have shown that dry conditions favour the formation of the more stable whewellite phase via weddellite dehydration (e.g. Frey-Wyssling, 1981). Whilst the temperatures experienced between SV and FC, and to a lesser extent, MQ, are similar, SV has the drier climate (Figure 6.4). It can therefore be concluded that the relative humidity experienced at each shelter probably accounts for the Ca-oxalate species occurrence at each of the sites.

Figure 6.5 shows the elemental composition, obtained using ICP-MS, of the water samples collected at each of the four sites. As stated earlier, these samples were collected from surface water either in, or in close proximity to, each of the study sites. They do not represent groundwater results and so the results can only be considered as guideline values for the possible elemental composition of the groundwater at each of the four sites.

The MQ results were collected from a variety of nearby sources and are presented separately. The other three sites have, however, been bulk analysed owing to the fact that they were collected in relatively similar conditions. Differences between the samples are easily apparent. The MQ samples

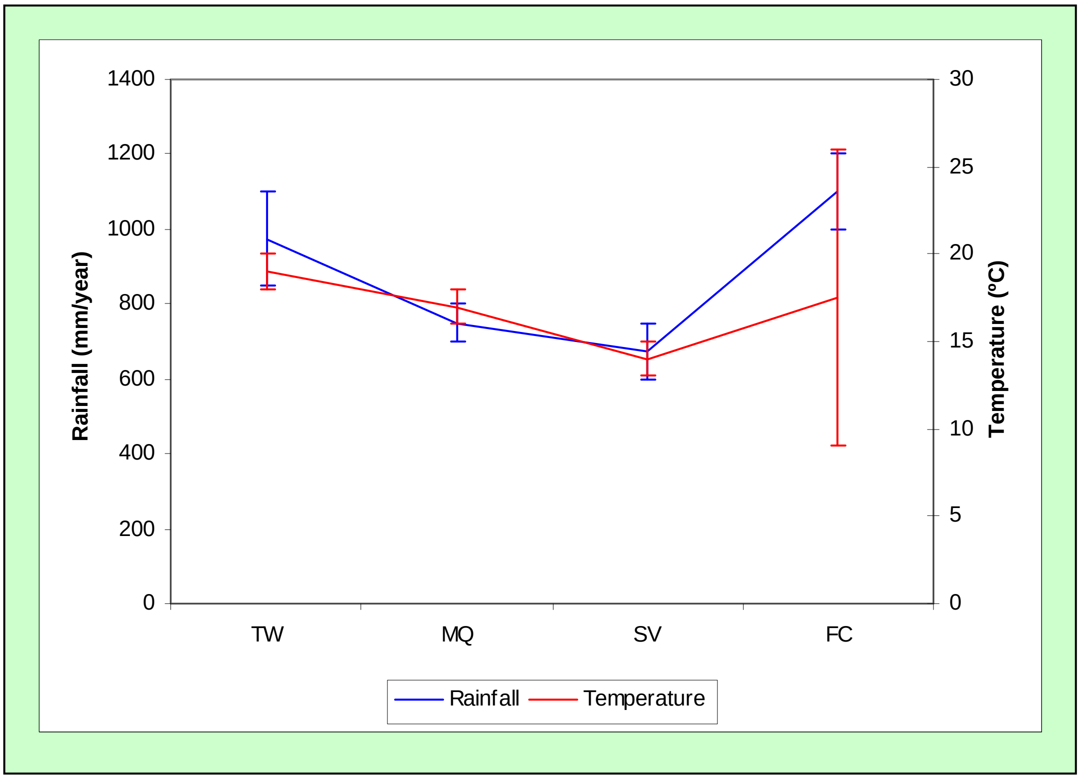


Figure 6.4: Annual maximum, minimum and average temperature and rainfall ranges for the four study sites (adapted from Eksteen *et al*., 1990).

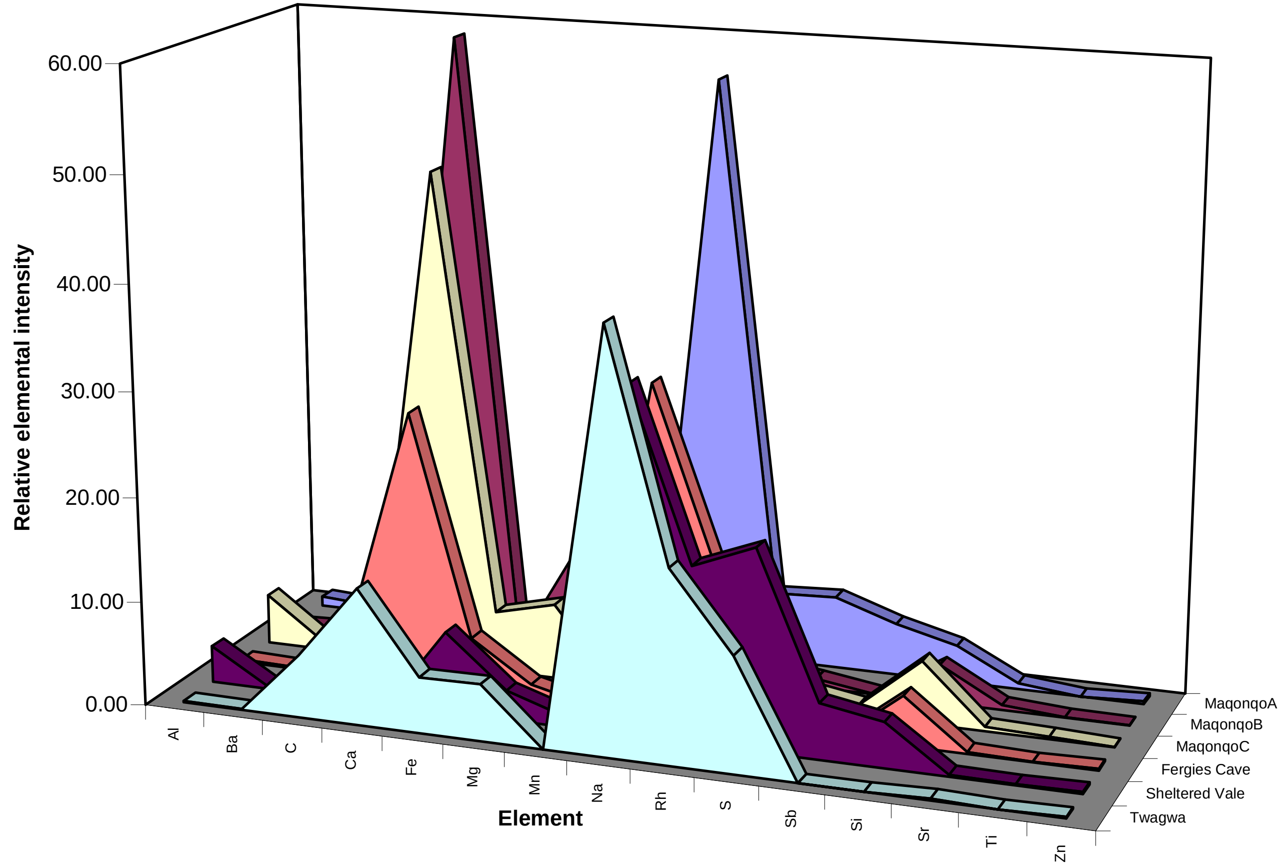
display an obviously high Ca content, whilst the other sites, although not as distinctive in their elemental composition, can still be seen to have distinguishing characteristics.

This trend is supported by the river water results obtained from each shelters associated drainage catchment (Table 6.1). In particular, the water samples obtained from the Buffalo River (which drains the MQ watershed) contain much higher Ca and S values than those determined for the other river samples indicating a potential source of these two elements in particular.

Table 6.1: A comparison of water sample data obtained from the rivers draining the catchments within which the shelters are located (adapted from Eksteen *et al*., 1990).

Locality	**Associated shelter**	**Sample point/no.**		**EC**	**pH**	**Na**	**Mg**	**Ca**	**F**	**Cl**	**NO_3**	**SO_4**	**PO_4**	**TAL$^{\sim}$**	**Si**	**K**	**NH_4**	**SAR**
				mS/m		**mg/l**												
Buffalo River Period 82-07-27 to 89-09-27	Maqonqo Shelter	Vaalbank V3M15	Ave	43.41	7.18	42.06	10.71	21.8	0.79	31.61	1.66	71.99	0.3	63.76	5.94	5.61	0.14	1.36
			Std.$^{\#}$	28.36	0.49	43.2	5.15	12.51	1.16	35.92	2.12	58.35	0.6	34.11	1.97	4.4	0.27	-
Little uThukela River Period 77-07-19 to 83-02-14	Fergies Cave	Drakensberg V1M39	Ave	6.98	3.74	2.26	5.72	2.14	0.69	0.46	1.67	0.49	20.51	14.92	2.4	0.13	0.05	0.18
			Std.	1.85	2.08	1.04	2.27	4.31	0.79	0.3	1.94	1.44	12.53	14.32	3.49	0.35	0.03	-
Mzimkulwana River No period/ sample numbers supplied	Twagwa Shelter	Gilbert Eyles Dam R01W	Ave	32.87	7.45	31.36	12.3	14.16	0.23	42.57	0.41	6.38	0.03	82.66	6.47	1.77	0.07	1.47
			Std.	7.53	0.49	7.68	3.25	3.8	0.09	11.34	0.53	7.38	0.04	25.36	2.26	0.66	0.06	-
		Gilbert Eyles Dam R0101	Ave	32.81	7.12	33.08	11.79	13.23	0.24	44.03	1.29	10.88	0.02	79.97	5.44	1.77	0.05	1.63
			Std.	7.43	0.58	9.88	3.13	4.77	0.09	15.21	5.23	12.88	0.03	25.24	2.15	0.39	0.04	-

$^{\#}$ - Std = Standard deviation.
$^{\sim}$ - TAL = Total Aluminium



	Al	Ba	C	Ca	Fe	Mg	nd	Na	Rh	S	nd	nd	Sr	Ti	Zn
▣ Twagwa	0.13	0.08	6.04	13.11	5.37	5.46	0.00	39.84	18.36	11.03	0.00	0.00	0.19	0.01	0.15
■ Sheltered Vale	3.52	0.08	5.49	nd	7.69	2.78	0.93	32.93	16.74	19.10	5.36	4.33	0.17	0.09	0.21
▣ Fergies Cave	0.25	0.12	6.29	26.40	5.20	1.36	nd	31.47	15.18	8.32	nd	4.75	0.16	0.04	0.16
▣ MaqonqoC	4.80	0.61	5.27	47.95	5.86	7.30	0.13	14.16	3.97	1.97	1.04	6.02	0.44	0.27	0.04
▣ MaqonqoB	0.01	0.24	5.95	59.51	0.93	11.10	nd	15.46	1.68	0.85	nd	3.67	0.46	0.04	0.01
▣ MaqonqoA	0.93	0.60	5.08	nd	1.75	11.00	0.90	56.01	6.71	7.02	5.05	3.58	0.58	nd	0.29

nd = Not detected

Figure 6.5: Main elements (% data from ICP-MS) in the surface water samples collected from the four study sites.

6.2.3.1 Maqonqo Shelter blank samples

The blank MQ EDX data are dominated by Ca, and, to a lesser extent, S and O, with only one sample indicating an above average Si content. The high Ca and S values are confirmed by the µ-XRD results, which indicate a predominant gypsum presence (accounts for between 15 and 100 % of every trace analysed). The dominant Ca-oxalate phase is weddellite, although this was found in only one sample. Of the 11 traces analysed, only four traces contained Ca-oxalates. The source of the Ca is, however, not fully understood. In an attempt to resolve this, the XRF analyses conducted on bulk wall samples collected at MQ were studied (Appendix A5.8.2). Elevated Ca values within these bulk samples indicate that the element probably originates from the local groundwater percolating through the rock substrate (Figure 6.5).

The very high values for S in the XRF rock samples indicate that the groundwater is also the source of this element. This is supported by the analyses of water samples from the Buffalo River (Table 6.1). This is not unexpected, for coal seams (which are common to the area) and the dark coloured carboniferous shales typically associated with the Ecca and Beaufort Karoo Supergroup rocks typically have S enriched groundwater associated with them (the pyrite coatings associated with the latter, when exposed, also result in elevated groundwater S contents).

The blank MQ µ-XRF data show a dominant influence of Sr. Whilst it was not immediately apparent from the µ-XRD data as to the source of the Sr, the bulk sandstone samples and the water samples analysed, both showed elevated Sr values (Appendix A5.8.4). This supports the contention that this element originates from the surrounding landscape. A mineral within which this element is often found is feldspar.

An apparent anomaly seems to exist between the µ-XRD and µ-XRF results and those produced using EDX. The first two techniques indicate a higher sandstone presence (both quartz and feldspar) than does the EDX data (indicated by a lower Si content). It must be remembered that the µ-XRF and µ-XRD analyses are run concurrently, using the same energy source, with their respective data being collected from the same point on the sample. Their two datasets are therefore intrinsically linked. Although the EDX data are collected from the same samples, the precise sampling locations will seldom be identical to those of the two aforementioned techniques. In addition, it is more difficult to accurately focus the X-ray beam onto the sample surface. The X-ray footprint is appreciably smaller than that of the EDX reduced window scan, thus the data will be more specific in nature, highlighting to a greater extent the differences existing between different sampling locations within the same sample. This, together with different elemental sensitivities displayed by each technique, are two of the factors responsible for the differences between the two datasets.

The presence of gypsum and weddellite give a good indication as to the climatic and chemical conditions found at the rock wall surface within the Shelter. Gypsum is susceptible to dissolution and removal by water. The presence of this mineral therefore indicates that sufficient water is in the system to allow for the movement of mobile Ca and S to the rock surface where deposition of gypsum occurs on evaporation. The high gypsum content present also indicates that the rock surface does not experience excessive surface water flow, either by rain-wash or seepage, which would result in a net loss of this mineral.

What is interesting about these blank samples, however, is that they lack other evaporite minerals that may be found in association with gypsum, namely bassanite and anhydrite (both dehydration products of gypsum). The lack of these minerals further attests to the humid and sheltered conditions experienced within the Shelter. This is enhanced by the fact that these samples have been shown to contain high Sr concentrations, an element that has been shown, via experimentation, to reduce the transition temperature at which gypsum converts to bassanite (Kushnir, 1982).

The presence of weddellite indicates that a) the ambient temperature within the Shelter (at the sampling point) is cool and moist enough to restrict the formation of whewellite; and b) the Shelter does not receive much direct sunlight. The resultant temperature changes would favour the dehydration of weddellite to form whewellite, which, with the exception of one trace, was not found. The exact source of the Ca-oxalate is not yet fully understood, although Mazel and Watchman (2003), who found these minerals in association with paint samples, suggest that they have a biological origin (see Section 3.5.9). They did not analyse blank samples, however. In the current study, no obvious signs of fungi, lichen or any other organism were present at the point of sampling, nor were they noted when the samples were observed using the SEM. This does not exclude the possibility that these agencies might have been present in the past, however. For further discussion of the possible origins and implications of these minerals with regards to MQ, the reader is referred to Appendix 3.2.

The higher quartz and feldspar contents found within the samples are to be expected. The samples were collected off Ecca sandstone, which is coarse grained and feldspathic in nature. A combination of larger and more irregularly shaped inert quartz crystals, together with a lower cementing component: quartz crystal ratio allows for greater friability within the Ecca sandstone (King, 1982). This sandstone is thus more susceptible to weathering relative to the other sandstone geologies discussed within this study.

6.2.3.2 Fergies Cave blank samples

The FC blank EDX samples are clearly distinct from the rest of the dataset, with their separation being driven primarily by their C and Ca content. In all EDX paint studies conducted to date in South Africa, the C value would normally be ascribed to one of a number of factors, including contamination and/or the method of sample preparation. However, when one considers the µ-XRD data (Figure 6.3), it is apparent that these sites lie along the weddellite/quartz: calcite gradient. Whilst both weddellite and calcite contain C and Ca, as can be seen in Appendix DIGITAL 1, neither of these minerals are present. This gradient is thus a reflection of sandstone: secondary deposit relationship.

Another factor apparent in Figure 6.1 is the lack of association of the samples with K, Si and Al, elements typically associated with quartz, mica and feldspar. This is indicative of a lack of sandstone ‘contamination’ within the samples. The µ-XRF data also substantiate this finding, with high Ca and correspondingly low Fe, Sr and Zn levels being determined (the latter elements most likely present in typical sandstone matrix minerals). The reduced presence of both sandstone and feldspar can be attributed to one or both of the following two factors: a) the relatively dense, compact nature of the Cave sandstone makes the surface more resistant to physical erosion when compared to the other sandstones considered within this study; and b) the site experienced a high rate of deposition, with the result that a majority of the sample collected is comprised of evaporite minerals. In either instance, a reduced sandstone presence was recorded.

Unlike the MQ site discussed previously, no XRF data for the composition of the bulk sandstone comprising the shelter wall was collected due to a lack of sampling permission. As a consequence, it is impossible to accurately determine the elemental sources found within the dominant minerals in the blank samples, though the water results again alluded to the groundwater as representing the main source. The relative proportions of the minerals present do, however, provide an insight into the climatic conditions present within the Shelter.

Of the two samples analysed using µ-XRD, it was found that one was totally dominated by whewellite, whilst the other contained a combination of whewellite and weddellite in similar proportions, with gypsum being found in lesser amounts (Appendix DIGITAL 1). With an average annual maximum temperature of 26 ^{o}C, and an average annual rainfall of between 1 000 and 1 200 mm p.a., the climatic conditions within the general geographical area of the Shelter greatly favour the formation of all three of these minerals. The fact that the two samples analysed showed different concentrations of these respective minerals, however, illustrates the dominating effect of the Shelter’s micro-climate over the evolution of each respective mineral, be it directly via deposition, or indirectly via the encouragement of organic growth. Whilst obvious signs of biological life were not noted (either visually or via the ESEM), the possibility that organisms might have had an historical influence cannot be discounted.

The presence of gypsum within the one sample indicates that the surface is sufficiently dry enough to allow for its deposition upon the surface of the wall. Its presence in only one of the samples would tend to indicate that the position of the sample without gypsum is subject to greater water flow, possibly being located along a line of weakness within the rock through which additional seepage occurs. These assumptions are supported by the µ-XRF data, which show that the Ca content within the sample without gypsum is approximately three times that with gypsum present (Ca is highly mobile in solution).

The dominance of whewellite suggests that the climatic conditions present within the Shelter favour its production, most notably the high temperatures. The higher degree of moisture found at the site would suggest that the manner in which the whewellite is produced is probably different to that suggested for MQ. This assumption is based on the fact that all of the papers concerning the evolution of Ca-oxalates referred to so far in this study were conducted in semi-arid to arid areas (e.g. Mawk and Rowe, 1998; Russ *et al*., 2000; Watchman *et al*., 2001). Under tropical conditions in Australia, however, Watchman (1990) determined that rainfall derived organic acids were responsible for the production of oxalate-rich crusts. Certain bacteria, which flourish in highly moist areas, have also been found to produce whewellite (Mawk and Rowe, 1998). Both of these pathways would more easily explain the presence of these minerals within this Shelter relative to MQ. Only C isotope analysis of these respective Ca-oxalates would shed more light on the origins of these minerals, however.

6.2.3.3 Sheltered Vale blank samples

Of the four sites investigated, the SV blank samples showed the least tendency to distinctly separate out from the rest of the sites in both the EDX and µ-XRF datasets. Whilst the other sites tended to align along a specific PCA gradient, the SV samples tended to occupy a median position relative to the other sites. Of the three blank samples analysed, two indicate a sandstone presence whilst the third indicates the presence of one (or more) of the Ca minerals already described above.

The µ-XRD data display a stronger degree of separation (Figure 6.3), driven primarily by the presence of kaolinite. It must be noted that only four of the eight traces analysed contained kaolinite, with the mineral representing less than an estimated 4 % of each trace within which it was found. This mineral has such a strong influence on the PCA diagram because of its limited distribution within the dataset as a whole.

The other minerals identified were, in decreasing abundance and dominance within the samples, whewellite, gypsum and quartz, and weddellite. Whewellite was by far the most dominant mineral (predominantly over 50 %). Both gypsum and quartz, whilst present in almost all of the samples, comprised between 5 and 45 % each. Weddellite was determined to represent between 5 and 15 % in only three of the traces. Thus, the samples are composed primarily of the evaporite-type minerals, with only minor sandstone ‘contamination’ being noted. What is interesting to note is that, whilst the quartz content might not always be high, it is present within almost all of the samples analysed. This was not the case for the other sites and could possibly indicate a higher degree of more uniform surface erosion/instability. The presence of kaolinite is also probably derived from the sandstone wall, although atmospheric deposition could also be a contributing factor (the water results tend to favour the former). Unfortunately, without chemical and mineralogical analyses of bulk samples of the Shelter wall, these two assumptions cannot be tested.

One of the samples is composed primarily of quartz and gypsum, with no Ca-oxalate being present. This highlights the variable distribution of the minerals both across the geological landscape, as well as within the rock shelters themselves. The presence of gypsum in all three of the samples does, however, indicate that the shelter wall is sufficiently dry so as to allow for its continued presence. Similar to FC, the source of both the Ca and the oxalate cannot be accurately determined with the data available. What is certain, however, is that the general microclimate experienced within the Shelter is relatively warm and dry, as these conditions promote the formation of both gypsum and whewellite.

6.2.3.4 Twagwa Shelter blank samples

In Figure 6.1, Si, Al and K are shown to have a strong association with one another, implying that they are derived from the same geological source, namely sandstone. The dominating Si influence corresponds with a dominating quartz fraction in sandstone, whilst the K and Al would be contained within feldspar. This trend is substantiated in Figure 6.2, which shows the TW samples in association with elements common to feldspar and other minerals present within sandstone matrices. Furthermore, the distribution of the TW samples is controlled by a number of minerals not encountered previously (Figure 6.3). All of these indicators imply that the samples are dominated primarily by sandstone material. Conspicuous is the lack of Ca-based minerals. Appendices A5.12.1 and 5.16 both show that these samples contain very low Ca contents. The water sample also displays a low Ca reading.

No Ca-oxalate or gypsum was found in any of the samples analysed. This is a marked difference when compared to the previously discussed sites. Even though there is no bulk sample data characterising the sandstone wall of the Shelter itself, the almost complete lack of Ca within the blank samples (both EDX and μ-XRF) indicates that this element is either very limited within the system, very efficiently leached from the system, or bound within a very stable mineralogical phase. As no mineral is completely immune to the combined actions of both chemical and physical weathering, the former postulation is assumed. It can therefore be concluded that any Ca-oxalate producing pathway that sources Ca from the rock substrate is effectively inhibited within this Shelter.

Ca-oxalates can still form naturally under conditions such as these, however, with Ca being derived from atmospheric deposition (Watchman, 1990). Wadsten and Moberg (1985) have shown that certain lichen produce Ca-oxalates even on Ca poor substrates, whilst Watchman (1990) contends that Ca-oxalates can also be formed inorganically at the rock surface after chemical reactions involving Ca and organic acids, both delivered to the rock surface via rainfall events. Whilst the protection of the rear wall of the Shelter prevents rainfall from reaching the surface (and hence severely limits this pathway as a possibility), the biological entities are inhibited by different factors i.e., moist and cool climates in the case of lichen (Russ *et al*., 2000) and dry, hot climates in the case of bacteria (Mawk and Rowe, 1998).

Twagwa Shelter experiences an average annual temperature of about 19 °C, and an annual rainfall of between 850 and 1 100 mm. The high relative humidity that this Shelter experiences is probably an inhibiting factor in the establishment of lichen that produce Ca-oxalate. Whilst the conditions seem to be suitable for bacterial growth, the lack of any Ca-oxalates implies the absence of both of these biological agents.

One final possibility that might explain the lack of any Ca minerals is just that the three sites sampled did not contain these minerals. Whilst only the analysis of additional samples would clarify this fully, the fact that three samples, each selected at random along the shelter wall, displayed no Ca mineral presence seems to suggest that the findings are likely to be representative of the Shelter as a whole. It must be noted that the high quartz readings obtained for this Shelter need not indicate that it is more susceptible to erosion than the others already referred to, but rather indicates the lack of deposited materials.

The following minerals were found within the samples analysed: quartz, muscovite, schlossmacherite, kaolinite, buserite and greigite. Whilst most of these minerals are probably derived from the sandstone bedrock, the presence of schlossmacherite is very unusual. Very little information is available concerning this rare mineral, and none describe the manner or under what conditions it forms. The few accounts reported all refer to this mineral being found in one specific copper-bearing gold mine called Emma Luisa in Guanaco, Chile. The rarity of this mineral, together with a lack of information on how and why it forms, make its discovery in this location very interesting. How the presence of this mineral will affect the rock art is, however, still to be determined.

6.2.3.5 Summary

The PCA diagrams used within this study emphasise trends inherent within the dataset. Once the trends have been highlighted, one must again refer to the datasets in order to correctly deduce the controlling factor(s) that result in the trend(s) highlighted. As each technique is specialised, looking at the results from each separately would only partly reflect the nature of the sample being studied. It is only when all the techniques are considered simultaneously can a more comprehensive understanding of each of the samples, and sites, be determined.

This section has also highlighted the importance of correctly identifying the mineralogical phases within which the elements identified reside so that the mobility of that element can be estimated. The findings will have a direct bearing on the development of measures for the protection/restoration of rock art. In addition, the presence (or absence) of the different minerals gives important clues about the site, such as the microclimate, the potential sources of the elements/minerals, and the susceptibility of the surface minerals to the different erosive mechanisms.

Three minerals that are of particular importance within this study are whewellite, weddellite and gypsum. Their presence within the blank samples strongly indicates that these minerals are of natural, and not anthropogenic, origin. It is therefore important that an understanding be gained of the effects that these minerals, both present and future, will have on the stability of the rock wall, and by default the paintings upon them.

In general, the following trends were determined for the four sites studied (Figures 6.6 and 6.7):

1. different climatological and geological locations influence the dominance (and possibly the chemical pathway) of the Ca-oxalate phases found within the shelters. This has important implications for conservation, dating and restoration methodologies that are being/have been considered. Citing these differences as an example, a 'one size fits all' approach to the management/study of rock art shelters is not recommended;
2. with the exception of MQ, the S contents for each of the shelters remained relatively constant. The S values recorded at MQ are ascribed to the elevated S levels in the groundwater associated with local coal seams. The high gypsum content resulted in a correspondingly low quartz content being recorded. Initially assumed to be an indicator of the sandstone's reduced susceptibility to erosion, it has subsequently been shown to be an indirect indicator of the sandstone's high porosity. The larger pore spaces and seepage planes within the sandstone lead to an increase in secondary deposition, and it is this depositional layer which 'masks' the inherent instability of the substrate;
3. the shelters were located within sandstone formations that decreased in geological age in the following order: TW, MQ, SV and FC. The degree of weathering within these respective sandstones generally increased from the oldest to the second youngest formation, with the youngest formation showing a similar resistance to weathering as that displayed by the oldest formation. In general, this trend is highlighted by the decrease in Si content within the samples (Figure 6.6). Refer to point 2) which explains why, even with an initial observed low Si value, MQ still conforms to this weathering trend;
4. an increase in the presence of both Ca and C occurs along the same geological age gradient mentioned above. The combined increase of these elements corresponds with an increasing presence of Ca-oxalates within the respective shelters (Figure 6.7). Climate and geology both influence this trend. The Ca present within the Ca-oxalate minerals in the blanks is derived from the rock substrate (this latter point is supported by the fact that all occurrences of Ca-oxalates in South Africa have been recorded in the presence of gypsum; a mineral associated with groundwater evaporation). This is, in turn, reflected in the Ca and S contents of the river water samples listed in Table 6.1; and
5. the combined use of a variety of techniques allows for the identification of trends that aid in the identification of the different origins of the samples collected.

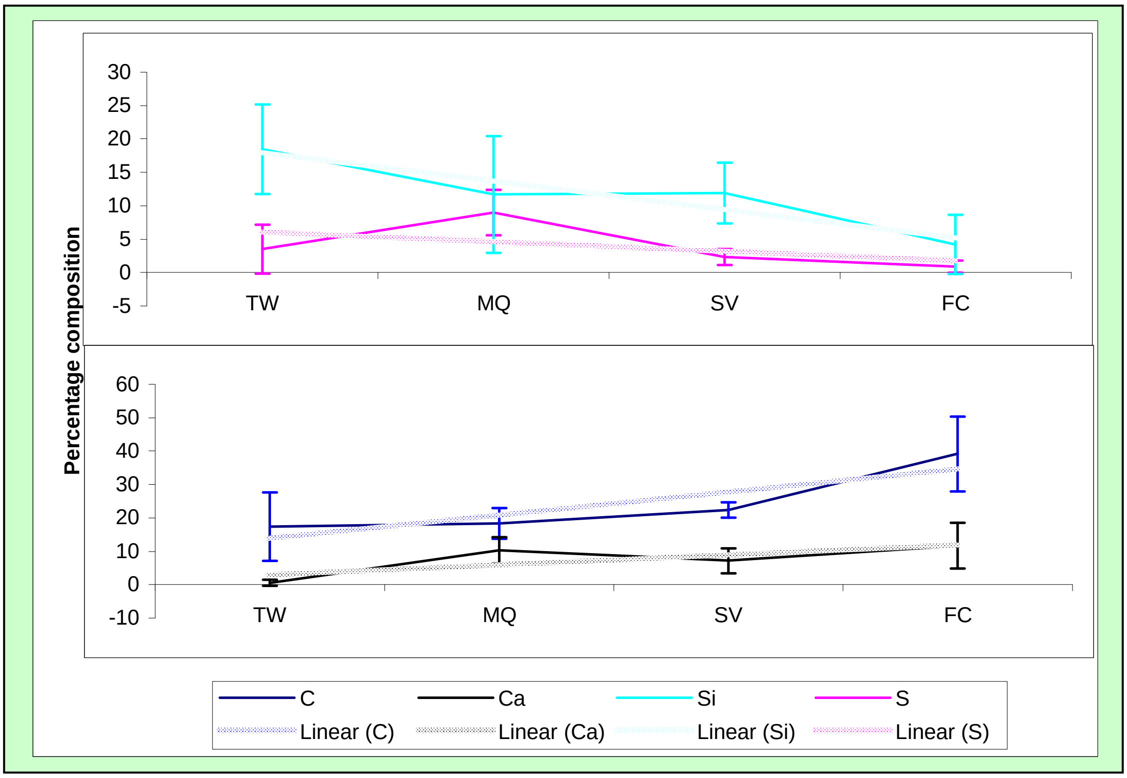


Figure 6.6: Average blank sample elemental values, with their associated standard deviations and trend lines, for the four shelters studied.

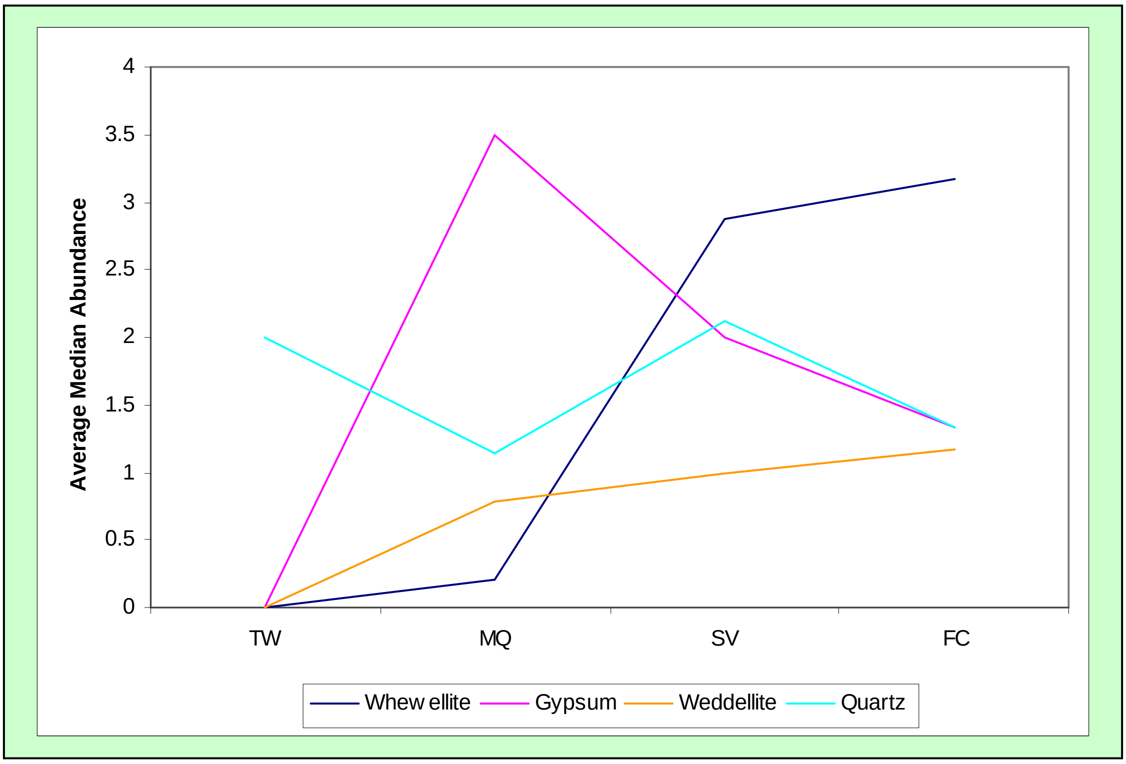


Figure 6.7: Relative mineralogical composition of the blank samples collected from the four study sites[1].

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[1] The results represent the data as listed in Appendix 5.10, only the relative percentages have been re-scaled as follows: 0 = not present; 1 = < 4 %; 2 = 5 – 14 %; 3 = 15 – 49 %; 4 = > 50 %.

6.2.4 Paint and blank samples from Maqonqo Shelter

The PCA analysis of the MQ EDX paint sample data is shown in Figure 6.8. It can be seen that the white, pink and orange colours show the strongest tendency to aggregate. The distribution along PCA1 (43.9 %) is predominately driven positively by Fe and negatively by Ca and to a lesser extent S. Effectively, the paint colour distribution is graded along the PCA1 axis, moving from the reds, yellows and oranges at high Fe values, through the pink colours to white as the Fe content decreases and the Ca and S contents increase.

This trend is again reflected, although not as dramatically, in the µ-XRF data (Figure 6.9). Iron dominates the sample distribution, accounting for 88.4 % of the variance displayed. The ‘over-influence’ of Fe relative to that displayed in Figure 6.8 is related to the technique’s inability to record elements of lower atomic mass i.e., C, Si, S and Al, all elements that are prominent in the EDX sample distribution.

The distribution of the samples in Figure 6.8 along the EDX PCA2 axis (27.2 % variance) is driven by the C content, which, according to data in Appendix DIGITAL 1, is located primarily within whewellite. Some of the recorded C content can possibly be ascribed to other factors including increased detection levels of C as a result of the reduced window scan technique, contamination of the samples via dust and biological residue from atmospheric deposition, and possibly even due to the presence of variable amounts of organics within the paint samples themselves. It must be noted, however, that only three samples (two red and one white) are responsible for C having such a dramatic effect on the variance of the dataset as a whole. A possible reason for this might be a result of beam penetration through and/or past the sample as a result of the sample being too thin/small. As all of these samples were shown to have both gypsum and whewellite featuring predominantly within their respective µ-XRD traces, however, the high C percentage recorded is probably due to a thicker deposition of these minerals in these three samples. The high variability of C within the sample set is thus a reflection of the variable deposition of these minerals across the rock surface.

The µ-XRD data featured in Figure 6.10 is harder to interpret. Several trends are, however, apparent. PCA1 (25.6 % variance) is driven by a linear gradient that exists between whewellite and haematite, gibbsite, bassanite, glushinskite and, to a lesser extent, gypsum. This reflects variations in whewellite deposition across the sandstone surface, which is in turn a reflection of the differing micro-climatic conditions within the site. The second, though less clearly defined trend, lies between the minerals goethite and haematite. This reflects differences in Fe oxide hydration states that in turn reflect the conditions under which their source geologies originally formed and weathered. This is manifest in a colour change from red (haematite) to yellow/orange (goethite). This gradient is further influenced by the presence of gibbsite, around which a majority of the orange samples are aggregated. This tends to indicate that at least two, or possibly three different mineralogies were utilised in the manufacture of the yellow, orange and red pigments, respectively.

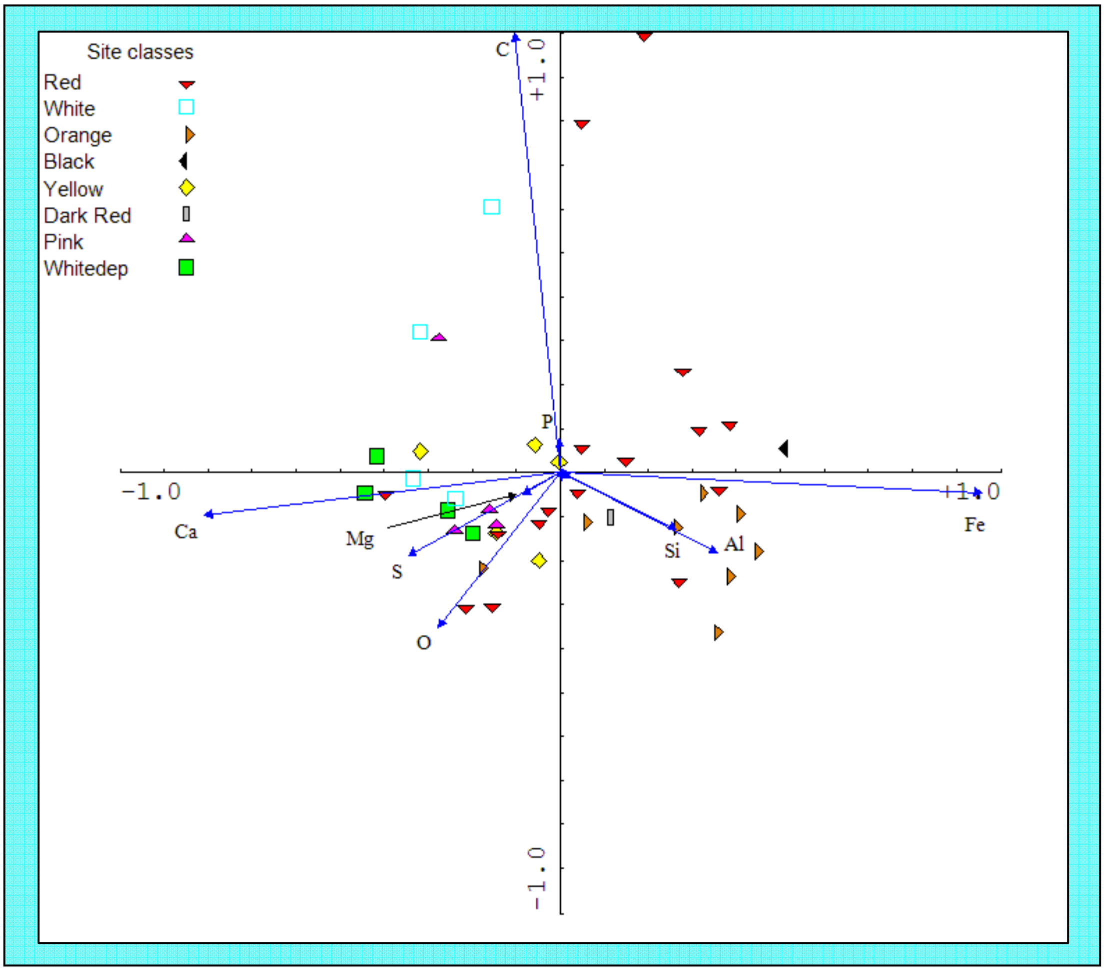

Figure 6.8: Average reduced window EDX data depicting individual paint colour and white deposit distribution for Maqonqo Shelter.
Eigenvalues: PCA1 – 43.9; PCA2 – 27.2; PCA3 – 15.8
Scaling = -2

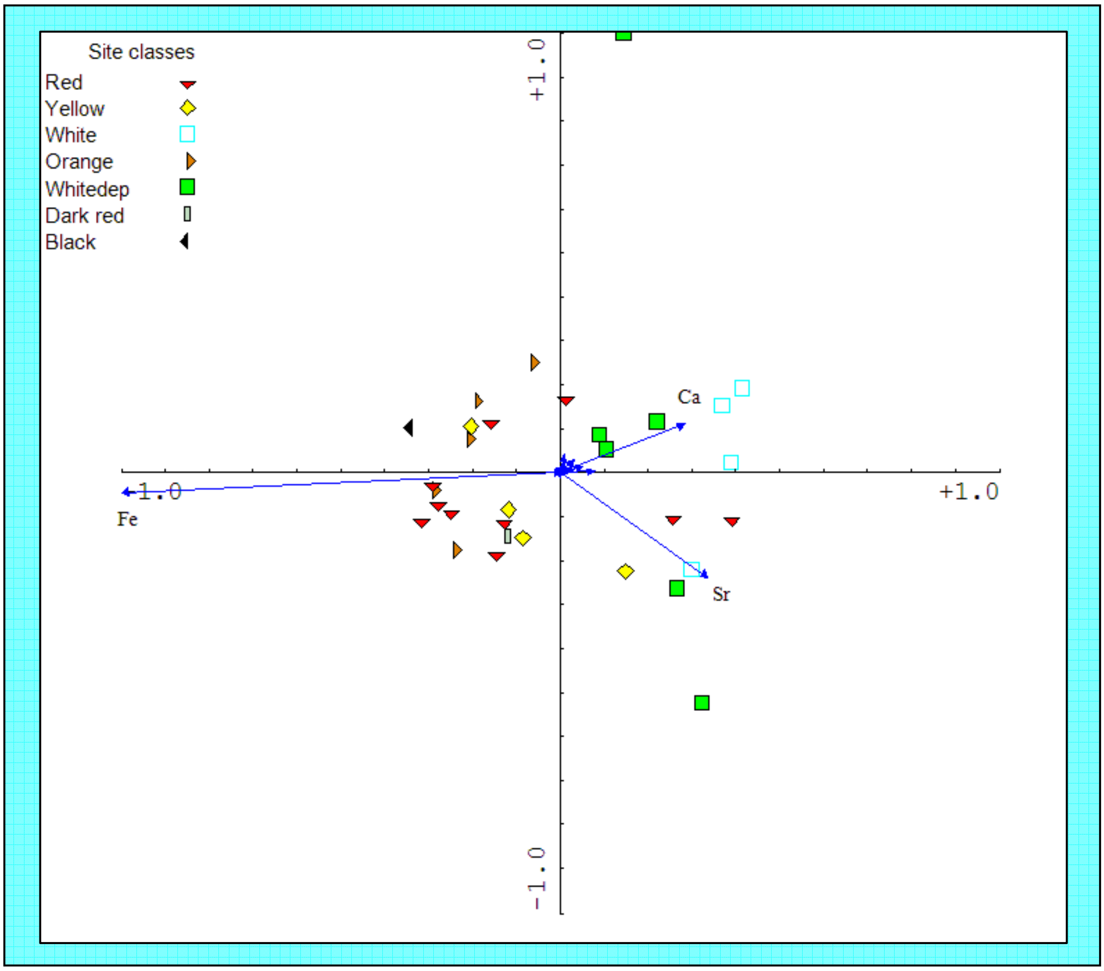

Figure 6.9: Micro-XRF data depicting individual paint colour and white deposit distribution for Maqonqo Shelter.

Eigenvalues: PCA1 – 88.4; PCA2 – 5.6; PCA3 – 2.8

Scaling = -2

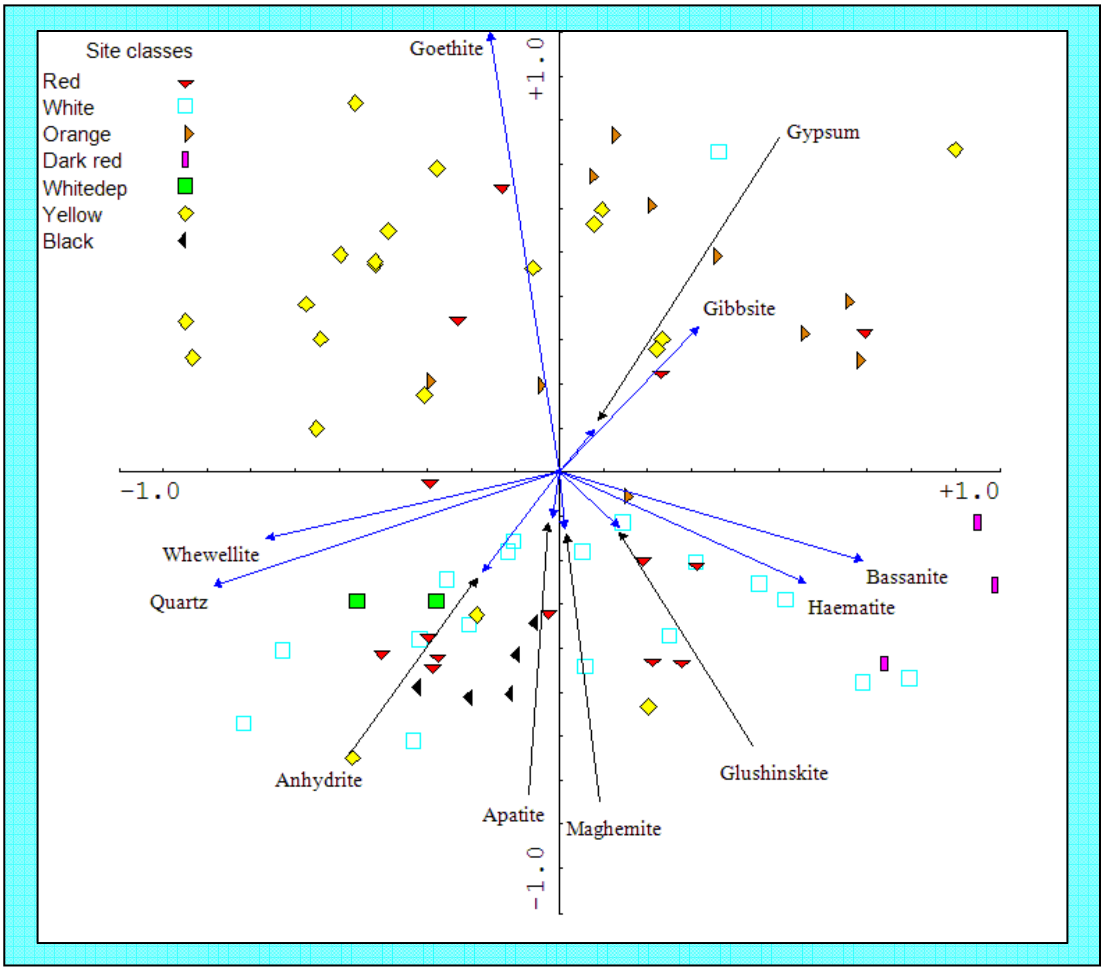

Figure 6.10: Micro-XRD data depicting individual paint colour and white deposit distribution for Maqonqo Shelter.

Eigenvalues: PCA1 – 25.6; PCA2 – 17.8; PCA3 – 14.6

Scaling = -2

The quartz content is the final influencing factor. The samples containing high quartz contents probably reflect low ‘true’ sample concentrations i.e., sandstone ‘contamination’ has been measured to the detriment of the ‘true’ sample. Possible reasons for the high quartz content have been given above (Section 6.2.1).

6.2.4.1 White colours

The white samples’ distribution within the EDX and µ-XRF PCA diagrams are predominantly governed by their Ca content, with S, C and Sr also having a moderate influence (Figures 6.8 and 6.9). Based on these data alone, Ca would be assumed to be present solely as gypsum; a conclusion reached by all but two of the previous studies on paint composition in South Africa (see Sections 3.5.3, 3.5.4, and 3.5.5). The µ-XRD analyses, however, show that the Ca is present within four separate mineralogical phases, namely gypsum, anhydrite, bassanite and whewellite (Appendix DIGITAL 1). Although the mineralogical data could only be obtained from 17 traces from four individual white paint samples[1], this awareness of different mineralogical phases for Ca has important implications on the current understanding of the susceptibility of the paintings to erosion, especially water action. Each of these minerals has its own solubility quotient, with gypsum being soluble in water, bassanite and anhydrite being less soluble than gypsum by a factor of 20 and 30 times, respectively, whilst whewellite is insoluble (see Appendix 6.3). All of these minerals are, however, readily soluble in dilute acid.

Although Ca-oxalates are sometimes found on cave and shelter wall surfaces, their origin is often hard to determine for they can be formed via a number of different mechanisms, many of which can occur concurrently (see Appendix 3.2). What is of importance here is the observed low occurrence of these minerals within the blank samples relative to the paint samples. Of the 88 MQ paint sample traces analysed, 47 contained whewellite, with only four of the 20 paint samples analysed showing no Ca-oxalate presence at all (one white, red, dark-red, and orange sample, respectively). It is interesting to note at this point that a majority of the traces in which no Ca-oxalates were detected contained elevated levels of haematite (25 of the 40 traces without Ca-oxalates), a trend noted earlier in Section 3.5.9. The remainder of the samples were dominated by either gypsum or gibbsite. This might be an indication of differences in paint recipes based on colour, or a reflection of the ages of the pigments sampled.

Gypsum was the mineral that consistently dominated the µ-XRD traces obtained of the white paint, white deposit and blank samples, accounting for between 25 and 100 % of each trace while the

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[1] Whilst µ-XRF data were obtained for most of the samples analysed, the results obtained for a majority of the µ-XRD analyses proved to be less than satisfactory. This is an indication that either the sample size analysed was insufficient to allow for an accurate mineralogical determination, or that the mineralogical component of the samples was poorly crystalline. As the µ-XRF results for the same traces were resolved with greater success, it is plausible to assume the latter.

presence of whewellite was shown to be more sporadic in nature (Appendix DIGITAL 1). Whilst being found in a majority of the white paint samples, only one of the 14 traces collected from the four blank samples contained any whewellite (estimated to average between 15 and 49 %). Similarly, only three traces (all from the same sample), showed a weddellite presence (ranging between 15 and 100 %). In general, however, the blank samples are shown to be primarily composed of gypsum.

The white paint samples on the other hand, while also containing gypsum, showed much higher whewellite:gypsum ratios, a trend reflected in Appendix DIGITAL 2 (Figure 6.11). Whilst this disparity could be ascribed to differences in the microclimate within the Shelter, the large degree of consistency shown between the samples to the detriment of the blank samples tends to eliminate this as a possibility. Two possible explanations for this distinct separation are that a) the whewellite was incorporated into the paint during its manufacture, and/or b) the primary paint components underwent chemical weathering which has resulted in deposition of secondary minerals i.e., the whewellite was deposited post the painting event. In order to determine which of these above two scenarios is the most likely, the double sampling points were examined in order to determine whether or not whewellite is ubiquitous throughout the sample (the reader is referred to Section 6.2.5 for a more comprehensive discussion concerning both the results and the criteria required for the result of these tests to be valid).

The presence of whewellite within the white pigment of the repeat samples, Paint 9A and Paint 9B, not only indicates that this mineral is inherently present within the white paint, but as its presence increases with increasing paint depth, it indicates that this mineral was actively sought by the artist as a primary component of the pigment used. The gypsum content, conversely, increases with decreasing paint depth. This indicates that the recorded gypsum of the surface sample represents a combination of both material formed *in situ* and paint derived material, and thus the recorded values for this mineral represent an ‘inflated’ value.

Quartz, only found in six of the traces, probably represents sandstone ‘contamination’ of the paint samples within which it was found (less than 40 % of each trace). Glushinskite, a Mn-oxalate, is derived via both chemical and biological processes in much the same way as Ca-oxalates, and is thus often found in association with them, though the latter are as a rule the dominant products formed (Graustein *et al.*, 1977; Favero-Longo *et al.*, 2005; Frost *et al.*, 2004; Kolo and Claeys, 2005). Unlike the Ca-oxalates, however, this mineral is highly soluble, with the solubility product of glushinskite being more than 1 000 times greater than that of the Ca-oxalates (Lide, 2002). Its presence is thus an indication of a combination of environment factors that have both favoured its formation (e.g. a high Mn:Ca ratio), as well as its retention, and that these conditions often only prevail in localised micro-environments.

The surface sample (Paint 9A) also contained a combination of gypsum, bassanite and anhydrite. These minerals represent mineralogical phase changes caused by dehydration. Sample 9B, a repeat

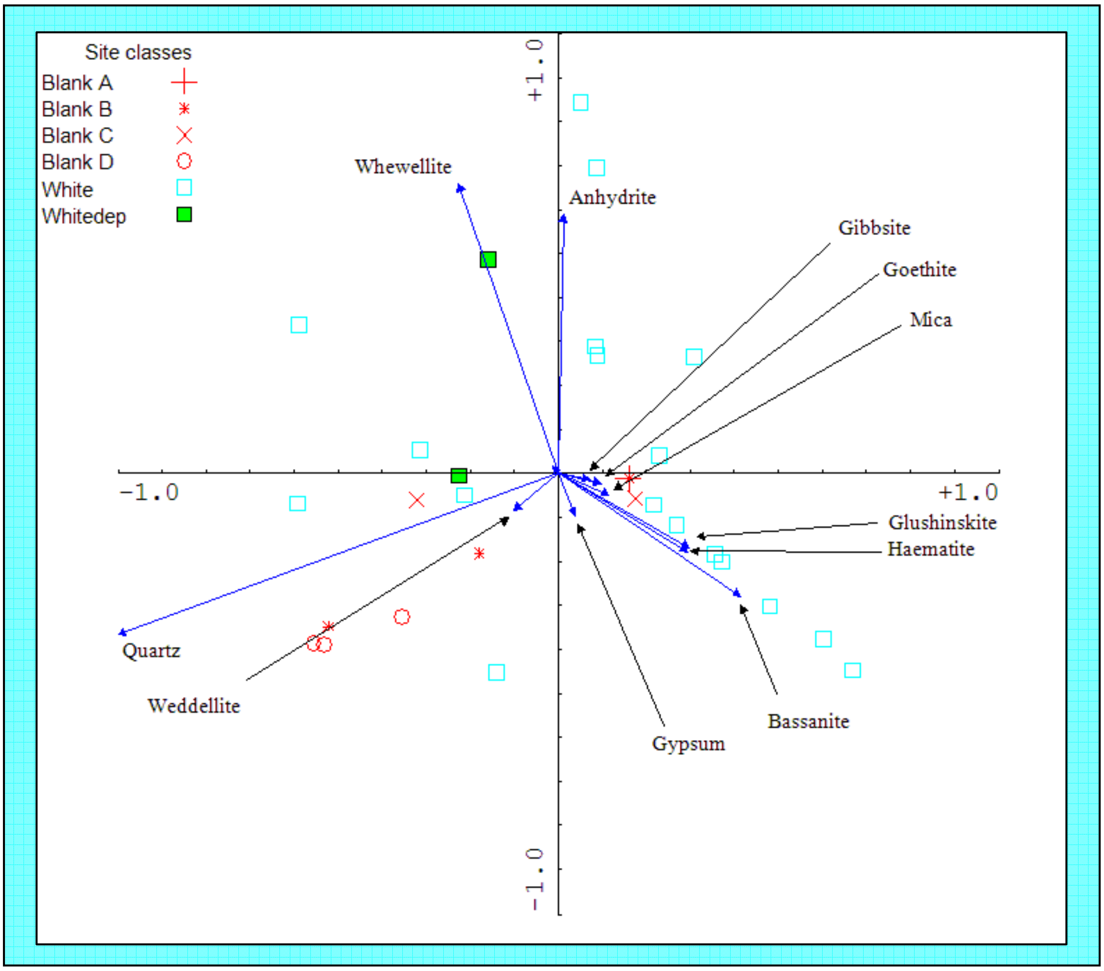

Figure 6.11: Micro-XRD data depicting the blank, white deposit and white pigment sample distribution for Maqonqo Shelter.

Eigenvalues: PCA1 – 33.6; PCA2 – 25.0; PCA3 – 13.9

Scaling = -2

sample collected at the same sampling point but representing a ‘deeper’ sampling pigment layer, is shown to contain only gypsum. Whilst it is common to find anhydrite in association with gypsum in natural depositions (Deer *et al.*, 1992), the manner in which the mineralogical fractionation seems to increase towards the surface of the paint sample tends to indicate that the gypsum has undergone a mineralogical transition driven by external environmental factors post the painting event.

Only three samples within the MQ paint dataset were shown to contain anhydrite (one white, orange and yellow sample, respectively), whilst none was found within any of the blank samples. Bassanite was found in association with anhydrite in all cases, with an additional four samples also containing this mineral (one dark red, two red and an additional white sample). Gypsum was found in all but five of the samples analysed. This ‘skewed’ recording of the three different phases of $CaSO_4$ is not unexpected, however, for gypsum dehydrates slowly to bassanite when exposed to air temperatures up to about 70 ^{o}C (though the exact activation temperature has been shown to be lowered in the presence of elevated Sr levels (Kushnir, 1982)), and to anhydrite only at temperatures above 200 ^{o}C (Deer *et al.*, 1992). The phase transition of gypsum to bassanite, and *vice versa*, is thus relatively fast, being dependent on normal fluctuations in local temperatures and atmospheric moisture levels. The phase transition of anhydrite to or from either bassanite and/or gypsum is a lot slower, and only results under very specific conditions.

During the course of the µ-XRD analysis, white deposits that were found in association with six different samples were also analysed (one black, two orange, two red and one yellow; see Table 6.2). Collectively, five traces were recorded and analysed, and are listed in Appendix DIGITAL 1 as ‘white deposit’. A comparison between the white deposit and white paint samples shows a high degree of similarity, with both datasets exhibiting similar mineral compositions, the primary difference being that whewellite exhibits a higher presence within the deposit samples (Figure 6.11). The white deposit samples are, for the same reason as the white paint samples mentioned above, distinct from the blank samples in that the blank samples contain almost no whewellite (Figure 6.12). These probably represent secondary deposition minerals; the gypsum from the shelter wall, the whewellite from a biological source (based on the same reasoning discussed above). Without C isotope analysis, however, this cannot be determined for certain.

Whilst it is impossible to distinguish between possible white deposits and white pigment in samples collected from white paintings, it is reasonably easy to identify them in the other paint colours analysed. The questions to be asked about these features are ‘what do they represent? Were they a) originally incorporated within the paints during their manufacture; b) natural depositional features derived from a shelter wall; or c) evaporite products that formed post the painting event?’ While it cannot be totally discounted, the distinct nature of the white deposit samples as compared to the blank samples indicates that the shelter wall is not the sole source of this material; gypsum is the only mineral consistently common to both the blank and white deposit samples. Interestingly, when one compares the mineralogical data obtained from the pigments associated with the white deposits,

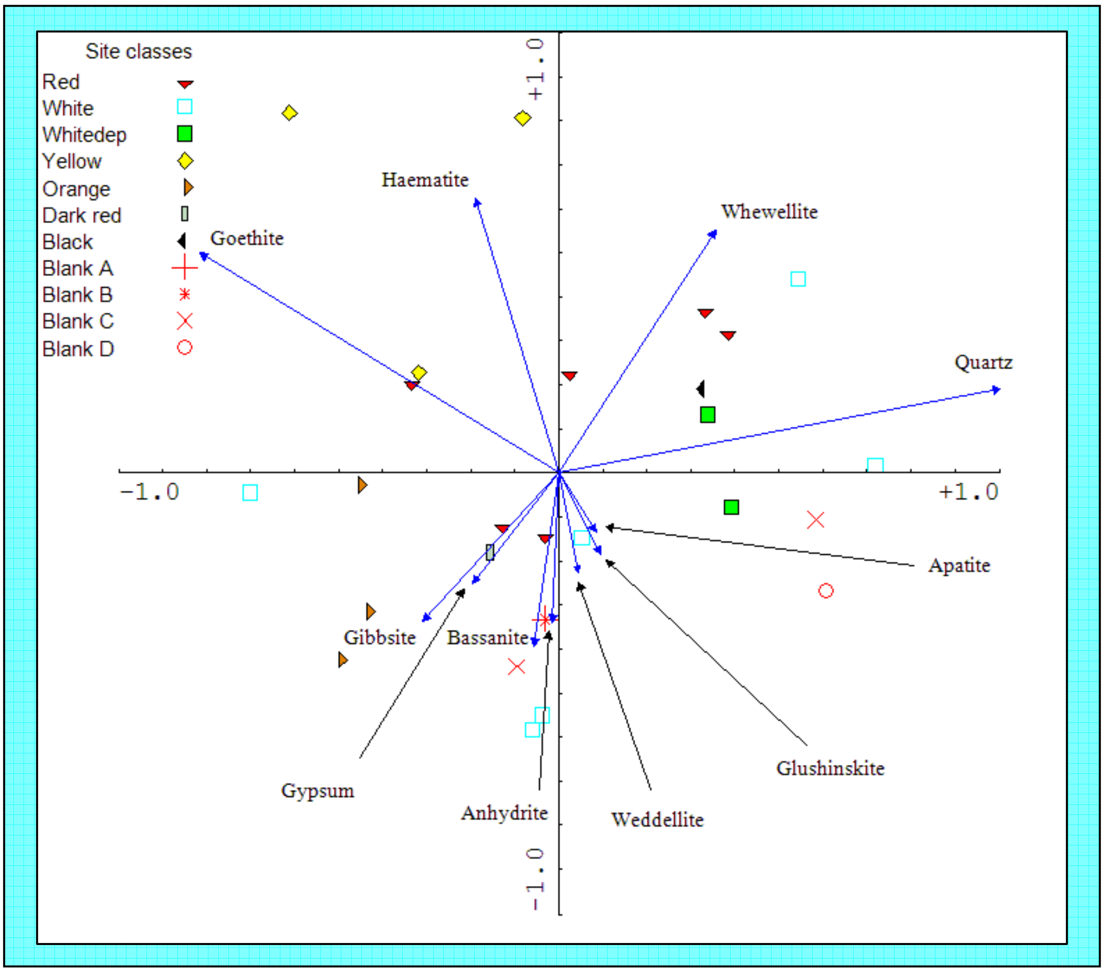

Figure 6.12: Mode micro-XRD data depicting individual paint colour, white deposit and blank sample distribution for Maqonqo Shelter[1].
Eigenvalues: PCA1 – 28.1; PCA2 – 21.8; PCA3 – 15.4
Scaling = -2

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[1] Where possible, mode values for each sample were used, otherwise averages were determined. In the cases where too few datum points were present, the individual traces were included (see Appendix 6.4).

Table 6.2: A comparison of the individual painting styles of the paintings in Maqonqo Shelter from which the white samples and white deposited material were collected.

Paint sample	Painting style*
Paint 2	White ‘deposit’. Original sampled image is a monochrome black human.
Paint 5	White ‘deposit’. Monochrome human figure overlying orange figure.
Paint 9A & B	Unshaded bichrome eland; white legs, head; orange torso; leg sampled.
Paint 10	Indiscernible monochrome image.
Paint 11B	White ‘deposit’. Original sampled image is an unshaded bichrome eland; white head, legs, yellow torso (area sampled). This is an ‘upper-surface’ sample.
Paint 12	Monochrome animal.
Paint 13 A & B	White ‘deposit’. Original sampled image is an orange monochrome animal (?). This represents the area adjacent to the suspected area of detachment of the Layer 7 exfoliated paint fragment (Paint 20).
Paint 14	White ‘deposit’. Original sampled image is an orange monochrome animal (?).
Paint 21	White ‘deposit’. Original sampled image is a red monochrome human.

* - See the images in Appendix DIGITAL 6.

the pigments were shown to contain gypsum and whewellite in similar proportions. The implications of this discovery to our understanding of the paint manufacturing techniques will be discussed in the red and yellow paints sections below.

Taking all of these factors into account, I propose that both the gypsum and whewellite found within the white paint samples were already present within the pigment when it was applied[1]. Furthermore, it seems probable that the gypsum and whewellite formed via two distinct mechanisms, suggesting that the paint might be a combination of two distinct pigment sources.

The most likely source for the gypsum would be rock exudates from sandstone shelters within the nearby vicinity to MQ. This theory has been proposed in recognition of the fact that there is, at present, no known source occurring within close proximity to the shelter[2]. This mineral has been shown to readily form within MQ, and would thus be expected to do so in a similar manner within the surrounding shelters. Maqonqo Shelter itself cannot be considered, for no exploitable gypsum deposits were noted within the Shelter during sampling.

The source of the whewellite is a lot more difficult to determine for a number of different biological and inorganic pathways result in its formation. The lack of this mineral within the blanks, yet its high concentrations both within and upon the white paints, tends to indicate that the mineral was added to the pigment already formed (this does not rule out the fact that additional whewellite could have formed subsequent to the painting event). It is possible that the whewellite formed in

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[1] Mazel and Watchman (1997) also found that gypsum was a primary component of the white paint sampled at Nkosanana Shelter. At Esikolweni Shelter, however, the primary component of the white paint was determined to be calcite.

[2] The closest recorded gypsum outcrop is found over 200 km away at the confluence of the Tugela and Nadi Rivers, where it is present as crystals, and as lumps of crystals, of particularly pure quality in clay and soil located upon a wide terrace of the Tugela River (Coetzee, 1976).

conjunction with the gypsum that was utilised in the manufacture of the white paints, but it is equally possible that an organic additive was utilised that either contained this mineral (e.g. the nesting chambers of termitaria: J. C. Hughes, pers. comm., 2007), or provided the material that allowed for its formation. The most likely scenario, however, is that these two minerals were sourced simultaneously from one geological location, with the most likely source being evaporite deposits from a shelter wall. Carbon isotope analysis is required to help resolve this anomaly, however.

It must be noted that this is just an hypothesis – there is as yet no evidence (either for or against) to suggest that this is the source of the white pigment. Neither does this suggest that phase changes have not occurred subsequent to the painting event, as is most likely evidenced by the findings associated with samples Paint 9A and Paint 9B mentioned above. It does, however, provide an explanation as to why the white paints seem to have a two-part composition namely, an inorganic source (including gypsum, bassanite and anhydrite) and an organic source (from which the secondary minerals, Ca-oxalates and glushinskite, were formed or were contained in).

This would also help to explain why Ca-oxalates were seldom found beneath the paint samples analysed by Mazel and Watchman (2003) – they simply were not there. In addition, this would explain the high detection rate of this mineral across a majority of the paint samples, and conversely, its minimal presence within the blank samples. Thus, based on these findings, I suggest that the presence of Ca-oxalates within the blank and paint samples have two different sources. This obviously has implications for the dating technique i.e., the Ca-oxalates would therefore represent (a) a relative age for each painting based on conversion rates of the organic additives within the paints by biological agents (if they were indeed used); (b) a minimum age if the Ca-oxalates formed post the painting event via inorganic processes; or (c) totally misleading dates if Ca-oxalates were specifically sourced and utilised in the manufacture of the paints e.g. the Ca-oxalates might have been formed over a 1 000 years ago, but only utilised 200 years ago by the artist. This would then be further complicated if more than one Ca-oxalate pathway were in operation at any one time. This also has important implications for the determination of the original paint constituents. For a further discussion on this point, the reader is referred to Appendix 3.2.

6.2.4.2 Orange colours

The orange samples collected tend to aggregate together within the PCA diagram based on both elevated Fe and, in particular, Al content (Figure 6.8). The average Fe content within the orange sub-set is greater than that recorded for the red samples, whilst the Al contents are, on average, between two and five times greater than those recorded for the rest of the paint dataset (Appendix A5.12.1). The average Ca content is about 6 %, with only two paint samples recording contents greater than 10%.

Unfortunately, the mineralogical composition of only three of the eight orange paint samples could be determined (Paint samples 6, 7 and 23). All four of the Ca-containing minerals determined within the white samples were also present within Paint sample 23 (namely gypsum, whewellite, bassanite and anhydrite). The presence of whewellite was found in only one trace in Paint sample 6, however, whilst none of the other Ca minerals were found in Paint samples 6 or 7.

Considering the Ca-containing minerals found within Paint sample 23, similarities between the composition and relative dominance of these minerals within this pigment and those recorded for the white and yellow pigments are interesting. This could indicate a number of different possibilities:

- The orange pigment was painted over a pre-prepared white pigment surface, following a painting technique that has been suggested by, for example, both Vinnicombe (1976) and Willcox (1984).
- A 'bulking' agent of similar composition to that of the white pigments was used in the manufacture of the paints.
- The Ca-minerals were deposited both before and after the painting event via natural processes alluded to in Section 6.2.4.1.

The lack of these same minerals in Paint samples 6 and 7 tends to negate all but the last of the three above-mentioned points. Although it is possible that different paint mixtures were utilised for the different images sampled, the thickness of the sample, the position of the images within the Shelter and the youth of the images are probably responsible for the absence of Ca-containing minerals. Both of these samples display the highest combined Al and Fe values recorded for the entire dataset, and correspondingly low Ca and S values. This indicates that these samples contain almost 'pure' inorganic pigment, upon which little or no gypsum or whewellite has, as yet, been deposited.

This has several implications, the most important of which is that all of these minerals are most probably present as a result of secondary deposition. From this it can be deduced that these minerals were most likely not present within the original paint when it was applied. A third conclusion that can be reached is that these paintings are all relatively recent. This theory is based on the assumption that the longer the image is upon the wall, the greater the time period to which the image is subjected to the secondary deposition of these minerals, which could possibly, though not necessarily, result in a more consistent distribution of these minerals across the painting surfaces. As these evaporite minerals display both an inconsistent presence and generally low percentage within the samples recorded, the obvious deduction is that the paintings are relatively young.

The one mineral common to the three samples analysed (Paints 6, 7, and 23), both in presence and dominance, is gibbsite. When looking at the elemental composition of these three samples, it is apparent that all display elevated Al contents (due to the gibbsite presence). As another orange paint sample, Paint 14, also displayed a similar elemental composition to these three samples, it can be assumed that all four samples share a similar origin.

The point is further supported when a comparison of the elemental data of these four samples is undertaken. As seen in Appendix A5.12.1, the average standard deviation within the orange dataset as a whole is 2.44. A comparison of only the samples with elevated Al contents reveals a drastic drop in the average standard deviation from 2.44 to 0.97. The high degree of similarity is further validated when one compares the recorded µ-XRF data obtained for Paint samples 6, 7 and 23 (Figure 6.13). As can be seen, not only do all three samples share a similar composition, but Paint samples 6 and 7 appear to be almost identical. When a comparison of the mode values determined for these same samples is made (Figure 6.13), the similarity between the samples is even further pronounced. This strongly indicates that, for the latter two samples at least, the same pigment was utilised in the production of both images.

There are few geological sources in the South African landscape that would offer both a high Al content together with an orange colour. Bauxitic material, and in particular ferruginous bauxite, contains goethite that is highly Al-substituted and orange in colour, whilst some saprolites also contain goethite with similar, though slightly lower Al-substitution (Fitzpatrick and Schwertmann, 1982). Both of these sources are relatively accessible, although some excavation would be necessary to reach some saprolites. Bauxite in particular is an obvious source for it is often found exposed as outcrops and is easily crushed, thus fulfilling two of the postulates set out in Section 5.2.4. Whilst the Al concentration within the orange dataset is highly variable, what is noted is that gibbsite represented a dominant mineralogical phase only within the samples containing these elevated Al values (Appendix DIGITAL 1). Of the two sources mentioned, saprolites do not contain elevated amounts of gibbsite. I therefore propose that the orange component of the paints pigments shown to contain elevated Al and a gibbsite presence was sourced from bauxitic material.

Two of the orange pigments do not contain elevated Al contents (Paint samples 4 and 24), indicating that they do not originate from bauxite. Typically found in association with bauxitic materials, however, are Fe nodules that range in diameter from between 2 and 5 cm and consist of a dark, hard rind and a brittle, much lighter (either red, yellow or orange) interior (Fitzpatrick and Schwertmann, 1982). Whilst the rinds typically contain higher Fe than do the interiors, the Al content tends to display the reverse trend. The analysis of a typical Fe nodule located near the Shelter (Sample 6) has shown that the black rind is composed predominantly of magnetite, whilst the interior material is composed of goethite, haematite and trace amounts of magnetite (Appendix 5.10). These similarities tend to suggest that the inner core of these nodules is the source of the orange pigment used within these images. The suspected pigment sources and painting styles are listed in Table 6.3.

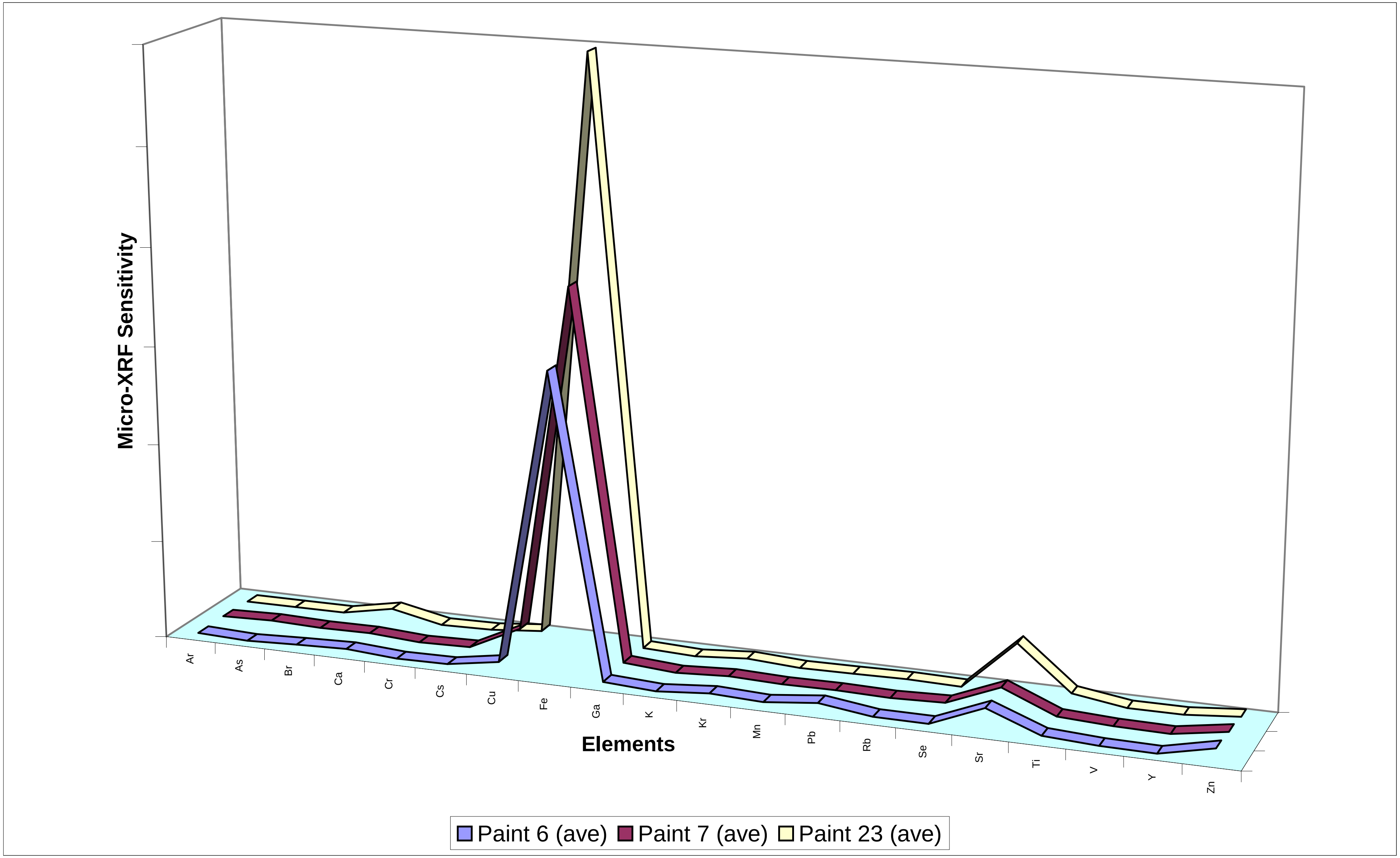

Figure 6.13: Micro-XRF data of Maqonqo Shelter paint samples 6, 7 and 23 (adapted from Appendix 5.16).

Table 6.3: A comparison of the individual painting styles of the paintings in Maqonqo Shelter from which the orange samples were collected.

Paint sample	Suggested pigment source	Painting style*
Paint 4	Fe nodules^	Unshaded bichrome eland; white legs, head; orange torso sampled.
Paint 6	Bauxitic material	Unshaded bichrome eland; white legs, head; orange torso sampled.
Paint 7	Bauxitic material	Indiscernible monochrome image.
Paint 11 B	Bauxitic material[#]	Orange ‘contaminant’ from underlying image. Original sampled image is an unshaded bichrome eland; White head, legs; yellow torso sampled.
Paint 14	Bauxitic material[$]	Indiscernible monochrome image.
Paint 20	Bauxitic material	Indiscernible monochrome image. This is a sample from the paint fragment excavated from Layer 7.
Paint 23	Bauxitic material[$]	Indiscernible monochrome image.
Paint 24	Fe nodules^	Indiscernible monochrome image.

* - See the images in Appendix DIGITAL 6.
^ - This determination is based on the relatively low Al content recorded using EDX.
# - One μ-XRD trace showed the presence of gibbsite.
[$] - This determination is based on the relatively high Al content recorded using EDX.

Another distinguishing feature of the orange samples suspected to have a bauxitic origin is that they contained elevated Ti contents relative to the other samples analysed (Appendices A5.12.1 and 5.16). This is consistent with the findings conducted on the three bauxitic samples collected within 15 km of MQ, as well as from a composite sample of bauxite collected from the Ngome area which, although located approximately 100 km away, was collected from a deposit considered to be typical of the bauxitic deposits found within KwaZulu-Natal (Brabers, 1976). The dominant minerals found within all of these samples were determined to be gibbsite, goethite, quartz, and chlorite, with smaller amounts of magnetite, ilmenite, orthoclase and haematite also being detected.

When compared with other bauxitic samples collected from around the country, it is clear that the KwaZulu-Natal samples display consistently higher Ti values (Table 6.4). The similarity existing between these samples and the orange paint pigments suggests that, not only was bauxite used in the manufacture of these paints, but the orange pigment sampled was sourced locally from within KwaZulu-Natal, and not ‘imported’ from other areas of the country via trade or population movement.

So far, two separate sources for the orange pigments have been suggested, with each relating to specific images. This suggests that at least two separate paint recipes were used for the creation of the orange paints found within MQ. Of the two resources, the Fe nodules represent the most easily accessible and widely distributed source, for they are commonly found within most of the drainage systems throughout the study area. The Fe nodule derived pigments, whilst not displaying as high a Ti content as those derived from bauxitic materials, still display a higher Ti content relative to the remaining paint pigments. Like the bauxitic samples, therefore, these pigments are suspected to have been collected locally.

The bauxitic material, although not uncommon within the landscape, tends to have a more limited distribution, often only being exposed within erosion dongas or found as part of highly weathered

Table 6.4: A comparison of XRF results for various different aluminous materials collected from around South Africa (adapted from Brabers, 1976).

	1	2	3	4	5		6		7		8	9	10	11
					A	B	A	B	A	B				
SiO_2	62.37	n.d.	44.54	54.68	10.9	18	56.5	49.65	46.11	46.98	10	16.08	18.25	13.35
Al_2O_3	17.35	30.5	49.27	26.33	33.9	29.9	27.83	34.8	34.65	32.03	25	45.95	22.14	42.99
Fe_2O_3	2.72	0.85	0.34	n.d.	31.6	31.6	3.03	1.35	3.9	6.1	36.2	34.01	51.61	38.53
FeO	n.d.	n.d.	2.01	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
MnO	0.09	n.d.	trace	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.6	0.26	0.07	0.11
CaO	1.57	n.d.	0.34	n.d.	n.d.	n.d.	0.12	0.11	9.11	7.93	0.1	0.05	0.35	0.05
MgO	0.83	n.d.	0.86	n.d.	n.d.	n.d.	0.2	0.2	2.19	1.14	0.1	0.48	0.91	0.41
Na_2O	1.19	13.2	0.24	0.17	n.d.	n.d.	0.2	0.25	1.32	1.26	n.d.	0.0	0.12	0.0
K_2O	13.63	4.7	0.8	8.65	n.d.	n.d.	0.44	0.23	n.d.	0.48	0.2	0.22	0.98	0.68
TiO_2	0.13	0.71	0.37	n.d.	3.6	2	1.61	1.58	1.75	0.63	4.3	2.68	3.93	2.75
SO_3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	trace	n.d.	n.d.	n.d.	n.d.	n.d.
S	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.14	trace	n.d.	n.d.	n.d.	n.d.
P_2O_5	n.d.	n.d.	0.11	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.65	0.7	0.34	0.49	0.38
H_2O+	n.d.	n.d.	0.62	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
H_2O-	n.d.	n.d.	0.26	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
CO_2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
F	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
L.O.I.	0.12	n.d.	n.d.	4	19.3	21	10.32	12.49	0.98	2.91	22.7	24.09	18.57	24.3
Total	100.00	n.d.	99.76	93.83	99.30	99.00	100.25	100.66	100.15	100.11	99.90	100.07	98.86	99.25

Key:

L.O.I. = Loss on Ignition.
n.d. = Not determined.
1 = Average of eight syenitic bodies from the Phalaborwa Complex.
2 = Average of two nepheline concentrates from coarse and fine ijolite, Spitzkop Alkaline Complex, Groblersdal District. [Total not given]
3 = Concentrate of andalusite from Toornkop 398 KS, Pietersburg District, cleaned of some contaminants.
4 = Average of eight samples of sericite from Palmietfontein 343 IP and Doornfontein 345 IP, Ventersdorp District.
5 A = Borehole sample of lateritic soil from Lisbon 531 KT, Pilgrims Rest District.
B = Borehole sample of lateritic soil from Mooigepierd 910, Lions River District.
6 A = Average of 10 samples from the upper plastic clay horizon, Klipfontein 83 IR, Boksburg District.
B = Average of 10 samples from the semi-flint clay horizon, Klipfontein 83 IR, Boksburg District.
7 A = Analysis of fly ash from Sasol.
B = Analysis of gasifer ash from Sasol.
8 = Analysis of a composite sample considered typical of bauxite from Mooiplaats 537, Ngome District.
9 = Bauxitic sample collected from Mpate (Appendixes 5.6 and A5.8.2).
10 = Weathered dolerite, sample 4, collected from area surrounding MQ (Appendixes 5.6 and A5.8.2).
11 = Weathered dolerite, sample 9, collected from area surrounding MQ (Appendixes 5.6 and A5.8.2).

doleritic intrusions typically located on the local hilltops. Small amounts of bauxitic material can, however, be collected from the weathering rinds of dolerite rocks that have a sporadic distribution across the landscape.

When comparing the painting styles with the suspected pigment sources, no discernable trends are seen with both suspected sources being used within both painting styles noted (Table 6.3). It is not inconceivable to assume that changes in painting style might also be reflected in changes in pigment sourcing/paint recipes. On the limited evidence available, however, it seems that either the painting styles within MQ were painted concurrently, and/or that the same inorganic pigment sources were used over a protracted period of time. Further sampling of additional sites within the area is required in order to clarify this point.

During the course of this discussion, one sample (Paint 20) has not yet been examined, even though it has a dominating influence on the variability in Ca, S and Si within the dataset as a whole. This sample is the suspected painted rock fragment that was excavated from Layer 7 of the deposit. The main distinguishing factor between this sample and the rest of the orange paint dataset is that it displays a greatly reduced Ca and S content. As a consequence, a greater percentage of the sandstone matrix contained within the sample was analysed, resulting in the elevated Si content recorded.

The lack of both Ca and S indicates that there is no gypsum present on the surface of the sample. This could have been lost either through the interaction of the gypsum with soil water within the deposit, or the gypsum seen on the wall samples only formed after this piece was dislodged from the wall (or both). In an attempt to compare the wall fragment with the orange samples without the influence of the evaporite minerals, the Ca, O and S values were reworked back into the remainder of the elements (see Appendix 5.15). The resultant PCA diagram, Figure 6.14, clearly shows how the four bauxitic samples cluster together with the remaining samples being widely spread out.

Based on this, it is again clear to see that there are at least two different pigment sources used in the production of the orange pigments. It is also clear that the wall fragment does not display a close affiliation with any of the other eight samples collected. A more detailed discussion as to why this is so is given in Section 6.2.5.

6.2.4.3 Yellow colours

Goethite, a mineral found within both the yellow and orange datasets, has been found to change colour from an orange-yellow to a true yellow with increasing Al-substitution (e.g. Fitzpatrick and Schwertmann, 1982; Jeanroy *et al.*, 1991), the degree and intensity of this colour change being moderated by the mineral’s crystal size (Bigham and Ciolkosz, 1993). However, as the paint sample distribution using EDX seems to indicate the reverse trend i.e., there is more Al on average in the oranges than the yellows (Figure 6.8), it is reasonable to assume that the Al variability between both datasets is directly attributable to variations in gibbsite content.

The yellow paint samples also display Ti contents that are comparable with those noted in the orange samples suspected of being sourced from the inner cores of Fe nodules. These similarities tend to suggest that the Al-goethite enriched yellow samples share a similar source, and originate from somewhere within the central to northern KwaZulu-Natal region.

Of the five yellow samples collected, Paint 29 and Paint 11A represent repeat samples collected at the same point and can therefore, for the purposes of this discussion, be considered to represent only one sample point (Paint 29 represents the ‘upper/surface’ paint layer). Paints 11B and 28, although separate samples, were collected from different locations on the same image as the repeat samples.

The remaining paint sample, Paint 10, represents a ‘contaminated’ sample, having originally been sampled for the white pigment from an image overlying an orange/yellow background. As such, this sample cannot be considered to be representative (see Appendix DIGITAL 6). As a result, effectively only one painted image was sampled. Thus, whilst this dataset does not allow for the comparison of yellows between different images, it does allow for an investigation of the heterogeneity of the painting upon the wall and, following on this, the robustness of the methodology being employed within the current study.

Figure 6.15 shows the EDX MQ paint sample data as displayed in Figure 6.8, only the yellow samples are labelled in order to highlight how each of these samples relates to one another. Immediately apparent is that the ‘contaminated’ sample, Paint 10, separates out from the rest of the yellow samples, with this separation being governed primarily by its S and O content. This is not surprising, for this sample was originally collected from a white painting that, as has already been shown in Section 6.2.4.1, is dominated by gypsum.

Paint 11A is also shown to separate out relative to the other yellow samples, with its separation being governed by its higher Si and Al content and, more importantly, its relatively lower C content (often directly related to the Ca-oxalate content). The µ-XRF data for this sample repeats this trend, with the only difference being that this sample is shown to have a lower Ca content relative to the other samples (Figure 6.16). The ‘upper’ of this repeat pair, Paint 29, displayed a higher C, but lower Ca and S content, from which can be inferred that the ‘surface’ paint sample contains a higher Ca-oxalate: gypsum ratio than the second, ‘lower’ sample, indicating a decrease in Ca-oxalate content with increasing paint depth, with the quartz and gypsum contents showing the reverse trend.

The increased presence of gypsum within the ‘lower’ paint sample is interesting, for it indicates that this mineral might represent an original paint constituent. The higher Si content could indicate the opposite, however, for an increasing quartz content could indicate an increased presence of the shelter wall within the sample. It is thus equally likely that the gypsum recorded here might represent a ‘contamination’ of the sample by gypsum that was originally upon the rock surface before the painting was created. Unfortunately, no additional samples were collected that would support one or the other of the above two hypotheses.

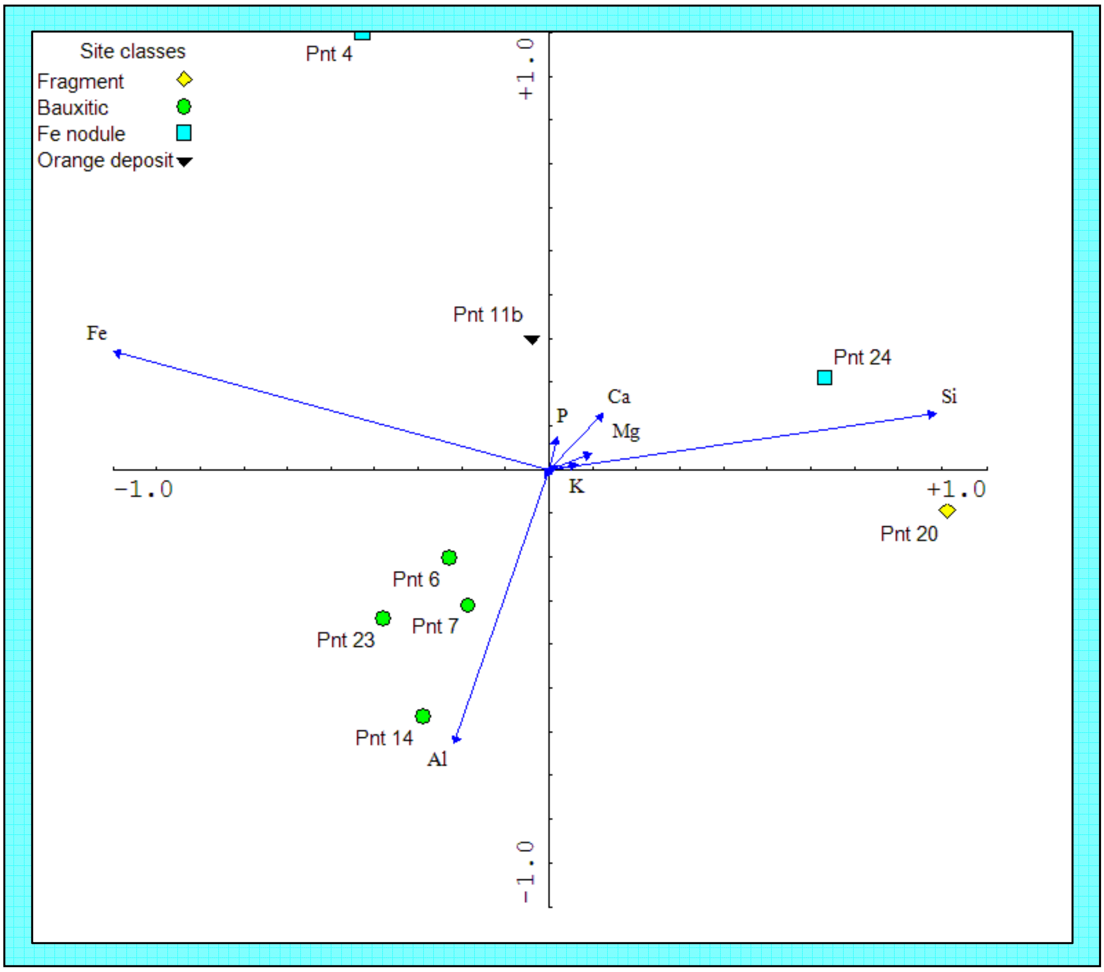

Figure 6.14: A comparison of the EDX Maqonqo Shelter orange paint samples and Paint 20, the exfoliated paint fragment.

Eigenvalues: PCA1 – 69.6; PCA2 – 18.8; PCA3 – 10.4

Scaling = -2

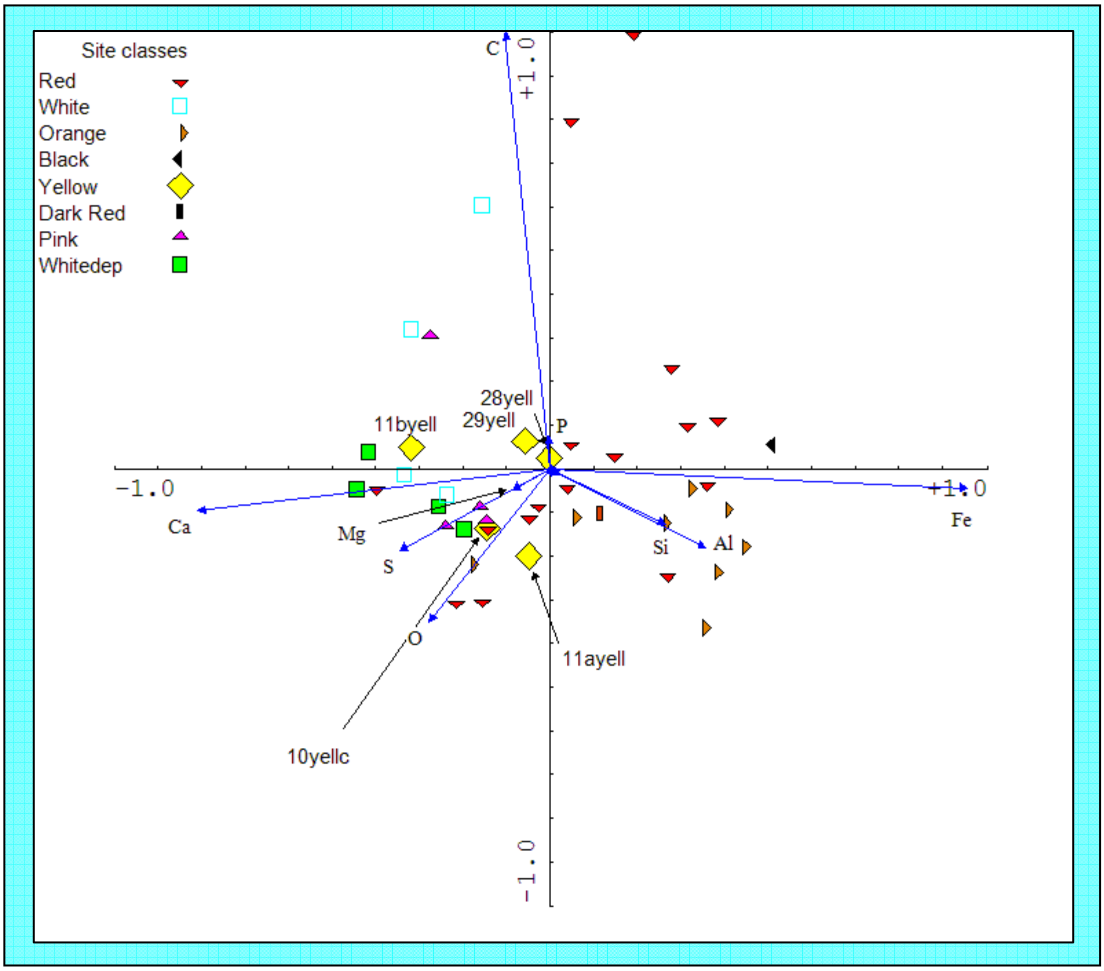

Figure 6.15: A comparison of the Maqonqo Shelter paint samples using EDX, highlighting the individual yellow paint samples.

Eigenvalues: PCA1 – 43.9; PCA2 – 27.2; PCA3 – 15.8

Scaling = -2

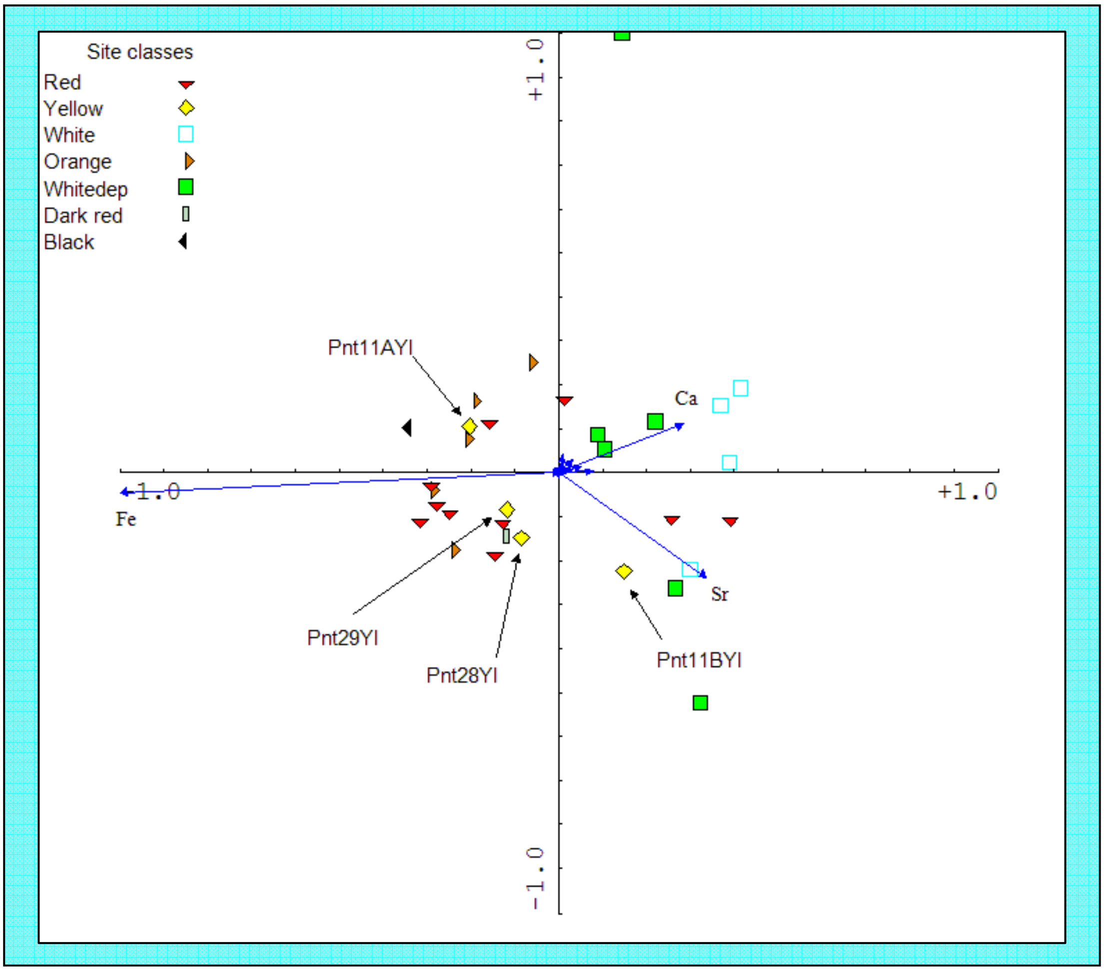

Figure 6.16: Micro-XRF data depicting the labelled yellow samples within the Maqonqo Shelter paint colour and white deposit dataset.

Eigenvalues: PCA1 – 88.4; PCA2 – 5.6; PCA3 – 2.8

Scaling = -2

A comparison of the three ‘upper’ surface samples (Paints 11B, 28 and 29) produces some interesting results. In both Figures 6.15 and 6.16, it can be seen that Paints 28 and 29 display very similar elemental compositions, whilst Paint 11B tends to have a higher Ca content. Although the mineralogical data for these samples show that all three of these samples have elevated gypsum and whewellite contents, Paint 11B is the only sample to also contain both bassanite and anhydrite; these latter minerals being the source of the elevated Ca contents recorded for this sample. The presence of these minerals, together with glushinskite (found only in Paint 28), can be attributed to localised deposition, thus further highlighting the high degree of variability that exists at the micro-environmental level upon a shelter wall. The photographs taken of Paint 11B’s sampling site substantiates this in that they show white surface accumulations located within the nearby vicinity (Appendix DIGITAL 6).

The dominance of whewellite within the surface samples, yet seemingly decreasing within increasing paint depth, supports the theory that this mineral formed upon the surface of the painting post the painting event. The consistent presence of this mineral within the samples analysed (and within the white deposits located amongst the sampled pigments) as opposed to the blanks collected from the same Shelter (Section 6.2.3), tends to indicate that the composition of the original paint pigment was instrumental in the formation of this mineral. The easiest way for this to be achieved would be if the mineral formed as a result of the bio-mineralisation of organic additives originally incorporated within the paint. If ^{14}C isotope analysis indicates that this mineral was the product of a biological pathway and not an inorganic pathway, this would clearly indicate that different preparation techniques were utilised for different paint colours. It would also have important implications with regards to possible dating of the images in question (see Appendix 3.2).

As all of the samples, with the exception of Paint 10, were collected from the same image, it is safe to assume that the samples share the same pigment composition. Whilst gypsum, whewellite and goethite are common to most of the traces collected from all three samples, the presence of haematite and gibbsite was a little more erratic. Although present within all the samples, haematite was only present within 9 of the 21 traces collected, and represented, on average, between 5 and 14 % of the total recorded mineralogical composition for each trace (Appendix DIGITAL 1). Gibbsite was found predominantly within Paint 29, with six of the seven traces being recorded within this sample (the remaining trace being recorded in Paint 11B). On average, this mineral represented between 15 and 49 % of the total mineralogical composition of each of the seven traces.

The decreased gibbsite content within Paints 11B and 28 can be due to one of two factors:

a) A larger percentage of the evaporite minerals was sampled in addition to the intended paint sample within both of these paint samples, thus resulting in lower recorded abundances of other minerals that might be present; or

b) The accidental sampling of the orange substrate underlying the paint pigment resulted in the introduction of gibbsite to the sample (see Appendix DIGITAL 6).

Whilst both of these factors influence the mineralogical composition of the pigments analysed, the latter seems the most probable reason for the prevailing presence of gibbsite within only one of the three samples analysed.

A consistent combination of goethite and haematite, together with a lower Al content, as compared to the gibbsite containing orange samples, tends to indicate that another source of goethite other than bauxite was used in the yellow paint's manufacture. As mentioned in the previous Section, Fe nodules contain a lower Al content than the bauxites whilst still reflecting elevated goethite contents. Furthermore, the nodules typically found within the central and northern KwaZulu-Natal environment also reflect the elevated Ti values typical of the bauxitic materials. The combination of these factors indicates that these samples were probably sourced from the inner cores of Fe nodules found locally within KwaZulu-Natal.

The EDX data collected from the yellow material on Paint 10 display a similar elemental composition to those of the previously discussed samples. Unfortunately, the µ-XRF and µ-XRD data collected for this material were not good enough to allow for the accurate identification of the minor elemental and mineralogical composition. However, even without this collaborative evidence, the similarities displayed within the EDX data of the yellow pigments, together with that of the painting styles of the two images, suggests that this is the case (Table 6.5).

Table 6.5: A comparison of the suspected pigment sources with the individual styles of the yellow paintings sampled in Maqonqo Shelter.

Paint sample	Suggested pigment source	Painting style*
Paint 10	Fe nodules^	Yellow 'contaminant' from underlying image. Original sampled image is a white leg (area sampled) of an unshaded bichrome eland (torso is orange).
Paint 11A & B, 28, 29	Fe nodules	Unshaded bichrome eland; white legs, head; yellow torso sampled.

* - See the images in Appendix DIGITAL 6.
^ - This determination is based on the relatively low Al content recorded using EDX.

6.2.4.4 Red colours

The red colours display the greatest degree of variation of all the colours analysed (Figure 6.8). Whilst this variability can be ascribed, in part, to the number of samples analysed (16), their distribution is governed primarily by their composition relative to the linear relationship existing between Fe and Ca (PCA1 = 43.9 % variability), with this distribution being further influenced by variable O and S contents within each of the respective samples. PCA2 (27.2 % variability) is driven almost exclusively by C content typically associated with a Ca-oxalate presence. Thus, over 70 % of the variability within the red colours is governed primarily by the ratio of the Fe and Ca containing minerals.

Figure 6.17 highlights the third strongest influencing variable(s) on the dataset as a whole (the 'y-axis') i.e., the almost linear relationship that exists between Si content and the 'combined' influence of Ca and Fe. PCA2 shows the linear relationship that exists between S and C. These trends can be re-interpreted as follows: PCA2 highlights the variability within the samples with regards to their gypsum: whewellite contents, and PCA3 highlights the change from quartz dominated (shelter wall) samples to pigment dominated samples, which, in turn, is indirectly an indication of the relative thickness of the overlying pigments and surface deposits upon the rock surface.

Only two other sample sets have a quartz content with a comparable influence on the dataset as that displayed within the red paint samples, namely the blank and black sample sets (the latter to be discussed later). This infers that the red samples collected were 'thinner' than those of the other datasets i.e., a greater percentage of the rock wall substrate was sampled in conjunction with the pigment due to the fact that there is insufficient pigment present between the sampling tape and the wall. Two hypotheses can be put forward to explain this phenomenon:

1) The pigment originally contained a greater percentage of quartz, either from the original source, or introduced during the manufacturing process i.e., when the original pigment was ground.
2) Due to the nature of the pigment and its method of manufacture, the pigment is absorbed into the uppermost layer of the rock substrate. Over time the paint residing upon the surface is reduced. Thus a painting is still seen, but when sampled, a greater percentage of quartz is collected along with the pigment.

Whilst neither of the aforementioned points can be conclusively accepted or rejected on the data available, based on the Si contents determined by EDX, it seems that the first hypothesis is unlikely, for the Si contents recorded for the red pigments are lower than those determined for the blank samples. Had Si been introduced to the paint during the manufacturing process, it is reasonable to assume that the reverse could be expected.

Personal observation has shown that a majority of the red paintings are present in the form of a 'stain'. The other pigments, namely yellow, orange and white, are almost always 'thicker' than the red paintings within the same shelter. The white pigments, in particular, seem to be applied in thick[1] layers, so much so that it is often possible to observe what can only be described as brush strokes (Appendix 6.1).

The combination of these observations together with the apparent dominance of gypsum within a majority of the red samples analysed, seems to support the second hypothesis. But is it the age of the painting or the nature of its pigments' source and paint manufacture, or both, which results in the

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[1] The term 'thick' refers to the visible applied paint pigment layer, which, in the case of the white pigments, is often at least 0.5 mm thick, but can be thicker.

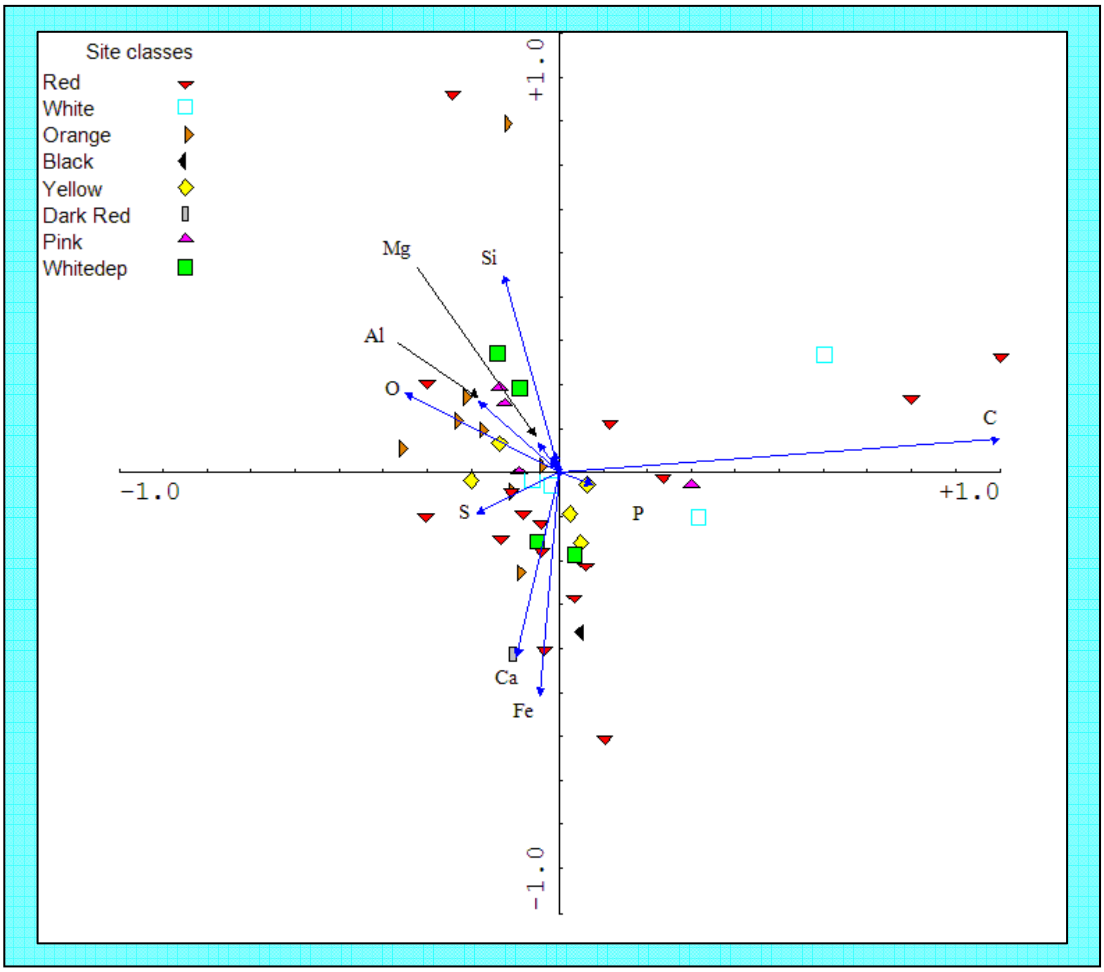

Figure 6.17: A comparison of the second and third EDX PCA dimensions for the Maqonqo Shelter paint samples.

Eigenvalues: PCA1 – 43.9; PCA2 – 27.2; PCA3 – 15.8

Scaling = -2

‘staining’ effect observed in the paintings? For a clue, one has to look at the surface deposits that are found in conjunction with the pigments, in particular the Ca-oxalates.

As has been commented in Section 6.2.4.1, Ca-oxalates, in particular whewellite, are found within a large proportion of the paint samples analysed, yet are almost totally absent from the blank samples, and it was from this fact that it was concluded that Ca-oxalates are inherently linked with the paint recipes and/or components. In Section 6.2.4.1, an argument was presented stating that the whewellite was present within the white pigment at the time of its application. This was supported by evidence supplied by the double sampling tests conducted on an image of this colour. Unfortunately, although a double sampling test was conducted on a red image, the lower repeat sample could not be resolved, in part due to the limited amount of paint material available for the second sampling.

Although it cannot be categorically concluded that whewellite was not an original constituent of the red images, this can be surmised from the relatively low Ca-oxalate: gypsum ratio recorded for all of the red samples (as compared to the white samples), together with their erratic distribution across the samples. These minerals are most probably the result of secondary deposition post the painting event, being derived from a process similar to that outlined in Section 6.2.4.3 (the Ca-oxalate presence within these samples is still sufficient to support the contention that they are present as a result of the paint constituents).

The thin nature of the paints, the erratic distribution of the whewellite, the dominance of gypsum and, to a certain extent quartz, all support the hypothesis that the paints are, at least in part, absorbed within the upper surface of the Shelter wall. This, together with the strong staining ability of haematite, is probably the single most important reason why the red pigments have outlasted images painted in other colours (the wall itself provides protection to the images). The fact that the pigment is absorbed into the shelter wall also gives an indirect indication as to the nature of the original paint mix i.e., fluid, as opposed to a more ‘paste-like’ consistency as has been described in the case of the white pigments.

This contention is supported by findings by Clarke (1958), who found that the red pigments tended to display considerably better bonding qualities than the yellows and whites. Haematite grains, being small, tend to penetrate the sandstone much easier than the yellow/orange ochreous pigments that tend to form hygroscopic layers upon the rock surface. Whilst the haematite grains are both mineralogically stable and display strong adhesive properties as a function of their mineralogical structure, the shrink-and-swell properties of the hygroscopic clays and the fluctuating water of hydration content within the gypsum/bassanite phases naturally lead to periodic flaking of the other pigments.

Of the original 13 samples analysed, the mineralogy of only six could be determined. As Paint 26 was collected from the same image as Paint 8A, however, effectively the mineralogy of only five individual images can be compared. Within these samples, it was found that haematite is not only common to all of the traces analysed, but it also represents the dominant mineralogical phase within most of these traces (between 15 and 49 % of the total recorded composition). Gypsum is the second most common (and dominant) mineral recorded, whilst goethite and whewellite are both only found in about half of the traces (though not necessarily the same ones).

Gibbsite was only found within one trace (Paint 12). It is probable that the sample analysed was derived from material underlying the original white target painting (see Appendix DIGITAL 6). This ‘contaminant’ material also contained both haematite and goethite in a ratio similar to those noted in previous yellow samples. In addition, this sample also has a relatively high Ti content relative to the remaining red samples, yet is similar to those determined for the yellow samples. As has been shown previously, this combination of minerals and elements indicates that this pigment was probably sourced from Fe nodules (Section 6.2.4.3). This is turn strongly suggests that this pigment is not a natural wall deposit, but represents a relic, highly eroded image that was over-painted by the white painting that was the original sampling focus (it has been included here for the sake of completeness).

However, even taking the influences of the shelter wall and the secondary surface deposition into account, there is still a high degree of variability recorded within the remaining red pigments, especially with regards to their Fe content (EDX data). There are at least four possibilities that could account for this. The first is that the San collected these paint pigments from a wide variety of sources, possibly over an extended period of time. The second possibility is that the San prepared the pigment using a variety of pigmentaceous materials, modifying the mixture with various components until the desired colour was obtained. In the case of a red pigment, any additional haematite would have gone unnoticed and subsequently been superfluous. The third is that the pigment was obtained from a geological source that has inherently variable Fe contents. A prime example would be the Fe nodules already discussed in the previous section.

A fourth possibility concerns the calcination of yellow pigments to produce red colours. This process has a long archaeological history in the northern hemisphere (see Chapter 3), but very few accounts have been described in southern Africa (Stanford, 1910; How, 1970). It is known that on heating to above 350 ^{o}C, goethite will dehydroxylate and convert to haematite. By controlling the temperature and the length of time the goethite is subjected to calcining, a variety of shades of red can be obtained. It has also been shown that calcination of natural goethites at < 500 ^{o}C forms haematite that retains the initial Al content of the original goethite up to a maximum 28 mole % Al (Wells *et al.*, 1989). This is almost double the natural Al-substituted haematite maximum of 16 mole % Al (Nahon *et al.*, 1977).

This process thus allows for the creation of high Al-substituted haematite together with a high Al-substituted goethite component, since it is probable that not all will have been converted during calcination due to the imperfect methods that would have been employed by the San painter. If this process had been practiced, and one source material (yellow) had been used, the Fe and Al contents of both the red and yellow samples could be very similar. It is highly probable, however, that the mineral maghemite would also be found to be present if the Fe sources were manipulated in this manner, again due to the manner in which the painter would have to manipulate the pigments i.e., over an open fire. As this was not the case, for these samples at least, this hypothesis is unlikely.

The results did show that almost all the red samples contain similar amounts of Al. This is of some interest because a) it has been shown that haematite can become redder with increasing Al-substitution (Barron and Torrent, 1984); and b) goethite can accept a greater degree of Al-substitution than haematite (Torrent *et al.*, 1980), with both being influenced by the haematite crystal size (Bigham and Ciolkosz, 1993). These two points in turn suggest that if the San actively searched for very red pigments then these pigments could contain elevated Al contents. However, the yellow and red samples contain similar amounts of Al and this therefore suggests that the red samples also contain goethite, an assumption confirmed by the µ-XRD analysis.

A complicating factor is that the colour of a sample is also determined by the ratio of goethite to haematite. It has been shown by Scheffer and Ludweig (1958) and Resende (1976) that between 1.0 % and 1.7 % haematite is all that is required to impart a rich red colour to a sample. This contrasts strongly with the lower pigmenting effect of goethite. Furthermore, it has been shown that no change in colour occurs above a ‘saturation’ percentage of either 10 % for haematite or 30 % for goethite when individually mixed with deferrated soil (Barron and Torrent, 1986). Due to the stronger pigmenting effect of haematite, goethite is often not visibly recognised as being present in pigments. Thus, quite large amounts of goethite may be present in the red samples, but the quantity of haematite in the yellow samples must, however, be very low to non-existent. This too was confirmed by the µ-XRD data.

Although the Fe content within the remaining red samples is still highly variable, the fact that the remaining elements display similar values throughout the sub-set could indicate that the red pigments were collected from more than one point, but possibly from only one geological source. A comparison of the minor elements (EDX) within the red and yellow pigments does highlight certain similarities, with the most noticeable being that of the recorded Ti contents within both datasets. With the exception of one trace (mentioned above), gibbsite is not, however, common to the red dataset. Fe nodules are therefore likely to be the source of the red pigments.

A comparison of the individual painting styles indicates that there is no specific style preference associated with the pigment source selection (Table 6.6). This could have several possible implications; either these materials were used interchangeably for all of these images at a similar time period or, the painting styles did not change, but the source of the pigment did. Of these two scenarios, the former would seem the most likely, especially if one accepts that the images were all created within a limited time period between 8 000 and 3 500 b.p. as has been suggested by Mazel (1996a). There is no evidence to substantiate this, however.

Table 6.6: A comparison of the suspected pigment sources against the individual styles of the red paintings sampled in Maqonqo Shelter.

Paint sample	Suggested pigment source	Painting style*
Paint 1	Fe nodules	Monochrome eland.
Paint 3	Fe nodules	Indiscernible monochrome image.
Paint 5	Fe nodules	Monochrome human.
Paint 8 A & B	Fe nodules	Indiscernible monochrome image.
Paint 9 A & B	Fe nodules	Red 'contaminant' from underlying image. Original sampled image is a white leg (area sampled) of an unshaded bichrome eland (torso is orange).
Paint 11 A & B	Fe nodules	Red 'contaminant' from underlying image. Original sampled image is a yellow torso (area sampled) of an unshaded bichrome eland (legs and head are white).
Paint 12	Fe nodules	Red 'contaminant' from underlying image. Original sampled image is an indiscernible white monochrome animal. Possible over-painted image.
Paint 13 A	Fe nodules	Red 'contaminant' from underlying image. Original sampled image is an indiscernible white monochrome figure. This area represents the suspected detachment point of the Layer 7 exfoliated paint fragment analysed (Paint 20).
Paint 20	Fe nodules	Red 'contaminant'. Original sampled image is an indiscernible orange monochrome figure. This is a sample from the paint fragment excavated from Layer 7.
Paint 21	Fe nodules	Monochrome human.
Paint 22	Fe nodules	Indiscernible monochrome image.
Paint 26	Fe nodules	Indiscernible monochrome image.

* - See the images in Appendix DIGITAL 6.

6.2.4.5 Other colours

Only one dark red sample was analysed, and as a result, no comments regarding its composition relative to the other colours can be made (with respect to variability). Similar in many respects to the red samples already analysed, this sample is distinguished in that it contains gibbsite, but not whewellite, goethite or magnetite. In addition, all of the traces obtained are dominated by gypsum, and to a lesser extent bassanite, with both haematite and gibbsite having a combined presence of about 20 % or less in all cases. As a result, the 'lesser' minerals (if they are present) are probably being 'masked' by the overwhelming dominance of the evaporite minerals. As a comparison, the red samples consistently display haematite contents of between 20 and 50 %. From a sourcing point of view, this sample's composition poses an interesting dilemma, for at first glance it does not seem to be sourced from the same geologies already discussed above. Even though gibbsite is present, lack of goethite precludes bauxite as a possibility. Furthermore, the lack of magnetite also precludes the use of the outer rinds of Fe nodules that typically display a dark colouration.

Taking the sampling photograph into consideration, it can be seen that the Shelter wall in the immediate vicinity of the image has a very orange colouring (Appendix 5.1). It is possible that the gibbsite recorded is actually an addition to the sample, being derived from the Shelter wall during the sampling procedure.

A clue as to a potential source is provided by the µ-XRF data, which show an elevated Mn content within the sample. Although a large variety of Mn minerals occur within the landscape (dependent on the source e.g., superficial Mn minerals vs. Mn minerals formed within soil environments), birnessite and lithiophorite are the most common (Dixon and Skinner, 1992). The only source (of which I am aware) that has, as its core constituents, haematite and Mn oxides, and which is easily accessible within the local landscape is plinthite. Formed as a result of the precipitation of soluble Fe in the soil zone that experiences fluctuating water levels, this material is characterised by the presence of mottles and nodules. These ‘products’ are typically dominated by a variety of Fe minerals but, due to the similarities in their chemistry, Mn can also be co-precipitated.

The dark red paint sample displays all the characteristics comparable with material sourced from plinthite; a high Fe content, and a significant Mn content (µ-XRF data). As the sample is dominated by haematite only, containing neither goethite nor maghemite, it is plausible that plinthite is the probable source of this pigment.

It must be noted that the plinthite derived material, whilst formed in a manner similar to that of the nodules suspected of being the source pigment for the red and yellow samples discussed above, is considered to represent a distinct pigment source. These mottles/nodules are generally much smaller in size, but more importantly have not been subjected to the same weathering conditions as the nodules located within the exposed dongas and river courses.

The pink samples seem to lie between the white and the Fe dominated colours of red, orange and yellow. Their slightly elevated Fe content in relation to their Ca and S content (when compared to the white pigments) suggests that the red and the white pigments were blended together to create the pink colours. The elevated gypsum content identified further supports this hypothesis.

The final colour to be considered is the black sample. It is strongly dominated by Fe, having the highest recorded Fe content of the entire paint dataset. In addition to this, the Mn content is much greater than almost all of the other paint samples. Most ethnographic (Table 3.1) and archaeological references strongly suggest that charcoal is the primary component in black pigments, with only one reference referring to magnetite and three to manganese as possible sources (Rudner, 1982). The C content of the black paint analysed here is similar to that of the rest of the paint dataset, thus suggesting that it is not the source of the black colouration. The mineralogical results indicate that, in addition to quartz, haematite and goethite being present in similar ratios to those displayed in the red samples, the black sample also contained maghemite, an Fe-oxide that displays a black hue.

The presence of maghemite is of particular interest, for this mineral is typically formed from Fe oxides, usually goethite, that have been subjected to temperatures between 300 and 500 ^{o}C (Schwertmann, 1985). The fact that this mineral is found in none of the other paint samples analysed, nor is it found in association with anhydrite, indicates that this mineral did not form upon the surface of the shelter wall, but rather that it was present within the paint pigment before it was applied. Two possibilities for its provenance exist, namely that it was either collected by the artist, or it formed during the paints' manufacture (a technique suggested by, among others, Dunn (1931), Ruan and Gilkes (1996) and Helwig (1997)).

Maghemite, when found in the natural environment, is considered to be the product of the interaction between goethite, fire and organic matter, and this is supported by the fact that it is typically only found in trace quantities in the upper surface of soil profiles. As such, it is not in any readily accessible form that would have been easily available to the San artist. The artist himself could have replicated the same conditions if he had access to a goethite pigment and an open fire. That fire was actually used in the manufacture of this paint pigment is very hard to prove, however, though some tantalising hints suggesting that this is in fact the case can be extracted from the data.

Firstly, the sample contains no goethite. The calcining of a goethite pigment, to achieve a black colouration, would have resulted in the creation of both haematite and maghemite, as is the case of this pigment. Secondly, the very presence of maghemite indicates that heat (via fire) has had some role to play in the creation of the pigment that was eventually utilised. Thirdly, the sample displayed a relatively high Mn content, which, as has been shown previously in this section, is typically associated with either plinthic material or Fe nodules. Fourthly, if one compares the EDX data collected for the black sample with that from a goethite rich Fe nodule inner core (Site 6B: Appendix A5.8.2), several similarities are easily apparent: 1) both reflect very high Fe contents; 2) both display relatively low Al contents (especially when compared to the other sampled pigment sources); and3) their respective Si and Mn contents are also comparable. Thus, whilst it cannot be categorically stated that fire was indeed used in the manufacture of this paint pigment, on the evidence available, this would appear the case.

Whilst it is recognised that too few of these less prominent colours were collected to allow for statistical comparison, Table 6.7 is presented below to indicate the suggested pigment sources and the associated painting styles of all of the colours discussed within this section.

6.2.4.6 Summation

This study has shown that the analysis of very small paint samples can lead to a greater understanding of factors that relate directly to the protection of San art. These include insights into the Shelter's microclimate, the ability of the pigments to withstand mechanical and chemical weathering, as well as providing clues into the probable sources of the pigments used within a painting's manufacture. Indications of biological additives are also suggested, but without a further investigation, these could not be verified.

Table 6.7: A comparison of the individual styles of the paintings in Maqonqo Shelter from which the black, dark red and pink samples were collected.

Paint sample	Paint colour	Suggested pigment source	Painting style*
Paint 2	Black	Fe nodules (inner core) [heated].	Monochrome human.
Paint 27	Dark red	Fe nodules (from plinthite).	Indiscernible monochrome image.
Paint 10	Pink	White pigment stained by an underlying red pigment.	Pink 'contaminant'. Original sampled image is a white monochrome animal.
Paint 11 a	Pink	Excess surface deposition upon a red pigment.	Pink 'contaminant'. Original sampled image is a yellow torso (area sampled) of an unshaded bichrome eland (legs and head are white).
Paint 13 a	Pink	Excess surface deposition upon a red pigment.	Pink 'contaminant'. Original sampled image is an indiscernible white monochrome figure. This area represents the suspected detachment point of the Layer 7 exfoliated paint fragment analysed (Paint 20).
Paint 15	Pink	Mixture of white and red pigments, collected from shelter wall surface deposited material and Fe nodules, respectively.	Monochrome human.

* - See the images in Appendix DIGITAL 6.

In general, it was shown that the results obtained from the analysis of paint pigment samples were influenced, to a greater or lesser extent, by the presence of four contributing components, namely the shelter wall, secondary wall deposits, secondary oxalate deposits, and the paint pigment itself (Figure 6.18). The shelter wall was represented mainly by quartz, although feldspars were also noted. The secondary wall deposits identified were gypsum, and to a much lesser extent, bassanite, and anhydrite. The secondary oxalate deposits, predominantly represented by whewellite, were found within a majority of the paint samples (weddellite and glushinskite were also noted in a few cases). The almost complete lack of these minerals within the blank samples raised some interesting questions, some of which were addressed in Section 6.2.3.1.

The determination of these key components and their respective influences on the results obtained is fundamental to the successful interpretation of the results. A complicating factor is that not all of these components need be present within a particular sample, their presence being dependent on a number of factors. These include the manner in which the paint pigment was manufactured, the age of the painting, the position of the painting within the shelter (i.e., is it exposed to the elements and/or located along a plane of weakness within the shelter wall), and the specific components that were utilised in the creation of the pigment, be they organic or inorganic, or both. They are also not necessarily easily distinguishable from one another. A brief description of each of these components follows.

The shelter wall:

As its name implies, this relates specifically to the nature and influence of the shelter wall on the composition of the paint pigment. In general, the primary minerals which are reflected within the pigments are quartz, and to a much lesser extent, feldspar. This does not mean to say that these minerals might not also reside within the original paint matrix but, based on the results obtained from both the blank samples as well as the double sample tests (which generally showed an increasing quartz content with increasing paint depth), it is reasonably safe to assume that this is not the case.

The paint pigment:

This component represents the remnants of the material applied to the wall by the San artist. The term ‘remnant’ is an important term to remember, for it is necessary to keep in mind that the images seen today have been in their current exposed position for an extended period of time, and thus have been subjected to a wide array of chemical, mineralogical and mechanical weathering processes. The degree to which each of these individual weathering processes has affected the pigments is dependent on a number of inter-related factors, namely the nature of the paint constituents, the manner in which the paints were applied, the position of the painting within the shelter, the nature of the microenvironment at the specific locality at which the painting is located, and the manner in which the shelter has been managed or utilised in the past.

This is most easily illustrated by comparing Appendix 6.1, which relates the relative durability of the individual paint colours based on observation by archaeologists, to Appendix 6.2, which highlights the colours of the pigments and the ages of burial stones. Based on this comparison, it is apparent that, under the right conditions, all the pigments can be preserved. As most San paintings exhibit variable degrees of weathering, and that the degree of weathering is strongly correlated to the paint colour, it can be inferred that certain pigments are more susceptible to weathering than others. This is further complicated by the fact that certain images of a certain colour appear to be more resistant to weathering than others, as is evidenced by photographs and tracings of images over a number of years (Figure 6.1).

The degree to which the pigment used within the manufacture of the paints affects the nature of the paint samples analysed is dependent on two factors, firstly the thickness of the paint pigment sampled (e.g. the red and orange pigments show a moderate and limited influence, respectively), and secondly, the nature of the sandstone formation upon which the paintings were created (see Section 6.2.3).

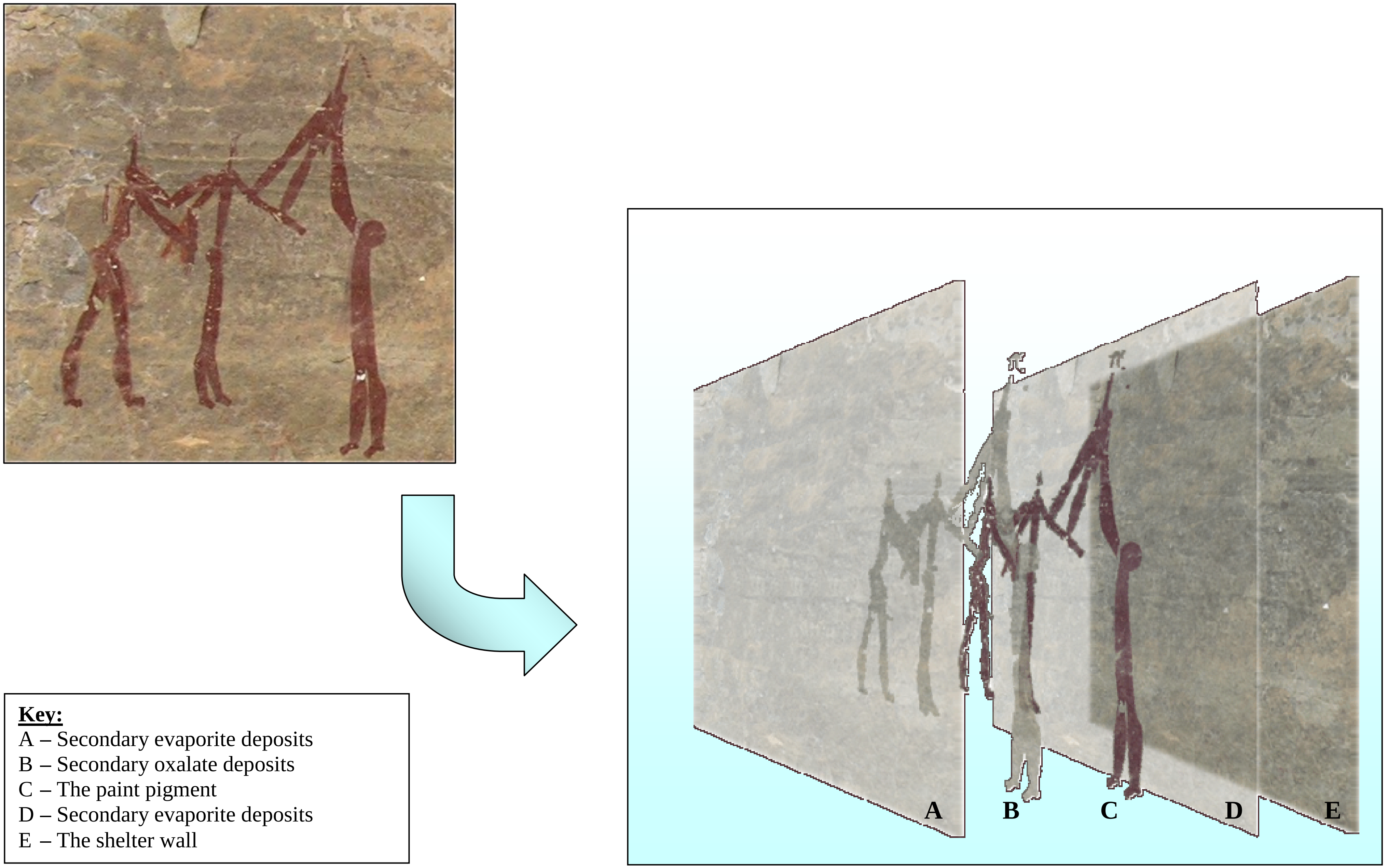

Figure 6.18: An example of a parietal San rock art painting split into its four component parts (A and D effectively represent a single continuous entity).

Figure 6.19: Successive tracings by P. Vinnicombe of a panel in Goodhope Shelter (1976). Today, only three of these images are visible. Represented here are predominantly light and dark red images.

Secondary evaporite deposits:

This component is repeated twice in Figure 6.18 illustrating that these minerals, which are precipitated periodically over time (dependent on the prevailing climatological regime), will exist upon the shelter wall both before and after the painting event. The mineralogical nature of this component is a function of the landscape within which the shelter is located, and as such, varies from shelter to shelter (see Section 6.2.3). The predominant mineral representing this component within MQ is gypsum, whilst its two associated derivatives, bassanite and anhydrite, are also shown to be present.

Due to the very nature of evaporite mineral precipitation, these deposits will never form a continuous and/or uniformly thick layer across the wall surface. In the case of MQ, whilst gypsum was found in a majority of the traces, it was seldom found in all of the traces obtained for a single paint sample. Its dominance within a sample also varied from trace to trace.

This variability was taken to the extreme when considering the gypsum derivatives, namely bassanite and anhydrite. The presence of these minerals is totally dependent on the micro-environment at the specific locality of the sampling point, and their distribution is thus highly variable. An example of this is shown in the results obtained for the orange painting sampled within this study. Paints 11B, 28 and 29 all represent surface samples collected from the image, yet only Paint 11B was shown to contain these minerals.

Oxalates, and in particular Ca-oxalates, can also form as part of this component, although in the case of MQ this seemed to be a rare occurrence. Mazel and Watchman (2003), in attempting to assign dates to paintings found in MQ, have determined ^{14}C dates for Ca-oxalate minerals that they assume to have formed as a function of this ***'secondary evaporite deposit'*** component. The results of the current study, however, indicate that the oxalates probably formed as a direct result of the paints presence, and not as a result of a natural accumulation over a prolonged period of time, indicating that the dates obtained are associated with the ***'secondary oxalate precipitation'*** component instead. The main difference between these two interpretations relates to the assumed accuracy of the dates relative to the painting event i.e., actually dating the painting (***'secondary oxalate precipitation'*** component) vs. giving approximate minimum or maximum date ranges (***'secondary evaporite deposit'*** component). Both studies do, however, agree that the mineralogical pathways involved in their creation are biological in origin, most likely via micro-organisms.

Secondary oxalate deposits:

The establishment of this as an individual component as a entity distinct from that of the ***'secondary evaporite deposit'*** component is based primarily on the fact that there is an unequal distribution of oxalate minerals, and in particular whewellite, existing between the paint and blank samples collected from MQ (53 % vs. 9 % presence, respectively). Unfortunately, a number of C pathways result in the formation of oxalate minerals, making it difficult to determine the true source of these minerals (see Appendix 3.2). In addition, these pathways need not be mutually exclusive and it is possible, in fact highly probable, that more than one of these pathways are in operation at any one time within a given shelter, the only controlling factors being the micro-environmental conditions experienced along the shelter wall. The one method that can be employed to help determine the specific pathway (and hence source) of a Ca-oxalate mineral within a specific sample is to use C isotope analysis.

Whilst this was not conducted within this study, Mazel and Watchman (2003) did run this analysis on some images collected from MQ. The results indicated that the Ca-oxalates that they analysed have a micro-biological origin. Unfortunately, the specific images that were sampled were not indicated, and it is thus impossible to associate these results with any of the samples used within this study. However, based on the results of the present study, and in particular the trend in whewellite distribution mentioned above, it is possible to assume that their results will also apply to the current dataset.

The dates obtained are not in question, but rather how they are interpreted. The Mazel and Watchman (2003) assumption is that the Ca-oxalates have formed on a continual basis, or at least on a periodic basis as indicated in the ***'secondary evaporite deposit'*** component discussed above. The lack of these minerals within the blank samples, together with the general lack of these minerals beneath the images (shown here and in the Mazel and Watchman (2003) study), tends to indicate the opposite, however, with the oxalates accumulating on the upper surfaces of the paintings.

The P content within the paints is significantly greater than that in the blank samples[1], as well as other pigment sources that were analysed separately. The elevated P contents may indicate that fungi, lichens and/or microbes were involved in the production of the Ca-oxalates, for these organisms have been shown to be natural accumulators of this element (Russ *et al*., 1999), further supporting the Mazel and Watchman (2003) findings. An interesting modern day account in which fungi were seen to form temporarily on the surface of newly created paintings made with paints containing organic additives also supports this hypothesis (F. Prins, pers. comm., 2006). This has yet to be verified, however.

Whilst the presence and interaction of the three aforementioned components have been known for some time, this is the first time that the ***'secondary oxalate precipitation'*** component is being suggested. If accepted, its presence will expand our current understanding of the manner in which paint pigments were manufactured, as well as having important implications on the interpretation of the results obtained from ^{14}C dating techniques i.e., the dates obtained could reflect dates comparable to the period of painting, for the Ca-oxalates could be expected to have formed soon after the painting event.

A limited source of pigments were determined to have been utilised within MQ, namely Fe nodules which were utilised for the dark red, red and two of the yellow pigments, gypsum for the white pigments, plinthite derived Fe nodules for the black pigment, and bauxite and/or bauxitic material in the manufacture of the orange and the remaining yellow pigments. Furthermore, it was found that Fe nodules and bauxitic material, originally derived from dolerite but now commonly residing within the Ecca Group found within KwaZulu-Natal, are unusual in that they typically display elevated Ti contents. From this it can be deduced that these specific pigments were collected locally and not imported.

The white pigments, in particular, are interesting for they appear to have been sourced, in part, from gypsum deposits collected from rock shelters. This deduction was based partly on the fact that no known local source of gypsum exists, but also on the fact that this mineral has the propensity to precipitate out along joint planes and lines of weakness within the local sandstone outcrops. This, therefore, represents the most probable source of the gypsum utilised within the white pigments. As no obvious gypsum exudates were noted within MQ, it was concluded that this material was sourced from another shelter.

Unlike the other paint pigments, whewellite within the white pigments was shown to increase with paint depth indicating that this mineral is also a primary component of the white pigment, and not just the result of chemical weathering. Two sources for the whewellite are proposed, the first

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[1] Interestingly, this seems to be a widely occurring phenomenon, with the images in Cougnac Cave showing P contents in excess of 1 % (Labeau, 1990).

being an organic additive, the second that the mineral was collected along with the gypsum. Carbon isotope analysis is required to further this line of inquiry. In either case, the composition of the white pigments within MQ display quite different characteristics to those suggested by both Wilson *et al.* (1990) and Peisach *et al.* (1991a), who stated that marine shell was utilised at the sites that they studied (see Chapter 3). This shows an obvious change in recipe with geographical distance.

The ubiquitous presence of gypsum throughout the paint dataset has important implications for the development of protection strategies, as this mineral is soluble in nature. Thus, in order to protect the chemical integrity of the area both beneath and above the paintings (components A and D in Figure 6.18), as well as the paintings whose composition incorporates gypsum, the application of water to the rock surface must be avoided.

Another factor that was highlighted during the course of this study is the degree to which the rock wall affords the individual pigments physical protection from mechanical weathering. This can be indirectly deduced by considering the relative quartz contents recorded for the different colours. In general, the blank, red and black samples displayed high quartz contents, the yellow samples displayed only a moderate content, and a minor presence was detected in the white pigments. The orange and dark red paints had no recorded quartz. Using the results of the blank samples as a standard i.e., a reference indicating the expected quartz content of a sample without pigment, an inverse relationship between quartz content and paint 'thickness' was determined. Thus, the paints with the higher quartz contents were determined to be 'thinner' than those without[1].

Several factors might have led to the varying thickness displayed throughout the paint dataset. The primary factor relates to the nature of the pigment used, whilst a secondary factor relates to the manner in which the pigments were applied to the surface. In the case of both black and red samples, haematite is the primary Fe-oxide mineral. This mineral has been shown to have a very high staining power, and as a consequence, very little pigment would be required in order to result in the creation of a red painting. The white paints, on the other hand, are by their nature not highly pigmentaceous i.e., a relatively large amount of the pigment is required in order to compensate for the lack of 'staining' power of its principal ingredient, gypsum. A third factor would relate to age, with the scarcity of paint being the end result of a combination of erosive forces removing a majority of the original paint.

Whilst the question as to whether the paint was originally applied as a thick or thin film is difficult to answer, inferences can be made based on the whewellite contents of the samples. It was found that whewellite appears to occur in greater concentrations at the surface of the paint samples (based on the results obtained from the double-sampling tests). As the presence of whewellite within the red and black samples was comparable to those of the remainder of the colours, it can be assumed

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[1] These trends reflect both personal and professional observation that has shown that a majority of red paintings present within rock shelters occur in the form of a 'stain'. The other paints, namely yellow, orange and white, are almost always 'thicker' than the red paintings present. The white paints, in particular, seem to be applied in thick layers (see Appendix 6.1).

that the sample collected represents the ‘original’ surface of the paint for, if a majority of an originally thick paint had been lost, then the whewellite would have been lost along with it. Thus, using the presence of whewellite as a reference, it seems probable that these paintings were created in a medium that was relatively fluid in nature. This, in turn, would facilitate the absorption of the paint into the upper surface of the sandstone wall.

At the opposite end of the spectrum, the white paints almost always seem to be applied as a thick paint, often retaining the relief of the original ‘brush’ strokes. The paints’ dominant component is gypsum, a mineral that is both highly crystalline in nature, as well as relatively susceptible to dissolution. Whilst the nature of the pigment and the manner in which it is applied resulted in the paint remaining prominent upon the rock surface, a combination of these two factors results in the maximum exposure of the paint to both mechanical and chemical erosion.

As a consequence of the aforementioned factors, the red and black paintings receive a degree of ‘protection’ from being absorbed into the rock wall, the result of a combination of the staining power of haematite, the nature of the pigment and the paint manufacturing technique. The other colours seem to be applied to the surface of the rock, rather than them being absorbed into it. The yellow and orange pigments do have some staining power. The orange pigments seem to be sourced from bauxite that is coarser than the red and the yellow pigments, and thus its absorption into the rock substrate is restricted to a greater extent. The white paints seem to be applied to the rock surface in the form of a ‘paste’.

Based on these conclusions, the paints can be ranked according to both their susceptibility to weathering, as well as by the degree of protection afforded the pigment by absorption of the paint into the sandstone shelter wall (listed from least to greatest): Red, yellow, and orange and white. This finding perfectly matches the sequence of paint colour ‘appearances’ as listed by a number of prominent archaeologists (e.g. Pager, 1971; Vinnicombe, 1976; Russell, 2000) (Appendix 6.1), as well as with the scientific deductions proposed by Van Rijssen (1987). Whilst this raises interesting questions, such as “Does this mean that the paintings were meant to last, or is it an ‘accident’ that the red pigments utilised would, as a by-product, last an extended period of time?,” this has practical implications regarding development of strategies for the protection of images of various colours. Physical weathering appears to be the primary threat to the paintings, with the more exposed colours being the most susceptible.

One of the most important findings in this study concerns the development of a good sampling regime that will allow for the collection of the maximum amount of reliable data, as well as having a minimal impact on the paintings. In addition, the collection of blank samples is vital for the characterisation of the secondary deposited materials associated with the ***‘secondary evaporite deposit’*** component discussed previously. This is driven by the fact that both the evaporite-type and underlying rock minerals have been shown to have a dramatic effect on the recorded mineralogical and elemental composition of the paint samples, especially when they are collected from different areas of the same image.

As indicated above, the influence of gypsum and the other evaporite-type minerals seems to decrease within increasing depth in the paint layer. Thus, in order to remove any possible external influences that might reflect upon the paint sample data, a two-step sampling regime is proposed in which double sampling at each sampling point is conducted. This would allow for the comparison of both the surface depositional features (if present) and the ‘true’ pigments. This strategy will have to be adopted to forestall the possibility that excess surface depositional features are present – it must be remembered that these are not necessarily apparent to the naked eye, and as a result of the sample size limitations, only a tiny amount need be present to have an adverse effect on the results.

Care must also be taken not to sample any underlying paint or rock substrate that might unduly affect the analyses. This is easier said than done, for it is impossible to pre-determine the effective sampling depth using the method described, but one way of mitigating this influence would be to sample thicker paints. As this would effectively mean that better preserved paintings will have to be sampled, careful thought must be taken as to which images must be sampled, and where on the image the sample will be collected.

In addition, it must be emphasised that these results have been obtained from paint samples that have already been exposed to a wide variety of chemical and mechanical interactions, and that any material that might have originally been present and subsequently removed via weathering will probably never be identified. As a consequence, it must be accepted that, even with today’s advances in science, we might never know the original paint pigment compositions utilised by the San artists.

Finally, the findings listed within this section refer exclusively to the paint samples collected from MQ, and might not necessarily apply to paints located in other shelters. The study of paints from additional shelters within the vicinity is needed in order to determine to what extent these findings apply to paints and shelters in general. In order to try and address this issue, paint and blank samples from three distant shelters were analysed, with the results being discussed in Section 6.2.6.

6.2.5 Double sampling tests (Maqonqo Shelter only)

The purpose of this section is to illustrate the effect of sampling depth on our ability to adequately quantify the nature of the paints and their individual components. As a consequence, this section will not deal specifically with the colours in question, but rather the nature of the sampling regime and the ways in which it could possibly influence the current results, as well as future research.

In order to allow for the accurate comparison of the pigments, one must understand the depositional and chemical dynamics that influence the eventual composition of the paint samples as recorded within the various experiments. An attempt to ‘filter’ out the secondary products could then be conducted, thus leaving only the paint pigment against which the field and/or excavated samples can be compared.

Factors to consider when comparing different paint pigments with one another include:

1) The thicker the original paint the greater the chance of extracting a more representative sample of less altered/modified pigment from a deeper layer. The thicker pigments tend to be associated with the younger paintings, and are usually represented by the white, orange, and sometimes black pigments. The red colours on the other hand, which are usually only present in the form of stains on the rock surface[1], are generally considered to represent the oldest paintings.
2) Related to the above point, the nature of the pigments within the painting experience differing degrees of weathering. This, in turn, affects the longevity of the image e.g. gypsum is more susceptible to weathering than haematite. The resistance of the pigment to mechanical erosion would also influence the amount of pigment that is recovered during the sampling process, this being further influenced by both the duration and degree of weathering the pigment has been subjected to.
3) The rock wall will weather, both in degree and nature, from point to point within a shelter. The degree of influence that this ‘contamination’ will impart upon the paint pigment analyses will, as a consequence, reflect this variance.
4) Microclimatic conditions within a shelter will favour the formation of a suite of evaporite minerals that are location specific.
5) The paint recipes could vary from painting to painting, resulting in either a lack of or presence of oxalate minerals within the ***‘secondary oxalate deposit’*** component as described in Section 6.2.4.6.
6) The amount of secondary deposition recorded on the surface of each image can vary from shelter to shelter, and is related to the age of the painting, the position of the painting within the shelter, the amount of exposure to both mechanical and chemical weathering, and the degree of tertiary deposition (external deposition such as dust, excreta etc.).

To illustrate how a sampling regime should be modified in order to mitigate the aforementioned factors, a comparison between an ‘ideal’ or ‘best-case’ painting and a ‘real’ painting surface sampling will be discussed (Figure 6.20). It must be noted that the layers described on Figure 6.20 are not present within all paintings, nor do the individual layers share a uniform thickness from painting to painting. Whilst the ‘ideal’ painting is hypothetical and represents the best-case scenario for paint sampling, in reality, the thicker the paint layer the closer one gets to this condition. The ‘real’ painting

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[1] Although red paintings are also considered to be amongst the youngest imagery, none of the generally accepted ‘old’ parietal images are considered to contain any of the other colours utilised by the San (Appendix 6.1).

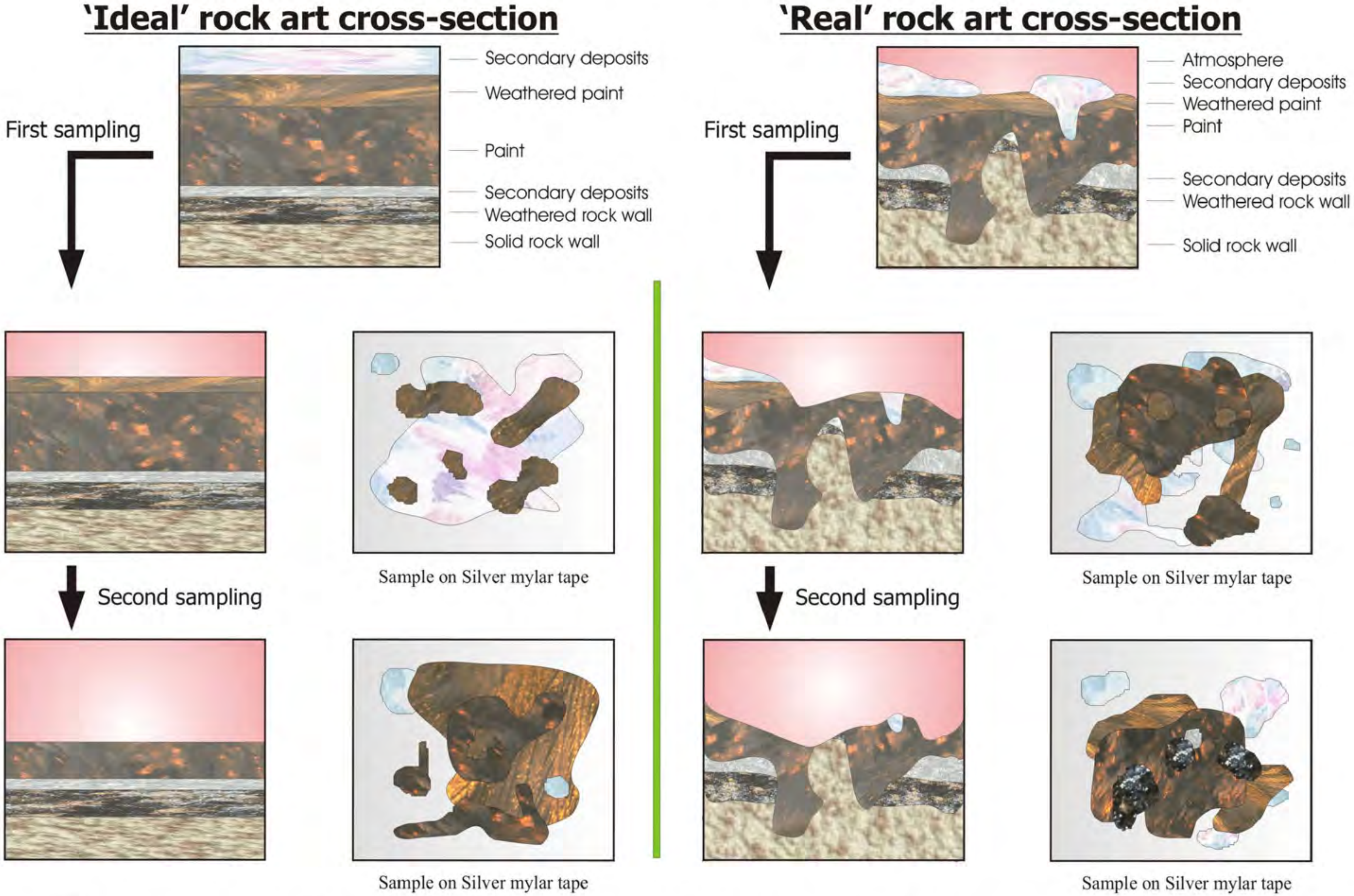


Figure 6.20: A comparison of 'idealised' and 'real' paint samples in cross-section, and the possible influences of the sampling regime on the samples obtained.

represents a much more life-like situation, with a more prominent rock substrate (at the microscopic level), as well as varying degrees of thickness (and presence) of the individual layers described. This is typical of a ‘thin’ painting, and can be expected to yield a smaller paint sample than the ‘ideal’ painting (less material to sample).

The two ‘paintings’ represent the opposite extremes of the spectrum, with the ‘ideal’ painting closely corresponding to the conditions displayed by the white and orange paintings, whilst the ‘real’ painting is more closely related to the red paintings. For comparative purposes, the reader is referred to Appendix 5.1. Note the amount of pigment recovered during the sampling procedure for the various colours. In both scenarios, a second sample allows for increased sampling of the ‘true’ paint pigment, with the influence of the secondary minerals being reduced.

In order to test these concepts, eight samples were collected from MQ (four duplicates). Although all of the data from these eight samples have been displayed (Figure 6.21), it is important to note that there are in fact only five ‘pairs’ of paint. For ease of discussion, I will comment on the trends highlighted by these pairs only, referring to the remaining colours only if they have some bearing on the results. The samples are labelled according to the painting sampled (represented by the number), as well as the order of the sampling: “top” denotes the first paint sample and “under” denotes the repeat sample. Paints 29 (top) and 11A (under) are the exception, for whilst these paints represent a double sampling pair, they were sampled over two sessions, and were thus assigned separate sample numbers.

Iron once again dominates the variability experienced within the EDX dataset, with its influence being countermanded by a combination of S and O contents lying at the opposite extent of the linear gradient (PCA1 = 54.1 % variance). PCA2 (22.8 % of the variance) is more difficult to interpret, but is primarily influenced by Ca, and to a lesser extent C. PCA1 illustrates the change in paint composition from a secondarily deposited material dominated to pigment dominated sample, whilst PCA2 indicates a change in the nature of the secondary depositional material i.e., either Ca-oxalate or gypsum (***secondary oxalate deposits*** vs. ***secondary evaporite deposits***: Section 6.2.4.6).

Figure 6.22 displays the average µ-XRF data collected for the Paints 29 (top), 11A (under), 9A (top) and 9B (under). Unlike the EDX data, however, this figure indicates that a linear gradient existing between Sr and Fe dominates the variability within the dataset, with the samples’ Ca content representing the second most dominant influencing element. The difference in trends recorded for the two techniques is due to the fact that S is not recorded within the µ-XRF data. Instead, Figure 6.22 indicates that the Sr content within all of the colours sampled decreases with increasing paint depth, with Fe displaying the inverse trend.

In Section 6.2.3.1 it was shown that the Sr content within samples is closely related to the deposition of gypsum. The µ-XRF results obtained within the double sampling analysis further supports this finding, for a comparison of the standardised Sr values (Appendix DIGITAL 3) of the blank and double sampling samples shows that similarities exist between the white pigments/ deposits

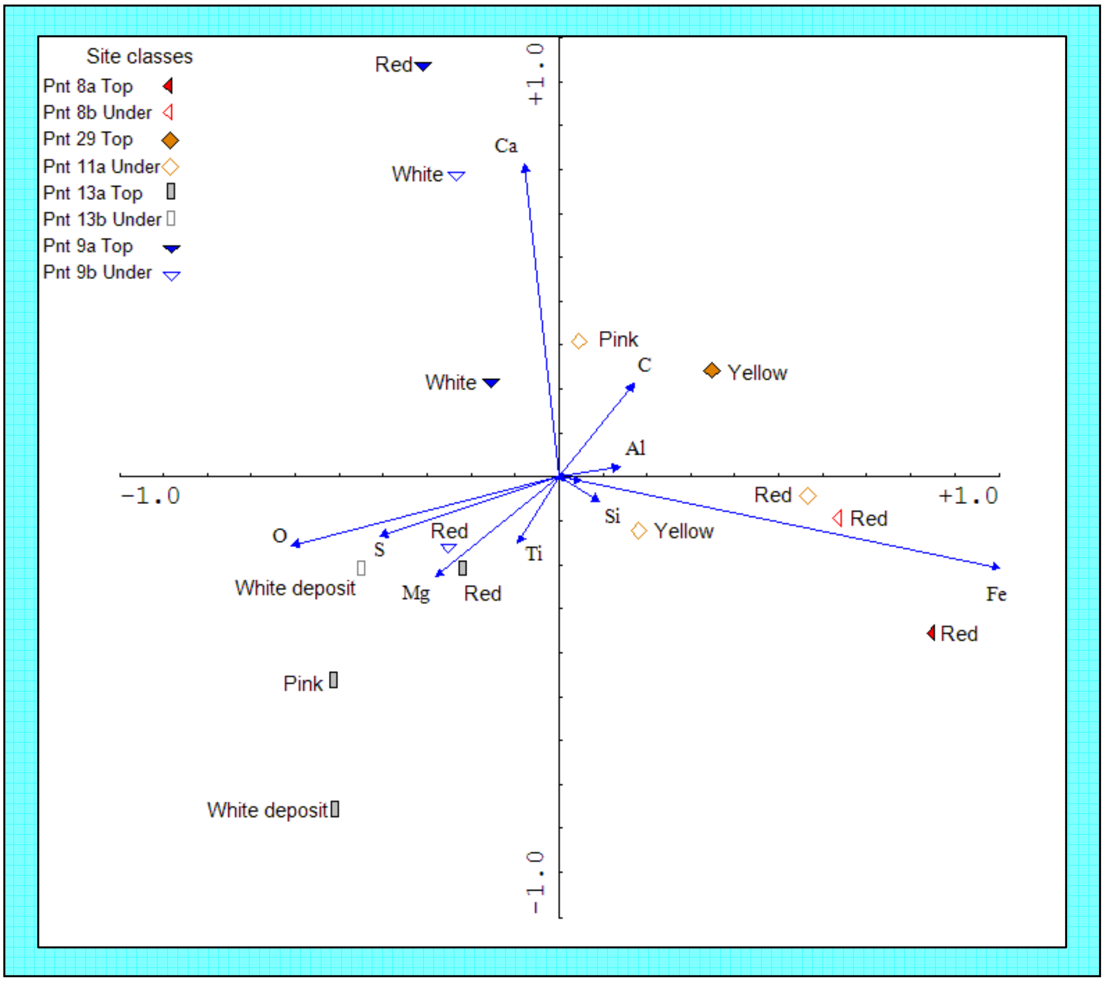
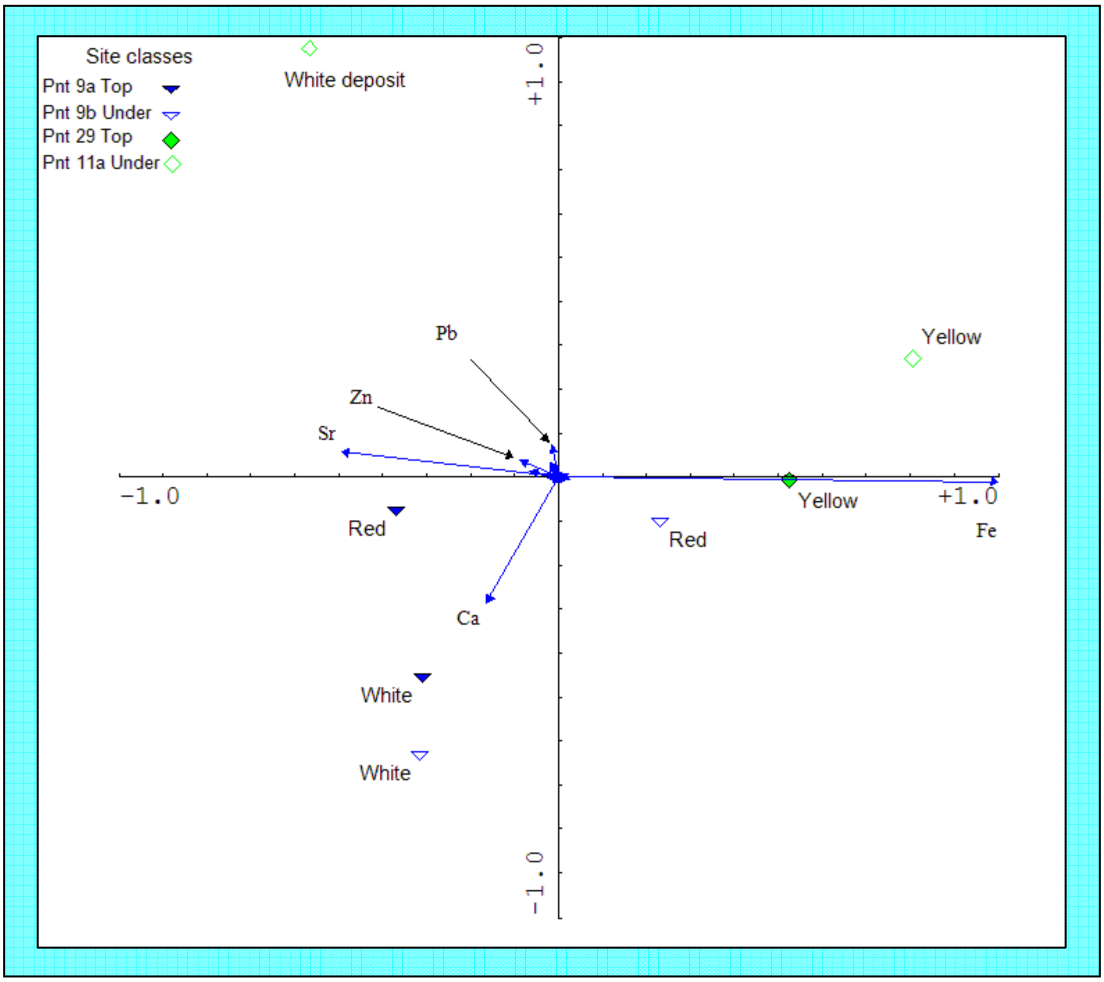


Figure 6.21: Average reduced window EDX data from 'duplicate' samples illustrating the effect of paint depth on the paint composition.

Eigenvalues: PCA1 – 54.1; PCA2 – 22.8; PCA3 – 11.3

Scaling -2



<u>Figure 6.22: Average standardised micro-XRF data from 'duplicate' samples illustrating the effect of paint depth on the paint composition.</u>
Eigenvalues: PCA1 – 87.3; PCA2 – 6.4; PCA3 – 3.7
Scaling -2

and the blank samples, with both being dominated by gypsum. The Sr contents within the yellow and red pigments are, however, significantly lower.

Finally, Table 6.8 lists both the individual and mode values for the µ-XRD data obtained for the double sampling samples. Unfortunately, mineralogical data could only be determined for four of the original eight samples analysed, with the data for only one ‘pair’ being resolved (9A and B; top and under, respectively).

The white samples (Paint 9A and B; top and under) show a dramatic increase in Ca with increasing paint depth in both Figures 6.21 and 6.22, with an associated minor decrease in Fe content. Figure 6.21 also indicates a shift from a Ca:C to Ca:S dominated mineralogical regime, as well as a decrease in Sr content, indicating a change from secondary deposited material to natural pigment with decreasing paint depth, a result confirmed by the µ-XRD data (Table 6.8). The dramatic shift in mineralogical content within the white pigment is thus reminiscent of the ‘ideal’ sample illustrated in Figure 6.20, and is probably the result of the paint thickness (and possibly youth).

At first glance, the EDX results obtained for the red paint samples appear to be contradictory for, whilst one of the red pigments (Paint 9) displays a decrease in Fe content and corresponding increase in Ca minerals with decreasing paint depth, the second red paint sample (Paint 8) exhibits the reverse trend. As Paint 9 was collected from a white image, this red pigment most likely represents a ‘contaminating’ element deposited on the surface of the image. Similarly, the yellow pair (Paint 29 ‘top’ and 11A ‘under’) show an increase in Fe, with an associated decrease in Ca, with increasing paint depth, highlighting the gradual change from a secondary mineral dominated to a ‘purer’ sample with increasing paint depth.

In all instances it was noted that the deposition of secondary minerals on the paints sampled has a dramatic influence on the results obtained. It is thus suggested that paint pigments should always be double sampled in an effort to reduce this effect. This approach would have several advantages. Firstly this would highlight both the nature of the surface contaminants associated with the pigment (both secondary oxalate and depositional components), and secondly will provide a relatively ‘pure’ sample that can be interrogated for provenancing and/or conservation purposes.

An example of how this approach was used within this study was when Paint 20, collected from a suspected paint fragment sample, was compared against a sample pair collected from the suspected point of detachment (Paints 13A and 13B; top and under, respectively). Due to their different localities, it could be expected that these two sample sets experienced vastly different microclimatic conditions (the pair exposed, the fragment buried).

As could be expected, the fragment did not show the presence of gypsum, nor any of the other evaporite minerals found within the wall samples. To allow for an accurate comparison between the orange pigments from all three samples, the depositional features encountered within the wall samples had to be accounted for. This would be more easily achieved with the comparison of the ‘under’ sample (the ‘top’ sample contained a greater proportion of the deposited material).

Table 6.8: A comparison of the individual and mode values obtained from the micro-XRD analyses conducted on the double sampling tests from Maqonqo Shelter.

Sample	Haematite	Goethite	Whewellite	Gypsum	Gibbsite	Anhydrite	Bassanite	Glushinskite	Quartz	Mica	Apatite
Paint 8A Red	2	3	0	2	0	0	4	0	0	0	0
	2	3	4	1	0	0	0	0	0	0	0
	1	2	0	3	0	0	0	0	0	0	0
	2	0	3	2	0	0	0	0	2	0	0
Mode Paint 8A Red	2	3	0	2	0	0	0	0	0	0	0
Paint 9A White	3	0	0	1	0	0	2	3	0	0	0
	0	0	3	1	0	3	0	0	0	0	0
	0	0	3	1	0	3	0	0	0	0	0
	3	0	0	2	0	0	3	2	0	2	0
	0	0	2	1	0	3	0	0	0	0	0
	0	0	0	1	0	3	2	0	0	0	0
	0	0	2	1	0	0	0	0	0	0	0
	0	0	0	2	0	0	0	1	0	0	0
Mode Paint 9A White	0	0	0	1	0	0	0	0	0	0	0
Paint 9B White	0	0	1	2	0	0	0	0	2	0	0
	0	0	2	2	0	0	0	0	0	0	0
	0	0	0	1	0	0	0	0	0	0	0
	2	0	0	2	0	0	0	0	0	0	0
Mode Paint 9B White	0	0	0	2	0	0	0	0	0	0	0
Paint 29 Yellow	0	3	0	1	0	0	0	2	0	4	0
	0	3	1	0	4	0	0	0	3	0	0
	3	2	2	1	2	0	0	0	0	0	0
	3	2	2	2	2	0	0	0	0	0	0
	0	3	4	1	0	0	0	0	0	0	0
	2	3	2	0	0	0	0	0	4	0	2
	0	4	1	2	3	0	0	0	4	0	0
	0	2	2	1	2	0	0	0	0	0	0
	0	3	3	1	0	0	0	0	4	0	0
	0	3	4	1	0	0	0	0	0	3	0
	0	3	2	1	0	0	0	2	3	3	0
	0	3	2	0	2	0	0	0	3	0	0
Mode Paint 29 Yellow	0	3	2	1	0	0	0	0	0	0	0

These subjective values are determined according to the method outlined in Appendix 5.9.

Figure 6.23 shows Paint 20 in relation to the double sampled pairs. Unfortunately, the fragment sample still separates out very distinctly from all of the paint samples, not just the Paint 13 pair to which it was suspected to be related. This distinction is driven primarily by the Ca to Si gradient that exists between the wall derived samples and the fragment (58.7 % variance). Four possible conclusions can be drawn from this result. Firstly, the fragment did not originate from the position from which the Paint 13 pairing was collected; secondly, the fragment was not painted, but only exhibited a slight enrichment of Fe; thirdly, the original pigment has been lost due to weathering; and fourthly, the Ca minerals within the wall sampled pigments still exert too dominant an influence on the results (see Appendix 5.15).

6.2.6 A comparison of the paint samples from all four of the sample sites

The primary reason behind the collection of the paint and blank samples from the three additional sites was to offer comparative material against which the MQ samples, and the techniques used in their analysis, could be compared. This was done in order to determine if the suite of techniques employed within this study were sensitive enough to detect differences between sample groups that are likely to be distinct from one another. As a consequence, the data obtained from these three

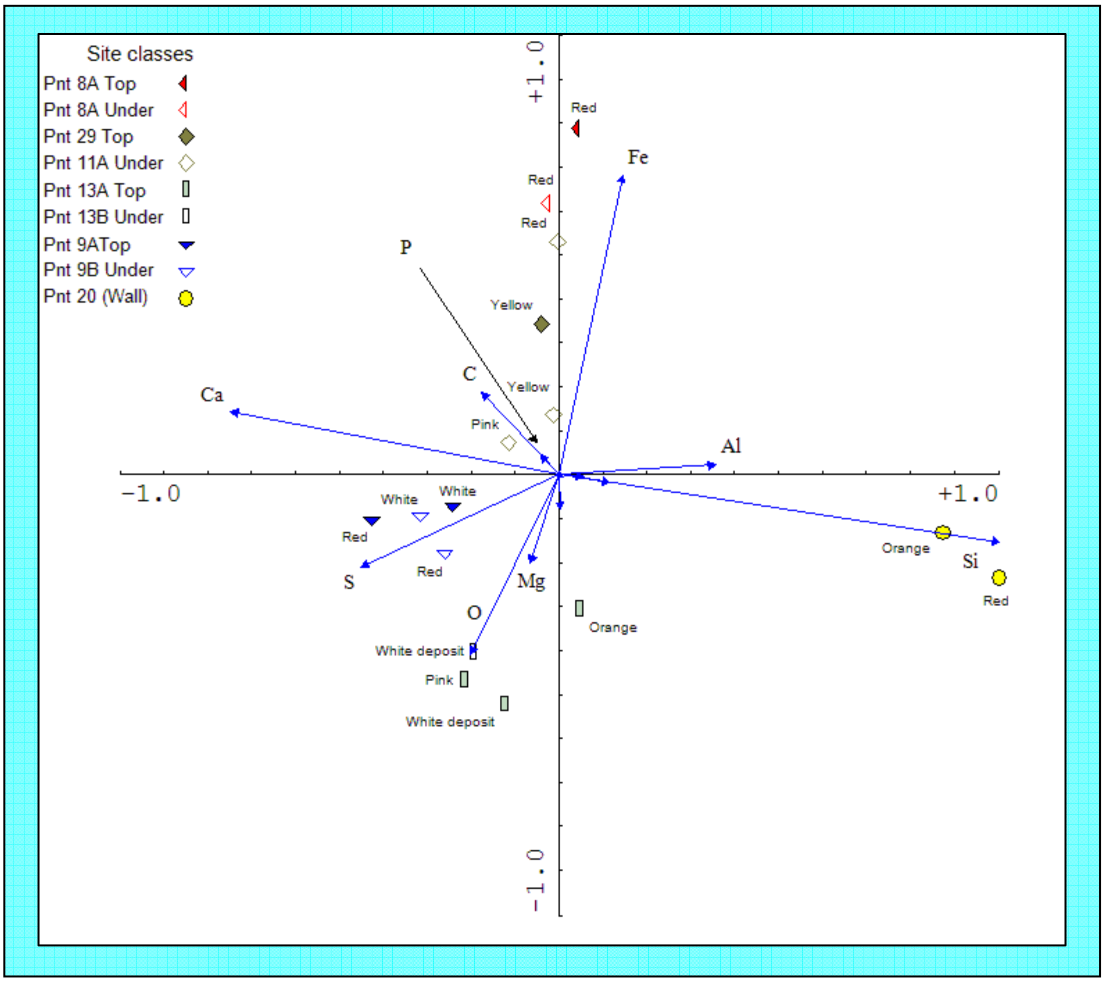


Figure 6.23: Average reduced window EDX data highlighting the differences between the paint fragment (Paint 20) and the duplicate samples.

Eigenvalues: PCA1 – 58.7; PCA2 – 23.5; PCA3 – 9.0

Scaling –2

additional shelters should not be considered to be representative samples from the respective shelters in question. The analysis of additional images of the same and additional paint colours should be conducted within the same, and surrounding, shelters before any claims of this nature can be made.

These samples do, however, allow for the determination of the effect that a variety of geologies and climatic conditions impart upon the rock art at different localities and, although it was not the primary aim, also offer some insight into the nature of the red and white pigments specific to the selected shelters. From these data, potential differences in weathering experienced by each shelter can be determined, with these being brought about by a combination of factors including different pigment sources, different environmental conditions, and, potentially, different paint pigment manufacturing techniques.

As only a few samples could be collected from the three additional sites, it was decided that three samples of both red and white images should be collected, in addition to the three blank samples that have already been discussed in Section 6.2.3 (for the reasoning as to why these specific colours were selected, the reader is referred to Section 4.2.2).

Figure 6.24 shows the comparison of the red and white EDX data collected from all four shelters. A very clear distinction between the paint sample datasets is shown to exist between the four shelters in question, with the distribution of the paint samples mirroring those displayed by the blank samples for each of the respective shelters (Section 6.2.3). In general, what distinguishes the sites from each other is the relative dominance of one key component of the overall paint samples' composition. In the case of the MQ samples, the ***paint pigment component*** tends to dominate the samples (Fe-oxide minerals for the reds and gypsum for the whites). The ***shelter wall component*** dominates TW's results (probably more accurately interpreted as a lack of secondary deposited minerals), whilst both the SV and FC samples are dominated by secondary deposits, oxalates in the case of FC (indicated by the higher C contents) and a combination of oxalate and evaporite minerals in the case of SV.

The ability to differentiate between different regions and paint colours is not unique to this study, however. When analysed using PCA, Van Rijssen's (1990; Section 3.5.3) data produce a similar trend (the data were standardised to 100%). A 5 % exclusion rate was applied to the data to account for two outliers noted in the original analysis[1]. Figure 6.25 shows the comparison of all the paint data (as were listed in Van Rijssen's (1990) paper). Immediately apparent is that the same trend determined within this study, with regard to pigment colour separation along Ca, Si and Fe lines, is also repeated with the Van Rijssen dataset.

In addition, it can also be seen that, in general, the Lesotho samples tend to be Ca dominated, whilst the eastern Cape samples show elevated Si contents. Showing similar trends are the FC and TW samples, respectively. This is not surprising as these sites are within the same general

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[1] These outliers, both black, contained very high Mn contents, an element that, with the exception of one other sample, was not recorded within the rest of the dataset. By removing these 'extreme' samples, the distributional trends existing within and between the remaining paint samples can more easily be determined.

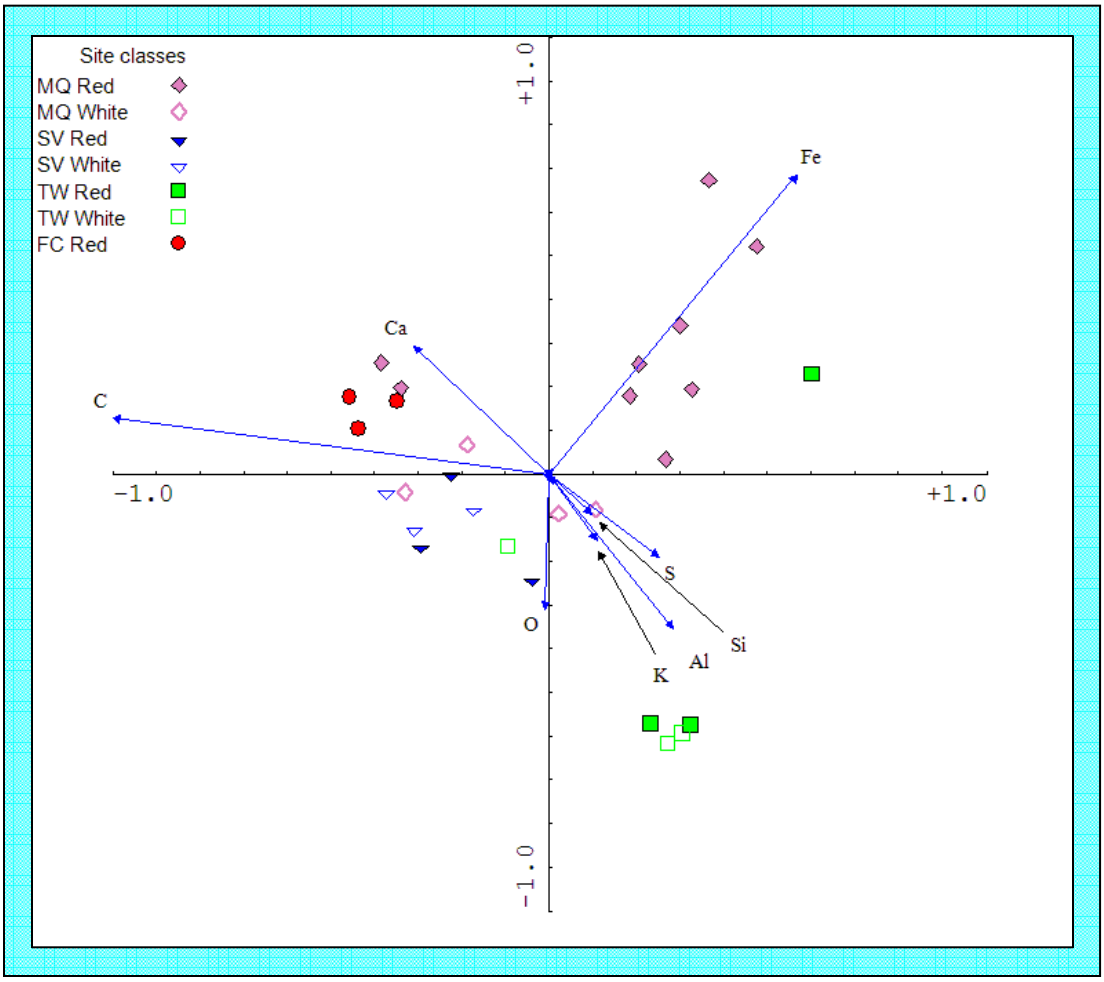

Figure 6.24: Average reduced window EDX data comparing the red and white samples from all four shelters.

Eigenvalues: PCA1 – 46.6; PCA2 – 25.3; PCA3 – 18.2

Scaling –2

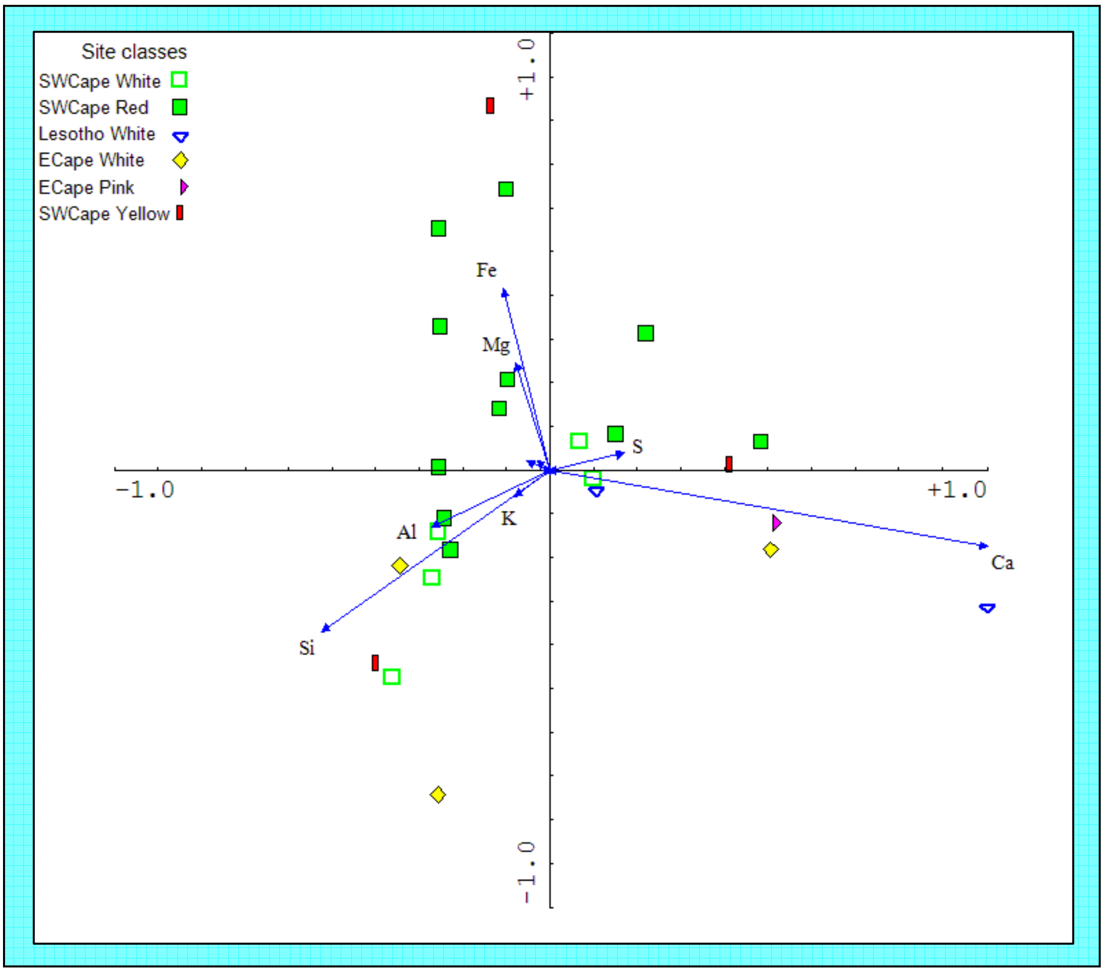

Figure 6.25: Van Rijssen's (1990) EDX derived site and paint colour distribution - subject to a 5% exclusion rate.

Eigenvalues: PCA1 – 52.7; PCA2 – 15.8; PCA3 – 11.9
Scaling = -2

geographical landscape, and probably originate from similar geologies. Unfortunately, as no information regarding the specific positions of the shelters sampled could be sourced, no further trends can be deduced that will add further to this study.

In a general sense, the distribution seen in Figure 6.24 (and Figure 6.25) validates both the methodology and the techniques utilised within this study. For a greater understanding as to the nature of the pigments in question, however, a closer examination of the individual pigments is required. Figure 6.26 displays the compositional trends displayed within all of the white samples analysed by the three primary techniques used in this study.

All three of the datasets show a clear distinction between the three[1] sites sampled, with the µ-XRD dataset most strongly highlighting the distributional dissimilarities. In general, the primary difference between the SV and MQ white samples is one related to the presence of secondary minerals i.e., whilst the white samples from both shelters are dominated by whewellite and gypsum (indicating that these minerals were probably present within the pigments when they were applied), the presence of quartz, sanidine and apatite in the SV samples indicates a degree of shelter wall ‘contamination’, with anhydrite, bassanite and glushinskite indicating climatic variations favouring various evaporite depositional regimes.

The white TW paint samples, like the associated blank samples, display a minimal presence of the secondary deposited minerals common in the other shelters studied. The one dominant mineral found, however, is minamiite. The absence of this mineral in the blank samples would indicate that this mineral originates from the original pigment source. Unfortunately, very little information describing this mineral is available, with none being available concerning its distribution, or possible source(s), within the South African landscape. It is known, however, that this is a rock forming mineral where acid, often ore-bearing, solutions have altered orthoclase feldspar-rich rocks[2]. Presumably then, this mineral can form as a precipitate.

Another interesting anomaly associated with these pigments is that the Zn contents recorded are generally between 10 to 40 times greater than those recorded for any of the other paint samples within the entire paint dataset. The source of this Zn has yet to be determined, but greigite, another mineral common to the white paints, is known to accumulate Zn as an impurity within its crystal structure[3].

The red paints, although not displaying as clear a separation between the shelters as was seen in the white sample dataset, also show a separation of the shelters based on the same elemental and mineralogical separations discussed above. A comparison between MQ, SV and FC again highlights the degree to which the secondary deposited minerals contribute to the separation of the sites from one another (Figure 6.27). As is the case with the white samples, SV is distinguished from MQ due to the presence of wall ‘contaminants’ i.e., quartz. Fergies Cave separates out as a result of the micro-

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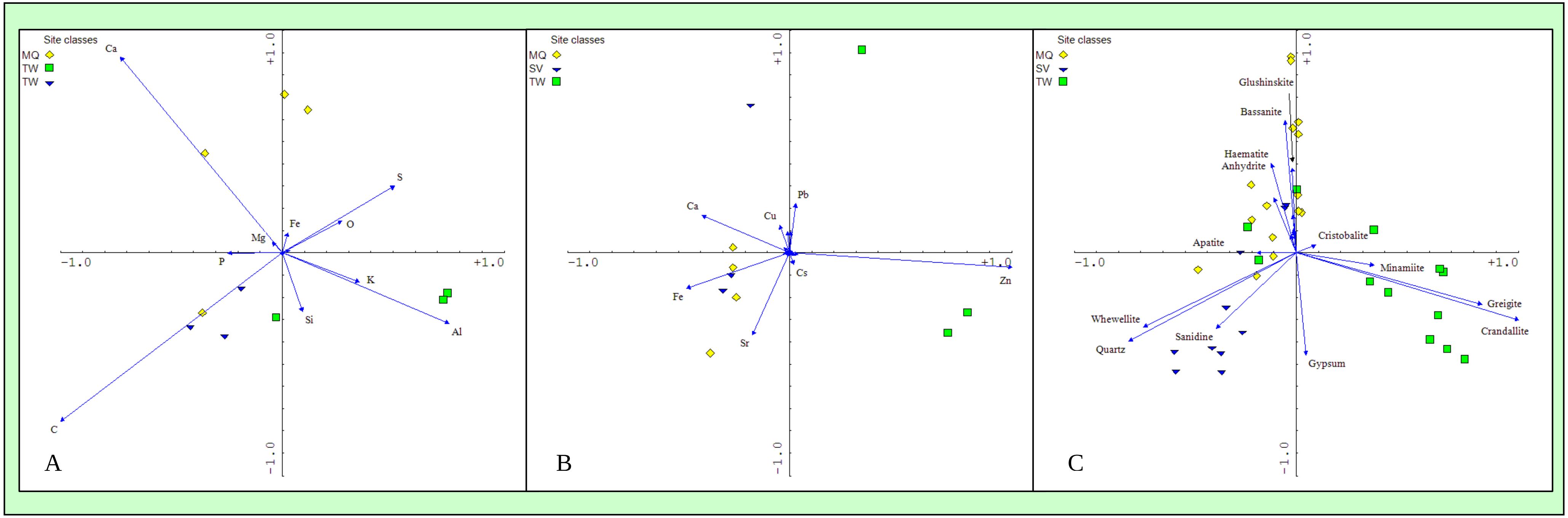
[1] No white samples were collected from Fergies Cave.

[2] http://www.webmineral.com/data/Alunite.shtml.

[3] http://www.mindat.org/show.php?id=1747.

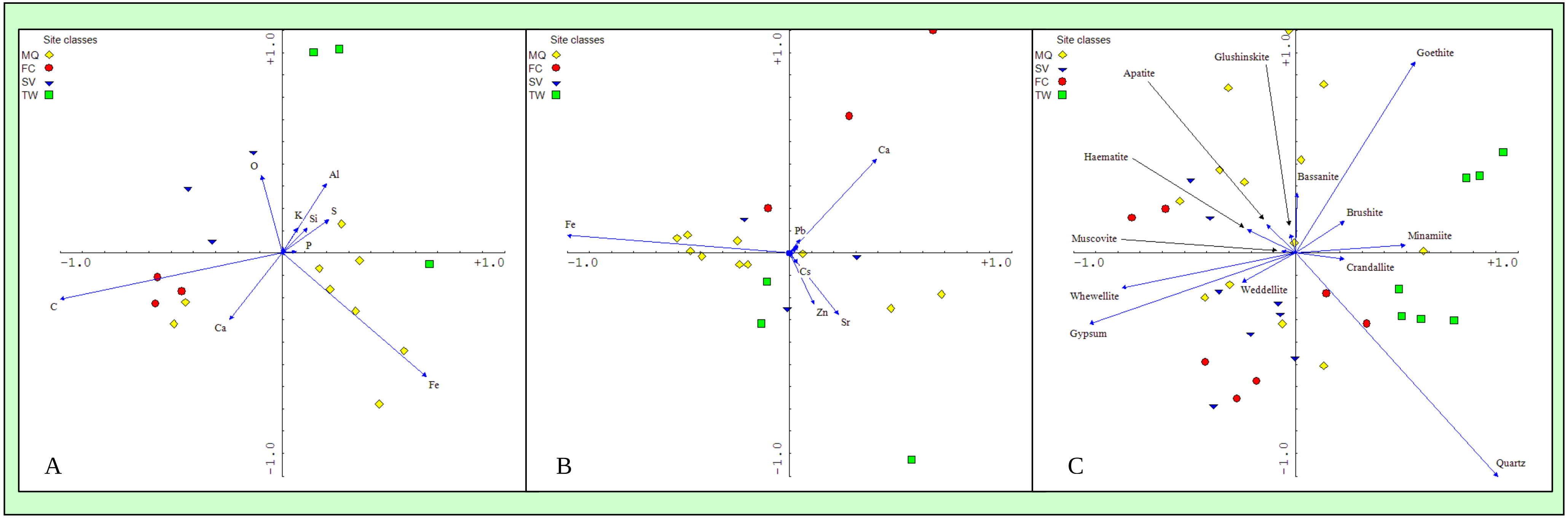


Eigenvalues: PCA1 – 52.2; PCA2 – 33.0; PCA3 – 9.1
Scaling –2

Eigenvalues: PCA1 – 78.5; PCA2 – 15.8; PCA3 – 3.0
Scaling –2

Eigenvalues: PCA1 – 33.9; PCA2 – 16.9; PCA3 – 11.9
Scaling -2

Figure 6.26: The results obtained from the A) average reduced window (EDX), B) average standardised micro-XRF and C) micro-XRD for all of the white samples collected from the three shelters sampled.



Eigenvalues: PCA1 – 55.0; PCA2 – 24.4; PCA3 – 14.0
Scaling –2

Eigenvalues: PCA1 – 71.9; PCA2 – 18.9; PCA3 – 5.7
Scaling –2

Eigenvalues: PCA1 – 32.0; PCA2 – 21.1; PCA3 – 11.3
Scaling -2

Figure 6.27: The results obtained from the A) average reduced window (EDX), B) average standardised micro-XRF and C) micro-XRD for all of the red samples collected from the four shelters sampled.

climatic conditions present within the Shelter which favour the formation of both whewellite and weddellite, the latter not typically found at the other three study sites.

The TW samples again indicate a change in pigment source and/or manner of paint manufacturing technique, for these red samples contain minamiite. As this mineral was not found within any of the blank samples collected at the site, it can only be deduced that this mineral represents part of the original paint pigment. As has already been discussed, however, this mineral is not red, but rather white. This mineral must therefore be present within the paint as an additive, the possible purpose being a bulking agent.

All four of the shelters show haematite as being the primary pigment within the red paints. With the exception of only one sample from TW, no goethite was found present within any of the red samples collected from the three additional sites. This could indicate one of two possibilities: 1) the pigment was sourced from a ‘pure’ haematite source, or 2) the pigments are the result of calcined goethite. As no maghemite was identified in any of the traces studied, this second possibility seems unlikely. Without an analysis of field samples collected from nearby vicinities of each of the respective shelters, however, potential sources for this pigment cannot, as yet, be postulated.

6.3 POTENTIAL SOURCING ANALYSIS FOR MAQONQO SHELTER

6.3.1 Introduction

Whilst Section 6.2.4 characterised the paint pigments sampled from MQ, this section attempts to characterise potential pigments that might have been utilised in their manufacture. In order to accomplish this, three separate but equally important datasets were created and analysed. The first includes the analysis of pigmentaceous material recovered from the MQ deposit. As this material was actively sought, and brought to the Shelter by the people who utilised the Shelter (either its inhabitants and/or regular users), this resource represents the most likely and easily accessible source of material against which the paint pigments can be compared. An additional advantage of using this resource relates to the fact that these materials have an associated ^{14}C date. Should it be determined that the pigments unique to one layer of the deposit closely resemble the pigment signatures determined for the paint samples, a possible indirect dating technique might be established.

In total, 5 931 unmodified pigmentaceous materials of variable size and geological origin were recovered from the MQ deposit (Mazel, 1996a). Due to a combination of factors, including sample size limitations, issues related to cultural heritage preservation and economic constraints, the original archaeometric study analysing these pigmentaceous materials was limited to 62 samples of > 2.5 g mass (Escott, 2000). The selection of these samples was further restricted to the first three depositional layers for two reasons, namely a) a majority of the deposit material recovered originated from these layers (1 918 pieces); and b) according to Mazel (1996a), the paintings within MQ were most likely created within the last 4 000 years, a time period against which the ^{14}C dates for these three layers correspond.

With access to µ-XRD and µ-XRF, the main limiting factor, namely sample size, was no longer an issue. As a result, the analysis of smaller samples previously avoided, but which were generally more ochreous in nature relative to the larger samples could now be conducted (i.e., samples <= 0.5 g in mass). Their selection was not restricted to the first three layers of the deposit, however, for the findings of the previous study (Escott, 2000) indicated that the large samples analysed did not represent the material from which the paint samples analysed were sourced. Samples from as many layers as possible were collected and analysed, with the only limitation on the number of samples analysed being the availability of synchrotron beam-time. In total, 51 samples were analysed from layers 1,2,3,5,6,7,9 and 11.

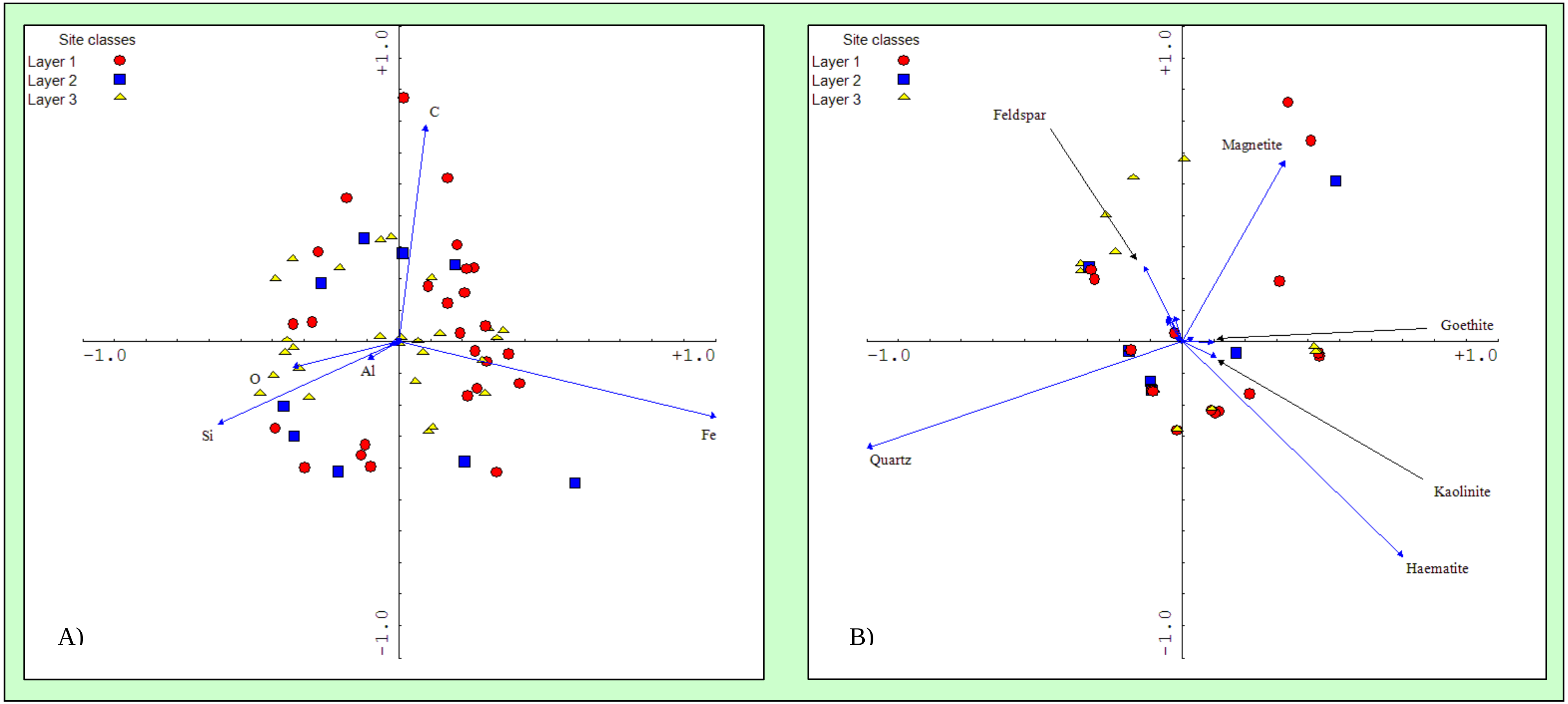
Although the data collected for the large excavated material has already been interrogated in a previous study (Escott, 2000), for the sake of completeness the analysis and findings have been reproduced in Section 6.3.2. Section 6.3.3 highlights the results obtained for the small excavated material collected and analysed during the course of the current investigation.

The second dataset consists of the collection and analysis of potential pigment sources from the immediate vicinity of MQ. Initially collected during the course of a previous study (Escott, 2000), these data have been reproduced in Section 6.3.4 to allow comparison with the paint, and large and small excavated samples. The collection of the samples within this dataset was based primarily on the pulverulence and colour richness of the samples in question, but was also guided by their relative accessibility within the landscape surrounding MQ. In total, 10 samples were collected and analysed.

Finally, samples were collected from six recognised pigment outcrops located within 50 km of MQ so as to allow for a greater sample set against which to compare both the paint and excavated pigmentaceous samples analysed. Five of these sites were Fe-ore outcrops whilst the sixth, Mpate, was bauxitic.

6.3.2 Large excavated pigmentaceous materials from Maqonqo Shelter

This section is adapted from previous work conducted by the author (Escott, 2000) and is included for completeness. As can be seen in Figure 6.28, a great deal of similarity exists between large pigmentaceous materials selected from the three layers. On closer inspection of the mineralogical data, however, a subtle change in geological composition with increasing depositional age is revealed. To illustrate this, the six mineralogical groupings identified within the dataset, together with their relative percentages within each layer, are listed in Table 6.9.



Eigenvalues: PCA1 – 67.4; PCA2 – 28.0; PCA3 – 3.9
Scaling –2

Eigenvalues: PCA1 – 41.8; PCA2 – 25.0; PCA3 – 11.1
Scaling –2

Figure 6.28: The results obtained from the A) average reduced window (EDX) and B) average standardised XRD datasets obtained from the large excavated pigmentaceous material collected from the first three deposit layers from Maqonqo Shelter.

Table 6.9: Mineralogical groupings and their relative percentages of the large pigments from the first three excavated layers.

Mineralogical grouping	Layer 1		Layer 2		Layer 3	
	No. Samples	Percentage	No. Samples	Percentage	No. Samples	Percentage
Quartz	2	7.7	2	22	4	14.8
Haematite	3	11.6	1	11	4	14.8
Quartz and Haematite	15	57.7	4	45	11	40.7
Magnetite	3	11.5	1	11	1	3.7
Quartz and Feldspar	2	7.7	1	11	7	26
Quartz and Goethite	1	3.8	0	0	0	0
Total	**26**	**100**	**9**	**100**	**27**	**100**

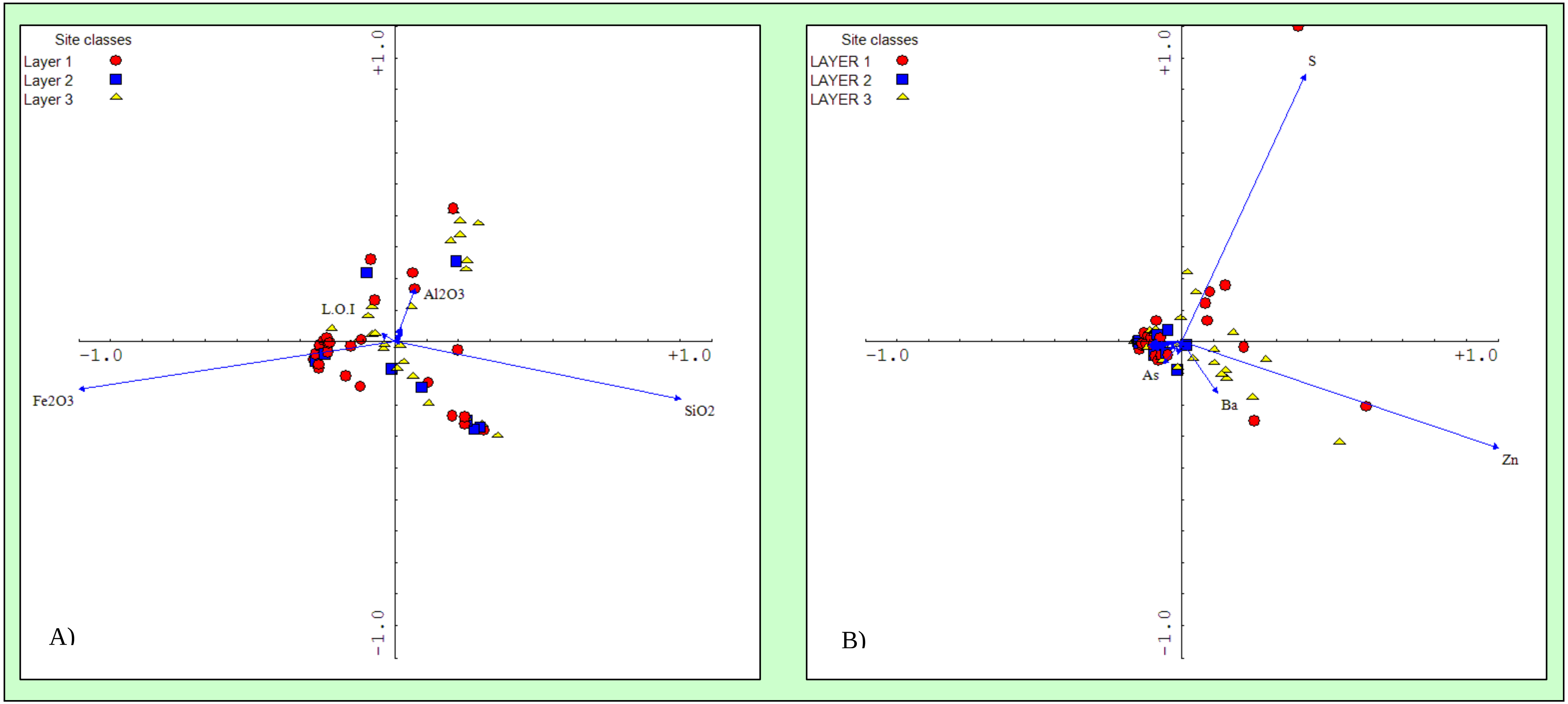
The dominant mineral phase that changed with increasing depth/age was feldspar. A majority of these samples with which feldspar was associated were determined to be of doleritic origin, with only one originating from snuffbox shale. These samples are shown to aggregate along the Al_2O_3 vertex in Figure 6.29A.

Samples containing magnetite also seem to become more dominant as the age of the excavated layer gets younger, though this tendency is not as prominent as that noted for the feldspars and could possibly be ascribed to a small sample size. In general, with the exception of the increase in dolerite samples in the third layer, very little discernable difference between the layers could be determined, indicating that the selection patterns for these samples remained relatively constant over time.

6.3.3 Small excavated pigmentaceous material from Maqonqo Shelter

The selection of these samples was based on the hardness (or more accurately the pulverulence) and colour richness. The one restriction placed on the development of this dataset related to practical time constraints i.e., due to limited access to the synchrotron, and the relatively low priority of the excavated material relative to that of the paint samples, only 63 samples were analysed (see Table 5.1).

The decision to expand the sampling regime to include all of the layers within the deposit was based on four criteria, namely a) the large sample set mentioned above showed little evidence of change in collection patterns over the time period encompassed by the first three layers; b) when the entire collection of excavated material is considered, a majority of the pieces that most closely align themselves with the criteria outlined in Section 5.2.4 were found to be less than 1 g in mass; c) as no definitive evidence was available at the time of sampling that conclusively proved that MQ’s images were created within the last 4 000 years, all possible dates, and therefore dated layers/spits, had to be



Eigenvalues: PCA1 – 94.6; PCA2 – 4.7; PCA3 – 0.3
Scaling –2

Eigenvalues: PCA1 – 50.7; PCA2 – 33.7; PCA3 – 7.4
Scaling –2

Figure 6.29: The results obtained from the A) major and B) minor standardised XRF datasets obtained from the large excavated pigmentaceous material collected from the first three deposit layers from Maqonqo Shelter.

considered; and d) when the larger samples were compared with the smaller excavated material, it was observed that the latter tended to be more pulverulent and ochreous in nature.

It was theorised, based on this last observation, that the larger pieces most probably represent waste lithic material discarded during the process of pigment manufacturing (whether for paint or some other, as yet undetermined, purpose). The smaller pieces, being more ochreous in nature, are more likely to represent the remnants of the original pigments than the larger samples analysed.

Whilst it has been assumed that both the large and small excavated materials represent relic fragments of a pigment manufacturing process, it is not assumed that the pigment produced was utilised for the creation of the paints, but could have been utilised for alternative purposes such as body decoration or the curing of animal skins.

Figure 6.30 shows the relationship between all of the small excavated materials (μ-XRF data). As expected, Fe dominates the distribution of the dataset as a whole. It is also clear that, with the exception of a few samples from layers 7 and 11, all of the samples analysed display very similar elemental compositions. Figure 6.31A supports this trend, with layer 7 again displaying the greatest compositional variance relative to the rest of the dataset. The three elements that resulted in the high degree of variance displayed within layer 7 and, to a lesser extent layer 11, are Pb, Ca and Sr. The source of these elements, or the minerals within which they reside is, however, difficult to determine.

The one sample that is shown to exert a dominating influence on the Ca/Sr vertices is sample 8 from layer 7. This sample also displayed a higher than average Pb content. Mineralogically, this sample was found to be composed primarily of calcite. As such, both the elemental and mineralogical compositions concur with the original assessment of the sample when it was originally selected for analysis; it was described as a ***white deposit***. The presence of calcite within this sample precludes it as having originated within MQ, for this mineral is unknown at this site. This sample most likely originates from an exposed Ecca sandstone surface within the local landscape.

The remaining ‘unique’ samples are comprised of a collection of Fe-enriched shale (Appendix 5.3). All of these samples display elevated Pb contents, suggesting that they too have been subjected to secondary depositional processes typical of geologies located along surface exposures. These factors suggest that these samples were collected from a specific geological source distinct from that noted for the rest of the small excavated materials.

What is interesting about these small samples is that their physical appearance tends to suggest that they originated from a rock outcrop as opposed to having been collected from a riverbed. This is evidenced by that fact that a majority of the large samples display sharp, angular edges as opposed to rounded edges that are typical of material subjected to river action. If one accepts that these large pieces represent waste lithic material removed from the ‘true’ pigment, judging by the size of these ‘waste’ pieces, the original rock would have to be relatively large. Though not impossible for large weathered rocks to be transported within river channels, an inspection of the local river channels has shown that the average rock size within these channels averages between 2 and 6 cm in diameter;

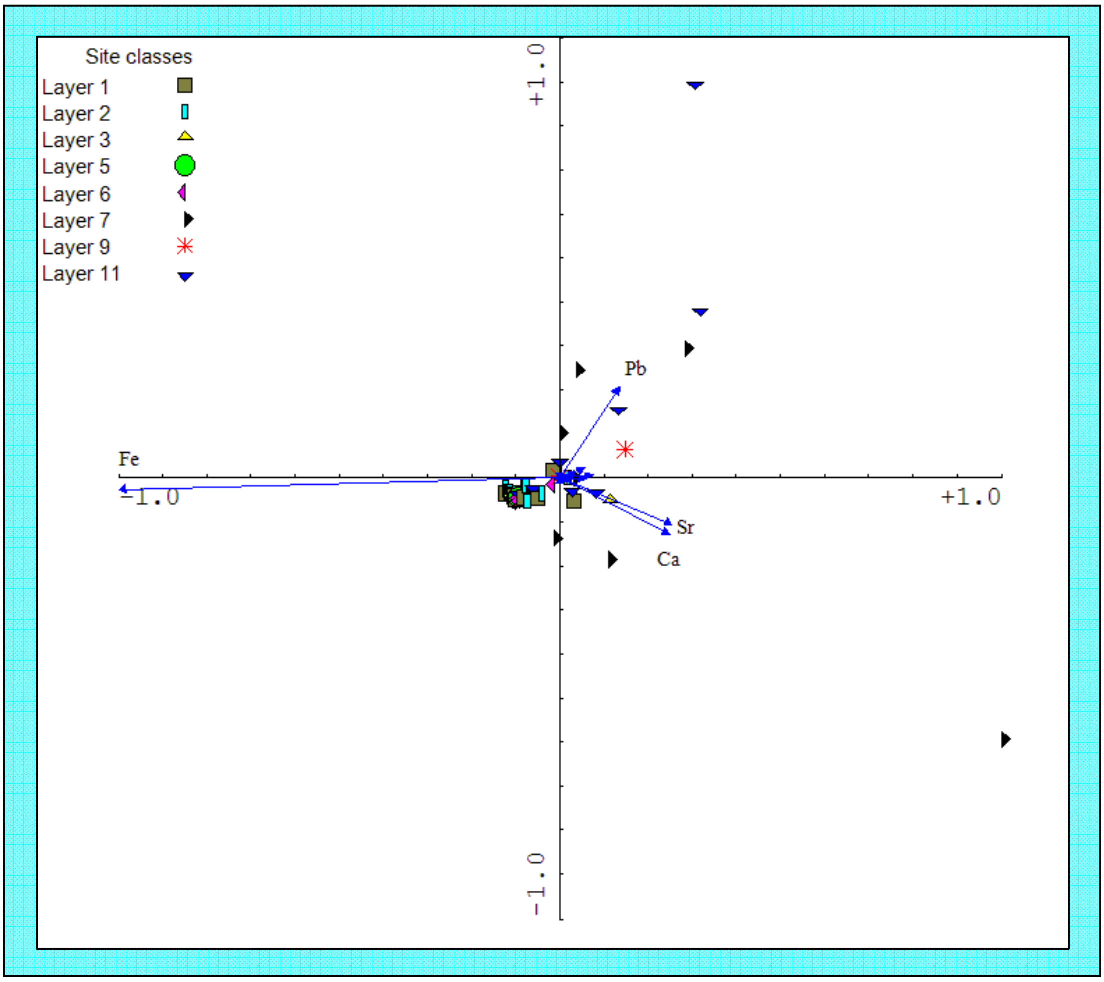
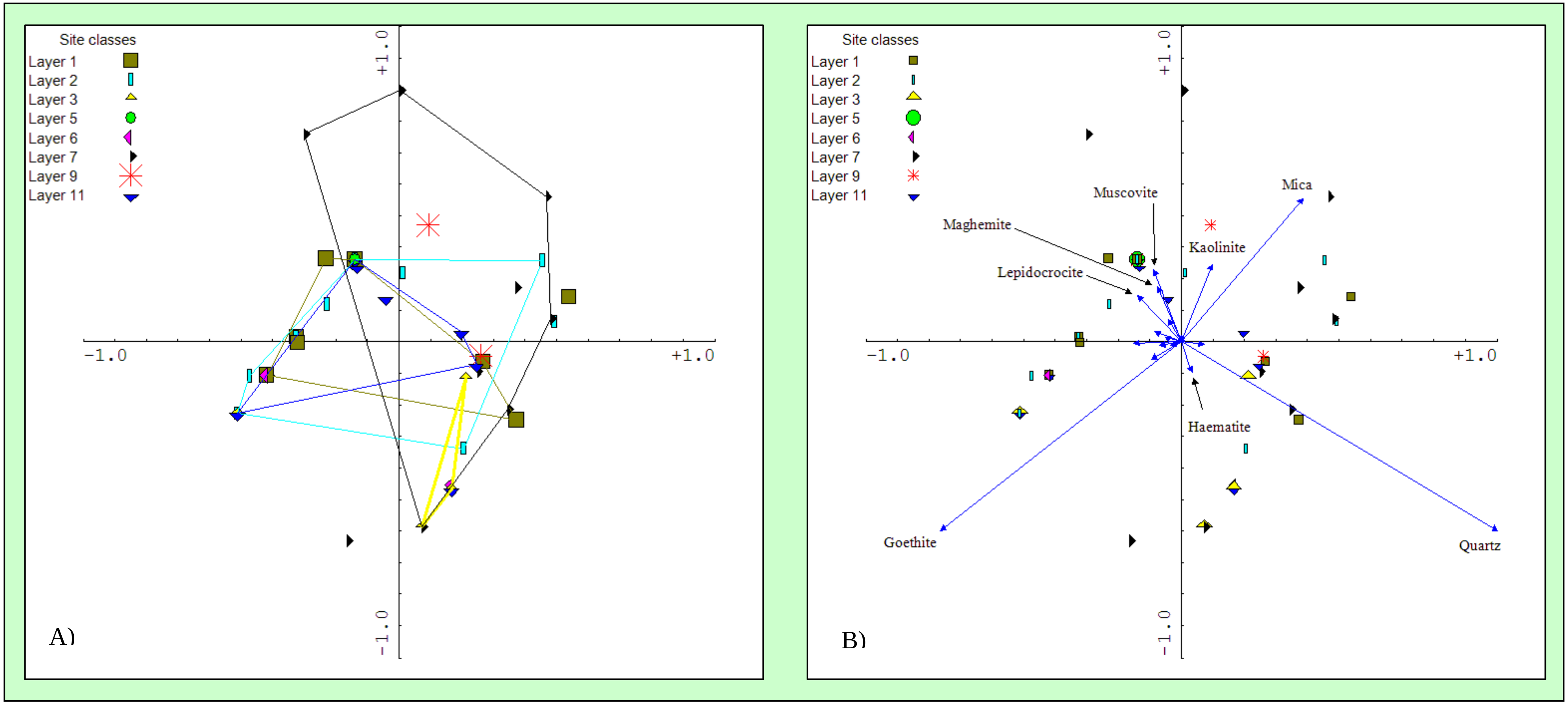


Figure 6.30: Micro-XRF datasets obtained from the small excavated pigmentaceous material collected from Maqonqo Shelter.

Eigenvalues: PCA1 – 89.0; PCA2 – 5.5; PCA3 – 2.6

Scaling -2



Eigenvalues: PCA1 – 30.2; PCA2 – 18.0; PCA3 – 17.1
Scaling –2

Eigenvalues: PCA1 – 30.2; PCA2 – 18.0; PCA3 – 17.1
Scaling –2

Figure 6.31: Modal micro-XRD data showing A) the relation between the layers and B) between the small excavated samples collected from Maqonqo Shelter.

roughly the same dimensions as the waste lithic material itself, suggesting that these materials were not sourced from the river channels.

It is also unlikely that a majority of the small excavated materials sampled originated from materials collected from a river channel. A majority of these pigmentaceous materials, whilst varying greatly in their x and y ordinates, display very similar z-axial distances, suggesting a similar source of sedimentary material (and effectively precluding the Fe nodules as a possible source). Furthermore, their high degree of pulverulence would result in their rapid destruction, even within a gently flowing current. These observations suggest that these materials were probably collected from a specific Fe-enriched shale outcrop.

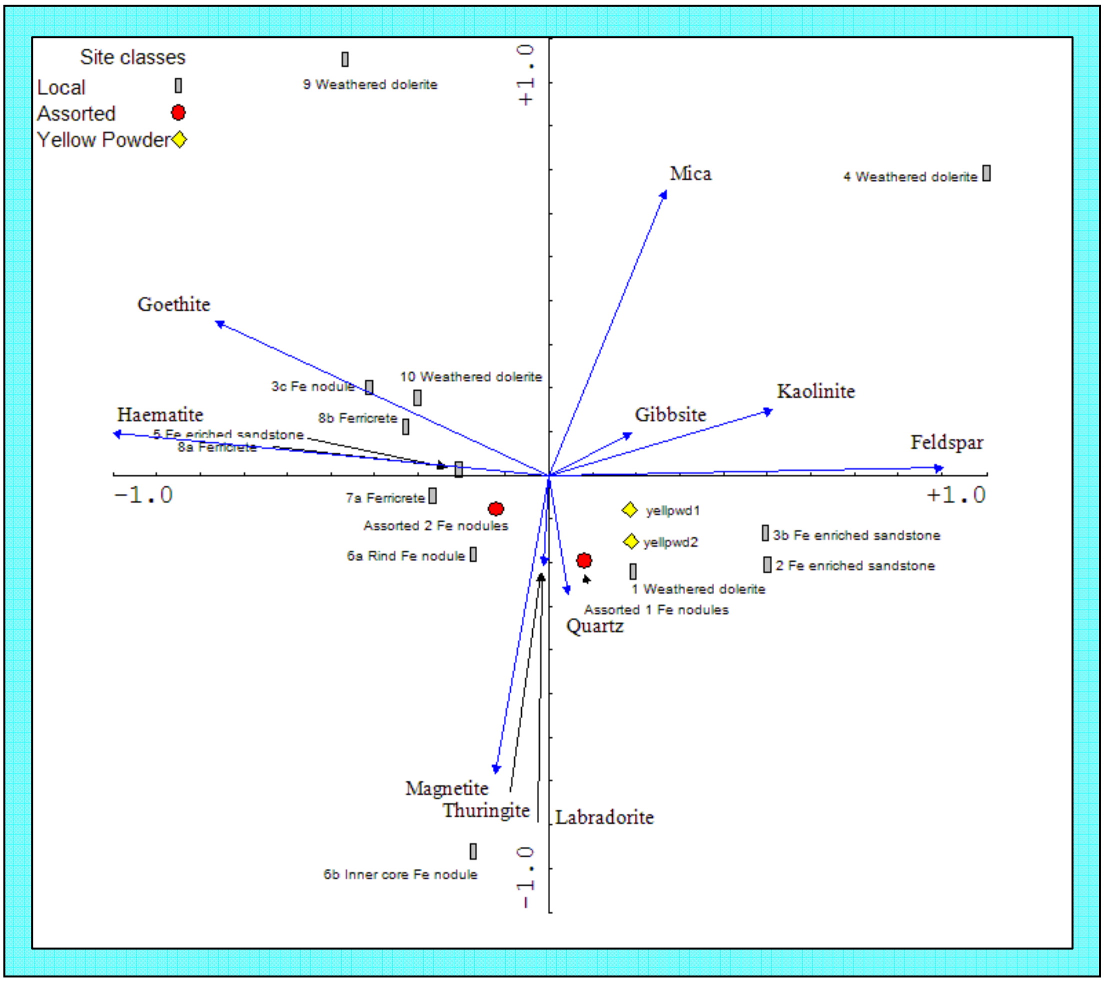
In general, with the exception of the few samples discussed above, the similarities displayed by the compositional and geological make-up of the small samples analysed from each layer suggests that there was little change in the selection criteria for these materials over the date-range determined for the deposit (about 300 years (Table 5.1)).

6.3.4 Local and distant field pigments from areas surrounding Maqonqo Shelter

As in Section 6.3.4, this section is adapted from Escott (2000) and included for completeness. At the time during which the local field sample set was collected, the only analytical work conducted on San rock art involved techniques that could only provide coarse semi-quantitative major elemental data. As a result, the only guidelines that could be used regarding possible paint pigment sources were based primarily on the fact that the coloured paints contained high Fe contents, whilst the white pigments showed elevated Ca. As outlined in Chapter 3, the ethnographic record was not very useful in this regard as the accounts were either too vague or non-existent, and thus could not provide any clues as to either the nature or source of the pigments utilised. As a result, certain assumptions had to be made when developing the sampling regime. For a more detailed description of these assumptions and the subsequent sampling regime employed, the reader is referred to Section 5.2.4.

Due to the broad nature of the sampling guidelines employed, the nature of the samples varied greatly with respect to their geology and locality within the landscape (Appendix 5.6). In general, five distinct geologies were sampled, namely Fe nodules (collected from within river channels), weathered dolerite and ferricrete (found as small localised outcrops), ferrihydrite deposits, and Fe enriched sandstones (exposed within the river channels). These samples were only analysed using standard XRD and XRF techniques due to time constraints. It is thus possible to compare these samples with the large excavated material datasets but not, unfortunately, with the paint samples or small excavated materials.

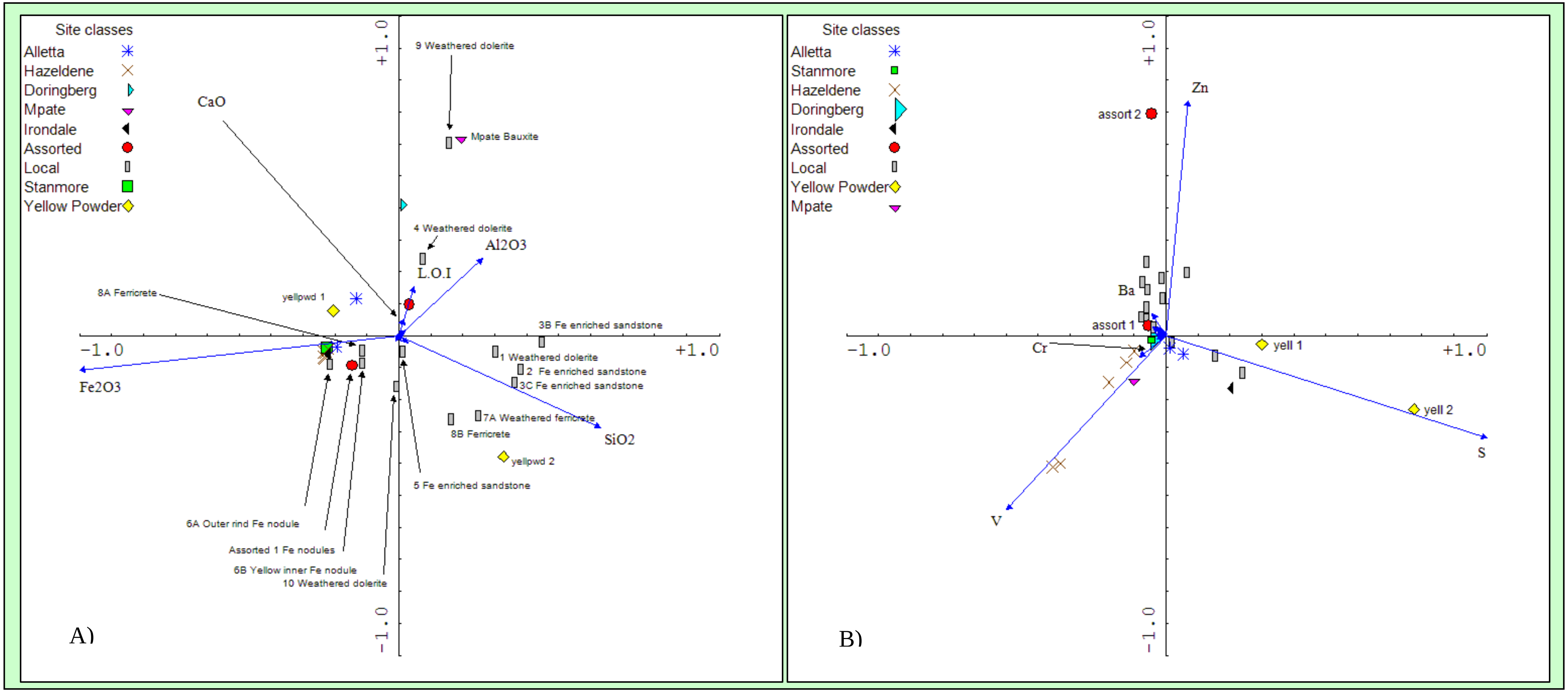
As would be expected, when these locally derived samples are compared against one another, they separate out quite distinctly based on their inherent geological inheritance (Figures 6.32 and 6.33). As their selection was based on their degree of weathering and perceived Fe content, it is not



<u>Figure 6.32: XRD data depicting the locally derived field samples surrounding Maqonqo Shelter.</u>

Eigenvalues: PCA1 – 50.0; PCA2 – 21.7; PCA3 – 9.4

Scaling -2



Eigenvalues: PCA1 – 82.7; PCA2 – 10.2; PCA3 – 5.0
Scaling –2

Eigenvalues: PCA1 – 40.7; PCA2 – 30.4; PCA3 – 17.0
Scaling –2

Figure 6.33: The A) major and B) minor XRF datasets for the local and distant field samples surrounding Maqonqo Shelter.

surprising that these factors play a dominant role in their distributions, both in the XRD and major XRF analyses. PCA1 (50 % variance) is an indication as to the degree of weathering exhibited within each of the samples analysed (Figure 6.32). As a consequence, samples of a similar geological origin, yet exhibiting different degrees of weathering, tend to have a wide distribution within the PCA diagram produced. PCA2, however, highlights two trends, the first being the subtle change in distribution between the haematite and quartz dominated samples i.e., the dolerites, ferricretes and Fe nodules vs. the Fe enriched sandstones. The second, more interesting trend involves the distinct separation of highly weathered material from more resistant material originating from the same sample.

It can clearly be seen that the inner 'core' sample analysed from one of the Fe nodules collected displays a unique mineralogical composition not only relative to the rest of the dataset as a whole (Figure 6.32), but also when compared to the sample analysed from material that comprised the 'rind' of the same sample (Paint 6B and 6A, respectively). This provides a clear example of how distinctive separate readings from individual samples collected from one source can be. If one uses the results collected from Paint 6 as an example, and assumes that the 'rind' of the nodule is 'waste' material while the 'inner core' represents the 'true' pigment, a sampling regime employed within the pigment sourcing study will have to take this possibility into account. The analysis of both the large and small excavated materials was conducted with this principle in mind.

In addition to the local field dataset (which was only collected from the drainage basin within which MQ is situated), samples were also collected from ore bodies located within 50 km of MQ shelter; recorded as distant field samples. This second dataset was created in order to highlight the degree of variability that might exist between a dataset composed of randomly collected weathered samples as opposed to samples collected from specific geological sources. With the exception of the Mpate sample (which is of a bauxitic nature), all of the distant field samples collected were from Fe ore outcrops. These samples were only analysed using standard XRF techniques due to time and financial limitations.

Figure 6.33A shows the major elemental data for the local and distant field samples. It can be seen that this PCA diagram is dominated by the Fe:Si and Al ratio. This effectively separates the sandstones, dolerites and Fe enriched shales from the Fe ore bodies and nodules, with the exception of the Doringberg sample. The Stanmore, Hazeldene and Irondale samples display almost identical characteristics, thus strongly suggesting that they belong to a similar geological formation. The Doringberg, and to a lesser extent the Alletta samples, are chemically different from the previously mentioned Fe ore bodies, possibly suggesting a different geological composition.

The Hazeldene, Stanmore and Irondale samples are very closely associated, whilst the Alletta and Doringberg samples are grouped separately. Geographically, the Hazeldene and Irondale sample sites are relatively close together (± 8 km apart), and their association suggest that these two sample sites are related. The Stanmore sample site is ± 15 km and ± 22 km distant from Irondale and Hazeldene, respectively, possibly indicating the opposite trend. It is interesting to note that the local samples display the most variability of the two datasets. It is probable that the varied degrees of weathering displayed by the local field samples relative to that of the ore bodies, has resulted in the high degree of variability (Figure 6.33).

Conversely, the Fe ore bodies tend to show a great deal of elemental ‘stability’ in both their major and minor elemental fractions. The Hazeldene samples are the one exception to this trend, however. The distinction between the five samples relates to their respective V contents. Whilst the high V contents within each of the samples clearly distinguishes this sample site from the rest of the local and distant field samples, the high degree of variability of this element within each of the individual samples results in their ‘separation’ in Figure 6.33B. Why such a high degree of variability was recorded is not fully understood, however. Only further analysis of additional samples from the same location might elucidate this phenomenon.

The strong distinction between the Hazeldene, Stanmore and Irondale samples and those from Alletta and Doringberg could indicate that these ores were formed during different geological events. This has important implications for future provenance work. If Fe ore bodies can be shown to be distinctly different from one another chemically, it would enable the determination of specific source points, as opposed to simply delineating certain generalised areas (assuming that the Fe ores were used in the manufacture of the paint pigments).

Figure 6.33B highlights a couple of interesting trends. Firstly, in a majority of the cases, samples gathered from a similar source tend to group together, as suggested in Figure 6.33A. The Assorted 2 and ferrihydrite samples tend to show the greatest degree of variability. The two ferrihydrite samples were collected differently, with one being sampled as a wet sample from run-off streams above the Shelter (yellow powder 1), with the other collected as a dry deposit (yellow powder 2). This latter sample has clear indications of sandstone contamination as a result of scraping from the rock surface, and these different provenances account for the apparent variability between these samples.

Both of the ferrihydrite samples also exhibit a great influence upon the dataset with regards to their S contents. This too is not unexpected, for both of these samples, by their very nature, are derived from deposits located along groundwater seepage points. As has been shown in Section 6.2.3.1, S is a ‘contaminating’ factor associated with the groundwater, which in turn is the direct result of the presence of coal seams and the dark coloured carbonaceous shales within the local surrounding geology.

In conclusion, the nature of the sampling regime inevitably resulted in the development of an unstructured field database, with no single geological formation being consistently collected over an extended area. Whilst many more samples are required in order to adequately determine similarities and differences between different geological materials, the trends displayed here support the methodology employed. With a greatly increased database (both in increased numbers of samples collected at each sample point, and a larger geographical distribution of sample points), the provenance of materials (cultural and geological) could be accomplished.

Before this can be conducted, however, the question of how the pigments were sourced first has to be established. As has been shown above, the choice of collection regime has a dramatic impact on our ability to accurately provenance the pigments utilised. The degree of weathering experienced within the locally derived samples had a much greater impact on the variability of the elemental and mineralogical compositions of the samples in question relative to the distant field samples. In either case, studies of this nature will have important implications for South African archaeology, which has as yet not attempted to source cultural material other than pottery. Additional work in this field is, however, envisaged for the future (see Chapter 8).

6.3.5 Excavated pigments and paints from Maqonqo Shelter

The primary reason for analysing the excavated pigmentaceous material was to determine whether or not this material could be related to the pigments used within the paints. As was shown in Section 6.2.4, however, the most likely source for the red, black and some yellow coloured pigments were Fe nodules (inner cores), dark red from plinthite, the orange from bauxite, and whites from gypsum based secondary surface deposits. Both the large and small excavated materials were, in the main, derived from shale, though some doleritic and Fe enriched sandstone material were also identified. As a result, it would be expected that little to no similarity should exist between the two pigment datasets.

In an attempt to determine if this is in fact the case, a comparison between the datasets was conducted. However, as was discussed above, the excavated material was further divided into two subsets in order to account for the different sizes of the materials selected. These two subsets were analysed using two separate micro-analytical techniques, namely EDX in the case of the large excavated samples, and µ-XRF and µ-XRD in the case of the small excavated samples. Whilst the MQ paint pigments were analysed using all of these techniques and can thus be compared with both the subsets on an individual basis, a direct comparison between all three datasets cannot be achieved due to data compatibility issues (see Appendix 5.15).

Figure 6.34 highlights the distinct separation of all of the MQ paint pigments analysed from the large excavated samples (using EDX). PCA1 (77.3 % variability) can be ascribed to a change in gradient between Fe dominated samples (the excavated material) and Ca and S influenced pigments (the paint samples), with Al also playing a minor role.

PCA2 (17.2 % variability) is most closely aligned with Si content, though the separation of the samples is driven primarily by the Fe-enriched sandstone materials analysed from the deposit as opposed to excess Si content recorded in the paint samples. Figure 6.34 is essentially a summary of all the trends noted up to this point within this study. Within this figure, it can clearly be seen that the Ca and S contents increase in content within the paint samples in the following order: black, orange,

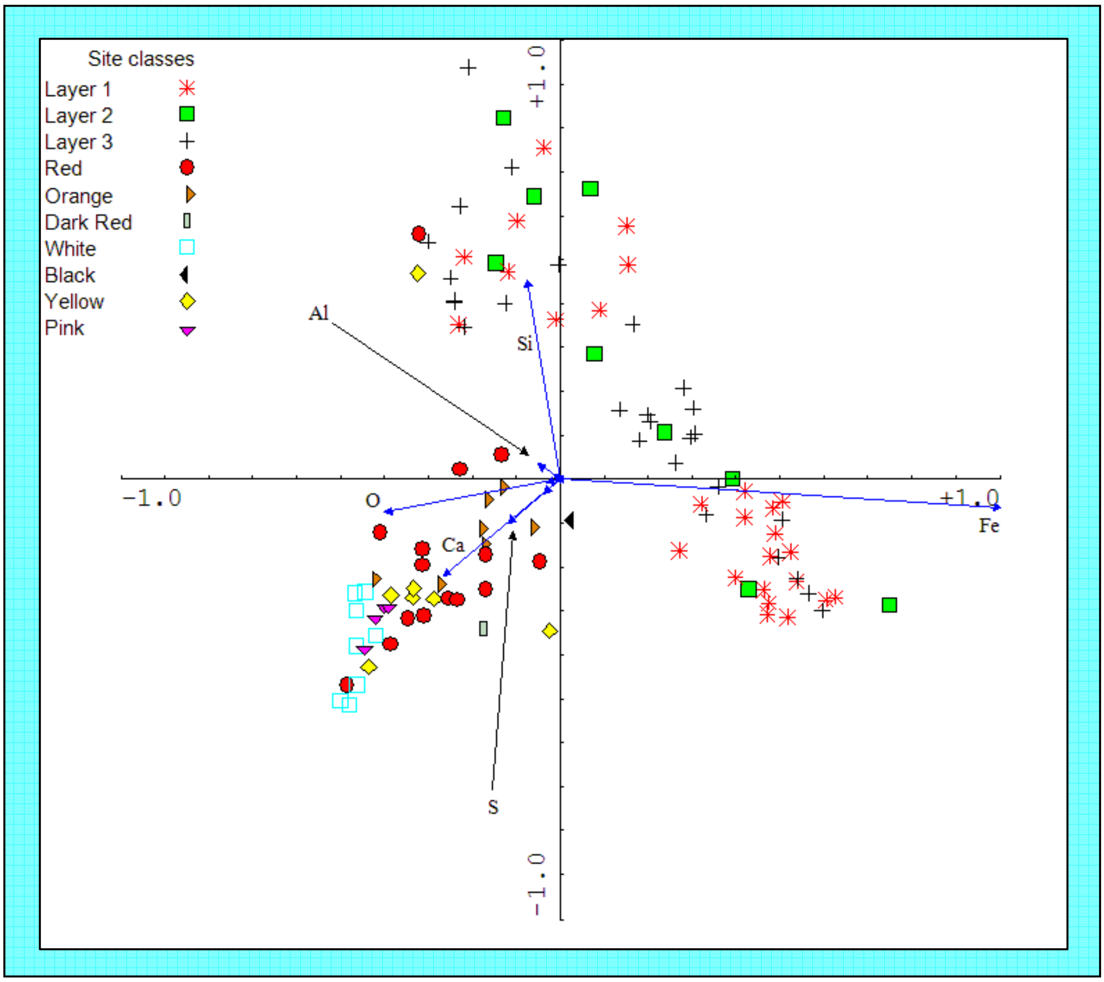


Figure 6.34: Average reduced window (EDX) for the paint and large excavated pigmentaceous material collected from Maqonqo Shelter.
Eigenvalues: PCA1 – 77.3; PCA2 – 17.2; PCA3 – 2.7
Scaling –2

yellow, pink and white (the red samples, which displayed the highest degree of variability, are distributed along this gradient). The Si content within these samples shows the reverse trend, indirectly indicating a ‘thinning’ of the sampled paint. Also evident is the similarity in composition between the three excavated layers sampled.

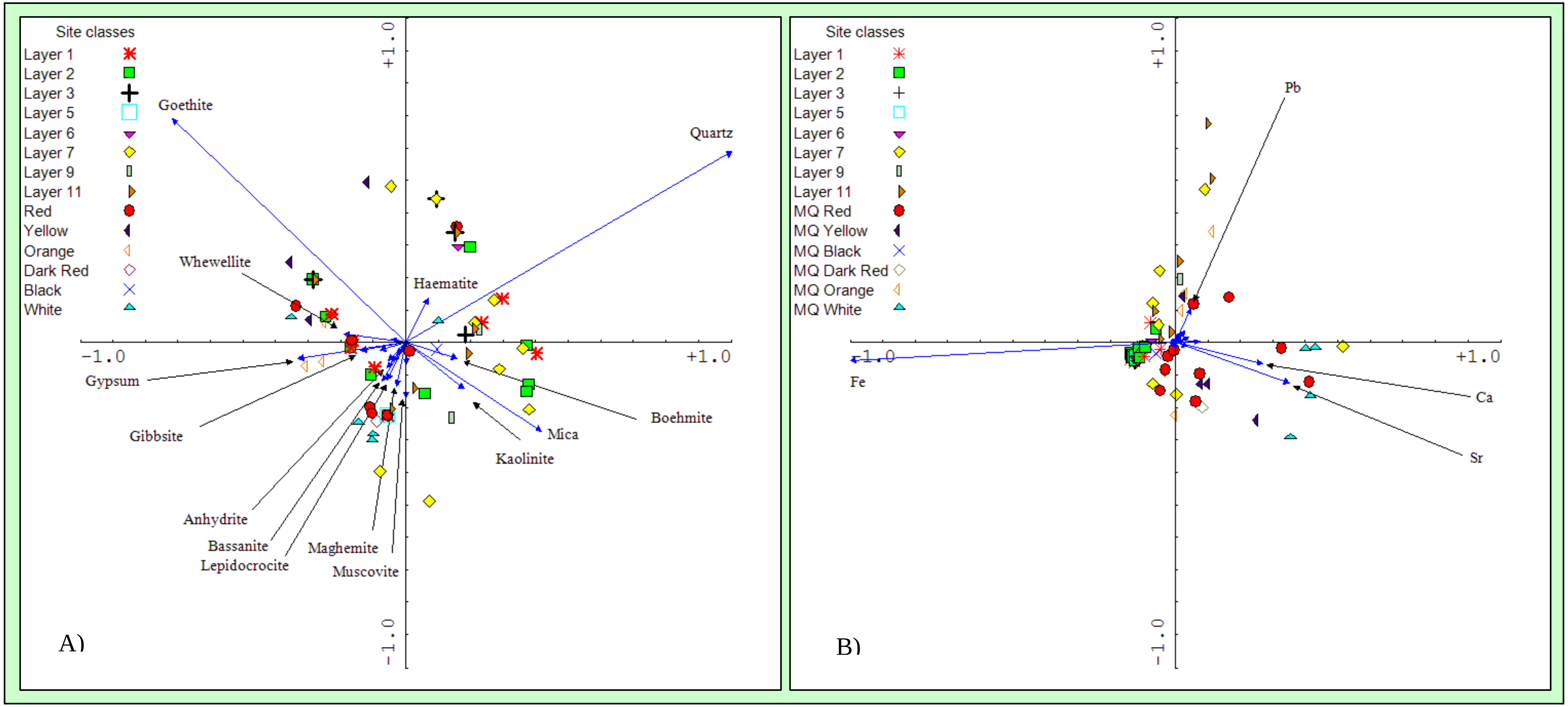
Figure 6.35, which depicts both the µ-XRD and µ-XRF data for the paint samples and the small excavated materials analysed, shows a similar separation between the paint and excavated samples. The µ-XRF data (Figure 6.35B) confirm the trends noted in Figure 6.34, namely that (a) there is little difference in pigmentaceous material composition with changing age/depth; (b) the paints and excavated materials separate out along a strong Fe:Ca gradient; and (c) there is a progressive increase in Ca content within the paint samples according to the paint colour from red, orange, yellow, pink to white. The µ-XRD data (Figure 6.35A) clearly show that the separation of these two datasets is based primarily on the presence of secondary deposited minerals within the paint samples analysed, namely whewellite, gypsum, anhydrite and bassanite.

The obvious conclusion that can be inferred from Figures 6.34 and 6.35 is that the paint sample data are significantly influenced by the presence of Ca and S, and that the presence of these elements effectively prevents a ‘true’ comparison between the inorganic pigments present within both datasets. In order to realise this goal, an understanding as to how the paints were manufactured is required, along with the manner in which the environment within which they reside has further influenced their elemental and mineralogical composition. Once this is achieved, it would theoretically be possible to ‘strip’ the additives and/or secondary deposited minerals from the data obtained for the paint samples, thus leaving the inorganic pigment utilised for comparison with potential pigment source materials (in this case, from the excavated deposit).

6.3.6 Data manipulation and compatibility

Before this form of data manipulation can be conducted, two vital pieces of information are required, namely a) a knowledge of the mineral composition of the paint samples analysed; and b) a knowledge of the mineralogical and elemental composition of the blank samples collected from within the same shelter. The blank data are a vital component in this process, for they indicate which minerals/elements were most likely to be present as a result of secondary deposition (see Section 6.2.3.1). In the case of the MQ paint samples, gypsum was the major secondary depositional mineral identified. The paint pigments, whilst also displaying a strong gypsum presence, also contain other secondary deposited minerals, namely whewellite, anhydrite and bassanite (see Section 6.2.4).

Several assumptions are made based on this information, namely a) that all of the Ca present within the samples resides exclusively within the secondary deposited minerals gypsum and whewellite; b) the remaining minerals identified are assumed to display a relatively homogeneous distribution throughout the paint sample i.e., the ratio of each of these remaining minerals remains



Eigenvalues: PCA1 – 28.7; PCA2 – 15.3; PCA3 – 13.0
Scaling –2

Eigenvalues: PCA1 – 93.3; PCA2 – 3.0; PCA3 – 1.2
Scaling –2

Figure 6.35: The results obtained from the A) micro-XRD (modal data) and B) average standardised micro-XRF datasets for the individual paint colours and small excavated pigmentaceous samples collected from Maqonqo Shelter.

constant relative to one another; and c) the elemental data recorded by each specific analytical technique are reasonably accurate, thus allowing for a removal of these minerals based on their stoichiometric ratios i.e., gypsum = Ca:S:6O and whewellite = Ca:2C:5O.

There are obvious flaws with regard to these assumptions, especially when considering the EDX data, the primary one being that the data are not quantitative. As a result, the reflected elemental proportions recorded, whilst being accurate enough to distinguish between paint samples both within and between different painted shelters, might not be accurate enough to allow for this form of data manipulation. Whilst the data recorded using µ-XRF can be considered to be more precise (although also semi-quantitative) than that of the EDX data (due to its smaller beam footprint), the fact that the paint samples have been shown to be heterogeneous in nature over very small distances does influence the degree of reliability of this form of data manipulation using this dataset.

Even when taking these factors into account, Figure 6.36 still shows a significant distinction between the paint and excavated material datasets, the only exception being displayed by the orange samples. This is not surprising for it has already been determined that the oranges have a bauxitic source, and thus would display a similar chemical signature to the weathered doleritic samples extracted from the excavated deposit.

As can be seen above, several of the datasets were analysed using a variety of different techniques, and as a consequence could not be directly compared with one another due to issues of ‘data compatibility’[1]. The reasons behind the techniques chosen to analyse each dataset are based on two factors, namely sample size limitations and analytical cost. The paint samples are always going to be restricted in size, and thus can only be analysed using the highly accurate, yet also costly, EDX, µ-XRD and µ-XRF techniques which are not always accessible to researchers.

The field samples, on the other hand, are not limited by sample size. However, in order to determine the degree of variability in both the chemical and mineralogical composition within a given area, a large number of samples have to be analysed. The cost of running such a large number of samples would be prohibitive if they were to be analysed in the same manner as the paint samples. Standard XRF and XRD analysis is much cheaper and is just as precise as the data produced during the analysis of the paint pigments.

This said, it is obvious that comparisons between these different datasets are needed in provenancing studies for it is the only way to determine the degree of similarity that might exist between San rock art pigments and suspected pigment sources. In the following chapter, an attempt is made to determine the degree to which the different techniques utilised within this study relate to one

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[1] Differences in energy sources and detector sensitivities within each of the techniques used are just some of the reasons why data from one technique might seem to be different to that obtained from another. It is also possible that the results obtained from two separate, but identical, machines utilising the same method of sample analysis might also differ due to differences in the general maintenance and the technical set-up of each machine. The only way to compensate for this is to run a standard sample through each of the machines, and subsequently determine corrective measures to account for any possible variations that might exist based on the data produced. This is attempted in Appendix 5.15.

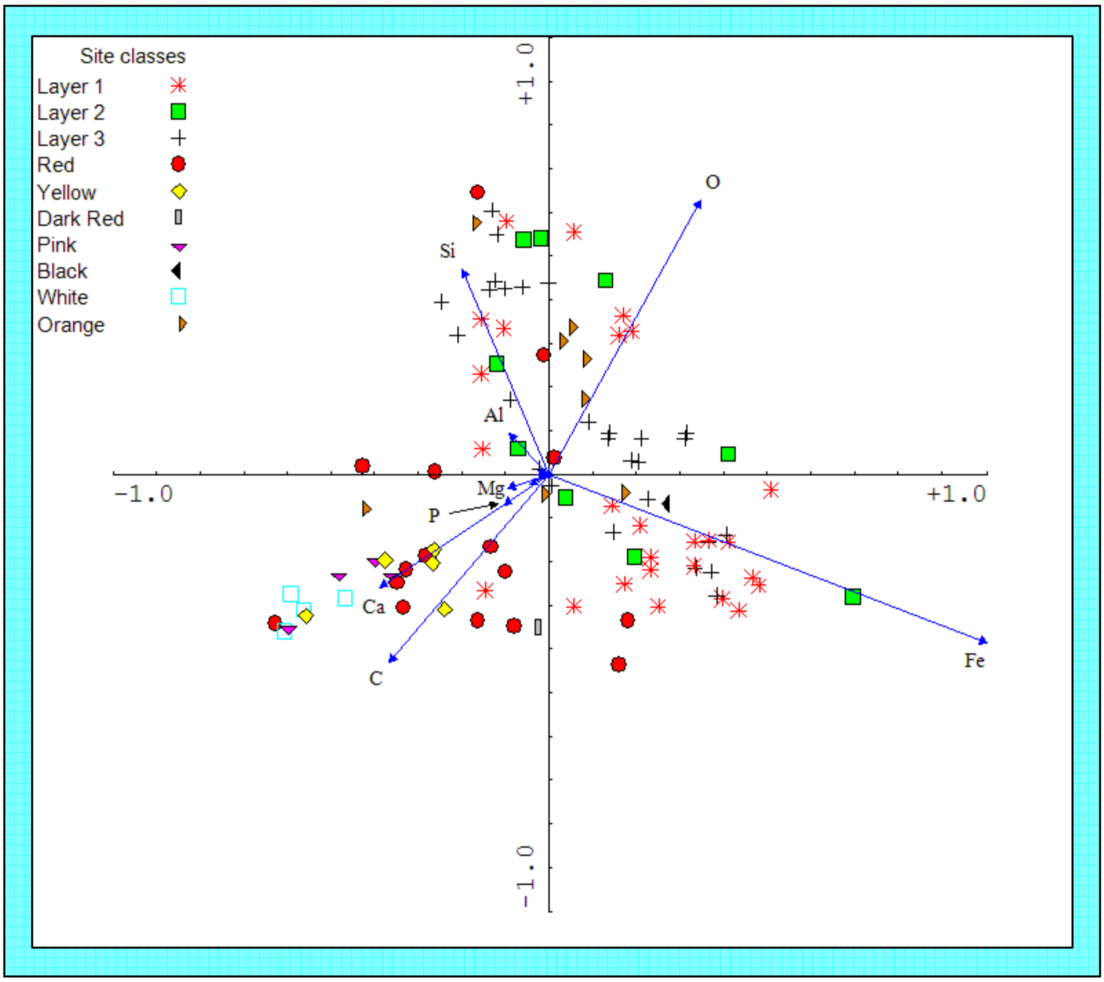

Figure 6.36: Average reduced window (EDX) for the paint and large excavated pigmentaceous material collected from Maqonqo Shelter; paints corrected for gypsum and whewellite.
Eigenvalues: PCA1 – 45.0; PCA2 – 31.3; PCA3 – 5.2
Scaling –2

another with respect to possible differences in sensitivity. There is then an attempt to analyse the data obtained between the individual datasets, after initially 'standardising' each of the datasets in order to make them compatible.

6.4 OVERALL CONCLUSION

A number of important observations have been made during the course of this study, with possibly the most important being the fact that the paints are extremely heterogeneous in nature at the microscopic level. Although this finding is not new, having been mentioned by Van Rijssen (1990), Wilson *et al.* (1990) and Peisach *et al.* (1991a), the manner in which the compositional data for the paints were recorded was not adequately addressed. As illustrated in Section 6.2.5, the manner in which the data are recorded has an important bearing on the reliability of the data thus obtained. The manner in which the data were manipulated varied[1] and as a result the final dataset used within each previous investigation cannot be considered comparable with those of the other studies. It unfortunately also calls into question the reliability of some of these results. The methodology developed within this study will ensure an increase in the reliability of the data recorded. A standardised approach would also allow for the comparison of data collected from a multitude of sources, thus greatly enhancing our archaeological knowledge, thus providing further justification for the original sampling of the paint pigments.

One of the important procedural adaptions that must be taken into account in future studies involves the adaption of the paint sampling technique itself. This study has shown that the influence of gypsum and the other evaporite minerals decreases with increasing paint depth. In order to accommodate for any possible external influences that might affect the paint sample data, a two-step sampling regime is proposed which would allow for the identification and comparison of any potential surface depositional features with the 'true' paint pigments. Furthermore, this approach should be adopted as a pre-emptive measure against the possible presence of excess surface deposits that might not be visually apparent. This is especially important when one considers paint samples that are relatively thick in nature. For obvious reasons, it might not be possible for thinner paint samples to be subjected to this sampling regime, due to a lack of available material.

In all of the studies conducted to date, almost all of the paint samples analysed have displayed elevated Ca contents, irrespective of the colour of the paint pigment. This has also been shown to be true in this study. The reasons for its presence have, however, varied, with suggestions of Ca being an additive derived from materials such as ground sea shells, burnt sea shells and bone (Peisach *et al.*,

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[1] In Van Rijssen (1990), a number of analyses were conducted, and the results averaged. No indication as to the use of spot or reduced window scans, nor the number of scans per sample, was mentioned. In Wilson *et al.* (1990), a number of spot and reduced window scans were taken, with the five most similar in composition being averaged. This method is statistically biased.

1991a), or a depositional product, such as gypsum or $CaCO_3$ (Van Rijssen, 1990). It was Van Rijssen (1990) who first noted the presence of gypsum within the paint samples (physical identification via SEM), with this finding later verified by Mazel and Watchman (1997). Some early results obtained by synchrotron analysis at Daresbury Laboratory in England (E. Pantos, pers. comm., 2000), as well as from the μ-XRD and μ-XRF data obtained at Brookhaven Laboratory, have shown that gypsum is indeed present in a majority of the paint samples in the present study.

The notion that gypsum was used as an additive was first introduced by Mazel and Watchman (1997), who noticed that the gypsum crystals in the paint samples were aligned with the brush strokes of the San painter. Had they formed subsequent to the painting event, then the crystal alignment would have occurred at right angles to the painted surface. The double sampling analysis discussed in Section 6.2.2 supports the idea that gypsum may be an additive, but only within the white samples. The results showed that the Ca content of the analysed paints increased with depth. Had the gypsum been present as a depositional feature, the opposite trend would have been noted. Gypsum does not necessarily account for the entire recorded S, however, as it has been shown that the MQ wall also contains an elevated S content (Appendix A5.8.4).

An additional Ca mineral, whewellite, was also found in a majority of the paints analysed using μ-XRD and μ-XRF. The presence of this mineral is interesting, for it is known to occur in most plants, being found within the plant cell vacuoles. In some plant species, the Ca is also found as insoluble carbonate, phosphate, or sulphate (Salisbury and Ross, 1992). This is interesting since Ca, S and P are the three defining elements that distinguish the paints from the other pigmentaceous materials studied (the excavated and field samples). This mineral is also known to be formed by microbes, fungi and lichen, some of which are also known to accumulate P.

In the light of the above information, and based on the fact that almost all of the paint samples display elevated Ca contents, the assumption made by Peisach *et al.* (1991a) that all of the Ca in the paints is highly mobile is rejected. If this were the case, then theoretically there would be very little Ca left in the paint samples. This is at odds with the findings presented by the other authors mentioned, as well as those of the current study.

Peisach *et al.* (1991a) also showed an elevated level of Ca within their paint samples, but tried to show that this was exclusively related to the lighter colours. From the results determined in this thesis, it is thought that this conclusion is slightly misleading. These findings, together with those of Van Rijssen (1990) and, to a lesser extent Wilson *et al.* (1990), show that Ca contents within most of the paint samples were relatively high, irrespective of colour. The only difference was that the red colours contained high Fe to Ca ratios, whilst the light colours (white and pink) displayed the opposite trend. No raw data were, however, supplied with the Peisach *et al.* (1991a) paper, and as a result, it is not possible to verify this point.

Another trend found to be consistent with the findings of previous papers, concerns the high variability in Fe content within the red sample dataset (see Sections 3.5.3 and 3.5.4). Wilson *et al.*

(1990) ascribe this variance to the degree of redness, the lighter colours containing the lowest Fe contents. Studies have shown that the Fe content of a sample does not necessarily determine the degree of redness, as only between 1.0 and 1.7 % haematite is required to induce a red colour (Scheffer and Ludweig (1958) and Resende (1976)).

Wilson *et al.* (1990) based their findings on the analysis of two colours, one light red and one dark red sample. The resultant graphs do highlight a difference in Fe content, with the lighter colour containing about 10 % less Fe. However, based on the red colour data collected both in this thesis and those presented in Van Rijssen (1990), this change in Fe content can be considered ‘normal’ i.e., paints of the same colour often show differences in Fe content equal to and greater than 10 %, while still maintaining the same hue. In order to identify any differences that might exist between the two samples, analysis of all the elemental data collected for each sample must be conducted. When these data are taken into account, the two samples do reflect a degree of similarity, but the light red sample contains a higher Si and Al content.

Aluminium contents were also noted as being relatively high in all the paints discussed by the different authors. Wilson *et al.* (1990) discounted the elevated Al and Si contents as ‘noise’ and these data were thus not considered when characterising the paint samples. Peisach *et al.* (1991a) actively eliminated Si and Al values by using absorbers. As has been shown in this thesis, however, Al content could be an indicator as to the nature of the original source material. When discussing the characterisation of the orange pigments, it was indicated that bauxitic material (high in both Fe and Al) could have been used in the manufacture of some of these pigments (see Section 6.2.4.2). By actively eliminating or discarding Si and Al as variables, important information regarding the pigment composition was lost.

The current study has shown that the black pigment contained a high Fe content, with a correspondingly low C content. The black colour, together with the high Fe content, initially suggests that the source material was either finely divided haematite or magnetite. The presence of maghemite, however, suggests that this colour was artificially created via the calcination of goethite, presumably obtained from the ‘inner’ core of an Fe nodule (see Section 6.2.4.5).

The finding that the black colours contain high Fe contents are supported by those of Mazel and Watchman (1997), whose analyses were based on Drakensberg samples, whilst Van Rijssen (1990) determined that a manganese oxide (pyrolusite) was the source of the black pigment in samples from the south-western Cape. Wilson *et al.* (1990) showed that their black sample was not sourced from a manganese-based compound, but suggested burnt bone instead (Coldstream Stone analysis – Eastern Cape coast).

The Coldstream Stone black pigments do contain Fe, but not as much as that recorded for the black paint sample analysed were (between 2 and 10 % as opposed to 27 %). When compared to a black sample from the Cederberg Mountains, a distinct difference in composition was noticed. The Cederberg sample contained very high Mn, thus showing great similarities with the results found by

Van Rijssen (1990). This is a very exciting finding, for it shows that the black paint recipes change with geographical location, with at least three different compositions now being identified.

Similarly, the white pigments analysed from MQ and SV indicate that gypsum and whewellite are the primary pigment components, indicating that they were probably sourced from shelter deposits. The white samples analysed from TW, whilst also sourced from shelter deposits, shows minamiite as being the primary mineral component. Van Rijssen (1990) found that the white pigments were derived from clays, whilst Wilson *et al.* (1990) and Peisach *et al.* (1991a) found that marine shells were used. With at least four different pigment sources being proposed for the white pigments, differences in recipes can also be assumed. As such, conservation/rehabilitation strategies have to take these differences into account, and must be adapted on a site-specific basis.

The excavated pigments, both large and small, displayed little change in geological composition over time, indicating that the sampling regime employed by the people who utilised MQ remained relatively unchanged over 6 000 years. When compared to the paint samples, a distinct difference between the two datasets was noted, even when the paint sample dataset was manipulated in order to remove the bias imposed by the secondary deposit materials upon its distribution. The paint samples analysed by Wilson *et al.* (1990) were also shown to be chemically distinct from the thirty-two large pieces of ochre analysed from the deposit. This finding raises an interesting question: what was the use of the excavated pigment if not for paint manufacture? A possible answer to this question is that the pigment was used for either personal adornment, and/or garment manufacture. Current evidence can neither support nor dismiss these possibilities.

The ethnographic record does provide tentative clues, however. Accounts are very vague regarding the locality of the paint manufacturing process, but inferences can be made from several accounts that they were manufactured outside of a shelter e.g. Kerik and Mapote (F. Prins, pers. comm. (2004), and How (1970), respectively). Whilst both of these accounts, both originating from the Lesotho/KwaZulu-Natal Drakensberg region, tend to favour the notion that the paints were manufactured outside of shelters, this ‘evidence’ is marginal at best, and cannot be categorically accepted as being representative of all paint manufacturing procedures. It does, however, explain why the material within the deposit does not seem to share any mineralogical or elemental characteristics with the inorganic pigments found within the paint samples. In either case, the lack of similarity between the paints and these excavated pigments leads one to question their original purpose.

The analysis of the field samples highlighted the differences in ‘behaviour’ of highly weathered material as opposed to ‘pure, fresh’ ore. The ‘purer’ the samples, the more tightly they clustered within the PCA diagrams, and thus the greater the prospects of provenancing material collected from these sources. Although these analyses showed that sourcing the material was a possibility using the adopted methodology, it also highlighted some shortcomings in the sampling regime employed. More field data are required, and with this, more samples at each sampling point have to be analysed (in order to determine the inherent variability within the sourced material). The larger the database, the greater the probability of sourcing the cultural materials under investigation, assuming that the pigments were sourced from distinct geological formations, as opposed to opportunistic scavenging of weathered material from the landscape.

Finally, whilst this study has managed to characterise the paint samples collected from the four shelters sampled, the primary success achieved here is the development and successful application of a methodology that will enable a more accurate analysis of future paint samples, as well as the development of guidelines enabling the development of successful sampling regimes to be employed in future provenancing work. Of primary importance is the manner in which the paint samples are originally sampled (double sampling is strongly suggested), whilst the use of blank samples is also essential.

CHAPTER SEVEN

INTER-TECHNIQUE COMPARISONS

7.1 INTRODUCTION

This chapter attempts to address some of the questions outlined at the end of Chapter 6, by comparing standardised datasets derived from the different experimental techniques. The ideal result would be that the trends highlighted will reflect those displayed in Chapter 6, thus both supporting the already derived trends, and also allowing for easier data manipulation in the future with fewer tests being required to highlight the trends noted.

Unfortunately, for reasons outlined in Appendix 5.15, only the EDX and major XRF elemental data can be compared with any reasonable degree of confidence. As such, this chapter will focus only on the two comparative models not yet attempted within this thesis, namely comparison of the MQ pigments with the local and distant field samples, respectively. As these latter two sample sets were collected using different criteria (see Sections 5.2.4), they will be discussed separately.

7.2 PAINT VS. LOCAL FIELD SAMPLES

In order to facilitate the comparison between the two distinct datasets (EDX and major XRF), the data were first standardized according to the method discussed in Appendix 5.15. Figure 6.1 shows the results obtained from the comparison, clearly highlighting the distinct nature of the two datasets. The main driving factor that ensures that the paint samples remain distinct from the field samples is the presence of Ca-containing minerals, which, as has been illustrated in Chapter 6, are represented mainly by gypsum and Ca-oxalates.

Even with this distinction, however, some samples do tend to closely align with some of the local field samples collected, in particular the samples that lie along the Si vertex. Unfortunately, rather than indicating the possible pigment source, this distribution most likely indicates rock wall contamination of the paint samples. A more plausible distribution concerns the close proximity of most of the orange (and some red) paint samples with the weathered dolerites. In order to more fully understand this apparent similarity, one must first account for the over-riding influence that the Ca minerals have on the dataset. In order to achieve this, the molar equivalents of whewellite and gypsum were reworked back into the dataset (as shown in Section 6.3.4), and the data re-interrogated.

It must be remembered at this point that this method of mineral ‘extraction’ from an existing EDX dataset is very crude, for it makes several assumptions that are impossible to accurately validate. Some of these assumptions include: a) that all of the Ca resides within whewellite and gypsum; b) that these minerals are present solely due to secondary depositional processes; c) the individual elemental

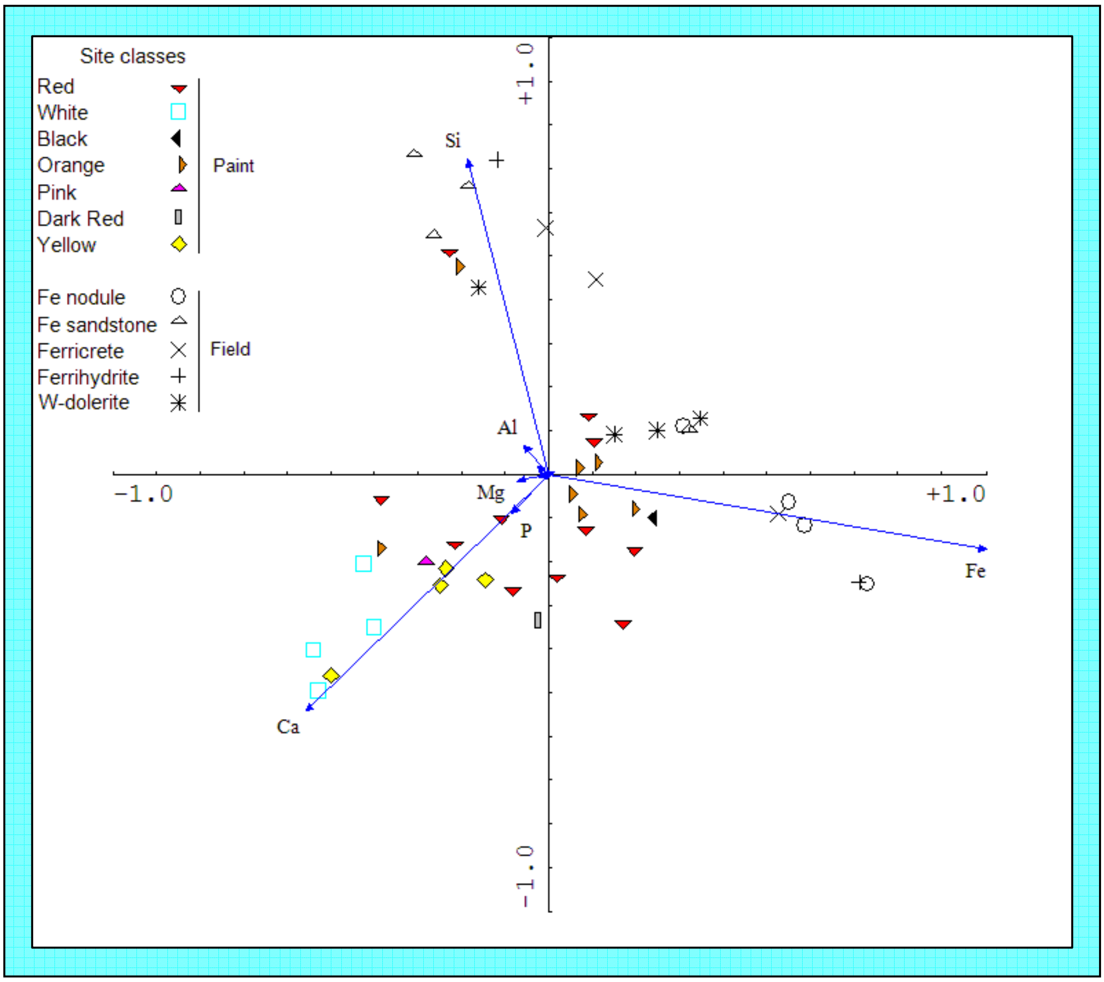

Figure 7.1: Comparison of the Maqonqo Shelter paint samples (EDX) with the local field samples (wet percentage XRF); W - weathered.
Eigenvalues: PCA1 – 55.2; PCA2 – 34.7; PCA3 – 7.8
Scaling –2

percentages presented within the EDX dataset were obtained with an equal degree of accuracy[1]; and d) as the percentage presence of an element decreases in a sample the associated error increases (see Appendix 5.12).

It is important to note that, whilst these assumptions can be considered to be valid for a majority of the paint pigments sampled, they are not as clear-cut in the case of the white (and pink) pigments. In Chapter 6, it was proposed that, as the white pigments are composed primarily of gypsum, and to a lesser extent by anhydrite, bassanite, and whewellite, they were sourced from secondary deposited material from a sandstone shelter located within the same geological landscape as MQ. As a result, the Ca-based minerals found within these pigments represent both the original pigment, together with secondary deposited materials formed within MQ.

Whilst not accurate, this process does, however, allow for a more realistic comparison of the two datasets than would be the case had this ‘extraction’ not been conducted. Finally, this process cannot be considered if no prior knowledge of the mineral composition (and the probable origins of these minerals) is known. Thus, the individual technique comparisons conducted in Chapter 6 are invaluable in this regard.

The resultant PCA, Figure 7.2, displays a similar distribution to Figure 7.1, but with the influence of the secondary deposited Ca now being limited, the distribution of the paint samples is no longer as distinct. The white, and to a lesser extent the pink samples which also contain gypsum as a primary component, still separate out from the locally derived samples, highlighting the differences in elemental sensitivity mentioned above. Several other individual paint samples also separate out due to a dominant Ca presence. This is most probably still the result of a Ca-oxalate presence that was not accounted for during the ‘extraction’ process.

The orange samples most strongly associate with the weathered dolerite samples. Dolerite rocks, when subject to weathering processes, tend to form a weathered outer skin of soft, orange material that is bauxitic in nature. These samples represent, for all intents and purposes, the precursors to bauxite. The similarities in the composition of the orange paints and these weathered samples is interesting, for it means that the orange pigments, like the yellows and reds, need not have been actively sourced from a specific geological formation/outcrop, but could also have been the result of opportunistic scavenging of loose pigmentaceous materials collected at random from the landscape.

This finding suggests that the provenancing of the orange pigments will be technically more difficult than was originally anticipated. On the other hand, from an archaeological point of view, this poses an interesting question – if these pigments were located within the general landscape in a manner similar to those used in the manufacture of the other pigments, why were they not utilised until relatively recently? Or were they used, but this paint weathers at a rate that is on a par with the

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[1] Some detectors favour the detection of certain elements to the detriment of others. As such, the correct ratio of elements cannot be assured, and thus the effectiveness of an ‘extraction’ of minerals based on their molar compositions may be greatly reduced.

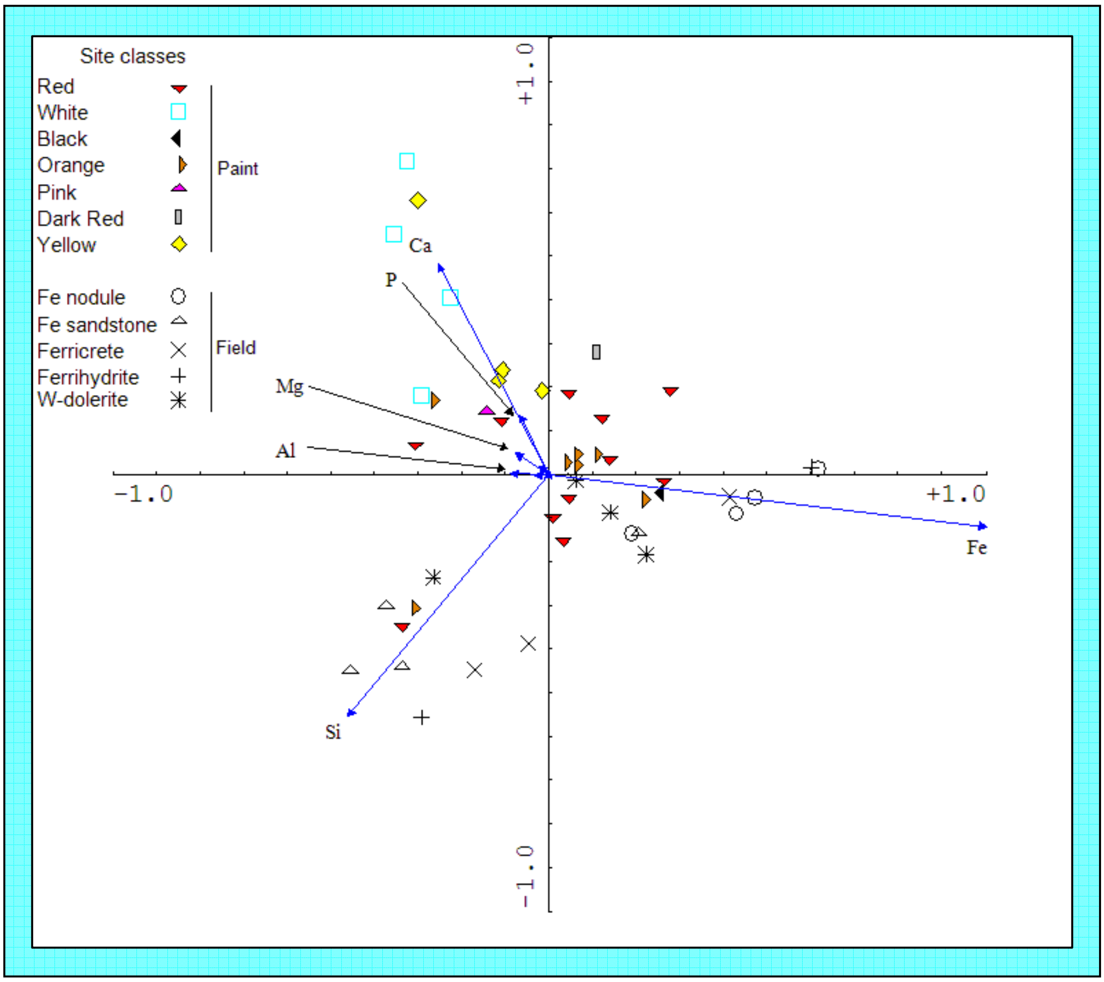

Figure 7.2: Comparison of the EDX Maqonqo Shelter paint samples (with whewellite and gypsum removed) with the local field samples (wet percentage XRF); W - weathered.

Eigenvalues: PCA1 – 59.3; PCA2 – 26.4; PCA3 – 10.1

Scaling -2

white pigments? Further work needs to be conducted in order to establish if this trend is real, however.

Of all of the colours depicted in Figure 7.2, the red colours show the greatest variability. This can be ascribed to a number of different factors, including patchy Ca-oxalate and gypsum deposition across the Shelter rock face, variable amounts of Si presence/contamination (due to differences in paint thickness), differences in weathering (which, in turn, could be related to age), and possibly differences in pigment source. What is interesting to note, however, is that none of the red samples have a strong relation to the Fe nodules. In addition, whilst they were all collected from within a similar vicinity, the Fe nodules themselves tend to display a varied distribution, although this is understandable considering that they were collected from within a river channel and would thus have been subjected to the extreme weathering/leaching conditions associated with this topographical feature.

Although there does not appear to be a definitive relationship between the red paint pigments and the Fe nodules, the tentative trend that does exist is a lot stronger than that recorded between the red paint pigments and the Fe ore bodies (Figure 7.2). This, together with the fact that the Fe nodule and red paint pigment data both tend to be highly variable in nature, still seems to suggest that these materials represent the pigment source for the red (and possibly some of the yellow) paint pigments. Further research into the variability of Fe nodule compositions both within and between watersheds is required, however, in order to try and determine if this pigment source does represent the correct source of the red paint pigments.

7.3 PAINT VS. DISTANT FIELD SAMPLES

This analysis followed a very similar analytical path as described in Section 7.2, with both the datasets being normalised to 100 % and then re-worked so that both shared the same elemental compositions. Figure 7.3 shows a similar distributional pattern to that found in Section 7.2, with the paint samples again remaining distinct from the field samples due to an over-riding dominance of Ca-based secondary depositional minerals, namely gypsum and Ca-oxalate. Figure 7.4 displays the same two datasets, with both the gypsum and Ca-oxalate ‘extracted’ from the EDX data. It is interesting to note that the only distant field sample that seems to display any degree of similarity with the paint dataset is that of Mpate.

This field sample, the only bauxitic sample collected, relates most strongly with the orange paint samples. As mentioned in Chapter 6, it was determined that these paints have gibbsite as a primary component, and as this mineral is most commonly found within bauxitic material, this most probably represents the source for this pigment. These same orange paint pigments also displayed a close affinity to the weathered dolerite samples collected from the local area surrounding MQ (Figure 7.1).

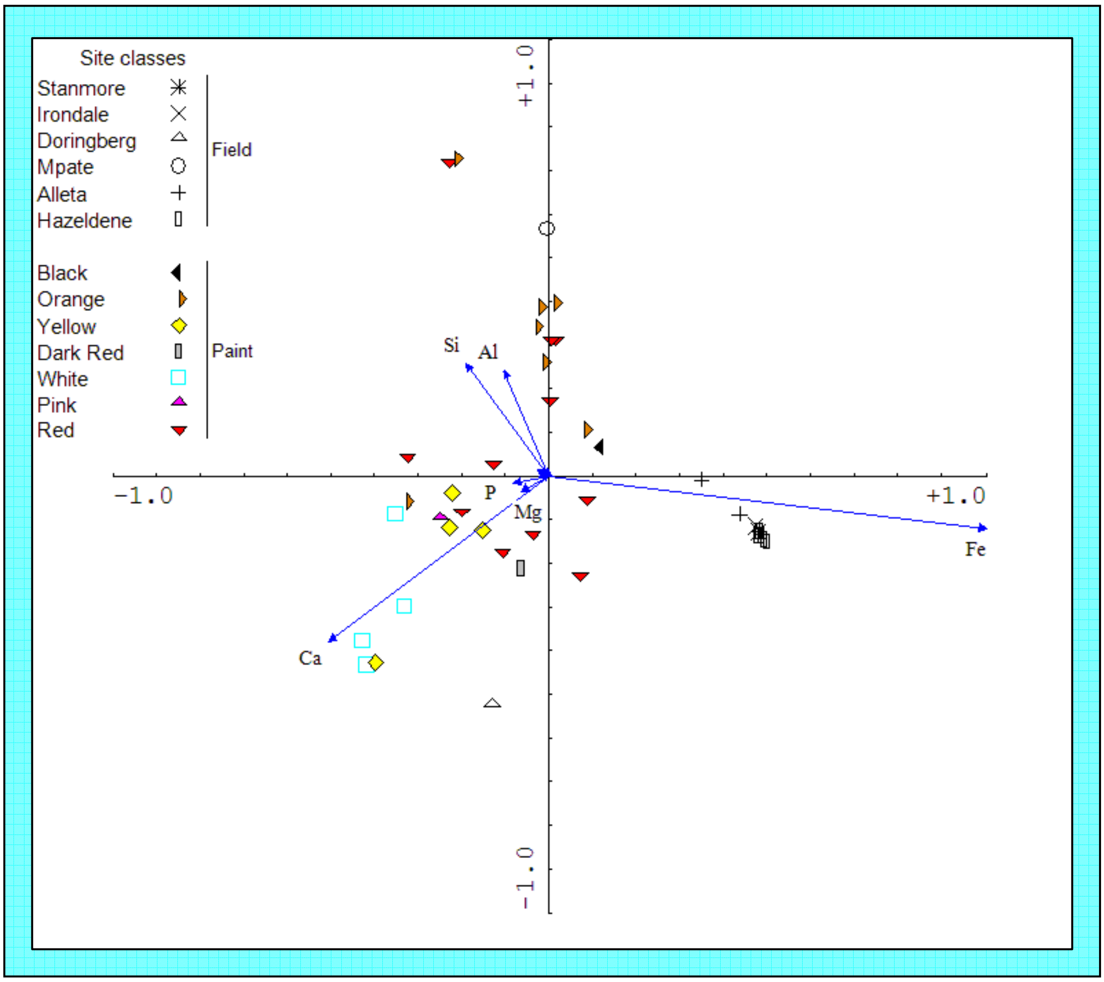

Figure 7.3: Comparison of the Maqonqo Shelter paint samples (EDX) with the distant field samples (wet percentage XRF).

Eigenvalues: PCA1 – 77.2; PCA2 – 16.7; PCA3 – 3.9

Scaling -2

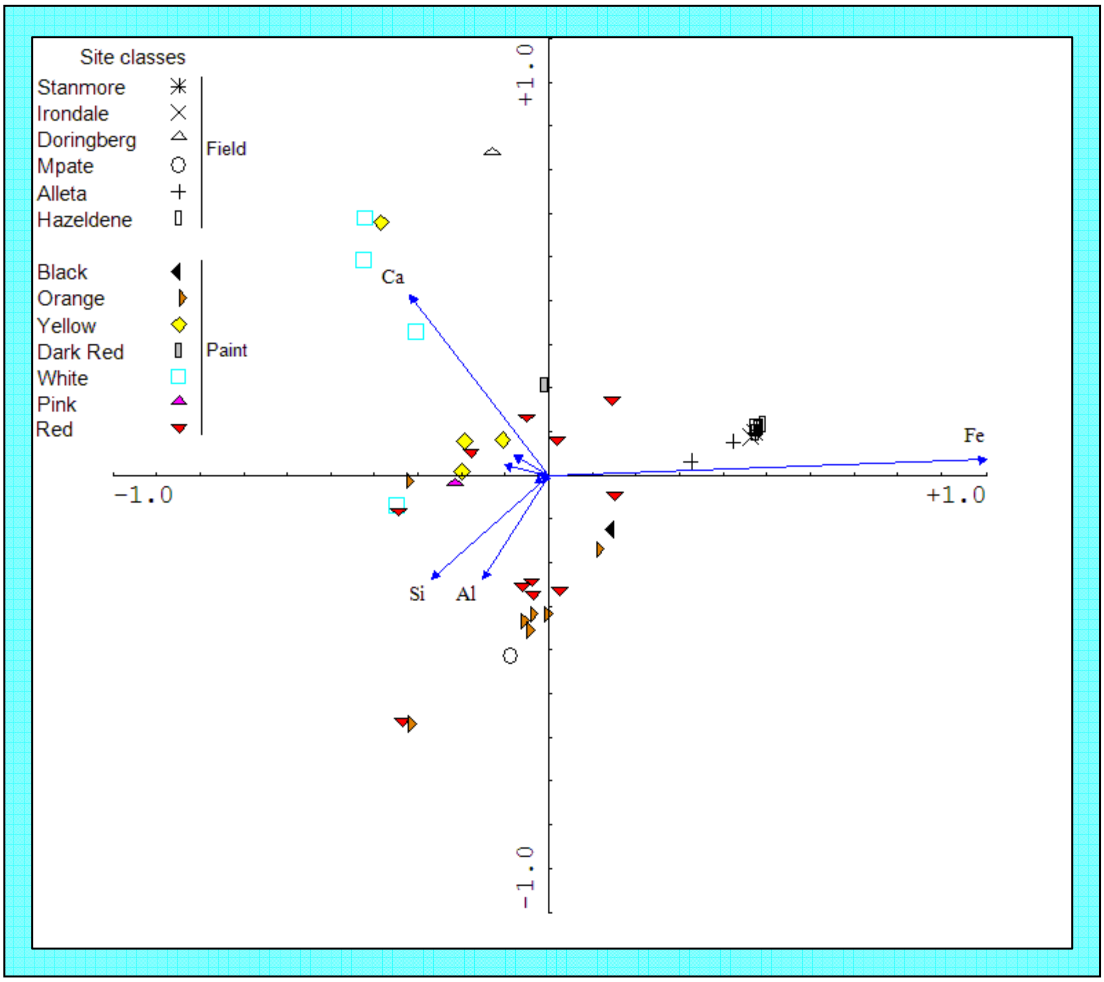

Figure 7.4: Comparison of the EDX Maqonqo Shelter paint samples (with whewellite and gypsum removed) with the distant field samples (wet percentage XRF).

Eigenvalues: PCA1 – 73.8; PCA2 – 17.3; PCA3 – 5.0

Scaling -2

Without an accurate means of comparing the µ-XRF and XRF data, however, there is no way to determine the degree of similarity/dissimilarity that might exist between these two bauxitic sources. As such, no definitive conclusion can be drawn regarding the specific source of this pigment (either a discrete source that was physically 'mined', or a haphazard collection of individual pigmentaceous materials from the general landscape).

Unlike the bauxitic sample, the Fe ore samples do not seem to share any similarity with the paint sample dataset. This could mean one of two things, either a) Fe ores, if they were utilised in the paints manufacture, were not sourced from any of these sites, or b) that Fe ore bodies were not utilised at all, but rather locally derived field material collected from river courses and/or surface exposures (loose as opposed to a coherent geological feature) were utilised instead. If one accepts this latter finding as being correct, then the trends displayed within this PCA diagram fully support the findings discussed in Chapter 6. Only further, and much more detailed analysis of the existing µ-XRD and µ-XRF data, together with the further analysis of additional field samples will aid in clarification of this point.

7.4 CONCLUSIONS

Based on the comparisons described in Sections 7.2 and 7.3, it appears as though, with the exception of the pigments used in the manufacture of the white and pink paints, the pigments utilised in the manufacture of the MQ paints were collected via the opportunistic gathering of materials from the general landscape as opposed to specific geological sources/outcrops. One possible exception to this would be the pigments utilised within the orange paints, which shared characteristics with bauxitic material collected from a recognised bauxite outcrop, located approximately 34 km away as the crow flies (Mpate), as well as with weathered dolerite samples collected from the landscape surrounding MQ.

This finding, whilst indicating that the possibility of provenancing the paint pigments is now more difficult, does suggest that a more intensive investigation into the variable nature of the possible pigment sources, both local and distant, is required. For example, Fe nodules from a wide variety of watersheds, both local and distant, should be analysed to determine just how distinct one watershed's pigments are relative to another. Using information gathered from this type of study, it might still be possible to provenance material back to individual watersheds, with these data providing valuable insights into possible migration and/or trading routes.

CHAPTER EIGHT

PROJECT SUMMATION

8.1 INTRODUCTION

Due to the size of the dataset, the number of different techniques used, and the complexity of the results discussed, it was thought applicable to concisely list the primary findings of this study within this chapter. These have been laid out in a similar manner to the ‘**AIMS AND OBJECTIVES’** listed in Chapter 2. Unless otherwise indicated, references to the discussions concerning each of the points listed below are given with each heading.

In addition, this Chapter will also deal with future aims for this line of research. As no one has conducted research of this nature before in southern Africa, the number of possible future avenues of research is understandably large. In response to this, two broad categories have been created in order to facilitate the discussion.

8.2 SUMMARY OF THE MAJOR FINDINGS OF THIS WORK

8.2.1 Blank sample analyses

8.2.1.1 Maqonqo Shelter blank samples: Section 6.2.3.1

- Gypsum is the primary mineral identified;
- Both Ca and S originate from the groundwater;
- The lack of the evaporite minerals bassanite and anhydrite typically found in association with gypsum indicates that the climatic conditions within MQ are not conducive to their formation. This is further supported by the fact that, even with elevated Sr contents recorded, the transformation of gypsum into bassanite has not occurred;
- The higher quartz and feldspar content within the samples relative to the other three shelters indicate that Ecca sandstone is more friable than the other sandstone lithologies studied.

8.2.1.2 Fergies Cave blank samples: Section 6.2.3.2

- These samples showed elevated C and Ca contents associated with elevated whewellite contents;
- The high temperatures and moisture contents found at this location favour the formation of whewellite, though it probably formed in a different manner to that suggested for MQ (based on differences in climatic regimes experienced by both shelters);

- The low K, Si and Al contents, often associated with quartz, mica and feldspar, indicate a lack of sandstone ‘contamination’ within the samples. This indicates either a) the relatively dense, compact nature of the Cave sandstone makes the surface more resistant to physical erosion when compared to the other sandstones considered within this study, and/or b) the site experienced a high rate of deposition, with the result that a majority of the sample collected is comprised of evaporite minerals.

8.2.1.3 Sheltered Vale blank samples: Section 6.2.3.3

- The samples were composed primarily of the evaporite-type minerals, with only minor sandstone ‘contamination’ being noted (in the form of kaolinite);
- The minerals identified were, in decreasing abundance and dominance within the samples, whewellite (predominantly over 50 %), gypsum and quartz, and weddellite;
- The quartz content, whilst not always high, is present within almost all of the samples analysed. This was not the case for the other sites, and could possibly indicate a higher degree of more uniform surface erosion/instability.

8.2.1.4 Twagwa Shelter blank samples: Section 6.2.3.4

- The following minerals were found within the samples analysed: quartz, muscovite, kaolinite, buserite and greigite (sandstone derived), and schlossmacherite;
- These samples contain no Ca-based minerals, a marked difference from the other three sites sampled;
- The presence of the evaporite mineral schlossmacherite is of mineralogical interest for very little is known about it.

8.2.2 Maqonqo Shelter paint sample analyses

8.2.2.1 White paints: Section 6.2.4.1

- The white pigments were found to be composed primarily of Ca-based minerals;
- Ca is present within four separate mineralogical phases, namely gypsum (dominant), anhydrite, bassanite and whewellite;
- The distribution and dominance of these various Ca-based minerals within the paint samples has important implications for the current understanding of the susceptibility of the paintings to erosion, especially water action;

< The pigments, being gypsum based, are water-soluble;

< The pigments are not easily absorbed into the sandstone matrix;

< When comparing the results of the repeat samples, Paints 9A (top) and 9B (under), it was found that the gypsum content decreased with increasing paint depth, whilst whewellite displayed the reverse relationship;

< The Sr content within the two paint samples also decreased within increasing paint depth, further indicating a change from secondary deposited materials to natural pigment with increasing paint depth (Section 6.2.5);

< Whilst the above findings indicate that both of these minerals were already present within the white pigment when it was applied, the increased gypsum content in the ‘upper’ sample is, in part, the result of *in situ* secondary deposition;

< The most likely source for the white pigments would be rock exudates from sandstone shelter(s) within the nearby vicinity to MQ;

< The top sample (Paint 9A) contained a combination of gypsum, bassanite and anhydrite; the under sample contained only gypsum. This indicates that the gypsum has suffered surface dehydration post the painting event;

< Whilst the whewellite is thought to have been sourced along with the gypsum, another possible source would be addition of organic additives. In either case, as the initial manner of whewellite formation is, as yet, unknown, C isotope work is required to provide clarification of this;

< The ubiquitous distribution of whewellite throughout the sample makes the dating of the sample very difficult, especially if it were sourced from a deposit that formed prior to the paint’s manufacture (Appendix 3.2).

8.2.2.2 Orange paints: Section 6.2.4.2

< The average Fe content within the orange sub-set is greater than that recorded for the red samples;

< The Al contents are on average between two and five times the values recorded for the rest of the paint dataset;

< The mineralogical data could only be resolved for three of the eight samples analysed. Within these, only one sample (Paint 23) contained all four of the Ca-based minerals, gypsum, whewellite, bassanite and anhydrite. The traces resolved for Paints 6 and 7 only displayed a limited gypsum and/or whewellite content;

< Although different paint mixtures could have been utilised for the different images sampled, the thickness of the sample, the position of the images within the Shelter and the youth of the images are probably responsible for the absence of Ca-containing minerals;

< Paints 6 and 7 contain the highest combined Al and Fe values recorded for the entire dataset, and correspondingly low Ca and S values, indicating that these samples contain almost ‘pure’ inorganic pigment. Three deductions can be made, namely a) gypsum and whewellite are the result of secondary deposition post the painting event; b) these evaporite minerals were not present within the original paint pigment; and c) their lack of dominance within the samples analysed indicates that they have not yet formed, which in turn indicates that the images are relatively young when compared to the rest of the paint dataset;

< The one mineral common to the three samples analysed, both in presence and dominance, is gibbsite;

< The strong degree of similarity in both the elemental and mineralogical composition of Paints 6 and 7 strongly indicates that the same pigment was utilised in the production of both images. This could imply that they share similar ages and, possibly, the same artist;

< All of the samples displayed elevated Ti levels;

< There are two suspected pigment sources. A majority of the paints analysed displayed an elevated Al content and contained gibbsite, suggesting that they were sourced from bauxitic material. Two of the samples (Paints 4 and 24) did not contain high Al contents, however. It was determined that these latter two samples were probably sourced from the soft inner ochreous material found within Fe nodules;

< As both the Fe nodules and the bauxitic material derived from materials located within the Ecca Group within KwaZulu-Natal have been shown to contain elevated Ti levels, at levels consistent with those displayed within the paint samples analysed, the pigment sources were most likely sourced within the central to northern KwaZulu-Natal region;

< No trend distinguishing a particular painting style with a specific pigment source was noted. Two possibilities thus exist, a) both painting styles within MQ were painted concurrently; and/or b) the same inorganic pigment sources were used over a protracted period of time;

< The wall fragment does not display a close affiliation with any of the eight samples collected.

8.2.2.3 Yellow paints: Section 6.2.4.3

< Four samples were collected from one image (three top and one under), thus allowing for an investigation of the heterogeneity of the painting upon the wall and, as a consequence, the robustness of the methodology being employed within the current study;

< Two of the samples (Paints 28 and 29) displayed very similar elemental compositions, whilst the last ‘top’ sample (Paint 11B) displayed a higher Ca content. This highlights the high degree of variability that exists at the micro-environmental level upon a shelter wall;

- The dominance of whewellite within the surface samples, yet seemingly decreasing with increasing paint depth, supports the theory that this mineral formed upon the surface of the painting post the painting event;
- A consistent combination of goethite and haematite, together with a lower Al and elevated Ti contents, indicate that these samples were probably sourced from the soft inner cores of Fe nodules found locally in KwaZulu-Natal.

8.2.2.5 Red paints: Section 6.2.4.4

- The red colours contained the highest degree of variation of all the colours analysed. Over 70 % of this variability is governed primarily by the relationship between the Fe and Ca containing minerals, the latter being dominated by gypsum;
- The quartz content is comparable with that of the blank sample set, from which can be inferred that the red samples collected are ‘thinner’ than those of the other datasets;
- The thin nature of the paints, the erratic distribution of the whewellite, the dominance of gypsum and, to a certain extent, quartz, all support the hypothesis that the paints are, at least in part, absorbed within the upper surface of the shelter wall. This, together with the strong staining ability of haematite, is probably the single most important reason why the red pigments have outlasted images painted in other colours;
- The fact that the pigment is absorbed into the Shelter wall also gives an indirect indication as to the nature of the original paint mix i.e., fluid, as opposed to a more ‘paste-like’ consistency as has been described in the case of the white pigments;
- Most of the red samples contain similar amounts of Al to those in the yellow pigments. The µ-XRD data indicate that goethite is indeed present, though, due to the masking effect of haematite, this is not automatically noted;
- The similarity in Ti content to that of the yellow pigments, together with the mineral composition, tends to indicate that these pigments are also probably sourced from locally derived Fe nodules. Though only one geological source has been suggested, the high degree of variability experienced regarding the Fe content within the samples could indicate that these pigments were collected from a number of different locations, and/or the source materials had been subject to variable degrees of weathering. Differences in painting ages might also account for this variation;
- A comparison of the individual painting styles indicates that there is no specific style preference associated with the pigment source selection.

8.2.2.6 Dark red paint: Section 6.2.4.5

< Although similar in many respects to the red samples analysed, this sample contains gibbsite, but not whewellite, goethite or magnetite;

< All of the traces obtained are dominated by gypsum, and to a lesser extent bassanite, with both haematite and gibbsite having a combined presence of about 20 % or less in all cases;

< The low Al content precludes bauxite as a possible pigment source;

< The lack of magnetite precludes the use of the outer rinds of Fe nodules;

< This sample displays an elevated Mn content. The only source (of which I am aware) that has, as its core constituents, haematite and Mn oxides and, which is easily accessible within the local landscape, is plinthite.

8.2.2.7 Pink samples: Section 6.2.4.5

< Their slightly elevated Fe content relative to their Ca and S content (when compared to the white pigments) suggests that red and white pigments were blended together to create the pink colours;

< The elevated gypsum content identified further supports this hypothesis.

8.2.2.8 Black paint: Section 6.2.4.5

< It is strongly dominated by Fe, having the highest recorded Fe content of the entire paint dataset;

< The Mn content is also much greater than almost all of the other paint samples;

< In addition to quartz, haematite and goethite (the latter two present in ratios similar to those displayed within the red samples), the black sample also contained maghemite;

< Maghemite is an Fe mineral that is formed in the presence of heat and organic material. Whilst it cannot be categorically stated that fire was used in the manufacture of this paint pigment, this mineral’s presence is strongly suggestive of this;

< When comparing the EDX data collected for the black sample with that from a goethite rich Fe nodule inner core (Site 6B), several similarities are easily apparent: 1) both reflect very high Fe contents; 2) both display relatively low Al contents (especially when compared to the other sampled pigment sources); and 3) their respective Si and Mn contents are also comparable. This is thus the suggested Fe source from which the paint pigment was manufactured.

8.2.3 Results from the excavated pigmentaceous material (Maqonqo Shelter)

- The dominant mineral phase that changed with increasing depth/age amongst the large excavated material was feldspar, which reflected an increase in dolerite samples within the third excavated layer (Section 6.3.2);
- With the exception of a few samples from layers 7 and 11, all of the small excavated material analysed display very similar elemental compositions (Section 6.3.3);
- The physical appearance of the small excavated material tends to suggest that they originated from a rock outcrop as opposed to having been collected from a riverbed (Section 6.3.3);
- A majority of the small and large excavated materials were probably collected from a specific Fe-enriched shale outcrop (Section 6.3.3 and Section 6.3.2, respectively);
- Similarities displayed within the compositional and geological make-up of the samples collected from each layer suggest that there was little change in the selection criteria for both the small and large excavated materials for the duration of the Shelter's utilisation (Section 6.3.3 and Section 6.3.2, respectively).

8.2.4 A comparison of the excavated pigmentaceous material and the paint samples (Maqonqo Shelter)

- The distinction between the two datasets is based primarily on the presence of secondary deposited minerals within the paint samples analysed, namely whewellite, gypsum, anhydrite and bassanite (Section 6.3.5);
- Even when correcting the data to take the secondary evaporite minerals into account, a significant distinction still exists between the paint and excavated material datasets (Section 6.3.5);
- The only exception is the orange paints, which show some similarity to some of the excavated samples (weathered dolerite). Although they share similar geological characteristics, a more detailed study of the minor elemental composition of these two datasets is required in order to determine if they were, in fact, obtained from the same geological source (Sections 6.3.5 and 7.2).

8.2.5 Results from the Local and Distant field pigments collected from areas surrounding Maqonqo Shelter (Section 6.3.4)

- The degree of weathering experienced within the locally derived samples had a much greater impact on the variability of the elemental and mineralogical compositions of the samples in question when compared to the distant field samples;

- As expected, all the samples separated out according to their geological composition, a trend that supports the methodology employed.

8.2.6 A comparison of the field and the paint samples (Maqonqo Shelter) (Section 7.3)

- The only bauxitic sample collected showed a strong correlation to the orange paint samples;
- The Fe ore samples do not seem to share any similarity with the paint sample dataset;
- Based on the comparisons conducted, it appears as though, with the exception of the pigments used in the manufacture of the white and pink paints, the pigments utilised in the manufacture of the MQ paints were derived from the opportunistic gathering of materials from the general landscape as opposed to from specific geological sources/outcrops;
- One possible exception would be the pigments utilised within the orange paints. These paint samples shared characteristics with both the bauxitic material collected from a recognised bauxite outcrop, as well as with weathered dolerite samples collected from the surrounding landscape;
- This finding, whilst indicating that the possibility of provenancing the orange paint pigments is now more difficult, does suggest that a more intensive investigation into the variable nature of the possible pigment sources, both local and distant, is required.

8.2.7 A comparison of the paint samples from all four sample sites

8.2.7.1 White paint samples: Section 6.2.6

- Whilst the white samples from SV and MQ are dominated by whewellite and gypsum (indicating that these minerals were probably present within the pigments when they were applied), the presence of quartz, sanidine and apatite in the SV samples indicates a degree of shelter wall ‘contamination’, with anhydrite, bassanite and glushinskite indicating climatic variations favouring various evaporite depositional regimes;
- The TW white paint samples display a minimal presence of the secondary deposited minerals common in the other shelters studied. The one mineral that is dominant within these samples is minamiite. As this mineral was not identified within any of the blank samples collected, it is likely that this mineral originates from within the original pigment. Very little information describing this mineral is available, however, with none being available concerning its distribution, or possible source(s), within the South African landscape. As it is known that this mineral forms where acid, often ore-bearing, solutions have altered orthoclase feldspar-rich rocks, it is presumed that this mineral can form as a precipitate;

- The Zn contents recorded within the TW white paints are generally between 10 to 40 times greater than those recorded for any of the other paint samples within the paint dataset as a whole. The source of this Zn has yet to be determined, but greigite, another mineral common to the white paints, is known to accumulate Zn as an impurity within its crystal structure.

8.2.7.2 Red paint samples: Section 6.2.6

- Fergies Cave is distinguished from the remaining three shelters, in that these samples contain weddellite, in conjunction with whewellite. This mineral, not typically found at the other three sites, is the product of a climatic regime specific to this Shelter;
- The SV red samples could be distinguished from MQ red samples due to the presence of wall 'contaminants' in a manner similar to that described for the white samples;
- The TW samples indicate a change in pigment source and/or manner of paint manufacturing technique relative to the other sites, for these red samples contain minamiite. This mineral is not red, but white in colour, suggesting that this mineral must represent a paint additive (it is not present within the blank samples analysed);
- The red samples from all four shelters show haematite as being the primary pigment within the red paints;
- With the exception of only one sample from TW, no goethite was found within any of the red samples collected from the three additional sites. This could indicate one of two possibilities: 1) the pigment was sourced from a 'pure' haematite source, or 2) the pigments are the result of calcined goethite. Without further analysis of field samples collected from nearby vicinities of each of the respective shelters, however, potential sources for this pigment cannot be proposed.

8.2.8 Considerations for future paint sampling and analysis (Section 6.2.4.6)

- During the course of this study it was shown that four contributing components influenced the paint sample results i.e.,
    1) The rock wall - represented mainly by quartz, although feldspars were also noted;
    2) Secondary evaporite deposits – primarily consisting of gypsum, though bassanite, anhydrite and glushinskite were also present to a much lesser extent. Oxalates can also form part of this component, though in the case of MQ, this seems to be a rare occurrence;
    3) Secondary oxalate deposition - predominantly represented by whewellite, though weddellite was noted in a few cases. This component is recorded as a distinct entity based on the unequal distribution of oxalate minerals between the paint and blank samples collected from MQ (53 % vs. 9 % presence, respectively);

4) The paint pigment - This component represents the remnants of the material applied to the wall by the San artist.

< Not all of these components need be present within a particular sample, their presence being dependent on a number of factors including: a) the manner in which the paint pigment was manufactured; b) the age of the painting; c) the degree of exposure to weathering that the specific image has been subjected; and d) the specific components that were utilised in the creation of the pigment, be they organic or inorganic, or both;

< The collection of blank samples is vital for the characterisation of the secondarily deposited materials;

< The presence of secondarily deposited minerals decrease within increasing paint depth. To mitigate these potential influences, a two-step sampling regime is proposed in which double sampling is conducted at each sampling point. This would allow for the comparison of both the surface depositional features (if present) and the 'true' paint pigments;

< Care must be taken not to sample any underlying paint or rock substrate that might unduly affect the analyses. One way of mitigating this influence would be to sample thicker paint layers;

< The study of paints from additional shelters within the vicinity is needed in order to determine to what extent these findings apply to paints and shelters in general.

8.2.9 Inter-Technique Comparisons (Appendix 5.15)

8.2.9.1 EDX vs. XRF

< Although a large dataset was available, only nine samples were used to compare the two techniques;

< The XRF data were divided into '*dry elemental percentages*' and '*wet elemental percentages*', based on whether or not the Loss on Ignition value had been re-worked back into the data;

< Both datasets were normalised to 100 %;

< It was determined that, for all future comparisons between these two techniques, the '*wet elemental percentage*' data must be used as they most closely correlated with the recorded EDX data.

8.2.9.2 EDX vs. Micro-XRF

< Only data for three standard samples common to both datasets could be determined;

< After simplification of the datasets, only a few elements were common to both datasets, namely K, Ca, Ti, Mn and Fe;

< Fe accounted for more than 95 % of the inherent variance;

< Based on the information available, the two datasets are not comparable.

8.2.9.3 XRF vs. Micro-XRF

- Only data for three standard samples common to both datasets could be determined;
- Only five elements were common to both, namely Fe, Mn, Ca, K and Ti, within which Fe accounted for over 97 % of the inherent variance;
- Based on the information available, the two datasets are not comparable.

8.2.10 Overall conclusion (Section 6.4)

- This study has shown that, even with a small sample set (both in sample size and number), and on relatively poor quality samples, the combined use of chemical and mineralogical techniques allows for the distinction between the various sites to be made. Obviously, access to better (thicker) paint samples would only result in better results;
- The importance of correctly identifying the mineralogical phases within which the elements identified reside is highlighted, for this has a direct bearing on the susceptibility of the minerals to chemical and/or mechanical erosion and, subsequently, will have an important bearing on the development of strategies to prevent these forces;
- The durability of the individual pigments is most probably due to the nature of their pigments, as opposed to any purpose or design by the artists (compare the white and red pigments);
- The data obtained provide information about the individual shelters, including the microclimate experienced within each, the potential sources of the elements/minerals used in the manufacture of the paints, the nature of the sandstone matrix, and can also provide indirect information regarding the shelter’s susceptibility to erosion;
- The three minerals that were identified as being of particular significance are whewellite, weddellite and gypsum. Their presence within the blank samples strongly indicates that these minerals are of natural, and not anthropogenic, origin;
- Different climatological and geological locations influence the dominance (and possibly the chemical pathway) of the Ca-oxalate phases found within the shelters. This has important implications for conservation, dating and restoration methodologies that are being/have been considered;
- A majority of the MQ paint traces in which no Ca-oxalates were detected contained elevated levels of haematite (25 of the 40 traces without Ca-oxalates). The remainder of the samples were dominated by either gypsum or gibbsite. This might be an indication of differences in paint recipes based on colour, or a sign of painting age i.e., the whewellite has been lost from the older images;
- The unequal distribution of oxalate minerals between the paint and blank samples collected from MQ (53 % vs. 9 % presence, respectively) tends to indicate that the source of the organics utilised

in the formation of the oxalates probably originates from within the paints themselves. This would help to explain why Ca-oxalates were seldom found beneath the paint samples (Section 6.2.4.6);

< The above point has obvious implications for rock art dating, with the Ca-oxalates either representing a relative age for each painting based on conversion rates of the organic additives within the paints by biological agents (if they were indeed used), a minimum age if the Ca-oxalates formed post the painting event via inorganic processes, or totally misleading dates if Ca-oxalates were specifically sourced and utilised in the manufacture of the paints (Section 6.2.4.1);

< The soluble nature of gypsum, together with its ubiquitous presence throughout the paint dataset, means that the application of water to the rock surface should be avoided at all costs (Section 6.2.4.6);

< Physical weathering appears to be the primary threat to the paintings, with the colours that reside upon the sandstone surface being the most susceptible (Section 6.2.4.6);

< The synchrotron data have been shown to be invaluable in aiding in the characterisation of the pigments, whilst also fulfilling the other requirements of being non-destructive (post the sampling event), as well as only requiring very small sample sizes;

< More field samples are required in order to adequately determine similarities and differences between different geological materials and/or geological sources (Section 6.3.4);

< Citing the various differences listed above relating to differences in paint recipes, pigment sources, shelter geologies and climatic regimes, a ‘one size fits all’ approach to the management/study of rock art shelters is therefore not recommended.

8.3 FUTURE WORK

8.3.1 Inorganic Research

With regard to the paints, this study, like the few before it, has concentrated almost exclusively on their inorganic composition. This is vital for our understanding of the nature of the paints, but falls short of providing all the answers that conservationists and archaeologists alike desire i.e., what were the main components used to manufacture the paint and what were the sources of those components. In order to achieve this, one needs quantitative elemental and mineralogical data. As a means of obtaining this, the paint sampling strategy has to be modified slightly in order to allow for the collection of paint pigments that can be sectioned. Only once samples of known dimension can be obtained can quantitative data be accurately determined.

That said, further work on the existing µ-XRD data is required. A very detailed investigation of these data will give an indication as to the inherent crystal size of the haematite and goethite mineral fractions, among others. This is important for an understanding of potential sources, for variability in crystal size could give an indication as to possible source materials[1] and, possibly, manufacturing techniques[2]. Crystal size also influences hue and value of the colour, and a greater understanding of this component of the paint samples will aid in our understanding of the visual colour.

An additional avenue of research must try to resolve whether the paint constituents were heated. Although this form of pigment alteration has been mentioned in the literature it has not been investigated. This could have important implications on the sourcing of the mineral pigments used, as well as the methods employed in their manufacture. A variety of techniques are available which can be used in order to either support or refute the use of fire-amended materials as pigments (e.g. Ruan and Gilkes, 1996; Helwig, 1997).

A further development of this topic is the suggestion that the yellow pigments on shelter walls can be converted to red hues if conditions are suitable, and enough time has elapsed (Cook *et al.*, 1989). That particular study, conducted in Queensland, Australia, noted that the grain-size measurements of haematite in the paints and those forming from goethite ochre fragments were comparable. Upon investigation, it was determined that under conditions of low relative humidity, elevated temperatures and fine goethite crystal size, a change from yellow to red could occur naturally. This has important implications concerning the relative dating technique (see Section 6.2.1), in which the early red monochromes might have originally been yellow (or yellow and red). Although this process can be considered doubtful in the southern African region, it should still be investigated, especially when one considers the fact that not only were these shelters lived in (and would thus have had cooking fires), but also the areas in which the shelters are located are frequently exposed to veld fires.

Finally, the field dataset has to be greatly enlarged, with samples of each geological material (e.g. Fe ore, shale etc.) needing to be sampled over an extended area in order to determine if any changes in composition occur within these materials with increasing distance from the shelter. In addition, repeat samples have to be collected from each sample point in order to determine any possible variations in the source material being sampled. For this work, standard XRD and XRF can be used.

In conclusion, additional work needs to be conducted in the following areas: a) to determine if the pigments were modified via heating; b) to determine the source of the Ca-oxalates, for this will aid in determining the accuracy of the ^{14}C dates obtained; c) the field database needs to be greatly enlarged, and notes on the variability of the geological material, both at source and over distance, have to be determined; c) all of these analyses should be conducted at a number of different sites situated in different geographical areas in order to allow for comparisons over distance; and, finally, d) to compare paint pigments collected from the four different painting regions (based on style; see Chapter 3.2) in order to determine if the different styles have associated paint recipes.

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[1] The shift in the d-spacing in relation to the metal substitution within the crystal structure would indicate specific sources e.g. the amount of Al, Cr, V etc. within the Fe oxides.

[2] As an example, it may be possible to distinguish between ‘natural’ and ‘manufactured’ haematite based on the level of ‘order’ displayed within their respective diffraction patterns (Helwig, 1997).

8.3.2 Organic Research

To the best of my knowledge, no work has yet been conducted in order to determine the possible organic nature of San paint pigments. This is surprising, considering the amount of literature detailing the conflicting reports as to the nature of the assumed organic binding medium.

Some work on the determination of archaeological organic material has been conducted in South Africa, but unfortunately none on the rock art pigments. A number of techniques can be used to assist in the determination of the organic component, including FTIR and gas chromatography (e.g. Scott *et al.*, 1996; Colombini *et al.*, 1999), and possibly reversed-phase high-performance liquid chromatography (RP-HPLC). This last technique is very sensitive, and can use extremely small samples – ideal for rock art research (Vallance, 1997).

In addition to these analyses, a further possibility is to create a set of ‘mock’ paints. These paints will use natural products that have been suggested in the literature. It is possible that by working in ‘reverse’ i.e., creating fake paints (a set of standards) against which the originals can be compared, the determination of the original pigments may be achieved.

8.4 CONCLUSIONS

An interesting facet of this study, although not directly addressed, concerns what the results do *not* show with respect to the compositional nature of the pigments analysed. Most texts available today list a number of pigment sources stated to have been utilised in the manufacture of the San parietal rock art. This study has shown that very few of these potential sources were utilised within the four shelters investigated. In addition, this study has also highlighted the presence of minerals about which little is known, yet which appear to be commonly associated with parietal rock art the world over.

The Ca-oxalates, present within a majority of the paint samples yet not in the blank samples, strongly indicate that organic components were originally present within the paints when they were first applied (these minerals representing alteration products derived via biological processes). This, together with the findings that calcination might also have been used in the manufacture of certain colours, both indicate just how much work in this field is still required in order to more fully understand the complexities associated with the San heritage.

The need for further research is clear, but it must be remembered that the paintings represent our national heritage, and as such are invaluable. As a result, the techniques to be used must be able to cope with very small samples, and should, as far as possible, be non-destructive. This would allow for the re-use of the samples in other, future, experiments. It is obvious that not all of the techniques mentioned herein will fulfil both of these requirements, and when this is the case, careful consideration as to the value of the data to be gained by the destruction of the sample as opposed to the loss of the sample for future research, must be taken.

However, if we are to gain a proper understanding as to the composition and manufacture of the paints, and by default all the associated information (e.g. determination of trading; relative dating techniques; determination of territorial boundaries, etc.), some balance will have to be achieved. The proposed research can, it is believed, achieve that balance.

Finally, the method by which the paint samples are collected and prepared should also be standardised, so as to allow for inter-study comparisons – something that cannot currently be reliably conducted.

REFERENCES

Abdel Aal, A. Y. (1998) **Mineral and chemical compositions of basalts in the neighbourhood of Giza, Egypt**. *J. Afr. Earth Sci.*, **26**: 101 – 117. In Mallory-Greenough, L. M., Greenough, J. D., Dobosi, G., and Owen, J. V. (1999) **Fingerprinting ancient Egyptian quarries: preliminary results using laser ablation microprobe - inductively coupled plasma - mass spectrometry.** *Archaeometry* **41**: 227 - 238.

Adams, F., Janssens, K. and Snigirev, A. (1998) **Microscopic X-ray fluorescence analysis and related methods with laboratory and synchrotron radiation sources.** *Journal of Analytical Atomic Spectrometry* **13**: 319 – 331.

Anderson, G. C. (1991) **Andriesgrond revisited: material culture, ideologies and social change.** (BA Hons. Th.), Department of Archaeology, University of Cape Town. Unpublished.

------------ (1994) The social and gender identity of hunters and herders in the southwestern Cape. (BA Masters. Th.), Department of Archaeology, University of Cape Town. Unpublished.

Anderson, K. A., Magnuson, B. A., Tschirgi, M. L., and Smith, B. (1999) **Determining the geographic origin of potatoes with trace-metal analysis using statistical and neural-network classifiers.** *Journal of Agricultural and Food Chemistry* **47**: 1568 - 1575.

Apthorp to Péringuey (1913) **South African Museum Correspondence 1913-19**. In Rudner, I. (1982) **Khoisan pigments and paints and their relationship to rock paintings.** *Annals of the South African Museum* **87**: 1 - 281.

Adan-Bayewitz, D., Asaro, F., and Giauque, R. D. (1999) **Determining pottery provenance: application of a new high-precision x-ray fluorescence method and comparison with instrumental neutron activation analysis.** *Archaeometry* **41**: 1 - 24.

Baines, T. (1842 – 53) **Journal of residence in Africa**. In Rudner, I. (1982) **Khoisan pigments and paints and their relationship to rock paintings.** *Annals of the South African Museum* **87**: 1 - 281.

Barron, V. and Torrent, J. (1984) **Influence of aluminium substitution on the color of synthetic hematites.** *Clays and Clay Minerals* **32** (2): 157 – 158.

------------ (1986) **Use of the Kubelka-Munk theory to study the influence of iron oxides on soil colour.** *Journal of Soil Science* **37**: 499 – 510.

Bassett, S. T. (2001) **Rock paintings of South Africa: Revealing a legacy.** David Phillip, Cape Town. ISBN 0-86486-500-7.

Beazley, M. J., Rickman, R. D., Ingram, D. K., Boutton, T. W. and Russ, J. (2002) **Natural Abundances of Carbon Isotopes (^{14}C, ^{13}C) in Lichens and Calcium Oxalate Pruina: Implications for Archaeological and Paleoenvironmental Studies.** *Radiocarbon* **44** (3): 675 – 683.

Bigham, J. M. and Ciolkosz, E. J. (Eds) (1993) **Soil Colour.** Madison, Wisconsin: Soil Science Society of America Special Publication 31. ISBN 0-89118-802-9.

Binneman, J. and Hall, S. (1993) **The context of four painted stones from the south-eastern and eastern Cape.** *South African Field Archaeology* **2**: 89 – 95.

Binneman, J. (1999) **Mummified Human Remains from the Kouga Mountains, Eastern Cape.** *The Digging Stick* **16** (2): 1 – 3.

Bish, D. L. and Post, J. E. (1988) **Quantitative analysis of geological materials using X-ray powder diffraction data and the Rietveld refinement method.** *Geol. Soc. Am. Abstr. Programs*, **20**: A223. In Jercher, M., Pring, A., Jones, P. G., and Raven, M. D. (1998) **Rietveld X-ray diffraction and X-ray fluorescence analysis of Australian aboriginal ochres.** *Archaeometry* **40**: 383 - 401.

Blundell, G. (2004) **Nqabayo's Nomansland: San Rock Art and the Somatic Past.** *Studies in Global Archaeology 2*. Uppsala. ISBN 91-973212-0-6.

Botha, G. A. (1992) **The geology and palaeopedology of late quaternary colluvial sediments in northern natal.** Memoir of the Geological Survey of South Africa No. 83, Council for Geoscience, Pretoria, South Africa. ISBN 1-875061-36-3.

Bousman, B. (1988) **Prehistoric settlement patterns in the Senqunyane Valley, Lesotho.** *South African Archaeological Bulletin* **43**: 33 - 37.

Bower, J. M. and Thorpe, A. G. (1976) **Human remains from Lake Mungo: discovery and excavation of Lake Mungo**, In Kirk, R. L. and Thorpe, A. G. (eds) (1976) **The Origin of Australians.** *Australian Inst. Aboriginal Stud.*, Canberra. In Jercher, M., Pring, A., Jones, P. G., and Raven, M. D. (1998) **Rietveld X-ray diffraction and X-ray fluorescence analysis of Australian aboriginal ochres.** *Archaeometry* **40**: 383 - 401.

Braak, C. J. F. and Smilauer, P. (1999) **CANOCO FOR WINDOWS V. 4.02:** Microcomputer Power, Ithaca, New York, The United States of America.

Brabers, A. J. M. (1976) **Aluminium.** In: Coetzee, C. B. (Ed.) (1976) **Mineral Resources of the Republic of South Africa.** Fifth edition, Department of Mines, Geological Survey, Handbook 7. ISBN 0 621 064351.

Breunig, P. (1986) **Archaeological research in the Upper Brandberg/Namibia.** *Nyame Akuma* **27**: 26 – 27.

Brown, A. G. (1985) **Traditional and multivariate techniques in the interpretation of floodplain sediment grain size variations.** *Earth Surface Processes and Landforms* **10**: 281 – 291.

Burkitt, M. C. (1928) **South Africa's past in stone and paint.** Cambridge University Press, London.

Butler, G. (2001) **Sister Mariya's account of San painting in the Tsolo District in the late 1920's and early 1930's.** *Southern African Field Archaeology* **10**: 16 – 18.

Cable, C. (1984) **Economy and Technology in the Late Stone Age of southern Natal.** Cambridge Monographs in African Archaeology 9, B.A.R. International Series 201, B.A.R. Publications, Great Britain.

Camp, K. G. T. (1999) **A Bioresource classification for KwaZulu-Natal, South Africa.** (MSc Agric. Th.) School of Applied Environmental Sciences, Range and Forage Resources, University of Natal, Pietermaritzburg, South Africa. Unpublished.

Cariati, F., Rampazzi, L., Toniolo, L. and Pozzi, A. (2000). **Calcium oxalate films on stone surfaces: Experimental assessment of the chemical formation.** *Studies in Conservation* **45**: 180 – 188.

Carter, P. L. (1970) **Late Stone Age Exploitation patterns in southern Natal.** *South African Archaeological Bulletin* **25**: 55 - 58.

------------- (1977) **The prehistory of eastern Lesotho.** (PhD Th.) University of Cambridge, United Kingdom. Unpublished.

CEM, (2000) **EDX (Energy Dispersive X-ray Micro-analysis).** A handout obtained from the Centre for Electron Microscopy, University of Natal, Pietermaritzburg, South Africa. Unpublished.

Clarke, J. D. (1958) **The Chifubwa Stream Rock Shelter, Solwezi, Northern Rhodesia.** *South African Archaeological Bulletin* **33**: 21 – 24.

Clarke, J. D. (1959) **The Prehistory of Southern Africa.** Penguin Books, Harmondsworth.

Clottes, J. (1993) **Paint analyses from several Magdalenian Caves in the Ariège region of France.** *Journal of Archaeological Science* **20**: 223 – 235.

------------- (1997) **New laboratory techniques and their impact on palaeolithic cave art.** *Memoirs of the California Academy of Sciences* **23**: 37 - 45.

Coetzee, C. B. (Ed.) (1976) **Mineral Resources of the Republic of South Africa.** Fifth edition, Department of Mines, Geological Survey, Handbook 7. ISBN 0 621 064351.

Colombini, M. P., Modugno, F., Giacomelli, M, and Francesconi, S. (1999) **Characterisation of proteinaceous binders and drying oils in wall painting samples by gas chromatography-mass spectrometry.** *Journal of Chromatography Amsterdam.* **846**: 133 – 124.

Conard, N. J., Breunig, P., Gonska, H. and Marinetti, G. (1988) **The feasibility of dating rock paintings from Brandberg, Namibia, with ^{14}C.** *Journal of Archaeological Science* **15**: 463 – 466.

Cook, N. D. J., Davidson, I. and Sutton, S. (1989) **Seeing red in Queensland.** *Nature* **342**: 487.

Council for Geoscience, (2002) **3028 KOKSTAD 1:250000 GEOLOGICAL SERIES.** Council for Geoscience, Private Bag X112, Pretoria.

Currlé, L. (1913) **Notes on Namaqualand Bushmen.** *Transactions of the Royal Society of South Africa* **3**: 113 – 120.

Davies, O. (1975) **Excavations of Shongweni South Cave: the oldest evidence to date for cultigens in southern Africa.** *Annals of the Natal Museum* **22** (2): 627 - 662.

Davis, J. C. (1973) **Statistics and data analysis in Geology.** Kansas Geological Survey, John Wiley and sons, Inc., New York. ISBN 0 471 19895 1.

de Decker, R. H. (1981) **The Geology of the Kokstad Area: Explanation Sheet 3028 (1:250000).** Geological Survey, Government Printers, Private Bag X85, Pretoria.

de Laporte to Péringuey (1914) **South African Museum Correspondence 1913-19**. In Rudner, I. (1982) **Khoisan pigments and paints and their relationship to rock paintings.** *Annals of the South African Museum* **87**: 1 - 281.

Deacon, J. (1994) **Rock Engravings and the Folklore of Bleek and Lloyd's /Xam San informants.** In: Dowson, T. A. and Lewis-Williams, D. (Eds) **Contested Images: Diversity in southern African rock art research.** Witwatersrand University Press, Johannesburg, South Africa. ISBN 1-86814-246-9.

Deacon, H. J., Deacon, J. and Brooker, M. (1976) **Four painted stones from Boomplaas Cave, Oudtshoorn District.** *South African Archaeological Bulletin* **31**: 141 – 145.

Deacon, J. and Dowson, T. A. (Eds) (1996) **Voices from the Past: /Xam Bushmen and the Bleek and Lloyd Collection.** Witwatersrand University Press, Johannesburg, South Africa. ISBN 1-86814-247-7.

Dean, W. R. J. (1989) **Ostrich.** In: Ginn, P. J., McIlleron, W. G., and Milstein, P. le S. (1989) **The complete book of southern African Birds.** Cape Town: Struik Winchester. ISBN 0 947430 11 3.

Deer, W. A., Howie, R. A. and Zussman, J. (1992) **An Introduction to the Rock forming Minerals**, 2nd Edition. Longman Scientific and Technical. ISBN 0 582 30094 0.

Del Monte, M. and Sabbioni, C. (1987) **A study of the patine called 'scialbatura' on imperial Roman marbles.** *Studies in Conservation* **32**: 114 – 121.

------------- (1988) **Weddellite on limestones in the Venice environment.** *Environmental Science and technology* **17**: 518 – 522.

Denninger, E. (1962) **Investigations of rock paintings in South West Africa, August - September 1962.** Laboratory reports nos. 93, 104, 105, 106. Copy in South African Museum library.

------------- (1966a) **Age determination of South African rock paintings in the Cape Province.** Report. Copy in the South African Museum library.

------------- (1966b) **Age determination of rock paintings in northern Transvaal (Limpopo Valley) and Natal (Drakensberg).** Report in Rudner, I. (1982) **Khoisan pigments and paints and their relationship to rock paintings.** *Annals of the South African Museum* **87**: 1 - 281.

------------ (1971) **The use of paper chromatography to determine the age of albuminous binders and its application to rock paintings.** *South African Journal of Science, Supplementary Special Issue* **2**: 80 – 84.

Dixon, J. B. and Skinner, H. C. W. (1992) **Manganese Minerals in Surface Environments.** In Skinner, H. C. W. and Fitzpatrick, R. W. (Eds) (1992) **Biomineralization processes of Iron and Manganese: modern and ancient environments.** *Catena Supplement 21.* Catena Verlag, Germany. ISSN 0722-0723.

Dornan, S. S. (1925) **The Tati Bushmen (Masarwas) and their Language.** In Rudner, I. (1982) **Khoisan pigments and paints and their relationship to rock paintings.** *Annals of the South African Museum* **87**: 1 - 281.

Dornan, S. S. (1925) **Pygmies and Bushmen of the Kalahari.** Seeley, Service and Co. (Ltd), London.

Dunn, E. J. (1931) **The Bushmen.** Charles Griffin and Co. (Ltd), London.

Du Toit, A. L. (1954) **The Geology of South Africa**, 3rd edition. Oliver and Boyd, London.

East, T. J. (1987) **A multivariate analysis of the particle size characteristics of regolith in a catchment on the Darling Downs, Australia.** *Catena* **14**: 101 – 118.

Edwards, D. (1967) **A plant ecological survey of the Tugela River Basin.** Pietermaritzberg: Natal Town and Regional Planning commission (Natal Town and Regional Planning Report vol. 10). *Botanical Survey of South Africa memoir 36.* In Mazel, A. D. (1996a) **Maqonqo Shelter: the excavation of Holocene deposits in the eastern Biggarsberg, Thukela Basin, South Africa.** *Natal Museum Journal of Humanities* **8**: 1 - 39.

Eksteen, Van der Walt and Nissen (1990) **KwaZulu catchments development potential study.** Department of Agriculture and Forestry, Private Bag X05, Ulundi, 3838. Section 9 (Catchment 310).

Ellenberger, V. (1953) **La fin tragique des Bushmen: les derniers homes vivants de l'Age de la Pierre.** Paris: Amiot-Dumont. Translation by Dr. Peter Mitchell.

Escott, B. J. (2000) **A mineralogical and chemical study of San rock paintings and discarded ochre in the Maqonqo Shelter, KwaZulu-Natal, South Africa.** Paper for Honours in Soil Science, University of Natal, Pietermaritzburg. Unpublished.

Favero-Longo, S. E., Castelli, D., Salvadori, O., Belluso, E. and Piervittori, R. (2005) **Pedogenetic action of *Lecidea atrobrunnea*, *Rhizocarpon geographicum* gr. and *Sporastatia testudinea* on serpentinized ultramafic rocks in an alpine environment.** *International Biodeterioration and Biodegradation*, **56** (1): 17 –27 and **56** (4): 250 – 251.

Fitte, P. (1990) **Comments on the analyses of the ochres from Cougnac.** *Rock Art Research* **7** (1): 17 – 18.

Fitzpatrick, R. W. and Schwertmann, U. (1982) **Al-substituted goethite – An indicator of pedogenic and other weathering environments in South Africa.** *Geoderma* **27**: 335 – 347.

Ford, B., MacLeod, I. and Haydock, P. (1994) **Rock art pigments from Kimberley region of western Australia: Identification of the minerals and conversion mechanisms.** *Studies in Conservation* **39**: 57 – 69.

Frey-Wyssling, A. (1981) **Crystallography of the two hydrates of crystalline calcium oxalate in plants.** *American Journal of Botany* **68**: 130-141.

Frost, R. L., Adebajo, M. and Weier, M. (2004) **A Raman spectroscopic study of thermally treated glushinskite--the natural magnesium oxalate dihydrate.** *Spectrochimica acta. Part A, Molecular and biomolecular spectroscopy* **60**(3): 643-51.

Gary, M., McAfee (Jr), R., and Wolf, C. L. (Eds) (1973) **Glossary of Geology.** American Geological Institute, Washington D.C. ISBN 0 913312 00 2.

Geological Survey, (1981) **2928 DRAKENSBERG 1:250000 GEOLOGICAL SERIES.** Government Printers, Private Bag X85, Pretoria.

------------- (1988a) **2830 DUNDEE 1:250000 GEOLOGICAL SERIES.** Government Printers, Private Bag X85, Pretoria.

------------- (1988b) **3030 PORT SHEPSTONE 1:250000 GEOLOGICAL SERIES.** Government Printers, Private Bag X85, Pretoria.

GeoMap, (2001) **GIANT'S CASTLE, MONKS COWL, Hiking Map No.3 1:50000.** Goldfields Press, Johannesburg.

Gillespie, R. (1997) **On human blood, rock art and calcium oxalate: further studies on organic carbon content and radiocarbon age of materials relating to Australian rock art.** *Antiquity* **71**: 430 – 437.

Goodwin, A. J. H. and van Riet Lowe, C. (1929) **The Stone Age cultures of South Africa.** *Annals of the South African Museum* **27**: 1 – 289.

Govindaraju, K. (1994) **Compilation of working values and sample description for 383 geostandards**. *Geostandards Newsletter Special Issue* **18**: 1 – 158.

Graustein, W. C., Cromack, K., Jr., and Sollins, P. (1977) **Calcium oxalate occurrence in soils and effect on nutrient and geochemical cycles.** *Science* **198**: 1252 – 1254.

Gray, C. J. (1906) **Report on Iron ore deposit, Prestwick, near Dundee, and Limestone deposit near Waschbank. Appendix B (a)** In Gray, C. J. (1907) **Report on the mining industry of Natal for the year 1906.** Commissioner of mines, Colony of Natal, "Times" printing and publishing company Ltd.

Hahn, T. (1879) **Felszeichnungen der Buschmänner.** In Rudner, I. (1982) **Khoisan pigments and paints and their relationship to rock paintings.** *Annals of the South African Museum* **87**: 1 - 281.

Hahn, T. (1881) **Tsuni-//Goam, the supreme being of the Khoi-Khoi.** In Rudner, I. (1982) **Khoisan pigments and paints and their relationship to rock paintings.** *Annals of the South African Museum* **87**: 1 - 281.

Hall, M. (1996) **Archaeology Africa.** David Philip Publishers (Pty) Ltd, Claremont, South Africa. ISBN 0 86486 302 0.

Hamilton, G. N. G. and Cooke, H. B. S. (1939) **Geology for South African Students: An Introductory Textbook.** Central News Agency Ltd, Johannesburg.

Harker, A. (1939) **Metamorphism – a study of the transformation of rock masses.** In Gary, M., McAfee (Jr), R., and Wolf, C. L. (Eds) (1973) **Glossary of Geology.** American Geological Institute, Washington D.C. ISBN 0 913312 00 2.

Hatch, F. H. (1910) **Report on Mineral Resources of Natal.** Colony of Natal, Part 1, Chapter 4, Richard Clay and Sons Ltd (Printers), London.

Hedges, R.E.M., Ramsey, C. B., van Klinken, G. J., Pettitt, P. B., Nielsen-Marsh, C., Etchegoyen, A., Niello, J. O. F., Boschin, M. T. and Llamazares, A. M. (1998) **Methodological issues in the 14C dating of rock paintings.** *Radiocarbon* **40** (1): 35 – 44.

Helwig, K. (1997) **A note on burnt yellow earth pigments: documentary sources and scientific analysis.** *Studies in Conservation* **42**: 181 – 188.

Hey, A. W. (1954) **Letter [on paints in rock art].** *South African Archaeological Bulletin* **9**: 140.

Hoffman. A. C. (1958) **New excavations in the Matjes River Rock Shelter.** *South African Museums Association Bulletin* **6** (13): 342 – 348.

Hoffman. A. C. (1971) Pers. Comm. In Rudner, J. (1971) **Painted Burial stones from the Cape.** In Schoonraad, M. (Ed.) **Rock Paintings of southern Africa.** *Supplement to the South African Journal of Science, Special Issue No. 2*, 54 – 61.

Hoffmann, B. A. and Bernasconi, S. M. (1998) **Review of occurrences and carbon isotope geochemistry of oxalate minerals: implications for the origin and fate of oxalate in diagenetic and hydrothermal fluids.** *Chemical Geology* **149**: 127 – 146.

How, M. W. (1970) **The mountain Bushmen of Basutoland.** 2nd Edition, Pretoria: J. L. Van Schaik Ltd.

Hughes, J. C. and Solomon, A. (2000) **A preliminary study of ochres and pigmentaceous materials from KwaZulu-Natal, South Africa: towards an understanding of San pigment and paint use.** *Natal Museum Journal of Humanities* **12**: 15 - 31.

Huwiler, K. (1972) **More light on rock paintings.** *Rhodesian Prehistory* **8**: 3 – 6.

Hyman, M., Turpin, S. A. and Zolensky, EM. E. (1996) **Pigment analyses from Panther Cave, Texas.** *Rock Art Research* **13** (2): 93 – 103.

Jeanroy, E., Rajot, J. L., Pillon, P., and Herbillon, A. J. (1991) **Differential dissolution of hematite and goethite in dithionite and its implication on soil yellowing.** *Geoderma* **50**: 79 – 94.

Jerardino, A. and Swanepoel, N. (1999) **Painted slabs from Steenbokfontein Cave: the oldest known Parietal art in southern Africa.** *Current Anthropology* **40** (4): 542 – 548.

Jerardino, A. and Yates, R. (1996) Preliminary results from excavations of Steenbokfontein Cave: implications for a re-characterization of megamiddens. *South African Archaeological Bulletin* **52**: 43 - 51.

Jercher, M., Pring, A., Jones, P. G., and Raven, M. D. (1998) **Rietveld X-ray diffraction and X-ray fluorescence analysis of Australian aboriginal ochres.** *Archaeometry* **40**: 383 - 401.

Johnson, T. (1957) **An experiment with cave-painting media.** *South African Archaeological Bulletin* **12**: 98 - 101.

Johnson, D. E. (1998) **Applied multivariate methods for data analysis.** Duxbury Press, New York, USA. ISBN 0-534-23796-7.

Johnson, M. R. (Ed.) (1996) **South African Code of Stratigraphic Terminology and Nomenclature.** 4th edition, South African Committee for Stratigraphy, Council for Geoscience, Pretoria, South Africa. ISBN 1-875061-29-0.

Jolly, P. (1986) **A first generation descendant of the Transkei San.** *South African Archaeological Bulletin* **41**: 6 - 9.

Jones, P. (1984) **Red ochre expeditions an ethnographic and historical analysis of Aboriginal trade in the Lake Eyre Basin.** *J. Anthropol. Soc. South Australia,* **22**(7): 3 – 10, and **22**(8): 10 – 19. In Jercher, M., Pring, A., Jones, P. G., and Raven, M. D. (1998) **Rietveld X-ray diffraction and X-ray fluorescence analysis of Australian aboriginal ochres.** *Archaeometry* **40**: 383 - 401.

Kaplan, J. M. (1989) **45 000 Years of Hunter-Gatherer history in Natal as seen from Umhlatuzana Rock Shelter.** *South African Archaeological Society Goodwin Series* **6**: 3 – 16.

------------- (1990) **The Umhlatuzana Rock Shelter sequence: 100 000 years of Stone Age history.** *Natal Museum Journal of Humanities* **2**: 1 - 94.

Karathanasis, A. D. and Hajek, B. F. (2001) **Elemental Analysis by X-ray Fluorescence Spectroscopy.** In Sparks, D. L. (Ed.) **Methods of Soil Analysis. Part 3 - Chemical Methods.** Book Series number 5, Soil Science Society of America and American Society of Agronomy, Madison, Wisconsin.

King, L. (1982) **The Natal Monocline.** 2nd edition, University of Natal Press, Pietermaritzburg, South Africa. ISBN 0 86980 314 X.

Kingsley, C. S. (1975) **A new stratigraphic classification implying a lithofacies change in the Table Mountain Sandstone in southern Natal**. *Transactions of the Geological Society of South Africa* **78**: 43 – 55.

Kolo, K. and Claeys Ph (2005) **In vitro formation of Ca-oxalates and the mineral glushinskite by fungal interaction with carbonate substrates and seawater.** *Biogeosciences* **2**: 277 – 293.

Krüsemann, J. P. (2000) **Philips EDX Microanalysis Course.** Practical Session Tasks version 3.1

Kushnir, J. (1982) **The partitioning of seawater cations during the transformation of gypsum to anhydrite.** *Geochimica et Cosmochimica Acta* **46**: 433 – 446.

L'Breuil, (1930) **Premiéres Impressions de Voyage sur la prehistoire Sud-Africaine.** In Mason, A. Y. (1933) **Rock paintings in the Cathkin Peak area, Natal.** *Bantu Studies* **7**: 131 – 158.

Labeau, M. (1990) **Physical and chemical analysis of prehistoric paints in Cougnac cave.** *Rock Art Research* **7** (1): 12 – 16.

Lange, O.L., Green, T.G.A. and Ziegler, H. (1988) **Water status related to photosynthesis and carbon isotope discrimination in species of lichen genus Pseudocyphellaria with green or blue-green photobionts and in photosmbiodemes.** *Oecologia* **75**: 494- 501.

Le Maire, R. W. (Ed.), Bateman, P., Dudek, A., Keller, J., Lameyre, J., Le Bas, M. J., Sabine, P. A., Schmid, R., Sørensen, H., Streckeisen, A., Wooley, A. R. and Zanettin, B. (1989) **A Classification of Igneous Rocks and Glossary of Terms: Recommendations of the International Union of Geological Sciences Subcommission on the Systematics of Igneous Rocks**. Blackwell Scientific Publications, Oxford. ISBN 063202593X.

Lebzelter, V. (1930) **Die Vorgeschichte von Süd und Südwest-afrika. Wissenschaftliche Ergebnisse einer Forschungsreise nach Süd und Südwest-afrika in den Jahren 1926 – 1928.** In Rudner, I. (1982) **Khoisan pigments and paints and their relationship to rock paintings.** *Annals of the South African Museum* **87**: 1 - 281.

Lee, R. B. (1979) **The !Kung San: men, women and work in a foraging society.** Cambridge University Press. ISBN 0 521 22578 7.

Lewis-Williams, J. D. (1980) **Ethnography and iconography: aspects of southern San thought and art.** *Man* (n.s.) **15**: 467 - 482.

------------- (1983) **The rock art of southern Africa.** Cambridge: Cambridge University Press. ISBN 0 521 24460 9.

------------- (2003) **Images of Mystery: Rock art of the Drakensberg.** Double Story Books, Cape Town, South Africa. ISBN 1-919930-06-X.

Lewis-Williams, J. D. and Dowson, T. A. (1989) **Images of Power: Understanding Bushmen rock art.** Southern Book Publishers, Cape Town, South Africa. ISBN 1 86812 196 8.

------------- (1992) **Rock painting of the Natal Drakensberg.** University of Natal Press, Pietermaritzburg, South Africa. ISBN 086980 869 9 (No. 5)

------------- (Eds) (1994) **Contested Images: Diversity in southern African rock art research.** Witwatersrand University Press, Johannesburg, South Africa. ISBN 1-86814-246-9.

Lewis-Williams, J. D. and Pearce D. (2004) **San Spirituality: Roots, expression, and social consequences.** African Archaeological Series xxvii. Altamira Press, Walnut Creek, California. ISBN 0-7591-0432-8.

Lide, D. R. (Ed.-in-chief) (2002) **CRC Handbook of Chemistry and Physics, 2002/2003 edition.** CRC Press, Boca Raton, New York. ISBN 0-8493-0483-0.

Linstrőm, W. (1981) **The Geology of the Drakensberg area: Explanation Sheet 2928 (1:250000).** Geological Survey, Government Printers, Private Bag X85, Pretoria.

------------- (1987) **The Geology of the Dundee area: Explanation Sheet 2830 (1:250000).** Geological Survey, Government Printers, Private Bag X85, Pretoria.

Loubser, J. H. N. (1992) **Materials used by Bushmen to make rock paintings.** *Culna* **42**: 16 – 17.

Loxton, R. F., Hunting and Associates (1971) **Report on a Survey of the Natural Resources of Natal South Coast (European owned land). Supplement to the Maps.** The Town and Regional Planning Commission, Pietermaritzburg. TS 57/69.

Lui, Q., Zhang, B., Shen, Z. and Lu H. (2006) **A crude protective film on historic stones and its artificial preparation through biomimetic synthesis.** Article in Press for Applied Surface Science, available online at www.sciencedirect.com.

Lyon, T. D. B. and Baxter, M. S. (1978) **Stable carbon isotopes in human tissues.** *Nature* **273**: 750 –751.

Magennis to Péringuey (1915) **South African Museum Correspondence 1913-19**. In Rudner, I. (1982) **Khoisan pigments and paints and their relationship to rock paintings.** *Annals of the South African Museum* **87**: 1 - 281.

Mallory-Greenough, L. M., Greenough, J. D., Dobosi, G., and Owen, J. V. (1999) **Fingerprinting ancient Egyptian quarries: preliminary results using laser ablation microprobe - inductively coupled plasma - mass spectrometry.** *Archaeometry* **41**: 227 - 238.

Manly, B. F. J. (1994) **Multivariate statistical methods: A primer.** 2nd edition. Chapman and Hall, London. ISBN 0 412 60300 4.

Mason, A. Y. (1933) **Rock paintings in the Cathkin Peak area, Natal.** *Bantu Studies* **7**: 131 – 158.

Mawk, E. J. and Rowe, M. W. (1998) **Effect of water on Lower Pecos River rock paintings in Texas.** *Rock Art Research* **15** (1): 12 – 16.

Mazel, A. D. (1989a) **Changing social relations in the Thukela Basin, Natal 7000 – 2000 b.p.** *South African Archaeological Society Goodwin Series* **6**: 33 – 41.

------------- (1989b) **People making history: the last ten thousand years of hunter-gatherer communities in the Thukela Basin.** *Natal Museum Journal of Humanities* **1**: 1 - 168.

------------- (1992) **Collingham Shelter: the excavation of late Holocene deposits, Natal, South Africa.** *Natal Journal of Humanities* **4**: 1 – 51.

------------- (1993) **KwaThwaleyakhe Shelter: the excavation of mid and late Holocene deposits in the central Thukela basin, Natal, South Africa.** *Natal Museum Journal of Humanities* **5**: 1 - 36.

------------- (1994) **Dating the Collingham Shelter rock paintings.** *Pictogram* **2** (6): 33 – 35.

------------- (1996a) **Maqonqo Shelter: the excavation of Holocene deposits in the eastern Biggarsberg, Thukela Basin, South Africa.** *Natal Museum Journal of Humanities* **8**: 1 - 39.

------------- (1996b) **Dating the Paint: Revealing the age of Natal Drakensberg rock art.** *Optima* **42** (2): 16 – 19.

------------- (1997) **Mzinyashana Shelters 1 and 2: excavation of mid and late Holocene deposits in the eastern Biggarsberg, Thukela Basin, South Africa.** *Natal Museum Journal of Humanities* **9**: 1 - 35.

Mazel, A. D. and Watchman, A. L. (1997) **Accelerator radiocarbon dating of Natal Drakensberg paintings: results and implications.** *Antiquity* **71**: 445 - 449.

------------ (2003) **Dating rock paintings in the uKhahlamba-Drakensberg and the Biggarsberg, KwaZulu-Natal, South Africa.** *Southern African Humanities* **15**: 59 - 73.

Meiring, A. J. D. (1953) **The Matjes River Shelter; Evidence in regard to the introduction of rock painting into South Africa.** *Researches of the National Museum, Bloemfontein,* **1**: 77 – 84.

Menu, M. and Walter, P. (1992) **Prehistoric Cave painting PIXE analysis for the identification of paint "pots".** *Nuclear Instruments and Methods in Physic Research* **B64**: 547 – 552.

Minzoni-Déroche, A., Menu, M., and Walter, P. (1995) **The working of pigment during the Aurignacian period: evidence from Üçagizili cave (Turkey).** *Antiquity* **69**: 153 - 158.

Mirmehdi, M., Chalmers, A., Barham, L. and Griffiths, L. (2001) **Automated Analysis of Environmental Degradation of Paint Residues.** *Journal of Archaeological Science* **28**: 1329 – 1338.

Mitchell, P. J. (1995) **Revisiting the Robberg: New results and a revision of old ideas at Sehonghong rock shelter, Lesotho.** *South African Archaeological Bulletin* **50**: 28 - 38.

Mozeik, O. (1910) **Die Malereien der Buschmänner**. Berlin: Dietrich Reimer. In Rudner, I. (1982) **Khoisan pigments and paints and their relationship to rock paintings.** *Annals of the South African Museum* **87**: 1 - 281.

Muller to Péringuey (1914) **South African Museum Correspondence 1913-19**. In Rudner, I. (1982) **Khoisan pigments and paints and their relationship to rock paintings.** *Annals of the South African Museum* **87**: 1 - 281.

Nahon, D. C., Janot, C., Karoff, A. M., Paquet, H., and Tardy, Y. (1977) **Mineralogy, petrography and structures of iron crusts (ferricretes) developed on sandstones in the western parts of Senegal.** *Geoderma* **19**: 263 – 277.

Nisbet, E. G. and Pearce, J. A. (1977) **Clinopyroxene composition in mafic lavas from different tectonic settings.** *Contributions Mineral. Petrol.*, **63**: 149 – 169. In Mallory-Greenough, L. M., Greenough, J. D., Dobosi, G., and Owen, J. V. (1999) **Fingerprinting ancient Egyptian quarries: preliminary results using laser ablation microprobe - inductively coupled plasma - mass spectrometry.** *Archaeometry* **41**: 227 - 238.

Opperman, H. (1987) **The Later Stone Age of the Drakensberg Range and its Foothills.** Cambridge Monographs in African Archaeology 19, B.A.R. International Series 339, B.A.R. Publications, Great Britain.

Ouzman, S. and Wadley, L. (1997) **A history in paint and stone from Rose Cottage Cave, South Africa.** *Antiquity* **71**: 386 - 404.

Pager, H. (1971) **Ndedema: a documentation of the rock paintings of the Ndedema Gorge.** Graz: Akademische Druck, Austria.

Partridge, T. C., Avery, D. M., Botha, G. A., Brink, J. S., Deacon, J., Herbert, R. S., Maud, R. R., Scholtz, A., Scott, L., Talma, A. S., and Vogel, J. C. (1990) **Late Pleistocene and Holocene climatic change in southern Africa.** *South African Journal of Science* **86**: 302 – 306.

Pearce, D. G. (2001) **Harris Matrices in southern African rock art: towards a chronology of the San rock art of Maclear District, Eastern Cape Province.** (BA Hons. Th.), Department of Archaeology, University of the Witwatersrand. Unpublished.

------------- (2002) **The Tierkloof burial stones: the art and context of painted stones in the Eastern Cape, South Africa.** (BA Msc. Th.), Department of Archaeology, University of Witwatersrand. Unpublished.

------------- (2003) **The Tierkloof Painted Buriel Stones.** *South African Journal of Science* **99**: 125 – 127.

Peisach, M., Pineda, C. A., and Jacobson, L. (1991a) **Nuclear analytical study of rock paintings.** *Journal of Radioanalytical and Nuclear Chemistry* **151**: 221 -227.

Peisach, M., Pineda, C. A., Jacobson, L., and Loubser, J. H. N. (1991b) **Analytical study of pottery from Soutpansberg.** *Journal of Radioanalytical and Nuclear Chemistry* **151**: 229 -237.

Péringuey to Daily Dispatch (1913) **South African Museum Correspondence 1913-19**. In Rudner, I. (1982) **Khoisan pigments and paints and their relationship to rock paintings.** *Annals of the South African Museum* **87**: 1 - 281.

Péringuey to De Laporte (1913) **South African Museum Correspondence 1913-19**. In Rudner, I. (1982) **Khoisan pigments and paints and their relationship to rock paintings.** *Annals of the South African Museum* **87**: 1 - 281.

Plug. I. (1996) **The hunter’s choice: faunal remains from Maqonqo Shelter, South Africa.** *Natal Museum Journal of Humanities* **8**: 42 - 52.

Pomiès, M. P., Menu M., and Vignaud, C. (1999) **Red palaeolithic pigments: natural Hematite or heated Goethite?** *Archaeometry* **41**: 275 - 285.

Porat, N. and Ilani, S. (1998) **A Roman period palette: Composition of pigments from King Herod’s palaces in Jericho and Massada, Israel.** *Israel Journal of Earth Sciences* **47**: 75 - 85.

Prins, F. E. (1994) **Living in two worlds: the manipulation of power relations, identity and ideology by the last San rock artist in Tsolo, Transkei, South Africa.** *Natal Museum Journal of Humanities* **6**: 179 – 193.

Resende, M. (1976) **Mineralogy, chemistry, morphology and geomorphology of some soils of the central plateau of Brazil.** In Torrent, J., Schwertmann, U., Fechter, H., and Alferez, F. (1983) **Quantitative relationships between soil colour and hematite content.** *Soil Science* **136**: 354 - 358.

Rivera, E. R. and Smith, B. N. (1979) **Crystal morphology and 13carbon/12carbon composition of solid oxalate in cacti.** *Plant Physiology* **64**: 966 – 970.

Roberts, N. (1916) **Rock Paintings of the northern Transvaal.** *South African Journal of Science* **13**: 567 – 573.

Ruan, H. D. and Gilkes, R. J. (1996) **Micropore formation in heated synthetic Al-goethites from a ferrous system.** *Clay Minerals* **31**: 75 – 79.

Rudner, I. (1982) **Khoisan pigments and paints and their relationship to rock paintings.** *Annals of the South African Museum* **87**: 1 - 281.

------------- (1983) **Paints of the Khoisan rock artists.** *South African Archaeological Society Goodwin Series* **4**: 14 - 20.

Rudner, J. (1971) **Painted Burial stones from the Cape.** In Schoonraad, M. (Ed.) **Rock Paintings of southern Africa.** *Supplement to the South African Journal of Science, Special Issue No. 2*, 54 – 61.

Rudner, J. and Rudner, I. (1973) **A note on early excavations at Robberg.** *South African Archaeological Bulletin* **28**: 94 – 96.

Russ, J., Palma, R. L., Loyd, D. H., Farwell, D. W. and Edwards, H. G. M. (1995) **Analysis of the rock accretions in the Lower Pecos region of south-western Texas.** *Geoarchaeology* **10** (1): 43 – 63.

Russ, J., Palma, R. L., Loyd, D. H., Boutton, T. W. and Coy, M. A. (1996) **Origin of the Whewellite-Rich Rock Crust in the Lower Pecos Region of Southwest Texas and its significance to Paleoclimatic Reconstructions.** *Quaternary Research* **46**: 27 – 36.

Russ, J., Kaluarachchi, W. D., Drummond, L. and Edwards, H.G.M. (1999) **The Nature of a whewellite-rich rock crust associated with pictographs in southwestern Texas.** *Studies in Conservation* **44**: 91 – 103.

Russ, J., Loyd, D. H., and Boutton, T. W. (2000) **A paleoclimate reconstruction for southwestern Texas using oxalate residue from Lichen as a paleoclimate proxy.** *Quarternary International* **67**: 29 – 36.

Russell, T. (2000) **The application of the Harris Matrix to San rock art at Main Caves North, KwaZulu-Natal.** *South African Archaeological Bulletin* **55**: 60 - 70.

Salisbury, F. B. and Ross, C. W. (1992) **Plant Physiology.** 4th edition. Wadsworth Publishing Company, Belmont, California. ISBN 0 534 15162 0.

Sampson, C. G. (1967) **Excavations at Glen Elliot Shelter, Colesberg District, Northern Cape.** *Memoirs of the National Museum, Bloemfontein, vol. 2*, **5**: 127 – 209.

------------ (1974) **The Stone Age Industries of the Orange River Scheme and South Africa.** *Memoirs of the National Museum, Bloemfontein*, **6**: 1 – 288.

Scheffer, F. E. W. and Ludweig, F. (1958) **Zur Frage der Eisenoxidhydrate im Bodem**. In Torrent, J., Schwertmann, U., Fechter, H., and Alferez, F. (1983) **Quantitative relationships between soil colour and hematite content.** *Soil Science* **136**: 354 - 358.

Schoute-Vanneck, C. A. and Walsh, R. C. (1959) **The shell middens at the Ingane River mouth, Natal south coast.** *South African Archaeological Bulletin* **53**: 43 - 55.

Schmidt, S. (1996) **The relevance of the Bleek/Lloyd Folktales to the general Khoisan traditions.** In: Deacon, J. and Dowson, T. A. (Eds) (1996) **Voices from the Past: /Xam Bushmen and the Bleek and Lloyd Collection.** Witwatersrand University Press, Johannesburg, South Africa. ISBN 1-86814-247-7.

Schulze, D. G. and Bertsch, P. M. (1995) **Synchrotron X-Ray Techniques in Soil, Plant, and Environmental Research.** *Advances in Agronomy* **55**: 1 – 66.

Schwertmann, U. (1985) **Occurrence and formation of iron oxides in various pedoenvironments.** In Stucki, J. W., Goodman, B. A. and Schwertmann, U. (Eds) **Iron in Soils and Clay Minerals.** D. Reidal Publishing Company, Dordrecht, Holland. ISBN 90-277-2613-2.

Schwertmann, U. and Taylor, R. M. (1977) **Iron Oxides.** In Dixon, J. B. and Weed, S. B. (Eds) **Minerals in Soil Environments.** 2nd edition. Soil Science Society of America, Madison, Wisconsin, U.S.A. ISBN 0 89118 765 0.

Scott, D. A., Newman, M., Schilling, M., Derrick, M. and Khanjian, H. P. (1996) **Blood as a binding medium in a Chumash Indian pigment cake.** *Archaeometry* **38**: 103 – 112.

Segal, B. (1935) **A possible base for “Bushman” paint.** *Bantu Studies* **9**: 49 – 51.

Singer, R. and Wymer, J. (1969) **Radiocarbon Date for Two Painted Stones from a Coastal Cave in South Africa.** *Nature* **224**: 508 – 510.

Smith, B. N. and Epstein, S. (1971) **Two categories of 13C/12C ratios for plants.** *Plant Physiology* **47**: 380 – 384.

Soil Classification Working Group, (1991) **Soil Classification: a taxonomic system for South Africa.** Memoirs on the Agricultural Natural Resources of South Africa No. 15, Department of Agricultural Development, Pretoria, South Africa. ISBN 0-621-10784-0.

Solomon, A. (1997) **The myth of ritual origins? Ethnography, mythology and interpretation of San rock art.** *South African Archaeological Bulletin* **52**: 3 - 13.

------------ (1999) **Meanings, models and minds: a reply to Lewis-Williams.** *South African Archaeological Bulletin* **54**: 51 - 60.

Somerville, W. (1799 – 1802) **William Somerville's narrative of his journeys to the eastern Cape frontier and to Lake Lattakoe 1799 – 1802. With introductions, map and notes by E. & F. Bradlow.** Cape Town: The Van Riebeeck Society, 1979. ISBN 0 620 04232.

Stanford, W. E. (1910) **Statement of Silayi, with reference to his life among the Bushmen.** *Transactions of the Royal Society of South Africa.* 1908 – 1910, **1**: 435 – 440.

Stevenson-Hamilton, J. (1929) **The Low-veld: its wild life and its people.** Cassell and Co., Ltd, London.

Strobel, B. W. (2001) **Influence of vegetation on low-molecular-weight carboxylic acids in soil solution: A Review.** *Geoderma* **99**: 169 – 198.

Surveyor General, (1981) **2830 HELPMEKAAR 1:50000 Map.** Second edition. Government Printers, Private Bag X85, Pretoria.

Thomas, R. J. (1988) **The Geology of the Port Shepstone Area: Explanation Sheet 3030 (1:250000).** Geological Survey, Government Printers, Private Bag X85, Pretoria.

Tobias, P. V. (Ed.) (1978) **The Bushmen: San hunters and herders of southern Africa.** Human and Rousseau Publishers, Cape Town. ISBN 0-7981-0668-9.

Torrent, J., Schwertmann, U., and Schulze, D. G. (1980) **Iron oxide mineralogy of some soils of two river terrace sequences in Spain.** *Geoderma* **23**: 191 - 208.

Vallance, S. L. (1997) **Applications of chromatography in art conservation: techniques used for the analysis and identification of proteinaceous and gum binding media.** *Analyst* **122**: 75R – 81R.

Van der Merve, N. J., Sealy, J. and Yates, R. (1987) **First accelerator carbon-14 date for pigment from a rock painting.** *South African Journal of Science* **83**: 56 – 57.

Van Riet Lowe, C. (1952) **Archaeological Survey: The Distribution of Prehistoric rock engravings and paintings in South Africa.** Department of Education, Arts and Science. (Archaeological Series; no. 7), Government Printer, Pretoria, South Africa.

Van Rijssen, W. J. (1987) **Painting in Peril.** *South African Archaeological Bulletin* **42**: 5 - 9.

------------ (1990) **Analysis of South African rock art pigments by X-ray fluorescence spectroscopy (EDS)**. *South African Archaeological Bulletin* **45**: 58 -59.

------------ (1994) **Rock art: the question of authorship.** In: Dowson, T. A. and Lewis-Williams, J. D. (eds) **Contested Images.** Witwatersrand University Press, pp 159 – 175. ISBN 1-86814-246-9.

Verrecchia, E. P., Dumont, J. and Verrecchia, K. E. (1993) **Role of calcium oxalate Biomineralisation by fungi in the formation of calcretes: A case study from Nazareth, Israel.** *Journal of Sedimentary Petrology* **63**: 1000 – 1006.

Vinnicombe, P. (1976) **People of the Eland: Rock paintings of the Drakensberg Bushmen as a reflection of their life and thought.** Pietermaritzburg, University of Natal Press. ISBN 0 86900 054 X.

Von M Harmse, H. J., van der Watt, H. v H., van Rooyen, T. H. and Burger, R. D. U. T. (1984) **Glossary of Soil Science Terms.** The Soil Science Society of South Africa. V&R Printing Works (Pty) Ltd, Pretoria. ISBN 0 86979 568 6.

Wadsten, T. and Moberg, R. (1985) **Calcium Oxalate Hydrates on the surface of Lichens.** *Lichenologist* **17**: 239 – 245.

Watchman, A. (1990) **A summary of occurrences of oxalate-rich crusts in Australia.** *Rock Art Research* **7** (1): 44 – 50.

------------- (1991) **Age and Composition of oxalate-rich crusts in the Northern Territory, Australia.** *Studies in Conservation* **36**: 24 – 32.

------------- (2001) **Dating oxalate minerals in rock surface deposits.** Proceedings of the 7th Australian Archaeometry Conference.

Watchman, A., Ward, I., Jones, R. and O'Connor, S. (2001) **Spatial and compositional variations within finely laminated mineral crusts at Carpenter's Gap, an Archaeological site in tropical Australia.** *Geoarchaeology* **16** (7): 803 – 824.

Ward, I., Watchman, A., Cole, N., and Morwood, M. (2001) **Identification of minerals in pigments from aboriginal rock art in the Laura and Kimberley regions, Australia.** *Rock Art Research* **18** (1): 15 – 23.

Watts, I. (2002) **Ochre in the middle stone age of southern Africa: ritualised display or hide preservative?** *South African Archaeological Bulletin* **57**: 1 – 14.

Wells, L. H. (1933) **The Archaeology of Cathkin Park: Introductory.** *Bantu Studies* **7**: 113 – 129.

Wells, M. A., Gilkes, R. J. and Anand, R. R. (1989) **The formation of corundum and aluminous hematite by the thermal dehydroxylation of aluminous goethite.** *Clay Minerals* **24**: 513 – 530.

Wendt, W. E. (1976) **'Art Mobilier' from the Apollo 11 cave, South West Africa: Africa's oldest dated works of art.** *South African Archaeological Bulletin* **31**: 5 - 11.

Wiedemann, H. G. and Bayer, G. (1988) **Formation of whewellite and weddellite by displacement reactions.** *American Laboratory* **20**: 54 – 61.

Willcox, A. R. (1956) **Rock paintings of the Drakensberg.** London, Max Parrish.

------------- (1963) **The Rock Art of South Africa.** Thomas Nelson and Sons (Africa) (Pty) Ltd, Johannesburg.

------------- (1975) **The Archaeology of the Drakensberg.** The Natal Town and Regional Planning Commission, Pietermaritzburg, South Africa. ISBN 0-909232-04-0.

------------- (1976) **Southern land: The pre-history and history of southern Africa.** Purnell and Sons (SA) Pty Ltd, Johannesburg, South Africa. ISBN 360 00324 9.

------------- (1984) **The Drakensberg Bushmen and their art: with a guide to the rock painting sites.** Drakensberg Publications, Winterton, Natal, South Africa. ISBN 0 620 07419 1.

Williamson, B. S. (2000**) Direct testing of rock painting pigments for traces of Haemoglobin at Rose Cottage Cave, South Africa.** *Journal of Archaeological Science* **27**: 755 – 762.

Wilson, M. L., Rijssen, W. J. J., and Gerneke, D. A. (1990) **An investigation of the 'Coldstream Stone'.** *Annals of the South African Museum* **99**: 187 - 213.

Wright, J. B. (1971) **Bushmen raiders of the Drakensberg, 1840 - 1870: a study of their conflict with the stock-keeping peoples in Natal.** University of Natal Press, Pietermaritzburg, South Africa.

Yates, R., Golson, J. and Hall, M. (1985) **Trance Performance: the rock art of Boontjieskloof and Sevilla.** *South African Archaeological Bulletin* **40**: 70 – 80.

Yates, R. J., Manhire, A. and Parkington, J. E. (1994) **Rock painting and history in the southwestern Cape.** Dowson, T. A. and Lewis-Williams, J. D. (eds) **Contested Images.** Witwatersrand University Press, pp 29 – 60. ISBN 1-86814-246-9.

Yates, R. and Jerardino, A. (1996) **A fortuitous fall: early rock paintings from the west coast of South Africa.** *South African Journal of Science* **92**: 110 - 110.

Yu, K. N. and Miao, J. M. (1998) **Multivariate analysis of the energy dispersive X-ray fluorescence results from blue and white Chinese Porcelains.** *Archaeometry* **40**: 331 - 339.

APPENDICES

APPENDIX 3.1

A SUMMARY OF DENNINGER'S REPORTS (1962; 1966A; 1966B; 1971).

Khomas Hochland, Namibia, 1962, Laboratory reports 93 and 104:

- Silica 'crusts' found on the paintings of Khomas Hochland, and at Spitskoppen and the Brandberg.
- Lime was not found.
- The pigments contain dark and light ochres with high Si contents. The white pigment consisted of pure $CaSO_4$.
- Several groups of paintings were distinguished in which one, two, three, four, and in one case, six amino acids were identified. The latter was interesting as it was obtained from a dark brown pigment, probably ochre mixed with blood and used within the previous 50 years prior to analysis. Denninger (1962;p4) states that:

"In paintings that have been fixed with blood, the iron which is complexly bound in the haemoglobin of the blood at first darkens the colour. After a few centuries, the iron of the haemoglobin, which up till then shows up dark to reddish-brown, starts forming the lighter brown methaemoglobin in which the iron occurs as a trivalent ion-bound element. Since such iron-brown paintings, which have shown themselves to be very old by the absence of amino acids (over 2 000 years), have been found at other sites, especially in the Brandberg, it can be concluded that blood has been used as a fixative not only in the Khomas Hochland, but also in the Brandberg area."

The present author has located no evidence that can substantiate either of these two statements.

- The remaining three groups of two (a majority), three and four amino acids were dated to between 200 and 600 years old.

Erongo Mountains, and the "Gross" and "Klein" Spitskoppe, Namibia, 1962, Laboratory reports 105 and 106:

- Brown iron pigments were used, together with charcoal (black). Very fine quartz particles were used to lighten the burnt ochre in some cases (as a white pigment). Generally, the white pigment consisted of pure $CaSO_4$.
- Blue pigment on paintings in Klein-Ameib was considered to be either dumortierite or arfvedsonite. Azurite was not considered, as Cu was not detected. Graphite was found on another painting at the same site, but this represented pencil markings left from tracing the images.

- The amino acid groupings were similar to those found in the Khomas Hochland area, and thus are also dated to between 200 and 600 years old.
- A considerable amount of $CaCO_3$ was found on the paint samples as crusts.
- A very dense, smooth surface was found over some of the samples, and assumed to be hyrax excrement.

Paintings in the Tsisab Ravine, Brandberg, and Cave of the "White Lady", Namibia, 1962, Laboratory report 107:

- Iron oxides (as burnt and light ochre), sometimes with high Si contents, were used as pigments. $CaSO_4$ was used for the white pigment, whilst charcoal was used for black.
- Five samples contained three amino acids (about 350 years), two samples one, and two groups of nine samples showed two (600 to 900 years) and no amino acids, respectively. The paintings of the "White Lady" belong to the oldest of the paintings examined.
- As for the samples without amino acid detection, Denninger states:

"Since in all other samples, without exception, the use of protein containing fixing agents could be deducted from the presence of amino acids, it may be concluded that the samples in which no amino acids could be determined were painted with similar fixatives."

Based on this assumption, an age of more than 2 000 years was assigned to these paintings. No other evidence that can substantiate this claim was given.

Paintings in the south-western Cape, South Africa, 1966a:

Two test paintings were analysed i.e., a painting of a three-masted galleon (known to have been used from the 16th to the 18th century), and one of Voortrekker troops (dated to roughly 1850 A.D.). The first painting displayed a sinter layer of silicic acid gel over a reddish-brown pigment composed of quartziferous, red haematite. Four amino acids gave a chromatographic date of 200 ± 50 years. The pigment obtained from the Voortrekker image was composed of quartziferous, natural burnt ochre that was covered by a thin, sinter layer. The image also contained four amino acids, giving a chromatographic date of 200 ± 50 years. The applicability of chromatographic analysis was based on these two findings.

The following information was determined for paintings within the greater western Cape region. In order to reduce repetition, only the determined ages are presented (according to Table 2.3 in Chapter 3).

- Farm Alpha, on the Olifant River, south-western Cape:

The dark, reddish-brown and yellow cattle, and the white and red-brown images nearby, displayed no sinter. The red-brown pigment was composed of a natural burnt ochre whilst the yellow pigment was a raw ochre; both were highly siliceous. The white, coarse-grained pigment was composed of $CaSO_4$ mixed with fine quartz particles. The four amino acids present give an age of 200 ± 50 years.

Older images (400 ± 100 years) were also found. The line paint was composed of quartziferous, natural burnt ochre.

- Farm Kriedouwkrans, on the Olifant River, south-western Cape:

The pigments used included natural burnt ochre and charcoal. A sinter layer on the surface of the images was noted. A date of 200 ± 50 years was determined.

- Paintings near Brakfontein, south-western Cape:

Dated to 400 ± 100 years, the very thin, red-brown paintings were composed of quartziferous, natural burnt ochre and red iron oxide (probably haematite). A sinter layer was noted.

- Farm Dasclip, near Porterville, south-western Cape:

Three groups of paintings were determined. The first consisted of thinly painted, red-brown animals and a galleon of the 18th century, all of which were dated to 200 ± 50 years. A sinter layer was noted. The second group of paintings (dated to 100 ± 20 years) did not show any sinter. A group of thinly painted, reddish-brown humans (400 ± 100 years) displayed a brilliant sinter. In all cases, the pigment used was highly quartziferous, natural burnt ochre.

Samples received from Mr H. Rabinowitz:

- Waterfall, Citrusdal, south-western Cape:

The red-brown image was composed of natural burnt ochre and dated to 400 ± 100 years. A sinter layer was noted.

- Farm Monte Cristo, Koue Bokkeveld, south-western Cape:

The yellow paint was composed of yellow ochre dated to 400 ± 100 years. No sintered layer noted.

- Stompiefontein, near Ceres, south-western Cape:

It was here that the Voortrekker horses and carriages were located. Very few sinters noted. The pigments used were quartziferous, natural burnt ochre and raw ochre (200 ± 50 years).

Some elongated human figures were found in association with the first paintings mentioned. These latter images were not painted onto the surface, however, but rather ‘drawn’ onto the rock with quartziferous, red haematite. They are assumed to be much older than the first set of images as they display a well-developed sinter, but as no albuminous binding medium was used, no date could be determined.

- Farm Rietfontein, Winkel Haaks River, south-western Cape:

The brown, human images were composed of brown, unburnt ochres that contained a high proportion of clay. They were dated to 400 ± 100 years. They displayed a brilliant sinter.

Samples received from Mr T. Johnson:

- Sample 232: Drilrivier, Brandewyn River, Parkhuis, south-western Cape:

Red-brown, fine and close paint, brilliant, with sinters. Pigment: quartziferous, natural burnt ochre. Age: 400 ± 100 years.

- Sample 239: Nuoredam, Parkhuis, south-western Cape:

1) Very thin red-brown painting on quartzite. Pigment: natural burnt ochre, quartziferous. Age: none – sample too small.
2) Dark red-brown paint, fine particles. Pigment: red iron oxide (haematite, quartziferous). Age: 100 ± 20 years.

- Sample 226: Nardousberg, Brakvlei, Clanwilliam, south-western Cape:

1) Thin, black painting with little binding medium. Pigment: charcoal black. Age: none – sample too small.
2) Red-brown layer of paint on quartzite, fine particles. Pigment: red iron oxide (haematite), quartziferous. Age: 200 ± 50 years.

- Sample 91: Klein Pakhuis, Oliviershoogte, Cape Province:

Black layer of paint, small particles. Pigment: charcoal black. Age: none – sample too small.

- Sample 180: Boontjieskloof, Pakhuis, Cape Province:

Red-brown, very thin layer of paint on quartzite, fine particles. Pigment: red iron oxide (haematite), quartziferous. Age: 400 ± 100 years.

- Leeuwenvlakte, Konetokkeveld, Cape Province:

Yellow, dull layer of paint, fine particles. Pigment: raw ochre, highly quartziferous. Age: 200 ± 50 years.

Paintings in the northern Transvaal (Limpopo Valley) and Natal (Drakensberg), South Africa, 1966b:

I was unable to obtain a copy of this report. The following information is quoted directly from Rudner's (1982) review.

- Paintings in the Limpopo Valley, Limpopo province:

The red pigments were 'ferric oxides, as haematite and bloodstone haematite' with a considerable amount of quartz; burnt ochres, quartziferous or clayey. Yellow was from yellow ochre (ferric oxide), and the violet pigments were mixed ferric oxides; white was quartziferous gypsum.

- Paintings in the Ukhahlamba- Drakensberg, KwaZulu-Natal:

Some white paintings (gypsum) did not contain amino acids, or a binder had not been used. Brown and reddish-brown pigments were quartziferous ferric oxide ('bloodstone haematite') or burnt ochre; white was china clay. (The pigment for yellow was not given.)

APPENDIX 3.2

NOTES ON Ca-OXALATES.

Introduction

Calcium oxalates, comprising whewellite ($CaC_2O_4.H_2O$) and weddellite ($CaC_2O_4.2H_2O$), are probably the most common, and least understood, of the minerals found in association with parietal rock art worldwide. Besides the many pathways, both organic and inorganic, that can result in their formation, these minerals are also found in a myriad of different sources/locations, including termiteria (J. C. Hughes, pers. comm., 2007), plants (Albert Frey-Wyssling, 1981; Hedges *et al.*, 1998), kidney stones (Hedges *et al.*, 1998), micro-organisms (Watchman, 1990; Russ *et al.*, 1995; Mazel and Watchman, 2003) and, of course, on rock surfaces (Cariati *et al.*, 2000; Lui *et al.*, 2006). Most of the papers that have analysed parietal rock art have attempted to address the obvious questions of "how did this mineral form?" and "does this mineral represent part of the original paint or is it a secondary depositional product?" These questions, or more specifically their answers, will have important implications for both rock art conservation and dating.

Manner of formation

The formation of Ca oxalates is driven by a relatively simple chemical reaction in which Ca combines with oxalate. What makes the study of these minerals so contentious within the field of rock art research, however, involves the conflicting hypotheses regarding the locality of this chemical reaction (i.e., *in situ* upon the paint/rock surface vs. from an external source), together with the disputed manner of production (i.e., were they derived via an inorganic or organic pathway). What further complicates matters is that there are very few clues which would indicate which scenario is correct, for these minerals form within both tropical and temperate climates, and are found upon a variety of different substrates, including siliceous sandstones (South Africa: this study; Mazel and Watchman, 2003), limestones (Texas: Russ *et al.*, 1995), granodiorite (Australia: Watchman, 1990) and granite (Argentina: Hedges *et al.*, 1998).

In addition, the source components, namely Ca and oxalate, are also derived from a number of different sources, with the Ca originating either from the rock (Australia: Ford *et al.*, 1994; Texas: Russ *et al.*, 1995), the groundwater (South Africa: this study; Mazel and Watchman, 2003), and atmospheric deposition (Australia: Watchman, 1991). The oxalates can be formed either on rock surfaces via epilithic and endolithic cyanobacteria (Del Monte and Sabbioni, 1988), lichens (Del Monte and Sabbioni, 1987), atmospheric deposition via rainwater (Watchman, 1991), through the displacement reactions on the surface of gypsum crystals (Del Monte and Sabbioni, 1987), or derived from localised groundwater i.e., via root exudates or the decomposition of organic matter (Hofmann and Bernasconi, 1998; Strobel, 2001).

Finally, different forms of oxalate can be found at different locations within the same shelter, their form being determined by the inherent environmental and chemical conditions found at each point within the shelter (Watchman *et al*., 2001). Whewellite, the most common and stable form of Ca oxalate, is the most widely distributed form of this mineral species. This mineral, together with another common secondary deposited mineral gypsum, is commonly found within shelters that experience drier conditions (Ford *et al*., 1994). Weddellite, on the other hand, is generally formed under wetter, cooler conditions, and often dehydrates to whewellite as conditions become drier due to its lower chemical stability (Del Monte and Sabbioni, 1987). Finally, during the course of this study, another oxalate was also identified at Twagwa Shelter (glushinskite [$MgC_2O_4.H_2O$]). This rare oxalate only forms under very specific conditions, a primary condition being that Mg is the dominant available cation in solution at the point of formation, and that this situation must remain for extended periods of time (Verrecchia *et al*., 1993). Kolo *et al.* (2005) also showed that, unlike the Ca oxalates, this mineral is not actively produced by fungi, but forms rather as a result of the inorganic reactions between exuded oxalates and the rock substrate upon which the fungi resides. Once formed, however, it is insoluble.

With so many potential mechanisms for oxalate formation, it is important to have a technique to aid in the determination of which of the above mentioned pathways are present within a particular shelter, and more specifically, within the paint sample being analysed. The technique at the forefront of this avenue of research involves the study of the isotope values for C extracted from the oxalates. Various studies have shown that oxalates formed via different chemical pathways tend to display different C isotope values (Table A3.2.1).

As can be seen in Table A3.2.1, however, broad categories representing the different photosynthetic pathways can be established with a relatively high degree of reliability, whilst those minerals formed via inorganic pathways are more variable and tend to be more site specific (see the rock crust values). In order to accommodate for this potential variability, analyses of ‘blank’ wall samples from the shelter being studied must also be conducted.

The most commonly studied source of Ca oxalate is that produced via lichens and micro-organisms, primarily because they are known to a) exist on the surface of, amongst other things, rocks, from which they derive their nourishment; and b) they are known to produce Ca oxalates as a means of disposing of excess Ca (Wadsten and Moberg, 1985; Kolo and Claeys, 2005). A further contributing factor was that, in a number of rock art studies, it was noted that the paint samples also registered elevated P contents, an element that is known to be accumulated by both (this study; Watchman, 1990; Ford *et al*., 1994; Russ *et al*., 1999.).

Table A3.2.1: Examples of carbon isotope values as displayed by a variety of different sources (adapted from Hoffman and Bernasconi, 1998)

Sample type	**Phase**	**Oxalate δ^{13}‰**	**Reference**
Cacti	Oxalate	- 8.1 ± 0.6(5)$^{\#}$	Rivera and Smith, 1979
Cacti	Ca-oxalate	-10.3 (1)$^{\#}$	Hedges *et al*., 1998
Rock crust	Whewellite	-11.8 (1)$^{\#}$	Hofmann and Bernasconi, 1998
Lichen (Switzerland)	Whewellite	-11.7 (1)$^{\#}$	Hofmann and Bernasconi, 1998
Living Lichen thalli	Oxalate	[-35 to –14]	Lange *et al*., 1988
Lichen (USA)	Whewellite	-10.6 ± 1.9(18)$^{\#}$	Russ *et al*., 1996; 2000
Rock crusts formed from past lichens	Oxalate	[-6.8 to –13.7]	Beaszley *et al*., 2002
Human urinary concretions	Whewellite	-18.3 ± 0.7(19)$^{\#}$	Lyon and Baxter, 1978
C4 plants	Oxalate	~ -12(?)$^{\#}$	Smith and Epstein, 1971
C3 plants	Oxalate	~ -28(?)$^{\#}$	Smith and Epstein, 1971
Algae and bacteria	Oxalate	~ -28(?)$^{\#}$	Hedges *et al*., 1998
Sediment derived (diagenetic)			
Natural deposit along a water seep	Whewellite	+1(1)$^{\#}$	Hedges *et al*., 1998
Hoheneggelsen, Germany	Whewellite	8.7(1)$^{\#}$	Hofmann and Bernasconi, 1998
Milan-Monroeville, USA	Whewellite	1.9(1)$^{\#}$	Hofmann and Bernasconi, 1998
Kladno, Czech Republic	Whewellite	11.2(1)$^{\#}$	Hofmann and Bernasconi, 1998

\# - Number of samples analysed.
[ ] – Indicates that a range was supplied, though no data regarding the number of analyses was given.

Paint samples collected from Maqonqo Shelter (the primary site of the current study) were analysed by Mazel and Watchman (2003). Stable carbon isotope values of ~ -15‰ were determined for the paint samples, indicating that a micro-organic pathway resulted in their formation. The elevated P contents noted within the paint samples within this and other studies tend to support these findings (e.g. Hyman *et al*., 1996[1]). It is interesting to note that the P values within the blank samples analysed here were much lower than those in the paints, and so too was the recorded Ca oxalate content.

Hedges *et al*. (1998) conducted a similar study in Argentina, and found that the blank samples analysed, whilst containing 50 times less whewellite than the paint samples analysed, also displayed a different isotopic composition. Their conclusions: a) whewellite can form naturally within the shelter, though at low concentrations; b) the whewellite in the paints and the natural deposit formed via two separate pathways; and c) these pathways can be identified by their respective δ^{13}C values.

The similarities between these trends and those displayed within the current study indicate that a similar situation is also present within Maqonqo Shelter, though, unlike the Hedges *et al*. (1998) study, whewellite was not sourced from cacti (suspected to have been utilised in the manufacture of the paints) but was rather produced via micro-organisms. In either case, however, these studies both show that Ca oxalates present within a single shelter can originate from at least two separate chemical

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[1] This paper also identified elevated P contents associated with the paint pigments analysed. Although they concluded that this is most probably present as a result of bone fragments being introduced to the paint medium, Ca phosphate minerals were not identified using micro-particle X-ray diffraction. It seems possible that the presence of this element is thus also due to biological accumulation processes.

pathways and, for these two shelters at least, the pathways seem to be dependent on the presence/absence of the paint pigments themselves. These factors can have important implications for the dating of parietal rock art, as will be discussed below.

Persistence

Calcium oxalates are insoluble in water, and are thus highly persistent. It is this feature that makes these minerals of great interest for dating techniques. It is also this feature which has made these minerals a focal point of a more unconventional science, one in which they are used to aid in the protection of rock wall surfaces.

It is well documented that historic stone monuments are under threat from anthropogenic pollution and, as a consequence, many scientific endeavours have been attempted to halt this degradation. As oxalate has also been shown to be more acid resistant and not as susceptible to the degradation caused by acid gases (Del Monte and Sabbioni, 1987), scientific studies have attempted to use these minerals as a preventative measure. As an example, Lui *et al*. (2006), who have shown that stone inscriptions on historic monuments in China have been preserved well for more than 1000 years via micro-organism produced whewellite, have attempted to replicate the formation of these films via artificial means. The initial results of the study have proved positive.

The one drawback of using this method as a protective measure in rock art, however, is that it will effectively eliminate the possibility of determining dates for the images in question. As a result, all the pros and cons regarding the utilisation of this form of ‘protection’ have to be considered carefully before it is employed.

Rock art dating considerations

So far it has been established that a wide range of mechanisms result in the formation of Ca oxalates. It has also been shown that the potential exists for all of them to operate within a given shelter at any one time, dependent on the prevailing environmental and chemical conditions being experienced within the particular shelter (and even a particular section of a shelter). It has also been noted that these conditions can change with the passage of time, reflecting the changes in the prevailing environmental conditions experienced by the shelter.

With all of these potential influences on the dates obtained, it would seem impossible to accurately date any oxalate material sampled. Biologically derived Ca oxalates, however, provide the one form of oxalate from which accurate dates can be derived, provided that it can be proven that the C contained within the mineral was sourced directly from the atmosphere (a C source which is considered to be relatively ‘constant’) and not from the micro-organic metabolism of older carbonate or bicarbonate.

Due to the size of the samples to be analysed, together with the obvious potential to easily contaminate the samples with ‘modern’ C, the extraction and dating of the C contained within these minerals must be conducted with the highest degree of caution and precision. Even with this high degree of vigilance in the sampling and analysis procedures, errors are known to occur. As an example, a whewellite sample was analysed by three different laboratories, using the same techniques, under identical conditions, and the same equipment, yet produced three different dates: 45 500 b.p., 36 500 b.p. and 31 470 b.p. (Watchman, 2001). Whilst it is not yet fully understood as to why the dates were different, it is clear that the material is indeed ancient, as was expected. From this example, it is clear that dates obtained from the analysis of Ca oxalates should provide a guideline value only, and too much reliance should not be placed on the specific dates themselves.

Even when taking all of the above-mentioned factors into consideration, certain assumptions have to be made when attempting to interpret the dates obtained from any given site. Russ *et al*. (2000), for example, in using oxalate derived dates in order to reconstruct palaeoclimatic conditions for southern Texas, had to assume that a) the oxalate was produced only during dry climatic conditions; b) multiple episodes of oxalate production can be distinguished in samples selected for radiocarbon dating; and c) bicarbonate from the substrate was not metabolised by the lichen. Mazel and Watchman (2003), in dating the Maqonqo Shelter paints have assumed that the Ca oxalates were produced via micro-organic processes, and that these processes are continuous over time. The lack of Ca oxalates within the blank samples analysed in the present study tends to contradict this theory, however. Whilst it seems plausible that the Ca oxalates were produced via micro-organisms, the association of these minerals almost exclusively with the paint samples tends to indicate that they formed as a direct result of the presence of the paint samples themselves. As such, the dates obtained probably reflect a more accurate time for the creation of the imagery analysed, and not just a time ‘bracket’ of minimum and maximum ages as suggested by Mazel and Watchman (2003).

Wiedemann and Bayer (1988), in laboratory experiments, found that oxalate can replace gypsum if the environmental conditions are favourable. As the oxalates could come from any number of sources, any dates obtained from these samples would not relate at all with either the age of the surface deposits and/or paintings, but would relate only to the age of the original oxalic acid formation. The analysis of blank rock wall surface deposits will help determine if these processes are in fact in operation within the shelter under study.

Finally, it is imperative to determine that no other organic source is present within the paint sample prior to oxalate dating, for anomalous dates could be determined. This can be accounted for by first pre-treating the samples using the permanganate oxidation technique which effectively removes the oxalate component alone from the sample for accelerator mass spectroscopy (AMS) dating (Gillespie, 1997).

Factors to consider

Before any conclusions are made as to how the presence of Ca oxalates will affect our interpretation of the paint components, manufacturing techniques, and possibly the derivation of reliable dates, it is imperative to determine the nature and source pathway of the mineral in question. In order to accomplish this, groundwater, rock and blank rock wall surface samples need to be collected and analysed in order to determine if the source components (i.e., either the Ca and/or oxalate) are present. This is a quick and easy way of eliminating potential pathways along which they could have formed.

Secondly, the carbon isotope results for the minerals must be obtained if dates are to be ascertained. Ideally, an organic pathway, such as via micro-organisms and lichens will be determined, for it has been shown that the ^{14}C dates obtained from oxalates produced via these mechanisms are reliable, both for the determination of dates and for the determination of palaeoenvironmental conditions under which they formed (Beasley *et al*., 2002). Work will still have to be done in order to determine if these organic producers were present within the shelter on an episodic or permanent basis, however, for this will in turn affect the interpretation of the dates obtained i.e., whether the dates accurately reflect the period of paint creation, or rather a maximum/ minimum time range, the latter dependent on the location of the oxalates in relation to the paint sample (either on the surface of the paint or below the pigment but upon the rock surface, respectively).

It must also be remembered that these processes need not occur independently of one another, and it is quite possible that the Ca oxalates present within a shelter might be the result of a combination of these pathways. Their variable deposition within a shelter, together with the potential for the dominance of individual pathways to alternate over time, must also be taken into consideration.

This science is obviously still in its infancy, and a lot more work is required to determine all of the conditions that favour the formation and persistence of these minerals, as well as the development of more reliable methods of identifying the chemical pathways of formation. As such, the dates obtained must be scrutinized to the highest degree, and even then must still be considered as representing a guideline figure only. As technology and our understanding of the chemistry involved increases, however, the information that can be gleaned from these minerals will greatly increase our understanding of parietal rock art around the world, the manner in which they were created, with what, and at what time.

APPENDIX 3.3

A NOTE ON THE PROBLEMS OF ACCURATELY QUANTIFYING PIGMENT COLOUR.

Although the accurate characterisation of paint pigment colour is essential, it is often difficult to achieve due to a number of contributing factors including the time of day (influences the quality of visible light, with dawn and dusk lending a distinct orange hue to images and midday, with its increased glare, lending a lighter intensity to the image), the weather (influences glare), the position of the image within the shelter (shaded or exposed), the colour of the rock substrate (influences the perceived image colour) and, of course, observer bias (i.e., one person's dark orange is another's light red).

A quantitative method for paint pigment colour determination is required for, as was indicated in Chapter 6, the colour of a pigment often provides clues as to its original source. As it is sometimes very difficult to determine the colour once it is mounted on the stub, this has to be determined during the sampling process. A hand-held colour spectrophotometer would help greatly in this regard, for it takes into account the ambient lighting conditions when determining a quantifiable value for the pigment colour in question.

This form of pigment/image analysis lends itself to the process of digital recording and image processing. A quantifiable pigment colour value allows for the determination of the 'true' image colour. Photographic images can thus be manipulated to reflect this 'true' colour, thus allowing for a more accurate recording of the image. Images from different shelters, or even from different positions within the same shelter, can be compared from a 'standard' position, thus allowing for a more accurate comparison.

Finally, the combined use of a spectrophotometer and digital photography will enable studies concerning the weathering effects on paint pigment colour over extended periods of time. For this form of research, it is essential that the different temporal images can be compared against each other from a common 'standard' colour 'base' i.e., the pigment colours have to be able to be precisely and accurately quantified before any potential changes in colour can be determined. For more information on this innovative approach to rock art studies, see Mirmehdi *et al.* (2001).

APPENDIX 4.1

AN EXPANDED GEOLOGICAL DESCRIPTION OF THE FOUR STUDY SITES.

Introduction

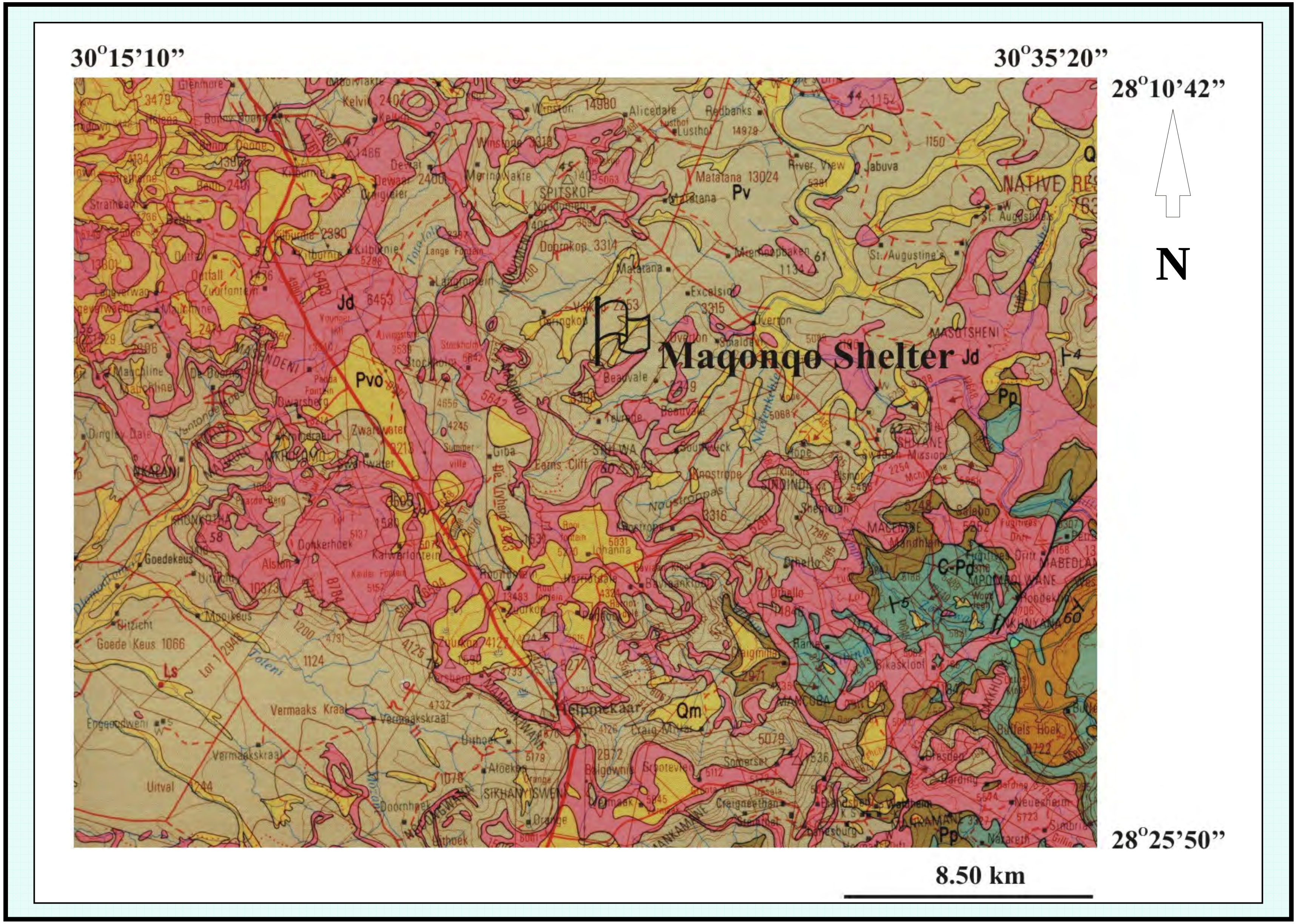
This appendix has been written to provide additional information regarding the geology present in and around each of the respective study sites. A short glossary of geological terms is provided in the beginning of this thesis. Unless otherwise stated, all co-ordinates are presented using CAPE 1880 datum.

4.1.1 Geology associated with Maqonqo Shelter

Maqonqo Shelter is situated on the Vryheid Formation of the Ecca Group. This Formation is dominated by medium- to coarse-grained sandstones and grey micaceous shales that were deposited under deltaic conditions (Linstrőm, 1987; Geological Survey, 1988a). Coal seams are also found, and are particularly common within the greater Dundee region (Geological Survey, 1988a; Camp, 1999), although they thin out as one moves south and south-west (Linstrőm, 1987). Overlying this Formation is the Volksrust Formation, the second member of the Ecca Group shown on Map A4.1. It is comprised mainly of blue-grey and black, well-laminated shale, though fine-grained siltstone is known to occur in places. Phosphate nodules are a characteristic feature of this deposit (Linstrőm, 1987). The third member of the Ecca Group is the Pietermaritzburg Formation. This Formation, which underlies the Vryheid Formation, is comprised mainly of fairly uniform dark-grey, blue or black shale that varies in thickness throughout the area (Linstrőm, 1987). Dolerite outcrops occur sporadically within this Group.

Overlying the Ecca Group is the Estcourt Formation, composed of massive or cross-bedded, fine- to coarse-grained feldspathic sandstone, sandy shale and shale interbedded with basal black or carbonaceous shale (Linstrőm, 1987). This Formation contains many fossil leaves, as well as molds of freshwater bivalves. The plant and animal species encountered tend to indicate that this Formation was laid down under cool, temperate fluvio-deltaic conditions (Linstrőm, 1987). The cross-bedding within some of the sandstones indicates a material source area to the north or north-east of its current location.

The Masotcheni Formation comprises semi-consolidated, basal boulder beds and yellow-brown, sandy clays. Probably of Quaternary age (Botha, 1992), this Formation is commonly exposed in erosion dongas, and highly eroded river channels, over large areas of the interior of KwaZulu-Natal.



Map A4.1: Geology of the local region surrounding the Maqonqo Shelter study site (Geological Survey, 1988a).

Key to Lithology

Symbol	Formation	Description	Symbol	Formation	Description
Qm	Masotcheni	Basal boulder bed; yellow-brown sandy clay	Pv	Vryheid	Medium to coarse-grained sandstone; grey micaceous shale; coal
Jd		Dolerite; Dolerite dyke (—)	Pp	Pietermaritzburg	Dark-grey shale
Pe	Estcourt	Dark blue-grey shale; carbonaceous in places; fine- to coarse-grained sandstone	C-Pd	Dwyka	Tillite; minor shale, varved shale and sandstone
Pvo	Volksrust	Shale; siltstone	Z-Rns	Nsuze	Quartzite, tuff, basaltic lava, subordinate conglomerate

Key to Economic Data

Symbol	Description	Symbol	Description
●	Occurrence	Ls	Limestone

Additional Data

Contour interval 50 m

Beneath the Ecca Group lies the Dwyka Formation, which in turn overlies the Nsuze Group. The Dwyka is comprised of massive tillite – the material deposited with the melting and retreating glaciers. The rock is fine-grained, and has a blue-grey to greenish matrix within which erratics of various sizes occur.

The Nsuze Group is a lot more complex, consisting of six different Formations comprised of alternating sedimentary and volcanic rocks. The Bomvu Formation, the lowermost of the six formations, is composed of clean, well-bedded, orthoquartzitic sandstone. The Nhlebela Formation overlies this, and consists of a relatively thin sequence of dark-green amygdaloidal lava. The Thembini Formation is comprised of an interlaminated sequence of mudstone, shale and siltstone, where the shale is finely laminated and green or grey in colour. The Chobeni Formation is comprised of a quartz-dolomite sequence of rocks. The Bivane Formation comprises a thick sequence of amygdaloidal lava. The uppermost Formation, the Taka Formation, is found in the valley of the Taka and Buffalo Rivers, and is composed of inliers of ferruginous shale with intercalated quartzite.

A variety of ore bodies, which could potentially have been utilised as pigment sources, have been known for many years. In many cases, their limited area and quality have prevented them from being commercially mined. All of the sites mentioned within this document do, however, have one aspect in common, and that is that the materials from each of these deposits are all naturally exposed and would thus have been readily accessible to the San i.e., no mining would have been required.

Iron ore deposits are known to occur throughout the region, notably in an arc from the north-east to the north-west of MQ, with the nature of the deposits being as diverse as their localities (Hatch, 1910; Coetzee, 1976). The Fe is generally present as haematite, siderite, magnetite, and limonite[1] or, more commonly, as a mixture of these. Although most of these deposits are of a high-grade, the seams are small and are thus not generally commercially viable (Hatch, 1910). As a general rule, the one defining characteristic that is common to all of these outcrops is that, when crushed, they tend to give a red to reddish/brown hue. The possibility therefore exists that these outcrops might have been the source for the red paint found within MQ.

A limestone deposit is known to be located approximately 19 km E.S.E. of Wasbank Station (approximately 38 km from MQ), near the Helpmekaar-Dundee road (Gray, 1906). Several dongas have cut into the deposit, and, in places, the thickness of the deposit is greater than 6 m above the bed of the donga, and presumably extends beneath it. The quality of the material varies from calcareous clay to almost pure limestone. All of the deposit is, however, siliceous, thus making it generally unsuitable for use as a flux in iron smelting. Due to the fact that the boundaries of this deposit are not well defined, and great variations in the structure, thickness and quality of the material can be seen, no accurate figure as to the quantity of the deposit can be given (Gray, 1906).

Bauxitic material is known to occur as isolated outcrops on the crests of some of the higher hills in the area. As these deposits are small and thus of little or no economic value, they have not been highlighted in Map A4.1. However, due to the nature of their formation (highly weathered dolerite), these deposits are exposed and easily accessible, and thus represent a possible orange pigment source. No kaolin or clay deposits of any sort are known within the greater Dundee-Helpmekaar-Vryheid area.

4.1.2 Geology associated with Fergies Cave Shelter

The oldest formation is the Estcourt Formation, and is one of the two members of the Beaufort Group that are represented on Map A4.2. It is composed of erodible dark-coloured shale and relatively more resistant grey-blue sandstone. These materials were deposited under reducing conditions at a time when the landscape was dominated by extensive alluvial flats and swamps, and when temperatures were warmer than those experienced during deposition of the preceding Ecca Group (King, 1982). As one nears the top of the Formation, however, red mudstones start to appear, indicating that the conditions of deposition gradually became drier (Linstrőm, 1981).

The Tarkastad Subgroup, the second member of the Beaufort Group represented, is comprised of fine-grained sandstone, alternating with maroon, green and blue mudstone. Unlike the Estcourt deposits, these were deposited under relatively dry conditions by moderate- to slow-flowing streams on an extensive alluvial plain (Linstrőm, 1981).

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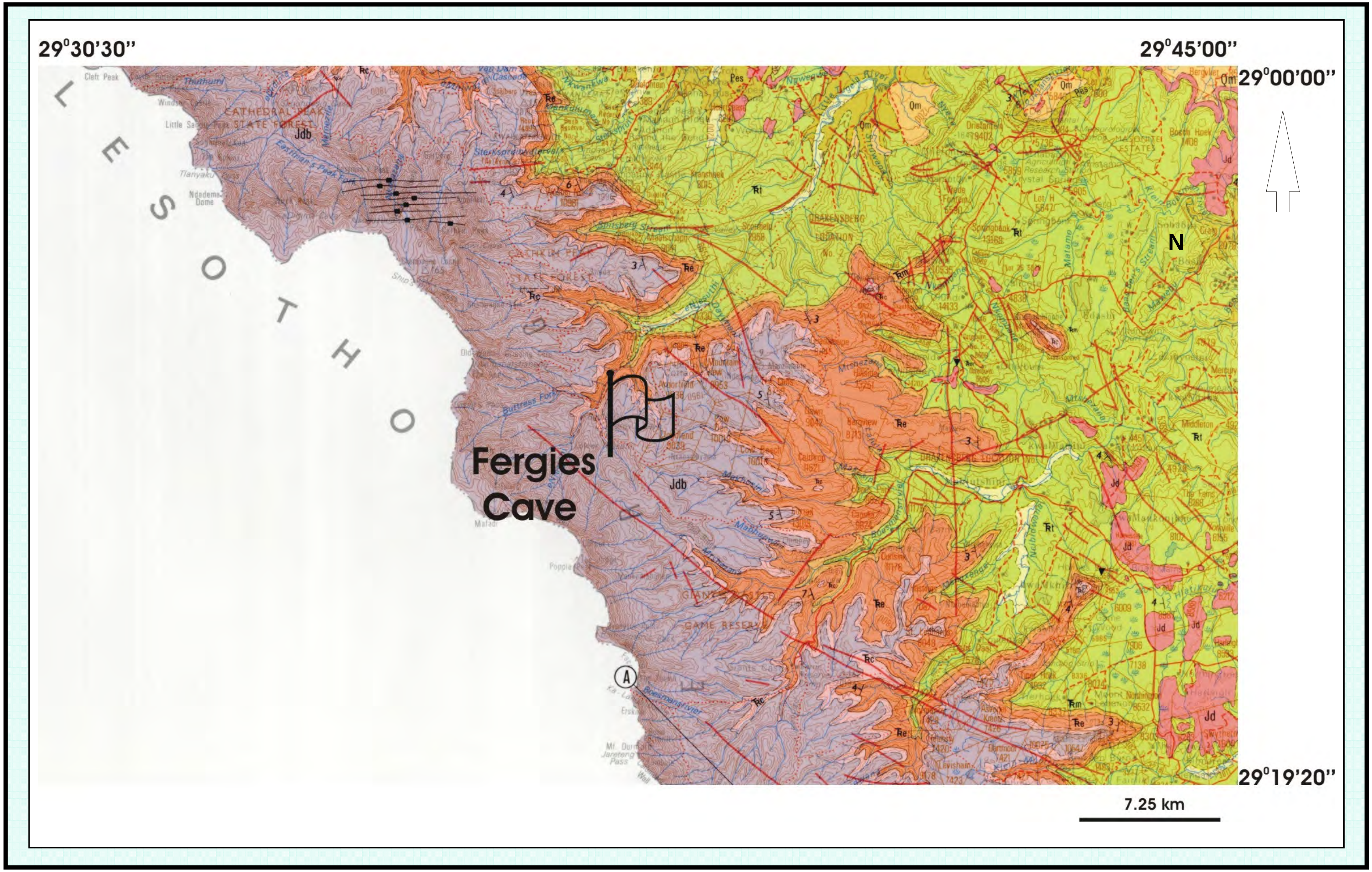
[1] The term limonite is generally used as a field term by geologists, and is used to denote a mixture of goethite (α-FeOOH), subordinate lepidocrocite (ɣ-FeOOH) and adsorbed water (Coetzee, 1976). It is, however, no longer an acceptable mineral term (Schwertmann and Taylor, 1977).



Map A4.2: Geology of the local region surrounding the Fergies Cave study site (Geological Survey, 1981).

Key to Lithology

Symbol	Formation	Description	Symbol	Formation	Description
		Alluvium	TRe	Elliot	Maroon, green and blue-grey mudstone; fine- to medium-grained sandstone
Qm	Masotcheni	Partly consolidated sediments; laterite; clay	TRm	Molteno	Coarse-grained glittering sandstone with thin grit beds; green, grey and maroon sandstone; Carbon rich beds
Jd		Dolerite; Dolerite dyke (—)	TRt	Tarkastad	Fine to medium-grained sandstone; maroon, green and blue mudstone
Jdb	Drakensberg	Basaltic lava	Pes	Estcourt	Dark-grey shale (often Carbon rich); siltstone; sandstone
TRc	Clarens	Yellow to pale-red fine-grained sandstone			

Additional Data

Contour interval 50 m

▼ Diatreme

—•— Joint

Overlying the Beaufort Group is the Stormberg Group, comprising the Molteno, Elliot, Clarens and Drakensberg Formations. The Molteno Formation is comprised of coarse-grained sandstone alternating with grey, green and maroon mudstone and grey shale (Linstrőm, 1981). Abundant secondary growth on the quartz grains gives a characteristic sparkling effect to the sandstone when exposed to sunlight (de Decker, 1981). The feldspathic component of the sandstones is easily weathered, thus resulting in the characteristic pockmarked surface (de Decker, 1981). It is thought that this Formation is a result of deposition from moderate- to fast-flowing rivers and streams that originated from the south (de Decker, 1981; Linstrőm, 1981; King, 1982). As a result, this Formation thins and finally disappears altogether as one moves northward. Several minor coal seams are known to occur at various levels within this Formation, although most are not of economic importance (de Decker, 1981).

Lying above this Formation is the Elliot Formation. It is comprised of maroon, and sometimes grey, mudstone that alternates with sandstone, all deposited by rivers in a much drier climate than that experienced during the formation of the Molteno deposits (de Decker, 1981; Linstrőm, 1981). This Formation also differs from the Molteno Formation in that it extends the full length of the Drakensberg, thus indicating a different erosional source(s). It is interesting to note that the number of sandstone layers varies from place to place, and that the grain-size in the sandstones tends to increase in diameter as one moves down the Formation.

Next in the sequence is the Drakensberg Formation. Unlike all of the previously mentioned sedimentary deposits, the Drakensberg Formation has volcanic origins, having been formed as a result of the break-up of Gondwanaland. This Formation was not formed during a single event, however, as is evidenced by the presence of brown palaeosols that are found between some of the lava flows, as well as by valleys that were carved into some of the flows only to be filled in by new volcanic material (de Decker, 1981). This delayed depositional rate tends to indicate that the lava was delivered to the surface primarily via fissures and not by a central volcanic vent. This is further substantiated by the presence of numerous dolerite dykes that cut through both the lava and the underlying sedimentary layers. This Formation is comprised predominantly of basalt, but sporadic deposits of sandstone similar to those found in the Clarens Formation are known to occur (Linstrőm, 1981).

The Masotcheni Formation was formed in the Quaternary period, and occurs sporadically throughout the area. As mentioned previously, this is comprised of semi-consolidated colluvial and alluvial deposits, the physical conditions of which facilitate easy erosion (Linstrőm, 1981). Most of the dongas found in the area are as a direct result of the presence of this Formation.

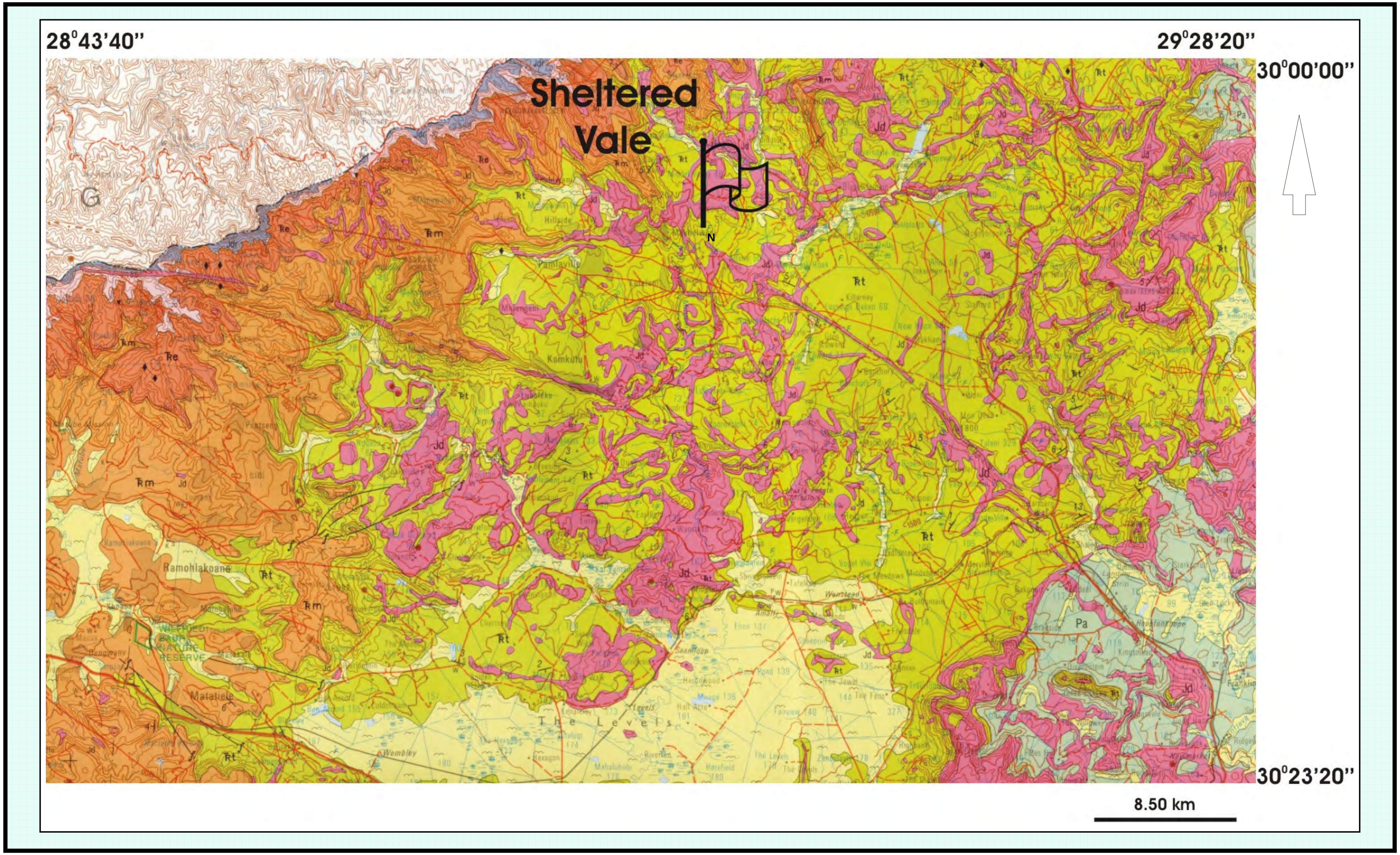
No economically viable mineral deposits are known to occur in the area (Coetzee, 1976; Linstrőm, 1981). As mentioned previously, however, small coal deposits are known to occur. Also, due to the large number of dolerite dykes found throughout the landscape, Fe ore (in the form of nodules and veins) and bauxite (highly weathered dolerite) can also be found in isolated pockets.

4.3 Geology associated with Sheltered Vale Shelter

The Estcourt Formation found in the central Drakensberg and the Adelaide Subgroup in the southern Drakensberg occupy the same stratigraphic position, but differ from one another lithologically as well as sedimentologically (Linstrőm, 1981). Whereas the Estcourt Formation is composed of dark-coloured shale and sandstone (Linstrőm, 1981), the Adelaide Subgroup is composed of grey, blue, green and reddish-brown mudstone alternating with blue-green feldspathic sandstone (de Decker, 1981). Essentially, the Adelaide Subgroup was deposited in alluvial flood plains that existed under relatively dry conditions, whilst the Estcourt Formation was deposited under reducing conditions under fluvio-deltaic conditions (Linstrőm, 1981). The Adelaide Subgroup grades into the Estcourt Formation as one moves northwards, reflecting the differences in the depositional environments experienced within the landscape at the time when both were deposited. The SV site is located in the Tarkastad Subgroup (see Map A4.3)

4.4 Geology associated with Twagwa Shelter

As can be seen from Map A4.4, the geology to the east of the shelter is more complex than that at the other sites. The Leisure Bay Formation is the only super-structural gneiss formation from this period to exist within the study area. All the other members of this period represent intrusive rock forms that formed as a result of the various deformation periods that occurred pre- and post-continental break-up. These intrusive units are quite variable in composition and lithostratigraphy, and as a result are sub-divided into fifteen lithostratigraphic units, with only five of these being represented on Map A4.4.



Map A4.3: Geology of the local region surrounding the Sheltered Vale study site (Council for Geoscience, 2002).

Key to Lithology

Symbol	Formation	Description	Symbol	Formation	Description
🟨		Alluvium	TRe	Elliot	Red and purple mudstone; medium-grained yellowish white and red sandstone
Jd		Dolerite; Dolerite dyke (—)	TRm	Molteno	Coarse- to fine-grained yellowish brown sandstone with thin pebble beds; bluish and grey mudstone and shale with occasional coal seams
Jdr	Drakensberg	Basaltic lava with subordinate agglomerate	TRt	Tarkastad	Medium- to fine-grained yellow and grey sandstone; red, purple and blue-green mudstone
Jc	Clarens	Pale-orange to pink fine-grained sandstone	Pa	Adelaide	Grey, greenish-grey and brownish-red mudstone; yellow and grey fine-grained sandstone

Additional Data

Contour interval 50 m

♦ Kimberlite

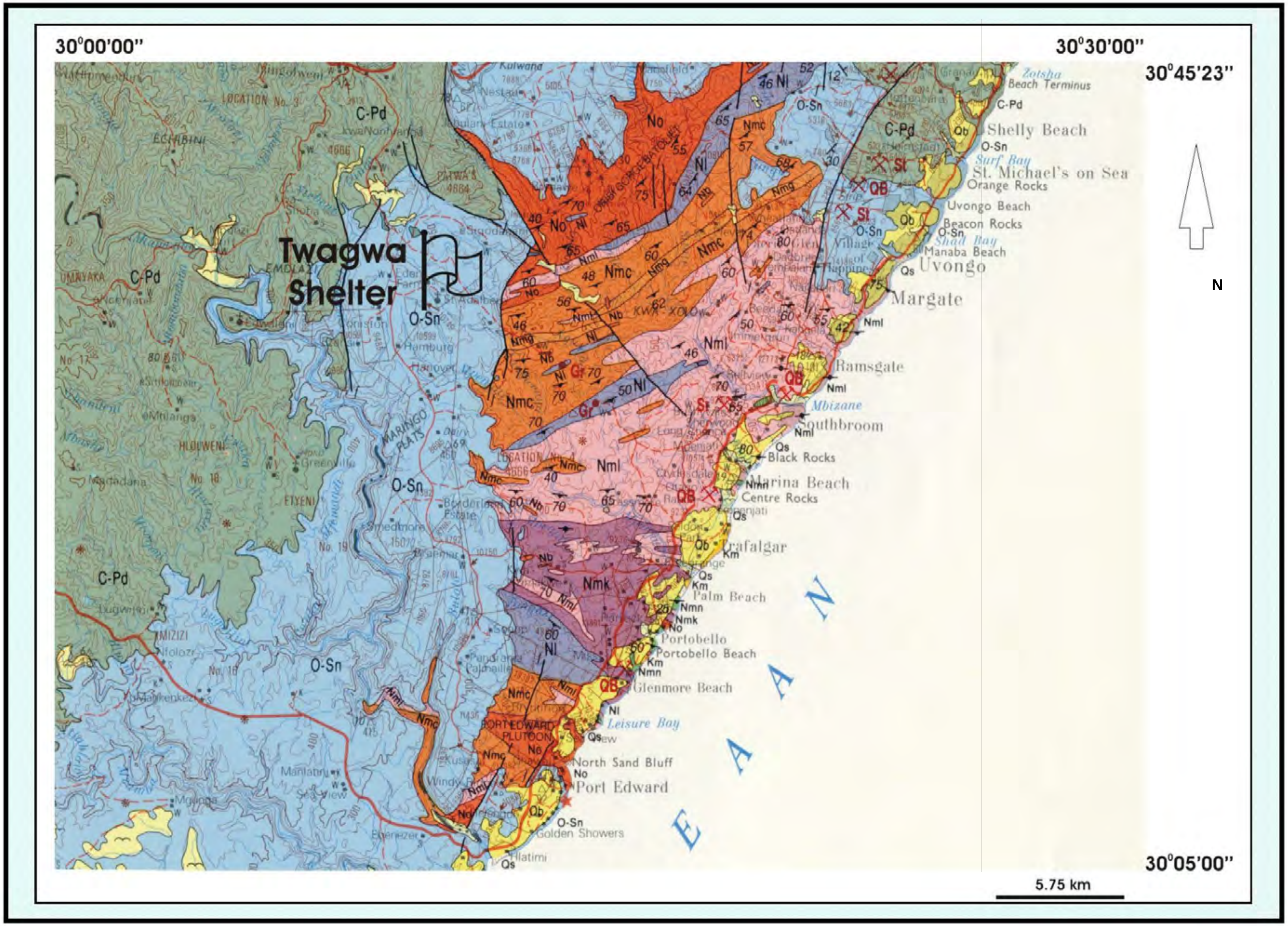
— Fault

- - Inferred or concealed fault

These suites, listed in geological sequence from oldest to youngest, are as follows: the Mkomazi Gneiss, the Munster Suite, the Margate Complex, the Oribi Gorge Suite, and the Belmont Suite. Due to the high degree of compositional variability that exists within and between these different intrusive rock formations, only a brief description will be given.

For a more detailed description, the reader is referred to Thomas (1988) from which the following is extracted.

1. The Mkomazi Gneiss Suite is composed of megacrystic, garnet-biotite, augen gneisses and foliated granites, with an overall composition of between 20 – 35 % quartz and sodic plagioclase, and 5 % garnet.
2. The Munster Metabasite Suite is composed of mafic gneisses, with the main lithologies being comprised of coarse-grained, mafic, granoblastic, though strongly foliated, biotite-, hypersthene-, augite- and plagioclase-bearing rocks of broadly dioritic aspect.
3. The Margate Complex is composed of three main lithological phases (as yet un-named), the garnet-bearing, leucocratic phase being dominant. The rocks of this phase are medium-grained, pink and pale grey, gneissose leucogranites in which garnet, as small grains, is conspicuous. The leucococratic, garnet-biotite, augen gneisses represent the second phase of the Margate Complex, and are composed of grey, coarse-grained, garnetiferous, biotite, augen leucogneisses that contain elongated white, simply twinned, K-feldspar augen (20 x 10 mm). The final phase is composed of dark-green, medium-grained charnockite.



Map A4.4: Geology of the local region surrounding the Twagwa Shelter study site (Geological Survey, 1988b).

Key to Lithology

Symbol	Formation	Description	Symbol	Formation	Description
🟨		Alluvium	No	Suite = Oribi Gorge	Very coarse-grained porphyritic granite, charnockite
Qs		Beach sand	Nml	Complex = Margate	Light pink and grey gneissose garnet leucogranite, migmatite
Qb	Berea	Red sand, subordinate white, yellow and brown sand, basal conglomerate	Nmg	Complex = Margate	Leucocratic garnet-biotite augen-gneiss
Km	Mzamba	Fossiliferous, fine-grained sandy limestone, grey sandstone, calcareous siltstone, shale and clay, hard shelly limestone, grit, conglomerate	Nmc	Complex = Margate	Medium-grained charnockite
C-Pd	Dwyka	Diamictite, subordinate varved shale	Nmn	Suite = Munster	Hypersthene-biotite diorite, monzonorite, locally porphyritic
O-Sn	Natal Group Sandstone	Red-brown, coarse- to fine-grained arkose to subarkose, light-grey quartzarenite, micaceous sandstone, grit, conglomerate, subordinate siltstone and mudstone	Nmk	Suite = Mkomazi gneiss	Garnet-biotite augen-gneiss
Nb	Suite = Belmont	Grey, fine-grained biotite microgranite	Nl	Leisure Bay	Garnet-cordierite-hypersthene-feldspar gneiss and granulite, subordinate two-pyroxene granulite; psammitic granulite and calc-silicate rocks; kinzigite

Key to Economic Data

Symbol	Description	Symbol	Description
⚒	Mine in production	Gr	Graphite
✕	Mine not in production	St	Stone aggregate
●	Occurrence	Qb	Building sand

Additional Data

Contour interval 50 m

- - - Inferred or concealed fault

---

4. The Oribi Gorge Suite is composed of very coarse-grained, porphyritic granitoids and charnockitoids. It is generally granitic in composition, though adamellitic, granodioritic and monzonitic compositions have been recorded. A striking feature of this suite is the presence of large (up to 100 mm), poikilitic K-feldspar (microcline or orthoclase perthite) phenocrysts within the rock matrices.
5. The Belmont Suite is composed of either fine-grained, homophanous grey biotite micrograntes when found in dykes, or of fine- to medium-grained, light grey, equigranular, fairly leucocratic, biotite granites when found as larger granitic plutons. Unlike most of the previous intrusive features mentioned above, garnet is a rare constituent within this suite.

Following the Namibian is the Ordovician/Silurian period, exclusively represented by the Natal Group Sandstone (Thomas, 1988), formerly known as the Table Mountain Sandstone (Loxton *et al.*, 1971; King, 1982). This group is highly resistant to weathering, resulting in the formation of spectacular cliffs and associated deep ravines. Many of the ‘flats’ within the area are formed on top of this group.

Although a majority of the southern units, known as the Margate facies, have not been as well defined as the northern units and as a consequence have not been ascribed formal formation status, one formation has been recognised (Thomas, 1988). The Msikaba Formation represents the entire Natal Group in the former Transkei region, and as such also represents the facies within which TW is located. The rocks, generally light grey in colour, are composed of a quartz-arenite association of grey, quartzitic sandstones, and conglomerates with minor feldspathic grits (Kingsley, 1975). The deposited material originated from the north-east in the northern part of the facies, whilst in the southern parts, the material seems to have been derived from the east (Thomas, 1988). Unlike the Hibberdene facies, however, the material was deposited under stable, shallow marine conditions (Kingsley, 1975). Although most of the kaolin and Fe oxides were removed prior to deposition, some residual kaolin can be found as spots and lenses within some of the sandstone outcrops (King, 1982).

The juncture of these two facies is easily noted at the coast, with the abrupt change from one to the other occurring close to the Mhlangankulu River mouth (Thomas, 1988). As one moves inland, however, the change is harder to determine, partly due to the sporadic nature of the sandstone outcrops (Thomas, 1988).

The only Permian Period geological formation present is the Dwyka Formation that covers quite an extensive area (Map A4.4). It generally overlies the Natal Group Sandstone, but has been found to over-step this latter formation and rest directly on top of the basement lithologies in certain areas. It is composed primarily of structureless tillite, which is itself composed of diamictite and an assortment of erratics that range in size from tiny grains up to boulders 0.5 m across (Thomas, 1988). The diamictite is considered to be a sub-glacial moraine deposit, whilst the erratics represent resistant rock types that pre-date the glaciation event. The melting and retreating glaciers laid down the eroded till which, over time and with pressure from the overlying Karoo formations, formed the tillite. These latter formations have subsequently been eroded away exposing the Dwyka tillite that can be seen today.

The only Cretaceous Period geological formation present is the Mzamba Formation. This fossiliferous formation consists of dirty grey, non-calcareous sandstones, mudstones, shales, and shelly limestones, and was deposited between 100 and 50 million years ago when that part of the landscape was originally submerged under the sea (King, 1982; Thomas, 1988). This period of deposition was halted only when the seabed underwent uplift, and there followed a period of about 30 million years during which little further deposition took place (King, 1982). Although found erratically distributed along the coastline, this formation has been identified in two boreholes more than 1 km inland beneath the Berea Formation, thus highlighting the fact that this deposit was originally more extensive (Loxton *et al.*, 1971; Thomas, 1988).

After this period of uplift, the seabed was again submerged and the Miocene stratum was deposited (not present within the area of study). This period of submergence did not last long, however, with the sea again retreating with the uplifting of the seabed (King, 1982). About 5 million years ago, during the Pleistocene, the sea again covered this area and deposited lime-rich sandstones (King, 1982). The sea then withdrew in stages, exposing these soft sandstones to weathering, resulting in the development of loose sands that formed the precursors to the Berea and Coastal Dune Formations (Thomas, 1988).

The first of the Quaternary deposits, the Berea Formation, is comprised of poorly consolidated red, brown and, more rarely, yellow and white, well rounded, well sorted, medium-grained sands that contain a relatively minor clay fraction (Thomas, 1988). As mentioned previously, the original sandstones, and hence the sands derived from them, were originally calcareous in nature. These have weathered *in situ*, however, resulting in the release of Fe oxides (from which the colours are derived), the loss of the original calcareous nature, and the formation of clays (from the weathering of the feldspars originally present). The coastal dunes are characterised by lighter colouration, calcareousness, and little to no clay, as a direct result of the feldspars not having weathered yet (Loxton *et al.*, 1971).

The final two Quaternary deposits represented on Map A4.4 include Beach Sand and Alluvium. The Beach Sands are composed of medium- to coarse-grained white and cream sands rich in broken shell debris, quartz, feldspars, micas and amphiboles (Thomas, 1988).

The Alluvium deposits are much more variable, however, ranging in texture from sands to clays, and in thickness from about 6 m inland (along the river courses and on colluvial/alluvial toeslopes) to over 61 m in the infilled lower courses of the rivers in the immediate vicinity of the coast (Loxton *et al.*, 1971).

APPENDIX 5.1

DIGITAL IMAGES OF THE PAINT SAMPLES USED WITHIN THIS STUDY.

Digital images of the paint samples used in this study. Also shown are the sampling positions (with the relevant trace numbers) recorded during the μ-XRD and μ-XRF analyses.

A Sony Digital Monica, MVC-FD 88 model, with a 1.3 mega pixel capacity was used to capture the following images. The aluminium stubs in these images have a diameter of 11 mm.

Maqonqo Paint Samples


Paint 1


Paint 2


Paint 3


Paint 4


Paint 5


Paint 6


Paint 7


Paint 8A


Paint 8B


Paint 9A


Paint 9B


Paint 10


Paint 11A


Paint 11B


Paint 12


Paint 13A


Paint 13B


Paint 14


Paint 15


Paint 20


Paint 21


Paint 22


Paint 23


Paint 24


Paint 25


Paint 26


Paint 27


Paint 28


Paint 29


Paint 30

All blanks and the three additional sites paint samples

SV White 1

SV White 2

SV White 3

SV Red 1

SV Blank 2

F Blank 3

Tw Blank 1

Tw Blank 2

Tw Blank 3

Tw Red 3

Tw Red 1

Tw Red 2

Tw White 1

Tw White 2

Tw White 3

F Blank 1

MQ Blank C

MQ Blank D

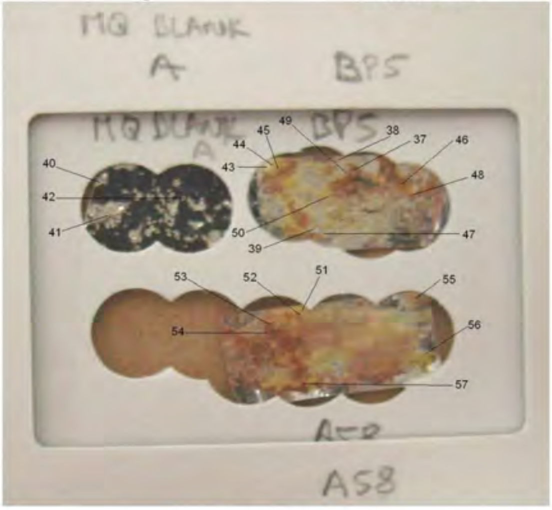
MQ Blank A

MQ Blank B

Photographs indicating the μ-XRF and μ-XRD sampling positions (with the associated trace numbers) on the Maqonqo paint samples

Image showing the dimensions of the sample cards shown in the following images.

MQ Blank A Paint 11B



Paint 28

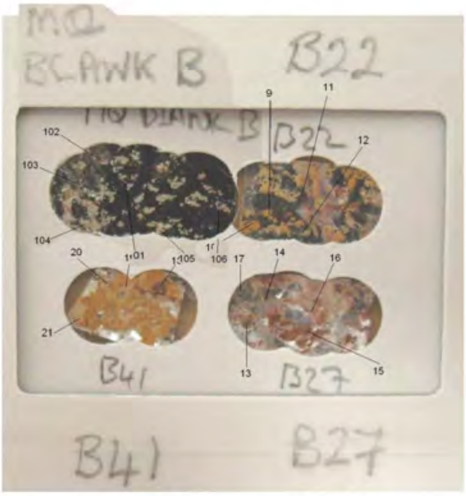
MQ Blank C

MQ Blank D

Paint 1 Paint 10

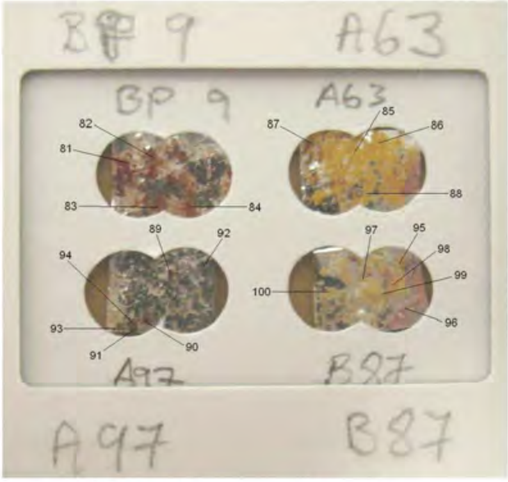
Si Mylar and C Blanks Paint 9A

MQ Blank B Paint 25



Paint 23 Paint 27

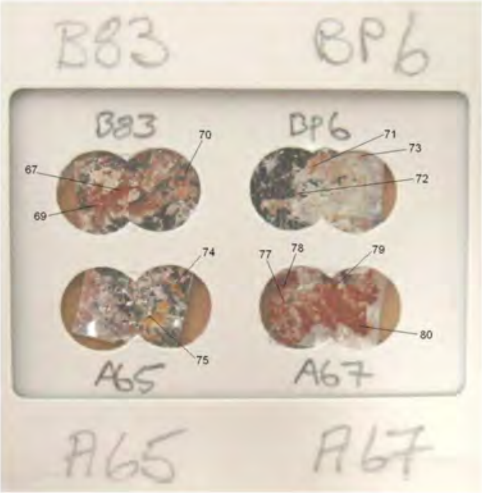
Paint 13B Paint 6



Paint 2 Paint 20

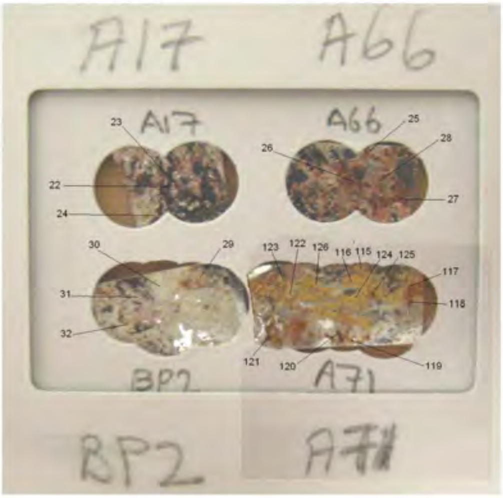
Photographs indicating the μ-XRF and μ-XRD sampling positions (with the associated trace numbers) on the Maqonqo paint samples (Cont.)

Paint 5 Paint 12



Paint 24 Paint 30

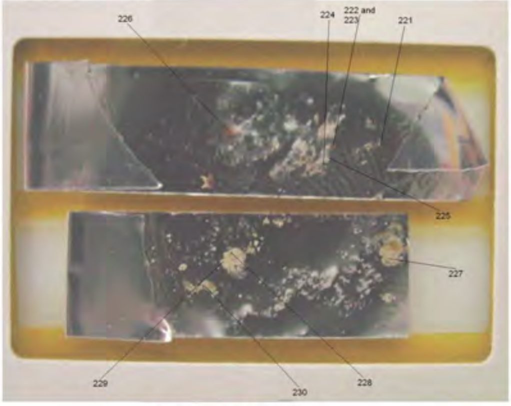
Paint 21 Paint 26



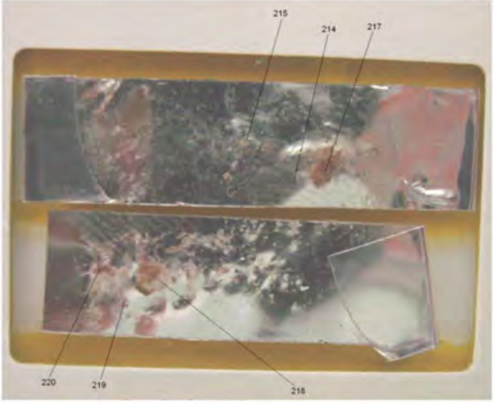
Paint 9B Paint 29

Photographs indicating the μ-XRF and μ-XRD sampling positions (with the associated trace numbers) on the additional sample sites.

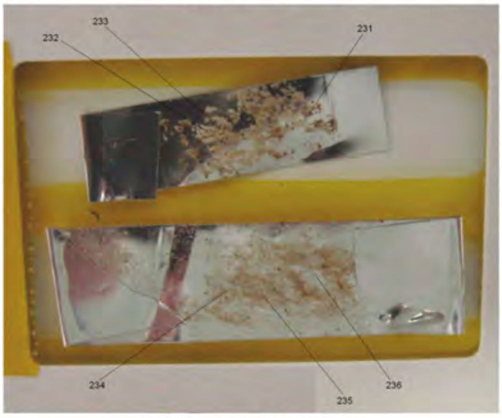
Fergies Red 1



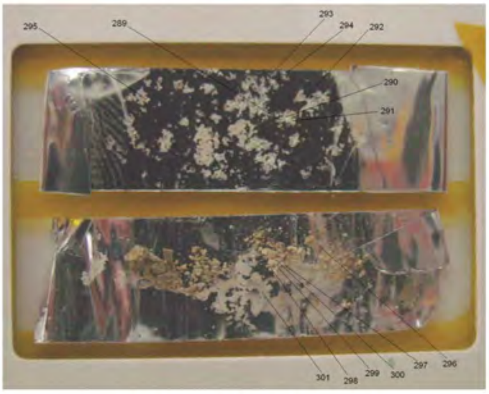
Fergies Red 2



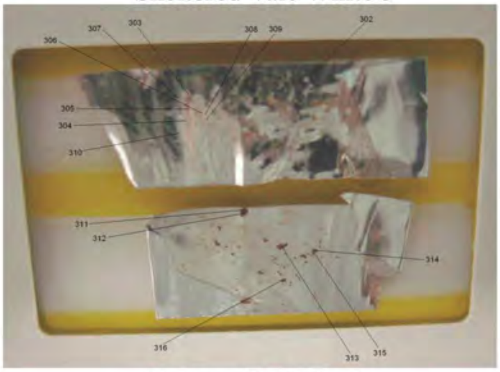
Fergies Blank 2
Sheltered Vale Blank 2



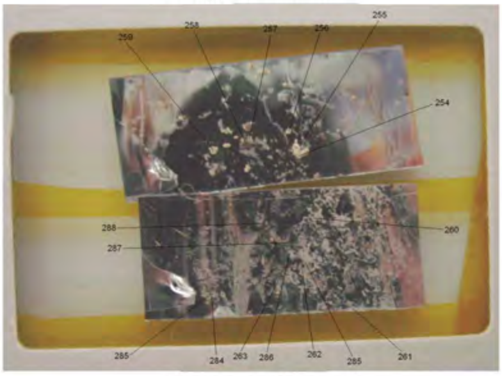
Fergies Red 3
Sheltered Vale White 1



Fergies Blank 3
Sheltered Vale White 3

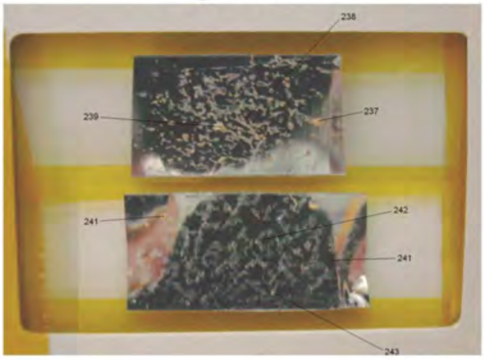


Sheltered Vale White 2
Twagwa White 1

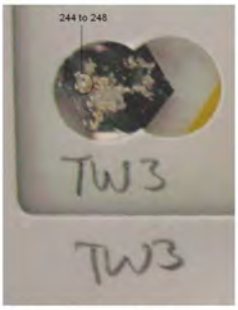


Sheltered Vale Red 1
Twagwa Blank 1

Twagwa White 2



Twagwa Blank 2



Twagwa White 3

APPENDIX 5.2

DIGITAL IMAGES OF THE LARGE EXCAVATED PIGMENTS USED IN THIS STUDY.

A Sony Digital Monica, MVC-FD 88 model, with a 1.3 mega pixel capacity was used to capture the following images. The paper clip in these images is 30 mm long.

Layer 1


No. 001


No. 022


No. 103


No.133


No. 243


No.272b

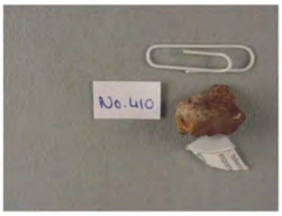

No. 278

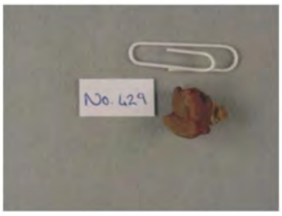

No. 330


No. 344


No 372


No. 400


No. 410


No. 429


No. 430


No. 440


No. 516


No. 562


No. 594


No. 751

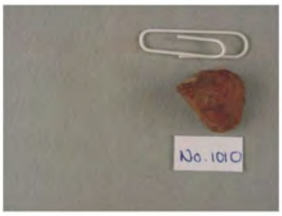

No. 797


No. 873


No.895


No. 912


No. 986


No. 1010


No 1035

Layer 2

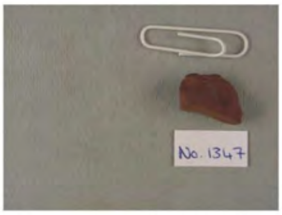

No. 1069


No. 1071

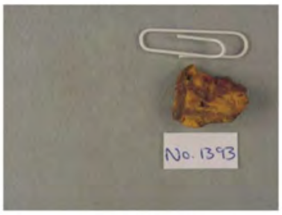

No. 1259

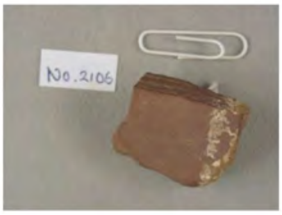

No. 1293


No. 1314


No. 1347


No. 1373


No. 1393


No. 2106

Layer 3


No. 1424


No.1534


No.1581


No. 1624


No.1638


No.1639


No.1659


No.1669


No. 1672


No. 1690


No. 1695


No. 1696


No. 1699


No. 1744


No.1779b


No. 1855


No. 1871


No.1874


No. 1904


No. 1920


No. 1921


No. 1939


No. 1942


No. 1943


No. 1944


No. 2074


No. 2075

APPENDIX 5.3

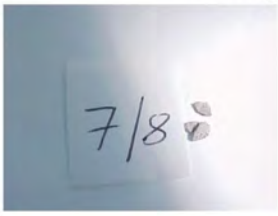
DIGITAL IMAGES OF THE SMALL EXCAVATED PIGMENTS USED IN THIS STUDY.

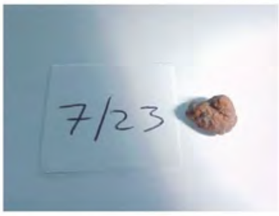
A Sony Digital Monica, MVC-FD 88 model, with a 1.3 mega pixel capacity was used to capture the following images. The sample from Layer 5 is 35 mm across. All image taken at the same distance.

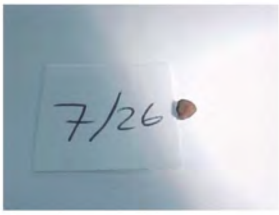
Layer 5

Layer 6

Layer 7

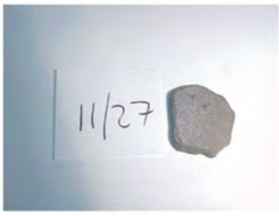


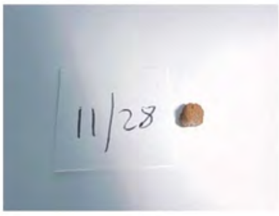


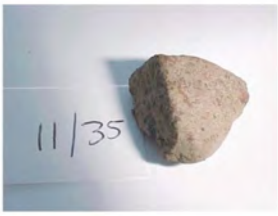


Layer 9

Layer 11

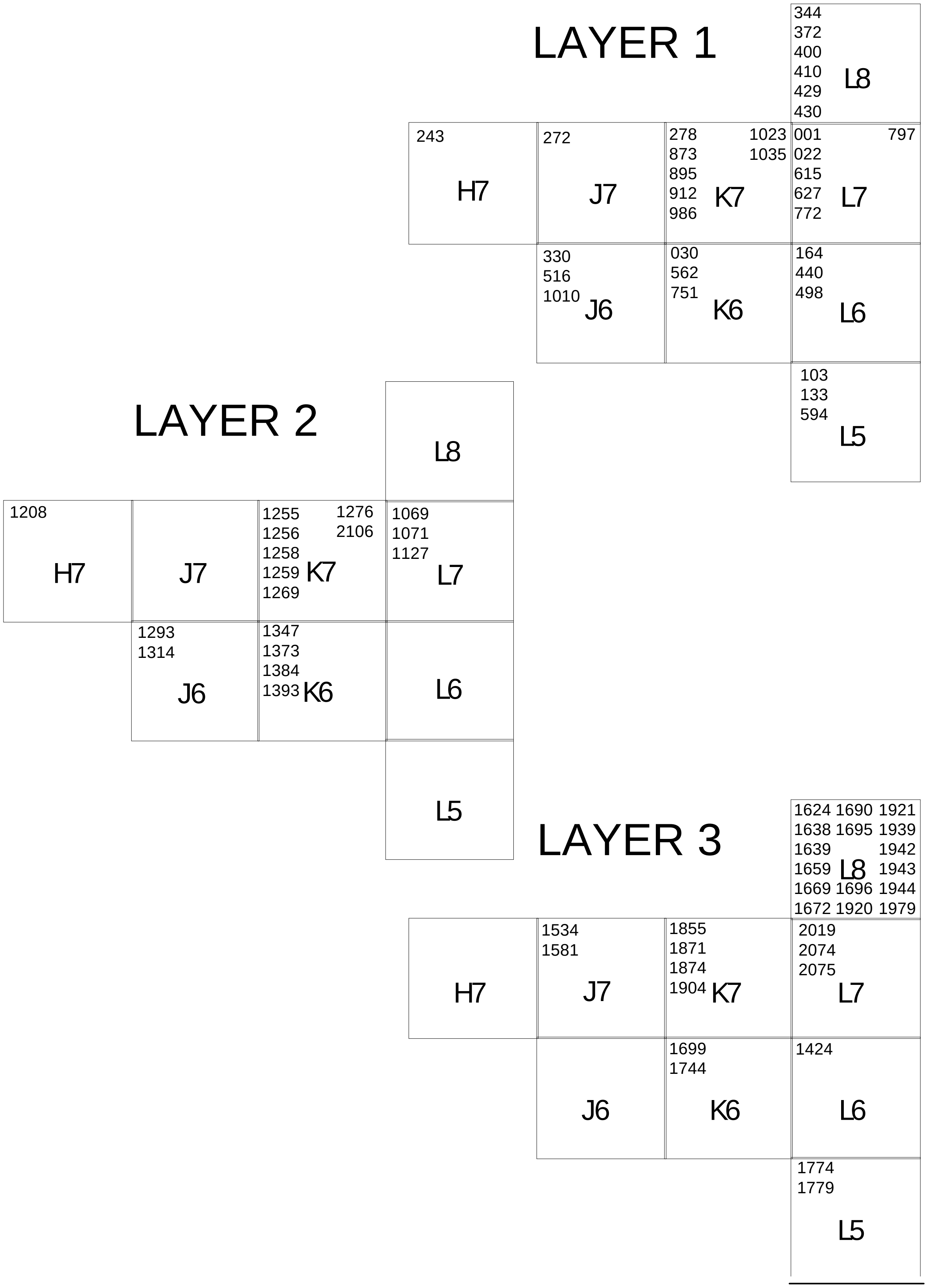






APPENDIX 5.4

MAQONQO SHELTER DEPOSIT SAMPLES - STRATIGRAPHIC LOCATIONS.



LAYER 5

			L8
H7	J7	5/28 K7	L7
	J6	K6	L6
			L5

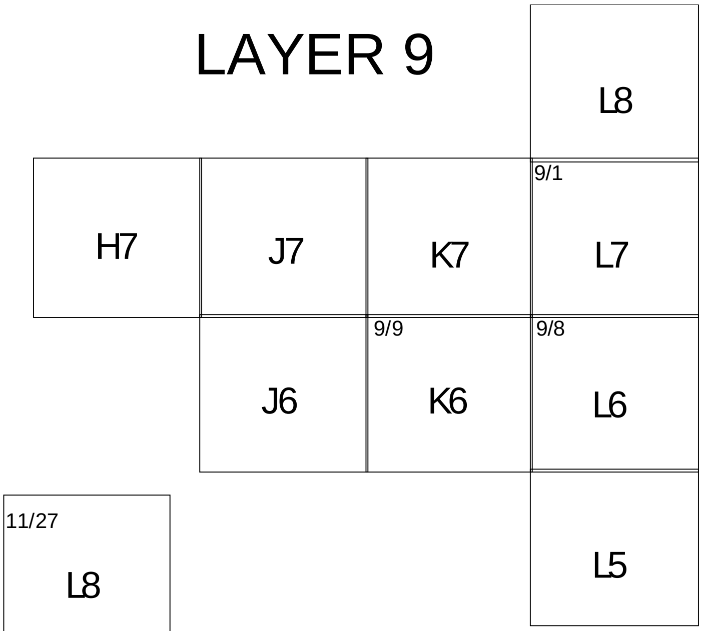
LAYER 6

			L8
H7	J7	6/5 6/6 K7	L7
	J6	K6	L6
			L5

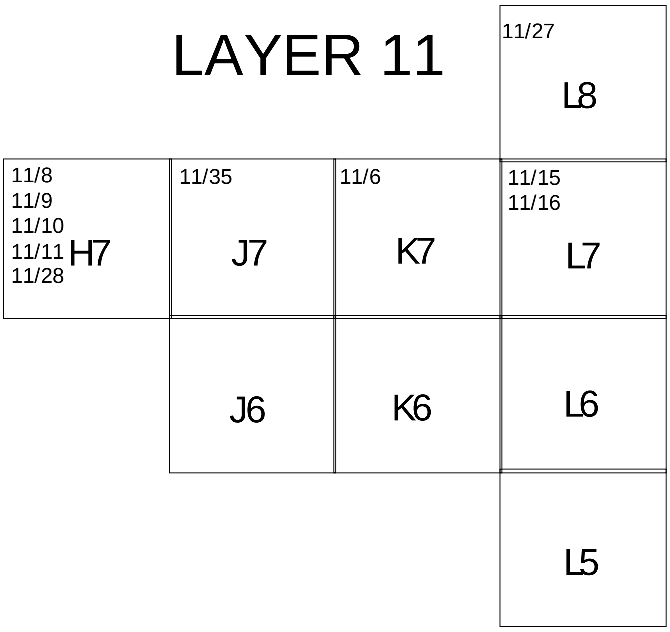
LAYER 7

			7/18 L8
Paint 20 7/20 7/23 H7 7/26	J7	7/15 K7	7/8 7/30 L7
	J6	7/11 7/12 K6	7/3 L6
			L5

LAYER 9



LAYER 11



APPENDIX 5.5

CO-ORDINATES FOR LOCAL AND DISTANT FIELD SAMPLES (CAPE 1880 DATUM).

LOCAL FIELD SITES	LATITUDE	LONGITUDE
Site 1	28^0 20’ 07’’ S	30^0 26’ 08’’ E
Site 2	28^0 20’ 05’’ S	30^0 26’ 15’’ E
Site 3	28^0 19’ 30’’ S	30^0 26’ 40’’ E
Site 4	28^0 18’ 51’’ S	30^0 26’ 55’’ E
Site 5	28^0 18’ 30’’ S	30^0 25’ 45’’ E
Site 6	28^0 19’ 05’’ S	30^0 25’ 25’’ E
Site 7	28^0 20’ 15’’ S	30^0 27’ 20’’ E
Site 8	28^0 19’ 10’’ S	30^0 27’ 25’’ E
Site 9	28^0 19’ 21’’ S	30^0 25’ 05’’ E
Site 10	28^0 19’ 30’’ S	30^0 24’ 52’’ E
Assorted Samples	28^0 19’ 24’’ S	30^0 28’ 15’’ E
Yellow Powder	28^0 20’ 15’’ S	30^0 26’ 15’’ E
DISTANT FIELD SITES	LATITUDE	LONGITUDE
Alletta Mine	28^0 03’ 00’’ S	30^0 14’ 25’’ E
Mpate	28^0 07’ 35’’ S	30^0 12’ 45’’ E
Stanmore Mine	28^0 01’ 50’’ S	30^0 17’ 05’’ E
Hazeldene Mine	28^0 10’ 10’ S	30^0 26’ 35’’ E
Doringberg	28^0 01’ 45’’ S	30^0 25’ 20’’ E
Irondale	28^0 09’ 40’’ S	30^0 21’ 25’’ E

APPENDIX 5.6

DIGITAL IMAGES OF THE SHELTER AND LOCAL FIELD SAMPLES USED IN THIS STUDY.

A Sony Digital Monica, MVC-FD 88 model, with a 1.3 mega pixel capacity was used to capture the following images. The paper clip in these images is 30 mm long.

APPENDIX 5.6

SAMPLE IMAGE	SAMPLE DESCRIPTION
Local Field Samples from around Maqonqo Shelter	
	Weathered dolerite
	Fe enriched sandstone
	Fe enriched sandstone
	Weathered dolerite
	Fe enriched sandstone
	Fe nodule - yellow sampled
	Weathered ferricrete

APPENDIX 5.6 - Continued

<table>
<tr><th>SAMPLE IMAGE</th><th>SAMPLE DESCRIPTION</th></tr>
<tr><td>
</td><td>Ferricrete</td></tr>
<tr><td>
</td><td>Weathered dolerite</td></tr>
<tr><td>
</td><td>Weathered dolerite</td></tr>
<tr><td>
</td><td>Wet paste (ferrihydrite)</td></tr>
<tr><td>
</td><td>Dry powder (ferrihydrite)</td></tr>
<tr><td></td><td>Assorted pigments from river valley</td></tr>
<tr><td colspan="2">Samples collected from within Maqonqo Shelter (A to E collected from the shelter wall, whilst F to G were sampled from surface derived samples)</td></tr>
<tr><td>
</td><td>Sample A - Sandstone wall</td></tr>
</table>

APPENDIX 5.6 - Continued

SAMPLE IMAGE	SAMPLE DESCRIPTION
	Sample B - Sandstone wall
	Sample C - Sandstone wall
	Sample D - Sandstone wall
	Sample E - Sandstone wall
	Sample F - Dolerite (weathered rind analysed)
	Sample G - Dolerite
	Sample H - Weathered dolerite

APPENDIX 5.7

DETECTION LIMITS AND ANALYTICAL ACCURACY ASSOCIATED WITH THE XRF DATA.

The following is a list provided by Mr R. Seyambu, School of Geological and Computational Sciences, University of KwaZulu-Natal, Durban who conducted the XRF analyses. The detection limits represent theoretical optima. It is likely that the actual limits obtainable on the equipment used are lower than indicated i.e., major oxides not less than 0.01%; trace elements not lower than 1 ppm.

ELEMENT	DETECTION LIMITS	ANALYTICAL ACCURACY	TUBE ANODE
Al_2O_3	0.005%	0.50%	Sc/Mo
CaO	0.0003%	0.20%	Sc/Mo
Fe_2O_3	0.001%	0.50%	Sc/Mo
K_2O	0.0003%	0.20%	Sc/Mo
MgO	0.011%	0.30%	Sc/Mo
MnO	0.001%	0.50%	Sc/Mo
Na_2O	0.018%	2%	Sc/Mo
P_2O_5	0.001%	0.20%	Sc/Mo
SiO_2	0.004%	0.20%	Sc/Mo
TiO_2	0.0004%	0.20%	Sc/Mo
As	0.001ppm	10%	Au
Ba	0.1ppm	20%	Cr
Cd	0.6ppm	10%	Au
Ce	0.13ppm	5%	Au
Cl	1ppm	10%	Cr
Co	0.1ppm	10%	Au
Cr	0.6ppm	5%	Au
Cu	0.2ppm	5%	Au
F	2ppm	10%	Cr
Ga	0.2ppm	10%	Au
La	0.5ppm	15%	Au
Mo	1ppm	10%	Au
Nb	0.1ppm	3%	Rh
Nd	0.3ppm	5%	Au
Ni	0.1ppm	5%	Au
Pb	0.1ppm	10%	Au
Rb	0.4ppm	2%	Rh
S	0.001ppm	10%	Cr
Sc	0.3ppm	10%	Cr
Sn	2ppm	10%	Au
Sr	0.3ppm	3%	Rh
Ta	3ppm	10%	Rh
Th	0.5ppm	20%	Rh
U	0.1ppm	20%	Rh
V	0.5ppm	10%	Au
W	0.5ppm	10%	Au
Y	0.3ppm	3%	Rh
Zn	0.3ppm	5%	Au
Zr	0.3ppm	3%	Rh

APPENDIX 5.8

RAW DATA FOR ALL STANDARD XRF ANALYSES.

Major elements

The major element analyses obtained from the XRF analyses were used in the statistical comparison between the paints and the local field samples, the excavated deposits and the field samples, as well as between all the field data. A comparison between the different pigments can be achieved without modifying the XRF data, as they have all been analysed under the same conditions. However, in an attempt to 'refine' the data a little more, these values were first normalised to 100 % before being analysed. This was done in order to standardise the data to allow for equitable comparisons to be made.

The normalisation process was achieved as follows (using SiO_2 from sample 1, Layer 1 as an example):

$$\text{Normalised } SiO_2 = \frac{(SiO_2\% \times 100)}{\text{Total Weight\%}} = \frac{(8.50\% \times 100)}{99.20\%}$$

$$\therefore \quad 8.57\ \% \text{ of total sample is } SiO_2$$

A direct comparison between the XRF and EDX results cannot be achieved, however, for the major element XRF data are recorded in WT%, whilst the EDX data are recorded as the atomic mass %. In order to allow for a direct comparison, the oxide data was converted to an atomic mass % using the following formulae (see 'Dry element%' in the following Appendices):

$$\text{Percentage Si in } SiO_2 = \frac{\text{Molar mass Si}}{\text{Molar mass } SiO_2} \times \frac{100}{1} = \frac{28.086}{60.074} \times \frac{100}{1} = 46.75\ \% \text{ of } SiO_2 \text{ is Si}$$

$\therefore$46.75 % of the 8.57 % (the weight percentage of SiO_2 normalised to 100 %) is Si

$$= \frac{8.57}{100} \times \frac{46.75}{1}$$

$$\therefore \quad 4.01\ \% \text{ Si in total sample (Dry)}$$

A direct comparison of these findings cannot be conducted with the results obtained for the paints, however, as these latter samples were examined whilst still in a hydrated state. Due to the nature of the XRF technique, any water (and other volatiles) that might be present within the sample are ‘lost’, with this loss being recorded as loss on ignition (L.O.I.). Thus, in order to allow for this comparison, the XRF results were re-calculated (using the normalised values) to take L.O.I. into account. This ‘wet’ value was worked out according to the following formulae (see ‘Wet element%’ in the following Appendices):

$$\text{Wet\% oxide} = \frac{(\text{Normalised oxide\% x L.O.I.\%})}{100} + \text{Normalised oxide\%}$$

$$= \frac{(8.57\%\ SiO_2 \text{ x } 3.09\% \text{ L.O.I.})}{100} + 8.57\%\ SiO_2$$

$$\therefore \quad 8.83\ \%\ \text{‘wet’ value for } SiO_2$$

This ‘wet’ SiO_2% was then re-calculated into the element form by the calculation given above, thus giving a ‘wet’ Si value of 4.13 % in 100 % total sample (Wet).

All of the XRF results with their corresponding calculations are given in the following Appendices (Note: elements for which no value was recorded, either because the element was not present or was present in a concentration below the machine’s detection limit are marked ‘nd’ indicating that the element was ‘not detected’.):

APPENDIX A5.8.1- XRF derived major element results large excavated pigments from Maqonqo Shelter
APPENDIX A5.8.2 - XRF derived major element results for the Maqonqo Shelter, local and distant field samples
APPENDIX A5.8.3 - XRF derived minor element results for the large excavated pigments from Maqonqo Shelter
APPENDIX A5.8.4 - XRF derived minor element results for the minor elements Maqonqo Shelter, local and distant field samples

APPENDIX A5.8.1

XRF derived major element results for the large excavated pigments from Maqonqo Shelter

ELEMENTAL COMPOSITIONS EXPRESSED AS A WEIGHT PERCENTAGE

COMMENT	LAYER	SAMPLE	SiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	TOTAL	L.O.I
RAW DATA	1	1	8.50	4.49	84.93	0.09	0.18	0.16	0.06	0.28	0.23	0.29	99.20	3.09
NORMALISED			8.57	4.53	85.61	0.09	0.18	0.16	0.06	0.28	0.23	0.29		
DRY ELEMENT %			4.01	1.20	29.94	0.07	0.11	0.12	0.02	0.12	0.14	0.06		
WET ELEMENT %			4.13	1.23	30.87	0.07	0.11	0.12	0.02	0.12	0.14	0.07		
RAW DATA		22	5.67	0.62	91.97	0.05	0.02	0.16	nd	0.02	0.04	0.03	98.58	5.87
NORMALISED			5.75	0.63	93.29	0.05	0.02	0.16		0.02	0.04	0.03		
DRY ELEMENT %			2.69	0.17	32.63	0.04	0.01	0.12		0.01	0.03	0.01		
WET ELEMENT %			2.85	0.18	34.54	0.04	0.01	0.12		0.01	0.03	0.01		
RAW DATA		103	38.71	10.98	38.25	0.43	4.05	3.95	1.15	1.11	0.90	0.17	99.69	4.13
NORMALISED			38.83	11.01	38.37	0.43	4.06	3.96	1.15	1.11	0.90	0.17		
DRY ELEMENT %			18.15	2.91	13.42	0.33	2.45	2.83	0.43	0.46	0.54	0.04		
WET ELEMENT %			18.90	3.04	13.97	0.35	2.55	2.95	0.45	0.48	0.56	0.04		
RAW DATA		133	66.40	8.47	22.66	0.01	0.14	0.22	0.09	1.19	0.31	0.26	99.76	4.78
NORMALISED			66.56	8.49	22.71	0.01	0.14	0.22	0.09	1.19	0.31	0.26		
DRY ELEMENT %			31.11	2.25	7.94	0.01	0.08	0.16	0.03	0.50	0.19	0.06		
WET ELEMENT %			32.60	2.35	8.32	0.01	0.09	0.17	0.04	0.52	0.20	0.06		
RAW DATA		243	5.79	2.40	85.10	0.31	0.31	2.26	nd	0.21	0.06	3.28	99.71	2.97
NORMALISED			5.81	2.41	85.35	0.31	0.31	2.27		0.21	0.06	3.29		
DRY ELEMENT %			2.71	0.64	29.85	0.24	0.19	1.62		0.09	0.03	0.72		
WET ELEMENT %			2.79	0.66	30.73	0.24	0.19	1.67		0.09	0.03	0.74		
RAW DATA		272	3.08	1.40	92.42	1.34	0.22	0.56	nd	0.35	nd	0.19	99.55	7.69
NORMALISED			3.09	1.41	92.84	1.35	0.22	0.56		0.35		0.19		
DRY ELEMENT %			1.45	0.37	32.47	1.04	0.13	0.40		0.15		0.04		
WET ELEMENT %			1.56	0.40	34.96	1.12	0.14	0.43		0.16		0.04		
RAW DATA		278	17.94	4.52	74.96	0.09	0.28	0.38	nd	0.41	0.26	0.08	98.90	3.69
NORMALISED			18.14	4.57	75.79	0.09	0.28	0.38		0.41	0.26	0.08		
DRY ELEMENT %			8.48	1.21	26.51	0.07	0.17	0.27		0.17	0.15	0.02		
WET ELEMENT %			8.79	1.25	27.48	0.07	0.18	0.28		0.18	0.16	0.02		
RAW DATA		330	74.95	0.48	24.06	0.02	0.01	0.04	nd	0.04	0.01	0.03	99.65	0.56
NORMALISED			75.21	0.48	24.14	0.02	0.01	0.04		0.04	0.01	0.03		
DRY ELEMENT %			35.16	0.13	8.44	0.01	0.01	0.03		0.02	0.01	0.01		
WET ELEMENT %			35.35	0.13	8.49	0.01	0.01	0.03		0.02	0.01	0.01		
RAW DATA		344	3.52	0.49	89.21	0.88	2.43	2.10	nd	0.11	0.03	0.23	99.00	4.91
NORMALISED			3.56	0.49	90.11	0.88	2.45	2.12		0.11	0.03	0.23		
DRY ELEMENT %			1.66	0.13	31.51	0.68	1.48	1.52		0.05	0.02	0.05		
WET ELEMENT %			1.74	0.14	33.06	0.72	1.55	1.59		0.05	0.02	0.05		
RAW DATA		372	8.76	3.62	85.81	0.11	0.38	0.12	nd	0.36	0.20	0.14	99.49	12.20
NORMALISED			8.80	3.64	86.25	0.11	0.38	0.12		0.36	0.20	0.14		
DRY ELEMENT %			4.12	0.96	30.16	0.08	0.23	0.09		0.15	0.12	0.03		
WET ELEMENT %			4.62	1.08	33.84	0.09	0.26	0.10		0.17	0.13	0.03		
RAW DATA		400	18.08	0.88	78.96	0.51	0.23	0.31	nd	0.10	0.02	0.59	99.68	0.86
NORMALISED			18.14	0.88	79.21	0.51	0.23	0.31		0.10	0.02	0.59		
DRY ELEMENT %			8.48	0.23	27.70	0.40	0.14	0.22		0.04	0.01	0.13		
WET ELEMENT %			8.55	0.24	27.94	0.40	0.14	0.22		0.04	0.01	0.13		
RAW DATA		410	5.27	1.14	91.77	0.18	0.05	1.09	nd	0.08	0.04	0.04	99.66	2.55
NORMALISED			5.29	1.14	92.08	0.18	0.05	1.09		0.08	0.04	0.04		
DRY ELEMENT %			2.47	0.30	32.20	0.14	0.03	0.78		0.03	0.02	0.01		
WET ELEMENT %			2.53	0.31	33.02	0.14	0.03	0.80		0.03	0.02	0.01		
RAW DATA		429	8.00	2.67	86.55	0.09	0.18	1.79	nd	0.06	0.12	0.03	99.49	1.78
NORMALISED			8.04	2.68	86.99	0.09	0.18	1.80		0.06	0.12	0.03		
DRY ELEMENT %			3.76	0.71	30.42	0.07	0.11	1.29		0.03	0.07	0.01		
WET ELEMENT %			3.83	0.72	30.96	0.07	0.11	1.31		0.03	0.08	0.01		
RAW DATA		430	5.62	4.23	87.68	0.11	0.51	0.16	nd	0.33	0.15	0.05	98.84	3.23
NORMALISED			5.69	4.28	88.71	0.11	0.52	0.16		0.33	0.15	0.05		
DRY ELEMENT %			2.66	1.13	31.02	0.08	0.31	0.12		0.14	0.09	0.01		
WET ELEMENT %			2.74	1.17	32.03	0.09	0.32	0.12		0.14	0.09	0.01		
RAW DATA		440	18.83	12.53	58.32	1.68	0.53	3.82	nd	0.67	0.49	2.17	99.04	1.57
NORMALISED			19.01	12.65	58.89	1.70	0.54	3.86		0.68	0.49	2.19		
DRY ELEMENT %			8.89	3.35	20.59	1.31	0.32	2.76		0.28	0.30	0.48		
WET ELEMENT %			9.03	3.40	20.92	1.33	0.33	2.80		0.29	0.30	0.49		
RAW DATA		516	50.27	17.50	13.84	0.16	5.76	7.10	1.52	1.71	1.40	0.22	99.46	2.07
NORMALISED			50.54	17.60	13.92	0.16	5.79	7.14	1.53	1.72	1.40	0.22		
DRY ELEMENT %			23.63	4.66	4.87	0.12	3.49	5.10	0.57	0.71	0.84	0.05		
WET ELEMENT %			24.12	4.75	4.97	0.12	3.56	5.21	0.58	0.73	0.86	0.05		
RAW DATA		562	3.77	1.63	89.34	1.60	0.39	0.71	nd	0.26	0.04	1.29	99.03	7.24
NORMALISED			3.81	1.65	90.22	1.61	0.39	0.72		0.26	0.04	1.30		
DRY ELEMENT %			1.78	0.44	31.55	1.25	0.24	0.51		0.11	0.03	0.28		
WET ELEMENT %			1.91	0.47	33.83	1.34	0.25	0.55		0.12	0.03	0.30		
RAW DATA		594	68.65	0.90	30.00	0.03	nd	0.27	0.05	0.02	0.03	0.03	99.99	1.68
NORMALISED			68.66	0.90	30.00	0.03		0.27	0.05	0.02	0.03	0.03		
DRY ELEMENT %			32.09	0.24	10.49	0.02		0.19	0.02	0.01	0.02	0.01		
WET ELEMENT %			32.63	0.24	10.67	0.02		0.20	0.02	0.01	0.02	0.01		
RAW DATA		751	84.00	0.43	15.12	0.02	0.02	0.02	0.07	0.03	0.01	0.02	99.73	0.42
NORMALISED			84.23	0.43	15.16	0.02	0.02	0.02	0.07	0.03	0.01	0.02		
DRY ELEMENT %			39.37	0.11	5.30	0.01	0.01	0.01	0.03	0.01	0.01	0.00		
WET ELEMENT %			39.54	0.11	5.32	0.01	0.01	0.01	0.03	0.01	0.01	0.00		
RAW DATA		797	42.00	13.07	39.38	0.16	0.53	0.07	0.09	4.01	0.49	0.03	99.83	2.86
NORMALISED			42.07	13.09	39.45	0.16	0.53	0.07	0.09	4.02	0.49	0.03		
DRY ELEMENT %			19.67	3.46	13.80	0.12	0.32	0.05	0.03	1.67	0.30	0.01		
WET ELEMENT %			20.23	3.56	14.19	0.13	0.33	0.05	0.03	1.71	0.30	0.01		
RAW DATA		873	25.70	0.98	72.75	0.09	nd	0.08	0.05	0.05	0.05	0.05	99.80	0.90
NORMALISED			25.75	0.98	72.90	0.09		0.08	0.05	0.05	0.05	0.05		
DRY ELEMENT %			12.04	0.26	25.49	0.07		0.06	0.02	0.02	0.03	0.01		
WET ELEMENT %			12.15	0.26	25.72	0.07		0.06	0.02	0.02	0.03	0.01		

XRF derived major element results for the large excavated pigments from Maqonqo Shelter - Continued

ELEMENTAL COMPOSITIONS EXPRESSED AS A WEIGHT PERCENTAGE

COMMENT	LAYER	SAMPLE	SiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	TOTAL	L.O.I
RAW DATA	1	895	23.88	7.07	59.05	0.70	2.60	2.75	0.73	0.85	0.52	0.18	98.33	4.77
NORMALISED			24.29	7.19	60.05	0.72	2.64	2.80	0.74	0.86	0.53	0.18		
DRY ELEMENT %			11.35	1.90	21.00	0.55	1.59	2.00	0.28	0.36	0.32	0.04		
WET ELEMENT %			11.89	1.99	22.00	0.58	1.67	2.09	0.29	0.38	0.33	0.04		
RAW DATA		912	2.37	1.63	93.92	0.33	0.06	0.25	nd	0.06	0.06	0.07	98.75	1.48
NORMALISED			2.40	1.65	95.11	0.33	0.06	0.25		0.06	0.06	0.07		
DRY ELEMENT %			1.12	0.44	33.26	0.25	0.04	0.18		0.03	0.04	0.02		
WET ELEMENT %			1.14	0.44	33.75	0.26	0.04	0.18		0.03	0.04	0.02		
RAW DATA		986	22.37	5.96	69.30	0.14	0.61	0.11	nd	0.40	0.16	0.09	99.15	3.73
NORMALISED			22.56	6.01	69.89	0.15	0.62	0.11		0.40	0.16	0.09		
DRY ELEMENT %			10.55	1.59	24.44	0.11	0.37	0.08		0.17	0.10	0.02		
WET ELEMENT %			10.94	1.65	25.36	0.12	0.38	0.08		0.17	0.10	0.02		
RAW DATA		1010	74.31	1.00	23.71	0.28	nd	0.17	nd	0.03	0.02	0.02	99.54	1.83
NORMALISED			74.65	1.00	23.82	0.28		0.17		0.03	0.02	0.02		
DRY ELEMENT %			34.90	0.27	8.33	0.22		0.12		0.01	0.01	0.00		
WET ELEMENT %			35.54	0.27	8.48	0.22		0.12		0.01	0.01	0.00		
RAW DATA		1035	55.26	3.52	39.36	0.02	0.12	0.19	0.14	0.97	0.10	0.03	99.71	1.20
NORMALISED			55.42	3.53	39.47	0.02	0.12	0.19	0.14	0.97	0.10	0.03		
DRY ELEMENT %			25.91	0.93	13.80	0.01	0.07	0.14	0.05	0.40	0.06	0.01		
WET ELEMENT %			26.22	0.95	13.97	0.01	0.07	0.14	0.05	0.41	0.06	0.01		
RAW DATA	2	1069	20.13	13.65	62.19	0.04	0.19	0.55	nd	0.58	1.57	0.27	99.15	9.68
NORMALISED			20.30	13.77	62.72	0.04	0.19	0.55		0.58	1.58	0.27		
DRY ELEMENT %			9.49	3.64	21.94	0.03	0.12	0.40		0.24	0.95	0.06		
WET ELEMENT %			10.41	4.00	24.06	0.03	0.13	0.43		0.27	1.04	0.07		
RAW DATA		1071	79.72	0.21	19.51	0.13	nd	0.08	0.03	0.01	nd	0.02	99.70	0.40
NORMALISED			79.96	0.21	19.57	0.13		0.08	0.03	0.01		0.02		
DRY ELEMENT %			37.38	0.06	6.84	0.10		0.06	0.01	0.00		0.00		
WET ELEMENT %			37.53	0.06	6.87	0.10		0.06	0.01	0.00		0.00		
RAW DATA		1259	3.25	0.90	92.99	0.58	0.30	0.50	nd	0.24	0.02	0.06	98.84	2.13
NORMALISED			3.29	0.91	94.08	0.59	0.30	0.51		0.24	0.02	0.06		
DRY ELEMENT %			1.54	0.24	32.90	0.45	0.18	0.36		0.10	0.01	0.01		
WET ELEMENT %			1.57	0.25	33.60	0.46	0.19	0.37		0.10	0.01	0.01		
RAW DATA		1293	75.23	0.67	23.07	0.01	nd	0.23	0.03	0.17	0.01	0.01	99.42	0.56
NORMALISED			75.67	0.67	23.20	0.01		0.23	0.03	0.17	0.01	0.01		
DRY ELEMENT %			35.37	0.18	8.12	0.01		0.17	0.01	0.07	0.01	0.00		
WET ELEMENT %			35.57	0.18	8.16	0.01		0.17	0.01	0.07	0.01	0.00		
RAW DATA		1314	55.73	11.00	15.18	0.17	7.12	5.44	1.53	1.66	1.60	0.12	99.55	1.37
NORMALISED			55.98	11.05	15.25	0.17	7.15	5.46	1.54	1.67	1.60	0.12		
DRY ELEMENT %			26.17	2.92	5.33	0.13	4.31	3.91	0.57	0.69	0.96	0.03		
WET ELEMENT %			26.53	2.96	5.41	0.13	4.37	3.96	0.58	0.70	0.97	0.03		
RAW DATA		1347	52.89	3.05	42.91	0.02	nd	0.02	nd	0.89	0.09	0.02	99.88	0.71
NORMALISED			52.95	3.05	42.96	0.02		0.02		0.89	0.09	0.02		
DRY ELEMENT %			24.75	0.81	15.02	0.01		0.01		0.37	0.05	0.00		
WET ELEMENT %			24.93	0.81	15.13	0.01		0.01		0.37	0.05	0.00		
RAW DATA		1373	81.76	0.24	16.85	0.02	nd	0.41	0.03	0.06	nd	0.02	99.40	0.57
NORMALISED			82.25	0.24	16.95	0.02		0.41	0.03	0.06		0.02		
DRY ELEMENT %			38.45	0.06	5.93	0.02		0.29	0.01	0.03		0.00		
WET ELEMENT %			38.67	0.06	5.96	0.02		0.30	0.01	0.03		0.00		
RAW DATA		1393	7.73	2.14	88.04	0.33	0.43	0.29	nd	0.44	0.13	0.10	99.62	10.02
NORMALISED			7.76	2.15	88.38	0.33	0.43	0.29		0.44	0.13	0.10		
DRY ELEMENT %			3.63	0.57	30.91	0.25	0.26	0.21		0.18	0.08	0.02		
WET ELEMENT %			3.99	0.63	34.00	0.28	0.29	0.23		0.20	0.08	0.02		
RAW DATA		2106	38.18	3.58	56.03	0.03	0.03	0.34	0.02	1.02	0.13	0.01	99.38	1.51
NORMALISED			38.42	3.60	56.38	0.03	0.03	0.34	0.02	1.03	0.13	0.01		
DRY ELEMENT %			17.96	0.95	19.72	0.03	0.02	0.24	0.01	0.43	0.08	0.00		
WET ELEMENT %			18.23	0.97	20.01	0.03	0.02	0.25	0.01	0.43	0.08	0.00		
RAW DATA	3	1424	51.12	17.83	14.26	0.18	4.79	6.18	1.80	1.69	1.56	0.21	99.63	4.26
NORMALISED			51.31	17.90	14.31	0.18	4.81	6.20	1.81	1.70	1.57	0.21		
DRY ELEMENT %			23.98	4.74	5.01	0.14	2.90	4.43	0.67	0.70	0.94	0.05		
WET ELEMENT %			25.01	4.94	5.22	0.15	3.02	4.62	0.70	0.73	0.98	0.05		
RAW DATA		1534	6.90	3.40	86.74	0.29	0.33	0.41	nd	0.74	0.08	0.29	99.18	6.98
NORMALISED			6.96	3.43	87.46	0.29	0.33	0.41		0.75	0.08	0.29		
DRY ELEMENT %			3.25	0.91	30.59	0.23	0.20	0.30		0.31	0.05	0.06		
WET ELEMENT %			3.48	0.97	32.72	0.24	0.21	0.32		0.33	0.05	0.07		
RAW DATA		1581	57.02	1.09	40.95	0.04	0.02	0.62	nd	0.12	0.01	0.02	99.90	1.14
NORMALISED			57.08	1.09	40.99	0.04	0.02	0.62		0.12	0.01	0.02		
DRY ELEMENT %			26.68	0.29	14.34	0.03	0.01	0.44		0.05	0.01	0.00		
WET ELEMENT %			26.98	0.29	14.50	0.03	0.01	0.45		0.05	0.01	0.00		
RAW DATA		1624	56.31	15.47	12.49	0.13	5.16	5.74	1.84	1.16	1.43	0.16	99.89	4.91
NORMALISED			56.37	15.49	12.50	0.13	5.17	5.75	1.84	1.16	1.43	0.16		
DRY ELEMENT %			26.35	4.10	4.37	0.10	3.12	4.11	0.68	0.48	0.86	0.03		
WET ELEMENT %			27.64	4.30	4.59	0.10	3.27	4.31	0.72	0.51	0.90	0.04		
RAW DATA		1638	21.39	5.47	70.80	0.19	0.54	0.27	nd	0.46	0.24	0.06	99.42	3.86
NORMALISED			21.51	5.50	71.21	0.19	0.54	0.27		0.46	0.24	0.06		
DRY ELEMENT %			10.06	1.46	24.90	0.15	0.33	0.19		0.19	0.14	0.01		
WET ELEMENT %			10.45	1.51	25.87	0.15	0.34	0.20		0.20	0.15	0.01		
RAW DATA		1639	33.02	5.47	59.18	0.18	0.69	0.16	0.15	0.57	0.15	0.04	99.61	3.98
NORMALISED			33.15	5.49	59.41	0.18	0.69	0.16	0.15	0.57	0.15	0.04		
DRY ELEMENT %			15.50	1.45	20.78	0.14	0.42	0.11	0.06	0.24	0.09	0.01		
WET ELEMENT %			16.11	1.51	21.60	0.14	0.43	0.12	0.06	0.25	0.09	0.01		
RAW DATA		1659	32.69	4.80	57.96	0.49	0.43	0.58	0.32	1.01	0.25	0.24	98.76	4.02
NORMALISED			33.10	4.86	58.69	0.50	0.44	0.59	0.32	1.02	0.26	0.24		
DRY ELEMENT %			15.47	1.29	20.52	0.38	0.26	0.42	0.12	0.42	0.15	0.05		
WET ELEMENT %			16.09	1.34	21.35	0.40	0.27	0.44	0.13	0.44	0.16	0.06		

XRF derived major element results for the large excavated pigments from Maqonqo Shelter - Continued

ELEMENTAL COMPOSITIONS EXPRESSED AS A WEIGHT PERCENTAGE

COMMENT	LAYER	SAMPLE	SiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	TOTAL	L.O.I
RAW DATA	3	1669	63.00	18.63	2.96	0.01	nd	0.07	1.71	12.95	nd	0.03	99.37	1.21
NORMALISED			63.40	18.75	2.98	0.01		0.07	1.72	13.03		0.03		
DRY ELEMENT %			29.64	4.96	1.04	0.01		0.05	0.64	5.41		0.01		
WET ELEMENT %			29.99	5.02	1.05	0.01		0.05	0.65	5.47		0.01		
RAW DATA		1672	40.52	3.77	54.31	0.05	0.52	0.35	0.11	0.15	0.13	0.03	99.94	4.08
NORMALISED			40.54	3.77	54.34	0.05	0.52	0.35	0.11	0.15	0.13	0.03		
DRY ELEMENT %			18.95	1.00	19.00	0.04	0.31	0.25	0.04	0.06	0.08	0.01		
WET ELEMENT %			19.73	1.04	19.78	0.04	0.33	0.26	0.04	0.06	0.08	0.01		
RAW DATA		1690	63.05	15.83	13.22	0.22	2.30	1.41	0.69	1.19	1.57	0.12	99.61	7.79
NORMALISED			63.30	15.89	13.27	0.22	2.31	1.42	0.69	1.19	1.58	0.12		
DRY ELEMENT %			29.59	4.21	4.64	0.17	1.39	1.01	0.26	0.50	0.95	0.03		
WET ELEMENT %			31.89	4.53	5.00	0.18	1.50	1.09	0.28	0.53	1.02	0.03		
RAW DATA		1695	62.09	15.87	11.61	0.06	1.99	1.71	2.85	1.84	1.35	0.16	99.54	4.40
NORMALISED			62.38	15.94	11.66	0.06	2.00	1.72	2.86	1.85	1.36	0.16		
DRY ELEMENT %			29.16	4.22	4.08	0.05	1.21	1.23	1.06	0.77	0.81	0.04		
WET ELEMENT %			30.44	4.40	4.26	0.05	1.26	1.28	1.11	0.80	0.85	0.04		
RAW DATA		1696	54.09	15.04	11.01	0.17	5.08	9.30	2.76	1.03	1.19	0.17	99.85	1.91
NORMALISED			54.17	15.06	11.03	0.17	5.09	9.31	2.76	1.03	1.19	0.17		
DRY ELEMENT %			25.32	3.99	3.86	0.13	3.07	6.66	1.03	0.43	0.71	0.04		
WET ELEMENT %			25.81	4.06	3.93	0.14	3.13	6.78	1.04	0.44	0.73	0.04		
RAW DATA		1699	26.63	6.48	63.95	0.14	0.77	0.15	0.01	0.37	0.27	0.06	98.82	3.83
NORMALISED			26.95	6.56	64.71	0.15	0.78	0.15	0.01	0.37	0.27	0.06		
DRY ELEMENT %			12.60	1.74	22.63	0.11	0.47	0.11	0.00	0.16	0.16	0.01		
WET ELEMENT %			13.08	1.80	23.50	0.12	0.49	0.11	0.00	0.16	0.17	0.01		
RAW DATA		1744	53.09	16.33	18.00	0.09	4.29	3.73	1.26	1.76	1.28	0.22	100.06	4.51
NORMALISED			53.06	16.32	17.99	0.09	4.29	3.73	1.26	1.76	1.28	0.22		
DRY ELEMENT %			24.80	4.32	6.29	0.07	2.59	2.66	0.47	0.73	0.77	0.05		
WET ELEMENT %			25.92	4.51	6.57	0.07	2.70	2.78	0.49	0.76	0.80	0.05		
RAW DATA		1779	23.14	6.39	63.95	0.04	0.30	0.35	0.05	3.40	0.78	0.36	98.77	8.79
NORMALISED			23.43	6.47	64.75	0.04	0.30	0.35	0.05	3.44	0.79	0.36		
DRY ELEMENT %			10.95	1.71	22.64	0.03	0.18	0.25	0.02	1.43	0.48	0.08		
WET ELEMENT %			11.91	1.86	24.63	0.03	0.20	0.28	0.02	1.55	0.52	0.09		
RAW DATA		1855	90.43	0.29	9.11	0.02	nd	0.02	0.05	0.03	nd	0.01	99.95	0.48
NORMALISED			90.48	0.29	9.11	0.02		0.02	0.05	0.03		0.01		
DRY ELEMENT %			42.29	0.08	3.19	0.01		0.01	0.02	0.01		0.00		
WET ELEMENT %			42.50	0.08	3.20	0.01		0.01	0.02	0.01		0.00		
RAW DATA		1871	75.14	0.83	23.31	0.03	0.03	0.19	0.06	0.11	nd	0.03	99.73	0.84
NORMALISED			75.34	0.83	23.37	0.03	0.03	0.19	0.06	0.11		0.03		
DRY ELEMENT %			35.22	0.22	8.17	0.02	0.02	0.14	0.02	0.05		0.01		
WET ELEMENT %			35.51	0.22	8.24	0.02	0.02	0.14	0.02	0.05		0.01		
RAW DATA		1874	27.84	6.58	62.56	0.17	0.96	0.22	nd	0.63	0.23	0.07	99.40	4.77
NORMALISED			28.01	6.62	62.94	0.17	0.97	0.22		0.63	0.23	0.07		
DRY ELEMENT %			13.09	1.75	22.01	0.13	0.58	0.16		0.26	0.14	0.02		
WET ELEMENT %			13.72	1.84	23.06	0.14	0.61	0.17		0.28	0.15	0.02		
RAW DATA		1904	2.67	1.10	92.35	0.57	0.30	0.69	nd	0.16	0.03	0.31	98.18	7.18
NORMALISED			2.72	1.12	94.06	0.58	0.31	0.70		0.16	0.03	0.32		
DRY ELEMENT %			1.27	0.30	32.90	0.45	0.18	0.50		0.07	0.02	0.07		
WET ELEMENT %			1.36	0.32	35.26	0.48	0.20	0.54		0.07	0.02	0.07		
RAW DATA		1920	82.76	0.54	15.52	0.02	0.07	0.75	nd	0.06	0.01	0.02	99.73	1.29
NORMALISED			82.98	0.54	15.56	0.02	0.07	0.75		0.06	0.01	0.02		
DRY ELEMENT %			38.79	0.14	5.44	0.02	0.04	0.54		0.02	0.01	0.00		
WET ELEMENT %			39.29	0.15	5.51	0.02	0.04	0.54		0.03	0.01	0.00		
RAW DATA		1921	39.81	5.99	51.01	0.12	0.88	0.38	nd	0.63	0.20	0.04	99.06	3.32
NORMALISED			40.19	6.05	51.49	0.12	0.89	0.38		0.64	0.20	0.04		
DRY ELEMENT %			18.79	1.60	18.01	0.09	0.54	0.27		0.26	0.12	0.01		
WET ELEMENT %			19.41	1.65	18.61	0.09	0.55	0.28		0.27	0.12	0.01		
RAW DATA		1939	23.67	7.85	61.36	1.50	1.23	1.50	0.12	0.83	0.30	0.80	99.17	4.20
NORMALISED			23.87	7.92	61.87	1.51	1.24	1.51	0.12	0.84	0.31	0.81		
DRY ELEMENT %			11.16	2.09	21.64	1.17	0.75	1.08	0.04	0.35	0.18	0.18		
WET ELEMENT %			11.63	2.18	22.55	1.22	0.78	1.13	0.05	0.36	0.19	0.18		
RAW DATA		1942	42.99	4.63	50.24	0.07	0.61	0.11	0.11	0.80	0.14	0.07	99.76	2.85
NORMALISED			43.09	4.64	50.36	0.07	0.61	0.11	0.11	0.80	0.14	0.07		
DRY ELEMENT %			20.14	1.23	17.61	0.05	0.37	0.08	0.04	0.33	0.08	0.02		
WET ELEMENT %			20.72	1.26	18.11	0.05	0.38	0.08	0.04	0.34	0.09	0.02		
RAW DATA		1943	41.55	9.93	42.46	1.56	3.45	0.17	nd	0.08	0.28	0.06	99.53	5.10
NORMALISED			41.75	9.98	42.66	1.57	3.47	0.17		0.08	0.28	0.06		
DRY ELEMENT %			19.51	2.64	14.92	1.22	2.09	0.12		0.03	0.17	0.01		
WET ELEMENT %			20.51	2.77	15.68	1.28	2.20	0.13		0.04	0.18	0.01		
RAW DATA		1944	48.59	3.68	46.39	0.16	0.53	0.15	0.01	0.21	0.13	0.06	99.92	2.50
NORMALISED			48.63	3.68	46.43	0.16	0.53	0.15	0.01	0.21	0.13	0.06		
DRY ELEMENT %			22.73	0.97	16.24	0.12	0.32	0.11	0.00	0.09	0.08	0.01		
WET ELEMENT %			23.30	1.00	16.64	0.13	0.33	0.11	0.00	0.09	0.08	0.01		
RAW DATA		2074	8.47	5.18	83.10	0.32	0.33	0.41	nd	0.66	0.11	0.56	99.13	7.49
NORMALISED			8.54	5.23	83.83	0.32	0.33	0.41		0.67	0.11	0.56		
DRY ELEMENT %			3.99	1.38	29.32	0.25	0.20	0.30		0.28	0.06	0.12		
WET ELEMENT %			4.29	1.49	31.51	0.27	0.22	0.32		0.30	0.07	0.13		
RAW DATA		2075	6.32	2.31	89.07	0.35	0.22	0.39	nd	0.38	0.04	0.28	99.36	6.99
NORMALISED			6.36	2.32	89.64	0.35	0.22	0.39		0.38	0.04	0.28		
DRY ELEMENT %			2.97	0.62	31.35	0.27	0.13	0.28		0.16	0.02	0.06		
WET ELEMENT %			3.18	0.66	33.54	0.29	0.14	0.30		0.17	0.02	0.07		

APPENDIX A5.8.2
XRF derived major element results for the Maqonqo Shelter, local and distant field samples

ELEMENTAL COMPOSITIONS EXPRESSED AS A WEIGHT PERCENTAGE

COMMENT	SAMPLE	SiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	TOTAL	L.O.I
		SHELTER SAMPLES											
RAW DATA	SHELTER A	77.00	6.17	2.92	0.01	0.37	3.66	0.20	3.22	0.14	0.38	94.07	6.26
NORMALISED		81.85	6.56	3.10	0.01	0.39	3.89	0.21	3.42	0.14	0.40		
DRY ELEMENT %		38.26	1.74	1.09	0.01	0.24	2.78	0.08	1.42	0.09	0.09		
WET ELEMENT %		40.66	1.84	1.15	0.01	0.25	2.95	0.08	1.51	0.09	0.09		
RAW DATA	SHELTER B	83.31	7.12	0.43	0.02	0.18	1.71	0.31	4.47	0.38	0.10	98.04	3.98
NORMALISED		84.98	7.26	0.44	0.02	0.18	1.74	0.32	4.56	0.39	0.10		
DRY ELEMENT %		39.72	1.92	0.15	0.02	0.11	1.25	0.12	1.89	0.23	0.02		
WET ELEMENT %		41.30	2.00	0.16	0.02	0.12	1.30	0.12	1.97	0.24	0.02		
RAW DATA	SHELTER C	82.82	6.20	1.84	0.01	0.22	2.15	0.21	3.37	0.10	0.21	97.12	5.13
NORMALISED		85.28	6.38	1.89	0.01	0.23	2.21	0.22	3.47	0.11	0.22		
DRY ELEMENT %		39.86	1.69	0.66	0.00	0.14	1.58	0.08	1.44	0.06	0.05		
WET ELEMENT %		41.91	1.78	0.70	0.00	0.14	1.66	0.08	1.51	0.07	0.05		
RAW DATA	SHELTER D	86.04	7.03	0.24	0.07	0.07	0.51	0.33	4.02	0.16	0.10	98.57	2.70
NORMALISED		87.29	7.13	0.24	0.08	0.07	0.52	0.33	4.08	0.16	0.10		
DRY ELEMENT %		40.80	1.89	0.09	0.06	0.04	0.37	0.12	1.69	0.10	0.02		
WET ELEMENT %		41.90	1.94	0.09	0.06	0.04	0.38	0.13	1.74	0.10	0.02		
RAW DATA	SHELTER E	86.30	7.34	0.38	0.02	0.09	0.20	0.44	3.78	0.33	0.10	98.97	2.80
NORMALISED		87.20	7.42	0.38	0.02	0.09	0.20	0.44	3.82	0.34	0.10		
DRY ELEMENT %		40.76	1.96	0.13	0.01	0.05	0.14	0.16	1.59	0.20	0.02		
WET ELEMENT %		41.90	2.02	0.14	0.01	0.06	0.15	0.17	1.63	0.21	0.02		
RAW DATA	SHELTER F	38.91	13.87	36.17	0.18	1.42	2.27	0.28	3.13	1.60	0.32	98.16	14.89
NORMALISED		39.64	14.13	36.85	0.19	1.45	2.31	0.29	3.19	1.63	0.33		
DRY ELEMENT %		18.53	3.74	12.89	0.14	0.87	1.65	0.11	1.32	0.97	0.07		
WET ELEMENT %		21.29	4.30	14.81	0.17	1.00	1.90	0.12	1.52	1.12	0.08		
RAW DATA	SHELTER G	53.60	18.03	13.17	0.12	4.47	4.05	1.47	2.84	1.45	0.20	99.41	9.76
NORMALISED		53.92	18.14	13.25	0.12	4.50	4.07	1.48	2.86	1.46	0.20		
DRY ELEMENT %		25.20	4.80	4.63	0.09	2.71	2.91	0.55	1.19	0.87	0.04		
WET ELEMENT %		27.66	5.27	5.09	0.10	2.98	3.20	0.60	1.30	0.96	0.05		
RAW DATA	SHELTER H	47.30	12.34	30.97	0.67	1.80	0.78	0.07	2.28	3.01	0.33	99.53	9.44
NORMALISED		47.52	12.40	31.12	0.68	1.81	0.78	0.07	2.29	3.02	0.33		
DRY ELEMENT %		22.21	3.28	10.88	0.52	1.09	0.56	0.03	0.95	1.81	0.07		
WET ELEMENT %		24.31	3.59	11.91	0.57	1.19	0.61	0.03	1.04	1.98	0.08		
		LOCAL FIELD SAMPLES											
RAW DATA	SITE 1	45.53	17.25	23.15	0.15	5.20	4.77	1.36	0.67	1.36	0.15	99.59	10.03
NORMALISED		45.72	17.32	23.25	0.15	5.22	4.79	1.37	0.67	1.37	0.15		
DRY ELEMENT %		21.37	4.58	8.13	0.11	3.15	3.42	0.51	0.28	0.82	0.03		
WET ELEMENT %		23.51	5.04	8.94	0.12	3.46	3.77	0.56	0.31	0.90	0.04		
RAW DATA	SITE 2	54.00	18.35	13.09	0.22	5.13	4.90	1.89	1.07	1.15	0.10	99.90	8.10
NORMALISED		54.05	18.37	13.10	0.22	5.14	4.90	1.89	1.07	1.15	0.10		
DRY ELEMENT %		25.27	4.86	4.58	0.17	3.10	3.51	0.70	0.44	0.69	0.02		
WET ELEMENT %		27.31	5.25	4.95	0.18	3.35	3.79	0.76	0.48	0.75	0.02		
RAW DATA	SITE 3B	58.03	25.16	4.74	0.06	1.82	0.63	0.97	6.30	1.27	0.08	99.06	14.65
NORMALISED		58.58	25.40	4.78	0.06	1.84	0.64	0.98	6.36	1.28	0.08		
DRY ELEMENT %		27.38	6.72	1.67	0.04	1.11	0.45	0.36	2.64	0.77	0.02		
WET ELEMENT %		31.39	7.71	1.92	0.05	1.27	0.52	0.42	3.03	0.88	0.02		
RAW DATA	SITE 3C	55.54	17.97	17.53	0.41	1.29	0.49	1.40	4.38	0.83	0.07	99.91	10.67
NORMALISED		55.59	17.99	17.55	0.41	1.29	0.49	1.40	4.38	0.83	0.07		
DRY ELEMENT %		25.99	4.76	6.14	0.32	0.78	0.35	0.52	1.82	0.50	0.02		
WET ELEMENT %		28.76	5.27	6.79	0.35	0.86	0.39	0.58	2.01	0.55	0.02		
RAW DATA	SITE 4	18.25	22.14	51.61	0.07	0.91	0.35	0.12	0.98	3.93	0.49	98.86	18.57
NORMALISED		18.46	22.40	52.21	0.07	0.92	0.35	0.12	0.99	3.98	0.50		
DRY ELEMENT %		8.63	5.93	18.26	0.06	0.56	0.25	0.05	0.41	2.38	0.11		
WET ELEMENT %		10.23	7.03	21.65	0.07	0.66	0.30	0.05	0.49	2.83	0.13		
RAW DATA	SITE 5	22.37	8.28	63.12	0.83	1.25	1.07	0.31	1.78	0.43	0.30	99.73	11.05
NORMALISED		22.43	8.30	63.29	0.83	1.25	1.07	0.31	1.78	0.43	0.30		
DRY ELEMENT %		10.49	2.20	22.13	0.64	0.76	0.77	0.12	0.74	0.26	0.07		
WET ELEMENT %		11.64	2.44	24.58	0.71	0.84	0.85	0.13	0.82	0.29	0.07		
RAW DATA	SITE 6A	3.74	1.26	93.08	0.31	0.26	0.14	nd	0.17	0.04	0.09	99.09	2.77
NORMALISED		3.77	1.27	93.93	0.31	0.26	0.14		0.17	0.04	0.09		
DRY ELEMENT %		1.76	0.34	32.85	0.24	0.16	0.10		0.07	0.03	0.02		
WET ELEMENT %		1.81	0.35	33.76	0.25	0.16	0.10		0.07	0.03	0.02		
RAW DATA	SITE 6B	13.58	3.55	80.84	0.64	0.27	0.17	nd	0.40	0.11	0.08	99.63	8.82
NORMALISED		13.63	3.56	81.14	0.64	0.27	0.17		0.40	0.11	0.08		
DRY ELEMENT %		6.37	0.94	28.38	0.50	0.16	0.12		0.17	0.07	0.02		
WET ELEMENT %		6.93	1.03	30.88	0.54	0.18	0.13		0.18	0.07	0.02		
RAW DATA	SITE 7A	51.13	10.85	35.58	0.13	0.22	0.14	0.12	1.00	0.49	0.13	99.80	9.68
NORMALISED		51.23	10.87	35.65	0.13	0.22	0.14	0.12	1.00	0.49	0.13		
DRY ELEMENT %		23.95	2.88	12.47	0.10	0.13	0.10	0.04	0.42	0.30	0.03		
WET ELEMENT %		26.27	3.16	13.67	0.11	0.15	0.11	0.05	0.46	0.32	0.03		
RAW DATA	SITE 8A	12.12	2.85	79.80	2.22	0.54	0.75	0.07	0.39	0.16	0.02	98.93	12.92
NORMALISED		12.25	2.88	80.66	2.24	0.55	0.76	0.07	0.39	0.16	0.02		
DRY ELEMENT %		5.73	0.76	28.21	1.74	0.33	0.54	0.03	0.16	0.10	0.00		
WET ELEMENT %		6.47	0.86	31.85	1.96	0.37	0.61	0.03	0.18	0.11	0.00		
RAW DATA	SITE 8B	44.41	6.25	46.67	0.34	0.33	0.19	0.20	1.03	0.36	0.03	99.80	10.50
NORMALISED		44.50	6.26	46.76	0.34	0.33	0.19	0.20	1.03	0.36	0.03		
DRY ELEMENT %		20.80	1.66	16.35	0.26	0.20	0.14	0.07	0.43	0.22	0.01		
WET ELEMENT %		22.98	1.83	18.07	0.29	0.22	0.15	0.08	0.47	0.24	0.01		
RAW DATA	SITE 9	13.35	42.99	38.53	0.11	0.41	0.05	nd	0.68	2.75	0.38	99.25	24.30
NORMALISED		13.45	43.31	38.82	0.11	0.41	0.05		0.69	2.77	0.38		
DRY ELEMENT %		6.29	11.46	13.58	0.09	0.25	0.04		0.28	1.66	0.08		
WET ELEMENT %		7.82	14.25	16.88	0.11	0.31	0.04		0.35	2.06	0.10		
RAW DATA	SITE 10	25.39	3.44	67.10	0.33	1.04	1.11	0.11	0.58	0.18	0.18	99.47	9.85
NORMALISED		25.53	3.46	67.46	0.33	1.05	1.12	0.11	0.58	0.18	0.18		
DRY ELEMENT %		11.93	0.92	23.59	0.26	0.63	0.80	0.04	0.24	0.11	0.04		
WET ELEMENT %		13.11	1.01	25.91	0.28	0.69	0.88	0.05	0.27	0.12	0.04		

XRF derived major element results for the Maqonqo Shelter, local and distant field samples - Continued

ELEMENTAL COMPOSITIONS EXPRESSED AS A WEIGHT PERCENTAGE

COMMENT	SAMPLE	SiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	TOTAL	L.O.I
RAW DATA	ASSORTED 1	10.67	1.56	84.44	2.03	0.13	0.19	nd	0.24	0.11	0.02	99.39	8.54
NORMALISED		10.74	1.57	84.96	2.05	0.13	0.19		0.24	0.11	0.02		
DRY ELEMENT %		5.02	0.42	29.71	1.59	0.08	0.14		0.10	0.07	0.00		
WET ELEMENT %		5.45	0.45	32.25	1.72	0.09	0.15		0.11	0.07	0.00		
RAW DATA	ASSORTED 2	21.07	13.39	59.52	2.11	0.54	0.39	0.08	0.38	0.97	0.19	98.63	21.19
NORMALISED		21.36	13.58	60.35	2.14	0.55	0.40	0.08	0.39	0.98	0.19		
DRY ELEMENT %		9.99	3.59	21.10	1.66	0.33	0.28	0.03	0.16	0.59	0.04		
WET ELEMENT %		12.10	4.35	25.58	2.01	0.40	0.34	0.04	0.19	0.71	0.05		
RAW DATA	YELLOW POWDER 1/	4.42	0.86	92.88	0.04	0.08	0.70	0.31	0.20	0.02	0.08	99.59	30.27
NORMALISED	FERRIHYDRITE	4.44	0.86	93.26	0.04	0.08	0.70	0.31	0.20	0.02	0.08		
DRY ELEMENT %		2.07	0.23	32.62	0.03	0.05	0.50	0.12	0.08	0.01	0.02		
WET ELEMENT %		2.70	0.30	42.49	0.04	0.06	0.65	0.15	0.11	0.02	0.02		
RAW DATA	YELLOW POWDER 2/	65.01	4.07	27.37	0.07	0.23	0.54	0.50	1.87	0.18	0.08	99.92	20.67
NORMALISED	FERRIHYDRITE	65.06	4.07	27.39	0.07	0.23	0.54	0.50	1.87	0.18	0.08		
DRY ELEMENT %		30.41	1.08	9.58	0.06	0.14	0.39	0.19	0.78	0.11	0.02		
WET ELEMENT %		36.70	1.30	11.56	0.07	0.17	0.47	0.22	0.94	0.13	0.02		
	DISTANT SAMPLES												
RAW DATA	STANMORE	1.83	2.54	94.01	0.38	0.29	0.06	nd	0.03	0.06	0.51	99.71	5.53
NORMALISED		1.84	2.55	94.28	0.38	0.29	0.06		0.03	0.06	0.51		
DRY ELEMENT %		0.86	0.67	32.97	0.29	0.18	0.04		0.01	0.04	0.11		
WET ELEMENT %		0.91	0.71	34.80	0.31	0.19	0.05		0.01	0.04	0.12		
RAW DATA	IRONDALE	3.23	1.81	93.38	0.12	0.24	0.05	nd	0.03	0.08	0.30	99.24	6.35
NORMALISED		3.25	1.82	94.10	0.12	0.24	0.05		0.03	0.08	0.30		
DRY ELEMENT %		1.52	0.48	32.91	0.09	0.15	0.04		0.01	0.05	0.07		
WET ELEMENT %		1.62	0.51	35.00	0.10	0.16	0.04		0.01	0.05	0.07		
RAW DATA	DORINGBERG	0.56	0.16	49.84	0.31	15.63	32.46	nd	0.01	0.03	0.27	99.27	33.49
NORMALISED		0.56	0.16	50.21	0.31	15.74	32.70		0.01	0.03	0.27		
DRY ELEMENT %		0.26	0.04	17.56	0.24	9.49	23.37		0.00	0.02	0.06		
WET ELEMENT %		0.35	0.06	23.44	0.32	12.67	31.20		0.01	0.02	0.08		
RAW DATA	MPATE	16.08	45.95	34.01	0.26	0.48	0.05	nd	0.22	2.68	0.34	100.1	24.09
NORMALISED		16.07	45.92	33.99	0.26	0.48	0.05		0.22	2.68	0.34		
DRY ELEMENT %		7.51	12.15	11.89	0.20	0.29	0.04		0.09	1.60	0.07		
WET ELEMENT %		9.32	15.08	14.75	0.25	0.36	0.04		0.11	1.99	0.09		
RAW DATA	ALLETTA 1	5.17	1.32	90.56	0.48	0.44	0.44	nd	0.05	0.06	0.52	99.04	11.44
NORMALISED		5.22	1.33	91.44	0.49	0.44	0.44		0.05	0.06	0.53		
DRY ELEMENT %		2.44	0.35	31.98	0.38	0.27	0.32		0.02	0.04	0.11		
WET ELEMENT %		2.72	0.39	35.64	0.42	0.30	0.35		0.02	0.04	0.13		
RAW DATA	ALLETTA 2	8.31	4.75	82.52	1.01	1.03	1.11	nd	0.35	0.15	0.62	99.85	29.88
NORMALISED		8.32	4.76	82.64	1.01	1.03	1.11		0.35	0.15	0.62		
DRY ELEMENT %		3.89	1.26	28.90	0.79	0.62	0.79		0.15	0.09	0.14		
WET ELEMENT %		5.05	1.64	37.54	1.02	0.81	1.03		0.19	0.11	0.18		
RAW DATA	HAZELDENE 1	2.42	0.72	94.60	0.63	0.46	0.28	nd	0.02	0.03	0.11	99.28	8.07
NORMALISED		2.44	0.73	95.29	0.64	0.46	0.28		0.02	0.03	0.11		
DRY ELEMENT %		1.14	0.19	33.32	0.49	0.28	0.20		0.01	0.02	0.02		
WET ELEMENT %		1.23	0.21	36.01	0.53	0.30	0.22		0.01	0.02	0.03		
RAW DATA	HAZELDENE 2	2.38	0.41	95.98	0.18	0.33	0.14	nd	0.02	0.03	0.05	99.52	7.2
NORMALISED		2.39	0.41	96.44	0.18	0.33	0.14		0.02	0.03	0.05		
DRY ELEMENT %		1.12	0.11	33.73	0.14	0.20	0.10		0.01	0.02	0.01		
WET ELEMENT %		1.20	0.12	36.16	0.15	0.21	0.11		0.01	0.02	0.01		
RAW DATA	HAZELDENE 3	3.05	0.88	94.40	0.28	0.24	0.10	nd	0.01	0.05	0.18	99.2	10.49
NORMALISED		3.07	0.89	95.16	0.29	0.24	0.10		0.01	0.05	0.18		
DRY ELEMENT %		1.44	0.23	33.28	0.22	0.15	0.07		0.00	0.03	0.04		
WET ELEMENT %		1.59	0.26	36.77	0.24	0.16	0.08		0.00	0.03	0.04		
RAW DATA	HAZELDEDE 4	1.89	0.54	96.48	0.15	0.31	0.09	nd	0.02	0.04	0.05	99.57	8.58
NORMALISED		1.90	0.54	96.90	0.15	0.31	0.09		0.02	0.04	0.05		
DRY ELEMENT %		0.89	0.14	33.89	0.12	0.19	0.06		0.01	0.02	0.01		
WET ELEMENT %		0.96	0.16	36.79	0.13	0.20	0.07		0.01	0.02	0.01		
RAW DATA	HAZELDENE 5	2.34	0.79	95.10	0.47	0.23	0.10	nd	0.01	0.04	0.03	99.11	5.41
NORMALISED		2.36	0.80	95.95	0.47	0.23	0.10		0.01	0.04	0.03		
DRY ELEMENT %		1.10	0.21	33.56	0.37	0.14	0.07		0.00	0.02	0.01		
WET ELEMENT %		1.16	0.22	35.37	0.39	0.15	0.08		0.00	0.02	0.01		

APPENDIX A5.8.4

XRF derived minor element results for the Maqonqo Shelter, local and distant field samples (ppm)

SAMPLE	ROCK TYPE	As	Ba	Ce	Co	Cr	Cu	Ga	La	Nb	Nd	Ni	Pb	Rb	S	Sc	Sr	Th	U	V	Y	Zn	Zr
SHELTER SAMPLES																							
SHELTER A	Sandstone	6.7	14.1	nd	nd	8.3	1.3	7	14	2.1	nd	30	10	81.9	56266	nd	195.1	1.7	2.3	2.3	6.4	970.6	74.7
SHELTER B	Sandstone	8.6	16.9	6	18	17.5	3.6	3	5.1	8	nd	59	10	130.7	14248	nd	173.3	5.8	1	2	9.6	953.3	114.3
SHELTER C	Sandstone	0.1	14	nd	nd	10.3	2.7	3	4.5	2.2	nd	25	9	95.4	23518	0.9	158.2	4.1	0.3	3	5.7	1062	71.6
SHELTER D	Sandstone	0.8	9.5	12	18	19.5	1.2	13	24	1.5	nd	37	8	120.6	8682	nd	121.1	2	nd	2.5	13.6	860.8	91.3
SHELTER E	Sandstone	4.6	16.1	4	17	10.8	1.6	8	11.4	3.9	nd	35	8	100	6629	5.8	101.9	3.8	nd	3.1	9	960.4	175.1
SHELTER FLOOR SAMPLES																							
SHELTER F	Dolerite	630.7	517.9	nd	1	84.2	22	83	88.9	11.4	7	54	30	52.7	5239	nd	122.3	9.6	3.9	46.4	11.4	551.1	241.6
SHELTER G	Dolerite	162.1	207.1	1	23	103.2	23.1	30	66.2	12.4	nd	15	31	43.1	22977	9.4	92.1	5.4	1.4	41.5	43.7	365	206.7
SHELTER H	Dolerite	566.6	781.3	nd	63	125.1	23.8	161	47.8	24.5	16	125	45	48.1	1043	6.9	87.8	13.7	0.2	17.7	27.1	468.6	400
LOCAL FIELD SAMPLES																							
SITE 1	Dolerite	280.8	309.8	16	43	111.2	26.7	39	75.4	13.2	nd	33	27	14.8	466	29.5	129.5	5.7	1.9	36.8	39	918.6	181.7
SITE 2	Sandstone	258.6	198.7	22	57	80	28.4	56	146.9	10	nd	14	26	37.7	410	25.2	129.2	5.2	nd	37.9	34.9	1315.4	166.3
SITE 3B	Sandstone	120	151.1	88	198	101.9	26.8	14	33.2	23.9	nd	46	32	227	71	121.6	130.9	33.5	7.4	56.3	64.4	1104.7	285.2
SITE 3C	Dolerite	75.6	125.4	63	123	115.2	21.9	24	32.7	15.5	nd	35	25	151.9	70	104.3	104.3	7.2	2.9	11.4	46.7	1487	164.9
SITE 4	Dolerite	344.3	1227.8	nd	nd	48.7	78.8	59	32.5	8.6	7	70	41	32.4	2228	nd	5.8	3	nd	273	8.1	285.7	202.4
SITE 5	Sandstone	40.2	432.6	131	86	132.2	45.6	5	27	8.7	1	41	28	60	880	248.1	83.7	7.9	1.2	0.7	86	1601.4	73.2
SITE 6A	Fe nodule	nd	81.2	nd	nd	21	15.2	7	0.2	4.7	nd	64	17	13	270	0.8	10.1	6.5	2.7	nd	22.7	255.2	34.4
SITE 6B	Fe nodule	217.3	1148.5	29	5	54.9	21.9	32	56.3	3	8	73	20	19.3	172	82	30.2	10.8	4.7	13.6	47.2	871.6	37
SITE 7A	Ferricrete	247.9	443.1	6	74	10.7	12.1	43	13.4	7.7	10	80	19	52.1	63	11.9	17.9	10.9	2.1	16.7	17.2	335.7	274.9
SITE 8A	Ferricrete	0.9	50.3	16	56	32.4	4.2	145	22.7	2.3	nd	21	12	19.6	1502	36.8	20.6	3.7	nd	0.9	23.9	220.3	32
SITE 8B	Ferricrete	40.6	196.6	44	95	84.3	11.3	108	47.5	5.3	1	53	17	42.2	145	57.9	31.7	8.2	3.1	6.6	39	361.9	151.5
SITE 9	Dolerite	628.8	824.2	nd	nd	31.4	88.3	64	23.2	12.5	9	72	39	22.3	720	nd	12.5	3.8	0.4	68.5	5.7	115.5	231.9
SITE 10	Dolerite	1.1	806.3	nd	1	37.1	10.9	2	10.4	2.3	7	40	13	26.1	148	0.9	52.3	6.2	2.9	0.7	22.5	539.9	20.6
ASSORTED 1	Shale	0.2	23.8	nd	nd	12.2	2.2	232	22.3	0.6	nd	31	15	12	166	62.1	17	10.3	0.4	nd	19.4	247.8	27.5
ASSORTED 2	Shale	57.1	760.7	98	256	120.9	55.3	142	78.6	3.1	3	76	21	19.5	101	137.9	17.5	2.8	10.5	223.9	60.4	4575.9	86
YELLOW POWDER 1/ FERRIHYDRITE	Ferrihydrite	0.6	87.7	nd	nd	0.2	2.9	1	nd	3.5	nd	18	2	7	2366	5.3	59.1	5.8	0.5	nd	14.8	844.9	40.4
YELLOW POWDER 2/ FERRIHYDRITE	Ferrihydrite	25.2	82.8	nd	18	15.7	5.3	14	nd	1.7	nd	31	10	50.3	5389	1.2	72.2	nd	nd	nd	10.2	853.8	135.7
DISTANT SAMPLES																							
STANMORE 1	Iron ore/Haematite	nd	29.6	nd	nd	17.7	1.9	10	0.6	0.7	nd	16.8	45	1.1	251	12.1	8.1	2.4	nd	32	14.9	30.7	16.4
IRONDALE 1	Iron ore/Haematite	nd	37.9	nd	nd	287.9	0.5	11	7.5	2.4	nd	20.7	29	6.3	1992	8.9	5.8	1	1.9	245.6	12.7	11.2	31.1
DORINGBERG 1	Iron ore/Haematite	nd	242.7	nd	nd	9.1	nd	nd	nd	0.3	nd	9.1	nd	2.2	236	nd	95.1	nd	nd	3.1	3.2	8.5	nd
MPATE 1	Bauxite	nd	174.8	nd	183	2896.6	131.1	30	nd	7.1	nd	49.9	4	6.5	473	126.1	nd	nd	nd	657	9.9	33.6	131.6
ALLETTA 1	Iron ore/Haematite	nd	153.2	nd	nd	14.5	1.9	5	nd	1.4	nd	19.5	26	4.5	611	4	21.5	3.2	nd	16.5	8.6	6	24.4
ALLETTA 2	Iron ore/Haematite	nd	133.1	nd	1	4.2	4	6	nd	0.6	nd	14.8	28	12.7	885	3.2	28	0.7	nd	20.7	10	10.8	34
HAZELDENE 1	Iron ore/Haematite	12	287.7	nd	27	37.6	0.1	5	nd	nd	nd	0.1	22	1.4	89	3.7	25.7	nd	nd	3598.3	21.6	16.6	3.2
HAZELDENE 2	Iron ore/Haematite	nd	120.8	nd	4	26	0.5	8	4.3	nd	nd	1.8	62	2.3	86	1.1	12	nd	nd	391.1	11.9	0.9	7.8
HAZELDENE 3	Iron ore/Haematite	5	182	nd	103	311.8	28.1	6	8.6	2.6	nd	97	17	2	71	14	2.4	1.4	nd	1267.2	37.8	31.7	12.5
HAZELDEDE 4	Iron ore/Haematite	4	34.8	nd	47	97.6	3.5	1	9.7	0.6	nd	3.7	38	2.1	89	2.5	9	7.3	nd	690.5	18.4	2.5	14.6
HAZELDENE 5	Iron ore/Haematite	23	463.2	nd	59	38.4	6.7	6	85.4	0.5	nd	24.9	69	3.3	184	1.8	20.3	1.2	nd	3451.4	39.8	11.4	6.9

APPENDIX 5.9

THE DETERMINATION OF PRESENCE-ABSENCE-DOMINANCE OF MINERALS WITHIN THE PAINT AND PIGMENT SAMPLES.

The µ-XRD data were collected on the synchrotron, and stored as chi files (X-Y data). These files were then viewed using JADE 3.1 (Materials Data Incorporated) and the mineralogy determined. An example of these 2-D traces is given in Figure A5.9.1.

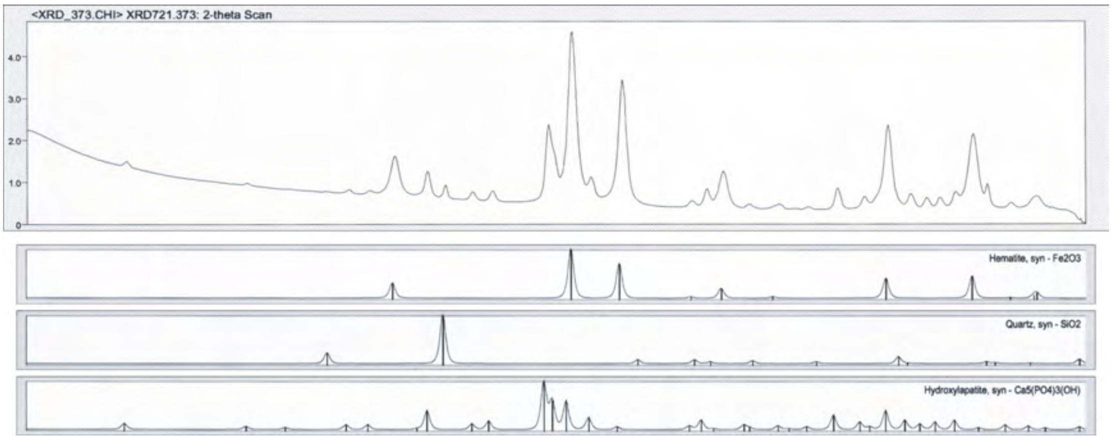


Figure A5.9.1. The micro-XRD trace (no. 373) obtained for a piece of excavated pigment from Layer 7. Standards for the three minerals determined to be present (Haematite – Fe_2O_3; Quartz – SiO_2; and Hydroxylapatite – $Ca_5(PO_4)_3(OH)$) are shown below.

As can be seen in Figure A5.9.1, the presence of haematite, quartz and hydroxylapatite has been determined. The percentage presence of each of these minerals relative to one another was then determined by comparing the peak strengths of each of the minerals present. These percentages were then rated according to the scale as represented in Table A5.9.1. In this example, the percentages were determined to be as follows: Haematite = 2; Quartz = 3; and Hydroxylapatite = 2.

A complete list of this qualitative data is presented in Appendix Digital 1.

Table A5.9.1: The scale used to determine the relative mineralogical proportions.

Assigned numeric value	Relative proportion
1	Dominant mineral phase (50 – 100 %)
2	Moderate mineral presence (15 – 49 %)
3	Low mineral presence (5 – 14 %)
4	Trace mineral presence (<4 % - just recognizable)
0	No mineralogical presence (0 %)

It is important to note that these proportions are determined for each mineral relative to one another within the same trace. It is not possible to gain any reliable information using the same procedure for minerals determined to be in one or more additional traces, primarily because not all of the traces are of the same quality (limited sample size and poor sample crystallinity are the two most common factors that result in a poorly defined trace).

In order to accommodate for this bias in the mineral dataset, the quality of the traces was rated according to the scale as presented in Table A5.9.2. In this way, the total dataset was 'subdivided' into categories of increasing error[1]; the higher the category number, the lower the degree of confidence in the results of comparison (the lower the 'resolution', the greater the chance that trace minerals might not have been recorded). In Chapter 5, various analyses were conducted using all the data, as well as groups of these categories. This allowed for a more accurate assessment of the dataset as a whole. An example of each scalar point listed in Table A5.9.2 is produced in Figure A5.9.2.

Table A5.9.2: The scale used to determine the quality of the mineralogical traces

Assigned numeric value	Trace Quality
1	Best – Clearly identifiable mineral phases
2	Medium – Traces visible, but not very strong
3	Poor – Only the strongest peaks are visible
4	None – Just the background 'noise' visible

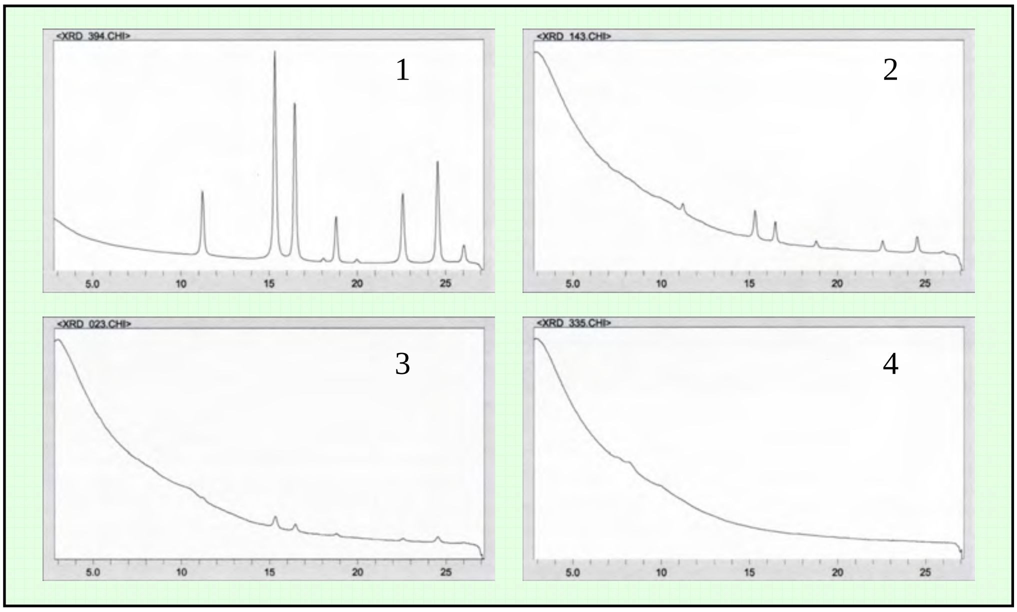


Figure A5.9.2. Four traces (trace numbers 394, 143, 023, and 335) highlighting the differences in variable quality; the numbers associated with the traces also represent the categories into which each trace was categorised. Only one mineral is present, namely haematite.

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[1] In this case, 'error' refers to the degree of characterisation of the mineral in question i.e., how accurately does the µ-XRD trace portray the mineralogical composition of the sample being studied. This relates directly to the ability of the author to determine the similarities/differences that might exist between the different materials under study, and relates directly on the ability to source the material in question.

APPENDIX 5.10

APPENDIX 5.10 (Cont.)

APPENDIX 5.11

METHODOLOGY EMPLOYED TO MINIMISE THE EFFECTS OF SAMPLE HETEROGENEITY USING EDX, WITH REFERENCE TO THE OTHER TECHNIQUES.

In order to counter the inherent micro-heterogeneity of the paint dataset, the first task was to modify the analytical sampling techniques in a manner that would best capture and reflect the overall composition of the paint samples accurately, as well as to allow for reproducibility of the findings so obtained. The following section thus focuses not only on the Maqonqo Shelter paint samples, but also the procedures and methodology adopted in order to facilitate the creation of a paint database used within this investigation.

When the high degree of heterogeneity within the paint samples was noted, the sampling regime employed when using EDX was modified to include a greater number of datum points (five reduced window and nine spot scans) in an attempt to decrease the amount of variability. Analysis of the data thus obtained showed that the spot scans displayed a much higher degree of variation than the reduced window scans (Figure A5.11.1 and Figure A5.11.2). In Figure A5.11.1, it can be seen that the reduced window points (solid symbols), although still displaying some degree of variability, are more closely associated with one another than are the spot data (open symbols). This differential distribution of data points is a result of the sampling technique employed.

A spot scan requires precise focussing of the electron beam on one particular part of the sample under study, and is, as a result, specific to that point. If, for example, a quartz grain should be analysed, the results would reflect a very high amount of Si and the other elements present within the sample as a whole will not be detected. If the beam were focussed a few micrometres to the side of this scan point where no quartz grain was present, the results would reflect this. As a result of this high degree of variability over small distances, the two separate analyses of the same sample would be reflected as two distinct samples after PCA analysis, and thus an aggregation of individual paint samples, or even paint colours, would not be achieved. The spot scan analyses were therefore considered too specific for the purposes of this study, and thus, these data were not used. They do, however, reflect the inherent variability of the paint at the sub-micron level.

A reduced window scan is a more generalised scanning technique in which the researcher predefines a selected rhomboidal target area on the sample surface. During analysis, the beam is raster scanned within the rhomboid's boundaries thus giving an averaged result for that predefined area. The advantage of this technique is that the 'extreme' variability noted in the spot analyses is tempered. These scans are still variable (see Figure A5.11.1), but not to the degree shown by the spot scan data.

This variability is partially attributed to the composition of the paint samples themselves, but also to the fact that the paint samples are neither uniformly flat nor thick. Both these factors affect the ability of the secondary electron detector to accurately determine the elemental composition of a

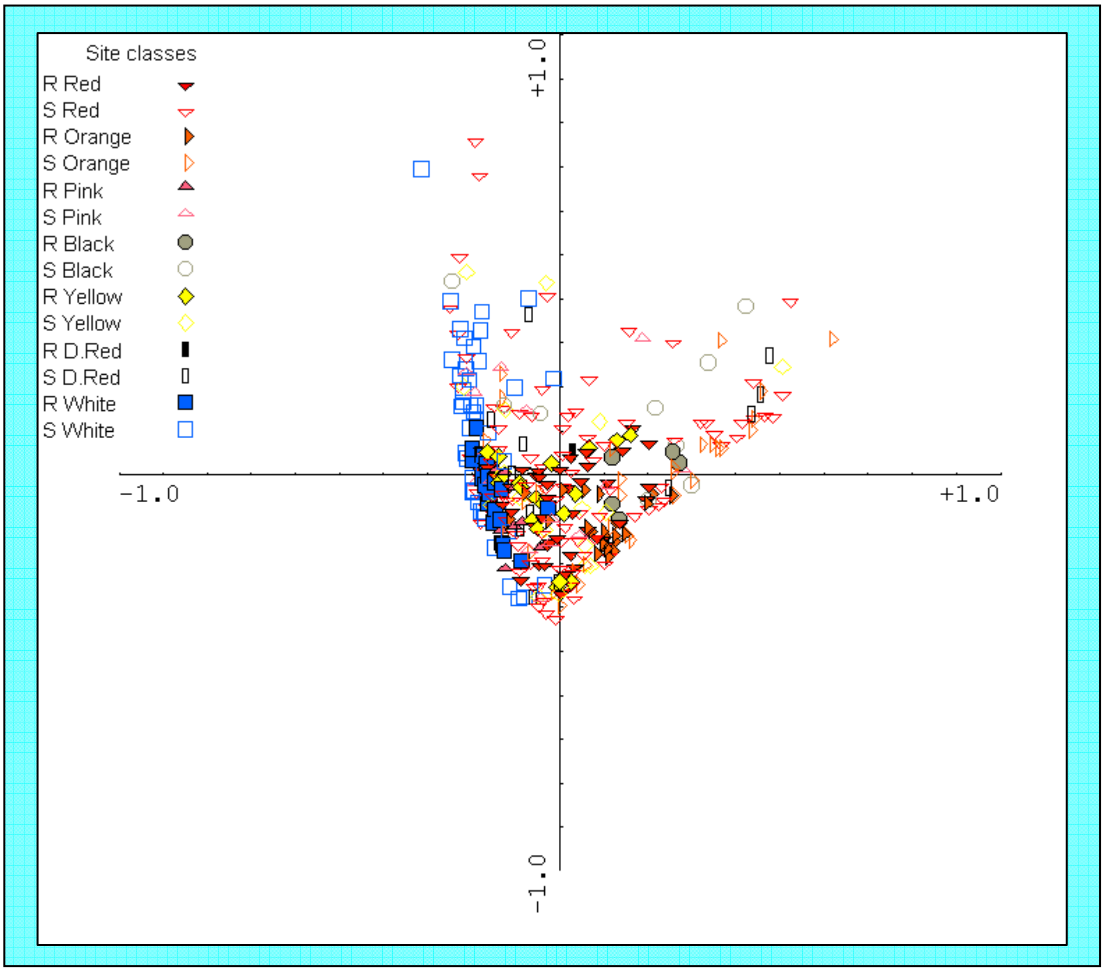

Figure A5.11.1: All reduced window (R) and spot (S) EDX data of the individual Maqonqo Shelter paint colours– sample distribution.
Eigenvalues: PCA1 – 46.5; PCA2 – 25.5; PCA3 – 10.3
Scaling = -2

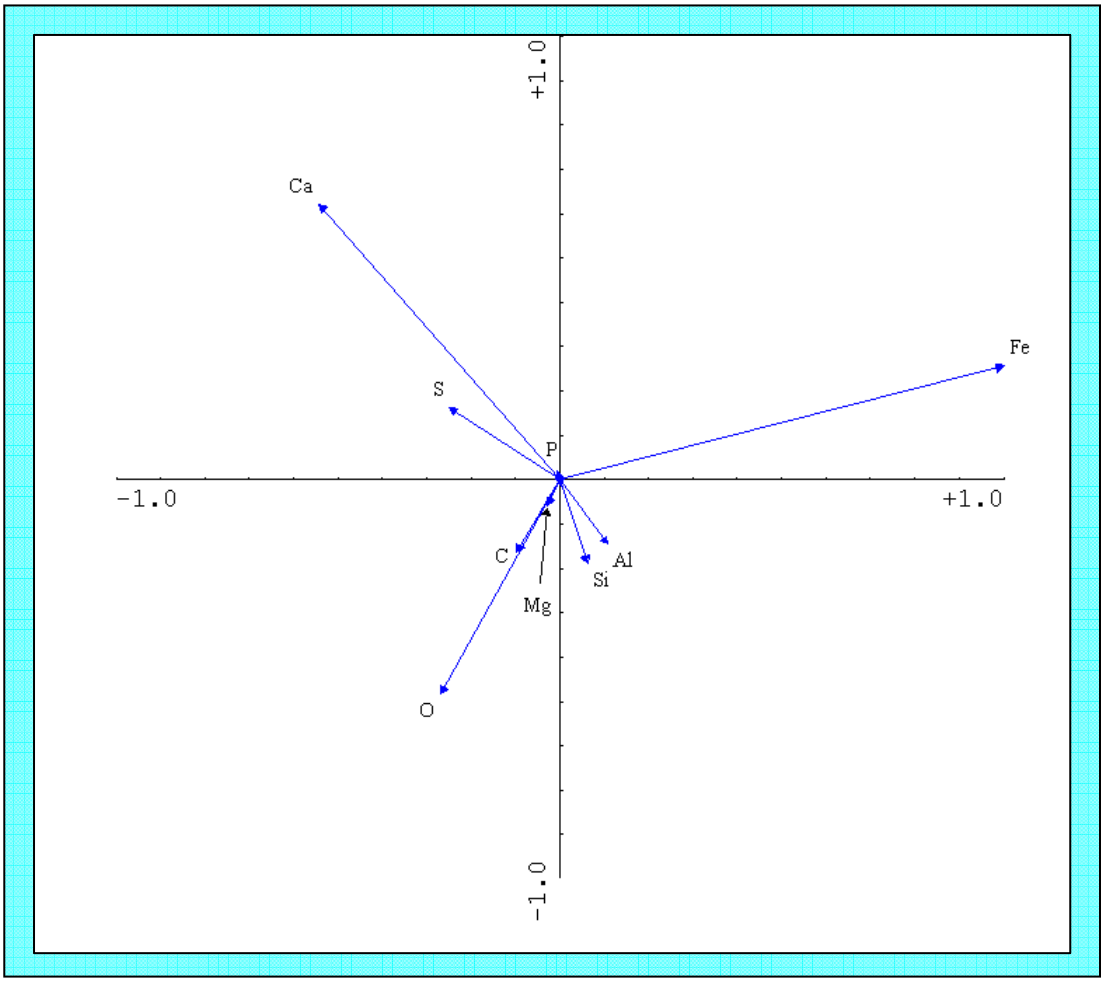

Figure A5.11.2: All reduced window and spot EDX data of the Maqonqo Shelter paint sample set– element distribution.

Eigenvalues: PCA1 – 46.5; PCA2 – 25.5; PCA3 – 10.3

Scaling = -2

sample. In addition, due to the nature of the sampling technique, the paint sample does not cover the entire stub surface. This, together with beam penetration through the thinner portions of the paint samples, results in some of the carbon tape background also being scanned with the resultant elevated C levels (Figure A5.11.2). Although these problems are noted, there is no simple way to correct them, especially when one has to conform to the sampling restrictions as discussed in Section 5.2.2. These problems notwithstanding, it has been determined that the reduced window scans best represented the 'average' composition of the paint samples, and have, for this reason, been used throughout this study.

Even with the removal of the spot scan data it was still too complicated to investigate the trends that exist within the remaining dataset (see Figure A5.11.1). It was therefore decided to further simplify the data by averaging the reduced window scan values for each colour on each stub. This was done in order to reduce the complexity of the PCA diagrams so that they are more easily interpreted. These averages, together with their associated standard deviations, are given in Appendix 5.12.

Unlike the EDX technique, however, the X-ray beam width used in the capture of data in both of the µ-XRF and µ-XRD techniques is fixed, moving through machined focussing slits that deliver a focussed beam to the sample. This cannot be altered without significantly affecting the performance of both of the techniques and the reproducibility of the results thus obtained. As a result, the only option was to analyse the samples in replicates of three or more, with the number of replicates being dependent on the amount of sample available.

A very important point to note is that the two techniques were run concurrently, with the data captured by both representing two facets of information obtained from the same spot on the sample, thus making both data sets directly related to one another. As a result, the data within one dataset should never be interrogated without consulting the results of the other technique – the two synchrotron datasets are intrinsically linked.

The µ-XRF data were captured as a series of 2D graphs from which peak-to-area relationships were determined. These semi-qualitative data were then captured, and where possible, averaged according to the criteria and guidelines as discussed in Appendix 5.13. The resultant data representing both the good and moderate data as defined in Appendix 5.16 are presented in Figure A5.11.3.

In the case of the µ-XRD technique, the data were also captured in a 2D graph format. Using FIT2D© software[1], these graphs were converted into 2D diagrams from which the mineralogy of the samples was determined. Unfortunately, without knowledge of the exact dimensions of the samples under study, a quantitative value indicating the abundance of these minerals could not be determined. As a result, the percentage abundance of the minerals indicated in Figure A5.11.4, and those referred to throughout this study, was determined on a subjective basis only. The reader is referred to Appendix 5.9 for a more detailed discussion on how these relative abundances were determined. Appendix Digital 1 lists the results used within the analysis presented.

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[1] FIT2D v10.132, copyright 1987-2001, Andy Hammersley, European Synchrotron Research Facility beam-lines (ESRF) (www.esrf.fr/computing/expg/subgroups/data_analysis/FIT2D/).

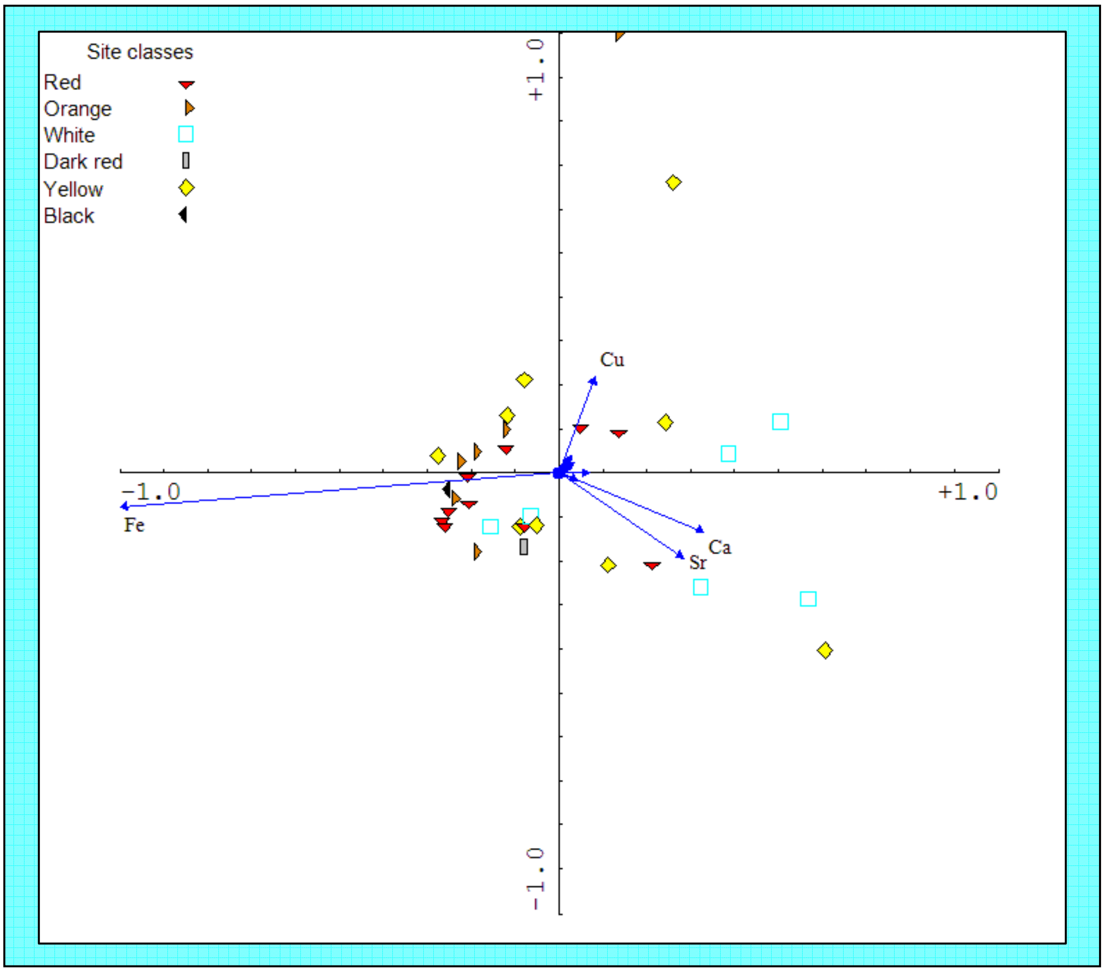

Figure A5.11.3: Micro-XRF data depicting individual Maqonqo Shelter paint colour distribution.

Eigenvalues: PCA1 – 87.6; PCA2 – 8.3; PCA3 – 1.3

Scaling = -2

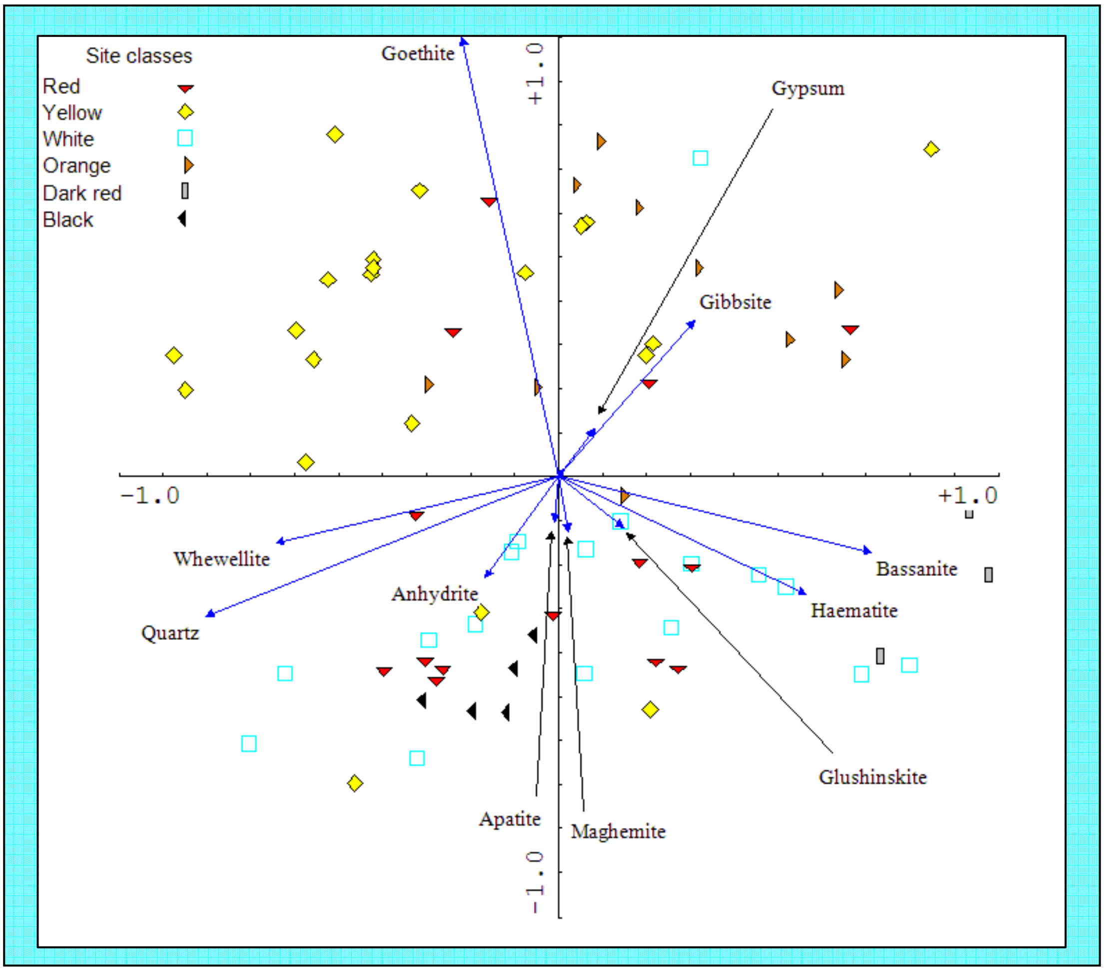

Figure A5.11.4: Micro-XRD data depicting individual Maqonqo Shelter paint colour distribution.

Eigenvalues: PCA1 – 25.6; PCA2 – 17.9; PCA3 – 14.6

Scaling = -2

APPENDIX 5.12

SEMI-QUANTITATIVE RESULTS OBTAINED FROM EDX.

The results of the EDX area given as a weight percentage (normalised to 100 %). These results, although relatively accurate, are considered to be only reliable above a minimum detection level of 1 000 ppm. The relative degree of error associated with the results obtained can be approximately determined according to the following table (CEM, 2000):

Results in weight %	Relative % i.e., 'The error could be up to'
100 - 20	5
20 - 5	10
5 - 1	20
1 - 0.2	50 - 100

It is for this reason that no trace elements were used for comparative purposes between the paints and the excavated samples; the latter's elements having been accurately detected in ppm by XRF. The following results were obtained by averaging between three and nine separate reduced window scans, all conducted at the same magnification. Though the standard deviation for each element was calculated, only the original quantified value for each element was used when the data were statistically analysed.

The data displayed here represent only the averaged reduced window scan data that were used in the analyses within this study. The raw spot and reduced datasets have not been included as they are too large to reproduce here (just under 570 individual scans). Section 5.2.2 explains how this dataset was selected/created.

The paint samples are listed according to colour; from the darkest (black) to the lightest (white). This was done so that trends that occur along this colour spectrum would be more easily discernable. For the entire dataset, refer to the file called 'APPENDIX DIGITAL 4' on the CD provided. Whilst in the electronic version of this data, the "no data" values are represented as "0.00", in the summary table presented here, they have been removed for the sake of clarity.

APPENDIX A5.12.1

Average semi-quantitative EDX paint and blank results from all four sites

MAQONQO SHELTER PAINT SAMPLES													
BLACK													
Paint Sample	**C**	**O**	**Na**	**Mg**	**Al**	**Si**	**P**	**S**	**K**	**Ca**	**Ti**	**Mn**	**Fe**
Pnt 2	11.55	36.03	0.60	0.89	3.83	8.42	2.73	1.08	0.93	5.40	0.25	0.74	27.55
DARK RED													
Paint Sample	**C**	**O**	**Na**	**Mg**	**Al**	**Si**	**P**	**S**	**K**	**Ca**	**Ti**	**Mn**	**Fe**
Pnt 27	8.82	39.58	0.39	0.76	4.29	4.46	1.59	5.88	0.66	15.32	0.14	0.31	17.79
RED													
Paint Sample	**C**	**O**	**Na**	**Mg**	**Al**	**Si**	**P**	**S**	**K**	**Ca**	**Ti**	**Mn**	**Fe**
Pnt 1	14.37	40.05	0.45	0.75	5.79	10.78	5.92	0.57	1.53	1.82	0.33	0.27	17.36
Pnt 3	34.32	37.24	0.64	0.68	2.14	5.93	2.03	0.92	0.81	6.82	0.38	0.29	7.80
Pnt 5	9.78	41.74	0.79	1.19	2.44	8.79	1.87	9.69	0.88	13.39	0.29	0.06	9.08
Pnt 8a	12.44	38.74	0.71	0.92	2.24	6.33	1.98	6.58	0.72	11.56	0.28	0.40	17.07
Pnt 8b	13.78	40.24	0.67	0.85	2.35	6.09	1.87	6.01	0.65	13.25	0.24	0.33	13.65
Pnt 9a 'contamination'$^{\$}$	12.78	45.51	0.75	1.16	1.54	3.88	1.07	8.24	0.60	23.08	0.16		1.23
Pnt 9b 'contamination'	5.67	47.29	0.47	3.08	1.93	4.57	1.11	12.34	0.36	16.18	0.18		6.14
Pnt 11a 'contamination'	11.26	41.85	0.66	1.13	4.58	6.02	2.06	4.18	0.74	14.37	0.41		12.77
Pnt 11b 'contamination'	9.26	42.21	0.80	1.10	3.71	6.29	1.48	8.31	0.61	18.08	0.19	0.17	7.77
Pnt 12 'contamination'	10.02	44.06	0.55	3.27	4.47	4.22	5.49	3.78	0.59	13.47	0.41	0.10	9.57
Pnt 13a	5.70	46.52	0.70	1.66	4.03	11.18	1.53	9.15	1.18	14.03	0.30	0.48	3.53
Pnt 20	6.18	42.10	0.75	1.34	8.56	26.84	0.30	0.13	1.50	1.96	0.72	4.24	5.41
Pnt 21	39.43	33.95	0.37	0.80	2.37	7.66	1.55	0.96	0.73	1.52	0.21	0.47	9.96
Pnt 22	18.92	40.58	0.32	0.36	9.26	4.78	2.02	0.90	1.02	5.39	0.47	0.18	15.79
Pnt 26	10.01	37.97	0.32	0.50	2.32	7.40	1.86	5.47	0.78	8.33	0.21	0.34	24.49
Pnt 30	13.27	35.20	0.23	0.90	2.87	3.71	0.95	3.78	0.80	12.53	0.18	0.17	25.32
AVE*	14.20	40.95	0.57	1.23	3.79	7.78	2.07	5.06	0.84	10.99	0.31	0.47	11.68
SD**	9.55	3.80	0.19	0.82	2.31	5.55	1.50	3.79	0.32	6.19	0.14	1.02	6.95
ORANGE													
Paint Sample	**C**	**O**	**Na**	**Mg**	**Al**	**Si**	**P**	**S**	**K**	**Ca**	**Ti**	**Mn**	**Fe**
Pnt 4	8.86	40.07	0.68	0.73	4.80	8.36	2.19	4.15	0.90	5.46	0.42	0.13	23.24
Pnt 6	7.52	42.57	0.72	0.84	14.23	8.05	2.58	1.06	0.99	1.89	0.92	0.21	18.41
Pnt 7	6.28	43.43	0.95	1.05	14.22	7.72	2.38	2.55	1.12	2.81	0.66	0.30	16.52
Pnt 11b 'contamination'	10.03	44.85	0.38	2.37	6.68	5.90	1.58	3.02	0.71	12.31	0.33	0.25	11.62
Pnt 14	3.39	44.90	0.44	1.25	16.10	6.30	1.03	3.58	0.46	4.60	0.71	0.56	16.67
Pnt 20	9.89	42.41	0.92	1.78	10.44	23.12	0.44	0.31	2.05	1.91	0.63	0.30	5.81
Pnt 23	11.78	43.03	0.19	0.62	13.07	5.28	1.29	1.44	0.68	5.25	0.69	0.18	16.51
Pnt 24	8.43	49.20	0.43	1.60	3.94	7.82	2.44	7.48	0.70	14.04	0.26	0.25	3.42
AVE*	8.27	43.81	0.59	1.28	10.44	9.07	1.74	2.95	0.95	6.03	0.58	0.27	14.02
SD**	2.58	2.66	0.27	0.60	4.72	5.79	0.78	2.25	0.49	4.65	0.22	0.13	6.65
YELLOW													
Paint Sample	**C**	**O**	**Na**	**Mg**	**Al**	**Si**	**P**	**S**	**K**	**Ca**	**Ti**	**Mn**	**Fe**
Pnt 10 'contamination'	10.19	45.87		3.18	2.96	6.60	1.38	10.00	0.63	13.10	0.29	0.31	5.53
Pnt 11a	8.02	44.61	0.25	0.97	6.86	6.69	1.50	7.00	1.01	14.28	0.36		8.48
Pnt 11b	14.10	40.96	0.98	1.14	2.57	4.50	1.71	6.47	1.01	23.00	0.39	0.25	2.92
Pnt 28	13.46	42.08	0.22	1.74	3.67	5.87	1.45	6.71	0.75	12.83	0.19	0.22	10.81
Pnt 29	14.95	42.82	0.12	0.62	5.49	6.27	0.99	3.86	0.90	15.14	0.35	0.18	8.30
AVE*	12.14	43.27	0.31	1.53	4.31	5.99	1.40	6.81	0.86	15.67	0.32	0.19	7.21
SD**	2.93	1.97	0.38	1.01	1.81	0.89	0.26	2.18	0.17	4.20	0.08	0.12	3.04
PINK													
Paint Sample	**C**	**O**	**Na**	**Mg**	**Al**	**Si**	**P**	**S**	**K**	**Ca**	**Ti**	**Mn**	**Fe**
Pnt 10 'contamination'	20.27	37.82	1.00	1.10	1.94	4.48	5.17	8.11	0.54	17.91	0.13		1.52
Pnt 11a 'contamination'	11.12	44.47		1.00	5.26	6.55	1.36	6.27	0.97	17.17	0.33		5.49
Pnt 13a 'contamination'	11.06	50.32	0.54	7.11	1.58	3.99	1.19	9.96	0.58	11.40	0.23		2.06
Pnt 15	10.76	48.96	0.63	5.73	1.87	4.77	1.24	8.51	0.59	10.30	0.14	1.74	4.77
AVE*	13.30	45.39	0.54	3.73	2.66	4.95	2.24	8.21	0.67	14.20	0.21		3.46
SD**	4.65	5.63	0.41	3.15	1.74	1.12	1.95	1.52	0.20	3.90	0.09		1.96
WHITE													
Paint Sample	**C**	**O**	**Na**	**Mg**	**Al**	**Si**	**P**	**S**	**K**	**Ca**	**Ti**	**Mn**	**Fe**
Pnt 9a	12.19	45.41	0.69	2.32	2.18	4.98	1.31	9.19	0.60	16.63	0.24	0.09	4.17
Pnt 9b	13.29	43.72	0.83	1.23	2.20	5.38	1.53	9.30	0.61	20.15	0.26	0.05	1.47
Pnt 10	29.60	41.57		2.58	2.16	4.77	4.38	2.38	0.73	10.07	0.25	0.12	1.44
Pnt 11b white deposit	14.44	43.11	0.64	0.79	1.42	3.13	1.45	8.21	0.63	24.73	0.11		1.37
Pnt 12	20.22	38.76	0.89	1.72	1.38	2.50	8.25	4.50	0.39	20.27	0.05	0.05	1.04
Pnt 13a white deposit	10.38	48.51	0.58	4.88	1.74	4.86	1.11	11.28	0.70	8.52	6.01	0.16	1.28
Pnt 13b white deposit	12.15	48.11	0.71	5.38	2.01	5.39	1.13	10.13	0.70	12.79	0.23		1.25
Pnt 14 white deposit	12.67	47.10	0.37	1.21	1.07	3.80	0.87	4.23	0.40	26.73	0.15	0.32	1.06
AVE*	15.62	44.53	0.59	2.51	1.77	4.35	2.50	7.40	0.59	17.49	0.91	0.10	1.63
SD**	6.36	3.40	0.28	1.73	0.44	1.08	2.58	3.25	0.13	6.66	2.06	0.11	1.04

APPENDIX A5.12.1 (Cont.)

Average semi-quantitative EDX paint and blank results from all four sites

BLANK SAMPLES FROM ALL FOUR SHELTERS													
MAQONQO SHELTER													
Blank Sample	**C**	**O**	**Na**	**Mg**	**Al**	**Si**	**P**	**S**	**K**	**Ca**	**Ti**	**Mn**	**Fe**
MQ Shelter Blank 1	17.82	44.17	0.44	0.59	2.82	8.24	0.69	10.86	0.62	12.29	0.19		1.27
MQ Shelter Blank 2	15.96	44.49	0.36	0.51	2.16	6.86	0.83	12.47	0.52	14.43	0.17		1.25
MQ Shelter Blank 3	14.71	44.67	0.55	0.88	2.14	24.79	0.51	4.75	0.51	5.25	0.20		1.04
MQ Shelter Blank 4	24.90	42.07	0.49	1.18	2.37	6.90	0.83	7.89	2.61	9.23	0.21	0.08	1.24
AVE*	18.35	43.85	0.46	0.79	2.37	11.70	0.71	8.99	1.07	10.30	0.19		1.20
SD**	4.55	1.20	0.08	0.30	0.32	8.75	0.15	3.41	1.03	3.98	0.02		0.11
FERGIES CAVE SHELTER													
Blank Sample	**C**	**O**	**Na**	**Mg**	**Al**	**Si**	**P**	**S**	**K**	**Ca**	**Ti**	**Mn**	**Fe**
Fergies Cave Blank 1	30.42	43.56	0.31	0.59	1.34	2.69	0.40	0.31	0.37	19.16	0.11		0.73
Fergies Cave Blank 2	51.85	35.12	0.33	0.22	0.36	0.71	0.26	0.43	0.34	10.12	0.01		0.25
Fergies Cave Blank 3	35.18	39.08	0.72	0.78	3.61	9.23	0.59	1.93	0.70	5.77	0.21		2.23
AVE*	39.15	39.25	0.46	0.53	1.77	4.21	0.42	0.89	0.47	11.68	0.11		1.07
SD**	11.25	4.22	0.23	0.28	1.67	4.46	0.16	0.90	0.20	6.83	0.10		1.04
SHELTERED VALE SHELTER													
Sheltered Vale Blank 1	19.75	50.61	0.83	1.65	4.87	14.68	0.21	1.86	0.78	2.99	0.17		1.61
Sheltered Vale Blank 2	23.63	39.64	1.20	1.22	5.17	14.39	0.78	1.37	1.19	8.01	0.34	0.26	2.90
Sheltered Vale Blank 3	23.70	49.74	0.49	0.64	2.58	6.68	0.47	3.63	0.51	10.43	0.12		1.00
AVE*	22.36	46.66	0.84	1.17	4.21	11.92	0.49	2.29	0.83	7.14	0.21		1.84
SD**	2.26	6.10	0.36	0.51	1.42	4.54	0.29	1.19	0.34	3.80	0.11		0.97
TWAGWA SHELTER													
Twagwa Blank 1	14.50	42.73	0.77	0.77	12.58	12.76	1.18	7.71	5.15		0.22	0.08	1.54
Twagwa Blank 2	8.89	46.23	0.69	0.61	10.84	25.84	2.15	1.12	2.69		0.10		0.89
Twagwa Blank 3	28.80	38.87	0.61	0.79	6.71	16.79	0.46	1.61	1.15	1.61	0.32		2.28
AVE*	17.39	42.61	0.69	0.73	10.05	18.46	1.26	3.48	3.00	0.54	0.21		1.57
SD**	10.27	3.68	0.08	0.10	3.02	6.69	0.85	3.68	2.02	0.93	0.11		0.70
PAINT SAMPLES FROM THE THREE ADDITIONAL SITES													
RED													
Paint Sample	**C**	**O**	**Na**	**Mg**	**Al**	**Si**	**P**	**S**	**K**	**Ca**	**Ti**	**Mn**	**Fe**
Fergies Cave Red 1	31.39	44.06	0.55	0.21	0.75	1.95	0.39	0.57	0.38	17.09			2.51
Fergies Cave Red 2	32.79	39.61	0.34	0.37	1.55	3.48	0.34	0.60	0.37	17.57	0.16	0.01	3.10
Fergies Cave Red 3	30.02	42.04	0.60	0.43	1.06	4.07	0.19	0.68	0.29	15.42	0.04		5.17
AVE*	31.40	41.90	0.50	0.34	1.12	3.17	0.31	0.62	0.35	16.69	0.07		3.59
SD**	1.38	2.23	0.14	0.11	0.41	1.09	0.11	0.06	0.05	1.13	0.08		1.39
Sheltered Vale Red 1	26.20	40.80	0.77	0.47	2.96	8.89	0.56	2.81	0.64	12.31	0.13	0.02	3.44
Sheltered Vale Red 2	28.99	47.62	0.90	0.82	3.38	6.85	0.70	0.71	0.55	7.60	0.24		1.64
Sheltered Vale Red 3	20.26	48.49	0.74	0.71	2.88	11.89	1.18	3.90	0.43	6.61	0.15		2.79
AVE*	25.15	45.64	0.80	0.66	3.07	9.21	0.81	2.47	0.54	8.84	0.17		2.62
SD**	4.46	4.21	0.08	0.18	0.27	2.54	0.33	1.62	0.11	3.05	0.06		0.91
Twagwa Red 1	14.32	47.66	1.37	0.94	13.72	5.21	1.54	8.64	4.54				2.06
Twagwa Red 2	8.33	36.59	0.92	1.15	9.84	10.19	1.34	4.77	3.31	0.38	0.29	0.52	22.36
Twagwa Red 3	10.97	44.36	1.04	0.81	14.38	9.77	2.04	8.36	5.59	0.31	0.24	0.09	2.03
AVE*	11.21	42.87	1.11	0.97	12.65	8.39	1.64	7.26	4.48	0.23	0.18	0.20	8.82
SD**	3.00	5.68	0.24	0.17	2.45	2.76	0.36	2.16	1.14	0.20	0.16	0.28	11.73
WHITE													
Paint Sample	**C**	**O**	**Na**	**Mg**	**Al**	**Si**	**P**	**S**	**K**	**Ca**	**Ti**	**Mn**	**Fe**
Sheltered Vale White 1	29.62	41.73	0.54	0.58	3.90	9.30	0.38	3.06	0.66	9.26	0.16		0.82
Sheltered Vale White 2	23.18	40.05	0.72	0.55	3.47	15.62	0.27	0.24	1.67	12.55	0.21		1.46
Sheltered Vale White 3	31.11	40.19	0.54	1.57	1.67	4.04	6.58	3.15	0.73	9.53	0.09	0.11	0.67
AVE*	27.97	40.66	0.60	0.90	3.01	9.65	2.41	2.15	1.02	10.44	0.15		0.98
SD**	4.22	0.93	0.10	0.58	1.18	5.80	3.61	1.66	0.56	1.83	0.06		0.42
Twagwa White 1	12.97	44.98	1.10	0.70	14.37	7.15	1.18	10.27	6.11	0.06	0.12		0.98
Twagwa White 2	22.48	38.00	0.92	0.70	7.84	9.77	6.22	2.08	2.25	7.90	0.19		1.71
Twagwa White 3	11.89	43.49	0.97	0.76	14.30	8.29	0.92	10.50	6.48	0.51	0.18	0.04	1.36
AVE*	15.78	42.16	1.00	0.72	12.17	8.40	2.78	7.62	4.94	2.82	0.16		1.35
SD**	5.82	3.67	0.10	0.03	3.75	1.32	2.99	4.80	2.34	4.41	0.04		0.37

*AVE - The average value of each paint/blank/pigment sample group.

**SD - The standard deviation of each sample group. It must be remembered that the sample values themselves are averages, and thus these values cannot be considered to be 'real', but they do give an indication of the variability within the samples as a whole. By averaging the SD's for each colour sub-set, a very rough indication as to the overall stability of the respective sub-set can be determined i.e., the lower the number, the higher the stability of the sub-set.

$^{\$}$'contamination' - Refers to the possible introduction of an additional pigment (of a different nature) from an underlying image to that of the original sample.

NOTE: Paints 25 and 27 were not included as only spot data could be obtained for these samples.

APPENDIX A5.12.2

Average semi-quantitative EDX Maqonqo Shelter wall, shelter and large excavated layer samples results

MAQONQO SHELTER BULK WALL SAMPLES

Sample	C	O	Na	Mg	Al	Si	P	S	K	Ca	Ti	Mn	Fe
Sample A	29.79	34.97	0.23	0.50	2.76	19.94	0.37	2.48	2.00	3.98	0.17	0.08	2.72
Sample B	11.22	40.37	0.39	0.53	4.84	32.60	0.17	1.16	4.13	2.98	0.34	0.20	1.10
Sample C	15.83	38.79	0.36	0.61	4.24	27.78	0.27	1.80	2.98	3.47	0.20	0.10	3.59
Sample D	10.67	40.26	0.51	0.48	5.35	35.81	0.12	0.77	3.82	0.96	0.17	0.36	0.74
Sample E	20.85	38.34	0.73	0.52	4.74	29.22	0.26	0.64	2.94	0.35	0.29	0.04	1.09

MAQONQO SHELTER FLOOR SAMPLES

Sample	C	O	Na	Mg	Al	Si	P	S	K	Ca	Ti	Mn	Fe
Sample F	18.49	29.38	0.20	0.95	6.52	11.78	0.12	0.15	2.27	1.25	0.75	0.38	27.76
Sample G	15.58	38.19	0.72	1.24	11.00	17.67	0.16	0.68	3.04	1.56	0.64	0.12	9.42
Sample H	14.97	31.16	0.25	1.13	6.78	14.09	0.17	0.11	1.51	0.61	1.33	0.71	27.21

MAQONQO SHELTER SAMPLES

LAYER 1

Sample	C	O	Na	Mg	Al	Si	P	S	K	Ca	Ti	Mn	Fe
1		24.41	0.27	0.46	4.03	9.34	0.23		0.38	0.20	0.27	0.11	60.32
22	19.93	23.06	0.16	0.29	0.70	3.21	0.27	0.08	0.10	0.22	0.09	0.46	51.46
103		38.13	1.61	2.47	12.38	26.91	0.30	0.14	1.82	3.61	0.87	0.06	11.72
133		33.23	0.57	0.67	7.17	23.20	0.25		1.59	0.33	0.26	0.27	32.43
243	15.06	23.43		0.55	2.42	4.86	0.08		0.39				53.20
272	12.47	21.04		0.26	1.10	2.23	0.04	0.09	0.43	0.38	0.08	1.44	60.45
278	16.39	23.02	0.18	0.39	2.45	6.06	0.06	0.05	0.43	0.33	0.25		50.40
330	4.20	29.46		0.33	0.94	29.86		0.10	0.08	0.08			34.96
344	27.35	22.07	0.25	1.06	0.53	1.03		0.12	0.13	0.85		0.71	45.90
372	17.39	25.83	0.20	0.42	1.42	4.11	1.65	0.05	0.27	2.86		0.26	45.54
400	23.26	24.02	0.12	0.18	0.43	8.52				0.13		0.11	43.25
410	39.79	20.39	0.08	0.15	0.94	1.46				0.24		0.23	36.73
429	11.48	22.88	0.31	0.33	2.04	8.43	0.10		0.12	1.08	0.12	0.43	52.69
430	24.22	22.58	0.06	0.52	2.21	4.16			0.31	0.15	0.07	0.18	45.50
440	9.00	22.38	0.27	0.86	3.52	7.76	0.98	0.10	0.63	2.75	0.24	1.92	49.58
516	14.19	35.64	1.37	2.25	11.20	18.59	0.22	0.22	1.83	3.41	0.72	0.23	10.12
562	26.92	24.74		0.26	0.68	1.12	0.36		0.14	0.33	0.04	1.00	44.42
594	36.22	28.71		0.09	0.62	15.56			0.05	0.20			18.57
751	28.96	31.74			0.75	22.63							15.93
797	16.75	33.11	0.25	0.79	7.90	21.07			3.76	0.08	0.30	0.28	15.72
873	50.39	21.22	0.10	0.09	0.42	3.34				0.10	0.03		24.33
895	16.24	20.20	0.32	0.58	1.03	2.07	0.18	0.28	0.45	0.91		1.05	56.68
912	30.42	22.38			2.16	2.21			0.08	0.50		0.70	41.58
986	24.22	26.10		0.60	3.45	6.98			0.37	0.13	0.15	0.31	37.73
1010		36.08		0.39	1.32	37.08	0.06			0.18		0.54	24.37
1035		29.47	0.32	0.49	3.90	27.34	0.04		1.47	0.43	0.23	0.27	36.07

LAYER 2

Sample	C	O	Na	Mg	Al	Si	P	S	K	Ca	Ti	Mn	Fe
1069		25.91	0.29	0.54	7.95	10.25	0.17		0.60	0.52	0.91	0.38	52.49
1071	25.17	30.81			0.41	25.23				0.09			18.30
1259		17.99	0.23	0.50	0.95	1.90	0.14		0.29	0.47	0.15	0.96	76.40
1293		32.43	0.25	0.36	1.09	33.97		0.05	0.35	0.35	0.07		31.08
1314		38.48	0.88	4.11	5.05	27.31	0.32	0.25	2.14	2.50	1.63	0.38	16.96
1347	30.67	27.90	0.21	0.28	1.92	14.53			0.82		0.12	0.08	23.49
1373	8.02	35.60	0.11	0.41	0.82	36.59			0.26	1.04			17.17
1393	27.35	24.96	0.32	0.43	1.36	2.34		0.03	0.41	0.30	0.09	0.48	41.96
2106	28.87	25.24	0.15	0.17	1.99	10.64	0.03		0.85	0.26	0.18	0.10	31.49

LAYER 3

Sample	C	O	Na	Mg	Al	Si	P	S	K	Ca	Ti	Mn	Fe
1424	10.73	37.60	1.29	1.65	12.55	19.04	0.05	0.07	1.53	3.05	0.72	0.25	11.45
1534	19.20	22.04	0.18	0.36	2.18	2.97	0.11		0.66	0.26	0.15	0.42	51.49
1581	17.81	28.00	0.08	0.32	1.45	19.46			0.27	0.71		0.11	31.81
1624	12.26	38.05	1.38	1.80	10.24	20.96			0.77	3.27	0.71	0.17	10.42
1638	17.84	25.51	0.29	0.71	3.03	8.66	0.13	0.10	0.47	0.25	0.19	0.36	42.43
1639	15.05	26.80	0.30	0.96	3.48	12.01			0.62	0.19	0.21	0.39	40.01
1659	10.42	22.29	0.24	0.50	2.91	7.15	0.10		0.87	0.46	0.23	0.74	54.08
1669	20.66	34.79	1.59	0.22	8.03	21.12	0.12	0.10	7.97	0.16			5.26
1672	30.67	27.49		0.49	2.14	10.10			0.16	0.26	0.07		28.63
1690	8.80	38.76	0.53	1.49	7.50	28.34	0.03	0.05	1.12	0.80	1.23	0.33	10.98
1695	24.71	35.50	1.57	1.08	6.09	19.31			1.16	0.75	0.79	0.14	8.88
1696	10.34	36.01	1.95	2.30	8.71	22.42			0.97	5.98	0.81	0.28	10.20
1699	16.45	28.74	0.10	1.14	5.20	12.59	0.44			0.22	0.17	0.38	34.59
1744	4.90	35.59	1.29	2.45	11.09	22.12	0.12	0.06	1.65	2.51	0.82		17.40
1779	4.26	26.84	0.51	0.54	5.66	13.10	0.09	0.06	3.40	0.40	0.48		44.69
1855	9.49	37.70		0.44	0.88	39.31							12.19
1871	26.79	30.01		0.29	0.83	20.86			0.19	0.33			20.71
1874	15.97	28.18	0.16	1.09	4.80	10.06	0.09	0.07	0.72	0.28	0.20	0.33	38.08
1904	19.12	21.40	0.37	0.49	0.78	1.37	0.28	0.21	0.22	0.44		0.55	54.77
1920	12.64	34.36	0.27	0.41	0.81	31.70		0.04	0.17	1.70	0.08		17.81
1921	4.16	26.66	0.22	1.29	5.24	15.38	0.13		0.91	0.59	0.32	0.54	44.56
1939	24.88	24.48	0.20	0.65	2.84	6.38	0.21	0.04	0.52	0.71	0.20	1.20	37.72
1942	11.60	26.64	0.22	0.67	2.93	15.97	0.05	0.05	0.84	0.14	0.23	0.33	40.30
1943	15.38	28.78		2.04	4.27	13.22			0.17	0.19	0.32	1.18	34.47
1944	30.19	27.98		0.54	2.06	11.76	0.03	0.03	0.29	0.17	0.16	0.31	26.51
2074	14.62	23.85	0.14	0.40	2.90	4.41	0.21		0.59	0.32	0.20	0.48	51.88
2075	18.14	22.59	0.08	0.28	1.57	2.27	0.14		0.39	0.24	0.06	0.43	53.82

APPENDIX 5.13

THE DETERMINATION OF THE MICRO XRF TRACE QUALITY AND ELEMENTAL COMPOSITION FOR THE PAINT AND PIGMENT SAMPLES.

Trace quality

The µ-XRF data were collected on the synchrotron, and stored as chi files (X-Y data). These files were then viewed using the ICP MCA Display Program[1] designed for IDL VIRTUAL MACHINE 6.0©[2]. The elemental composition of the samples was then determined using the 2D diagrams produced. Two examples of these 2-D traces (labelled) are given in Figure A5.13.1.

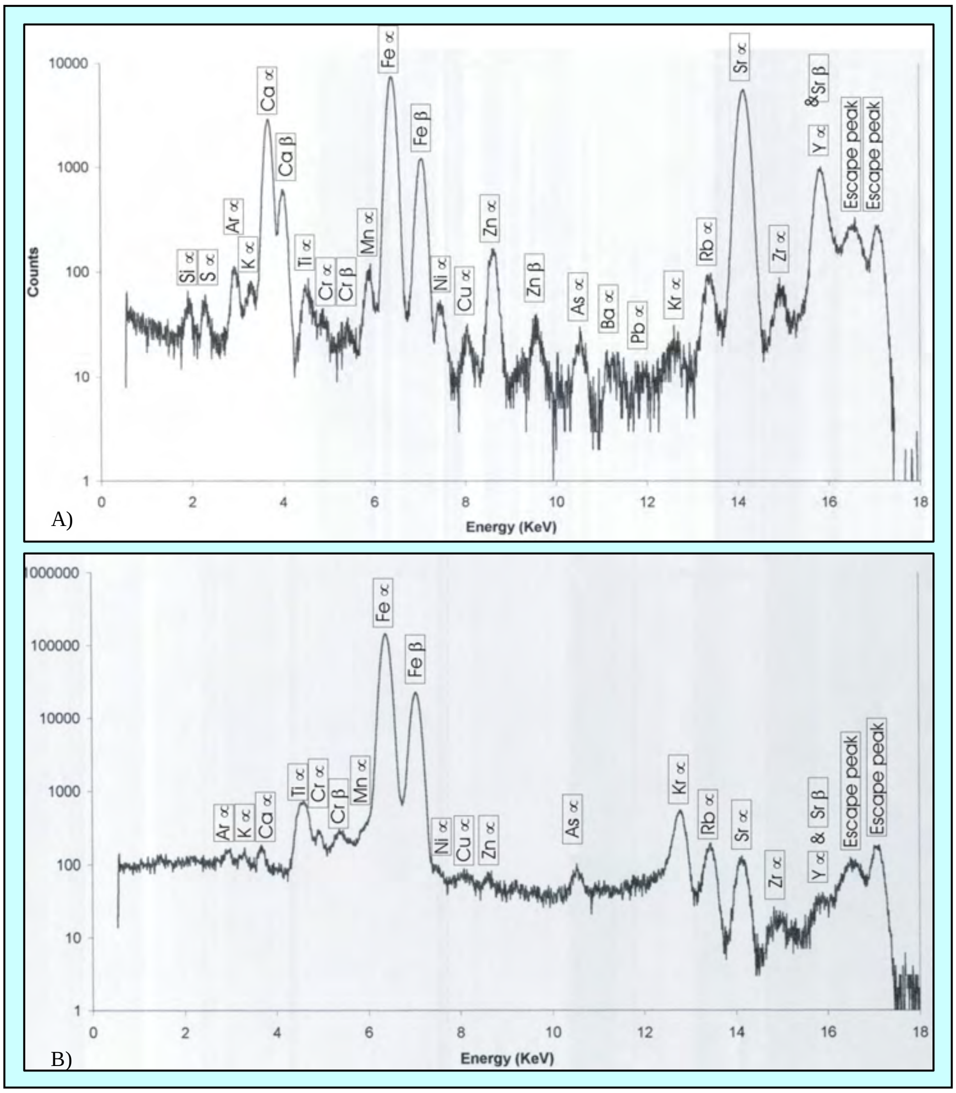

Figure A5.13.1 Examples of a good (A) and moderate (B) micro-XRF trace.

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[1] ICP MCA Display Program v4.3.17, written in Nov 2001 by Mark Rivers, Centre for Advanced Radiation Sources, University of Chicago.

[2] IDL VIRTUAL MACHINE 6.0, copyright 2003, produced by Research Systems Inc. (RSI). For more information see www.rsinc.com/IDL/.

The traces obtained for the samples analysed were classified as being good, moderate or poor. The traces classified as poor were not considered further within this study. The distinction between the foremost two categories is based on the perceived clarity of each trace i.e., how clearly the minor elements are represented, specifically between the KeV range of 7.5 and 12.5. As is illustrated in Figure A5.13.1B, the minor elements falling within this energy range can, in some cases, be lost beneath ‘white noise’. This perceived ‘loss’ of data could be attributed to either the nature of the sample (e.g. thickness, orientation, etc.) or the dominating presence of one or more element(s). In the case of this trace B, it would appear that Fe is dominating the spectrum to the detriment of the other elements, a fact that is supported by the high counts recorded on the y-axis. This finding is not a totally un-expected result, however, as this trace was determined from one of the Maqonqo Shelter excavated pigment samples.

Figure A5.13.1A is more representative of a majority of the elemental traces recorded during the course of this investigation, with this specific example being typical of most of the red paint samples analysed.

Elemental composition determination

This section is not intended to be a discussion on the theory of X-ray fluorescence, but rather discusses the manner in which the elemental compositional values used within this study were derived from the data obtained (e.g. the traces shown in Figure A5.13.1). As can be seen, the traces produced record both the alpha (α) and beta (β) peaks. As the alpha peaks represent the strongest peaks recorded for each element, the presence of each element, together with their respective presence was determined from this source of information only. It is, however, important to note that the beta peaks of particularly dominant species can dominate alpha peaks of additional elements also located at similar KeV’s. Unfortunately, these potential data are neither discernable, nor recoverable, using this technique.

Once the alpha peaks of the respective elements were identified, the traces were run through the ICP MCA program mentioned above. The program performed the functions listed below in the following order:

1) A best-fit baseline was fitted to the trace. This formed a basal line conforming to the base of the peaks. All the information recorded beneath this line is now no longer considered.
2) Best-fit ellipsoids were produced for each labelled element, the ellipsoids arising from the baseline to the highest recorded value of each respective element. An ellipsoid not fitting comfortably within the confines of a peak on the original XRF trace is indicative of an incorrectly labelled peak. The peak must be re-labelled.

3) Once all the peaks have been labelled and their ellipsoids fitted, the areas within each newly created peak (delimited by the baseline) were calculated. It is these area values that were used in the analyses discussed within this study.

As area values obtained for each element have no specific unit, they cannot be used to provide quantitative elemental data. These values do, however, allow for intra-technique comparisons. All of the area values for each trace were transferred to a spreadsheet and then standardized in order to facilitate analysis. In total, 361 individual traces were captured in this manner.

Whilst in some ways it is an advantage that an extraordinarily large body of data was collected during the course of this investigation, the large and varied dataset can, in some cases, be too complicated to allow for the easy identification of trends. In order to simplify the data to a greater extent, multiple data of like-colours from a single stub were averaged. The revised dataset thus contained a mixture of averaged and single values. It is on this modified dataset, as set out in Appendix 5.16, that the analyses produced within the main body of this study were based. The original dataset is set out in Appendix DIGITAL 3.

The following figures, using the data obtained for the Maqonqo Shelter paint samples, are shown in order to illustrate the validity of this adjustment. Figures A5.13.2 and A5.13.3 represent the individual datum points and averaged values, respectively. As is illustrated by both the eigenvalues and the distribution, and relative strengths, of the species' vertices represented within each of the figures, the averaging of the data has very little influence on the overall trends displayed by the dataset as a whole.

In order to determine the effect of trace quality on the results, the dataset was sorted into good and moderate traces. This was done for two reasons: a) the separate and combined analyses of these two respective categories would highlight the influence, if any, of the moderate traces on the dataset as a whole; and b) a 'purer' dataset might lead to less cluttered figures of higher data quality i.e., the trends identified would best reflect the true nature of the samples analysed. Figures A5.13.4 and A5.13.5, representing the good and moderate trace data respectively, are used in conjunction with Figure A5.13.3 to illustrate this effect.

Figure A5.13.4 displayed similar eigenvalues and vertices distribution and strengths as those in Figures A5.13.2 and A5.13.3. Figure A5.13.5, however, does display a degree of variation, although not great, relative to the three previous diagrams. Trace quality does, therefore, impart a influence upon the projected PCA trends. However, when considering both the limited number of moderate samples and the marginal influence of this subset on the sample distribution within the combined dataset tests (Figure A5.13.3), this influence can be considered to be minimal. The separation of the dataset based on trace quality is therefore not considered further within this study. The distinction is, however, still highlighted in Appendix DIGITAL 3.

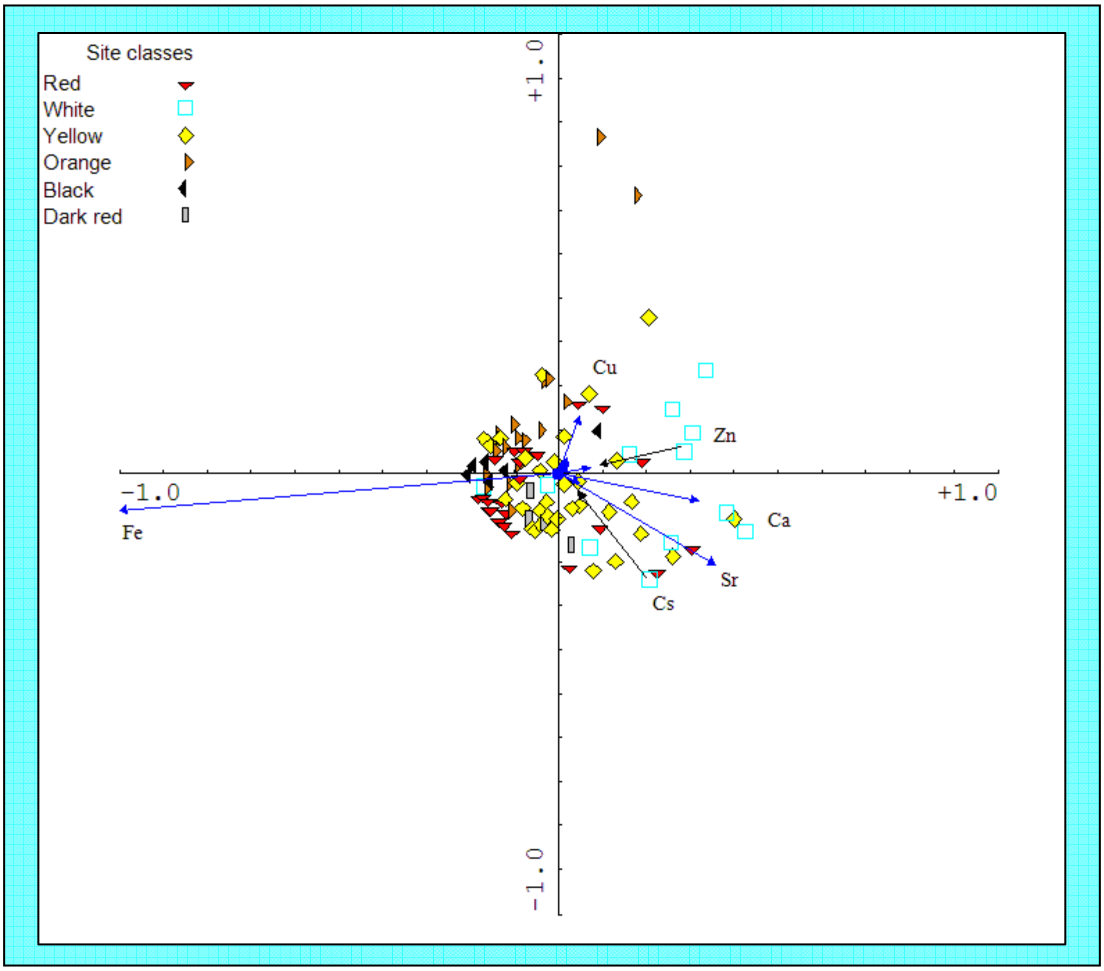


Figure A5.13.2: All datum points for the paint samples collected from Maqonqo Shelter as determined using micro-XRF.

Eigenvalues: PCA1 – 89.2; PCA2 – 5.5; PCA3 – 2.2

Scaling = -2

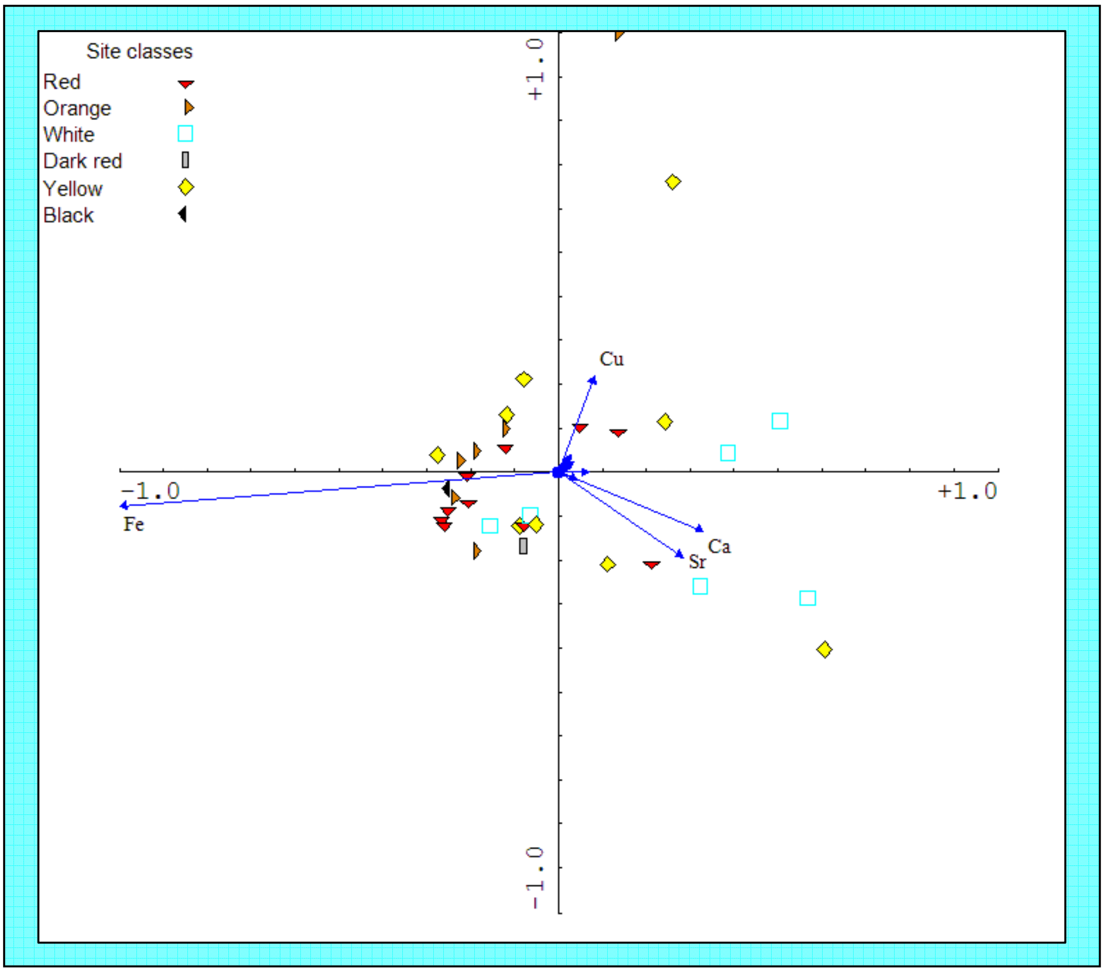


Figure A5.13.3: Sample distribution based on the combined average values obtained for the paint samples collected from Maqonqo Shelter as determined using micro-XRF.

Eigenvalues: PCA1 – 87.6; PCA2 – 8.3; PCA3 – 1.3

Scaling = -2

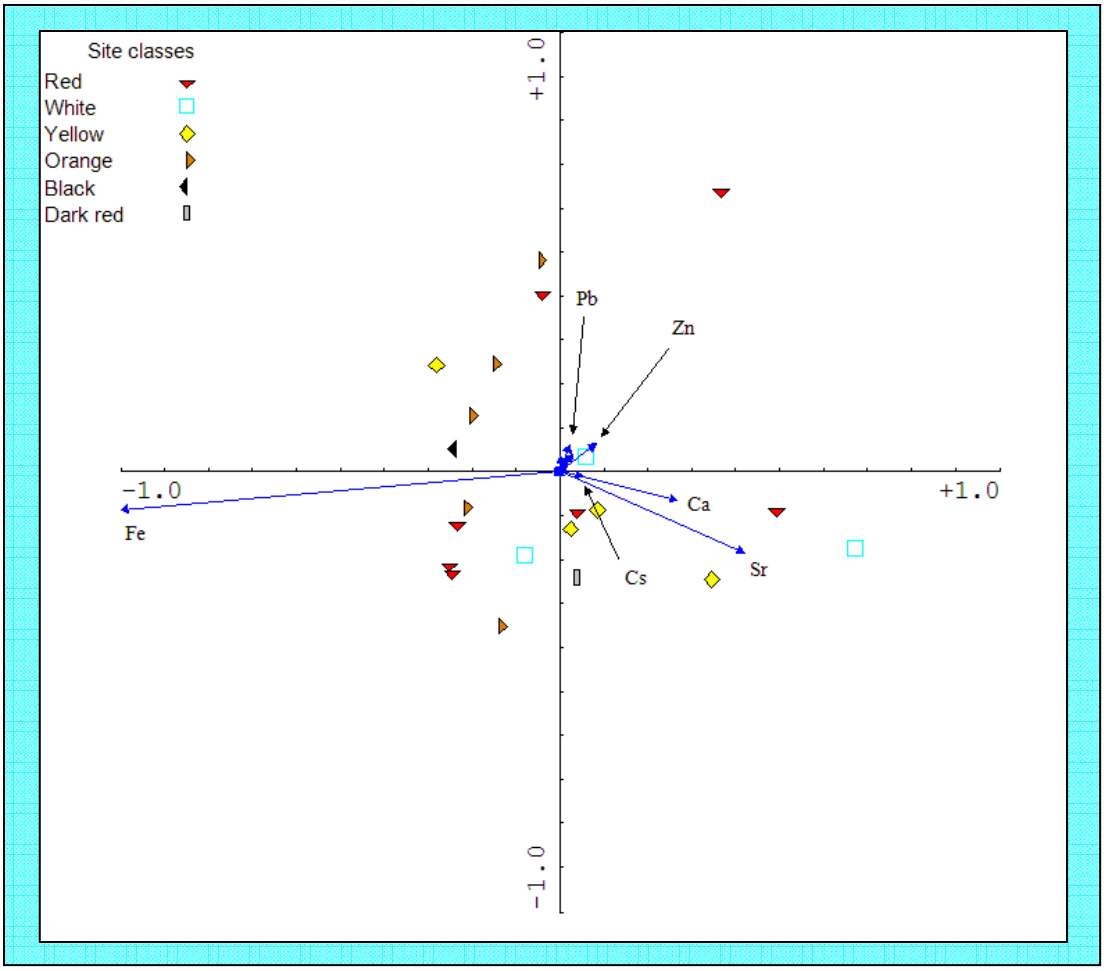


Figure A5.13.4: Sample distribution based on good trace average values recorded for the paint samples collected from Maqonqo Shelter as determined using micro-XRF.
Eigenvalues: PCA1 – 93.5; PCA2 – 4.4; PCA3 – 1.0
Scaling = -2

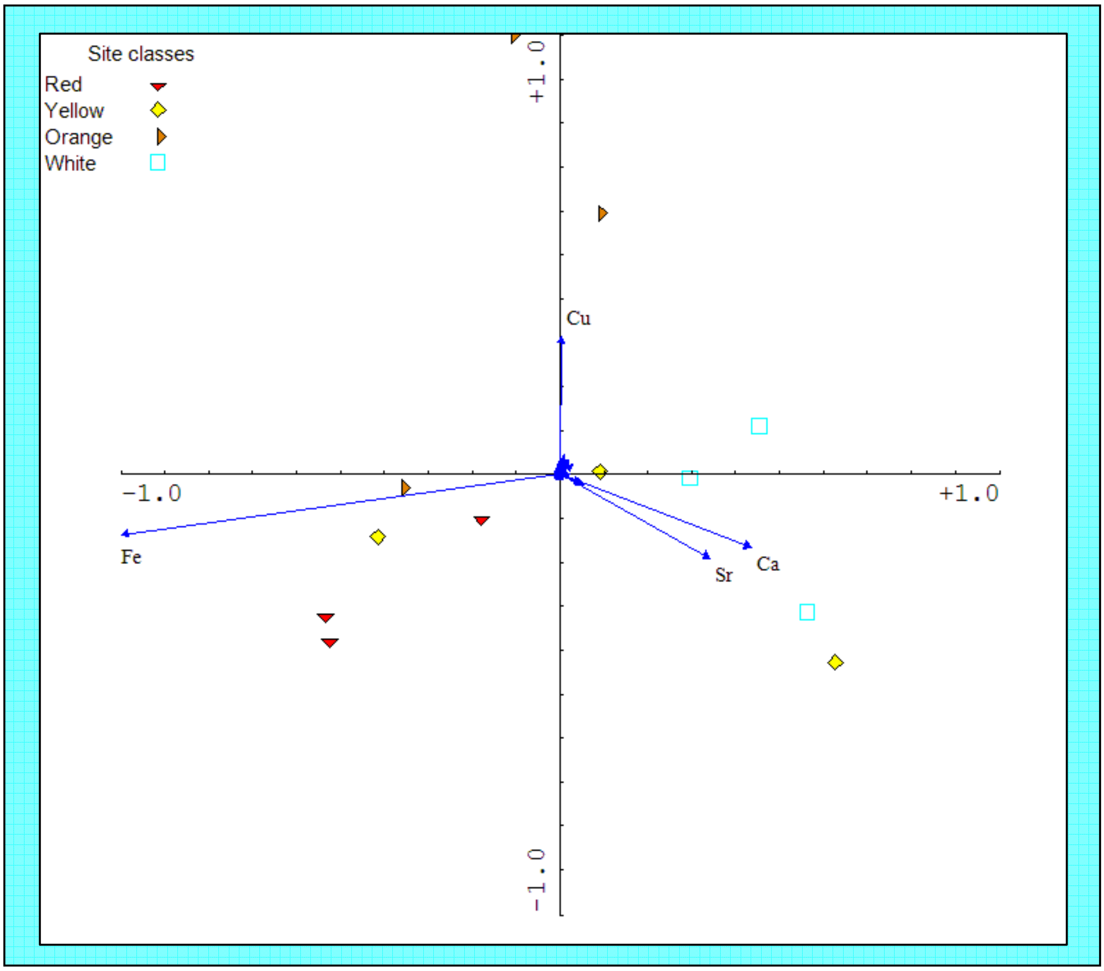


Figure A5.13.5: Sample distribution based on the average values obtained from the moderate traces recorded for the paint samples collected from Maqonqo Shelter as determined using micro-XRF.

Eigenvalues: PCA1 – 83.0; PCA2 – 12.0; PCA3 – 2.2
Scaling = -2

APPENDIX 5.14

MODE VALUES FOR THE SEMI-QUALITATIVE MICRO-XRD RESULTS OBTAINED FOR THE MAQONQO SHELTER SMALL EXCAVATED PIGMENTS SAMPLES.

This appendix contains the mode data for the µ-XRD data listed in Appendix DIGITAL 1. These data were used in order to simplify the PCA diagrams.

APPENDIX 5.14

MODE VALUES FOR THE SEMI-QUALITATIVE MICRO-XRD RESULTS OBTAINED FOR THE MAQONQO SHELTER SMALL EXCAVATED PIGMENTS SAMPLES.

Sample Name	Layer	Haematite	Goethite	Gibbsite	Quartz	Maghemite	Mica	Muscovite	Feldspar	Anatase	Lithiophorite	Lepidocrocite	Clinochlore	Apatite	Kaolinite	Rutile	Calcite	Boehmite
M30	1	1																
M164		1	2															
M165		2	2															
M772		1			4		4											
M1023		1	3															
M627		2			4													2
M1255		1	3				4											
S498		4			3										2			
M1208	2	2			1										2			
M1256		2	1															
M1258		1	2															
M1269		1	4															
M1276		1	3								3							
M1384		2	2		4										3			
M1393		1																
S2106		1			4		3		3									
S1347		1																
M1227		1			3		4											4
M1774	3	1	2		4													
M2019		1	3		4													
S1979		1			3											4		
M1939		1	4															
M28	5	1																
M5	6		2	1	4													2
M6		1	3															
M30	7	1	3		4													
M11		2			4									2				
M12		1			3		4								4			
M26		1				4	4							2				
M30		1			3		3											
M15		2	4		3								2					
M18			1					4				4			4			
M20		3			3										1			
M23		3			3										1			
S8					4		3										1	
M8	9	1																
M9		3			3										2			
M1					2			4							3			
M6	11	1	2		4													
M9		1	4															
M11		2																
M8		1																
M16		1	3															
M27		1			3			3										
M28		2			3										1			
S35		2			1					3								

NOTE:

M = Mode value

S = When no mode could be determined, the individual sample was used and is listed here

Only the good and moderate trace data has been reproduced here.

APPENDIX 5.15

INTER-TECHNIQUE COMPARISONS.

Introduction

The three techniques used to determine the elemental compositions of samples analysed operate using fundamentally distinct principles, and hence exhibit unique characteristics that have to be taken into consideration when attempting to conduct inter-technique comparisons. The first factor to consider is that each technique tends to display different sensitivity levels for individual elementals, though the degree of sensitivity is often dependent on the nature of the detector used[1]. Secondly, the techniques exhibit unique elemental detection "ranges", with some only able to identify elements that represent over 1 % of the overall sample composition, whilst others can determine the presence of all the elements present within a sample no matter how small a presence they represent, so long as the elements examined have an atomic number greater than 16. Finally, the format in which the data is recorded differs from technique to technique, with the results being presented as either oxides, element weight percentages or as parts per million.

Due to these differences in each of the techniques, the resultant datasets produced cannot be directly compared with one another, but must first undergo a certain degree of manipulation. However, as is almost always the case when data are manipulated, questions about the reliability of the results so obtained arise. In order to forestall this, it is customary to analyse a set of 'standards' by the different techniques and identify, and possibly account for, any possible discrepancies that might arise should the datasets be compared.

In order to minimise the potential bias that might be imparted upon a manipulated dataset(s), only two techniques can be compared at one time. As was the case in Chapter 6, however, the results obtained from only one comparison should not be consulted on an individual basis. Instead, it is strongly suggested that, should the same samples be analysed using all three of the techniques mentioned, the results should be obtained from a comparison of all three techniques in turn, as well as individually, so as to produce the most accurate answer for the particular question being posed.

Within this study elemental datasets were gathered from three separate analytical techniques, namely EDX, XRF and µ-XRF. For ease of explanation, each combination of comparisons will be discussed separately.

---

[1] For the different levels of accuracy displayed by the various techniques, the reader is referred to Appendix 5.7 (XRF) and 5.12 (EDX). The µ-XRF data is generally accurate to between 5 and 10 ppb for each element (Adams *et al.*, 1998).

EDX vs. XRF comparison

During the course of this study, all of the paint and large excavated samples were analysed using EDX. Whilst it is clear that the paint samples had to be analysed using this technique due to sample size limitations, the analysis of the large excavated samples was conducted solely to allow for a comparison between the paint and deposit materials. These samples, along with the local and distant field samples, were also analysed using XRF in order to try and identify possible pigment sources. The fact that the large excavated samples were analysed using both techniques thus allows one to determine the compatibility between the two datasets. Should it be determined that the datasets are compatible, this would allow for the comparison of the paint samples not only with the local and distant field samples, but also with field sample data collected subsequent to the completion of this study.

The techniques in question differ greatly in the manner in which their data are presented, with the elemental composition being expressed as element weight percentages by EDX, but as oxides and parts per million by XRF (for the major and minor elements, respectively). As the EDX data only contain major elements, however, only the major XRF data can be used for comparative purposes. Only the average reduced window data collected using EDX will be used for reasons outlined in Appendix 5.11. In order to prepare the data for comparison, certain manipulations first have to be made to the XRF dataset. An example of these calculations is given in Appendix 5.8, whilst the resultant values derived for each of the major XRF elements are given in Appendix A5.8.1.

At this point it can be noted that C, O and S, whilst recorded using EDX, are not recorded by the major XRF data. These elements were therefore ‘re-worked’ back into each of the remaining elements on a proportional basis, and the resultant values normalised to 100 %. Only when each dataset contains the same elemental descriptions, and have been normalised to 100 %, can the compatibility of the two datasets be tested.

A sample set consisting of Layer 2 large pigment data was used to test the comparability of the EDX and XRF datasets (a total of eight samples). For this test, the normalised EDX data were compared, using PCA, with both the calculated *dry* and *wet elemental percentages*. The resultant diagram (Figure A5.15.1) clearly shows that a similar distribution pattern occurs within the EDX and major XRF datasets, but that it is the ‘*wet elemental percentage*’ that most closely correlates within the recorded EDX data[1]. This is not surprising, however, for whilst the samples are analysed in an unmodified state using EDX, the method of sample preparation required for major XRF elemental analysis results in the ‘alteration’ of the original sample via heat - hence the L.O.I. value. Future comparisons between datasets derived from these two techniques must therefore take this into account.

---

[1] An identical distributional pattern is unlikely to be achieved, due to the heterogeneous nature, even at the micro-level, of the samples being analysed.

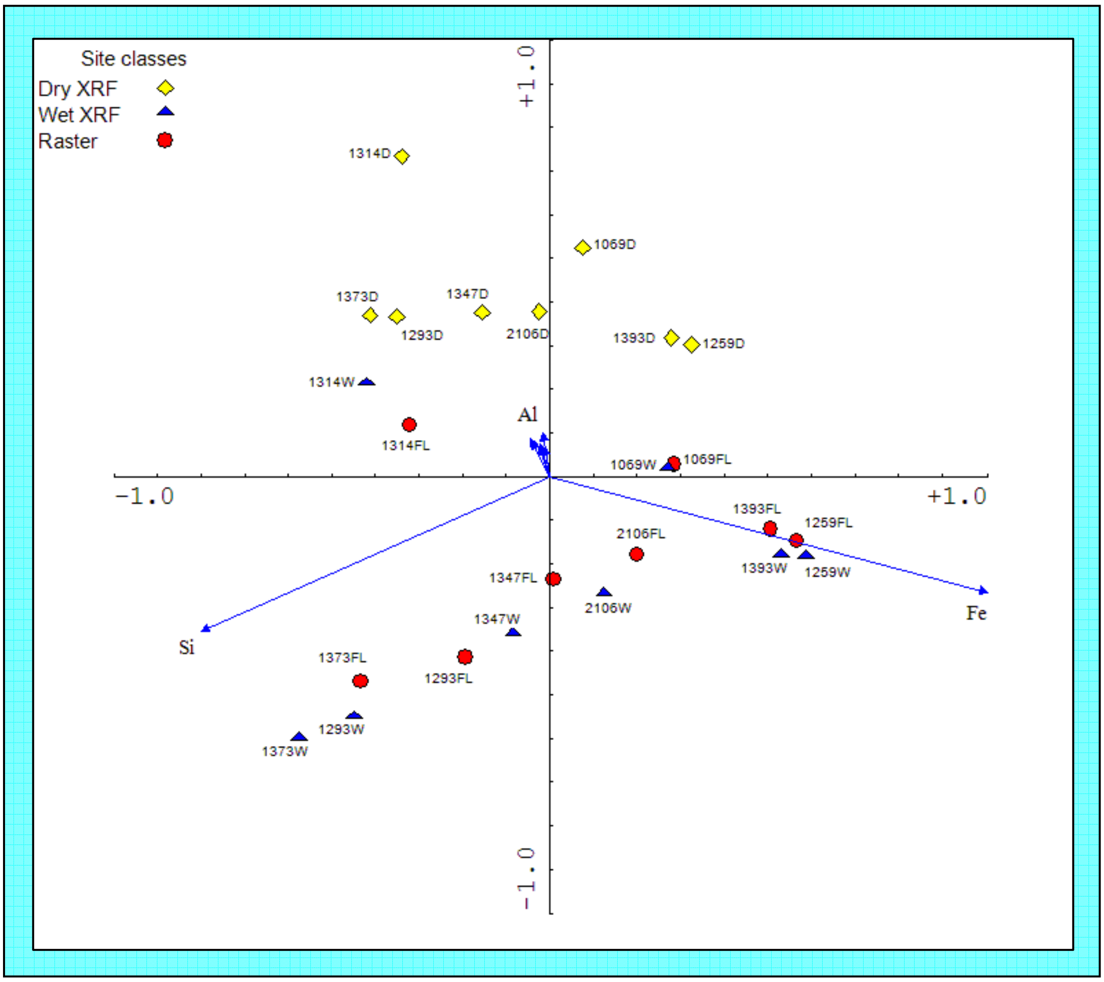


Figure A5.15.1: Average reduced window EDX data compared with the ‘dry’ and ‘wet’ XRF data manipulations.

Eigenvalues: PCA1 – 86.2; PCA2 – 12.8; PCA3 – 0.8

Scaling -2

EDX vs. micro-XRF comparison

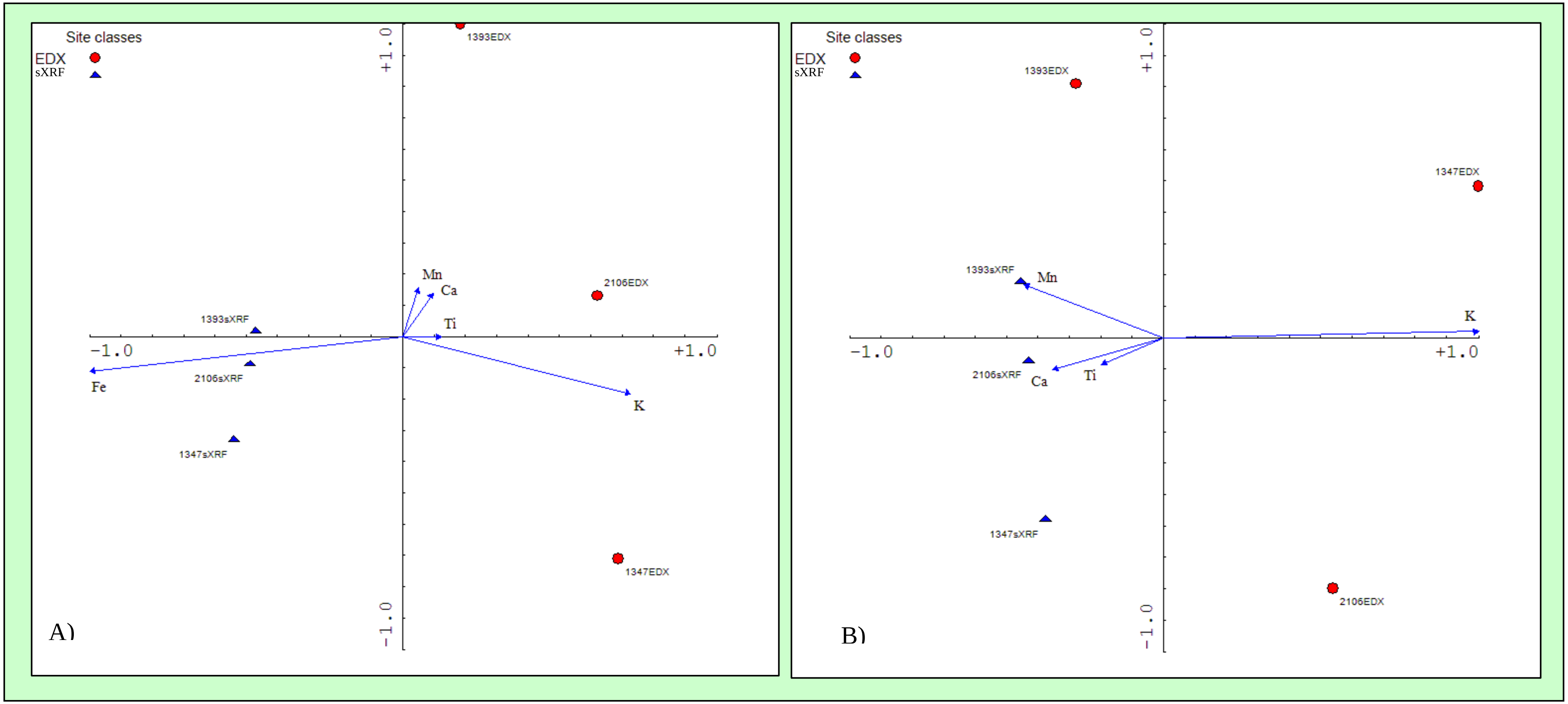
Unlike the EDX data, which are recorded as weight elemental percentages, the µ-XRF data are recorded as ‘counts’, an unmodified, arbitrary unit that reflects the number of ‘X-ray hits’ the detector received whilst the sample was held in the X-ray beam for the pre-determined 150 second time period. Each sample (and even each individual trace) will reflect a different overall ‘count total’, with the count being dependent on many different factors, including a) the ‘thicker’ the sample under the beam, the greater the count; b) the higher the average atomic number within the sample, the more sensitive the sample trace (‘light elements’, such as O and S, don’t ‘reflect’ as well as the ‘heavier elements’ such as Fe); and c) the more crystalline the mineral, the greater the reading.

Whilst the counts do not initially provide comparable trace information, they do establish the relative proportions of the individual elements to one another within the individual traces. It is thus a simple process to standardise the dataset as a whole via the conversion of all of the traces into weight percentages. It was this standardised dataset that was used in the µ-XRF PCA investigations discussed in Chapter 6.

Whilst both the µ-XRF and EDX datasets are now recorded as elemental weight percentages, only a few elements are common to both datasets. These include K, Ca, Ti, Mn and Fe. In order to attempt a comparison, all of the remaining ‘non-common’ elements were re-worked back into these five elements in the same manner as described in the previous section. In addition to this highly simplified comparable dataset, only three of the initial five samples that were analysed using both techniques could be resolved using µ-XRF (all were resolved using EDX), thus severely limiting the size of the ‘comparable’ dataset.

This very small dataset was then interrogated using PCA (Figure A5.15.2A). As was expected, Fe, which is dominant in more than 95 % of all of the samples analysed, dominates the diagram. Even with this, however, it is clear to see that there is no similarity exhibited by the two datasets. Figure A5.15.2B, in interrogating the two datasets without the overall influence of Fe, further illustrates this dissimilarity.

There are several reasons as to why the two datasets are not comparable (in their current state). The most probable lies in the relative sizes of the respective technique’s beam footprints. The EDX reduced window scan is a ‘generalist’ scan, recording data from a pre-determined beam footprint that is generally between 0.5 and 1.0 mm in both length and breadth. The µ-XRF technique, on the other hand, has a circular beam footprint with a diameter of approximately 0.05 mm (very similar to the EDX’s spot analysis). The high degree of precision that this latter beam footprint displays, coupled with the high degree of heterogeneity present within the samples and a variable sample thickness, results in a high degree of variability within the traces, with this variability being reflected within the resultant dataset as a whole (see Appendix 5.11 – although this discusses the EDX spot data, the principles are identical).



Eigenvalues: PCA1 – 93.7; PCA2 – 5.5; PCA3 – 0.7
Scaling –2

Eigenvalues: PCA1 – 94.6; PCA2 – 3.3; PCA3 – 2.1
Scaling –2

Figure A5.15.2: A comparison of the datasets obtained from both the average reduced window EDX and micro-XRF technique (µ-XRF), containing A) all elements and B) all elements excluding Fe.

The reasons as to why the two sample sets are, as yet, incompatible can be rectified if careful consideration to sample preparation is given e.g. thicker samples could allow for cross-sections of known thickness to be taken. This, coupled with a beam footprint of a known diameter allows for the quantitative analysis of the samples under study. More analyses collected from each sample would also aid in the establishment of a more generalised reading for each sample. Whilst these suggestions will aid in any future work using these micro-analytical techniques, within the confines of this study these two datasets can only be considered on an individual basis.

XRF vs. micro-XRF comparison

After both of these datasets were standardised (i.e., both normalised to 100 % and converted to weight percentages), not only were only three of the standard samples present within both datasets, but also only five elements were common to both, namely Fe, Mn, Ca, K and Ti. As seen above, it was found that the Fe content was by far the most dominant of all the elements listed, accounting for over 97 % of each of the samples. As a consequence, Fe was left out of the PCA analysis of the two datasets (as per the reasoning outlined in the above section). Even with the removal of Fe (Figure A5.15.3), it can still be seen that the two datasets are not compatible, for the same reasons as outlined in the previous section.

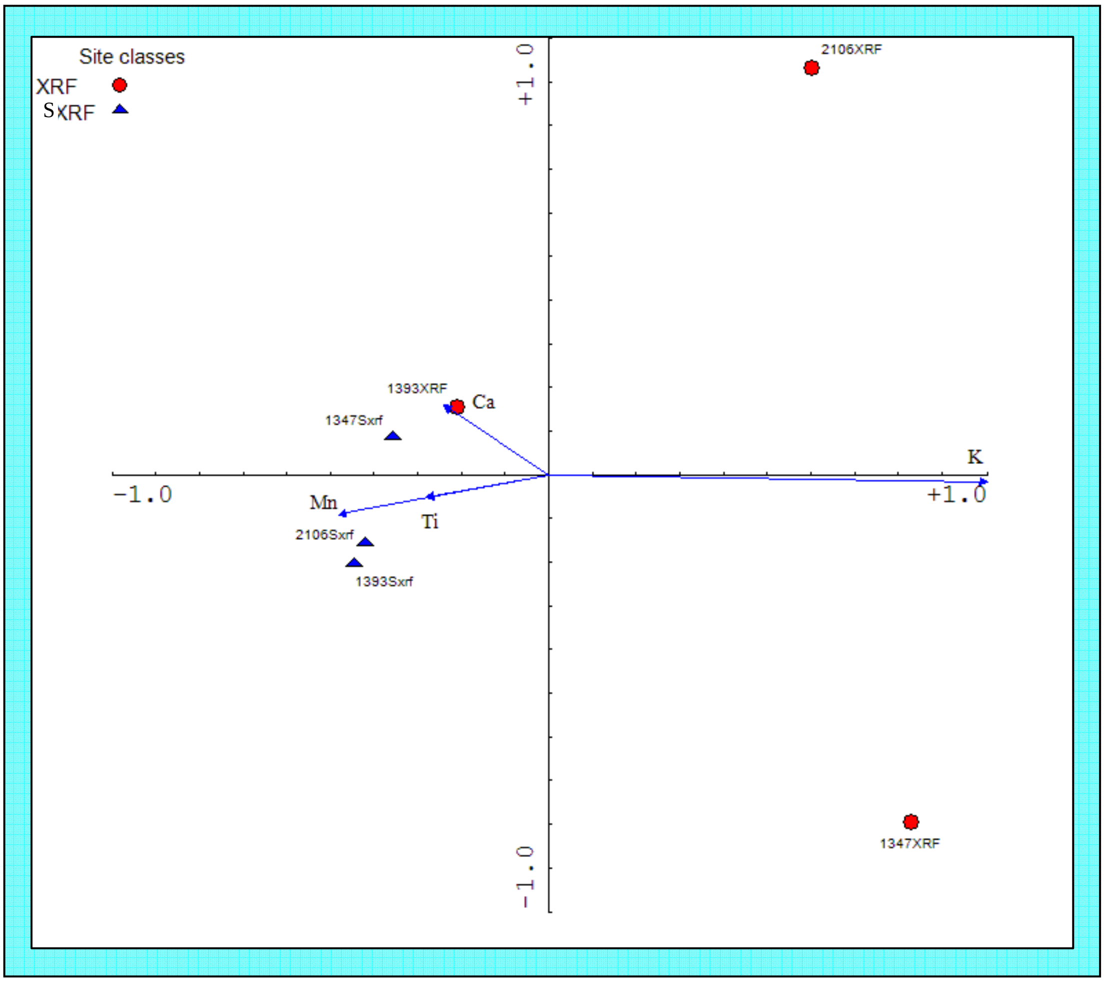


Figure A5.15.3: A comparison of the standard XRF and micro-XRF techniques, Fe excluded.
Eigenvalues: PCA1 – 96.2; PCA2 – 2.6; PCA3 – 1.2
Scaling -2

APPENDIX 5.16

AVERAGE SEMI-QUANTITATIVE MICRO-XRF RESULTS (PPM) OBTAINED FOR THE BLANK, PAINT AND EXCAVATED PIGMENT SAMPLES FROM ALL FOUR SHELTERS.

For the entire dataset, refer to the file called ‘APPENDIX DIGITAL 3’ on the CD provided.

(Note: null values, represented as ‘0.00’, indicate that the element totally absent from the sample or present in a concentration beneath the sensitivity of the apparatus. However, these values null values have been retained so that the table can be immediately incorporated into a statistical package for analysis. Whilst in the electronic version of this data, the “no data” values are represented as “0.00”, in the summary table presented here, they have been removed for the sake of clarity.).

APPENDIX 5.17

QUANTITATIVE RESULTS (PPT) OF THE SURFACE WATER SAMPLES OBTAINED USING ICP-MS.

Sample	Rh	Li	Be	B	C	Na	Mg	Al	Si	S	Ca	Sc	Ti	V	Cr	Mn	Fe
Maqonqo A	1463078	125		2441	1107156	12215134	2399143	202599	780839	1531923		1156		400	30524	195919	381701
Maqonqo B	1463078	224		740	5187084	13473061	9676684	6278	3200000	744218	51865652	4438	36179	5796	28985		814178
Maqonqo C	1463078	330	5	794	1942542	5217744	2689208	1769742	2218823	727735	17670902	3940	98427	4785	17245	48641	2158891
Twagwa	1478187	91	5	542	486242	3206937	439202	10650		888254	1055351	1147	403	169	4747		432303
Sheltered Vale	1478187	185	5	1600	484513	2907548	245298	310888	382529	1686049		3158	8032	1215	16999	82527	679072
Fergies Cave	1478187	86	1	146	612730	3065045	132590	24290	462276	809855	2571052	2216	3500	699	1794		506762

Cont.

Sample	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	Rb	Sr	Y	Zr	Nb	Mo
Maqonqo A	420	14458	8401	63649			108	6760	9003		22214	127515	124	102	1	302
Maqonqo B	283	1817	1805	6536			86	12956	6183			401071	141	67		299
Maqonqo C	723	4999	2354	13424			43	8476	1420		2819	162131	1116	1647	409	538
Twagwa	158	2858	2196	12250	54	82	29	372	3683		854	15283	36			
Sheltered Vale	623	9303	4280	18631	157			52	1916	99	1469	15107	1050	1041		677
Fergies Cave	469	2893	3863	15581	231		10	13062	1035		1157	15645	90	1		391

Cont.

Sample	Pd	Ag	Cd	In	Sn	Sb	I	Xe	Cs	Ba	La	Ce	Pr	Nd	Sm
Maqonqo A	18	26			169	1100696	9800	458	76	131207	312	44	33	105	1
Maqonqo B		33			175	107	9257	1004	8	207798	56		16		
Maqonqo C		28	10		422	382416	2791		322	226390	1333	2541	535	1243	348
Twagwa		24					454	448	41	6337	50	18	11	42	
Sheltered Vale		42		3		472921	890	900	34	6947	684	1238	245	672	210
Fergies Cave						107	199	1612	12	11777	45	50	9	56	

Cont.

Sample	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf	Ta	W	Os	Pt
Maqonqo A	26		7	1					3	12		63		
Maqonqo B	16		3			17			6	6		11		
Maqonqo C	114	275	42	244	42	40	1	89	24	47	19	85		
Twagwa	11		12		19		23		9	19	1	175	8	3
Sheltered Vale	73	131	29	84	19	73	23	30	11	46	4	173		
Fergies Cave			1		19		17		6	16		46		

Cont.

Sample	Au	Hg	Tl	Pb	Bi	Th	U
Maqonqo A				435		9	
Maqonqo B							1300
Maqonqo C	27		73	1255	13	848	663
Twagwa		218				17	11
Sheltered Vale		3	9		110	353	144
Fergies Cave						2	3

NOTES:

Elements not tested for: H He N O F Ne Cl Ar K

Elements not present within any of the samples: P Ru Rh Te Re Ir

APPENDIX 5.18

SOME THEORETICAL ASPECTS OF PRINCIPAL COMPONENTS ANALYSIS.

This form of analysis examines the interactions between various variables, in this study major and minor elements, and expresses these as "... a linear combination which is most efficient in accounting for the greatest amount of total variance between fractions" (Davis, 1973). It uses a mathematical procedure to create a new set of uncorrelated variables from the original set of variables (Johnson, 1998). This can be formed on either a sample variance-covariance matrix or, as was used within this study, a correlation matrix.

The variables are expressed as a series of vectors in space, with the eigenvectors of the matrix indicating the orientation of the variables, and the eigenvalues indicating the length (Botha, 1992). The variables are weighted according to their contribution to the variance between the samples, with the 'principal attribute' (i.e., axis 1 or the x axis) defining the most variation (Brown, 1985). The closer a variable is weighted to zero, the less these variables are related to the variation (East, 1987).

Occasionally, these newly created variables, or principal attributes, are interpretable, but this is by no means the norm (Johnson, 1998). Wherever possible in this study, an interpretation for each of the principal attributes is given. In order to facilitate the easy comparison of the PCA tests, the data were forced into a scatter diagram in which the axes ranges were predetermined to –1 to 1, respectively. In order to accomplish this, a scaling factor had to be introduced to the data. This factor has been given in association with each of the diagrams.

APPENDIX 6.1

A COMPARISON OF SOME PROPOSED RELATIVE DATING TECHNIQUES.

<table>
<tr><th>Reference</th><th>Area</th><th>Age</th><th colspan="28">Oldest > > > Youngest</th></tr>
<tr><td>L’Breuil, 1930</td><td>Eastern Free State</td><td rowspan="5">Style</td><td>Monochrome</td><td>Monochrome</td><td colspan="3">Monochrome</td><td>Monochrome</td><td colspan="3">Monochrome</td><td>Monochrome</td><td colspan="2">Bichromes</td><td>Shaded polychromes (beautiful)</td><td colspan="2">Bichrome (good technique)</td><td colspan="2">Monochrome (good technique)</td><td colspan="2">Polychromes (better art)</td><td>Polychromes (bad art)</td><td colspan="2">Bichromes</td><td>Monochrome</td><td colspan="3">Monochrome</td><td>Monochrome</td><td>Monochrome</td></tr>
<tr><td>Mason, 1933</td><td>Cathkin Peak</td><td colspan="3">Monochrome</td><td colspan="4">Monochrome</td><td colspan="4">Unshaded polychrome 1</td><td colspan="3">Some shaded polychrome 2</td><td colspan="4">Shaded polychrome 3 (best imagery)</td><td colspan="3">Shaded polychrome 4 (decreasing quality; seldom more than two colours used)</td><td colspan="4">Shaded polychrome 5 and bichrome (decreasing quality; seldom more than two colours used); Unshaded mono- and bichrome</td><td colspan="3">Monochrome (inferior)</td></tr>
<tr><td>Pager, 1971</td><td>Ndedema (based on Eland superposition)</td><td colspan="4">Unshaded monochrome</td><td colspan="4">Unshaded bichrome</td><td colspan="4">Shaded bichrome</td><td colspan="4">Shaded polychrome</td><td colspan="4">Shaded polychrome</td><td colspan="4">Unshaded polychrome</td><td colspan="4">Unshaded mono- and bichrome</td></tr>
<tr><td>Vinnicombe, 1976</td><td>Southern Drakensberg</td><td colspan="7">Monochrome</td><td colspan="7">Bichrome</td><td colspan="7">Shaded polychrome</td><td colspan="7">Monochrome</td></tr>
<tr><td>Russell, 2000</td><td>Main Caves North, Central Drakensberg</td><td colspan="4">Monochrome and Bichrome</td><td colspan="4">Bichrome and Polychrome</td><td colspan="4">Shaded polychrome and bichrome</td><td colspan="4">Monochrome</td><td colspan="4">Shaded polychromes</td><td colspan="4">Monochrome</td><td colspan="4">Bichrome and polychrome</td></tr>
<tr><td>Mason, 1933</td><td>Cathkin Peak</td><td rowspan="3">Application</td><td colspan="3">-</td><td colspan="4">-</td><td colspan="4">Thick/clear brush lines</td><td colspan="3">-</td><td colspan="4">Fine brush lines</td><td colspan="3">Fine brush lines</td><td colspan="4">-</td><td colspan="3">Thick smear</td></tr>
<tr><td>Vinnicombe, 1976</td><td>Southern Drakensberg</td><td colspan="7">Stain</td><td colspan="7">Stain or thin film</td><td colspan="7">Thick/clear brush lines</td><td colspan="7">Thin film</td></tr>
<tr><td>Russell, 2000</td><td>Central Drakensberg</td><td colspan="4">Stain</td><td colspan="4">-</td><td colspan="4">Thick paint and brushstrokes</td><td colspan="4">-</td><td colspan="4">-</td><td colspan="4">-</td><td colspan="4">-</td></tr>
<tr><td>L’Breuil, 1930</td><td>Eastern Free State</td><td rowspan="5">Colour</td><td>White</td><td>Yellow</td><td colspan="3">Pale red</td><td>Black</td><td colspan="3">Pale red</td><td>Dark red</td><td colspan="2">Red and white</td><td>-</td><td colspan="2">Red, brown</td><td colspan="2">Black</td><td colspan="2">-</td><td>-</td><td colspan="2">Black and white</td><td>Strong red</td><td colspan="3">Ochreous yellow</td><td>White</td><td>Orange red</td></tr>
<tr><td>Mason, 1933</td><td>Cathkin Peak</td><td colspan="3">Yellowish-white (naturalistic)</td><td colspan="4">Faint red</td><td colspan="4">Dark red, yellow or yellowish white</td><td colspan="3">Yellow-brown and white, yellow</td><td colspan="4">Red, brown, yellow and white</td><td colspan="3">Red and chalky white</td><td colspan="4">Shaded polychrome = Yellow, orange, orange-brown, and dark red; Unshaded mono- or bichrome = Orange, white</td><td colspan="3">Chalky white, red or black</td></tr>
<tr><td>Pager, 1971</td><td>Ndedema (based on Eland superposition)</td><td colspan="4">Red*</td><td colspan="4">Red*- white or red*-red*</td><td colspan="4">Red*- white or red*-red*</td><td colspan="4">Red*-white-black, or red*-red*-white or red*-red*-white-black</td><td colspan="4">All 4, 3 and 2 pigment colour schemes containing yellow or orange</td><td colspan="4">All other 3-colour schemes, also bichrome’s of red* and black</td><td colspan="4">Monochromes are black, white, orange, bright red, yellow; Bichromes are black-white or bright red-white</td></tr>
<tr><td>Vinnicombe, 1976</td><td>Southern Drakensberg</td><td colspan="7">Black/maroon</td><td colspan="7">Red, sometimes white (usually lost)</td><td colspan="7">Red, white, orange, black, yellow, brown</td><td colspan="7">Increased black, white, orange and yellow use instead of red</td></tr>
<tr><td>Russell, 2000</td><td>Central Drakensberg</td><td colspan="4">Monochrome = Dark purple, Orange, brown; Bichromes = Dark purple and white</td><td colspan="4">Bichrome = Red and white; Polychrome = purple/maroon, white, black</td><td colspan="4">Polychrome = pink, brown, purple, orange, black, white; Bichrome = orange, brown. Black for details</td><td colspan="4">White</td><td colspan="4">-</td><td colspan="4">Pink, brown-red</td><td colspan="4">Bichrome = yellow, white; Polychrome = yellow, white, black</td></tr>
</table>

* - Comprise all dull reds including pink, red, maroon, dark maroon and chocolate.
\- - Information not given.

APPENDIX 6.2

A COMPILATION OF KNOWN DATED BURIAL STONES, *ART MOBILIER* AND PARIETAL ROCK ART.

Age	Colour	Style	Shelter	Locality	Reference
Wilton industry = about 9000 b.p. to present	Black, red	Black monochrome humans (4), stone was originally painted red on the side of the images	Knysna Eastern Head Cave (burial stone)	Knysna District, Cape Province	Goodwin and van Riet Lowe (1929)
6 310 ± 250 B.C. (doubtful)	Red, Black	Engravings on shelter wall with pigment rubbed into them. (Buried and layers dated)	Chifubwa Stream Rock Shelter	Solwezi, Northern Rhodesia [Zambia]	Clark (1958)
Between 5 400 ± 250 B.P. and 7 750 ± 300 B.P. (considered doubtful); Date from C from stone = 5 600 ± 200 B.P. (Hoffman pers. comm. to Rudner, 1971)	Red	Monochrome humans (water worn burial stone)	Matjes River Shelter (burial stone)	Plettenberg Bay, Cape Province	Meiring (1953); Hoffman (1958); Hoffman (pers. comm.: cited in Rudner, 1971)
2 285 ± 105 B.P.	Black, with thin white lines	Monochrome human; bichrome dolphins (black with white lines on underbellies)	Klasies River Mouth Complex, Cave 5 (water-worn pebbles)	Klasies River Mouth, Cape Province	Singer and Wymer (1969) [see also Binneman and Hall, 1993]
4 110 ± 160 B.P. (obtained from a lower layer. The painting is probably closer to the first age)	Red	Monochrome oval grid pattern on both sides [out of context – Binneman and Hall, 1993]			
8 260 ± 720 B.P.	Red	Monochrome (Burial stone)	Wilton Caves	Albany District, Cape Province	Rudner (1971)
235 ± 80 B.P. (slab fell therefore maximum date)	Red	Monochrome animals and grid pattern (Parietal art in slab scar)	Glen Elliot Shelter	Colesberg District, north-eastern Cape	Sampson (1967; 1974)
1 925 ± 33 B.P.	Black	Monochrome humans (12) (Table Mountain Sandstone slab)	Cave D/Guanogat Cave	Robberg Peninsula, Knysna District, Cape Province	Rudner and Rudner (1973)
1 955 ± 75 B.P. (above stones)	Red	Monochrome antelope, monochrome square (on slab of limestone)	Boomplaas Cave (buried stones covering pits)	Near Cango Caves, Oudtshoorn, Cape Province	Deacon *et al*. (1976)
	Black, white	Bichrome of eland			
	Red	Monochrome ostrich with human legs and feet (quartzite river cobble)			
6 400 ± 75 B.P.	Red, white	Mainly smear and animal (?) (broken quartzite river cobble)			
Three dates obtained: 26 300 ± 400 B.P. 26 700 ± 650 B.P. 28 400 ± 450 B.P.	Black	Monochrome (animal with human legs)	Apollo 11 Cave	Huns Mountains, south-western Namibia	Wendt (1976)
	Black	Outline of rhino			
	Black, red	Black lines on a red patch			
	Red, (?)	Antelope with red lines over it			
	White, black	Bichrome zebra (?)			

APPENDIX 6.2 (Cont.)

A COMPILATION OF KNOWN DATED BURIAL STONES, *ART MOBILIER* AND PARIETAL ROCK ART.

Age	Colour	Style	Shelter	Locality	Reference
520 ± 50 B.P. (Dated wasp nest therefore is a minimum date)	Red	Monochrome human	Lufthöhle	Amis Gorge, Upper Brandberg, Namibia	Breunig (1986)
500 ± 140 B.P.	Black	Monochrome human legs (finger painting)	Boontjieskloof (parietal art)	Clan William District, Cape Province	Van der Merwe *et al.* (1987)
3 900 ± 50 B.P.	Red	Monochrome antelope	Klasies River Mouth Complex, Cave 5 (wall fragment)	Klasies River Mouth, Cape Province	Binneman and Hall (1993)
6 430 B.P. (error not given)	Black	Monochrome human (?)	Groot Kommandokloof Shelter (wall fragment placed in burial cairn)	Near Grahamstown, Cape Province	
650 ± 50 B.P. (minimum date)	White, red	Monochrome rhebuck (white), polychrome rhebuck and eland neck and head, and some monochrome human figures (red)	Collingham Shelter (wall fragments fallen into deposit)	Drakensberg, KwaZulu-Natal	Mazel (1992; 1994)
Between 1 800 ± 50 B.P. and 1 830 ± 50 B.P. (dates of layers above and below layer in which slab found)	Black	Monochrome humans (3) and smudges			
330 ± 90 B.P.	Orange and white	Unshaded bichrome	Esikolweni Shelter (parietal art)	Cathedral Peak, KwaZulu-Natal	Mazel (1996b); Mazel and Watchman (1997)
420 ± 340 B.P. (high error makes this date unreliable)	Orangey white (cream)	Shaded (?) bichrome	Clarke's Shelter (parietal art)	Drakensberg, KwaZulu-Natal	
3 510 ± 50 B.P. above slabs 3 635 ± 30 B.P. between slabs 3 640 ± 60 B.P. beneath slabs	Red, white	Monochrome human (2) Bichrome human (1) (white kaross, red body)	Steenbokfontein Cave	Near Lambert's Bay, Cape Province	Yates and Jerardino (1996)
	Red, white	Monochrome legs and hips of humans (3). One bichrome human has white decorations			
1930 ± 20 B.P. from branches within the burial	Yellow, red	Yellow human figures; red patches	Tierkloof Cave	Tierkloof Farm, Kouga Mountains, Eastern Cape Province	Binneman (1999); Pearce (2003)

APPENDIX 6.3

MINERAL AND CHEMICAL NOTATIONS, AND SOLUBILITY VALUES.

Only the minerals for which the solubility products and/or solubility in grams per 100 cc could be found have been listed.

TABLE A6.3: MINERAL AND CHEMICAL NOTATIONS, AND SOLUBILITY VALUES (LIDE, 2002).

Mineral	Mineral notation	Chemical notation	Solubility Product Constant (K_{sp})	Solubility in grams per 100 cc		Other solvents
				Cold water	Hot water	
Alunite	Potassium Aluminium Sulphate Hydroxide	$(K,Na)Al_3(SO_4)_2(OH)_6$	…	…	…	slightly soluble in acid
Anatase	Titanium Oxide	TiO_2	…	insoluble	insoluble	Soluble in H_2SO_4, alkali; insoluble in acid
Anhydrite	Calcium Sulphate	$CaSO_4$	$4.93\ 10^{-5}$	0.209^{30}	0.1619^{100}	soluble acid; NH_4 salts, $Na_2S_2O_2$, glycerin
Apatite	Calcium Phosphate Hydroxide	$Ca_5(PO_4)_3(OH)$	…	…	…	soluble in acid, HCl
Aragonite	Calcium Carbonate	$CaCO_3$	…	0.00153^{25}	0.00190^{75}	soluble in acid, NH_4Cl
Barite (Baryte)	Barium Sulphate	$BaSO_4$	$1.08\ 10^{-10}$	0.000222^{18}	0.000336^{50}	0.006 s 3% HCl; slightly soluble in H_2SO_4
Bassanite	Calcium Sulphate Hydrate or Calcium Sulphate HemiHydrate	$2CaSO_4.H_2O$ or CaSO4.½H_2O	$3.14\ 10^{-5}$	0.3^{20}	slightly soluble	soluble in acid, NH_4 salts, $Na_2S_2O_3$, glycerin
Boehmite or Böhmite	Aluminium Oxide Hydroxide	γ-AlOOH or AlO(OH)	…	insoluble	insoluble	soluble in hot acid, hot alkali
Brushite	Calcium Hydrogen Phosphate Hydrate	$CaHPO_4.2H_2O$	…	0.0316^{26}	0.075^{100}	Insoluble in alcohol; soluble acid
Calcite	Calcium Carbonate	$CaCO_3$	$3.36\ 10^{-9}$	0.0014^{25}	0.0018^{75}	soluble in acid, NH_4Cl
Cristobalite	Silicon Dioxide	SiO_2 (at 500 °C)	…	insoluble	insoluble	soluble in HF; very slightly soluble in alkali
Gibbsite	Aluminium Hydroxide	α-$Al(OH)_3$	…	insoluble	insoluble	soluble in acid, alkali; insoluble in alcohol
Glushinskite	Manganese (II) oxalate dihydrate	$MgC_2O_4.2H_2O$	$1.70\ 10^{-7}$	…	…	…
Goethite	Iron Hydroxide	FeOOH	$4.87\ 10^{-17}$	…	…	soluble in HCl
Greigite	Iron Sulphide	Fe_3S_4	6.10^{2} (K_{spa})	…	…	…
Gypsum	Calcium Sulphate Dihydrate	$CaSO_4.2H_2O$	$3.14\ 10^{-5}$	0.241	0.222^{100}	soluble in acid; NH_4 salts, $Na_2S_2O_2$, glycerin
Haematite	Iron Oxide	Fe_2O_3	…	insoluble	insoluble	soluble in HCl, H_2SO_4, slightly soluble HNO_4
Lepidocrocite	Iron Oxide Hydroxide or Iron Oxide Hydrate	FeO(OH) or $Fe_2O_3.xH_2O$	…	insoluble	insoluble	soluble in acid; insoluble alcohol, ether
Magnetite		Fe_3O_4	…	insoluble	insoluble	soluble in concentrated acid; insoluble in alcohol, ether
Quartz	Silicon Oxide	SiO_2	…	insoluble	insoluble	soluble in HF; very slightly soluble in alkali
Rutile	Titanium Oxide	TiO_2	…	insoluble	insoluble	soluble in H_2SO_4; alkali, insoluble in acid
Strontianite	Strontium Carbonate	$SrCO_3$	$5.60\ 10^{-10}$	0.0011^{18}	0.065^{100}	0.12 aqua CO_2; soluble in acid, NH_4 salts
Tschermigite	Ammonium Aluminium Sulphate Hydrate	$NH_4Al(SO_4)_2.12H_2O$	…	15^{20}	very soluble	soluble in dilute acid; insoluble in alcohol
Whewellite	Calcium Oxalate Hydrate	$CaC_2O_4.H_2O$	$2.32\ 10^{-9}$	insoluble	insoluble	soluble in acid, insoluble in acetic acid

APPENDIX 6.4

MODE VALUES FOR THE SEMI-QUALITATIVE MICRO-XRD RESULTS OBTAINED FOR THE PAINT AND BLANK SAMPLES COLLECTED FROM ALL FOUR SHELTERS.

This appendix contains the mode data for the µ-XRD data listed in Appendix DIGITAL 1. These data were used in order to simplify the PCA diagrams.

APPENDIX 6.4

MODE VALUES FOR THE SEMI-QUALITATIVE MICRO-XRD RESULTS OBTAINED FOR THE PAINT AND BLANK SAMPLES COLLECTED FROM ALL FOUR SHELTERS.

Sample Name	Paint Colour	Haematite	Goethite	Whewellite	Gypsum	Gibbsite	Anhydrite	Bassanite	Glushinskite	Quartz	Muscovite	Feldspar	Clinochlore	Minamiite	Schlossmacherite	Weddellite	Apatite	Kaolinite	Crandallite	Greigite	Sanidine
MPaint 2	Black	2		1						2											
MPaint 5	Red	2		3	2					2											
MPaint 6	Orange		3			1															
MPaint 7	Orange		2		4	2															
MPaint 8A	Red	2	3	4	2																
MPaint 9A	White				1		3														
MPaint 9B	White			2	2																
SPaint 10	Red	3		2	1				2												
MPaint 10	White				1			3													
MPaint 11B	Yellow	4	4	2	2																
SPaint 12	White	2	3		4	2															
SPaint 12	White	3		3	2					3							2				
SPaint 21	Red	1																			
MPaint 23	Orange		2		2	2															
SPaint 26	Red	2	2																		
SPaint 26	Red	2	2							4											
MPaint 27	Dark red	3			1			3													
MPaint 28	Yellow	3	4	2	2					3											
MPaint 29	Yellow		3	2	1																
MPaint 30	Red	2			2																
MWhite Twagwa 1														1					4	3	
MWhite Twagwa 2																	1				
MWhite Twagwa 3					3									2					3	3	
MRed Twagwa 1		2	4							4				2							
MRed Twagwa 2		1								3									4		
SRed Twagwa 3		2								4				2							
SRed Twagwa 3		3								4				1							
SRed Fergies 1		2		2	4					3						3					
SRed Fergies 1		2		2	4					4						2					
SRed Fergies 2		3		1						4											
SRed Fergies 2		4		1	3											3					
MRed Fergies 3		3		2	4					4						2					
MSheltered Vale White 1				1						3											
MSheltered Vale White 2				2	2					2											4
SSheltered Vale White 3				4	3					4							2				
SSheltered Vale White 3				4	2					4							2				
MSheltered Vale Red 1		2		2	3					4											
MSheltered Vale Red 3		3		2	2					3							3				
SMQ BLANK A					1																
SMQ BLANK A					1																
MMQ BLANK B					1																
SMQ BLANK C				2	2				2	3											
SMQ BLANK C					3																
MMQ BLANK D					2					4						1					
MTwagwa Blank 1										2					1						
STwagwa Blank 2										4	1										
STwagwa Blank 3											1							2			
STwagwa Blank 3										1											
MFergies Blank 1				1																	
SFergies Blank 3				1	3					2											
SSheltered Vale Blank 1		3								2		2									
SSheltered Vale Blank 1					1					3			2								
MSheltered Vale Blank 2				1	3					3						3					
MSheltered Vale Blank 3				1	2					3								4			

NOTE:
M = Mode value
S = When no mode could be determined, the individual sample was used and is listed here
Only the good and moderate trace data has been reproduced here.

Qualitative standard XRD results of the analyses conducted on the large excavated pigments, and the shelter and local field samples.

Excavated Pigment Samples

Layer 1

Sample description	Haematite	Goethite	Gibbsite	Quartz	Maghemite	Mica	Muscovite	Feldspar	Kaolinite	Magnetite	Oligoclase	Mackelveyite	Thuringite	Illite	Labradorite
Ochre 1	1			3					4						
Ochre 22	1	3		2											
Ochre 103	4			1			4	2							
Ochre 133	3			1			4								
Ochre 243	1			2					4						
Ochre 272	1	4													
Ochre 278	1			2					4						
Ochre 330	2			1											
Ochre 344	4									1					
Ochre 372	3	2		2											
Ochre 400	1			1											
Ochre 410	1			3					4						
Ochre 429	1			2					4						
Ochre 430	1			3					4						
Ochre 440	1			3				4	4	2					
Ochre 516	4			1		4		3							
Ochre 562	1	4													
Ochre 594	3			1											
Ochre 751	3			1											
Ochre 797	3	4		1			3								
Ochre 873	1			2											
Ochre 895	3						4			1					
Ochre 912	1								4						
Ochre 986	1			2					4						
Ochre 1010	3			1											
Ochre 1035	2			1			4								

Layer 2

Sample description	Haematite	Goethite	Gibbsite	Quartz	Maghemite	Mica	Muscovite	Feldspar	Kaolinite	Magnetite	Oligoclase	Mackelveyite	Thuringite	Illite	Labradorite
Ochre 1069	2			1		3									
Ochre 1071	3			1											
Ochre 1259	2									1					
Ochre 1293	3			1											
Ochre 1314	4			1		3		3							3
Ochre 1347	2			1			4								
Ochre 1373	3			1											
Ochre 1393	2	1		3											
Ochre 2106	2			1			3								

Layer 3

Sample description	Haematite	Goethite	Gibbsite	Quartz	Maghemite	Mica	Muscovite	Feldspar	Kaolinite	Magnetite	Oligoclase	Mackelveyite	Thuringite	Illite	Labradorite
Ochre 1424		4		1											3
Ochre 1534	1					4									
Ochre 1581	3			1											
Ochre 1624				2		3		4				2			
Ochre 1638	1			1											
Ochre 1639	2			1											
Ochre 1659	1			2			4								
Ochre 1669				3				1							
Ochre 1672	2			1											
Ochre 1690				1											
Ochre 1695				1											
Ochre 1696				2											
Ochre 1699	2			1											
Ochre 1744				1											
Ochre 1779	2			1											
Ochre 1855	3			1											
Ochre 1871	3			1											
Ochre 1874	2			1											
Ochre 1904	1	4													
Ochre 1920	3			1											
Ochre 1921	2			1											
Ochre 1939	4			2						1					
Ochre 1942	2			1											
Ochre 1943	2			1									2		
Ochre 1944	2			1											
Ochre 2074	1													4	
Ochre 2075	1														

Qualitative standard XRD results of the analyses conducted on the large excavated pigments, and the shelter and local field samples.

Shelter samples

Sample description	Haematite	Goethite	Gibbsite	Quartz	Maghemite	Mica	Muscovite	Feldspar	Kaolinite	Magnetite	Oligoclase	Mackelveyite	Thuringite	Illite	Labradorite
A				1				3							
B				1				4							
C				1				4							
D				1				3							
E				1				3							
F				1											
G		4		1				3							
H				1											

Local field samples

Sample description	Haematite	Goethite	Gibbsite	Quartz	Maghemite	Mica	Muscovite	Feldspar	Kaolinite	Magnetite	Oligoclase	Mackelveyite	Thuringite	Illite	Labradorite
Yellow powder 1															
Yellow powder 2				1											
Assorted sample 1	1			2											
Assorted sample 2	2	1		2											
Site 1				2											
Site 2				2				3							
Site 3 b)				1				3							
Site 3 c)	3	3		1											
Site 4			2	2		4		4	4						
Site 5	2	2		2											
Site 6 a)	3									1					
Site 6 b)	2	1		3						4					
Site 7 a)	4			1											
Site 8 a)	2	2		2											
Site 8 b)	3	2		1											
Site 9	4	4	1	2		4									
Site 10	2	3		1											

APPENDIX A5.8.3

XRF derived minor element results for the large excavated pigments from Maqonqo Shelter (ppm)

SAMPLE	LAYER	As	Ba	Ce	Co	Cr	Cu	Ga	La	Nb	Nd	Ni	Pb	Rb	S	Sc	Sr	Th	U	V	Y	Zn	Zr
1	1	7.3	613.2	nd	nd	12.6	18.2	5	28.3	0.9	4	21	11	13.1	68	4.3	23.6	5.5	2.1	0.2	12.2	123.3	33.2
22		4.7	118.6	nd	nd	5.2	3.1	nd	4.2	1.2	3	nd	10	8.5	146	1.5	40.6	6.9	2	4.1	9.3	192.7	6.4
103		135.8	165	1	28	99	16.5	93	68.1	7.4	nd	11	25	35.3	571	6.5	113.1	6.4	1.8	18.1	36.8	507.6	149.5
133		88.7	354.5	nd	1	12.5	7.3	nd	5.1	5.8	9	62	8	39.6	101	nd	25.6	13.2	3.5	4.7	6.2	272.9	142.8
243		58.6	234.3	nd	nd	5	8.8	nd	89.1	3.2	5	8	13	12.9	79	nd	11.8	8.9	2.6	22.8	11.3	76.9	25.1
272		0.7	866	nd	14	46.6	8.4	133	80.4	0.3	2	37	13	12.1	8.4	32.5	80.8	10.2	0.9	7.3	14.9	1121.3	9
278		85.8	168.3	nd	nd	11.1	10.8	nd	20.5	4.5	nd	37	14	19.9	130	nd	12.1	7.3	0.1	4.4	11.9	114	43.9
330		20	22.6	nd	nd	1.2	1.2	3	33.4	0.3	nd	nd	2	4.8	19	nd	3.4	3.8	2.1	0.3	2.9	17.3	0.7
344		nd	253.8	nd	nd	14.9	20.7	21	5.6	1.4	nd	22	13	12.1	381	0.4	82.1	7.4	9	nd	19.6	918.1	10.5
372		3.6	90.7	25	nd	16.3	4.6	nd	1.3	1.8	1	nd	13	11	630	53	142.1	0.3	2.4	3.8	49.3	506.5	22.5
400		10.6	65	nd	nd	6.1	4.8	nd	52.6	1.1	2	nd	5	4.7	33	nd	5.2	4.3	2.3	1.5	4.4	10.3	5.4
410		49.6	128.4	nd	nd	nd	15.8	nd	30.9	3.4	3	13	17	11.7	33	nd	8.2	10.6	4.8	14.8	7.3	57.4	12
429		0.7	112.2	nd	62	0.2	3.8	nd	7.3	4.7	3	nd	13	5.1	45	33.7	29.1	7.2	2.5	0.3	9.4	59.1	18.8
430		85	149.5	nd	nd	35.5	14.6	nd	198.3	3.2	4	13	17	18.9	87	6.3	14.1	6.9	2.8	1.9	8.5	173.2	22.6
440		37.4	115.3	nd	34	33.7	12.8	16	1.9	3.4	nd	15	14	31.2	432	28.2	99.1	11.7	3.8	1.4	32	566.7	42.7
516		160.1	250.3	6	31	112.1	27.2	56	109	6.3	nd	8	25	33.9	782	3.1	131	0.5	1	72.9	30.9	621.4	169.9
562		nd	440.6	nd	nd	53.2	9.6	1	nd	8.4	5	98	15	16.8	435	14.2	96.9	16	12.1	nd	31.2	2108.8	38.1
594		3.1	30.8	nd	nd	18.7	0.7	nd	4.1	0.2	30	171	3	2.1	43	1.9	3.8	2.6	1.1	3.9	2	38	6.6
751		12.5	13	nd	nd	4.3	0.4	4	39.1	0.5	nd	nd	2	2.4	17	1.7	1	0.5	0.1	3.3	3.1	33.5	0.6
797		477.1	108.7	nd	9	23.2	21.2	nd	76.4	6.4	nd	1	21	236	43	0.6	9.3	6	2.1	1	14.5	273	94.7
873		16.5	99.1	nd	nd	3.8	3.5	nd	11.9	1.4	4	1	11	4.9	117	3.7	5.9	6.1	3.5	0.1	7.3	40	13.3
895		9	103.2	nd	nd	44	9.2	8	10.5	2.7	nd	8	23	17.8	2740	0.1	81.5	0.8	nd	0.6	24.4	564.1	68.2
912		7.1	77.1	nd	nd	7.2	7.4	nd	10	1.3	nd	30	15	6.9	242	1.3	14.5	4.5	4.2	0	12	124.5	7.9
986		117.8	236.8	nd	24	19.4	17.8	48	235.2	2.4	7	6	23	17.7	154	nd	12.5	5.5	1.5	13.7	10.9	85.5	31.9
1010		249.8	253.1	nd	nd	12.3	0.7	nd	4.1	0.3	nd	35	7	5.2	30	nd	6.2	3.1	2.2	3.9	6.5	20.8	4.5
1035		86.8	40.8	nd	nd	2.5	6.5	2	19.5	2.3	nd	10	13	52.6	31	nd	23	6.6	3.4	0	6.4	268.2	20.4
1069	2	266.8	1091.7	nd	nd	41.5	14.1	2	41.8	3	9	95	29	15.8	148	nd	44.9	7.8	3.4	34.8	5	288.6	134.6
1071		7.2	11.5	nd	nd	0.1	1.2	nd	18.4	0.9	nd	8	1	0.8	19	nd	1.8	0.2	0.7	1.2	3.4	37.1	2.7
1259		0.3	98.5	nd	nd	10.3	12.8	35	nd	1.2	nd	4	13	9.8	219	nd	29.5	2.4	1	nd	13	242.8	17.8
1293		44.6	24.5	nd	nd	9.3	0.7	nd	2.4	0.5	nd	4	4	7.8	36	nd	3.9	1.6	1.5	1.7	2.1	28.2	3.1
1314		407.4	266.6	nd	23	126.8	20.7	35	74.3	15.1	3	24	26	70.2	264	nd	111.3	2.7	0.8	10.7	33.8	441.9	225.3
1347		91.3	34.4	nd	nd	nd	4.4	nd	19	0.2	nd	9	7	41.1	3	nd	11.3	2.9	3.2	nd	4.6	204.3	18.6
1373		13.1	21.6	nd	nd	2.6	0.1	2	15.2	0.9	nd	9	nd	0.5	38	nd	7.2	0.4	0.2	3.1	3.2	28.7	5.5
1393		4.6	159.4	nd	14	23.4	108	10	42.8	5.3	1	13	13	19.9	173	3.2	40	2.5	0.1	2.5	34.5	164.9	87.8
2106		118.9	72.6	nd	nd	nd	7.1	nd	9.2	0.4	nd	24	12	45.1	70	nd	23.4	8	2	nd	6	295	24.1
1424	3	187.3	304.1	nd	17	103.5	28.5	70	149.1	7.1	nd	7	26	32.7	215	5.5	191.2	1.7	0.8	56.6	25.4	726.1	175.8
1534		15.9	180.5	nd	nd	27.5	6.7	8	nd	3.1	4	1	16	23.5	347	0.7	45.3	2.3	6.7	0.1	15.3	306.1	24.5
1581		65.7	108.9	nd	nd	nd	4.2	nd	nd	0.4	nd	4	8	7.9	35	5.6	13	5.5	2.9	nd	5.1	32.3	8.2
1624		135.6	209.6	16	31	99.1	21.4	30	61.9	13.2	nd	23	26	45.4	186	7	169	5	0.3	26.2	40.9	853.6	216.9
1638		161	108.3	nd	5	33.2	10.4	nd	59.7	0.4	4	8	14	31.4	5	0.3	19.4	3.5	3.1	0.1	10.2	440	37.8
1639		72.2	85.5	nd	nd	40.6	9.4	3	66.6	2	nd	15	15	51.2	16	nd	15.5	8.5	7.6	nd	7.8	274.3	29.6
1659		8.8	343.5	nd	nd	59.7	25.9	nd	8.3	5.4	nd	2	15	45.5	385	2.1	69	5.6	3.7	3.4	36.9	1135.7	97.6
1669		44.5	76.2	nd	2	5.3	0.2	20	14.1	0.3	45	150	20	469.5	180	0.9	65.6	nd	0.7	2.6	8.3	141.1	4.8
1672		84.8	80.4	nd	4	40	7.8	4	112.8	1.8	nd	33	12	18.8	nd	1.1	19.4	1.9	1.7	nd	4.3	287.8	22.6
1690		479.5	313.3	nd	17	154.4	33.4	59	136.8	14.9	6	33	29	63.2	141	nd	111.3	7	0.1	31.2	37.2	1152.6	234.8
1695		221.3	344.3	12	24	128.5	33	47	111.3	6.2	2	9	20	44.4	113	1.8	129.3	2.1	nd	73.9	22.6	2013.5	149
1696		127.3	208.1	14	22	108.5	21.2	62	92.9	6.3	nd	2	25	16	132	1.6	278.6	4.2	2.6	64.3	30.2	885.6	149.2
1699		137.8	146.3	nd	7	31.3	11.8	15	118.5	1.8	3	1	10	24.5	43	nd	14.1	4.7	1.3	7.6	13.3	115.3	58.2
1744		431.9	260.6	7	29	136.6	23.5	40	94.1	10.7	nd	9	25	45.8	322	12.9	140	4.6	0.5	26.2	34.7	694.9	188.6
1779		28.8	526.2	nd	8	74.7	5.9	4	48.2	15.1	33	155	15	126.4	184	2.8	104.4	20.9	8.9	1	61.1	784.7	345
1855		19.1	12.9	nd	nd	1.5	0.4	4	10.3	1.3	nd	nd	1	1.5	3	nd	1.1	1.5	1.3	3.7	2.6	1.9	1.2
1871		19	22.3	nd	nd	5.1	0.6	10	54.8	1.2	nd	nd	3	4.8	36	51.7	5.2	1.7	1	8.3	3.5	17.2	3.2
1874		231.5	118.9	nd	nd	82.4	19.9	18	600.8	4.6	3	6	24	29.2	719	nd	24.3	2.5	2.5	1.7	10.9	309.1	44.6
1904		4.7	6236.6	nd	nd	24.3	2.8	85	12.8	1.6	13	43	9	5.3	286	23.6	84.2	3.2	1	1.6	29.7	710.5	15.2
1920		31.5	19.9	nd	nd	3.4	2.3	nd	26.1	0.9	nd	nd	2	3.5	15	nd	15.2	0.1	0.6	1.6	2.9	42	13.2
1921		252.4	93	nd	nd	54.2	16.9	10	281.1	0.4	3	4	14	25.1	182	nd	23.3	7.1	1.6	12.8	11.3	172.3	36.4
1939		52	144.4	nd	11	29.6	16.2	2	1.8	4.5	1	8	12	39	430	2.1	86.8	11.7	1.8	1.1	33	812	44.5
1942		109.3	69.8	nd	nd	26.9	8.6	17	68	2.7	nd	7	11	56.5	90	nd	13.1	7.8	nd	11.8	8.1	287.3	22.4
1943		315	105.9	nd	nd	87.9	13	13	106	3.1	1	nd	19	3.5	138	nd	31	5.8	1.6	8.1	9	550.6	52.9
1944		63.9	97.1	nd	6	24.6	6.8	3	43.9	2.7	4	10	9	23.4	177	nd	12.9	11.9	2.1	5.2	6.7	141.4	20.7
2074		70.6	200.2	nd	3	24.3	7.1	7	0.4	1.5	11	16	12	29.7	587	20.1	35.2	2.7	2.1	0.1	27.9	375.8	16.4
2075		0.6	303.9	nd	nd	13.6	11.1	nd	1.8	1.9	5	17	15	12.8	171	1.9	33.8	8	4.7	1.6	15.2	334.5	16.3

APPENDIX 5.16

Average semi-quantitative micro-XRF results (ppm) obtained for the blank, paint and excavated pigment samples from all four shelters.

MAQONQO SHELTER PAINT SAMPLES

Paint sample	Paint colour		Al	As	Br	Ca	Cd	Ce	Cr	Cs	Cu	Fe	Ga	Ge	K	Kr	Mn	Ni	Pb	Rb	Se	Sr	Th	Ti	V	Y	Zn
Paint 2	Black	Pnt2Blc	0.15		0.17	2.57			0.41	0.13	0.22	88.18	0.86	0.35	0.96	0.64	1.52		0.81	0.59	0.15	3.56		0.13	0.41	0.21	0.72
Paint 5	Red	Pnt5Red	0.22		0.74	4.38	0.14		0.27	1.19	0.95	71.26	0.22	0.31		0.97	0.58		1.63	0.47	0.58	13.27		0.13	0.75	0.34	3.68
Paint 6	Orange	Pnt6Org	0.57		0.65	1.22			0.26	0.44	3.50	76.65	0.82		0.84	1.36	0.75		2.25	0.49	0.48	6.22		1.13	0.26	0.85	3.35
Paint 7	Orange	Pnt7Org	0.66	1.22	0.72	0.72	0.15			0.27	9.24	74.28	1.29		0.27	1.15	0.53		0.55	0.43	0.80	4.90		0.83	0.25	0.90	1.97
Paint 8A	Red	Pnt8ARed	0.26		0.30	2.12			0.60	0.27	0.46	84.50	0.67			0.66	0.96		0.73	0.48	0.71	7.32		0.91	0.33	0.97	1.60
Paint 9A	White	Pnt9AWht	0.41		0.98	16.99	0.12	0.34	0.15	3.14	1.52	37.96	0.37		0.46	0.89	0.85		1.65	0.67	0.76	28.68		0.47		0.30	4.57
	Red	Pnt9ARed	0.20		0.82	9.22	0.35	0.78	0.78	2.39	1.98	37.46	0.27			0.60	0.75		1.20	0.20	0.43	21.49		0.12		0.16	2.55
Paint 9B	White	Pnt9BWht	0.73		1.00	21.24		0.69		2.95	1.47	29.49	0.52	0.47		1.82	0.62		2.16	0.87	0.51	26.28		1.24	0.74	0.18	8.52
	Red	Pnt9BRed	1.25		3.34	7.83		0.17		0.58	4.83	58.12				2.25	1.82		3.16	0.58		1.74		0.17		0.83	5.83
Paint 10	Red	Pnt10Red	1.82		2.55	16.82	0.34		0.28	2.89	3.83	28.82	0.95			3.56	0.76	0.51	2.75	0.86	2.43	27.78	0.19	0.27	0.33	0.11	3.18
	White	Pnt10Wht	1.53		2.39	22.41	0.19	0.83	0.19	2.61	3.92	26.31	1.33		0.53	3.76	1.38		3.56	0.71	1.72	23.13	0.29	0.76	0.23	0.74	5.98
Paint 11A	Yellow	Pnt11AYl	0.73		2.23	1.37	0.46	0.18	0.24	0.47	2.55	75.52	1.31		0.95	1.45	0.50		2.77	0.82	1.12	5.77		0.29		0.88	2.75
Paint 11B	Yellow	Pnt11BYl	0.29		0.26	11.38		0.27		2.46	1.53	49.77	0.45		0.76	0.65	1.57		1.43	0.73	0.54	24.11		0.56	0.26	0.19	3.85
Paint 12	White	Pnt12Wht	2.69	7.61		16.74				2.81	5.97	28.86	1.45		0.12	3.16	0.73			0.73		21.55		0.35		0.12	5.15
	Red	Pnt12Red	0.88		0.24	4.28	0.88	0.66	0.20	1.22	0.79	73.41	0.31	0.38	0.38	0.39	0.61		0.63	0.54	0.27	14.67		0.39	0.75	0.13	1.54
Paint 20	Orange	Pnt20Org	1.39		2.93	2.68			0.22	0.56	4.46	62.38	1.52	0.11	0.70	1.77	1.33		3.89	3.54	0.19	5.75		2.66	0.43	0.28	3.38
Paint 21	Red	Pnt21Red	0.64		0.18	0.56				0.59	0.88	8.63	0.75			1.13	0.59		2.48	0.35		9.14	0.12	0.18	0.95	0.85	2.19
Paint 22	Red	Pnt22Red	0.53		0.92	2.47			1.75	0.63	1.89	71.29	0.62			1.28	0.53	7.64	1.57	0.32	0.70	6.53		1.22	0.32	0.95	0.83
Paint 23	Orange	Pnt23Org	0.14	0.15	0.22	1.74			0.14	0.31	1.86	84.55	0.33			0.58	0.16		0.30	0.38	0.30	7.46		1.13	0.69	0.75	0.89
Paint 24	Orange	Pnt24Org			0.38	3.67					0.12	81.83	0.62			0.25	0.45		0.15	0.12	0.92	12.32				0.62	0.50
Paint 26	Red	Pnt26Red	0.48		0.14	0.30				0.68	1.69	83.36				0.90	0.83		1.66	0.32	0.71	8.13		0.12	0.89	0.17	2.16
Paint 27	Dark red	Pnt27Drd	0.15	0.34	0.34	6.16	0.42			1.23	0.62	71.29	0.28	0.22		0.44	1.40		0.63	0.26	0.33	15.93		0.13	0.17	0.74	1.50
Paint 28	Yellow	Pnt28Yl	0.22	0.33	0.67	4.86		0.15	0.69	1.73	1.26	67.94	0.43			0.54	0.73		0.92	0.99	0.29	15.23		0.53	0.19	0.18	3.62
Paint 29	Yellow	Pnt29Yl	0.19		0.34	5.89	0.15	0.50	0.82	0.86	1.35	7.89	0.48	0.14	0.91	0.48	0.55		1.18	0.85	0.34	13.46		0.54	0.95	0.15	1.87
Paint 30	Red	Pnt30Red	0.97		0.18	1.33			0.24	0.27	0.12	87.61				0.42	0.56		0.25	0.59	0.78	8.50		0.67	0.25	0.85	0.40

BLANK SAMPLES FROM ALL FOUR SITES

Sample name			Al	As	Br	Ca	Cd	Ce	Cr	Cs	Cu	Fe	Ga	Ge	K	Kr	Mn	Ni	Pb	Rb	Se	Sr	Th	Ti	V	Y	Zn
Maqonqo Shelter Blank A		MQBla	1.99	1.97		27.24				1.99	3.73	24.15	2.65		0.36	3.28	0.45		3.56	2.19		2.98		0.86	0.54	0.17	4.62
Maqonqo Shelter Blank B		MQBlb	1.29	1.43	0.64	2.68			0.43	2.14	2.87	25.60	1.93	1.48	0.28	2.57	0.64		4.64	1.43	1.14	24.37	0.23	1.29	0.42	0.27	4.47
Maqonqo Shelter Blank C		MQBlc	1.28		2.63	12.98		0.13	0.19	2.15	3.73	23.48	1.74		4.24	3.34	0.48		5.66	9.88	0.17	3.00		1.56	0.53	0.50	4.53
Maqonqo Shelter Blank D		MQBld	0.82		3.55	13.43	0.57	0.39		4.15	3.43	2.76	0.62	0.29	1.34	2.98	2.80		3.39	2.47	1.30	27.43	1.88	0.62		1.62	6.22
Fergies Cave Blank A		FCBla	2.39			67.38			0.32		3.79	6.58	4.65			2.76	0.72		5.16	0.61		1.75		0.67	0.14		3.61
Fergies Cave Blank B		FCBlb	11.61		2.93	8.80					5.86	8.80				14.52			17.97	3.88	8.65	2.93		2.26			1.32
Fergies Cave Blank C		FCBlc	3.54		3.19	2.82				0.13	5.87	27.98	4.76		0.96	5.39	0.24		5.95	2.62		6.98		2.85	0.58		8.37
Twagwa Shelter Blank A		TWBla	0.31		0.64		0.75	0.11		3.29	0.87	23.14	1.32	0.17	2.13	0.95	0.72	0.46	2.28	5.14	1.94	28.20		5.50	1.63	1.00	18.85
Twagwa Shelter Blank B		TWBlb	0.87		1.00		1.32	0.52	0.99	8.62	1.98	22.67	0.68	1.27	2.57	2.14	0.62		7.26	2.96	0.18	31.55		1.35		0.74	11.55
Twagwa Shelter Blank C		TWBlc	1.15		3.23	1.27	0.81			0.65	4.42	46.80	2.36		1.57	1.99	1.28		5.16	12.57		5.91	0.13	3.17	0.87	0.90	4.64
Sheltered Vale Blank A		SVBla	2.88			3.71			0.30	0.45	5.83	59.24	1.24		1.94	2.76	1.19		6.14	3.38	0.82	3.54		2.65	0.46		5.12
Sheltered Vale Blank B		SVBlb	0.45		0.65	17.42	0.66			1.12	2.53	29.91	0.76	0.73	0.36	1.54	8.14		4.82	1.27	0.23	2.61		1.38	0.47	0.87	6.76
Sheltered Vale Blank C		SVBlc	0.77		0.88	21.74	0.58	0.35	0.29	3.51	1.45	22.32				1.21	0.83		18.29	1.26	1.26	23.24		0.39		0.24	2.66

PAINT SAMPLES FROM THE THREE ADDITIONAL SITES

Sample name	Paint colour		Al	As	Br	Ca	Cd	Ce	Cr	Cs	Cu	Fe	Ga	Ge	K	Kr	Mn	Ni	Pb	Rb	Se	Sr	Th	Ti	V	Y	Zn
Fergies Cave Red 1	Red	FCRed1	1.49			41.87			0.12	0.45	3.16	35.23	0.63			2.75			6.58	0.64	0.59	4.52		0.47	0.52	0.66	1.58
Fergies Cave Red 2	Red	FCRed2	1.54			24.89			0.46		3.68	5.75	0.60	0.82	0.22	2.35	0.32		5.53	0.72	0.46	4.40		1.17	0.47	0.21	1.69
Fergies Cave Red 3	Red	FCRed3	1.20		0.34	9.26	0.49		0.98	0.34	2.49	66.24	0.43	0.69		2.53	0.20		4.92	0.65	0.94	6.33		0.19	0.13	0.68	2.80
Twagwa Shelter Red 1	Red	TWRed1	0.24		0.33	0.24		0.55	0.18	0.93	0.45	66.68	0.94		0.83	0.58	0.42		1.76	0.66	0.63	11.16		0.25	0.49	0.28	14.20
Twagwa Shelter Red 2	Red	TWRed2	0.93		2.32	0.55		0.12	0.46	0.35	1.28	63.62	0.66		1.23	1.16	1.12		2.11	4.49	0.29	7.14		4.83	0.68	0.29	6.19
Twagwa Shelter Red 3	Red	TWRed3	0.47		0.38	0.67		0.32		4.36	0.64	31.94	0.22		1.97	1.00	0.86		2.62	0.76	0.54	24.25	0.15	0.73		0.56	27.47
Twagwa Shelter White 1	White	TWWht1	0.25		0.13	0.35	0.68	0.22		3.66	0.38	12.43			2.52	0.33	1.59	1.84	1.85	0.90	0.58	2.59	0.95	0.34		1.69	47.53
Twagwa Shelter White 2	White	TWWht2	6.56			17.19				1.13	6.19	1.47				6.79	0.23		14.93	1.90		5.43				0.45	28.54
Twagwa Shelter White 3	White	TWWht3	0.66			1.95	0.43	0.36		4.37	0.67	6.72			2.43	0.88	1.87	0.37	2.28	0.96	0.76	2.80	0.27	0.22		1.59	5.87
Sheltered Vale Red 1	Red	SVRed1	0.17			4.76	0.24	0.16	0.35	2.67	0.57	62.88	0.43		0.28	0.56	0.63		1.19	0.63	0.22	23.44		0.22		0.13	1.55
Sheltered Vale Red 2	Red	SVRed2	0.74		0.15	5.53			0.12		1.81	7.61	0.59		0.45	1.92	0.78		4.53	3.98		3.66		2.00	0.93	0.17	3.79
Sheltered Vale Red 3	Red	SVRed3	0.39			14.56	0.21	0.32	0.55	1.58	1.59	48.32	0.18	0.88	0.15	1.32	1.34		3.40	1.46	0.96	2.52	0.11	0.33		0.51	2.93
Sheltered Vale White 1	White	SVWht1	0.79			19.19	0.45	0.13		2.85	2.78	24.28	1.75		0.37	1.70	0.53		5.69	2.31	3.17	27.18	0.17	1.91	0.52	0.27	4.32
Sheltered Vale White 2	White	SVWht2	0.43			21.77	0.25	0.19		3.30	2.15	23.61	1.54		1.39	0.91	0.89		2.96	5.68	0.75	29.21	0.12	0.88	0.43	0.89	2.85
Sheltered Vale White 3	White	SVWht3	3.13			23.18		0.52	0.29	0.85	8.78	23.39	0.47		1.67	3.93	1.55		9.40	3.55		1.25		1.77	0.43	0.18	7.43

WHITE DEPOSIT SAMPLES

Sample name			Al	As	Br	Ca	Cd	Ce	Cr	Cs	Cu	Fe	Ga	Ge	K	Kr	Mn	Ni	Pb	Rb	Se	Sr	Th	Ti	V	Y	Zn
Paint 2		Pnt2WD	0.23		0.35	8.29				1.43	2.28	51.33	1.18	0.70	1.68	1.91	1.18		3.13	7.18	0.35	14.83		0.46	0.29	0.46	3.53
Paint 5		Pnt5WD			0.63	23.62	1.79			5.95	1.66	45.71	0.39	0.32	1.84	0.83	7.37		2.95	2.93	0.44					0.44	4.25
Paint 11A		Pnt11AWD	1.18		0.46	2.19	0.67	1.90	0.16	3.87	1.78	32.52	0.58		0.25	2.66	1.17		5.45	0.66	0.72	3.89	0.69	0.65		0.91	8.78
Paint 11B		Pnt11BWD	0.29	0.13	0.32	15.43	0.54	0.19	0.22	3.19	1.57	4.72	0.26	0.68		0.55	0.82		1.57	0.53	0.53	28.52		0.66	0.24	0.16	3.84
Paint 21		Pnt21WD	1.70		0.66	6.41				0.99	4.30	49.75	1.64			1.56	0.58		4.11	1.15		14.72	0.74	2.71	0.66	0.41	8.59
Paint 28		Pnt28WD	1.24	3.55	1.29	9.68		0.33	0.29	1.37	5.45	39.97	3.20			2.15	0.66		0.56	1.29	8.85	16.89		0.54		0.83	3.43
Fergies Cave Red 1		FCRed1WD	2.38			64.70			0.22	0.72	4.69	4.55				4.35			8.67	0.74	0.44	5.41		0.62	0.86	0.40	2.31
Fergies Cave Red 2		FCRed2WD	2.72			32.74			0.54		4.21	33.56				2.85	0.27		1.33	0.68		6.93		1.22	0.54	0.48	2.99
Twagwa Shelter Red 3		TWRed3WD	0.55		0.42	0.79		0.42		6.48	0.55	11.15	0.36		5.94	0.97	0.97		4.00	0.67	0.55	4.00	0.12	0.42	0.12	0.55	34.79
Sheltered Vale Red 2		SVRed2WD	0.14			7.55	0.35		0.35	1.59	0.76	63.44	0.32			0.32	0.53		2.58	1.87	0.42	16.13	0.35	0.81	0.25	0.78	2.15
Sheltered Vale Red 3		SVRed3WD	1.98			31.17		0.66	0.22	1.27	3.73	17.14			0.20	3.74	0.77		7.57	1.43	1.98	24.40		0.33		0.22	4.94

MAQONQO SHELTER EXCAVATED PIGMENT SAMPLES

Sample name			Al	As	Br	Ca	Cd	Ce	Cr	Cs	Cu	Fe	Ga	Ge	K	Kr	Mn	Ni	Pb	Rb	Se	Sr	Th	Ti	V	Y	Zn
Ochre 30		30lyr1	0.49			0.64			0.23			97.85			0.23	0.36	0.32		0.29	0.47		0.63		0.35	0.23	0.94	0.29
Ochre 164		164lyr1	0.96			0.11				0.44		94.57	0.43		0.53	0.43	1.42	0.45	0.86	0.67		1.86		0.89	0.97	0.38	0.90
Ochre 315		315lyr1	0.83			0.74			0.14			96.25				0.46	0.52			0.79		1.24			0.35	0.41	
Ochre 498		498lyr1	0.15		0.35	0.20			0.37	0.70	0.46	88.86	1.12		0.61	0.33	0.25		0.52	1.73		1.56		2.41	0.46	0.33	1.24
Ochre 627		627lyr1	0.69		0.36	0.58			0.28	0.22	2.54	86.16	0.28		0.13	0.44	0.24		0.66	0.39	0.35	5.44		0.99	0.30	0.25	0.46
Ochre 772		772lyr1	0.64			0.16			0.23	0.32		96.24	0.24		0.66	0.42	0.32	0.12	0.32	0.63	0.12	1.66		0.68	0.36	0.20	0.43
Ochre 1023		1023lyr1	0.57			0.13		0.97		0.92		92.17			0.24	0.40	3.13		0.80	0.76		2.68		0.13	0.15	0.18	0.61
Ochre 1127		1127lyr2	0.38		0.26	0.26		0.12	0.59	0.73	0.23	91.37	0.26		0.25	0.38	1.34	1.00	0.25	1.44	0.19	2.49		0.31	0.15	0.36	0.47
Ochre 1208		1208lyr2	0.44		0.11	0.28			0.29	0.12	0.16	86.82	0.38		0.23	0.44	0.87	0.59	0.73	1.46	0.46	3.72		2.48	0.53	0.61	0.84
Ochre 1255		1255lyr2	0.54			0.25			0.14	0.58	0.27	94.27			0.67	0.39	1.92			0.79		2.17		0.72	0.28	0.16	0.59
Ochre 1256		1256lyr2	0.34			0.88			0.27			95.93			0.23	0.54	0.49		0.68	0.83		1.56		0.46	0.13	0.66	0.82
Ochre 1258		1258lyr2	0.54			0.93			0.25	0.45		96.49			0.22	0.49	0.40		0.89	0.67		1.65		0.11	0.37	0.19	0.67
Ochre 1269		1269lyr2	0.34			0.85			0.22		0.90	96.84				0.40	0.46		0.17	0.67		0.86		0.63	0.66	0.42	0.39
Ochre 1347		1347lyr2							0.40			97.62				0.83				0.75		0.40	0.59	0.79		0.40	
Ochre 1384		1384lyr2	0.44		0.83	0.18			0.12	0.48	0.16	94.31	0.19		0.44	0.48	0.26		0.55	0.79	0.96	1.51		0.65	0.24	0.17	0.18
Ochre 1393		1393lyr2	0.63			0.81			0.13		0.77	96.91				0.83	0.44			0.76		0.54		0.42		0.37	0.77
Ochre 1396		1396lyr2	0.35	0.44		0.12						97.49				0.37	0.48		0.59	0.58		0.58		0.43	0.94	0.22	0.34
Ochre 2106		2106lyr2	0.72			0.48						97.18				0.60	0.24		0.48	1.29		0.60		0.48	0.48	0.96	
Ochre 1774		1774lyr3	0.33			0.12			0.29			97.17				0.34	0.42		0.27	0.59		0.98		0.64	0.37	0.18	0.27
Ochre 1979		1979lyr3	0.39		0.24	0.97			0.14	1.17	0.57	79.79	0.52	0.21	0.36	0.54	0.68		1.32	1.72		7.88		1.50	0.18	0.23	1.63
Ochre 2019		2019lyr3	0.45			0.18			0.30			96.88			0.12	0.37	0.30		0.24	0.49		1.32		0.62	0.50	0.21	0.29
Ochre 5/28		28lyr5	0.40		0.18	0.99			0.33	0.43		95.76			0.36	0.38	0.26		0.39	0.98	0.79	1.60		0.12	0.77	0.31	
Ochre 6/5		5lyr6	0.13			0.33			0.23	0.83	1.21	89.27	0.48		0.87	0.76	0.27		0.67	1.15		2.99		1.52	0.36	0.16	0.33
Ochre 6/6		6lyr6	0.67			0.27			0.38	0.50		95.58			0.46	0.49	0.45		0.13	0.74		1.68		0.52	0.73	0.52	0.16
Ochre 6/7		7lyr6	0.75			0.21			0.32	0.64		95.58			0.64	0.57	0.48			1.11		1.33		0.75	0.64	0.36	
Ochre 7/3		3lyr7	0.29			0.19			0.13	0.42	0.23	96.16			0.25	0.48	0.34		0.69	0.77		1.65		0.64	0.25	0.12	0.74
Ochre 7/8		8lyr7			2.50	28.40			0.14	1.37	1.56	15.74	2.21		1.13	1.37	0.81		4.43	6.49		26.25		1.37	0.85	1.13	5.42
Ochre 7/11		11lyr7	0.43		0.30	2.90	0.20			0.87	0.15	81.15				0.30	0.36		1.25	0.27		11.48		0.67	0.73	0.20	0.38
Ochre 7/12		12lyr7				0.17			0.42		0.42	94.14	0.29		0.11	0.37	1.45		0.42	1.14		1.66		0.56	0.13		0.72
Ochre 7/15		15lyr7	0.14			0.25			0.42	0.86	0.75	88.17	0.42		0.12	0.66	0.36	1.27	2.63	1.68		1.62		1.39	0.25	0.25	0.44
Ochre 7/18		18lyr7	0.16			0.16	0.27		0.26	0.58	0.13	84.86	0.27		0.89	3.00	1.74		5.69	0.59	0.58	0.74	0.26	0.36	0.22		0.56
Ochre 7/20		20lyr7	0.13		0.32	0.42			0.17		0.94	85.89	0.48	0.20	0.43	0.44	0.74		0.58	1.31		3.15		3.33	0.67	0.36	0.81
Ochre 7/23		23lyr7	0.27		13.64	0.99		0.43	0.28	0.93	1.32	65.13	0.75	3.52	0.17	0.43	0.52		3.93	1.69		2.54		3.57	0.59	0.28	1.27
Ochre 7/26		26lyr7	0.19		0.23	1.29	0.57		0.22	0.29		9.59				0.47	0.53		0.86	0.48		6.24		0.54	0.70	0.17	0.14
Ochre 7/30		30lyr7	0.52			0.12			0.50	0.54		95.81			0.18	0.33	0.16		0.54	2.27		0.90		0.18	0.37	0.40	0.62
Ochre 9/1		1lyr9	0.11		0.37	0.31			0.25		0.37	88.17	0.46		0.65	0.49	0.50	0.18	0.61	1.33		2.30		2.18	0.49	0.32	1.53
Ochre 9/8		8lyr9				0.26			0.64	0.32	0.27	94.79			0.13	0.51	0.46		0.16	0.92		1.66		0.64	0.13	0.37	0.26
Ochre 9/9		9lyr9	0.47		2.83	0.63			0.46	0.35	1.59	76.13	1.44	0.19		0.75	0.46		0.96	3.28		3.68		3.85	0.84	0.41	1.72
Ochre 11/6		6lyr11				0.19			0.25	0.25		96.27				0.42	0.29		0.41	0.60		1.72		0.72	0.34	0.27	0.16
Ochre 11/8		8lyr11	0.20			0.68			0.96	0.12	2.77	77.29				4.91	0.23		3.12	2.84		1.54		0.14	0.15	0.33	5.62
Ochre 11/9		9lyr11	0.52			0.82			0.24	0.43		96.62				0.40	0.47		0.28	0.55		1.57			0.81	0.13	
Ochre 11/10		10lyr11			0.75	0.51			0.40	0.13	0.68	82.82	0.66		0.42	0.50	0.47	0.27	0.78	1.42		5.82		3.44	0.74	0.55	1.26
Ochre 11/11		11lyr11										95.39				0.89	1.77			0.78		0.89		0.37	0.74	0.18	
Ochre 11/15		15lyr11			0.65	0.29			0.19	0.27	0.39	86.40	0.29	0.36		0.74	0.50		0.74	1.71		4.44		1.47	0.39	0.80	0.53
Ochre 11/16		16lyr11	0.85		0.77	0.83			0.47	0.55	0.71	92.72	0.39		0.27	0.46	0.30		0.25	0.62	2.53	1.45		0.29	0.52	0.22	0.11
Ochre 11/27		27lyr11	0.83		2.63	0.33		0.53	0.88	0.58	0.18	88.00	0.35	0.26	0.41	0.43	0.13		0.83	3.51		1.46		0.56	0.73	0.34	0.30
Ochre 11/28		28lyr11	0.49		0.18	1.53			0.52	0.23	1.82	63.93	2.30	0.11	0.52	0.90	0.69	0.45	8.36	9.13		3.93		4.17	0.94	0.45	1.56
Ochre 11/35		35lyr11				1.34		0.64	0.64	0.20		65.83				0.57	0.42		23.68	0.64		5.91		0.17		0.30	0.83