Magnetic susceptibility as an indicator of layering in soils at Bonamanzi Game Ranch, KwaZulu-Natal, South Africa

by

TANYA LYNN BARKER

Submitted in partial fulfilment of the academic requirements for the

degree of

Master of Environment and Development

in the

Centre for Environment and Development,

School of Applied Environmental Sciences,

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Abstract

All matter has a specific magnetic signal, due to their magnetic properties. These range from a high susceptibility to become magnetised (ferrimagnetic) to a low ability to be magnetised (diamagnetic). Magnetic susceptibility measures the degree to which a substance can be magnetised, and this can be used to identify minerals within material and used as an indicator for processes i.e., erosion. Therefore magnetic susceptibility has been widely used to investigate soil related research as the values obtained correspond with the types of magnetic minerals in the soil, mainly the iron oxides such as magnetite and maghaemite (higher MS), and haematite and goethite (lower MS). Thus MS acts as a signature for different types of soils allowing them to be categorised. The amount of magnetic minerals present in the soil is largely dependent on soil processes active in the profile and external factors, such as parent material.

Soil processes influence the type or amount of magnetic mineral in the soil, or the strength of the magnetic signal. Lower MS values are associated with horizons that have undergone gleying, eluviation, leaching and reductive weathering. Higher MS values are found in horizons that have undergone illuviation, and hydrolytic and oxidative weathering. Diamagnetic materials, such as calcium carbonate, decrease the magnetic susceptibility by diluting the magnetic signal.

The relationship between MS and iron in soil is influenced by both external factors such as parent material; climate; topography; land use history of the area and time. Similarly these factors significantly contribute to soil genesis and are highly interactive. Parent materials that are igneous are found to form soil with higher magnetic susceptibility, and sedimentary and metamorphic rocks form less magnetic soils. However, it has also been found that materials such as slate are related to soil with high susceptibility, which is argued to result from more rapid weathering and the release of iron in the ionic form. Climate has a direct affect on the soil processes that drive magnetic susceptibility, thus in warm tropical climates magnetic susceptibility is expected to have higher values. Topography has been shown to alter magnetic susceptibility values, and generally the top and foot of the slope have higher values than the slopes. Land-use history influences magnetic susceptibility as cultivation is

likely to disturb the soil causing magnetic susceptibility values to be lower due to mixing of the upper and lower soil layers. Time relates to the age of the soil and older soil either has large magnetic susceptibility values due to more prolonged pedogenesis, or the magnetic particles have weathered out of the profile and magnetic susceptibility is lowered.

Past research has found topsoil to have higher frequency dependent magnetic susceptibility than lower soil horizons. Frequency dependent magnetic susceptibility measures fine-grained ferrimagnetic particles with grain sizes between 0.013 and 0.027μm. Two measurements at low and high frequency (0.46 and 46 kHz respectively) are used to calculate frequency dependent magnetic susceptibility. These are measured using a Bartington MS2B sensor and certain measures need to be taken in order to obtain an accurate measurements of magnetic susceptibility. Frequency dependent magnetic susceptibility values are influenced by factors including burning, organic matter and pedogenesis. However, the nature of contribution of these is still highly debated.

Many South African soils are considered to be old soils and the amount of magnetic minerals in these is unknown. It has been found that magnetic minerals such as maghaemite have been depleted due to erosion cycles. Very little research has been undertaken regarding the applicability of magnetic susceptibility for South African soils as most of the research on magnetic susceptibility in soils has been carried out in countries of the northern hemisphere, where soil materials are much younger than in South Africa.

The ability of frequency dependent magnetic susceptibility to differentiate between topsoil and subsoil allows it to be used as a method of assessing topsoil erosion. Topsoil erosion has a detrimental effect on the environment and it is vital a rapid field indicator is developed to assess erosion in order to curb the process.

Preface

The research described in this mini-dissertation was carried out at the Centre for Environment and Development, University of Natal, Pietermaritzburg, under the supervision of Dr. Nevil.Quinn and Professor Jeffery.Hughes.

The mini-dissertation represents the original work of the author and has not otherwise been submitted in any form for any other degree or diploma at any university. Where use has been made of the work of others it is duly acknowledged in the text.

Tanya L. Barker

Prof. Jeffery.Hughes

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Plate 1   Grid IV in the Bonamanzi trench displaying (a) the clear visible layering and (b) close-up of the iron concretions and calcium carbonate evident in the trench (area marked in (a)).

Chapter 1: Introduction, aims and objectives

1.1 Introduction

Soil is essential for plant, animal and human survival. However, this important contribution to life on earth is non-renewable and the increased pressure due to rises in human population growth is likely to threaten its sustainability (Doran *et al.* 1999). Topsoil erosion causes the soil system to lose its input of organic matter and nutrients, therefore topsoil loss can eventually lead to desertification (United Nations 1998). This has important implications for agriculture and thus food security; and for all connected ecosystems. Topsoil forms at a rate of approximately 10mm of soil per100 to 400 years (Doran *et al.* 1999), while natural or geological erosion of the soil occurs at approximately the same rate. Erosion due to anthropogenic factors, known as 'man-accelerated' erosion, is at a rate higher than that of soil formation (Bennett 1939 cited in Liggitt 1988). It is therefore essential that we recognise topsoil as a resource in South Africa and develop methods to conserve it.

Over the last 60 years topsoil has been found to exhibit high values of magnetic susceptibility compared to the subsoil (Le Borgne 1955 cited in Dearing *et al.*1986; Mullins 1977; Maher 1986; Thompson & Olfield 1986; Maher & Taylor 1988; Williams & Cooper 1990; Dearing *et al.* 1996b; Dearing *et al.* 1997; Smith 1999). Two measurements of magnetic susceptibility at high and low frequencies, i.e., the frequency dependent magnetic susceptibility, particularly show this relationship because of its ability to detect ultra-fine ferrimagnetic particles (Maher 1986; Eyre 1997; Dearing 1999) that occur in the topsoil due to pedogenesis (Thompson *et al.*1980; Maher 1986; Dearing *et al.* 1996a; Dearing *et al.*1996). From this, one can presume that frequency dependent magnetic susceptibility can be used to determine the magnetic susceptibility characteristics or magnetic signature of the topsoil compared to the subsoil. Following from this an indicator for topsoil loss can be created. However, the past research on magnetic susceptibility and topsoil has only been carried out in northern hemisphere countries, which has distinctly younger soils than those in Africa. Africa has escaped recent glaciation, which the northern hemisphere was affected by, resulting in the surface soils being exposed to weathering for approximately 100 million years (Fitzpatrick 1988). African soils' magnetic signature therefore, may not be as evident in the topsoil as those in the northern hemisphere (Plater

pers. comm. 2002) However, African soils are subjected to burning, which has been associated with a strengthening of magnetic susceptibility (Le Borgne 1955 cited in Dearing *et al.* 1986; Maher 1986; Thompson & Oldfield 1986; Dearing *et al.* 1996a; Dearing *et al.* 1996b; Oldfield 1999; Smith 1999), thus African topsoil could exhibit a magnetic signature that can be used as an indicator for topsoil loss.

1.2 Problem statement

Research in the northern hemisphere suggests that magnetic susceptibility measurements are a powerful tool for determining the characteristics of the soil, including differentiating between topsoil and subsoil. Topsoil conservation is an important issue facing South Africa and the measurement of frequency dependent magnetic susceptibility would be useful in determining the state of topsoil. Previous research has been undertaken in northern hemisphere countries which have distinctly different climates, paleogeomorphology, geology and soil. A key research need is therefore to explore the relationships between frequency dependent magnetic susceptibility and soil in South Africa. Past research has shown a marked increase in frequency dependent magnetic susceptibility for topsoil. This evident pattern is often exacerbated by past burning of the soil. Thus with South Africa's high exposure of soil to burning, it is expected that the magnetic susceptibility of the topsoil will be higher than the subsoil. This parameter can thus act as a magnetic signature for topsoil.

1.3 Aim

To explore the relationship between frequency dependent magnetic susceptibility and topsoil in KwaZulu-Natal.

1.4 Objectives

1. Determine whether frequency dependent magnetic susceptibility in topsoil is higher than the subsoil.

2. Evaluate magnetic susceptibility as an indicator of topsoil loss in soils in KwaZulu Natal, and the influences of organic matter and burning on magnetic susceptibility. Examine the iron mineralogy with the use of XRD (X-ray diffraction) to determine if the frequency dependent magnetic susceptibility is a reliable method for assessment of iron in the soil.

3. If evaluation is successful, attempt to produce a field method to aid detection of topsoil.

4. Recommend areas of further research that may add value to this field.

1.4.1 Hypothesis

For initial exploratory research the following hypothesis will be used:

The Null Hypothesis states that the mean of the topsoil's frequency dependent magnetic susceptibility (χ_{FD}) is equal to the mean of the subsoil's frequency dependent magnetic susceptibility.

The Alternative Hypothesis states that the mean of the topsoil's frequency dependent magnetic susceptibility differs to the mean of the subsoil's frequency dependent magnetic susceptibility.

$$H_o: \mu_{\text{Topsoil } \chi FD} = \mu_{\text{Subsoil } \chi FD}$$

$$H_1: \mu_{\text{Topsoil } \chi FD} \neq \mu_{\text{Subsoil } \chi FD}$$

For further explanatory research the following hypothesis will be used:

The Null Hypothesis states that the mean of the difference between topsoil and subsoil frequency dependent magnetic susceptibility is the same for eroded and non-eroded soils.

The Alternative Hypothesis states that the mean of the difference between topsoil and subsoil will differ for eroded and non-eroded soils.

$$H_o: \mu_{\text{diff}\chi FD \text{ eroded areas}} = \mu_{\text{diff}\chi FD \text{ non-eroded areas}}$$

$$H_1: \mu_{\text{diff}\chi FD \text{ eroded areas}} \neq \mu_{\text{diff}\chi FD \text{ non-eroded areas}}$$

The purpose for not stating the direction of the relationship in the alternative hypothesis is due to lack of prior research in this field in South Africa and thus the lack of certainty of these relationships.

1.5 Conceptual framework

This study will attempt to examine the relationship between magnetic susceptibility and topsoil in South Africa as a base for developing an indicator for topsoil loss. Past research, mainly in the northern hemisphere, shows a distinct difference in frequency dependent

measurements of the soil in topsoil and in subsoil, but the applicability of this to South African soils is unknown. Soil processes and other factors influencing magnetic susceptibility (the inputs) need to be examined, including organic matter and burning in order to understand the use of magnetic susceptibility in the field (the outputs) (Figure 1.2).

1.7 Assumptions and anticipated problems

The majority of the work carried out with frequency dependent magnetic susceptibility and topsoil has been carried out in the United Kingdom, and thus it is assumed that frequency dependent measurements will help explore soil characteristics in South Africa. However due to the vast differences in soil types, climate, greater amounts of burning and geological history, results may not show as prominent correlations of magnetic susceptibility to topsoil and subsoil. Nevertheless it is important that this issue in itself is investigated in order that future research may build upon the results found.

Figure 1.1: The inputs and outputs regarding magnetic susceptibility

Land use — cultivated / pasture lands

Atmospheric fallout (natural/ anthropogenic)

Soil age — old soils / young soils

single frequency

frequency dependent sensor

Bacteria

Iron

Carbonate

Measurements

Inputs

Organic matter

Increases burning

Burning

related

reduction/oxidation

Soil processes — leaching / weathering

resistance of parent material determines extent of weathering

Parent material

Magnetic susceptibility

field or lab work

past research and new data

Outputs

Indicators

topsoil erosion

slope processes

top soil

sub soil

bottom/ enclave

top/ steep sides

Soil horizon

Slope processes

Key:
+ : enhances magnetic susceptibility

− : decreases magnetic susceptibility

topsoil loss determined with sensor

Chapter 2: Magnetism

All matter has magnetic tendencies (Smith 1999) and this ability to place particles in to some sort of order has allowed the measurement of environmental characteristics (Thompson & Oldfield 1986). The first environmental investigations regarding magnetism originated with geophysists who were interested in examining past field changes and palaeomagnetism. Their research led to the understanding that specific minerals in rocks have greater magnetism than others. The origin of these magnetic properties lies within the atoms that compose the material (Smith 1999). The atom's electrons that spin on their own axes and rotate about an atom's nucleus create currents that cause a magnetic field to arise. Spin moments, however, completely dominate the magnetic field of natural iron oxides (Thompson & Oldfield 1986), which is the main focus of this literature review.

2.1 Magnetic properties

Different magnetisms occur in materials depending on the movement of electrons, and these have important implications for the magnetisation of substances.

2.1.1 Diamagnetism

Diamagnetism is displayed in substances with paired electrons. When a magnetic field is applied to the material the electron's orbits become aligned in the opposite direction to the external field and therefore it is a negative magnetic property. This magnetisation is lost when the applied field is removed as the electron orbits revert to a random state and no moment results (Smith 1999). The electron's spin moments do not contribute to the magnetisation of diamagnetic substances because the paired electrons cancel one another out. Diamagnetism is a weak magnetic property and thus tends to be inundated by other stronger magnetic behaviour. Commonly found natural diamagnetic minerals are quartz, feldspar and calcite (Thompson & Oldfield 1986). Other diamagnetic substances include plastic, organic matter, calcium carbonate and water (Dearing 1999).

2.1.2 Paramagnetism

In substances that have paramagnetic properties atoms occur with unpaired electrons, therefore a net magnetic moment results from both the spin and orbit of the electron. These electrons have little interaction because of the large distances between them (Smith 1999). The net magnetic moment is zero due to random electron movement. However, in the
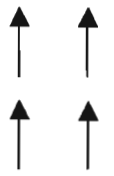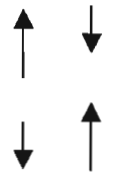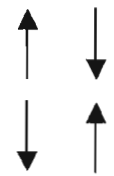
presence of an applied magnetic field, the spin magnetic moments align themselves with the field and a magnetic moment occurs in the same direction as the applied field. When the field is discontinued no magnetic moment results and alignment becomes random. Paramagnetic substances show weak magnetisation, although it is stronger than diamagnetic materials. A range of natural minerals has paramagnetic properties, including olivine, pyroxene, garnet, biotite and carbonates of iron and manganese. The inner electron shell of Mn^{2+}, Fe^{2+} and Fe^{3+} ions have unpaired electrons, which are largely responsible for the paramagnetic properties of many natural substances (Thompson & Oldfield 1986).

2.1.3 Ferromagnetism

Smith (1999) characterises ferromagnetic substances by unpaired electrons in atoms that are spaced at close, regular intervals. This allows for greater interaction to occur between the unpaired electron spins, resulting in an additive magnetising effect of ferromagnetism. This co-operative effect can occur in the absence of an applied field where spins align and cause spontaneous magnetisation and remanent magnetisation to occur. Magnetisation may result in a single crystal, but the overall magnetic moment of the sediment would be zero as other crystals have random orientation. The net magnetic moment, however, is larger than either the moment of the paramagnetic or diamagnetic substance (Smith 1999). Thompson & Oldfield (1986) recognise the above-mentioned factors, but characterise ferromagnetic materials by the drastic change in magnetic properties at a certain temperature known as the Curie temperature that acts as a threshold for magnetism. Below this point ferromagnetic materials can hold magnetism obtained by an external field. Above this temperature thermal energy enhances alignment and the substance acts as a paramagnetic material.

Different types of ferromagnetic behaviour are observable, and result from the position of atoms in the crystal lattice (Table 2.1).

Table 2.1: Ferromagnetic property types (based on Thompson & Oldfield 1989, Dearing 1999 and Smith 1999).

Ferromagnetic property type	Ferromagnetic (*senso stricto*)	Ferrimagnetic	Anti-ferromagnetic	Canted anti-ferromagnetic
General characteristics	Electrons are parallel and unpaired allowing for strong net magnetisation.	Two magnetic sites but anti-parallel magnetic moments with different strengths. Thus the sum of magnetic moments is overall greater and influences net magnetism direction.	Two anti-parallel sublattices with equal magnetic moments, thus spontaneous magnetisation is zero.	Some anti-ferromagnetic formation not exactly anti-parallel (known as spin canting) and thus small spontaneous net magnetisation occurs.
Diagram	↑ ↑ ↑ ↑ ↑ ↑	↑ ↓ ↑ ↓ ↑ ↓	↑ ↓ ↑ ↓ ↑ ↓	↗ ↘ ↗ ↘ ↗ ↘
Net magnetism direction	↑	↑	0	→
Example of mineral	Cobalt, nickel, chromium and pure iron and iron transition metals	Magnetite, maghaemites, pyrrhotite, greigite, titanomagnetite, titanohaematite	As for canted	Haematite, goethite

Magnetic susceptibility in a bulk sample is a measurement of the total magnetic attraction of all the minerals in the sample, or the magnetic moment induced by an applied field. The magnetic susceptibility is therefore the sum of the net magnetic susceptibility of the ferrimagnetic, canted antiferromagnetic, paramagnetic and diamagnetic particles (Dearing 1999). This measurement is therefore skewed as some particles have stronger magnetism values and will override those with weaker magnetism readings. Large quantities of diamagnetic substances, however, will dominate the susceptibility measurements. The highly magnetic mineral that dominates most susceptibility readings is magnetite (Fe_3O_4), which jumps to the magnet as it passes it, and therefore magnetite rich rocks, such as basalt, show a higher magnetism (Dearing 1999). From this it is understandable that the magnetic susceptibility of the material depends largely on the magnetic behaviour of the grains within the substance (Table 3.1).

Table 3.1: The magnetic behaviour of minerals (based on Dearing 1999).

Mineral/s	Magnetic behaviour	Location
Pure iron	ferromagnetic (high magnetic susceptibility)	Not usually found in the environment
Magnetite	ferrimagnetic (high magnetic susceptibility)	Found in igneous rocks, and in most sedimentary rocks
Maghaemite	ferrimagnetic (high magnetic susceptibility)	Found in tropical and sub-tropical soils
Haematite	canted antiferromagnetic (low magnetic susceptibility)	Few minerals in this category, but occur in rocks and soil and are responsible for the red colouration
Biotite Pyrite	paramagnetic (weak magnetic susceptibility)	Common in rocks and soils and contain iron
Quartz Calcium carbonate Organic matter Water	diamagnetic (weak or negative magnetic susceptibility)	Common in the environment

3. 1 Volume magnetic susceptibility

Detection of magnetic behaviour occurs when the substance is placed into a magnetic field. An unmagnetised material becomes magnetised as it aligns with the force field. Different substances will react differently, for example diamagnetic substances create a weak, negative magnetic field, while basalt containing a large amount of magnetite will have a strong, positive field. Similarly the substance's magnetic properties will affect the magnetism created by a magnetic field. Every substance has a characteristic relationship between the magnetic field applied and the quantity of induced magnetisation. This relationship can be expressed as a ratio termed volume magnetic susceptibility (Equation 1.1):

$$\kappa = M/H \tag{1.1}$$

This volume susceptibility is expressed as κ, whilst M is defined as the magnetic moment per unit volume of the sample and H is the applied external magnetic field (Thompson & Oldfield 1986; Dearing 1999). This equation formulates a dimensionless susceptibility measurement (Mullins 1977; Thompson & Oldfield 1986) and is expressed as SI units (Thompson & Oldfield 1986).

3.2 Mass specific susceptibility

Samples are usually taken of materials with different bulk densities, which is problematic for the comparison of κ values. Single samples are therefore expressed in terms of dry mass. Mass specific magnetic susceptibility is a ratio of the volume susceptibility (κ) and the sample density (ρ) (Equation 1.2).

$$\chi = \kappa/\rho \tag{1.2}$$

Mass specific susceptibility is calculated by dividing κ by the sample's bulk density, which is the mass of the sample divided by its volume. Volume of the samples used in the MS2B sensor is $10 cm^3$. However, it is important to note that bulk density is expressed in $kg\ m^{-3}$ (Thompson & Oldfield 1986, Dearing 1999). The measurement obtained through these calculations will be expressed as χ (chi) or χ_{LF} to indicate the reading was taken at low frequency. It is also important to note that χ is expressed as a value in units of 10^{-3}, 10^{-6} or

10^{-9}, and χ_{LF} is usually given as $10^{-6}m^3kg^{-1}$. This is easily obtained from a κ (10^{-5} SI) by dividing this value by the sample's mass (g) and dividing it by 10 (Dearing 1999).

3.3 Magnetic domains

Hysteresis and its associated characteristics are mainly dependent on the relative positions of magnetic domains. These are thus influential in the control of magnetism in naturally magnetic minerals (Dunlop 1981 cited in Thompson & Oldfield 1986). Weiss 1907 (cited in Thompson & Oldfield 1986) first proposed the concept of domains. He advocated that all material can be split up into various domains or areas, and that each such domain may have a different direction of magnetisation (Figure 3.1) and thus the net magnetisation would be zero. The various directions of fields in the domains cause domain walls to be a balance between conflicting forces, and of a relative thickness (Thompson & Oldfield 1986).
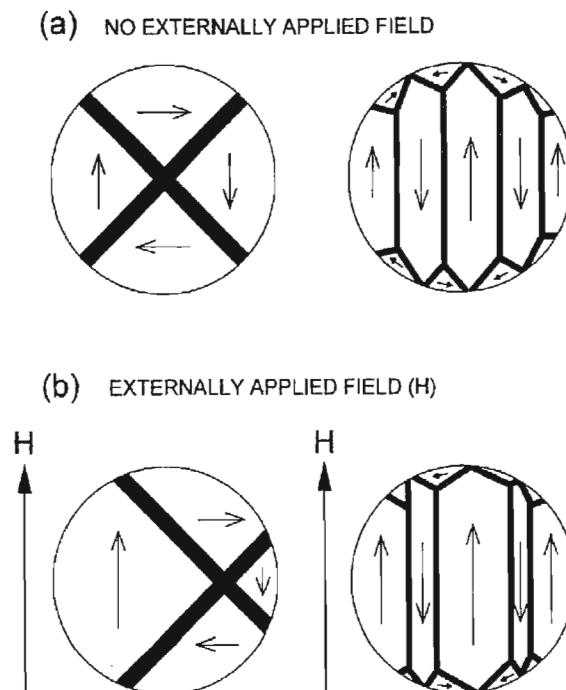
Figure 3.1: Schematic diagram of possible domain configurations for a spherical grain; LEFT-four domains, where magnetic moments form a closed loop; RIGHT-multi-domain grain (after Dankers 1978 cited in Smith 1999).

3.3.1 Single-domain behaviour

Small grained particles are only able to house single-domain grains that are unstable and easily flip their magnetic axis through 180°. However, if they are in a magnetic field they will spend time aligned to the field direction (Mullins 1977). Another important influence on causing them to flip their axis is thermal fluctuations that occur in the atoms within the crystal lattice. Temperature changes cause a spontaneous reversal of the direction of domain magnetisation. If grain sizes are larger and remanence decay occurs (called magnetic viscosity), a viscous single domain results. If only a slightly larger grain has remanence over stable geological time, a stable single domain is formed (SSD) (Smith 1999).

3.3.2 Multi-domain behaviour

In multi-domain grains (MD) the domain wall plays an important part in determining their magnetisation cycle. Initially a domain's walls will be situated at a minimum energy position. When a field is applied to a multi-domain grain, domain walls favour an increase in area of the domain with magnetisation in the direction of the external field (Thompson & Oldfield 1986). The domain walls form new configurations and some of the domains are rotated. During this process energy barriers may be crossed and a new minimum energy position will be obtained. This phenomenon is termed the Barkhausen jumps. This is an irreversible domain wall movement and can cause remanence to be induced in a grain. If domain walls do not cross the energy barrier, the domains are able to re-establish themselves once the applied field is removed (Smith 1999).

3.3.3 Superparamagnetic

Some ferromagnetic or ferrimagnetic grains are extremely small in diameter, 0.001-$0.01\,\mu m$, and have thermal vibrations with the same magnitude as their magnetic energy. These ultra-fine grained magnetic particles do not show signs of remanence or hysteresis, due to their constantly thermally reoriented magnetisation. However, when a field is applied they do display magnetism as well as superparamagnetic (SP) behaviour. This type of behaviour is stronger than paramagnetic magnetism, and the susceptibility of the SP grain is larger than a SSD or a multidomain grain (Bean & Livingston 1959 cited in Thompson & Oldfield 1968). This has important implications on susceptibility sampling, as its presence is likely to give higher magnetic susceptibility readings. Temperature is also

a key determinant of superparamagnetic behaviour. If these types of grains are at room temperature and are cooled they will then show properties of a ferromagnetic or ferrimagnetic SSD grain (Thompson & Oldfield 1986).

3.4 Ferrimagnetic particles

Ferrimagnetic particles occur as primary or secondary sources of the mineral. Primary ferrimagnetic iron oxides and sulphides are found in igneous rocks and they retain a large proportion of their magnetic properties. Secondary ferrimagnetic minerals occur due to processes such as burning, fossil fuel combustion, bacteria, soil formation, diagenesis and authigenesis (Thompson & Oldfield 1986; Dearing et al. 1996a; Dearing 1999).

Ferrimagnetic particles display properties of domains: single (SD), multi (MD) and superparamagnetic (SP). However, if a domain is large enough to have more than one domain but still shows evidence of only a single domain, the domain is termed pseudo-single domain (PSD) (Dearing 1999). These are usually evident when domains are altering from single domain to multidomain particles (Dearing et al. 1996a).

3.5 Frequency dependent magnetic susceptibility

Measurements of frequency dependent magnetic susceptibility rely on the principles of magnetic viscosity and relaxation time.

3.5.1 Magnetic viscosity

If temperature is kept constant then the volume susceptibility at a low frequency will increase linearly with an increase in the grain volume. Thermal energy serves to assist the external field and therefore create maximum magnetisation. However, thermal energy becomes less than the magnetostatic energy of the applied field at the critical volume or blocking volume, which ultimately causes the volume magnetic susceptibility to decrease. The stable single domain (SSD) state is then entered until the grain becomes large enough to accommodate greater magnetostatic energy. If a grain does increase its volume it will reach the pseudo-single domain state at the interface between the SSD and MD form. This causes the volume susceptibility to increase again and it becomes more constant in larger grain sizes. The boundary between SP and SSD also consists of a range of grain volumes, although these are narrower. In this range grains are in a transitional magnetic state and they show evidence of a time-dependent property that is measurable, called magnetic

viscosity (Dearing *et al.* 1996a, Dearing 1999). Magnetic viscosity is the loss or increase of magnetisation over time (Thompson & Oldfield 1986). When magnetic viscosity occurs due to the removal of an applied field and a grain loses its remanent magnetisation over a period of time, it is known as the grain relaxation time (Eyre 1997). This phenomenon arises before the grain obtains equilibrium of magnetisation (Dearing *et al.* 1996a).

Frequency-dependent susceptibility uses the relaxation time to compare induced magnetism with the aid of two frequencies. A frequency slower than relaxation time enables the grains to reach equilibrium, but a faster frequency results in non-equilibrium magnetism and therefore a lower susceptibility measurement is obtained at high frequency (Dearing *et al.* 1996a). Dearing (1999) suggests that the low frequency allows SP crystals near to the SSD particles to contribute to susceptibility. High frequency then prevents this as the domain boundary is moved causing SP grains on the boundary to become blocked in thus behaving as SSD and exhibiting low magnetic susceptibility (Maher 1986; Dearing *et al.*1996a).

3.5.2 Measurement of frequency dependent magnetic susceptibility

Frequency dependent magnetic susceptibility is calculated using the low and high frequency volume susceptibility measurements (0.46 and 4.6 kHz, respectively). It can either be expressed as mass specific dual frequency dependent susceptibility (χ_{FD}) (Equation 1.3) or as percentage frequency dependent susceptibility ($\chi_{FD\%}$) (Equation 1.4). In both equations κ_{LF} is the corrected low frequency volume susceptibility value and κ_{HF} is the corrected high frequency measurement, and both κ values are in units of 10^{-5} SI.

$$\chi_{FD} = \{(\kappa_{LF} - \kappa_{HF})/mass\} /10 \tag{1.3}$$

$$\chi_{FD\%} = \{(\kappa_{LF} - \kappa_{HF})/\kappa_{LF}\} \times 100 \tag{1.4}$$

Equation 1.3 gives χ_{FD} in units of 10^{-6} m^3 kg^{-1}, similar to χ in Equation 1.2 (Dearing 1999).

3.5.3 Frequency dependent magnetic susceptibility and superparamagnetic particles

Samples with significant SP grains have a frequency dependent magnetic susceptibility percentage ($\chi_{FD\%}$) of greater than six percent. Less than five percent indicates no SP grains or extremely fine grains (Dearing *et al.* 1996a; Dearing 1999). This relates to the findings that $\chi_{FD\%}$ only indicates the presence of medium SP grains, between 0.013μm and 0.027μm (Maher and Taylor 1988; Dearing *et* al. 1996a; Dearing *et al.* 1997) and the highest values for χ_{FD} are obtained from grains within this range and it decreases below and above these two boundaries (Dearing *et al.* 1996b; Eyre 1997) (Figure 3.2). However, this is advantageous as this narrow band of ferrimagnetic grains if detected will exclude any primary ferrimagnetic particles or those grains attributable to pollution (Dearing *et al.* 1996a).

Frequency dependent grains, such as SSD particles, depress the $\chi_{FD\%}$ value (Dearing *et al.* 1996a; Dearing 1999). Coarse-grained MD ferrimagnetic particles show a high χ_{LF} but zero for χ_{FD} (Dearing *et al.* 1996a). Ferrimagnetic particles play an important part in frequency magnetic susceptibility readings, especially magnetite that tends to dominate readings (Dearing 1999). Magnetite has a $\chi_{FD\%}$ usually from 14.5 to 16.9% and maghaemite's $\chi_{FD\%}$ values fall between 11.6 and 14.3% (Dearing *et al.*1997; Dearing 1999). Both these ferrimagnetic particles have SP grains which are related to their high $\chi_{FD\%}$ readings (Oldfield 1999). However, Dearing (1999) contradicts this by saying that samples with a $\chi_{FD\%}$ of over 14% are very rare and largely attributable to contamination of the sample or other error (Table 3.2). The $\chi_{FD\%}$ values can be used quantitatively as a measurement of the concentration of frequency dependent grains as SP particles (Table 3.2) (Dearing *et al.* 1996a). This also allows the calculation of frequency independent grains such as SSD particles (Table 3.2) (Dearing *et al.* 1997).

Dearing (1999) also attributes high $\chi_{FD\%}$ values to soils that have been burned, which is associated with magnetite and maghaemite formation (discussed in Section 4.3.2). High $\chi_{FD\%}$ values can also result if air-borne particles occur in the soil, due to natural or anthropogenic causes. This results in a high χ_{LF} reading that may effect the $\chi_{FD\%}$ value, therefore it is important that sampling is done on soils away from industrial areas (Dearing *et al.* 1996b).
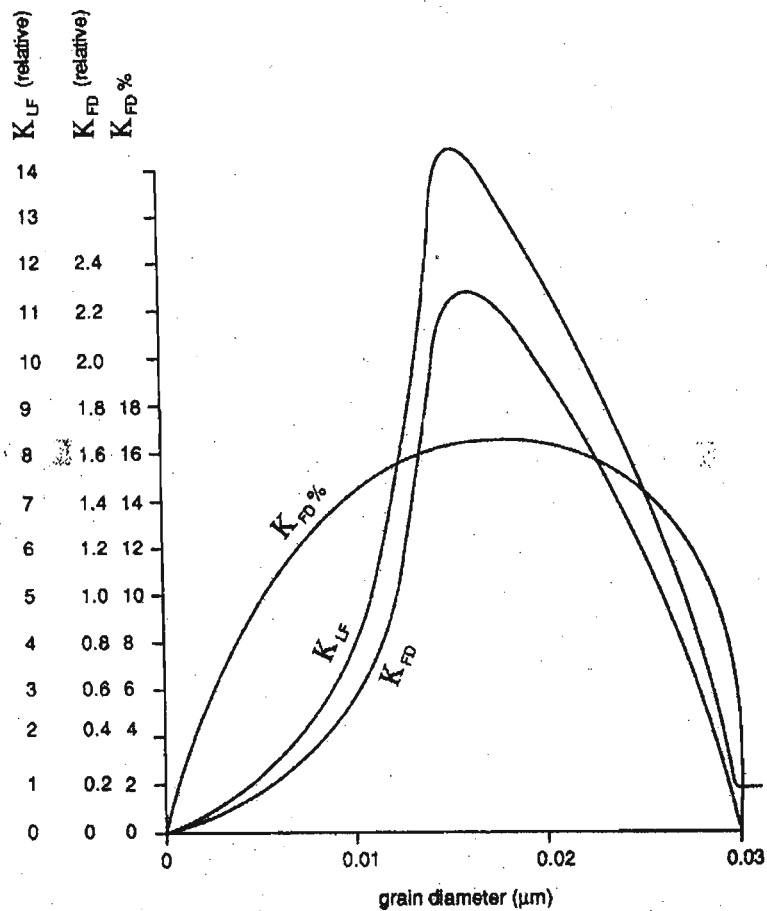
Figure 3.2: Distribution of grain sizes according to frequency dependent magnetic susceptibility values (Dearing *et al.* 1996b).

Table 3.2: Interpretation of frequency dependent susceptibility values, using χ_{FD} as an estimate of SP concentration (Dearing *et al.* 1997; Dearing 1999).

$\chi_{FD}\%$	$\chi_{FD}\%$ value	SP grains present	Percentage of SP grains
Low $\chi_{FD}\%$	<2.0	Virtually no SP grains	10% (indicates 90% SSD in the soil)
Medium $\chi_{FD}\%$	2.0 – 10.0	A mixture of SP and coarser grains, or SP grains <0.005μm	10-75%
High $\chi_{FD}\%$	10.0 – 14.0	Virtually all SP grains	>75%
Very high $\chi_{FD}\%$	>14.0	Erroneous measurement, anisotrophy, weak sample or contamination	Up to 100%

Chapter 4: Magnetic minerals

4.1 Magnetic minerals in the environment

Magnetic minerals in the environment are said by Thompson *et al.* (1980) and Thompson & Oldfield (1986) to transform and move between the atmosphere, lithosphere and hydrosphere. Transformation and deposition lead to authigenesis (new minerals are crystallised in the rock or sediment) (Figure 4.1). Oldfield (1999) criticises this concept as only placing the emphasis on old assumptions that magnetic minerals occur due to lithogenesis, pedogenesis, volcanic activity or industrial sources. He extends these categories of magnetic particle occurrence in the environment through production of magnetic materials by highlighting three processes.

- *Magnetic mineral formation through dissolution* which occurs mostly as a by-product from diagenesis (the alteration of a sediment to a sedimentary rock) of organic matter. This process is a result of deposition and thus is evident in a range of contexts such as deep-sea sediments and peat,
- *Magnetite produced by bacteria* living in largely aquatic habitats and formed through biomineralisation, and
- *Authigenic ferrimagnetic sulphide production* (mainly greigite) in waterlogged, freshwater, brackish and marine conditions (Oldfield 1999).

Although Smith (1999) advocates that past research has shown magnetic minerals in materials to be stable, he also stresses that it cannot be assumed as *in situ* processes (including authigenesis or diagenesis) or sampling procedures may cause mineralogical or chemical changes to be induced. Hilton *et al.* (1986 cited in Smith 1999) found that minerals magnetically enhanced by authigenesis or diagenesis substantially increase the magnetic properties of anaerobic sediments.
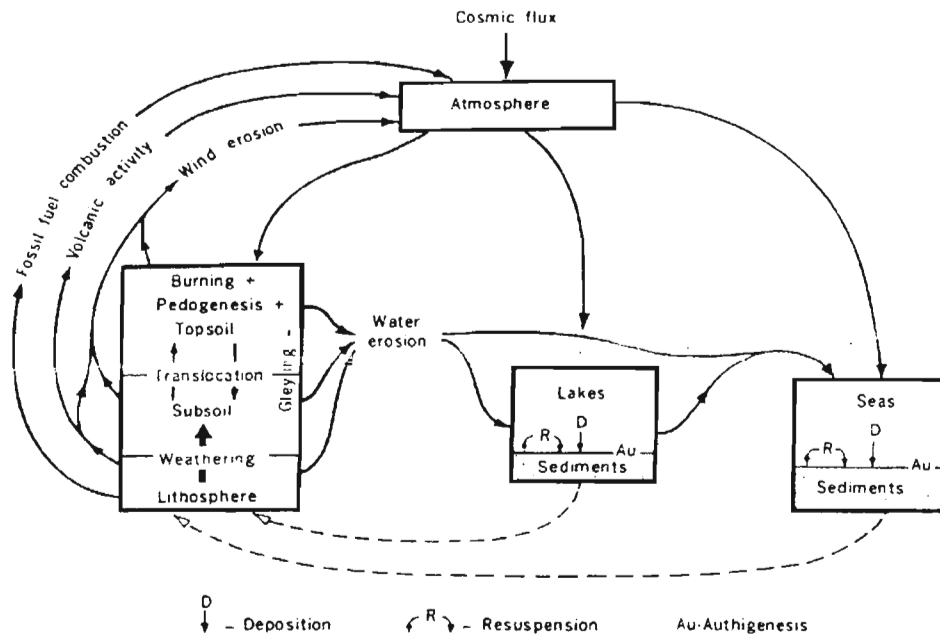
Figure 4.1: Simplified model of the movement of magnetic minerals between the atmosphere, lithosphere and hydrosphere (Thompson *et al.* 1980).

The major source of magnetic minerals to the environment is through the formation of ferromagnetic minerals. However, overall they are a small component in the composition of igneous and metamorphic rocks. Sedimentary rocks have magnetic minerals as particles within them that were formed during or after lithification. Rock-forming minerals that dominate are the silicates that are diamagnetic or paramagnetic. Rocks that have magnetic ions including Fe^{2+}, Fe^{3+} or Mn^{2+} and are largely paramagnetic (Smith 1999).

The greatest magnetic characteristics are evident in ferromagnetic oxides or sulphides (Nagata 1961 cited in Smith 1999). The most common form of magnetic minerals are the iron and iron-titanium oxides, which display ferrimagnetic and anti-ferrimagnetic behaviour. Other significant magnetic minerals include iron sulphides (such as pyrrhotite, greigite and pyrite) and iron hydroxides/oxyhydroxides (including goethite and lepidocrocite).

4.1.2 Iron

In the Earth's crust, iron is the fourth most abundant element, and therefore is an important constituent of rocks. It interacts with oxygen and silicon to produce many common rock-

forming minerals. The minerals that have magnetic properties are generally pure oxides of iron including magnetite, titanomagnetite, haematite and maghaemite. These iron oxides only compose a minority of the overall material of the rock in which they are greatly dispersed. These magnetic iron oxides determine the magnetic properties of the rock and if these oxides are in too small quantities then iron sulphides or manganese oxides may play a more important role. However, even in minimal quantities the magnetism of the iron oxides may dominate the weak magnetic behaviour of the paramagnetic silicates or hydroxides (Thompson & Oldfield 1986).

4.1.3 Iron Oxides

Environmental magnetic minerals can be split into two distinctly different groups. Firstly those minerals that form a spinel structure during crystallisation and secondly those that form a corundum structure during crystallisation.

4.1.3.1 The spinel group

Many oxides form with the spinel structure during crystallisation because it allows flexibility in the acceptance of cations. In this structure the oxygen framework is able to contract or expand, accommodating various sizes of cations. This enables vacancies in the lattice to occur that may become occupied by important cations in the spinel group resulting in a range of elements to arise. (Thompson & Oldfield 1986).

i) Magnetite (Fe$_3$O$_4$)

Magnetite is one of the most common magnetic minerals and is abundantly found in igneous rocks and in most metamorphic and sedimentary rocks. One unit cell is composed of eight tetrahedral sites occupied by Fe^{3+} cations, and 16 octrahedral sites filled by equal numbers of Fe^{3+} cations and Fe^{2+} cations. Magnetite occurs in the form of a primary mineral, resulting from igneous rocks, and as a secondary mineral due to biological processes (Thompson & Oldfield 1986). Biologically magnetite can be formed due to magnetostatic bacteria (Fassbinder et al. 1990 cited in Schwertmann & Fitzpatrick 1992). Magnetite is ferrimagnetic and has a Curie temperature of 580°C. At low temperatures magnetite also transforms magnetically, at about −150°C, and this results in an alteration in its electrical conductivity (Thompson & Oldfield 1986).

ii) Ulvospinel (Fe_2TiO_4) and titanomagnetites

Magnetite has the same spinel structure as titanomagnetite, but is composed differently. The sites that are filled by Fe^{3+} in magnetite are occupied by Ti^{4+} in ulvospinel. Ulvospinel also differs from magnetite in that it is antiferromagnetic, as the Fe^{2+} cations cancel each other out creating a net magnetic moment of zero. Solid solutions exist between ulvospinel and magnetite, and these are named the titanomagnetites (Figure 4.2) and include chromite. It is evident that an increase in titanium in the single domain titanomagnetites results in a steady loss in susceptibility. Multidomain titanomagnetites show less change with titanium increase and these oxides are more common in the environment (Thompson & Oldfield 1986).

iii) Maghaemite (Fe_2O_3)

Maghaemite has the same spinel structure as magnetite and chemical composition as haematite, but has a cation-deficient lattice (Thompson & Oldfield 1986). Maghaemite occurs in tropical and subtropical soils and is found occasionally in temperate soils. Maghaemite forms in various ways during soil formation and one mechanism is the addition of oxygen and oxidation of magnetite. A more common process of maghaemite formation is the altering of iron oxyhydroxides such as the heating of goethite when organic matter is present (Schwertmann & Fitzpatrick 1992). Maghaemite's most characteristic behaviour is its inversion when heated above approximately 300°C to haematite. This disenables the determination of its Curie temperature. However, the presence of impurities such as Na and Al allow the maghaemite structure to stabilise (Thompson & Oldfield 1986).

iv) Titanomaghaemites

Titanomaghaemites occupy the area on the ternary diagram (Figure 4.2) between the magnetite-ulvospinel and haematite-ilmenite boundaries. Their position in this area is related to two parameters i.e., the Fe:Ti ratio and the degree of oxidation (Thompson & Oldfield 1986).
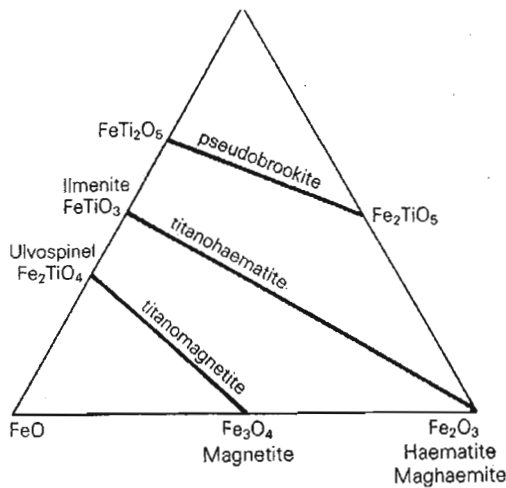
Figure 4.2: Ternary diagram of iron and titanium oxides showing the solid solution series (Thompson & Oldfield 1986).

4.1.3.2 The corundum group

The corundum group consists of cells that are rhombohedral as opposed to cubic as the spinel group (Thompson & Oldfield 1986).

i) Haematite (αFe_2O_3)

Haematite is an important magnetic mineral that forms in igneous rocks due to oxidisation of titanomagneties or the inversion of maghaemites at temperatures over 350°C (Smith 1999). Haematite in the form of fine grains exhibits a blood-red colour (Thompson & Oldfield 1986). Haematite is produced by the structural rearrangement and dehydration of ferrihydrite. Favouring this formation are high temperature, low water activity, high amounts of iron released from rocks and low concentrations of organic matter (Schwertmann & Fitzpatrick 1992). Haematite has a structure composed of Fe-O_3-Fe tetrahedra and the pair of iron ions has anti-parallel spin moments. This spin structure results in haematite's antiferromagnetic properties. Iron layers that lie adjacent to one another in the haematite lattice become coupled antiferromagnetically, but the spins of those in adjacent planes are not exactly antiparallel and thus a weak magnetic moment occurs. A net magnetic moment can also be accounted for by spin canting (Dzyaloshinsky 1958 cited in Thompson & Oldfield 1986). This creates a weak but stable magnetisation, due to the corundum structure. This is particularly important in palaeomagnetic studies. The Curie temperature of haematite is approximately 675°C and below −10°C spins move

out of alignment in pure crystals and at lower temperatures for impure crystals (Thompson & Oldfield 1986).

ii) Ilmenites and titanohaematites

Ilmenite is composed of Fe^{2+} layers with alternating Ti^{4+} planes, unlike haematite where all the layers consist of Fe^{3+} ions. Titanohaematites are common in nature and lie in the spectrum between ilmenite and haematite (Figure 4.2). Those titanohaematites closer to the ilmenite end of the spectrum, which also have alternate layers of Fe^{2+} and Ti^{4+} around oxygen layers, show magnetisation of antiparallel layers. Effectively these result in superparamagnetism at room temperature (Thompson & Oldfield 1986), although according to Smith (1999), ilmenite remains mostly paramagnetic.

iii) Pyrrhotite (FeS) and the iron sulphides

Another group of important magnetic minerals apart from the iron oxides are the iron sulphides. The most magnetic iron sulphide is pyrrhotite, which is ferrimagnetic. Pyrite (FeS_2) and is common in the environment and has paramagnetic behaviour. Greigite (Fe_3S_4) is rare and is largely found in freshwater where authigenesis has caused it to form (Thompson & Oldfield 1986).

4.1.3.3 Iron hydroxides and oxyhydroxides

i) Goethite (αFeOOH)

Goethite is a commonly found mineral and has a yellowish brown colour (Thompson & Oldfield 1986; Schwertmann & Fitzpatrick 1992). Goethite results due to the precipitation (involving primary rock minerals and biological by-products) and crystallisation of iron. High water activity in the surface and low temperatures are thought by Schwertmann (1985, 1988 cited in Schwertmann & Fitzpatrick 1992) to encourage goethite formation. However, Thompson & Oldfield (1986) advocate that it is more generally found in humid climates. Goethite is generally antiferromagnetic, however, oxygen ion vacancies can lead to uncompensated spins resulting in a weak magnetic moment. When goethite is heated to between 300 and 400°C it dehydrates to form haematite (Thompson & Oldfield 1986).

ii) Lepidocrocite (γFeOOH)

Lepidocrocite is less common than goethite but is widespread in young soils and sediments). Lepidocrocite is bright orange in colour and often indicates a lack of oxygen in the soil system due to excessive moisture. Lepidocrocite formation is suppressed by high carbonate concentrations that may favour goethite formation instead (Schwertmann & Fitzpatrick 1992). It cannot hold a magnetic remanence at normal temperatures but when heated at 250 to 350°C it breaks down and forms maghaemite (Thompson & Oldfield 1986).

4.1.3.4 Other magnetic minerals

Other minerals found in nature to carry magnetic remanence are the ferromanganese oxides and hydroxides, especially those along the jacobsite solid solution sequence that has the end members hausmannite (Mn_3O_4) and magnetite (Thompson & Oldfield 1986).

Table 4.1: Iron oxides in soils (after Schwertmann & Taylor 1977 cited in Maher 1986)

Mineral	Formula	Magnetic status	Reported environmental associations	Fe %	Mass specific Susceptibility ($10^{-6} m^3 kg^{-1}$)
Haematite	αFe_2O_3	Canted antiferromagnetic	Relatively dry, highly oxidised soils usually in areas of elevated temperate	70	0.27 ≈2
Goethite	$\alpha FeOOH$	Canted antiferromagnetic	Moister soils, abundant in well-drained temperature areas	63	0.35 ≈ 1.26
Maghaemite	γFe_2O_3	Ferrimagnetic	Abundant in highly weathered tropical/ sub-tropical soils	70	410, 420
Lepidocrocite	$\gamma FeOOH$	Paramagnetic	Occurs in poorly drained soils	63	0.5 –0.75
Magnetite	Fe_3O_4	Ferrimagnetic	Restricted occurrence, primary mineral or from burning	72	380 - 11116

4.2 Formation of natural magnetic minerals

All magnetic minerals have specific identifiable magnetic susceptibility values (Table 4.1). This is largely due to the the environment factors influencing their formation.

4.2.1 Parent material

4.2.1.1 Igneous rocks

Igneous rock is formed by the cooling and crystallisation of molten magma. The lava that cools quickly gives rise to fine grained volcanic rock, which is slowly cooled forms coarse grained plutonic rock. Igneous rocks have a variety of types of silica present but iron oxide is their vital component. Rocks with large quantities of silica, such as granite, are categorised as acidic. These rocks also have large amounts of quartz and feldspar. Rocks that are poor in silica, basic rocks, consist largely of feldspar, pyroxene and olivine crystals. These rocks are darker in colour than acidic rocks and tend to have higher iron oxide concentrations. In igneous rocks magnetite is one of the first formed crystals. Magnetite, produced due to cooling magma is usually titanium rich and may occur with ilmenite and titanomagnetite. Haematite is not as common in igneous rocks as magnetite and titanomagnetite, but when present gives the rock a red colour. Pyrrhotite is rare in igneous rocks and goethite result from the weathering of iron silicates and oxides (Thompson & Oldfield 1986).

i) Basalt

When basalt cools it contains usually either magnetite or ulvospinel, although a variety of end products can be formed depending on temperature dependent oxidation and rate of cooling (Smith 1999). High temperature oxidation alters the state of primary titanomagnetites to initially produce magnetite and ilmenite and, then progresses to form titanohaematite and lastly pseudobrookite is formed. Smith (1999) marks this as the Fe_3O_4-Fe_2TiO_4- Fe_2TiO_5- Fe_2O_3 quadrangle. Oxidation at lower temperatures, between 400 and 600°C, results in the formation of titanomagnetite (Thompson & Oldfield 1986). In oxygen-rich environments ilmenite, maghaemite and haematite tend to form as the rock cools. Haematite can also be formed by the oxidation of titanomagnetites or maghaemite's inversion (Smith 1999).

ii) Gabbro

In all gabbros iron is present mostly in the form of ilmenite, titanomagnetite or magnetite. These basic rocks tend to have undergone prolonged cooling and thus are coarse-grained with large iron-oxide grains. Titanohaematites are frequently found in transformed or

weathered gabbro. Gabbro contributes substantially to the composition of the ocean floor and the resultant titanohaematites may be associated with the ocean's magnetic anomalies (Smith 1999).

iii) Granite
The slow cooling of granite can eventually lead to large grained ilmenite and titanohaematite particles forming. Overall granites are poor carriers of remanence, and titanohaematite is the most significant magnetic component in granites. However, iron oxides tend to be less titaniferous in igneous rocks rich in silica (Smith 1999).

4.2.1.2 Sedimentary rocks
If material with magnetic particles is transported it will face both chemical and mechanical weathering, although these only persist for a certain period. These effects will alter the mineral's size, surface area and mechanical characteristics. However minerals such as magnetite and haematite are still likely to be identifiable. Processes that occur *in situ* material are also important in altering magnetic minerals, particularly reduction process resulting in solution, and oxidation that leads to precipitation (Thompson & Oldfield 1986).

Red beds or red sandstone are a distinct type of sedimentary material and owe their colour to haematite that stains their silica grains (Thompson & Oldfield 1986), therefore these grains only have a low iron oxide content (Maher 1986). Red beds consist of two groups of iron-titanium oxides of mineral assemblages: a fine-grained group containing the haematite pigment and secondly a coarse-grained group, predominantly haematite and maghaemite (Smith 1999). This type of haematite consists of large, black iron oxide grains, that form from the oxidation of magnetites (Thompson & Oldfield 1986).

Limestone has a very low but stable remanent magnetism. This is contributed mostly by magnetite, but also by goethite and haematite (Thompson & Oldfield 1986).

4.2.1.3 Metamorphic rocks
In some slates the major magnetic mineral has been found to be iron sulphide, but at higher grades of metamorphism magnetite may form. This type of magnetite is generally pure and exists as large crystals. Both magnetite and ilmenite in metamorphic rocks show coarse

grain sizes which have mainly multidomains and unstable palaeomagnetic remanence. Metamorphic rocks also contain members of the haematite-ilmenite solid solution (Thompson & Oldfield 1986).

4.2.2 Theories regarding the formation of fine-grained ferrimagnetic minerals

Many theories for the mechanisms that enrich the soil with fine-grained ferrimagnetic minerals have been formulated over the past 40 years and no consensus on any particular theory has occurred:

1. *Long-term weathering and pedogenesis:* leading to the concentration of primary ferrimagnetic minerals (Singer & fine 1989 cited in Dearing *et al.* 1996b). Since these are primary particles they should not dominate frequency dependent susceptibility readings (Dearing *et al.* 1996a).

2. *Accumulation of coarse airborne magnetic particles:* these are usually greater than $1\mu m$ and occur from pollution sources (Thompson & Oldfield 1986). The large size of these particles result in them not being detected by the frequency dependent magnetic susceptibility sensor (Dearing *et al.* 1996b).

3. *Anaerobic dissimilatory bacteria:* ultrafine-grained ferrimagnetic particles such as magnetite are thought to be produced by magnetostatic bacteria under anaerobic conditions (Lovely *et al.* 1987). However, it has been argued that oxygen is necessary for magnetite synthesis and growth (Blakemore *et al.* 1985 cited in Lovely *et al.* 1987.) Dearing *et al.* (1996b) argued that SP grains are not found in great quantities in waterlogged conditions, therefore this type of production of ferrimagnetic particles does not significantly contribute to the overall content of ultrafine-ferrimagnetic particles.

4. *Anaerobic formation of greigite (Fe_3S_4):* in connection with microbial reduction (Stanjek *et al.* 1994 cited in Dearing *et al.* 1996b). As stated above Dearing *et al.* (1996b) discredits this theory because ultrafine-ferrimagnetic grains are mostly found in freely drained soils.

5. *Thermal transformation:* due to natural fires and crop burning, iron oxides and hydroxides that are weakly magnetic are converted to highly magnetic ferrimagnetic particles, magnetite and maghaemite (Kletetschka & Banerjee 1995 cited in Dearing *et al.* 1996b; Le Borgne 1955 & 1960 cited in Oldfield 1999). (This is further discussed in Section 4.3.2).

6. *Abiological weathering of Fe(II):* results in oxidised magnetite or maghaemite, evident in synthetic experiments (Maher & Taylor 1987 cited in Dearing *et al.* 1996b; Maher & Taylor 1988). It is important to note that SFMs (secondary ferrimagnetic minerals) will also eventually weather away but if a new iron supply is available new SFMs will form (Dearing *et al.* 1996b).

7. *Formation of microcrystals of maghaemite or magnetite from weakly magnetic iron oxides and hydroxides:* this occurs due to reduction-oxidation cycles that take place in pedogenesis. This process is not well understood (Thompson & Oldfield 1986).

Dearing *et al.* 1996b adds a further category of "anaerobic microbial Fe reduction", but this can be seen as an overlap of the theory related to anaerobic dissimilatory bacteria. Conclusively only thermally transferred minerals can be seen to have a significant contribution to χ_{FD} and therefore is the only viable theory of formation of fine-grained ferrimagnetic minerals.

4.3 Influences on magnetic susceptibility

4.3.1 Underlying material

Samples with parent materials high in primary ferrimagnetic particles are thought to lead to high concentrations of SFMs in the soil. The availability of iron in the soil is important as it supplies new SFM through weathering. Materials such as igneous rocks, would thus show high readings of frequency dependent magnetic susceptibility as they have a high concentration of magnetite (Maher 1986). However, these soils may have large amounts of primary ferrimagnetic minerals and thus exhibit a high χ_{LF} reading (Dearing *et al.* 1996b). This may cause a large χ_{FD} measurement to result that is not truly representative of the SFM content of the soil. Igneous rocks supply iron to the soil in two ways: firstly primary magnetic grains are released into the soil, and secondly ionic iron is release from other iron bearing particles of the rock, especially ferromagnesian silicates (Maher 1986).

Research carried out in the United Kingdom has found that strongly magnetic soils with ultrafine-grained ferrimagnetic particles occur over material that has no concentration of primary ferrimagnetic particles (Maher & Taylor 1988). Strongly magnetic soils are evident over sedimentary and low-grade metamorphic substrates such as limestone and slate (Dearing et al. 1996b). This is evident in areas consisting of slate in Devon in the United Kingdom (Maher & Taylor 1988). Another important factor to note is that these areas lie south of the area most recently covered by glaciers, and thus are free of 'igneous erratics' that occur in the form of drift deposits (Dearing et al.1996b). The low levels of total iron in rocks such as chalk are thought to be compensated by rapid weathering (Atkinson 1957 cited in Dearing et al. 1996b) thus supplying high amounts of iron (Moukarika et al. 1991 cited in Dearing et al. 1996b). This is done by releasing iron in the ionic form that is either followed by oxidation leading to the precipitation of iron, or iron is taken into soil solution and is then precipitated in another section of the profile. Both of these rely on the oxidative conditions of the soil (Maher 1986). Usually soil with large amounts of calcium carbonate have low magnetic susceptibility values, but when dissolution occurs large amounts of magnetic minerals are left in the giving a high magnetic susceptibility value (Dearing et al.1996b). This shows that magnetism is masked by by minerals diamagnetic in nature, such as calcium carbonate (Thompson & Oldfield 1986; Dearing 1999). Although this is inconsistent with De Jong et al. (1998) who found higher χ_{FD} values in calcium carbonate rich soil.

Iron supply does not totally control soil magnetic susceptibility as other factors, such as weathering, also play an important role (Dearing et al. 1996b). Weathering relies on climatic controls in order to supply iron to the soil. Maher (1986) states that although the macroclimate may control the general release of iron, the "micro-environment pedoclimate" is important in determining its final composition. In soils the weathering processes that are dominant include hydrolysis and solution, and these are largely driven by precipitation (Dearing et al. 1996b).

4.3.2 Effects of burning

Oldfield (1999) advocates that if sufficient paramagnetic or imperfect anti-ferromagnetic iron is burnt at a temperature of greater than 400°C then the magnetic properties of the material will alter greatly. This occurs because of reduction-oxidation reactions, the gain

and loss of an electron, respectively. Reduction conditions occur due to heating and rapid cooling, causing magnetite to form. Oxidation then takes place, allowing maghaemite to result in a thin soil layer under the fire (Jonscher 1975; Kletetschka & Banerjee 1995 cited in Dearing *et al.* 1996b; Le Borgne 1955 & 1960 cited in Oldfield 1999). Maher (1986) includes organic matter in the combustion of the soil as an important factor in creating reducing conditions in the soil pores (Figure 4.3).
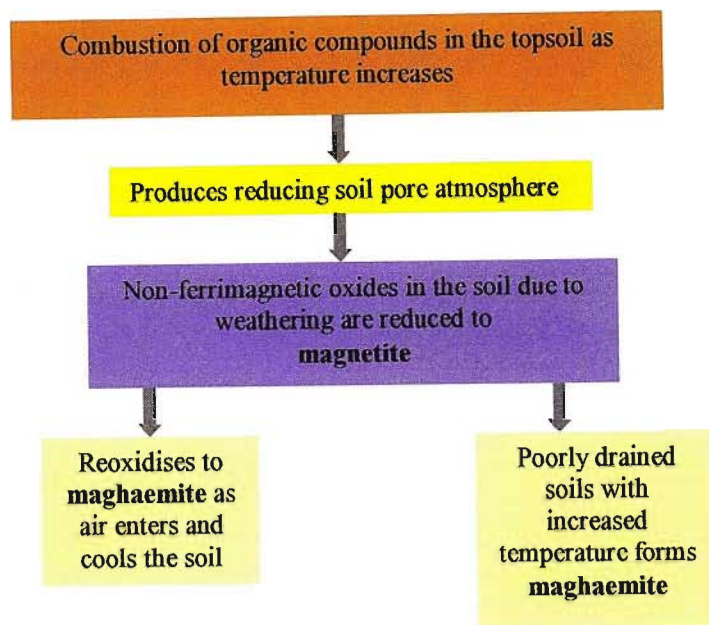
Figure 4.3: The formation of maghaemite due to burning (*after* Scheffer *et al.* 1959 cited in Maher 1986).

Research relating burnt soils to high $\chi_{FD\%}$ has been done extensively. Studies of sediment cores from Lago di Origlia, South Switzerland have found that $\chi_{FD\%}$ peaks correspond to charcoal peaks and thus catchment fires that caused viscous and SP grains to be present in the material (Oldfield 1999). A study in North Wales showed that soil, with no input of primary ferrimagnetic particles, burnt in forest fires had a maximum χ value of $36\mu m^3 kg^{-1}$ compared to a χ value of $0.13\mu m^3 kg^{-1}$ in unburnt areas (Maher 1986).

Dearing *et al.* (1996b) argue against burning as a major contributor towards increasing magnetic susceptibility in soils. Firstly, they argue that if crop burning causes an increase in the value of χ_{FD}, then arable land should have higher frequency dependent magnetic susceptibility than ley grasslands. However, the converse of this was found (Dearing *et al.*

1996b) as it was not taken into account that cultivation disrupts the pedogenic processes in the soil that result in the production of ultrafine-grained ferrimagnetic particles (Dearing *et al.* 1996a). Dearing *et al.* (1996b) propose as their second argument the findings of a study at Rothamsted Experimental Station where straw on adjacent plots was burnt or acted as control plots. The topsoil measurements in this study showed no significant differences in frequency dependent magnetic susceptibility following eight years of burning. Problems associated with these findings are that the burning was controlled, and natural fires are uncontrolled and thus may reach a higher temperature that could be conducive to the formation of ultrafine ferrimagnetic particles. The straw had also been cultivated and thus would be more spread out and less dense than natural vegetation, which may also contribute to higher temperatures in natural fires than those on cultivated land, lowering the production of ferrimagnetic particles. Dearing *et al.* (1996a) found that soil samples exposed to burning in the laboratory caused the $\chi_{FD\%}$ value to reach a high measurement of 12%. However this doesn't consider the interaction of environmental factors.

There is a strong interaction between burning, iron available, temperature and organic matter present (Thompson & Oldfield 1986; Dearing *et al.* 1996a). It is also thought that the soils most affected by burning are well drained (Thompson & Oldfield 1986). This can be linked to the findings that magnetite and maghaemite are often found in biologically active topsoil that is rich in organic matter (Le Borgne 1955 cited in Dearing *et al.* 1996a; Maher & Taylor 1988). This is related to the need to create a reducing atmosphere in the soil pores (Figure 4.3). Research has also found that in burnt areas the highest magnetic susceptibility readings were found around tree trunks, and this is related to the accumulation of organic matter (Maher 1986). A field experiment was carried out by burning soil profiles with an organic horizon to show the importance of organic matter because higher magnetic susceptibility measurements were obtained from the organic horizon than the inorganic horizon. The soil beneath the ashed organic layer was pink in colour (Longworth *et al.* 1979 cited in Thompson & Oldfield 1986), indicative of the change in composition of the iron oxides. Burnt topsoil can result in a range of colours: black, grey, pink or bright orange, depending on the amount of magnetic minerals formed. This occurs concurrently with a shift in multidomain magnetite to a high concentration of viscous and SP magnetite that occurs with a growing haematite component. This particular experiment found that mostly magnetite resulted (Thompson & Oldfield 1986), which goes against Borgne's (1955 cited in Oldfield 1999) theory that only maghaemite results from

burning. His theory can also be criticised for only examining maghaemite's formation though burning and anaerobic reduction (Jonscher 1975) when maghaemite occurs in smaller proportions in the environment to magnetite. There must thus be instances when maghaemite does not fully oxidise and magnetite remains.

Mullins (1977) also highlighted the importance of the availability of oxygen in burning. This can be linked to aiding the burning process and oxidation-reduction. Soil iron is yet another significant factor and the resultant ferrimagnetic particles are also thought to be more evident in iron-enriched subsoil (Maher *et al.* 1994 cited in Dearing *et al.* 1996a). Soils that are poor in iron gain minimal effects of enhancement by burning (Thompson & Oldfield 1986). This is an important point to note as it has important implications for fieldwork attempting to distinguish the topsoil from the subsoil using frequency dependent magnetic susceptibility.

Other factors that affect burning are the intensity of the fire. Fires that occur in the canopy only or low-intensity fires on the surface are not sufficient to alter surface minerals (Thompson & Oldfield 1986). Thompson & Oldfield (1986) express their concern in attributing ferrimagnetic particle formation to burning or pedogenesis because of the lack of sufficient means to differentiate the product of these two processes.

4.3.3 Topsoil

Research in the northern hemisphere found that there is a general inverse relationship in soil profiles between depth and χ_{FD} (Maher 1986) with magnetic susceptibility highest in the A horizon (Williams & Cooper 1990). Le Borgne (1955 cited in Maher 1986) and Jonscher (1975) term the abundance of ultrafine-grained ferrimagnetic particles formed by *in situ* conversions of iron oxides as 'soil enhancement'. This is attributed to the process of iron minerals, occurring as primary ferrimagnetic minerals or weakly magnetic forms of iron, being weathered to form ferrimagnetic grains through exposure to burning or pedogenesis (Figure 4.4) (Le Borgne 1955 cited in Thompson *et al.* 1980; Mullins 1977). Enhancement can be measured using X-ray diffraction (Longwoth 1977 cited in Thompson *et al.* 1980) and other methods including a frequency dependent magnetic susceptibility sensor.

Dearing *et al.* (1996a) found that pastures showed stronger frequency dependent magnetic susceptibility readings as the SFM pedogenic production was not as disturbed as in fields where ploughing occurred. Ploughing effectively vertically distributes the SFM thus mixing it with the subsoil (Dearing *et al.* 1996a).
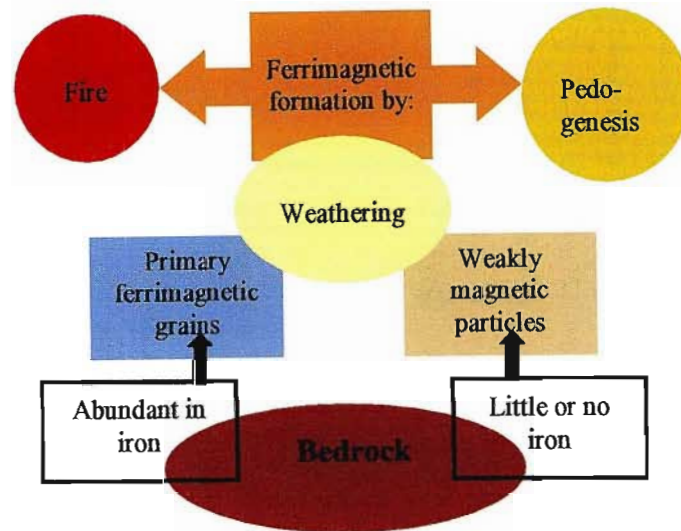
Figure 4.4: Formation of ferrimagnetic particles in the topsoil (*after* Le Borgne 1955 cited in Thompson *et al.* 1980; Mullins 1977).

4.3.4 Organic matter

Some researchers have found a correlation between magnetic susceptibility and organic matter. Neumeister & Peschel (1968 cited in Thompson & Oldfield 1968) obtained a correlation co-efficient of 0.64 between mass susceptibility and humus in the A horizon. Organic matter has also been found in low levels to encourage the reduction of iron that will allow for greater magnetic susceptibility of the soil to be measured. Thompson & Oldfield (1986) and Dearing *et al.* (1996b) support this idea and add that organic matter provides a substrate for microorganisms that aid the reduction of iron. This process is a function of soil temperature, water conditions, and quantity and type of organic matter. However, the mentioned process requires waterlogged conditions and magnetic susceptibility in these areas is very low, perhaps refuting the theory that organic matter leads to increased magnetic susceptibility.

Other researchers advocate that organic matter has diamagnetic properties (Williams & Cooper 1990) and thus results in a dilution of the magnetic signature (Maher 1986). Organic matter is also thought to play an important role in ferrimagnetic particles produced by burning (Maher 1986, Thompson & Oldfield 1986). This was disproved in a laboratory experiment using flour as a substitute for organic matter, due to its diamagnetic properties. The findings from the experiment were that maghaemite formation does not rely on organic matter alone but also is dependent on climatic conditions, freely draining soils and a high iron oxide content (Maher 1986).

Chapter 5: Measurement of magnetic susceptibility

5.1 Methods of measuring magnetic susceptibility

Magnetic susceptibility can be measured in various ways that supply different information regarding the sample mineralogy.

- *The low field susceptibility* is most commonly used and it gives a measurement using a low, single AC or DC magnetic field. This type of reading indicates the total ferrimagnetic mineral concentration. If ferrimagnetic minerals are not abundant then this measurement will supply information on the paramagnetic and canted antiferromagnetic minerals present.

- *High field susceptibility* refers to the measurement using a high DC field. This measurement is an indicator of the paramagnetic and canted antiferromagnetic minerals in the substance.

- *Frequency-dependent susceptibility* is the measurement of the difference in magnetic susceptibilities at high and low AC frequency. This measurement is useful in the detection of ultra-fine ferrimagnetic minerals within superparamagnetic dominant grains.

There is a variety in commercially obtainable equipment types but most users make use of the Bartington MS2 system for environmental research. This system is chosen more often because of its sensitivity for a range of applications, portable equipment for fieldwork and dual frequency alternative (Dearing 1999).

5.2 Bartington MS2 System

The Bartington MS2 System includes a meter and a range of alternative sensors. Each sensor can be used for a specific purpose and their uses include geology, soils, archaeology, hydrology, sedimentology, pollution and building materials. The meter expresses the magnetic susceptibility detected in cgs or SI (international susceptibility units measured in 10^{-5}SI). The meter calculates the susceptibility in either the range of 1.0 or 0.1, the latter being more precise (Dearing 1999). The different Bartington MS2 susceptibility sensors include:

- *The MS2B sensor* measures dual frequency magnetic susceptibility using a low frequency of 0.465kHz and a high frequency of 4.65kHz (Dearing *et al.* 1996a; Dearing 1999; Bartington 2001). This sensor measures samples in 10cm^3 tailor-made plastic pots or drill cores an inch long. This sensor comes in the form of a portable laboratory allowing fieldwork to be more convenient and allows for more rapid results that can be assimilated by environmental observations. It is used to identify the presence of ultrafine ferrimagnetic particles (Dearing 1999) that are present at the boundary of superparamagnetic and the stable single domain (Bartington 2001). This is particularly important for interpretation of information regarding weathering, soil formation, fossil soil categorisation and particle source investigations (Bartington 2001).

- *The MS2D loop* has a diameter of 185mm and is used for the quick assessment of surface substances, such as soils, rocks, and stream channels (Dearing 1999). The loop measures approximately the top 60mm of the surface (Bartington 2001). It is largely used for mapping and surveys (Dearing 1999), slope process studies and archaeological prospecting (Bartington 2001).

In the comparison of data received from the different sensors it is necessary to take into account that the measurements will vary due to the different field strengths, sample form and the effects of demagnetisation (Dearing 1999). Different sensors are used to highlight the presence of particular minerals (Caitcheon 1993) and this too needs to be acknowledged when comparing data from various sensors.

More accurate measurements using the Bartington sensors can be obtained in the method employed to: set-up the sensor, prepare the sample and measure the samples (Appendix I). All MS2 sensors are the most sensitive part of the entire system and therefore they should be used in a 'quiet' environment. These types of conditions should eliminate any changes in temperature or presence of electromagnetic fields or strong magnetic metals (Dearing 1999).

5.3 Frequency dependent magnetic susceptibility

Low-field AC susceptibility instruments measure the concentration of ferrimagnetic particles in the environment. These instruments are not able to distinguish between grain sizes or mineral types. Frequency dependent magnetic susceptibility has the ability to detect ultrafine ferrimagnetic particles that are indicative of SP grains lying at the SSD and

SP boundary (Maher 1986; Eyre 1997; Dearing 1999), which mainly are in the form of magnetite or maghaemite (Oldfield 1999). Other magnetic susceptibility instruments, including the MS2D loop's readings, are controlled by the concentration of ferrimagnetic particles which occur abundantly in rocks, soils, sediments and dust. Ferrimagnetic iron oxide particles include magnetite, maghaemite, titanomagnetite and titanomaghaemite (Dearing 1999).

5.4 Magnetic susceptibility measurements used in soil studies

The first studies of magnetism focused solely on environmental areas such as paleaomagnetism. Over the last 25 years magnetism has been found to be a useful means of investigating other environmental aspects (Smith 1999). Magnetism of environmental substances effects the concentration of magnetic minerals, which in turn tells us information regarding that material or the area in which it was found (Thompson *et al.* 1980). Magnetism is used in a broad variety of environmental studies from meteorology to soil science. In soil studies magnetism has been used for evaluating topics including topsoil (Williams & Cooper 1990; Dearing *et al.* 1997), slope processes (Williams & Cooper 1990), soil erosion in catchments (Hutchinson 1995) and the delineation of wetlands (Watson 2002). These areas of research depend on a measurement of magnetic susceptibility to determine the amount of magnetic mineral in the soil and this measurement acts as a signature for different types of soils.

Dearing (1999) identifies five ways in which magnetic susceptibility is useful to soil studies: Identifies the minerals present; quantifies concentration of minerals; categorises materials; determines the formation or transport processes; and develops fingerprints for specific materials.

Magnetic susceptibility measurements are increasingly being used in the field because of their ease of use, ability to be used on all substances, rapid and safe result, non-destructive nature, ability to be used in the laboratory or in the field and it is a complementary method to other types of analysis (Dearing 1999). However the frequency dependent magnetic susceptibility samples require augering and thus are not as "environmentally friendly" as the other types of magnetic susceptibility measurements. The convenience and rapid means of obtaining measurements allows the researcher to use a large sampling strategy as more measurements can be taken. Other methods tend to be expensive and time-consuming. The

ability to obtain results in the field allows for field data to be linked to observations, and this is especially important for research in remote areas that cannot easily be revisited (Dearing 1999).

Chapter 6: The factors of soil formation and their influences on magnetic susceptibility

Soil is an important resource and external and internal processes largely determine its composition. Soil can be defined as a "dynamic natural body with properties from combined effects of climate and biotic activities, as modified by topography, acting on parent materials over periods of time" (Brady & Weil 1999).

6.1 Soil formation

6.1.1 Factors influencing soil formation

Soils result from the interaction of weathering and various other variables including parent material, climate, living organisms, topography and time.

- *Parent material*: Soil characteristics are shaped by the parent material (Harpstead *et al.* 1997; Brady & Weil 1999; Singer & Munns 1999). Certain parent materials are more resistant to weathering than others due to the chemical and mineralogical make-up (Brady & Weil 1999; Singer & Munns 1999), hardness and porosity (Singer & Munns 1999). Granite, for example, has quartz particles which are resistant to weathering and thus forms a gritty sandy soil. Basalt, on the other hand, is less resistant to weathering and forms a clayey soil (Harpstead *et al.*1997). Hardness tends to decrease weathering of a rock but greater porosity will allow movement of water and acids through the material, thus increasing weathering (Singer & Munns 1999). Soil texture in turn affects the percolation of water within the soil, which changes the freedom of movement of the fine soil grains and nutrients through the profile (Brady & Weil 1999). Different minerals weather at various rates thus allowing for the formation of different products and soils. The differently sized minerals in the material determine the speed at which it can be weathered, for example generally those with greater surface areas are weathered more quickly (Singer & Munns 1999). Inorganic parent material can be formed *in situ* due to the weathering of residual material and rock, or material that has been transported and deposited in the area. Therefore parent material can be classed according to its depositional characteristics. These include colluvial debris which are transported downslope due to gravity, alluvial sediments that are deposited on the floodplain following a flood, and residual material that has been weathered in a

highly stable landscape (Brady & Weil 1999). Because these materials are unconsolidated after being transported and deposited they weather quicker than consolidated material (Singer & Munns 1999). Parent material is also influential in the type of vegetation evident in the landscape, and this in turn contributes to the litter and soil development of the area (Brady & Weil 1999).

As discussed in Section 4.2.1 parent material contributes largely to the type of magnetic minerals formed during pedogenesis and thus the MS of the soil. Thus soils with igneous parent material are likely to have higher MS values than other soils (Thompson & Oldfield 1986).

- *Climate*: Precipitation and temperature are the main climatic factors influencing soil formation (Harpstead *et al.* 1997; Brady & Weil 1999), as these influence the rate of chemical, physical and biological processes and thus the weathering of the material. Harpstead *et al.* (1997) view precipitation in this context as purely the amount of water inputting the system. However, Brady & Weil (1999) use the concept of effective precipitation focusing on not only the input of water into the system but the final amount that reaches the regolith (broken down material) and thus affects soil genesis (Figure 6.1). This system accounts for evaporation and loss due to plant uptake and runoff on slopes. Brady and Weil (1999) find that the higher the amount of effective precipitation the greater the amount of pedogenesis. They also suggest that excess water percolating in the soil carries dissolved and suspended grains from the upper to the lower horizons, where the soluble minerals are lost to runoff or groundwater. The greater amount of percolation thus enhances weathering and ultimately horizon differentiation of the soil profiles. In dry regions where the soluble salts are unable to be percolated to the lower parts of the soil, a build up of these salts occurs. In this way temperature interacts with precipitation in enhancing pedogenesis (Brady & Weil 1999).

Temperature doubles biochemical reactions with an increase of 10°C, which speeds up weathering processes and thus pedogenesis. Warm environments with large amounts of precipitation have more highly, deeply weathered, well-percolated soils and large amounts of plant growth, while in colder areas there is comparatively less profile development. Climate influences the types of vegetation present i.e., humid areas usually exhibit more trees, subhumid and semiarid areas are likely to have

grasslands and arid regions normally have shrubs and bushes for the majority of ground cover.

Pedogenesis is dependent on the interaction of water and temperature. Temperature and precipitation affect plant growth and organic material decomposition, thus increasing or decreasing organic matter content in the soil and, respectively, speeding up or inhibiting pedogenesis. Evaporation resulting from higher temperatures lowers the effective precipitation so that there will be less percolation of water through the soil and slower soil development rates than colder areas with the same rainfall (Figure 6.1 (a)). Seasonal variability in precipitation is seen by Singer and Munns (1999) as important in terms of the temperature of the soil when precipitation enters the soil and weathering occurs. For example weathering due to snow in cold winter soils will be less effective than rainfall in warmer summer conditions. Permeability of the soil influences the amount of water percolating within the soil, for example a coarse sandy soil will allow more movement of water than a tight clay (Figure 6.1 (b)), thus increasing the amount of soil development occurring (Brady & Weil 1999).
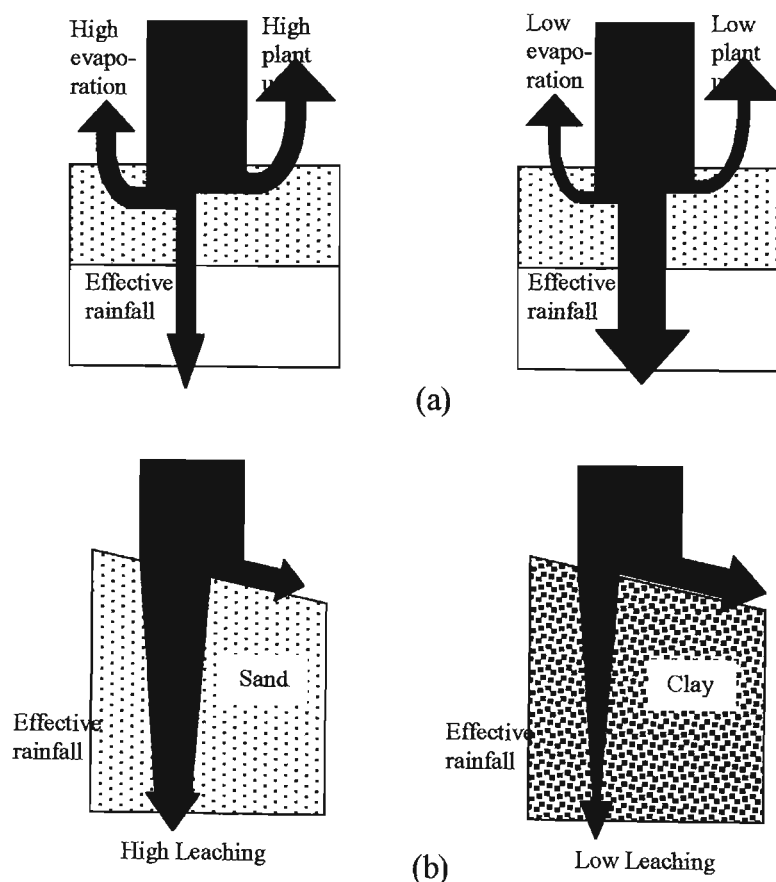
Figure 6.1: Effective rainfall due to (a) evaporation and plant use and (b) soil type (*after* Brady & Weil 1999).

Climate is an important factor in determining a soil's MS, for example large amounts of effective rainfall can lower MS due to dissolution (Thompson & Oldfield 1986).

- *Time*: Soil formation is affected by time and certain horizons will take different lengths of time to form. For example an A horizon will take a decade or more to develop while a B horizon in a humid environment will take more than 40 years (Brady & Weil 1999). The terms 'young' and 'mature' or 'old' soils are not related to the soil's age but the extent of profile differentiation and weathering in the soil (Leeper & Uren 1993; Brady & Weil 1999). Leeper & Uren (1993) refer to young soils as those in wetter climates or where weathering and percolation of water in the soil are continually active in the profile. This leads to the incorrect assumption that old soils have reached a point where no pedogenesis occurs (Leeper & Uren 1993). Older soil tends to exhibit a high clay content due to the physical and chemical breakdown of large grains (Harpstead *et al.* 1997). Older soils are more likely to be found in countries that were not exposed to event glaciation i.e., most of the southern hemisphere countries. In these countries residual parent material is exposed to soil forming processes for a longer period of time than transported materials, including soils affected by glacially deposited material in North America, Europe and Asia. The mineralogy of the younger soils will be closer to the parent material than in the unglaciated areas. The time the soil takes to form is dependent on many interacting factors, including climate, parent material, topography and living organisms. For example a soil in a warm climate with a high rainfall on parent material rich in easily weathered minerals will have more profile development and weathering than a steeply sloping environment in a cold climate with an impermeable parent material.

Time may influence MS as one theory for the concentration of primary ferrimagnetic minerals is due to long-term weathering and pedogenesis (Singer & Fine 1989 cited in Dearing *et al.* 1996b), therefore younger soils would display lower MS .

- *Topography:* The elevation, slope of the area and the overall landscape can accentuate or decrease climate's affect on weathering. Steep slopes allow for rainfall to runoff rather than infiltrate the soil, thus causing more erosion than pedogenesis (Brady & Weil 1999). Steep slopes have less effective precipitation entering the regolith than flatter landscapes (Brady & Weil 1999; Singer & Munns 1999). Therefore convex slopes are likely to have less developed soils than concave slopes where water can accumulate and infiltrate the soil. Plant cover is also a factor mediating the affect of erosion, as areas with less plant cover, as found in steep slopes of arid areas are less likely to have rain infiltrating the soil and will thus exhibit poorly defined shallow profiles (Brady & Weil 1999). The aspect of the slope will influence the absorption of solar energy and thus temperature of the slope. For example north-facing slopes in the southern hemisphere are warmer and less moist, thus having lower organic matter content and less weathering than south-facing slopes (Brady & Weil 1999; Singer & Munns 1999). Climate and vegetation do not interact alone with topography, parent material forms the basis for topography, e.g. resistant sandstone may form steep sloping ridges (Brady & Weil 1999).

Topography has been shown to have an effect on MS, with soil at the bottom of a slope having higher MS values than the upper slope soils (Dearing *et al.* 1986; de Jong *et al.* 1998).

- *Biota (living organisms):* The activity of organisms in the soil is enhanced by organic matter content increases, biochemical weathering, profile mixing, nutrient cycles and aggregate stability. Vegetation is important to the soil as it, firstly, protects the soil surface from erosion. Secondly, the leaves forming litter on the surface produce organic acids that dissolve iron and aluminium minerals. This allows for the movement of these elements down the profile and their accumulation in the B horizon, leading to horizon differentiation. The organic matter that is added to the soil varies with the type of vegetation, e.g. grasses add root material whilst trees contribute mostly leaves to organic matter. Therefore soils under grasslands have deeper A horizons and greater depth distribution of organic matter than those of forests (Brady & Weil 1999). Singer and Munns (1999) also acknowledge that

vegetation plays an important role in adding and removing ions and nutrients to the soil, which contribute to soil genesis.

Animals, including moles, earthworms and termites, burrow into the soil and bring this material to the upper layers, a process known as bioturbation (Brady & Weil 1999; Singer & Munns 1999). This allows for the soil to become mixed and thus lose the accentuation between the layers. However, it also allows for water and air to enter the soil more easily and so increases aggregate stability (Brady & Weil 1999). It could also be assumed that the increase of access of water to subhorizons, especially in otherwise impermeable soils, would allow for further soil development.

Magnetostatic bacteria have been shown to produce ultrafine-grained ferrimagnetic particles such as magnetite, thus increasing the MS of the soil. However these are thought to only occur in anaerobic conditions (Lovely *et al.* 1987). Large amounts of vegetation are likely to add high quantities of organic matter to the soil. The effect of this on MS is still debated. Thompson & Oldfield (1986) and Dearing *et al.* (1996b) argue that it decreases MS values while Maher (1986) and Williams & Cooper (1990) advocate it decreases measurements.

It is significant to remember that all the soil formation factors interact and the resultant soil will be an interplay of parent material, climate, time, topography and biota (Brady & Weil 1999; Singer & Munns 1999). Similarly MS relies on the interaction of these factors in the formation of magnetic minerals.

Chapter 7: Weathering and narrow processes of soil formation

Soils forms over time due to a gradual and continuous process, known as pedogenesis (Gerrard 2000). Soil originates from weathered parent material, which is largely dependent on the climate (Leeper & Uren 1993; Harpstead *et al.* 1997). This residual weathered rock known as the regolith, is then subjected to soil forming processes (Nortcliff 1983; Harpstead *et al.* 1997). Following these processes, layers in the soil known as horizons indicate the soil development that has occurred over time.

7.1 Soil profiles

Soil processes change both the parent rock material and organic matter-rich soil horizons (Figure 7.1). The topsoil (horizon A) is usually an accumulation of humus and is dark in colour with a mixture of mineral and organic matter and thus a large amount of biological activity occurs in this horizon (Singer & Munns 1999; Gerrard 2000). The chemical and physical properties of this horizon differ from the parent material because of the large amount of pedogenesis occurring in this horizon. However, if erosion of this layer takes place the soil development process becomes retarded (Brady & Weil 1999). A soil horizon that generally occurs below the A horizon is the E horizon consisting of soil leached of clay, Fe and Al (Harpstead *et al.* 1997; Gerrard 2000). The subsoil (B horizon) usually has a large percentage of clay, oxides and hydroxides of Fe and Al, due to the illuvial accumulation of elements from the leached horizon above (Singer & Munns 1999; Gerrard 2000). The B horizon acts as a transitional horizon from A to C (Gerrard 2000). In this horizon soil has undergone a large amount of pedogenesis and consequently there are no structural similarities between the soil in the B horizon and the parent material. Material is likely to accumulate in this horizon due to soil processes in the upper soil layers, therefore iron and aluminium oxides may be abundant in this horizon (Brady & Weil 1999). The C horizon is the section of the profile where the level of humus decreases greatly, and therefore this section is less affected by biological activity (Gerrard 2000). The C horizon consists largely of unconsolidated material (Harpstead *et al.* 1997) that retains the features of the parent material (Brady & Weil 1999). Over time the upper part of the C horizon may become weathered and thus become part of the solum (Brady & Weil 1999). The A, E and B horizons are known as the solum and are the soil profile section altered by soil-forming processes (Harpstead *et al.* 1997; Gerrard 2000). On the top of the A horizon there may be

plant residue termed the O horizon. This occurs when organic matter input exceeds transformation (Gerrard 2000). If the bedrock exists within a few meters of the surface it is referred to as the R horizon (Harpstead *et al.* 1997). Different horizons in the profile may have alternative geological origins, but is more likely that they will be of the same parent material (Leeper & Uren 1993). However this concept is based on northern hemisphere soils and does not always apply to South African soils.

Mullins (1977) advocates that different horizons of a profile will have specific magnetic signatures because of the various magnetic minerals within each horizon. However, a profile where most of these minerals have been leached out or are not well-developed may not show distinct variations in MS layering.

O	Loose leaves and organic debris, largely undecomposed
O	Organic debris, partially decomposed
A	A dark-coloured horizon of mixed mineral and organic matter with much biological activity
E	A light-coloured horizon of maximum eluviation
EB	Transitional to B but more like E than B: may be present
BE	Transitional to B but more like B than E: may be present
B	Maximum accumulation of silicate clay minerals or of sesquioxides and organic matter
BC	Transitional to C but more like B than C: may be absent
C	Weathered parent material, occasionally absent: formation of horizons may follow weathering so closely that the A, E or B horizon rests on consolidated rocks
R	Layer of consolidated rock beneath the soil

Figure 7.1: A profile illustrating the soil horizons (Gerrard 2000)

7.2 Soil processes: inputs, outputs, transformations and translocations

Soil processes may become disrupted due to climate or vegetation changes and erosion or deposition, which then either enhances or limits pedogenesis. Erosion may cause the soil to be stripped down to the C horizon, while deposition may form a new C horizon and the A horizon will transform into the subsoil. From this it is clear the processes operating in the soil can be categorised into inputs and outputs, which ultimately lead to transformations and transfers (Nortcliff 1983; Gerrard 2000) (Figure 7.2). The inputs largely occur from the surface soil, because of vegetation, water and dissolved minerals from precipitation, particles from wind and water erosion and mass movements including soil creep. Nortcliff (1983) also includes energy from sunlight and transformation (discussed below) by-products as inputs. Outputs are evident in soil erosion, throughflow, deep percolation of dissolved elements in water, nutrient uptake by plant's roots (Gerrard 2000), decomposition of organic matter and loss through respiration (Nortcliff 1983). Transfers refer to the transfer of clay, organic matter, iron and aluminium and calcium carbonate vertically down the soil. This results in layers losing minerals (eluvial layers) and an accumulation in other layers (illuvial layers). Transfers may also occur vertically upwards, for example during evaporation, and horizontally through the soil, such as on slopes. Transformations involve the breaking down of organic matter to form humus, and decomposition and weathering of the regolith's primary minerals leading to the release of the cations, largely calcium (Ca^{2+}), magnesium (Mg^{2+}) and potassium (K^+) (Nortcliff 1983).

The development of the various profiles occurs at varied rates due to differing environmental conditions. This is related to two fundamental assumptions: ongoing processes affect the soil's development, and the rate of pedogenesis varies over time. If the environment were to become stable, the soils would too reach a stable state. Consequently the soil can be viewed as developing in relation to the changes in the environment (Nortcliff 1983).
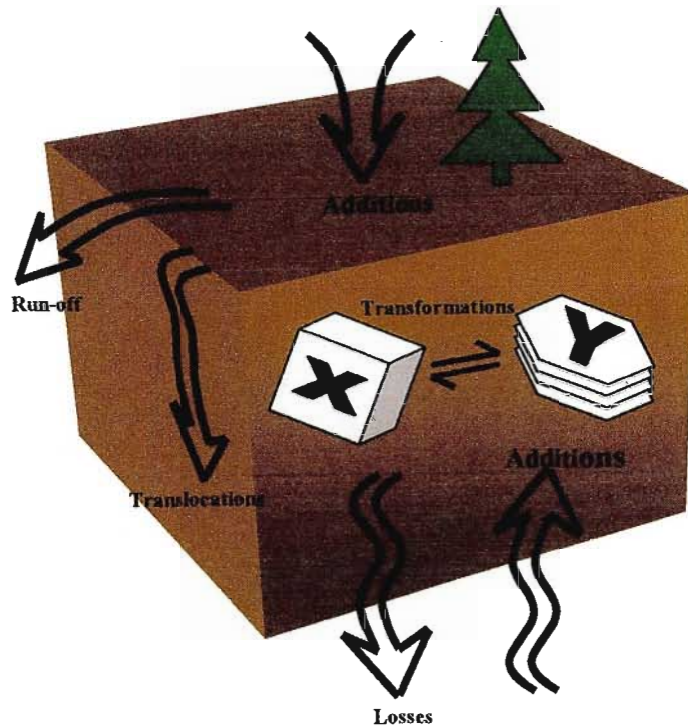
Figure 7.2: A schematic illustration of additions, losses, translocations and transformations as the fundamental processes driving soil profile development (*after* Brady & Weil 1999).

7.2.1 Transformation

Transformation involves the breakdown of organic matter and the change, decomposition or formation of soil minerals (Brady & Weil 1999). Transformation occurs in the processes of weathering, organic matter decomposition, the effects of waterlogging and soil ripening.

i) Physical weathering

The result of physical weathering is the breakdown of rocks ultimately to particles of silt and clay, thus disintegrating the material into minerals (Brady & Weil 1999). Physical weathering occurs due to:

- *Unloading*: creation of fissures due to reduction of pressure after erosion (Gerrard 2000) and further weathering occurs on the fissures through exfoliation and grain disintegration (Summerfield 1991).

- *Thermal processes*: temperature differences due to greater temperature on the outside of material than the core (Gerrard 2000) or cooling and heating related to

the time of day result in the minerals' expansion and contraction, that can cause fissures to develop (Gerrard 2000). Brady and Weil (1999) also suggest that the different expansion rate of various minerals leads to stress within the rock and ultimately the physical breakdown of the rock.

- *Processes that results in the expansion of the material's pores*: through ice (frost weathering occurs when water freezes in the pores) or salts (salt weathering results in the precipitation of salts in voids, the expansion of these crystals through heating or hydration). These processes ultimately shatter the rock (Summerfield 1991).

The extent of physical weathering on a material will depend mostly on the pore size, the greater the amount of micropores that are saturated the more weathering that will occur (Gerrard 2000).

ii) Chemical weathering

Chemical weathering releases and synthesises minerals occurring from material broken down due to physical weathering. The effects of chemical weathering are increased by water and its solutes, oxygen and organic and inorganic acids due to biochemical processes. Particle sizes decrease during chemical decomposition and may finally become dissolved in and lost to runoff or form different minerals that are resistant end products. The oxides of iron and aluminium and some silicate clays are examples of resistant end products as they persist after other minerals have been removed (Brady & Weil 1999). Soil formation is most greatly influenced by the following chemical weathering processes:

- *Solution*: water acts as a solvent for minerals (Summerfield 1991) and these are moved within the profile or they are lost (Gerrard 2000) depending on the mineral's solubility (Nortcliff 1983). A highly soluble soil constituent, such as calcium carbonate, will be dissolved by the water and completely removed from the soil. However, the least soluble minerals, for example quartz, remains as the soil's skeleton. Important to note is that the soil minerals may change due to transformation and interaction with other soil constituents.

- *Carbonation and other acid reactions*: acid increases weathering due to its ability to increase the activity of hydrogen ions in the soil water. This is evident when carbon dioxide, due to microbial and root respiration, is dissolved in water to produce carbonic acid which encourages the chemical decomposition of calcite in limestone.

$$CO_2 + H_2O \rightleftharpoons H_2CO_3$$

<div align="center">carbonation</div>

$$H_2CO_3 + CaCO_3 \rightleftharpoons Ca^{2+} + 2HCO_3^-$$
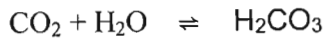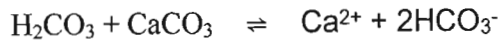
Carbonic acid Calcite (solid)   (solution) (solution)

Other stronger soil acids including nitric acid (HNO_3) and sulphuric acid (H_2SO_4) and organic acids are also active. These acids and hydrogen ions linked to clays may cause the chemical decomposition of soil minerals (Brady & Weil 1999).

- *Hydration*: is the absorption of water in the mineral lattice (Nortcliff 1983; Brady & Weil 1999; Singer & Munns 1999; Gerrard 2000), for example hydration of iron haematite results in goethite:

$$Fe_2O_3 + H_2O \rightleftharpoons 2FeOOH$$
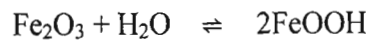
Haematite   Goethite

Hydration causes many minerals to expand, such as smectites, and shrink when water leaves the material (Singer & Munns 1999). Continuous hydration and dehydration can ultimately result in physical weathering (Singer & Munns 1999; Gerrard 2000).

- *Hydrolysis*: is the replacement of elements in minerals by hydrogen (H^+) ions and hydoxyl (OH^-) ions resulting from water (Nortcliff 1983; Singer & Munns 1999), leading to the break down of these minerals and the formation of a new clay mineral and by-products that are soluble. The by-product may then either move out of the soil through solution or remain in the soil by combining with other soil constituents creating new minerals (Nortcliff 1983). The addition of the H^+ or OH^- to the structure results in physical strain in the structure and increases weathering. Hydrolysis can be accentuated by lowering the pH of the soil, addition of decomposed organic matter, biochemical processes such as nitrification and high temperature (Singer & Munns 1999).

- *Oxidation/reduction*: occurs when an atom loses or gains an electron, respectively (Summerfield 1991; Gerrard 2000). Oxygen is able to accept electrons in the soil, but if it is not available then another element will act as the electron receptor. The former condition is termed aerobic and the latter refers to anaerobic conditions. Anaerobic conditions are usually found in waterlogged states of the soil. Oxidation,

therefore, results in soils with access to air or oxygenated waters. Oxidation favours well-drained soils, high temperatures, and the decomposition of organic matter (Gerrard 2000). One of the elements most commonly involved is iron and may lead to ironstone concretions. These ironstone gravels are usually absent from the parent material and thus have formed due to pedogenic processes. The formation of these is thought to be due to the reduction of iron in the form of Fe^{3+} to Fe^{2+} during waterlogging and an absence of oxygen (Leeper & Uren 1993). This is evident in the grey or bluish-grey colour of the soil occurring during reduction (Nortcliff 1983). In drier times oxygen enters the soil and Fe^{2+} is converted to ferric oxide, leading to a red soil. An important consideration is that if a soil has reached the extent of waterlogging to produce ironstone, it will exhibit the loss of necessary soil elements (Leeper & Uren 1993).

In aerobic conditions the iron in the rock, in the form Fe^{2+}, becomes oxidised to Fe^{3+} due to water and air exposure at the time of soil formation (Brady & Weil 1999). The oxidation process can cause strain within the mineral's crystal structure and thus weathering is accentuated (Singer & Munns 1999). Oxidation can also lead to the simultaneous oxidation to Fe^{3+}, such as the release of ferrous oxide from olivine and the instant oxidation to goethite.

<div align="center">
Hydrolysis

$$3MgFeSiO_4 + 2H_2O \rightleftharpoons H_4Mg_3Si_2O_9 + 2SiO_2 + 3FeO$$

Olivine (solid)   Water   Serpentine (solid) (solution) Fe oxide(solid)

Oxidation

$$4FeO + O_2 + 2H_2O \rightleftharpoons 4FeOOH$$

Fe oxide   Goethite
</div>
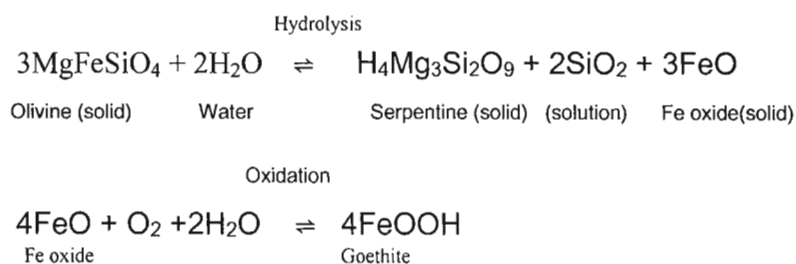
The change in colour of the soil is evidence of the altered minerals and oxidation and reduction of iron in the material (Brady & Weil 1999; Singer & Munns 1999).

- *Chelation or organic complexing*: occurs when bonds are created between metal atoms and organic molecules, resulting in the solubility of the metal. This can be seen in the weathering of surfaces covered by lichen. This process is particularly important for Fe (iron) and Al (aluminium) solubility (Gerrard 2000). This type of chemical weathering is particularly effective in speeding up the formation of soil (Brady & Weil 1999).

iii) Integrated weathering processes

Chemical and physical weathering processes may work simultaneously although they are separate processes. An example of this interaction is the hydrolysis of a primary mineral causing the release of ferrous iron (Fe^{2+}), followed by the oxidation to ferric iron (Fe^{3+}) which is hydrated to the form hydrous iron oxide. Hydrolysis or complexation of this substance produces soluble cations, silicic acid and aluminium or iron compounds. A humid environment would lead to the soluble cations and silicic acids to be lost to drained water where these may recombine to produce silicate clay and secondary minerals of silicate (Brady & Weil 1999).

Weathering is influenced by the climate it occurs in and physical weathering is more successful in dry, cool regions, while chemical weathering is most affective in wet and hot environments. The majority of weathering takes place simultaneously and thus increases the overall rate of weathering (Brady & Weil 1999).

iv) Organic matter decomposition

Organic matter decomposition is a significant transformation in soil. There are various factors that control it, including organic substrate quality and quantity which affect the pH (undecomposed matter has a low pH), soil moisture and amount of nutrients and energy available (the older the plant the less protein it has) and soil moisture, as it influences temperature, leaching and aeration and breaks down substrates through freeze-thaw processes (Gerrard 2000).

v) Waterlogging

Waterlogged conditions result when water movement in the soil is impeded or reduced to very slow rates. This then prompts reduction of the elements. Decomposition of organic matter is reduced due to the lowered pH levels and lack of oxygen resulting in slower anaerobic decomposition (Gerrard 2000).

vi) Soil ripening

Soil ripening relates to the physical, biological or chemical change in waterlogged or flooded soils that have dried out. Physical ripening refers to the contraction of the soil mass as it dries producing cracks, causing air to enter the soil and oxidation replacing reduction. From this chemical ripening will occur due to the oxidation of organic matter,

iron and manganese. Biological ripening results when the soil is mixed because of plants or animals and this is evident in coastal swamps where stratification is destroyed over time (Gerrard 2000).

vii) Magnetic susceptibility

Weathering has vastly different effects on the soil's MS, which is also influenced by factors such as parent material, climate and organic matter. This is illustrated by the following example. Weathering of igneous parent material leads to the change in state of iron from reduced Fe^{2+} to the oxidised form of Fe^{3+}. More commonly the iron's low solubility leads to its precipitation as an oxide or hydroxide. However, in oxygen-depleted environments iron may return to its reduced form allowing for a more soluble oxide form that allows for its movement within the profile to an area where it may be oxidised. Weathering of magnetite rich igneous material results in the formation of soil dominated by haematite and/or goethite. Soils that formed in environments of high temperatures, good aeration, fast decomposition of organic matter and frequent periods of high pH are richer in haematite. In cool, moist areas where pedogenesis occurs over longer time periods goethite is more likely to form. This is due to the dissolution of haematite, through reduction or chelation, and reprecipitation in more oxidising conditions (Thompson & Oldfield 1986).

7.2.2 Transfers/ translocations

The processes that cause the movement of inorganic and organic material within the soil are seen as transfer processes (Brady & Weil 1999; Gerrard 2000). Water and soil organisms are largely responsible for these processes. It is important to note that both transfers and transformations result in an accumulation of material in a soil horizon (Brady & Weil 1999).

i) Pedoturbation

Pedoturbation results when the soil is mixed and is either detrimental or significant to horizon development. Biological pedoturbation involves organisms such as earthworms that mix and aerate the soil. Non-biological pedoturbation includes wetting and drying sequences that can redistribute the soil and eventually lead to soil creep, and frost churning due to repeated frost and ice segregation causing organic matter to be forced deeper into the mineral layers (James 1970 cited in Gerrard 2000).

ii) Percolation and infiltration

Infiltration relates to the entering of water into the soil and percolation is the passage of the water through the soil. When water moves through the soil it displaces water previously in the soil (Gerrard 2000).

iii) Eluviation

Eluviation is the transfer of material in suspension, and involves the process of leaching and cheluviation. The process of leaching results when soluble soil substances are removed by percolating water. Different salts will be affected in different ways according to the climate. Sodium chloride ($NaCl$), sodium sulphate (Na_2SO_4) and calcium sulphate ($CaSO_4$) in a wet climate, are totally washed out of the soil. However, in dry climates the highly soluble sodium chloride is only leached down to the subsoil, while calcium sulphate occurs near the surface, sometimes in the form of crystalline gypsum (Leeper & Uren 1993).

The presence of bicarbonates in the soil determines its acidity, and includes Ca, Mg, K and Na. These elements are true bases and their loss results in an acidic soil, so that most wet climates tend to have more leaching and thus more acidic soils than drier areas. The clay constituents of Fe, Al and Si are also subjected to leaching in a soil profile. Si has been found to be more leached out of the soil over time. Fe and Al are more immobile, except when organisms are present and in acidic sandy soils, thus these elements tend not to leach down the soil profile (Leeper & Uren 1993).

Cheluviation refers to the process whereby soluble organic complexes cause the metal cations, especially iron and aluminium, to move to another part of the soil profile. Organic materials that cause cheluviation are firstly compounds washed directly from plant foliage or litter, and secondly the end products of the decomposition of the organic matter (Gerrard 2000).

iv) Illuviation

Illuviation is the accumulation of elements such as clay minerals, iron and aluminium oxides and hydroxides, and organic matter. The reason for this phenomenon is thought to be due to either a mechanical sieve effect, where the lower pore spaces of the soil will be filled with proportional sized material from upper horizons. A second school of thought

advocates that transferred material is chemically altered leading to decreased solubility and thus precipitation (Gerrard 2000).

The transfer of weathered particles in the soil is dependent on the rate of water movement through the soil. If the eluviation of the particles is slow, for example in waterlogged soils, weathering cannot supply particles for removal. On the other hand arid soils are poorly developed because of the lack of water movement within the soil (Nortcliff 1983).

Areas in a soil profile that have lost magnetic minerals due to transfers will display a lower MS while in comparison those areas of accumulation will show higher MS values. Pedoturbation was found to display a single peak in the profile within the mixed layer, the peak was thought to be situated where pedogenesis was enhanced by the presence of organic matter (Thompson & Oldfield 1986). However, this is contrary to the idea that organic matter lowers MS (Maher 1986; de Jong *et al.* 1998).

7.2.3 Inputs/ Additions

Additions are the inputs of material from external sources to soil that is developing, for example organic matter in the form of leaves, dust and soluble salts.

7.2.4 Losses

Losses refer to the material that is lost from the soil system, and includes leaching.

i) Leaching

Decaying plant residues form organic acids that are then percolated in the soil by water. This then initiates weathering processes by dissolving and leaching chemicals from upper to lower horizons. These are then precipitated in various horizons creating horizons with depleted or accumulated material. Substances that are dissolved are positively or negatively charged ions that result from the decomposition of organic matter and soil minerals. Many semi-arid areas experience leaching resulting in horizons with calcite ($CaCO_3$) or gypsum ($CaSO_4.2H_2O$) is present. In high rainfall areas the soluble material may be lost from the profile by entering drainage water. This removal of weathered material encourages weathering to occur, causing the soil profile to increase in acidity and lose the elements Ca, Mg and K. However, these may be absorbed by plant roots and thus

returned to the surface soil through litter ultimately lessening weathering and soil development processes (Brady & Weils 1999).

Soil horizons that have undergone leaching have been shown to have lower MS values. This is associated with the dissolution of magnetic minerals including haematite and maghaemite, which could ultimately lead to the formation of goethite (Schwertmann 1988 cited in CSIRO 1997). Goethite has a lower MS value and thus the overall MS of the horizon will decrease (Schwertmann & Taylor 1977 cited in Maher 1986).

Chapter 8: Major pedogenic processes

Nortcliff (1983) views the main pedogenic processes as a consequence of inputs, outputs, transfers and transformations occurring in the soil, resulting in specific soil profiles and morphology.

8.1 Erdefication

Erdefication results in a profile that is brown in colour, termed a brown earth, with no distinct contrasts in the profile. Weathering, wetting and drying, mixing resulting from plants and burrowing animals, humus formation from organic matter and the mineral matter mixing with organic matter physically and biochemically, result in erdefication. Consequently transformations can be identified as the major narrow soil processes that dominate in this type of soil. Erdefication is a soil system in a balanced state with the environment, where inputs are relatively balanced to outputs. It relies on input consisting of material and energy from the environment that it transforms and redistributes (Nortcliff 1983). Brown earth profiles only display χ peaks in the mixed A horizon because of the contact between decaying organic matter and soil minerals. The mixing of the A horizon is thought to be due to biological disturbance by earthworms (Thompson & Oldfield 1986).

8.2 Lessivage

Lessivage is often viewed as the further development of the soil from a brown earth, as it involves the leaching of clay minerals from the A horizon and accumulation in the B horizon. The resultant B horizon is termed an *argillic* hoizon and is notated as Bt. This process requires the addition of precipitation to the profile and transfer of the clay down the profile. Transformation does not play a significant role in this process and some clay may be lost to drainage water (Nortcliff 1983). The transfer of minerals to the B horizon is likely to result in a high MS in this soil horizon (Thompson & Oldfield 1986).

8.3 Podzolisation

Podzolisation results in a distinct profile of a bleached eluvial horizon above an accumulation zone in the upper B horizon. Podzols generally develop on parent material that is freely-drained, and often occur under grasslands or coniferous forests. The most important process within a podzol is the transformation of iron, aluminium and organic matter to a soluble form in the A horizon that allows illuviation of these to occur in the B

horizon. This process is thought to be assisted by chemicals present in litter or living plants. However, this is still contested and there are many other theories around the causes of the movement of these metals to the B horizon (Nortcliff 1983).

Podzol profiles were found to have the following MS characteristics in their profiles: thin layers of enhancement with χ peaks at the surface and minimum χ values, close to 0, in the rest of the horizon indicating an eluviated A horizon; and increases of χ in the B horizon evident of Illuviation (Thompson & Oldfield 1986).

8.4 Gleying

Gleying results when water is prevented from moving through the soil freely, due to a high water table such as in low-lying area, or a layer of impermeable material in the soil preventing downward drainage of the water. The waterlogging of the soil causes reduction to occur and this is accentuated by organic matter and microbial activity. These conditions allow for the transformation of certain minerals into a more soluble state, such as the insoluble Fe^{3+} is reduced to the soluble form of Fe^{2+} that is more easily transported in water. If waterlogging persists then some iron may be lost from the soil to drainage water. In most cases waterlogging is seasonal and therefore reduction and oxidation will occur at different periods of time. Consequently the appearance of the soil will appear mottled as orange and brown soil grains result from oxidation, whilst grey and bluish-grey soils indicate reduction. Gleyed areas due to groundwater are predominately wet and thus peds with orange exterior (soil aggregates) and grey interiors due to reduction are present. In areas where water is restricted due to a permeable layer (surface-water gleys) the gleyed area is able to dry out in certain seasons and thus the peds in this soil have an external grey surface with an orange or orange-brown interior (Nortcliff 1983).

Gleying in soils has been shown to decrease magnetic susceptibility, due to the dissolving or leaching out of ferrimagnetic particles from the horizon. The superparamagnetic particles are thought to be most susceptible to dissolution (Thompson & Oldfield 1986).

8.5 Calcification

In areas that receive moderate amounts of precipitation the calcium carbonate is transported from the upper section of the profile to the lower zones where it accumulates in a calcic horizon denoted as B_{ca}. These deposits of calcium carbonate in pores and fissures

are clearly evident as white specks among the soil. Areas that receive low-rainfall have a restricted output of water or dissolved minerals from the profile's base, including calcium carbonate (Nortcliff 1983). Calcium carbonate is a diamagnetic material and is thought to dilute the MS signal (Thompson & Oldfield 1986; Dearing 1999), therefore calcification can be expected to decrease MS in a profile.

8.6 Salinisation

Arid areas have a restricted movement of soil minerals within the profile due to the lack of rainfall. However, when the water table occurs near the surface of the profile there is an upward transfer of water and soluble salts due to evaporation. This leads to the accumulation of salts, known as salinisation, which enriches the surface layers of the soil and may cause surface salt crustations. The soil profile for this type of soil shows little differentiation, as the regolith is not greatly affected by pedogenesis (Nortcliff 1983). Salt is a paramagnetic substance and therefore salinisation is likely to lower enhancement in surface layers, thus decreasing MS values.

8.7 Ferrallitisation and ferrugination

The two processes of ferrallitisation and ferrugination occur in the tropics due to predominance of high rainfall and high temperatures. Ferrallitisation occurs when the soil is subjected to intense weathering leading to transformations of the soil minerals. Ferrugination involves less intense weathering leading to transformations and the loss of soluble salts. Iron is abundant in both soils and leads to their red colour and the occurrence of concretions in the soil (Nortcliff 1983). This high amount of iron evident in the soils will presumably lead to high MS values in these soil profiles.

8.8 Limitations to the literature –South African soils

All literature regarding frequency dependent magnetic susceptibility is based on measurements documented in northern hemisphere countries, mainly the United Kingdom. An important implication for the distribution of iron compounds in Southern Africa is palaeogeomorphology. From Palaeozoic times, southern Africa has escaped the glacial periods that affected the northern hemisphere. Therefore southern Africa's land surface has undergone weathering for more than 100 million years (Fitzpatrick 1988). The evidence of many erosion cycles can be seen on the KwaZulu-Natal coast. This is strongly contrasted

by the Drakensberg which is the oldest land surface preserved in KwaZulu-Natal (King 1959 cited in Maud 1965).

The old and 'new' soils in KwaZulu-Natal are linked by Fitzpatrick (1988) to the finding of specific iron compounds. Maghaemites depletion due to erosion cycles occurred largely at the coastal areas (Figure 8.1). The Lesotho plateau is characterised by large amounts of Ti-magnetite and ilmenite and different forms of Fe and Ti oxides with a poor crystalline structure (Fitzpatrick 1978). The soils in these conditions are relatively young and have parent materials that are rich in iron and exhibit high concentrations of magnetite and/or Ti-magnetite grains. The highlands (Drakensberg) and the mistbelt (Natal midlands) show a decrease in magnetite evident in older red and yellow soils (Fitzpatrick 1988). These red and yellow soils are highly eroded and weathered and are the result of iron being oxidised into the stable oxides haematite and goethite, respectively (Macvicar *et al.* 1984). This process also results in the depletion of magnetic oxides. These oxides may become coated by secondary weathered products and eventually will form glaebules. These glaebules are more commonly found in old soils rather than those which have undergone recent glaciation. These iron compounds are related to parent material and the resistance to weathering of these compounds. It is thought that they are related to igneous parent material or, in the secondary form, from pressure or heating in the presence of organic matter (Fitzpatrick 1988).

Many soil scientists in the past have advocated that high concentrations of iron oxide occur in warm, humid climates that are found in the tropical, equatorial or mediterranean climates. However, iron compounds have been located in southern Africa in a wide variety of climatic settings, including semi-arid zones. The African continent's passage through geological periods from eras of cold periods to warmer, wetter climates have encouraged the accumulation of iron in the soil (Fitzpatrick 1988).

South African soils have also been found to exhibit ferrimagnetic particles in the form of titanomaghaemite produced by the pedogenic weathering of titanomagnetite. Titanomagnetites are thought to be derived from basic igneous material. Titanomagnetites decompose on heating in air to greater than 200°C, while magnetite oxidises to maghaemite at a temperature between 150 and 250°C (Fitzpatrick & Le Roux 1975 cited in Thompson & Oldfield 1986). Therefore burning may have a significantly different effect on South

African soils to those of the Northern hemisphere that have ferrimagnetic particles largely in the form of magnetite. In this instance burning will decrease magnetic susceptibility.

A high clay content is often found in old soils, such as some South African soils, due to the physical and chemical breakdown of large grains (Harpstead *et al.* 1997). Some of KwaZulu-Natal's soils have coarse-grained topsoils due to eluviation (Macvicar *et al.* 1985). The frequency dependent magnetic susceptibility sensor only detects finely grained particles (below 0.03μm) (Dearing *et al.* 1996b), and therefore χ_{FD} may be of a very low value. The biggest limitation is the overall lack of evidence regarding magnetic susceptibility, especially frequency dependent magnetic susceptibility, for South African soils and this disallows any assumptions to be made regarding field measurements.
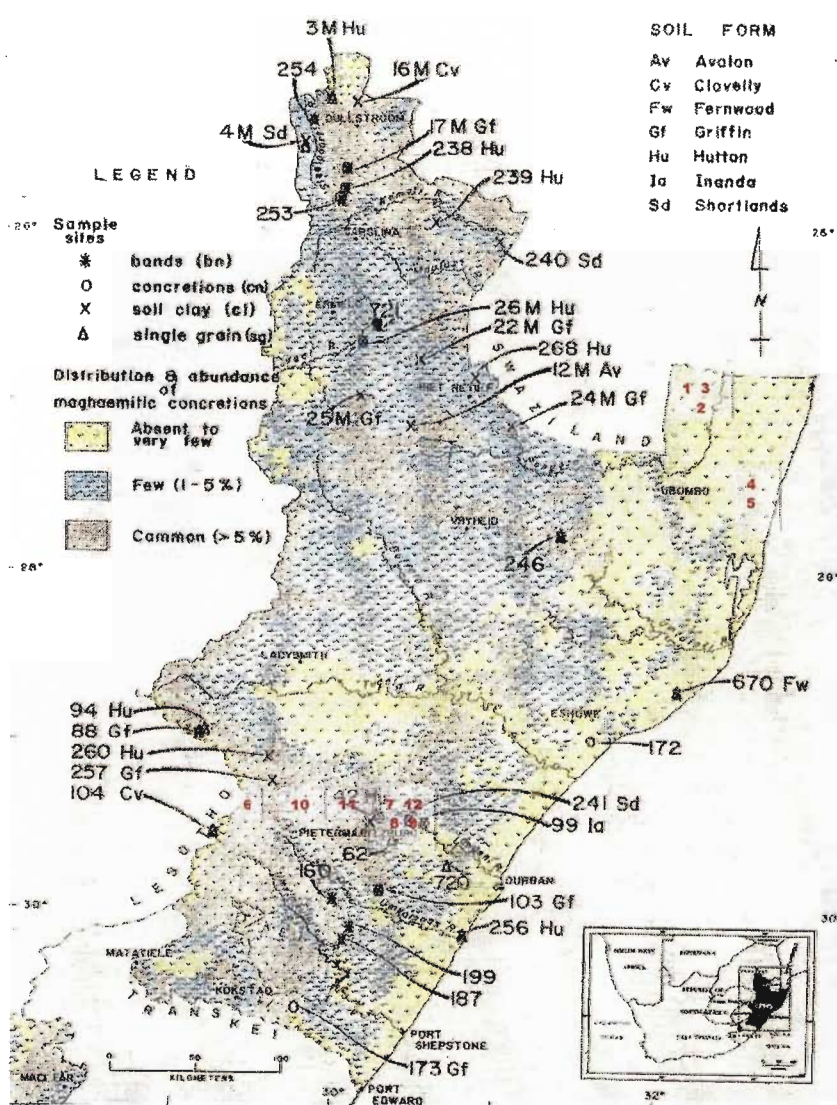
Figure 8.1: The distribution of maghaemite concretions (Fitzpatrick 1978).

8.5 Summary

Topsoil erosion is a pressing problem as it leads to desertification (United Nations 1998). Research from northern hemisphere countries has shown a correlation between frequency dependent magnetic susceptibility and topsoil (Le Borgne 1955 cited in Dearing *et al.* 1986; Mullins 1977; Maher 1986; Thompson & Oldfield 1986; Williams & Cooper 1990; Dearing *et al.* 1996b, 1997; Smith 1999) Therefore frequency dependent magnetic can be used as an indicator for topsoil loss. The applicability of this method in South Africa is not clear due to lack of research and thus needs to investigated.

Chapter 9: Methodology

9.1 Overview of methods to be used

Two methods shall be undertaken in the research, firstly an exploratory phase and secondly an explanatory phase. The exploratory phase will attempt to identify if a relationship exists between frequency dependent magnetic susceptibility and both topsoil and subsoil. If a relationship is detected than an explanatory phase shall be undertaken. The explanatory phase will aim to explore this relationship and examine it in terms of topsoil loss. Both methods will be carried out in KwaZulu-Natal.

9.2 The exploratory phase

The exploratory phase will be undertaken using purposeful sampling methods, this is sampling in areas with various parent material, landform settings, amount of organic material and a history of burning. All sampling will be carried out in areas with well-defined topsoil, in order that the relationship between frequency dependent magnetic susceptibility and topsoil and subsoil can be correctly documented. Sampling will be carried out using the Bartington MS2B frequency dependent magnetic susceptibility sensor and the MS2D loop. The Bartington MS2B frequency dependent magnetic susceptibility sensor detects ultra fine ferrimagnetic particles which, in past research has been found to correlate strongly to either topsoil or subsoil (Maher 1986; Eyre 1997; Dearing 1999). The Bartington MS2D loop is an easily operated field sensor that gives rapid measurements of surface magnetic susceptibility. The loop will be used so that its results can be correlated to the MS2B sensor to examine whether the loop can be used as a field method for topsoil loss evaluation. Samples of the soil will be taken at a depth of 10cm and 30cm and placed in plastic sample pots holding a volume of $10cm^{3}$. Samples are taken at these two depths, as 10cm will characterize the topsoil (A horizon) and 30cm should be representative of the sub-soil. An auger will be used to extract the soil from the desired depths and soil will be taken from the centre of the augered sample to minimise the risk of contamination. Plastic instruments will be used to place the soil samples in the sample pots, to avoid contamination of the soil with magnetic particles. Both samples will be examined using the Bartington MS2B dual frequency sensor that will measure the magnetic susceptibility of the samples at a low frequency of 0.46kHz and at a high frequency of 4.6kHz (Dearing

1999). The frequency dependency magnetic susceptibility of soil from different depths can then be used to determine the signature of the topsoil and subsoil in that geological region.

The data gathered will be statistically analysed to determine the following: firstly whether a significant relationship exists between the frequency dependent magnetic susceptibility and topsoil or subsoil, using a related t-test at the 0.05 level of significance. Secondly the magnetic susceptibility readings from both sensors will be separately correlated for the related sites of different parent material to evaluate if a magnetic signature for various parent materials exists. This shall be evaluated using Pearson's correlation co-efficient. Thirdly both sensors' frequency dependent magnetic susceptibility will be cross-correlated, using a related t-test at a 0.05 significance level, to determine if the MS2D loop is a reliable method of topsoil magnetic susceptibility assessment.

9.3 The explanatory phase

If a significant relationship is found with topsoil and frequency dependent magnetic susceptibility, then the explanatory phase of the research will be undertaken. This part of the research entails the selection of two areas, one eroded and the other showing no evidence of erosion, which consist of the same parent material and are exposed to the same amounts of burning and landform processes. On these areas a grid of 10m by 10m will be set up using string and plastic pegs, in order not to contaminate the magnetic susceptibility readings. A small sized grid will be used due to time constraints. The grid method allows for the large collection of site-specific data, which can later be statistically correlated to determine whether eroded areas have a lower difference in magnetic susceptibility between the topsoil and subsoil. The analysis of a greater amount of samples related to one area allows the data collected, and thus the relationship found, to be more reflective of that in the real world.

Two samples from each site, at both depths will be sent to the laboratory for X-Ray diffraction to determine the ferromagnetic minerals in the soil. These results will be correlated with the field results of frequency dependent susceptibility to determine their reliability as a method for detecting ferromagnetic particles in the soil. This is important as no past research regarding frequency dependent magnetic susceptibility has been previously carried out in South African soils. This method correlated with the magnetic

susceptibility measurements of frequency dependent magnetic susceptibility and low frequency magnetic susceptibility will indicate the validity of these methods in detecting topsoil loss in South Africa. Graphical representation will be used to illustrate these correlations.

Both the exploratory and explanatory research phases will be carried out in areas away from urban and industrialised areas to account for atmospheric fallout skewing the data. Data collection will be carried out in the same season to account for variations in soil moisture and pedogenic processes.

9.4 Triangulation

The study effectively employs triangulation by obtaining data through: frequency dependent magnetic susceptibility measurements, low frequency magnetic susceptibility loop readings and X-ray diffraction (figure 9.1). The use of all three methods aims to firstly evaluate the validity of the magnetic susceptibility methods for topsoil signature analysis in South Africa, and broaden the amount of information on topsoil in South Africa in order that a reliable signature can be established. All these methods rely on quantitative data for analysis, and thus the study falls within a positivist paradigm.
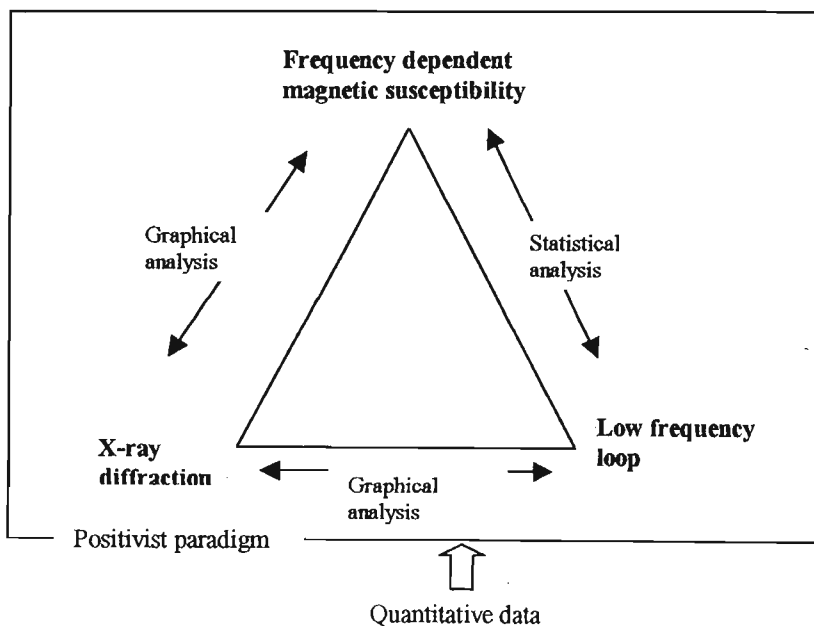
Figure 9.1 : Triangulation method used in the study

9.5 Validity and reliability of the instruments

The Bartington MS2D loop is a reliable method for examining magnetic susceptibility for a surface of 268.7cm^2 with a 50% response at a 15mm depth (Dearing 1999). The MS2D loop does not always provide valid measurements, especially in vegetated areas thus more than one reading is necessary and the mean taken as the total susceptibility (Watson 2002). The Bartington MS2B frequency dependent susceptibility sensor gives a reliable measurement of frequency dependent susceptibility if the sample pots are properly filled and samples are not contaminated by other sources of magnetic material. Readings from both the Bartington MS2B and MS2D may lose validity if instrumental drift occurs, which can be prevented by checking air readings between sample measurements (Dearing 1999).

9.6 Methodology process diagram
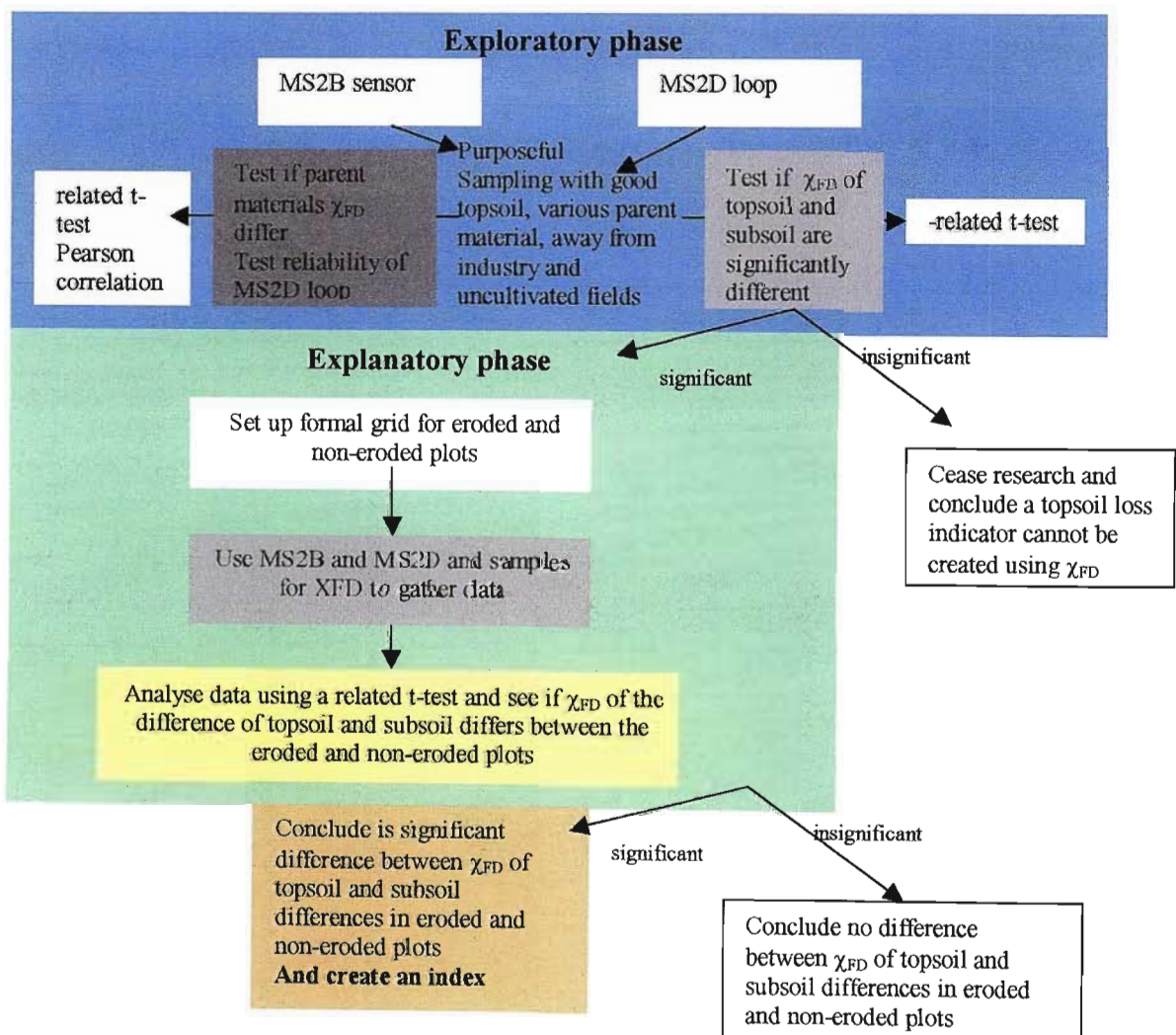
Figure 9.1: Methodology process diagram

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Appendix

Appendix I

A.1.Sample measurement with the MS2B sensor

A.1.1 Setting-up

The following points should be followed in order to gain maximum accuracy of results when setting up the MS2B sensor:

- Retain the sensor in a wooden or a plastic frame or stand the sensor's feet in a niche, in order to keep the sensor stable.
- Do not place sensor near metal objects including screws, coins, buttons, metal pens and jewellery.
- Do not place the sensor next to a transformer or main cable.
- Do not situate sensor near electronic equipment especially field generating equipment such as electric motors.
- Do not place near vibrating devices such as lift shafts or on the same bench as a motor.
- Keep the sensor away from any source that causes a variation in heat, such as draughts and sunlight. Also do not touch the sensor as this too results in a change in temperature of the sensor.
- Try to keep the temperature, which the sensor is working in, constant.

Drift may occur in very weak samples or in a noisy environment, but is not usual due to the stability of the MS2 sensor. To avoid drift:

- Switch the MS2B on ten minutes before use.
- Take air measurements for a long period once the sensor is placed on a suitable surface, in the 0.1 range. This process will help to highlight the sensor's drift and identify if there are any vibrations or magnetic fields which may undermine the sensors accuracy.
- During the day measure air for a minimum of one hour a day and preferably several hours during a full working day.
- If the environment is 'noisy', try other environments and take measurements at various times of the day. (Some researchers have found that measurements at night in rural areas are more 'quiet' than in inner cities at midday.)

A.1.2 Sample preparation

Sampling must be done so as to minimise any contamination from ferrous substances:

- Do not use iron spades, trowels or augers, or any material that has had contact with the metal. Instead use plastic or nylon alternatives such as plastic spoons and children's spades. Stainless steel and aluminium have a lower chance of causing contamination, but scrapings from these objects should be analysed to confirm this.
- Samples that have been exposed to metal in air filter or sieves need to be compared to non-magnetic powders after the same exposure.

The MS2B sensor can measure samples that are either wet or dry, including liquids. The most preferred sample preparation method is freeze-drying. Air drying can be carried out but requires to be undertaken at room temperature (approximately $25^{o}C$). Drying using an oven (up to a maximum of $35^{o}C$) can be used if the sample needs to be rapidly dried, but the even distribution of heat throughout the oven needs to be ensured (Dearing a,b). Air drying may cause changes in the mineralogy of the sample, for example goethite heated between 300 and $400^{o}C$ forms haematite (Thompson & Oldfield 1986). The plastic sample pots supplied can withstand temperatures of a maximum $40^{o}C$, and therefore oven-drying can occur in the sample pots. If the effect of temperature on the sample is uncertain, a comparison is needed to ensure the most representative results are obtained.

Frozen samples need to reach room temperature before measurements are carried out on them, as frozen samples could jeopardise sensor stability. To account for drift ice and water can be used.

The method of placing of material into the sample pot needs to be carefully carried out so that the sample is not contaminated. Plastic spatulas, spoons and commercial nylon presses can be used to place dried soil and sediment into the sample pots. After drying, samples need to be broken down either using a pestle and mortar, or a hammer with the sample wrapped in layers of plastic first. Soils can also be broken down using a ball mill that uses glass or ceramic beads in a revolving drum.

A.1.3 Sample size

The MS2B sensor has been calibrated to measure susceptibility of $10cm^3$ samples. If the pot is not filled or a pot of different volume is used, sample errors will arise. If pots of an alternative size are used the sample error can be calculated using a non-paramagnetic substance such as maganous carbonate ($MnCO_3$) in the different pots. If the samples taken are of a strong magnetic nature it is better to us half filled pots, but in calculating specific susceptibility the volume needs to be assumed to be $10 cm^3$ so as to avoid errors associated with small samples.

For best results from the MS2B sensor it is necessary to determine the optimum position for sample measurement. This can be done by continuously measuring a full, well mixed pot of highly magnetic material and simultaneously adjusting the sample platen height until the greatest magnetic susceptibility reading is obtained.

A.1.4 Sample measurement

The MS2 meter is used in conjunction with the other MS2 sensors and has the option of two measurement modes and measurement ranges. The measurement modes consist of button and continuous mode. The ranges available are 1.0 and 0.1, where the 0.1 range is ten times more sensitive but takes much longer to carry out a measurement. Normally measurements are taken using the 0.1 range, unless the samples are strongly magnetic. Instrumental drift between readings is important to recognise and this can be accounted for by carrying out air measurements between samples. The process shown in Figure A1.1 needs to be followed in order to carry out sample measurement using the MS2B sensor.

Dearing (1999) suggests that readings are firstly carried out on the LF (low frequency) range and then samples are all remeasured on the HF (high frequency) range. It is important that samples are measured with the same orientation in the sensor, which is easily done by marking the pots and aligning this mark with a part of the sensor. This will help to minimise the directional variations in the readings (Dearing *et al.* 1996a; Dearing 1999).

```
┌─────────────────────────┐   No        ┌──────────────────────┐
│ Turn switch to BATT      │───green────▶│ Recharge batteries   │
└─────────────────────────┘   light     └──────────────────────┘
            │
        Green light
            │
            ▼
┌──────────────────────────────────────────────────────────────┐
│ Chose range 0.1, select SI and place MS2B switch on LF        │
│ Leave for 10 minutes                                          │
│ Push button Z to zero- meter takes few seconds to take measurement │
└──────────────────────────────────────────────────────────────┘
            │
            │                                Not
            ▼                               close
┌──────────────────────────────────────────┐ to 0  ┌──────────────────────┐
│ Take reading of the air by pushing the M button │────▶│ Re-zero with Z and   │
└──────────────────────────────────────────┘       │ take a new air       │
            │                                       │ measurement          │
        Close to zero                               └──────────────────────┘
            │
            ▼
┌──────────────────────────────────────────────────────────────┐
│ Raise the MS2B platen and stand the sample pot on cut-out and │
│ lower sample into the MS2B sensor                             │
│ 2.1.1   Push the M button                                     │
│                                                               │
│ After a bleep remove the sample pot and record the reading value │
└──────────────────────────────────────────────────────────────┘
            │
            ▼
┌────────────────────────────────────┐
│ Take an air reading with the sensor │
│ empty using the M button            │
│ (it is not necessary to rezero the meter │
│ before the next measurement)        │
└────────────────────────────────────┘
```

Figure A1.1: The sample measurement process using the MS2B
(based on Dearing 1999)

The above process leaves the researcher with three measurements, that could be used to calculate drift if the two air readings were not zero, using the equation below:

$$\kappa(\text{corrected}) = \text{sample } \kappa - \{(\text{first air } \kappa + \text{second air } \kappa)/2\}$$

If the first air reading is not zero then either the sensor has not had enough time to warm up, or the sensor is close to metallic material. To decrease drift it is important that time between readings is kept constant and to a minimum. To increase the speed of readings the second air reading of a sample can act as the first reading of the following sample.

Another more precise method uses the following steps:

1. zero meter and switch to M
2. bleep 1-record the first air reading
3. place sample into sensor
4. bleep 2 –ignore
5. bleep 3 –record first sample measurement
6. bleep 4 –record second sample measurement
7. remove sample from sensor
8. bleep 5 –ignore
9. bleep 6 –record second air reading

The second air reading is again used for the first air measurement of the following sample. Magnetic susceptibility is found by subtracting the mean of the two air readings from the mean of the two sample measurements. This is a more time-consuming method but more accurately accounts for drift.

When samples of very weakly magnetic diamagnetic material are taken, the sample pot's properties may reduce the value of the sample. It is recommended that the sample pots are first measured empty to obtain a mean diamagnetic susceptibility reading that can be added to the magnetic susceptibility of the sample.

On the other hand if samples are highly magnetic, with a κ value of greater than 100 .10^{-5} SI, it is best to use the 1.0 range. It is important to note that with such samples a risk of the meter overloading and not displaying the correct value is possible, as the meter can only display values up to the value 9999. Values above this become truncated and thus the first digit related to tens of thousands is not displayed (Dearing *et al.* 1996a; Dearing 1999).

Generally samples that have a κ_{LF} of less than 10 and up to 25 are likely to generate large errors and therefore are not very useful. Differences between low and high frequency readings are around 1 – 10% or 0.4 units on the sensor.

A.2 Sample measurement with the MS2D

The MS2D is designed for outdoor use and therefore it doesn't need to be as carefully handled as the MS2B sensor. The only important consideration is to make sure that the connections are tightly assembled.

The sensor needs to be operated in the following way:

1. Attach the sensor to the meter that is then switched on, SI units and a range of 1.0 is normally chosen. Allow the meter to warm-up for approximately ten minutes.

2. Zero the sensor by holding it in the air (by pushing the Z button), at a minimum of 100cm from any objects. The display will becleared and the M button will then take an air measurement.

3. Position the loop onto the surface and take a reading using the M button.

4. Place the sensor in the air and obtain an air reading. Use the mean of the two air readings to adjust the magnetic susceptibility reading for drift, by subtracting this mean from the magnetic susceptibility value.

If a large number of sample readings are needed it could be more convenient to set the meter in continuous mode (Dearing 1999). Usually two or three readings are needed (because of variations of measurements) in order that a mean of these values can be taken as representative of the sample (Watson 2002). Dearing (1999) suggests that the loop should be positioned on the surface until a maximum reading is attained, which is usually after two or three bleeps.

The MS2D loop produces a magnetic field around the circular section of the loop that determines the magnetizability of the material it is placed over. This results in the loop being more sensitive to material within a close range of 5mm to its surface. However, a strongly magnetic material at a depth of 100mm will still make an important contribution to the susceptibility measurement. This has important implications for surfaces covered with diamagnetic material, such as leaves (Dearing 1999). Due to this Watson (2002) suggests removing as much vegetation from the surface as possible. It is also important to note that because of its circular shape the loop is least sensitive in the centre (Dearing 1999).

Magnetic susceptibility as an indicator of layering in soils at

Bonamanzi Game Ranch, KwaZulu-Natal, South Africa

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Abstract

Very little research has been undertaken regarding the applicability of magnetic susceptibility (MS) as a method for discriminating between horizons in South African soils. The aim of the research was to investigate the use of MS as an indicator of distinct visible layering in soils exposed in a trench at Bonamanzi Game Ranch (BGR), KwaZulu-Natal, South Africa. Certain trends were found in the trench, including the homogenising effect of bioturbation on MS; an increase in MS at the top of the heavy clay layer; and high κ_{LF} values and contrasting low χ_{FD} values for the fluvial gravel at the base of the trench. However, in repeat samples it was found that high variability of MS resulted. This variability was minimised slightly by crushing the samples to <2 mm, but crushing to a particle size lower than this was not advantageous. Variability was found not to be attributed to packing, pot orientation or remanent magnetisation. The MS of a uniform, residual soil was measured and displayed much lower variability than the Bonamanzi samples. Chemical analysis was undertaken to investigate the influence of dithionite extractable iron (Fe_{DCB}), oxalate extractable iron (Fe_{OX}), loss on ignition between 105°C and 400°C (LOI (105-400°C)), and loss on ignition between 700°C and 1000°C (LOI (700-1000°C)) on MS. When the residual soil samples were included in the regression analysis a strong relationship between Fe_{OX} and MS was evident. Using only the BGR samples resulted in a weak positive relationship between κ_{LF} and organic matter (LOI (105-400°C)) and a weak negative relationship with carbonate (LOI (700- 1000°C)). The in-sample variability reflects the balance between the influence of these factors both at the micro-scale within the soil and between different parts of the same layer within the trench. It appears that MS is not a suitable method for discriminating soil layers within a 'young' active soil environment.

1. Introduction

Magnetic susceptibility (MS) has been widely used in soil studies to evaluate *inter alia* topsoils (Williams and Cooper, 1990; Dearing et al., 1997), slope processes (Williams and Cooper, 1990), soil erosion in catchments (Hutchinson, 1995), and the delineation of wetlands (Grimley and Vepraskas, 2000). The values of MS obtained correspond with the types of magnetic minerals in the soil, mainly the iron oxides such as magnetite and maghaemite (higher MS), and haematite and goethite (lower MS) (Dearing, 1999a,b). Thus MS acts as a signature for different types of soils, categorising them according to processes of formation or transportation and composition matrix (Dearing, 1999b).

The relationship between MS and iron in soil is influenced by both external factors such as parent material (Thompson and Oldfield, 1986; Shenggao, 2000); climate (Mullins, 1977; Maher, 1986); topography (Dearing et al., 1986; Williams and Cooper, 1990; de Jong et al., 1998, 2000); burning (Jonscher, 1975; Maher, 1986; Thompson and Oldfield, 1986; Dearing et al., 1996a,b; Oldfield, 1999); land use history of the area (Dearing et al., 1996b; de Jong et al., 1998); and time (Akram et al., 1998), and by various soil constituents of which organic matter (OM) and carbonate are considered the most important (Maher, 1986; Thompson and Oldfield, 1986; Dearing et al., 1996b; Jong et al., 1998) .

Thompson and Oldfield (1986) and Dearing et al. (1996b) argue that OM increases MS values because it provides a substrate for micro-organisms that aid the reduction of iron, resulting in minerals in the soil with lower magnetic susceptibility. However,

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this process requires anaerobic conditions and it has been suggested that oxygen is necessary for magnetite synthesis and growth (Blakemore et al., 1985 cited in Lovely et al., 1987). Maher (1986) and de Jong et al. (1998) suggest that OM decreases MS measurements due to its diamagnetic properties thus diluting the magnetic signature. Similarly carbonate is a diamagnetic material and has been found to decrease MS values (Thompson and Oldfield, 1986; Dearing, 1999b). However, de Jong et al. (1998) found that calcium carbonate rich soils had a higher MS signal due to the formation of maghaemite as a result of oxidation of ferrous-carbonate.

Maher (1986) and Hanesch and Petersen (1999) used MS to identify horizons within the soil profile. This is possible because specific pedogenic processes are assumed to result in a decrease or an increase in the MS signature of the horizons. Lower MS values are associated with horizons that have undergone gleying, eluviation, leaching and reductive weathering (Thompson and Oldfield, 1986; de Jong et al., 1998). Higher MS values are found in horizons that have undergone illuviation, and hydrolytic and oxidative weathering (Thompson and Oldfield, 1986).

Most of the research on MS in soils has been carried out in countries of the northern hemisphere, where soil materials are much younger than in South Africa. Fitzpatrick's (1988) findings that maghaemite is depleted in South African soils due to the number of erosion cycles that the materials have undergone over many millions of years, indicates that MS might not be an effective method for horizon identification in South Africa. The usefulness of MS has not been tested in South Africa, where even 'young' pedogenetic processes may be operating on very old materials. An existing trench that exposed a number of clearly visible layers within the soil profile at Bonamanzi Game Ranch in KwaZulu-Natal presented an opportunity to investigate whether MS could distinguish these layers and assist in understanding the pedogenetic

history of the area. In addition, instrumental variables mentioned in the literature as being important for obtaining accurate κ_{LF} values and the effect of grinding on reproducibility of results were also investigated.

2. Materials and methods

2.1 Study site

The Bonamanzi Game Ranch (BGR) covers an area of 3950 ha and is located between 28° 01'S and 28° 05'S, and 32° 16'E and 32° 21'E in KwaZulu-Natal, South Africa (Fig. 1). The climate of the area varies from hot, humid summer conditions to mild, dry winters. The mean monthly maximum temperatures range from 29.5°C in summer to 25.9°C in winter. The hottest months, January and February, have an average maximum temperature of 30.6°C, and July has an average minimum of 9.9°C (Camp, 1995). The average annual rainfall is approximately 650mm but has varied from 400 mm to 1300 mm over the past 12 years (P. Prinsloo, personal communication, 2002). The topography of BGR can be divided into three main areas. The highest part is a central Quaternary sand ridge (maximum height 100 m) that is aligned approximately north-south. To the east and west of this ridge the landscape is lower in altitude i.e., in the east a wide gently sloping plain; to the west a broad, almost flat slope. The underlying geology consists mainly of Upper Cretaceous conglomerates, siltstones, sandstones and some shelly beds laid down between 85 and 65 million years ago. These rocks are, however, covered by a complex succession of alluvial sediments especially in the west. This western area can be subdivided into broadly three sections. The southern and northern sections are characterised by the

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occurrence of termitaria that are absent in the central part. In the south these termitaria are mainly covered by shrubby vegetation or grass; in the north many are vegetated with woody species while the intermounds are grass covered. In both areas some of the mounds are clearly active while others are apparently abandoned. A newly dug trench (17.5 m long with a maximum depth of 2.4 m) excavated between an active and an inactive mound in the northern area was chosen because of distinct visible layering in the profile (Plate 1).

2.2 Sampling strategy

Four grids intersecting vertically and horizontally every 20 cm were laid across particular parts of the trench wall (Fig. 2). Grid I begins at the middle of the inactive termite mound and stretches 100 cm across and 140 cm down; Grid II covers an area 180 cm across by 160 cm deep centred at about 460 cm from the centre of the inactive mound; Grid III is 40 cm in length and 160 cm deep about 990 cm from the centre of the inactive mound; Grid IV is the soil beneath half of the active termite mound, 20 cm across and 240 cm in depth. Soil samples (179 in total) were collected from the intersection of all grid lines using a geological pick ensuring that soil that came into contact with the pick was discarded. Similarly the soil from the face of the trench (outermost 10mm) was discarded and the samples were placed into plastic sampling bags.

2.3 Magnetic susceptibility

The soil collected was dry and therefore further air-drying was not necessary. Random samples from the sample bags were taken and placed in 10 cm^3 plastic pots

custom made for the Bartington MS2B dual frequency magnetic susceptibility sensor. Each sample was then tested twice at both high and low frequency, 4.6 and 0.46 kHz, respectively. Air measurements were also taken twice, to account for drift using Equation 1.1 (Dearing, 1999a,b):

$$\kappa = \{(\kappa_{ms\ reading\ 1} + \kappa_{ms\ reading\ 2})/2\} - \{(\kappa_{air\ reading\ 1} + \kappa_{air\ reading\ 2})/2\} \qquad (1.1)$$

Throughout Equation 1.1 κ (volume specific magnetic susceptibility) is expressed in SI units and gives an answer in 10^{-5} (Dearing, 1999a,b). The corrected low frequency volume specific magnetic susceptibility (κ_{LF}) and high frequency volume specific magnetic susceptibility (κ_{HF}) were converted to the frequency dependent magnetic susceptibility (χ_{FD}) using the mass of the soil (Equation 1.2):

$$\chi_{FD} = \{(\kappa_{LF} - \kappa_{HF})/mass\}/10 \qquad (1.2)$$

These χ_{FD} values are expressed in units of $10^{-6}\ m^3\ kg^{-1}$ (Dearing, 1999a,b).

Measurements of κ_{LF} give an indication of the presence of magnetic minerals in the soil, thereby providing information on the types of minerals in the material (Thompson and Oldfield, 1986; Dearing, 1999a,b). The χ_{FD} values relate to superparamagnetic particles with grain sizes between 0.013 and 0.027 µm (Maher, 1986; Dearing et al., 1996a; Dearing et al., 1997; Eyre, 1997). These secondary ferrimagnetic particles are thought to be indicative of pedogenesis (Maher, 1986; Maher & Taylor, 1988; Akram et al., 1998; Dearing, 1999a,b). Both κ_{LF} and χ_{FD} were assessed for their suitability as indicators for the various layers.

2.4 Natural in-sample variation

Three profiles (Grid I Profile D, Grid II Profile G and Grid II Profile J) were selected on the basis of the large within-horizon variations in the initial MS results. A single sample was again taken from each of the original sample bags and tested as before. In-sample variability was explored further by measuring three additional soil samples from each point in Grid II Profile G.

2.5 Effect of particle size

2.5.1 <2 mm

The samples taken from Grid II Profile G, were ground to <2 mm and placed into 30ml plastic vials. From these vials the 10 cm^3 sample pots were filled with soil and measured at both low and high frequency as before. After measurement the soil samples were returned to their respective vials and the sample pot refilled with soil from the same vial and remeasured as before. This process was repeated a further three times.

2.5.2 <0.5 mm

Soil from the first three intersection points of Grid II Profile G and two repeat samples of the first intersection point, were ground to <0.5 mm and their κ_{LF} values measured and compared to values obtained earlier.

2.6 Effect of packing, remanent magnetisation and sample pot orientation

The effect of packing was investigated using soil from all sample points in Grid II Profile G. The 10 cm^3 sample pots were filled to the top and then levelled with a ruler. Care was taken not to disturb or bump the sample pot whilst measuring or weighing. This was repeated twice more with exactly the same material.

To test for remanent magnetisation soil samples from Grid I Profile F (with sample Grid II D9 as a fluvial gravel as none was exposed in Profile F) and from the topsoil of Grid I Profile E and Grid II Profile G were taken from a 30 ml plastic vial filled with soil ground to less than 2 mm that had never been tested before and κ_{LF} and κ_{HF} measured. This was repeated three more times using a different subsample each time. If soil minerals had been magnetised whilst in the sensor and returned to the vial, subsequent MS readings of soil taken from the same vial would be expected to increase.

The effect of orientation was examined using samples from Grid II Profile G by placing the sample pot at four orientation points (0°, 90°, 180° and 270° from a point of reference) in the MS2B sensor.

2.7 Comparison with a residual soil

Five samples ground to <2 mm from the A horizon (0-20 cm) and B horizon (80-100 cm) of a highly weathered Hutton soil (Soil Classification Working Group, 1991), Typic Haplustult (Soil Survey Staff, 1992), from Howick, KwaZulu-Natal were tested for MS.

2.8 Chemical analysis

Soil samples from Grid II Profile G, Grid I Profile F (with sample Grid II D9 as a second fluvial gravel as none was exposed in Profile F) and the Hutton A and B horizons were analysed for dithionite extractable iron (Fe_{DCB}) (Mehra & Jackson, 1960) and oxalate extractable iron (Fe_{OX}) (Schwertmann, 1964). The iron extracted was measured by atomic absorption spectrophotometry on a Varian SpectraAA 250. Loss on ignition at $105°C$, $400°C$, $750°C$ and $1000°C$ was also determined. The loss on ignition between $105°C$ and $400°C$ (LOI ($105–400°C$)) was taken to represent OM, and that between $700°C$ and $1000°C$ (LOI ($700-1000°C$)) an estimate of calcium carbonate content.

2.9 Statistical analysis

Results were analysed using SPSS for Windows. This package was used to correlate chemical analyses with magnetic susceptibility using Pearson's correlation co-efficient, and for simple and multiple regression analysis.

3. Results and Discussion

3.1 Initial MS measurements

Certain trends are evident, including:

- Grid I Profile A is situated under part of the inactive termite mound and shows the homogenising effect biological disturbance has on χ_{FD} values (Fig. 3(a));

- an increase in χ_{FD} at the upper boundary of the heavy clay in the lower sections of some profiles (Fig. 3(b) and (c) at 80 and 100 cm, respectively); and

- the fluvial gravel exhibited the highest κ_{LF} measurements but had very low χ_{FD} values. This inverse relationship is evident in the graphical comparison of χ_{FD} and κ_{LF} values of the fluvial gravel (Fig. 3(c) and (d), respectively). This is in accordance with Shenggao (2000) who suggests that time can increase MS values, as the fluvial gravel may be as old as 20 million years (G. Botha, personal communication, 2002).

Large variations in magnetic susceptibility in samples from the same layer in adjacent profiles in various parts of the trench were apparent for both χ_{FD} and κ_{LF}. In previous publications a variation in κ_{LF} of 50×10^{-5} SI and an increase of χ_{FD} by 0.002×10^{-6} m^3 kg^{-1} were viewed as significant (Begét et al., 1990; Dearing et al., 1996b). The χ_{FD} values from samples of the same layer in adjacent profiles in various parts of the trench showed large differences. For example the soil in the B-horizon of Grid I E2 has a χ_{FD} value of 0.05×10^{-6} m^3 kg^{-1} while the adjacent sample, F2, has a χ_{FD}

value of 0.13×10^{-6} m^3 kg^{-1}. Similarly the ferricrete layer appeared visually to be fairly uniform and would be expected to give high values of similar magnitude. However, in Grid II the κ_{LF} value for ferricrete varies from 167.3×10^{-5} SI to 95.7×10^{-5} SI in adjacent Profiles F3 and E3. This apparently haphazard pattern of high and low MS values is evident in all the layers throughout the trench.

3.2 Mass specific magnetic susceptibility

The magnetic susceptibility measurement of κ_{LF} does not take into account the density of the sample. This can be achieved using Equation 1.3 to calculate a mass specific low frequency value in units of 10^{-6} m^3 kg^{-1} (Dearing, 1999a,b):

$$\chi_{LF} = (\kappa_{LF} / \text{mass}) / 10 \qquad (1.3)$$

However, the individual samples tended to have very similar masses of approximately 12 g and therefore this method did not serve to minimise the variance of MS. Consequently MS values were analysed in the form of κ_{LF}.

3.3 Natural in-sample variation

The κ_{LF} values of the Grid I Profile D and Grid II Profile J samples differed from the original set of MS values by a maximum of 56.5 % (Table 1). However, the increase in value for both κ_{LF} and κ_{HF} were relatively similar within the same sample. The five repeated measurements of samples from Grid II Profile G showed great variation with differences from the original κ_{LF} values of up to 366 %.

3.4 Effect of particle size

3.4.1 <2 mm

Values of κ_{LF} of soil crushed to <2 mm showed less variation than the original κ_{LF} values. However, the differences between κ_{LF} values of soil taken from the same sample set were still very high (Fig. 4).

3.4.2 <0.5 mm

In the literature there is no consistent particle size to which soil is ground for MS measurement purposes, e.g. grinding to <1 mm (Shenggao, 2000); <2 mm (de Jong et al., 1998, 2000); and the use of no grinding (Heller & Tung-sheng, 1982; Dearing et al., 1986). However, it was found that crushing the samples to a particle size of <0.5 mm did not decrease the variation within the soil samples and only altered the κ_{LF} values very slightly (Table 2). Therefore grinding soils to a particle size of <2 mm was adequate for MS measurement purposes as further grinding had no effect on the MS values measured.

3.5 Effect of sample pot orientation, packing and remanent magnetisation

Placing the sample pot at four distinctly different positions in the Bartington MS2B sensor showed the effect of pot orientation on κ_{LF} values to be negligible (Table 3). Packing and repacking the same soil into the sample pot was found to give repeatable values for κ_{LF} and made no difference regarding the large variations in κ_{LF} (Fig. 5).

Accounting for remanent magnetisation also did not lower sample variability, which was extremely high even though sub-samples had not been previously placed in the sensor (Table 4).

3.6 Comparison with a residual soil

If fluctuations in MS in the samples from the Bonamanzi trench are due to inherent variability within the soil layers, then a uniform, residual soil would not be expected to exhibit such large variations. A Hutton soil from Howick, KwaZulu-Natal was selected to compare with the in-sample variability found in the soils from Bonamanzi. This soil has undergone intensive weathering *in situ* and had few external factors affecting it except for long-term soil genesis. These samples show a maximum percentage change between κ_{LF} values of only 9.04 % for the topsoil and 8.19 % for the subsoil (Table 5).

3.7 Chemical analysis

Amounts of iron, OM and carbonates are often important in affecting magnetic susceptibility values and the high variability in MS values in the Bonamanzi samples may therefore be due to differences in the amounts of Fe_{DCB}, Fe_{OX}, OM and carbonates present.

The relationships between κ_{LF} values and the percentages of Fe_{DCB}, Fe_{OX}, LOI (105-400°C), and LOI (700-1000°C) were analysed and significant correlations at the 0.05 level for a two-tailed test, using Pearson's correlation coefficient, were found between all the individual variables and the κ_{LF} values. This shows that these variables influence MS and may be responsible for the variability measured in MS

within the soil samples. The relationship between LOI ($105\text{-}400^\circ C$) and percentages of both Fe_{DCB} and Fe_{OX} was also shown to be highly significant at the 0.05 level.

Simple regression analysis was carried out between the individual variables i.e., κ_{LF}, Fe_{DCB} and Fe_{OX}, LOI ($105\text{-}400^\circ C$) and LOI ($700\text{-}1000^\circ C$). The correlations between κ_{LF} and Fe_{DCB}, LOI ($105\text{-}400^\circ C$) and LOI ($700\text{-}1000^\circ C$) are very weak (Figs. 6 and 7). The only significant relationship is that between κ_{LF} and Fe_{OX} with an $R^2=0.81$ (Fig. 6a). Oxalate iron is considered to be non-crystalline but will include finely divided goethite and it may be that these forms of iron contributed more to κ_{LF} than crystalline iron removed by DCB. However, as seen in Figs. 6 and 7, these regression trend lines are controlled by the values of κ_{LF} greater than 800×10^{-5} SI, which are those from the Hutton soil. Removal of these values results in no correlation between the variables for the Bonamanzi samples alone. A possible explanation for this is that the Bonamanzi trench samples are lower in the range of MS and the Hutton soil is situated in the upper range of MS, leaving a large gap between the two sets of data in the regression graphs. If this is so, then a large number of samples taken from around the Province may fill this gap and confirm the trend shown in Fig. 6a.

Figs. 6b and 7b show each of the soil layers sampled and it can be seen that no layer appears at a consistent distance from the regression line, and it can be concluded that no specific layer in the trench exhibits a strong correlation between κ_{LF} and the measured variables. The haphazard scattering around the regression line of the samples from the various layers suggests that large in-sample variation is responsible for the differences of MS between the soil samples.

The inability of MS to differentiate between layers using the MS2B may be linked to the great variation of minerals and particle sizes within the individual soil samples,

including iron nodules and $CaCO_3$ concretions (Plate 1). These minerals have been shown to decrease and/or increase the susceptibility (Maher, 1986; Thompson and Oldfield, 1986; Dearing, 1999a,b; Shenggao, 2000).

The simple regression analysis shows that the LOI (105-400°C), that is assumed to be OM, is positively although weakly related to κ_{LF} (Fig. 7b), as advocated by Thompson and Oldfield (1986) and Dearing et al. (1996a,b). Other studies have found that organic carbon decreases MS values (Maher, 1986; de Jong et al., 1998). Similarly the LOI (700–1000°C) is weakly negatively correlated to κ_{LF} (R^2=0.027, Fig. 7b). However, if the samples from the fluvial gravel layers, which have high LOI (700-1000°C) values and yet are not visually calcareous in the field, are omitted a stronger negative trend is evident with an R^2=0.51. This negative influence of carbonate on MS agrees with Thompson and Oldfield (1986) and Dearing (1999a,b), but is contrary to de Jong et al. (1998).

An examination of the scatter plots of LOI (105-400°C) and LOI (700-1000°C) against MS supports the assumption that these estimate the percentage loss of OM and percentage loss of carbonate, respectively (Fig. 7b). The LOI (105-400°C) shows that the majority of samples that lost a high percentage of mass from heating between these temperatures were in the upper parts of the profile, where most OM is present. Similarly LOI (700-1000°C) shows that the soil in the lower layers of the profiles displayed the highest percentage loss which correlates with most carbonate occurring in this part of the profile (Plate 1).

3.8 Multiple regression

To investigate the overall effect of all the independent variables on κ_{LF} a multiple regression was carried out. This showed a highly significant R^2 of 0.87. Therefore κ_{LF}

is significantly influenced by the total interaction of Fe_{DCB}, Fe_{OX}, LOI (105-400°C), and LOI (700-1000°C). However, this regression included values from the Hutton soil. Excluding these values gave an R^2 of 0.17. Thus the interaction of all the measured variables only explained 17 % of the variance in κ_{LF} between the soil samples at Bonamanzi, and of this LOI (105-400°C) accounted for 15.7 %.

4. Conclusions

A number of variables mentioned in the literature as important for obtaining accurate κ_{LF} values, for example packing and placement position in the sensor (Dearing et al., 1996; Dearing, 1999a,b), had no effect either on reducing the variability of κ_{LF} or on the measured κ_{LF} values. Although it was determined that grinding soils to <2 mm decreased some of the variability in the measurements of κ_{LF}, additional improvements were not gained by further grinding, which also did not affect the κ_{LF} values measured.

Even though the soil layers in the Bonamanzi trench were clearly visible and distinct, MS could not be used as a successful method to differentiate them. It appears that within an active, alluvial soil environment, such as the area of the BGR trench, MS gives no indication of layering in the soil profile. The external factors that affect MS including parent material, climate, topography and time are the same variables that influence soil genesis. Thus MS is directly connected to all soil formation factors and this complex interaction means that it is unlikely that, especially in an active soil environment such as BGR, a single factor will be responsible for the trend in MS. In addition the internal factors considered important i.e., OM, carbonate and iron also interact and are themselves affected by the external factors.

The only strong positive relationship existing between the measured variables was that between κ_{LF} and Fe_{OX}. This relationship was spread across two very different soil environments and is only evident when the Hutton samples are included in the analysis. A regression analysis that included the Hutton samples found Fe_{OX} to contribute 81.3 % of the variance, whilst in a regression that only included BGR samples, Fe_{OX} accounted for <1 % of the variance, and LOI (105-400°C) was the dominant variable.

From the measurements obtained for the BGR samples it appears that OM increases and carbonate decreases κ_{LF}, and iron extracted by DCB and oxalate are unimportant. When a wider range of soils is considered (i.e., including the residual, highly weathered Hutton soil) then Fe_{OX} becomes the dominant variable in its affect on κ_{LF}. Thus it is possible that the effects of OM and carbonates are important in the 'young' active environment at BGR but become less important with time. The in-sample variability shown by the κ_{LF} values measured therefore reflect the balance between the influence of these factors, and perhaps others unmeasured (such as degree of hydromorphy), both at the micro-scale within the soil and between different parts of the same layer within the trench. It is clear that further MS measurements must be undertaken in soils from a range of pedogenic environments in South Africa to investigate whether the relationships suggested by this study can be confirmed.

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Table 1

In-sample variation in κ_{LF} measured in (a) Grid I Profile D; (b) Grid II Profile J; and (c) Grid II Profile G.

(a)

Sample	Depth (cm)	Original κ_{LF} (10^{-5}) SI	$\kappa_{LF}2$ (10^{-5}) SI	Percent change from original value
D1	0	103.7	64.4	-37.9
D2	20	74.4	65.6	-11.8
D3	40	118.4	51.6	-56.5
D4	60	51.0	71.7	40.7
D5	80	80.1	66.1	-17.5
D6	100	59.9	67.6	12.9
D7	120	49.5	68.0	37.3
D8	140	45.3	38.7	-14.6

(b)

Sample	Depth (cm)	Original κ_{LF} (10^{-5}) SI	$\kappa_{LF}2$ (10^{-5}) SI	Percent change from original value
J1	0	35.4	27.0	-23.7
J2	20	76.3	43.8	-42.7
J3	40	64.5	67.5	4.7
J4	60	93.0	63.6	-31.7
J5	80	62.1	47.6	-23.4
J6	100	49.8	47.0	-5.7
J7	120	48.9	63.9	30.6
J8	140	51.8	66.1	27.7
J9	160	53.7	46.3	-13.8

(c)

Sample	Depth (cm)	Original κ_{LF} (10^{-5}) SI	$\kappa_{LF}2$ (10^{-5}) SI	Percent change from original value	$\kappa_{LF}3$ (10^{-5}) SI	Percent change from original value	$\kappa_{LF}4$ (10^{-5}) SI	Percent change from original value	$\kappa_{LF}5$ (10^{-5}) SI	Percent change from original value
G1	0	31.3	33.5	6.9	74.2	137.1	34.0	8.5	81.4	160.1
G2	20	30.3	48.6	60.2	84.9	180.2	141.3	366.2	72.4	138.9
G3	40	165.9	83.6	-49.6	79.6	-52.0	79.8	-51.9	101.6	-38.8
G4	60	68.1	53.4	-21.6	33.2	-51.3	57.0	-16.2	50.3	-26.2
G5	80	36.0	52.2	44.9	58.8	63.3	50.7	40.8	61.6	71.0
G6	100	43.5	33.0	-24.2	41.5	-4.5	35.1	-19.3	44.3	1.8
G7	120	79.1	65.9	-16.6	38.1	-51.8	76.4	-3.4	52.5	-33.6
G8	140	72.9	97.2	33.4	79.5	9.1	133.7	83.5	73.2	0.5
G9	160	257.5	474.5	84.3	299.2	16.2	120.5	-53.2	222.7	-13.5

Table 2

The effect of crushing the soil to <0.5 mm on κ_{LF} values for selected samples from Grid II Profile G.

Sample	Depth (cm)	κ_{LF} of <2 mm soil (10^{-5} SI)	κ_{LF} of <0.5 mm soil (10^{-5} SI)	Percent change from original value (%)
G1 Repeat sample no.2 [a]	0	37.7	37.7	0.0
G1 Repeat sample no.4 [a]	0	110.4	116.1	5.2
G1	0	68.6	66.4	3.1
G2	20	51.2	49.3	3.6
G3	40	41.2	40.6	1.5

[a] From Table 4

Table 3

The κ_{LF} values of Grid II Profile G of the sample pot at four orientation points in the Bartington MS2B sensor.

Sample	$0°$ κ_{LF} (10^{-5} SI)	$90°$ κ_{LF} (10^{-5} SI)	$180°$ κ_{LF} (10^{-5} SI)	$270°$ κ_{LF} (10^{-5} SI)	Mean of κ_{LF} (10^{-5} SI)	Standard Deviation
G1	68.3	68.7	68.2	68.3	68.4	0.2
G2	51.7	51.8	52.2	52.3	52.0	0.3
G3	47.3	47.7	47.8	47.9	47.7	0.3
G4	70.3	70.2	69.8	70.3	70.2	0.2
G5	36.9	37.0	37.1	37.4	37.1	0.2
G6	32.3	32.5	32.4	32.4	32.4	0.1
G7	76.8	77.1	77.1	76.9	77.0	0.2
G8	54.4	54.0	54.3	54.7	54.4	0.3
G9	152.0	151.3	151.7	152.3	151.8	0.4

Table 4

The κ_{LF} values of sub-samples that had not been previously measured.

Sample	Soil description	$\kappa_{LF}1$ (10^-5 SI)	$\kappa_{LF}2$ (10^-5 SI)	Percent change from $\kappa_{LF}1$	$\kappa_{LF}3$ (10^-5 SI)	Percent change from $\kappa_{LF}1$	$\kappa_{LF}4$ (10^-5 SI)	Percent change from $\kappa_{LF}1$	Mean of κ_{LF}	Standard deviation
I F1	A horizon	80.0	80.7	0.8	90.8	13.5	94.8	18.5	86.6	7.4
I F2	B horizon	147.4	88.7	-39.8	116.2	-21.2	79.3	-46.2	107.9	30.6
I F3	Ferricrete	98.7	129.7	31.4	131.2	32.9	82.9	-16.1	110.6	23.8
I F4	Ferricrete	78.6	92.6	17.8	94.2	19.8	93.2	18.5	89.6	7.4
I F5	Boundary of ferricrete and clay	84.0	111.7	32.9	102.4	21.8	101.4	20.7	99.8	11.5
I F6	Clay with nodular carbonate	45.3	48.2	6.3	44.7	-1.4	66.1	45.9	51.1	10.1
I F7	Clay with nodular carbonate	79.3	57.6	-27.4	71.6	-9.7	39.2	-50.6	61.9	17.6
I F8	Clay with nodular carbonate	64.1	85.3	33.1	60.7	-5.4	42.2	-34.2	63.1	17.7
II D9	Fluvial gravel	91.1	83.0	-8.9	86.6	-5.0	106.4	16.7	91.7	10.3
I E1	A horizon	73.6	57.9	-21.3	84.95	15.4	44.75	-39.2	65.3	17.6
II G1	A horizon	43.4	37.7	-13.1	72.0	65.9	110.4	18.9	65.9	33.3

Table 5

The five repeated κ_{LF} values and their means and standard deviations for the A and B horizons of the Hutton soil.

	$\kappa_{LF}1$ (10^{-5} SI)	$\kappa_{LF}2$ (10^{-5} SI)	$\kappa_{LF}3$ (10^{-5} SI)	$\kappa_{LF}4$ (10^{-5} SI)	$\kappa_{LF}5$ (10^{-5} SI)	Mean of κ_{LF}	Standard deviation
A Horizon	868.9	789.9	800.2	816.2	834.6	822.0	31.2
B Horizon	858.6	899.2	935.5	900.2	896.4	898.0	27.2
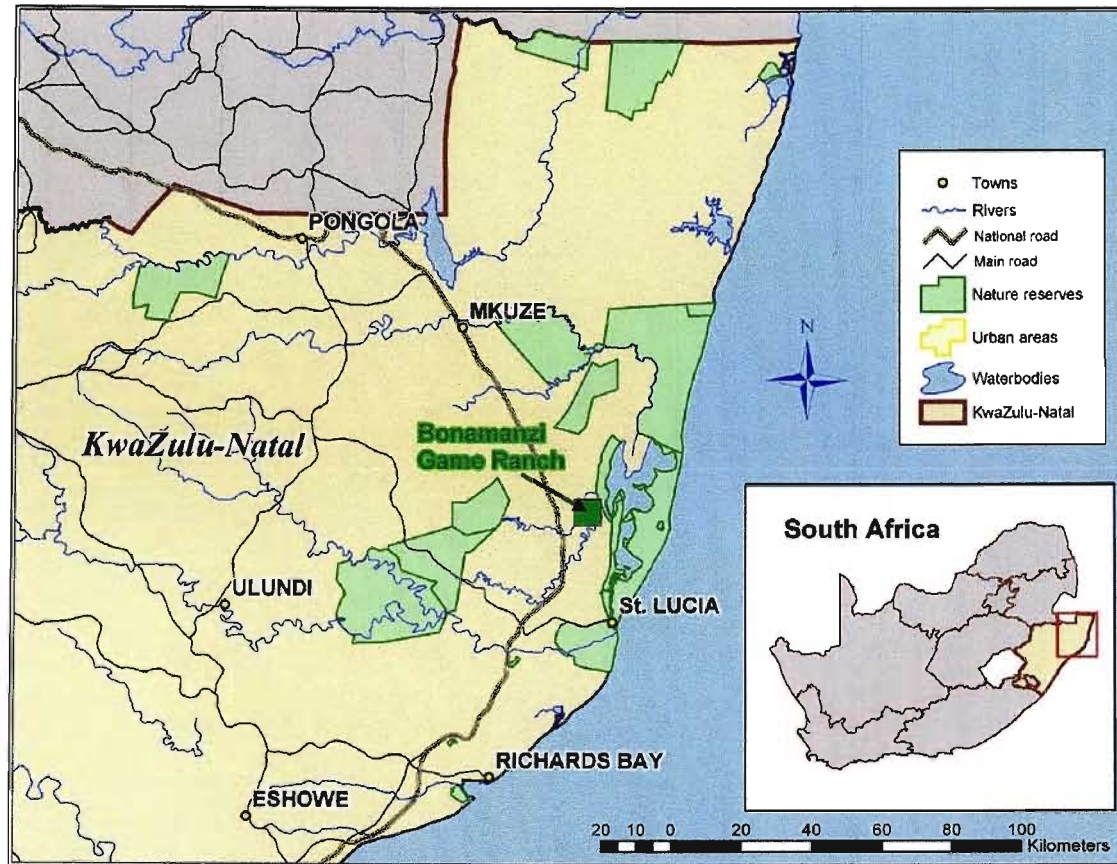
Fig. 1. Location of the Bonamanzi
Game Ranch in KwaZulu-Natal, South
Africa.
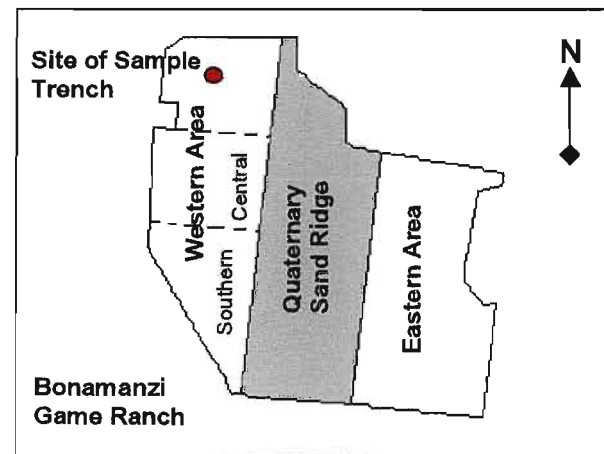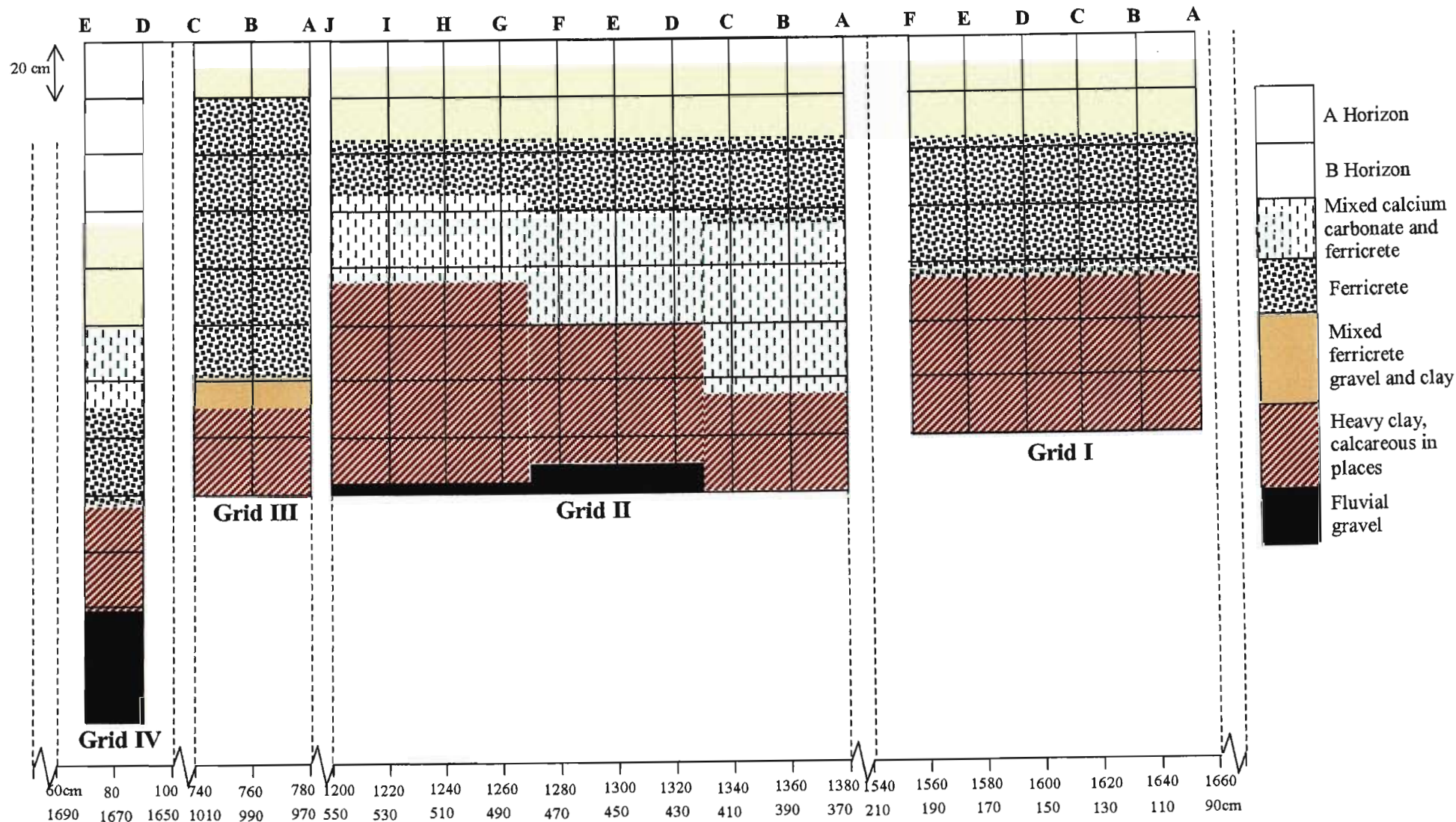
Fig. 2. Grid layout of the soil samples in the Bonamanzi trench.
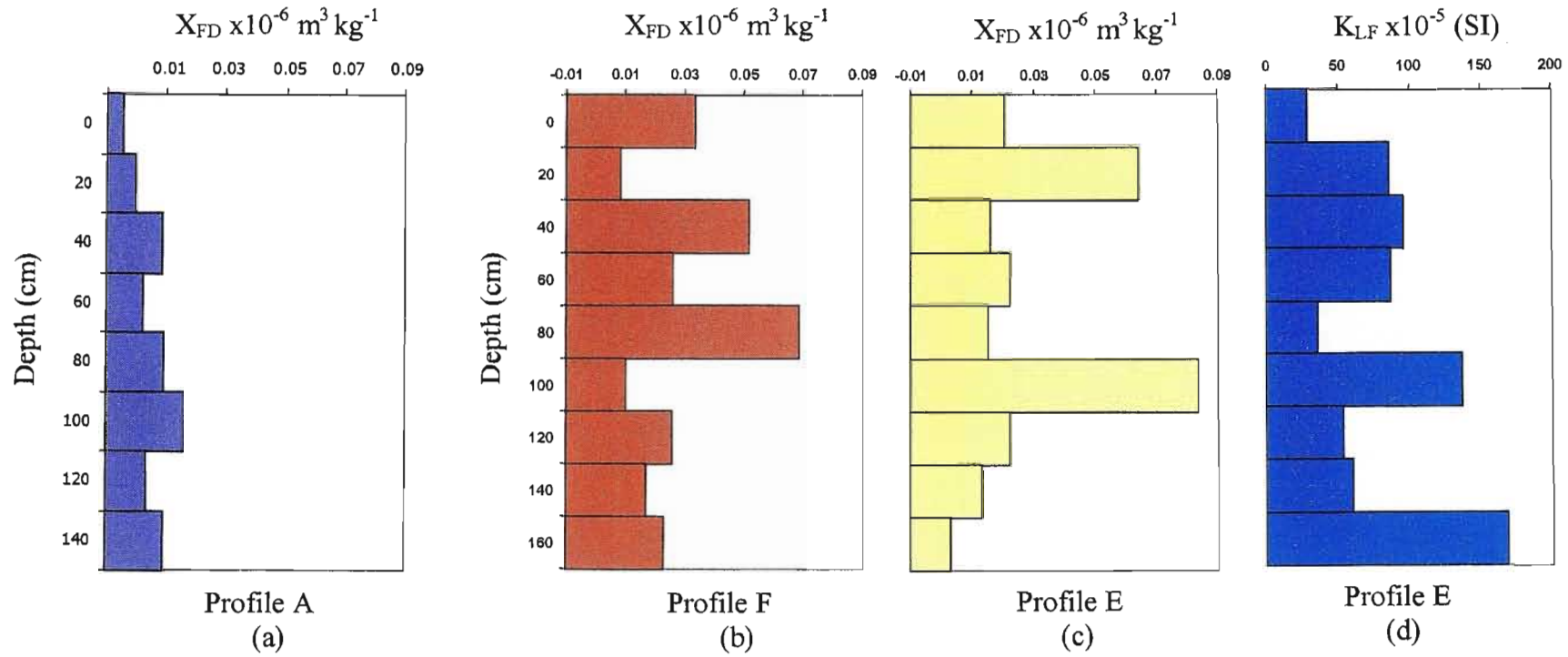
Fig. 3. Magnetic susceptibility trends in three profiles from the Bonamanzi trench, (a) Grid I

Profile A; (b) Grid II Profile F; (c) Grid II Profile E; and (d) κ_{LF} of Grid II Profile E.

(a) Original soil
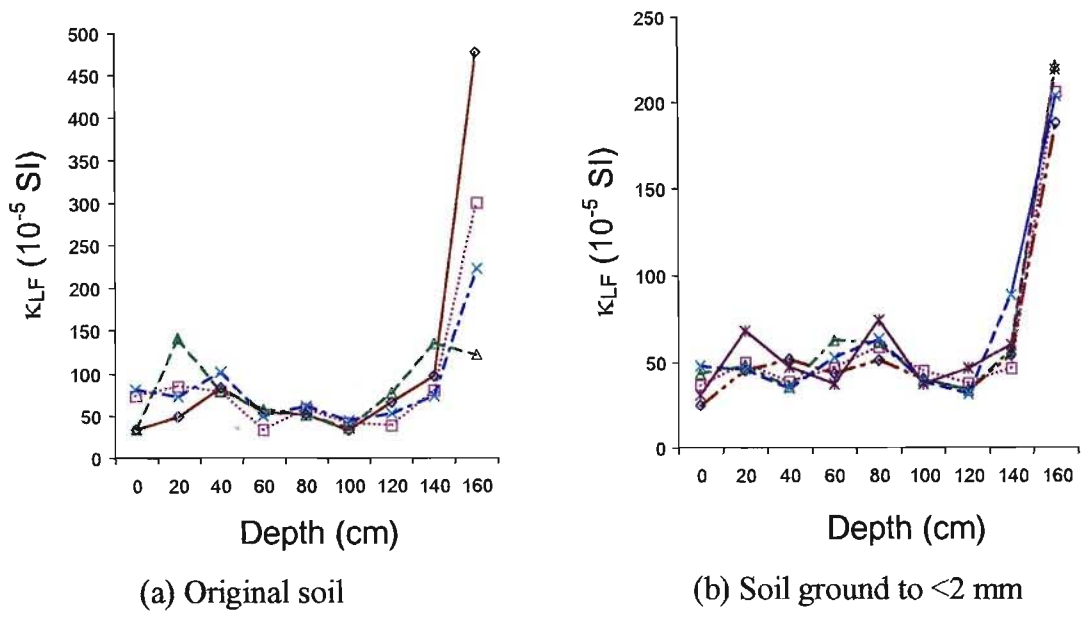
(b) Soil ground to <2 mm

Fig. 4. The variability of Grid II Profile G κ_{LF} values for (a) four repeat samples from the original soil and (b) five repeat samples ground to <2 mm.
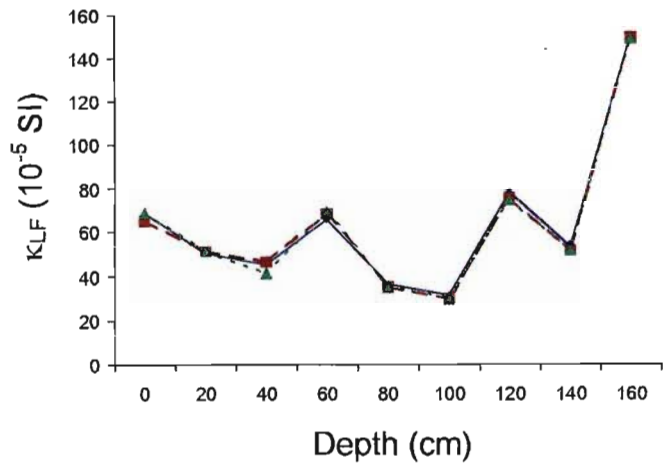
Fig. 5. The comparison of sample κ_{LF} values after the soil from Grid II Profile G was repacked three times using the same soil.
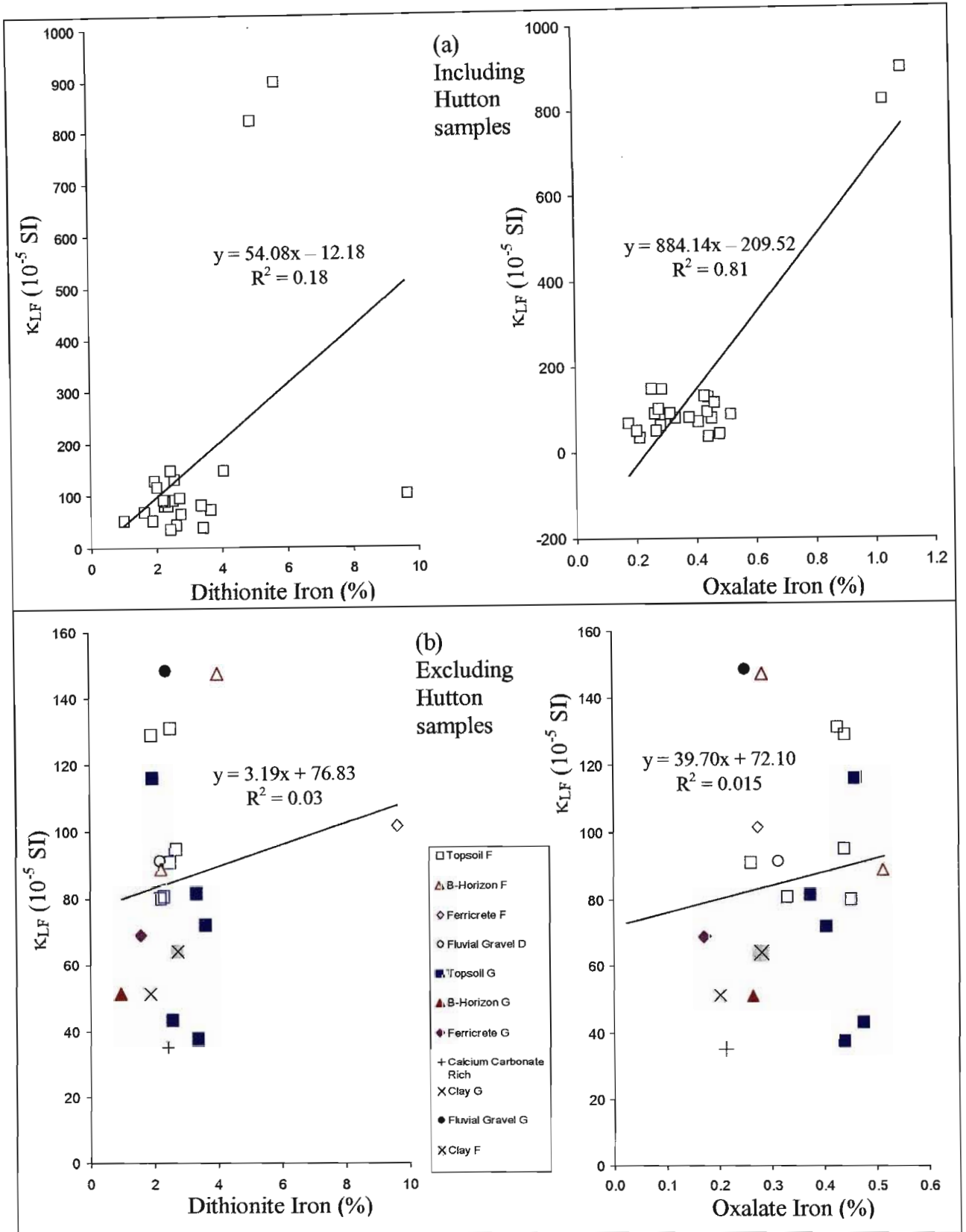
Fig. 6. The relationship between κ_{LF} and the means (n=2) of dithionite and oxalate extractable iron (a) including and (b) excluding the Hutton samples.
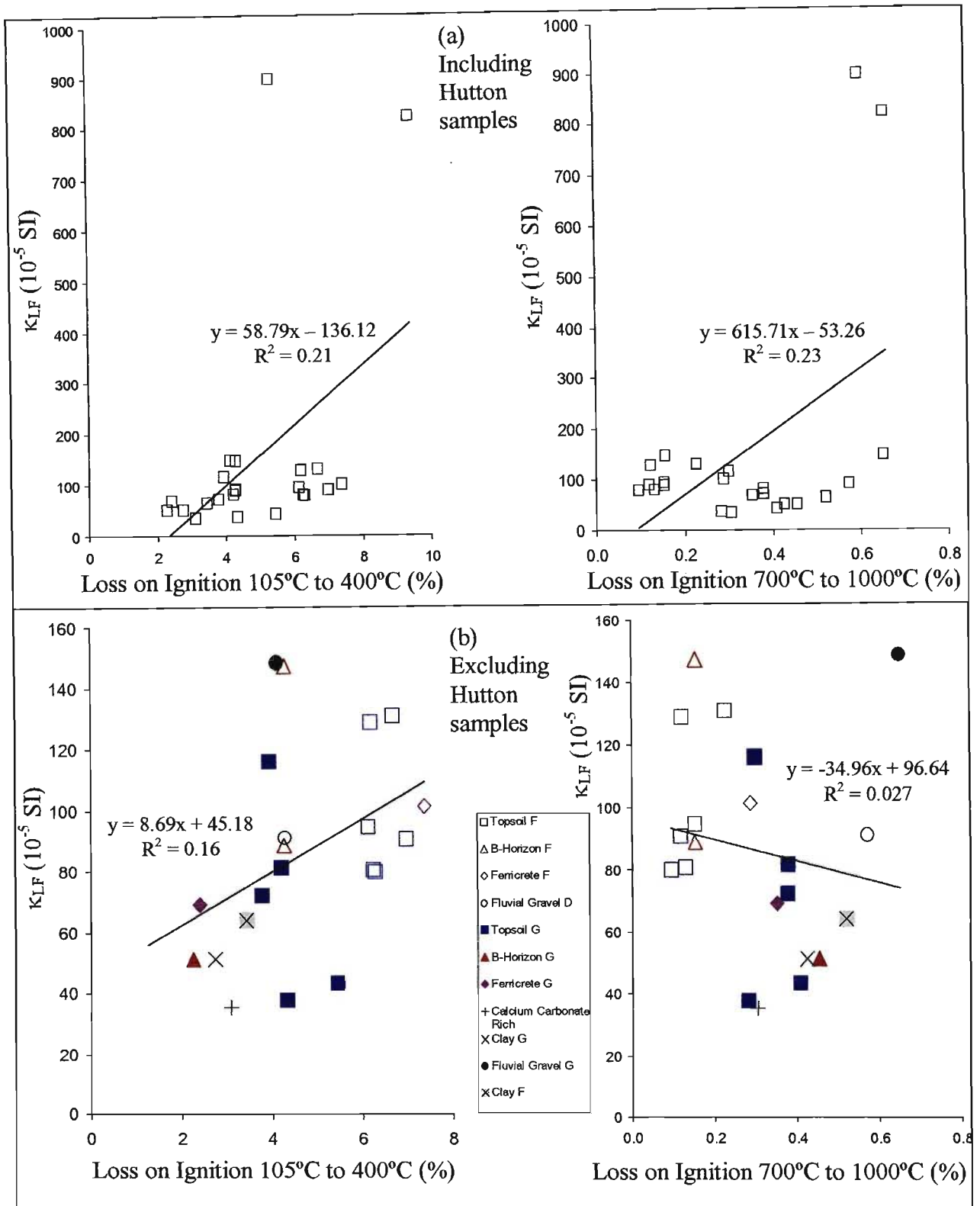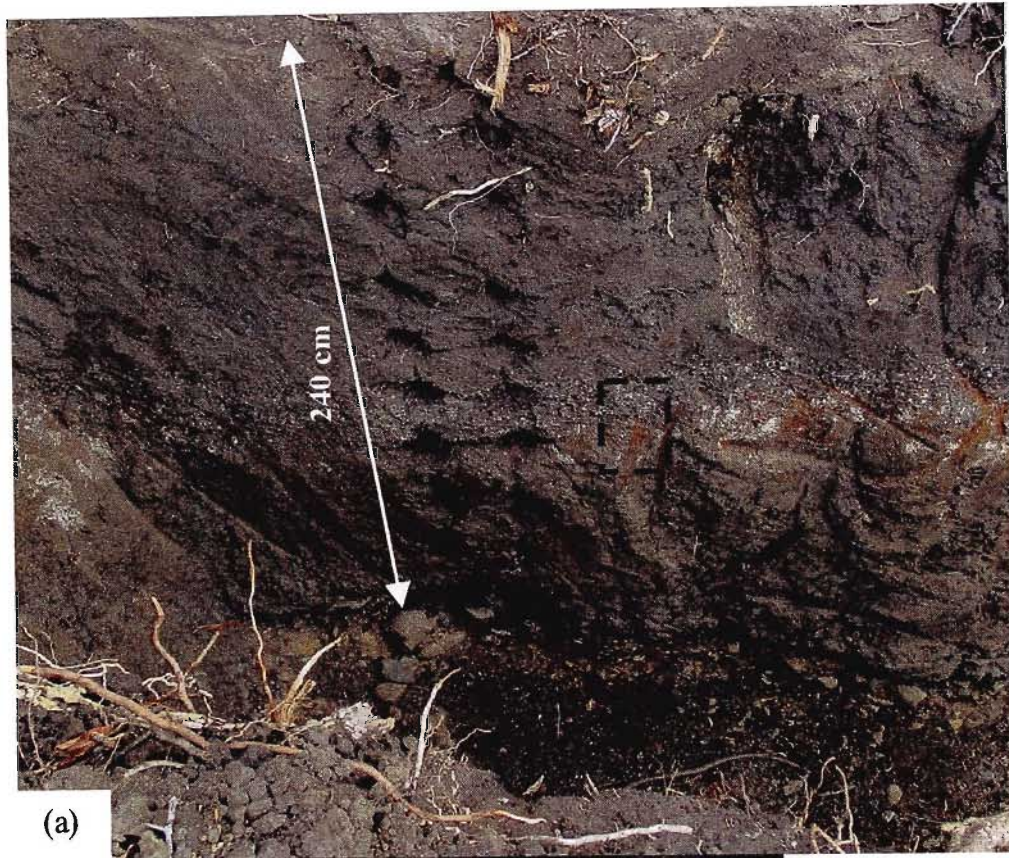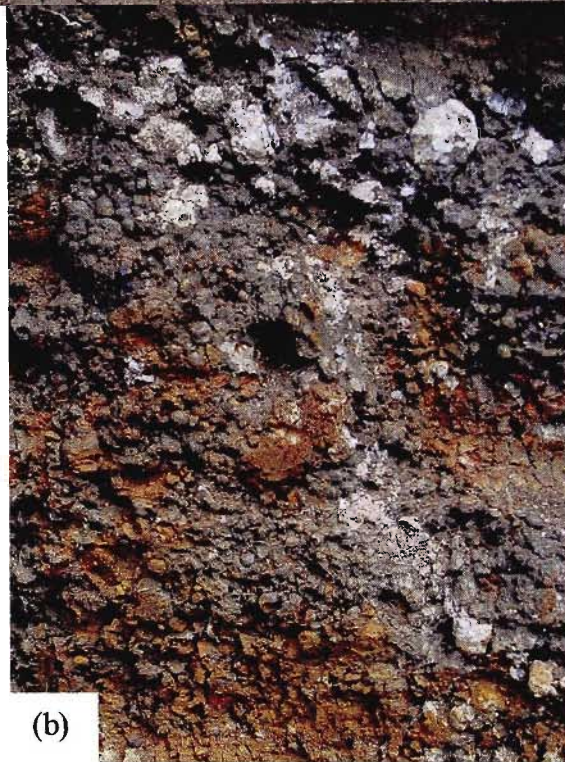
Fig. 7. The relationship between κ_{LF} and the means (n=2) of loss on ignition between105°C and 400°C and loss on ignition between 700°C and 1000°C (a) including and (b) excluding the Hutton samples.

Plate 1. Grid IV in the Bonamanzi trench displaying (a) the clear visible layering and (b) close-up of the iron concretions and calcium carbonate evident in the trench (area marked in (a)).