

Characterisation of soils by mineral magnetic measurements

B.A. Maher *

Department of Geography, University of Liverpool, P.O. Box 147, Liverpool L69 3BX (Gt. Britain)

Maher, B.A., 1986. Characterisation of soils by mineral magnetic measurements. *Phys. Earth Planet. Inter.*, 42: 76–92.

Processes of iron mineral authigenesis, diagenesis, and dissolution, in interaction with primary inputs of iron minerals, act to produce vertical differentiation of soil magnetic properties. Thus, magnetic iron oxides, in common with other iron forms, may both respond to and reflect soil forming processes. Investigation of the degree of detectable and persistent magnetic differentiation within different soil materials can provide insights into the nature and direction of distinct sets of soil processes. Evidence of clear association between magnetic variation and discrete types of soil environment also has applied significance, in several areas of environmental study: for example, the observed magnetic variation can be used to discriminate between individual soils and soil horizons, for the purposes of soil surveying, sediment 'tagging' and tracing, and empirical modelling of source-sediment linkages.

This paper reports the use of mineral magnetic techniques to characterise the iron oxide assemblages within soils of varying type and provenance. The effect of different pedogenic regimes have been investigated through measurement of a range of magnetic parameters (including magnetic susceptibility, frequency dependent susceptibility, and anhysteretic and saturation remanences).

Contrary to current pedological thought, but in accord with other, magnetically-based, studies (e.g., Mullins), the presence of magnetite/maghemite (typically of superparamagnetic-single domain grain size) within soils has been found to be an extremely widespread phenomenon. Its contemporary neof ormation within the soil environment is inferred. However, the input of artificially-generated ferrimagnetic material is indicated for one of the magnetically 'enhanced' soils examined here, and the possibility of extraneous sources of magnetite in topsoils should be considered before pedogenic processes of magnetic enhancement are inferred. From the data presented, discrimination of industrially-derived magnetic particles appears possible, on the basis of their very low levels of frequency dependent susceptibility (χ_{fd}), low anhysteretic remanence (*ARM*), and dissociation from the finer, clay-sized ($< 2 \mu\text{m}$) components of the soil.

Not the formation but the active dissolution of ferrimagnetic minerals is indicated for soils affected by the processes of gleying and podsolisation. Eluvial horizons of podsolised profiles demonstrate almost total loss of detectable magnetic content; variations in the form of the iron reprecipitated in the underlying illuvial layers may reflect differences in the pedological characteristics of these horizons. Within gleyed (waterlogged) soils, processes of magnetite dissolution appear to be grain size-specific; preferential reduction of those grains of ultrafine (superparamagnetic) and fine (single domain) magnetic grain size is indicated. Where soil forms a major contributor to catchment sediment loads, this has significance in the area of source-sediment modelling. Soil derived from permanently wet or highly leached catchment areas is unlikely to contribute to peaks in the magnetic content of deposited sediments; further, only those erosional processes that operate at a faster rate than those of magnetic depletion will have the capacity to produce peaks in sediment ferrimagnetic concentrations such as have been observed within the historical magnetic record.

1. Introduction

Although not a major component (in quantitative terms) of most post-glacial soils, iron is of immense importance in processes of soil profile

development. The many forms in which it occurs significantly affect several of the physical properties of the soil; soil colour, structure and fabric are all notably influenced by variations in iron mineral forms and distributions. In the oxide form, iron may also act as either a potential source or sink of plant nutrients and soil pollutants, through the adsorption of ions, some of which may be incorpo-

* Present address: Department of Geophysics, University of Edinburgh, Mayfield Road, Edinburgh, Gt. Britain.

rated into the oxide structure. Iron attains significance for profile development both through its mobility and its sensitivity to ambient environmental conditions; these properties are conferred by its ability to change valence state, to form complexes with other soil components, and to form a wide range of environmentally-specific oxide phases.

The specificity of response of the various oxide forms to ambient environmental and micro-environmental regimes potentially presents to the soil scientist a record of the disparate directions and pathways of pedogenesis. Awareness of the value of differential and possibly diagnostic soil iron speciation has led to increasing efforts to characterise distributions and forms of iron within

TABLE 1

Mineral magnetic parameters and instrumentation

K, χ	<p>Magnetic susceptibility: the ratio of magnetisation induced to intensity of the magnetising field. This is measured <i>within</i> a small magnetic field (c. 0.1 mT), and is reversible (i.e., no remanence is induced). Can be measured on a volume (K) or mass specific (χ) basis. Roughly proportional to the concentration of ferrimagnetic minerals within a sample</p> <p>^a Instrumentation: Single sample susceptibility sensor Units: K (dimensionless), χ ($\text{m}^3 \text{kg}^{-1}$)</p>
χ_{fd}	<p>Frequency dependent susceptibility: the variation of susceptibility with frequency. This parameter indicates the presence of grains lying at the stable single domain/superparamagnetic boundary; at higher frequencies of measurement, a proportion of these grains will become blocked in, and will no longer contribute to χ as superparamagnetic but as single domain grains. Values of high-frequency χ (χ_{HF}) can thus be expected to be proportionally lower than χ_{LF} values. Expressed here as a % of χ_{LF}:</p> $\frac{\chi_{LF} - \chi_{HF}}{\chi_{LF}} \cdot 100 = \chi_{fd}\%$ <p>^a Instrumentation: Dual frequency (1 and 10 Kh) susceptibility sensor</p>
<i>ARM</i>	<p>Anhyseretic remanent magnetization: if a sample is subjected to a decreasing alternating field with a small steady field super-imposed, it acquires an anhyseretic remanence. This parameter is sensitive both to the concentration and grain size of ferrimagnetic minerals in a sample</p> <p>^b Instrumentation: Anhyseretic magnetiser (max. a.c. field 100 mT, direct field 0.04 mT). Units: $\text{Am}^2 \text{kg}^{-1}$</p>
<i>SIRM</i>	<p>Saturation isothermal remanent magnetisation: the highest level of magnetic remanence that can be induced in a sample by application of a high field. <i>SIRM</i> is an indicator of the volume concentration of magnetic minerals in a sample, but also responds to grain size variations.</p> <p>^b Instrumentation: Pulse magnetiser (max field 880 mT), fluxgate magnetometer Units: $\text{Am}^2 \text{kg}^{-1}$</p>
$SIRM/\chi$	<p>The ratio of these two parameters can be diagnostic of either mineralogy type (e.g., a low—theoretically zero—ratio indicates the presence of paramagnetic minerals) or where samples have similar mineral types and concentrations, the dominant magnetic grain size.</p>
$(B_0)_{cr}$ $IRM_{-x}/SIRM$ 'S'	<p>Demagnetisation parameters: obtained by applying one or more reversed magnetic fields to a previously saturated sample. The reverse field strength (mT) required to return a magnetised sample from its <i>SIRM</i> to zero is termed the coercivity of remanence $(B_0)_{cr}$. The loss of magnetisation at other selected backfields can be expressed as a ratio, $IRM_{-x}/SIRM$ (giving a result between +1 to -1); the ratio obtained using $IRM_{-100 \text{ mT}}$ (a backfield which discriminates between ferrimagnetic and antiferromagnetic mineral types) has been termed the 'S value'</p> <p>Instrumentation: Pulse magnetiser (pm), fluxgate magnetometer Units: $(B_0)_{cr}$ (mT)</p>

^a Bartington Instruments Ltd.^b Molspin Ltd.

different profile types; (e.g., Kodama et al., 1977; Bigham et al., 1978). Access to the pedogenic information held by these soil components is hindered, however, by their analytically unfavourable properties of generally low concentrations, very small grain size, and poorly developed crystallinity. Extractions of iron by theoretically selective reagents are routinely performed in soil analyses; more quantitative methods of analysis resort to increasingly sophisticated and expensive techniques, such as differential X-ray diffraction (Schulze, 1981) and Mössbauer analysis (Goodman, 1980; Longworth and Tite, 1976).

The application of mineral magnetic techniques to soil studies presents a new opportunity to characterise certain areas of the soil iron oxide system, although it should be noted that the focus of these techniques may not necessarily coincide directly with that of other methods, such as those noted above. If it can be shown that the magnetic iron oxides, in common with other iron forms, are responsive to and reflective of soil-forming processes, mineral magnetic techniques may provide a new means of access to this pedogenic information.

2. Mineral magnetism

'Mineral magnetism' is the term that has been given to the investigation of the non-directional

magnetic properties of materials, which arise from their inherent iron mineralogy and granulometry. It involves the measurement of both the in-field and remanent responses of the material under study to a series of externally applied magnetic fields. Many of the parameters thus obtained derive from palaeo- and rock-magnetic studies; however, for the purposes of rapid and simple characterisation of large numbers of natural samples, the methodology has until now preferentially used a restricted range of room temperature magnetic measurements. Table I gives a brief summary of the parameters and instrumentation used within this study.

3. Soil iron oxides

The minerals of major interest in magnetic studies are the iron oxides. Within the soil, these minerals can exist as discrete fine particles or grains, as aggregated concretions, or as very fine-grained material coating other grain or void surfaces (Taylor et al., 1983). Table II lists the most commonly occurring soil iron oxides, together with their magnetic status and reported environmental associations.

The factors controlling the forms and distributions of soil iron assemblages may be expected to be similar to those affecting other soil properties,

TABLE II
Iron oxides in soils

Mineral	Formula	Magnetic status	Reported environmental associations
Haematite	$\alpha\text{Fe}_2\text{O}_3$	Canted antiferromagnetic	Relatively dry, highly oxidised soils, usually in areas of elevated temperature
Goethite	αFeOOH	Canted antiferromagnetic	Moister soils, abundant in well-drained temperature areas
Maghemite	$\gamma\text{Fe}_2\text{O}_3$	Ferrimagnetic	Abundant in highly weathered tropical/sub-tropical soils
Lepidocrocite	γFeOOH	Paramagnetic	Occurs in poorly drained soils
Ferrihydrite	$5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}^a$	Paramagnetic	Poorly drained and podsolised soils
Magnetite	Fe_3O_4	Ferrimagnetic	Restricted occurrence, primarily derived or from soil firing.

^a After Schwertmann and Taylor, 1977.

with parent material, climate, biological action, drainage, relief and time each playing a role. In addition, however, extraneous sources of iron oxide minerals may contribute to the soil magnetic record, notably through the effects of soil combustion, and from atmospheric fall-out of natural and/or industrially-derived magnetic particles.

4. Materials and methods

To investigate the degree of detectable and persistent magnetic differentiation possessed by different soil materials, a range of measurements has been performed on a large number of soils of varying type and provenance.

Samples were obtained from cores of soil (extracted using rigid plastic drain piping of 6.5 cm diameter) and also from excavated soil pits, the use of ferrous implements being avoided where possible. All samples were oven-dried overnight at a temperature no higher than 40 °C (to avoid possible thermal alteration of the initial soil oxide assemblage), gently disaggregated with a pestle and then sieved to exclude particles larger than 2 mm. Between 5–10 g of each soil were packed firmly into pre-weighed cylindrical plastic sample holders of 10 cc volume, and immobilised by packing with clean foam.

5. Magnetic differentiation

Figures 1–4 illustrate, for a range of soil profile types, the variation with profile depth of a number of the magnetic parameters defined in Table I. All but two of these soils are British in origin, the exceptions are derived from an arid and a semi-arid zone in the western U.S.A. (Table III). Profiles have been illustrated which represent several, contrasting major British soil regimes, including strongly brunified, podsolised and gleyed soils, together with two intergrade profile types. From these diagrams, distinct variation of magnetic properties both within and between the soils is readily apparent. Similar measurements have been made on large numbers of soil samples; the profiles and data presented here have been selected to

TABLE III

Location and classification of soils sampled

Sample code	Location	Soil type
ArdG	Ardnamurchan, W. Scotland	Gley
ArdF	Ardnamurchan, W. Scotland	Acidic brown earth
Geir	Gwdyr Forest, N. Wales	Peaty ranker
PSBE	Pinkery Farm, Exmoor, U.K.	Brown earth
ExPod	Pinkery Farm, Exmoor, U.K.	Stagnopodsol
HarW	Hardwick Wood, Cambs., U.K.	Brown pelosol
Sway	Sandiway, Cheshire, U.K.	Brown sand
PD	Painted Desert, Arizona, U.S.A.	
DG	Fredonia, Arizona, U.S.A.	

demonstrate magnetic differentiation arising from distinct types of magnetic and pedological input, the contributions and effects of which are discussed in turn below.

6. Parent material input

The results of weathering processes are indicated by mineralogical, chemical and grain volume changes in the developing soil as compared with the unaltered underlying parent material. Weathering, and the consequent release of iron to the soil system, is dependent on the type of substrate available and the stability of its constituents under prevailing environmental conditions. Weathering may act *indirectly* on the amounts of iron oxides in soils by either relative concentration or dilution of these mineral phases. For example, selective loss of diamagnetic and paramagnetic minerals (such as calcium carbonate and the pyroxenes), through dissolution and removal from the profile, may produce greater magnetic concentrations. Conversely, the new production of non-ferrimagnetic phases (such as organic matter) will effectively dilute the magnetic signal.

A developing soil profile may inherit significant quantities of resistant, primary magnetic iron oxides from its weathering substrate, where this contains these mineral species. An igneous bedrock, for example, may contain magnetite (or, more commonly, titanomagnetite) in concentrations up to c. 10%. In contrast, a sedimentary

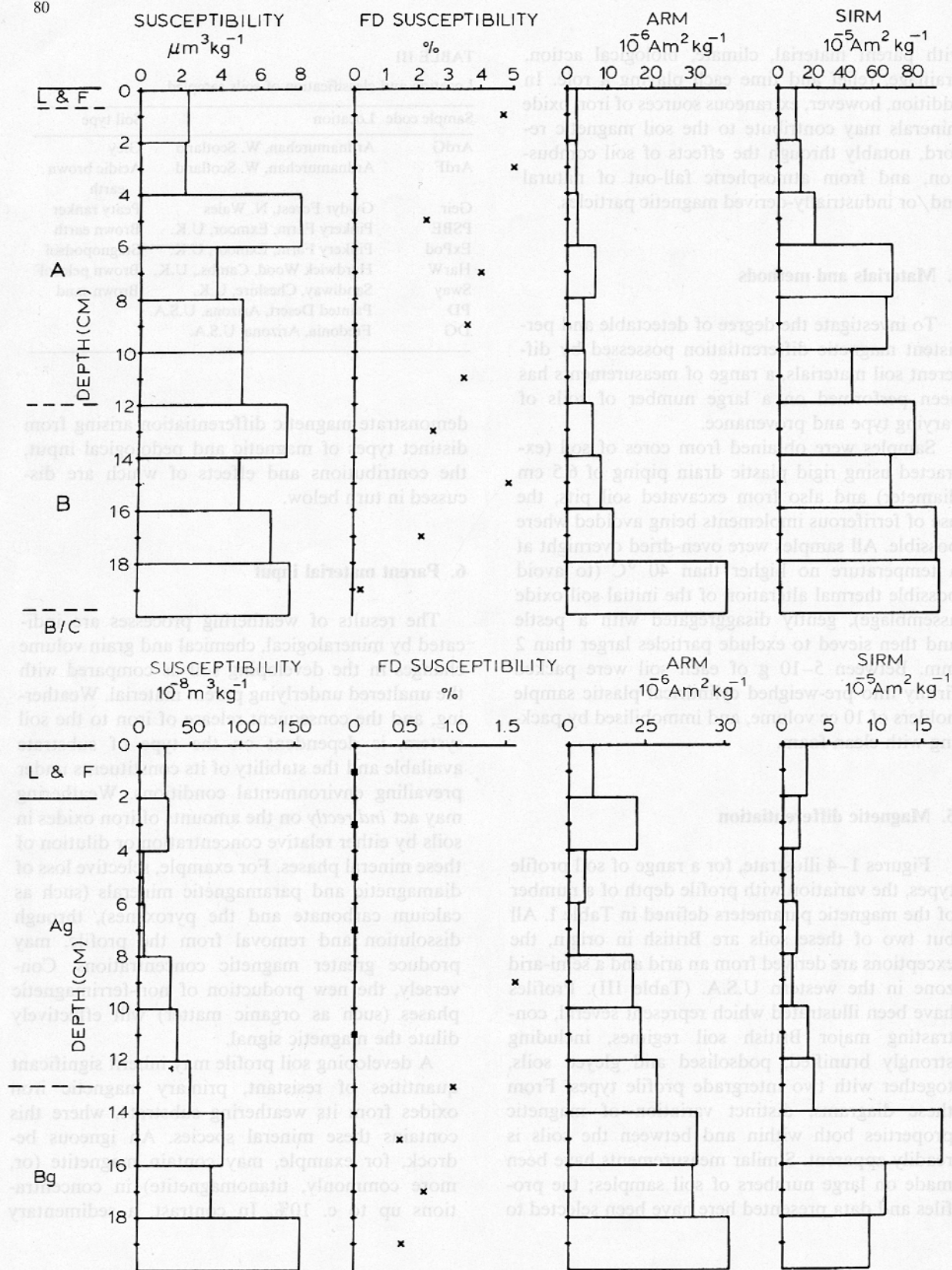


Fig. 1. Profiles developed on doleritic parent material, Ardnamurchan, W. Scotland, demonstrating primary magnetic input: (a) acidic brown earth profile; and (b) gleyed profile.

substrate, such as red sandstone, may contain considerably lower concentrations of iron oxide (this particular rock type deriving its ferruginous colouration from finely disseminated grains of haematite coating the individual grains of silica). In the case of the igneous material, the effect of weathering is twofold: firstly, the resistant primary magnetic grains are released at the weathering front into the developing surficial soil; secondly, ionic iron is liberated from the other iron-bearing minerals of the rock, notably from the ferromagnesian silicates.

Even where parent materials are devoid of primary iron oxide phases, weathering processes will act to liberate iron, in the ionic form, into the soil system. Subsequent to its release from mineral

lattices, this iron may be oxidised and precipitated in situ; alternatively, it may be taken into the soil solution (as Fe^{2+}) and precipitated elsewhere in the profile, depending on the oxidative status of the soil micro-environment.

In summary, the contribution of weathering to the distribution, nature and concentration of soil iron oxides can include the release of primary magnetic grains, but everywhere provides a pool of liberated iron cations, which may then crystallise into the iron oxide phases most stable with respect to the ambient soil environment.

The primary input of magnetite to an acidic brown earth soil developed on doleritic parent material is illustrated in Fig. 1a, where marked increases occur in the values of χ , ARM and

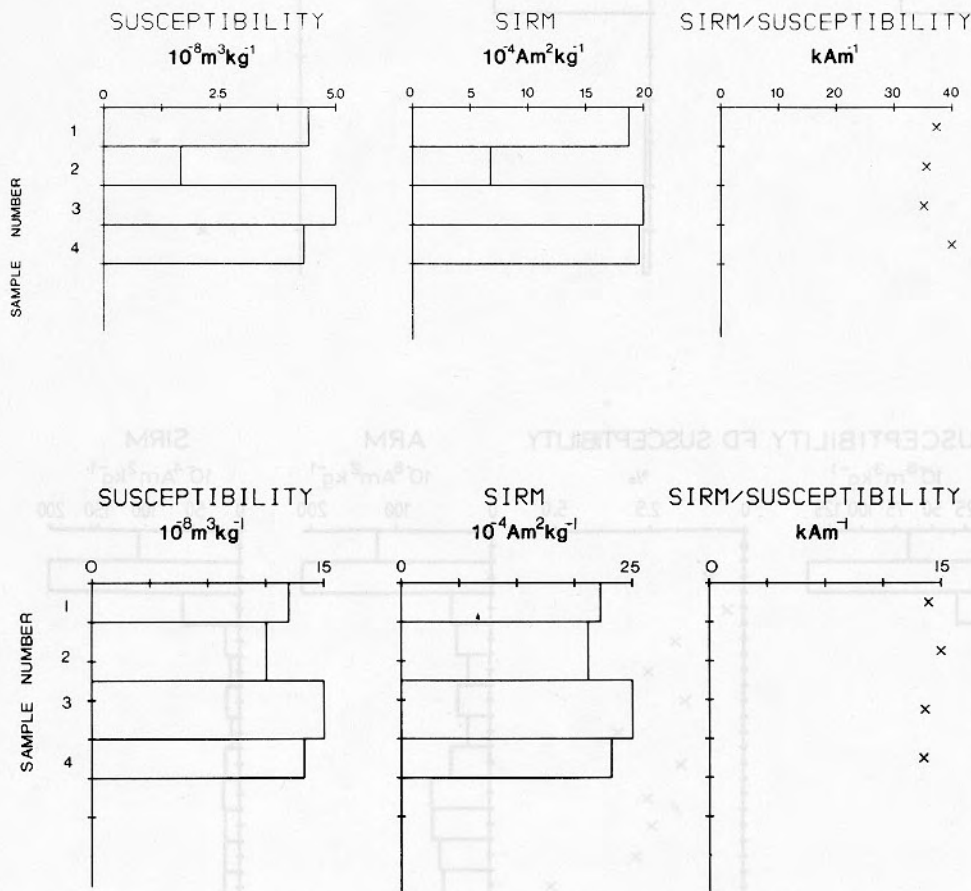
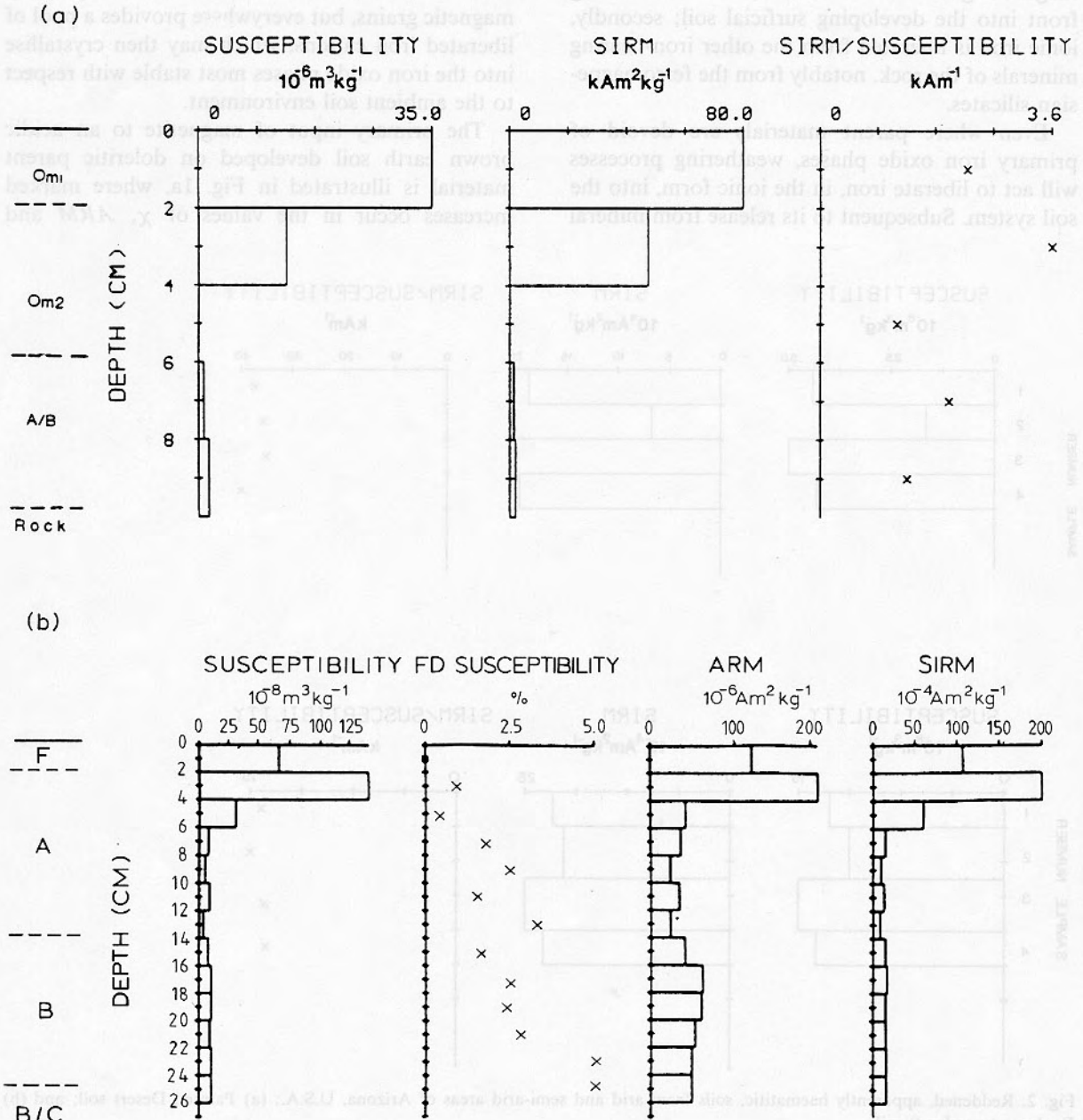


Fig. 2. Reddened, apparently haematitic, soils from arid and semi-arid areas of Arizona, U.S.A.: (a) Painted Desert soil; and (b) Fredonia (grassland) soil.

SIRM toward the profile base. There is close correspondence between *SIRM* and χ at all depths (producing *SIRM*/ χ ratios of c. 8 kAm^{-1}), suggesting a dominantly monomineralic magnetic contribution. The pattern of a steady increase in χ with depth is interrupted by particularly high val-

ues at depths of 4–6 cm ($8 \mu\text{m}^3 \text{ kg}^{-1}$) and at 12–14 cm ($7 \mu\text{m}^3 \text{ kg}^{-1}$), which indicate localised increases in ferrimagnetic concentration. The presence of grains of superparamagnetic dimensions is indicated by the occurrence of measurable values of χ_{fd} throughout most of the profile. Unlike χ ,



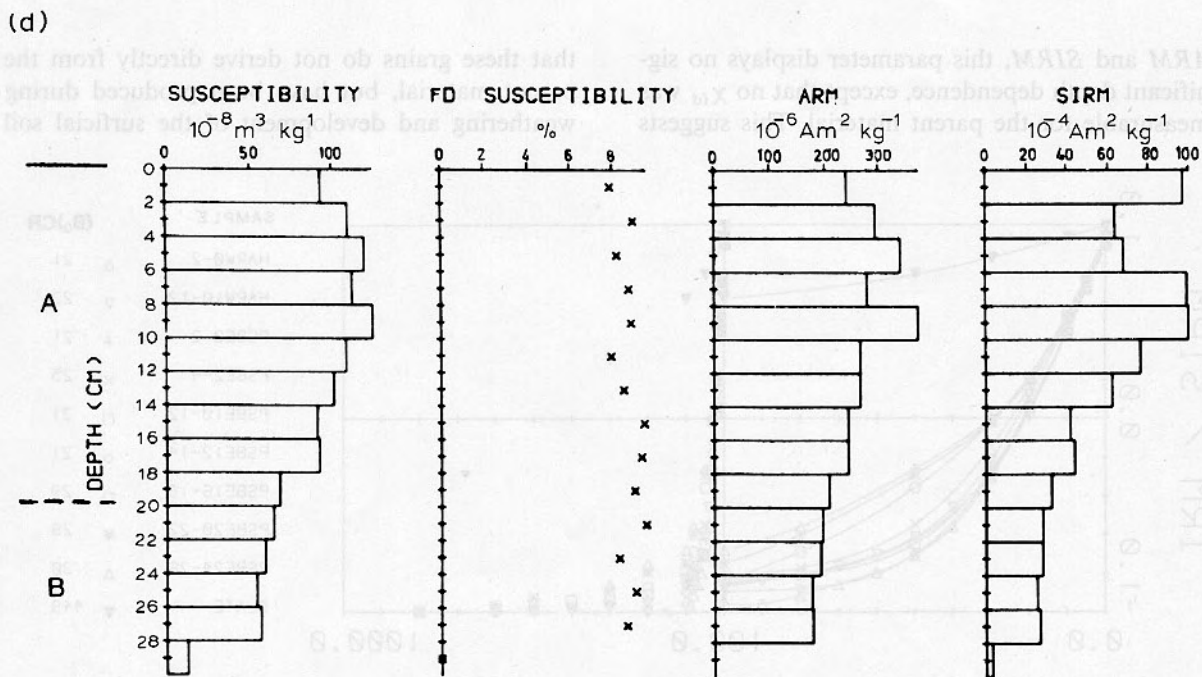
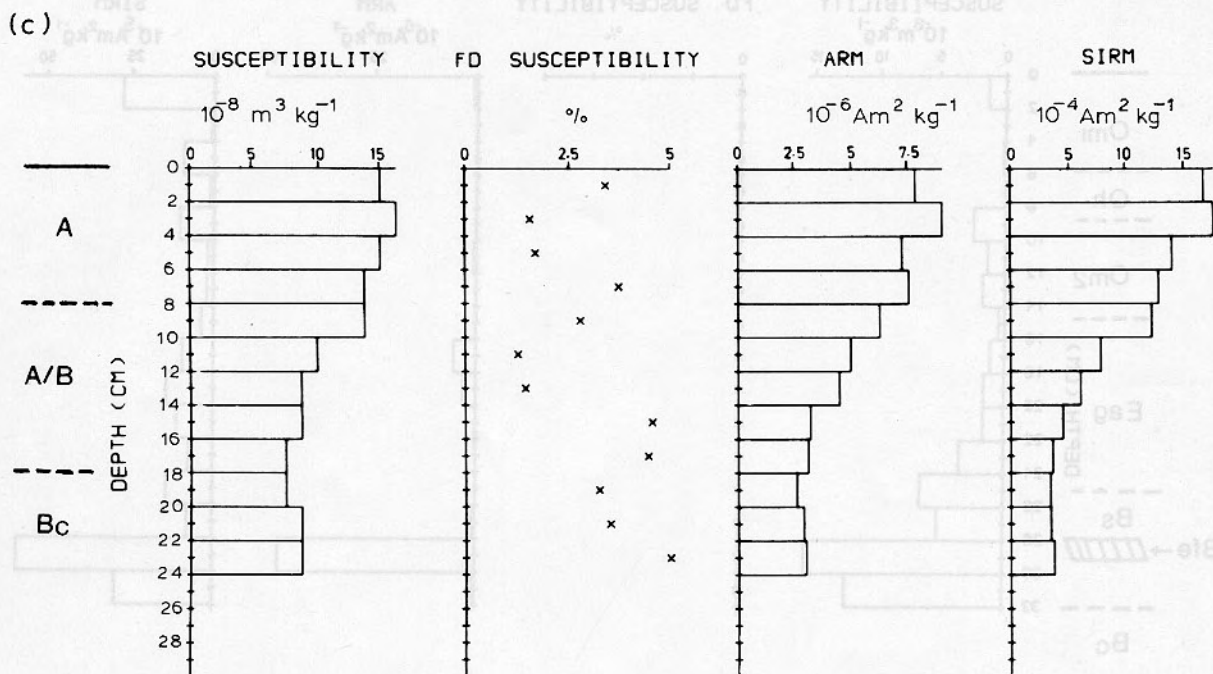


Fig. 3. Temperate zone profiles demonstrating upper soil magnetic enhancement: (a) Burnt peaty ranker soil, Geirionydd, N. Wales; (b) Brown sand profile, Sandiway, Cheshire; (c) Brunified pelosol, Hardwick Wood, Cambs.; and (d) Slope brown earth, Exmoor.

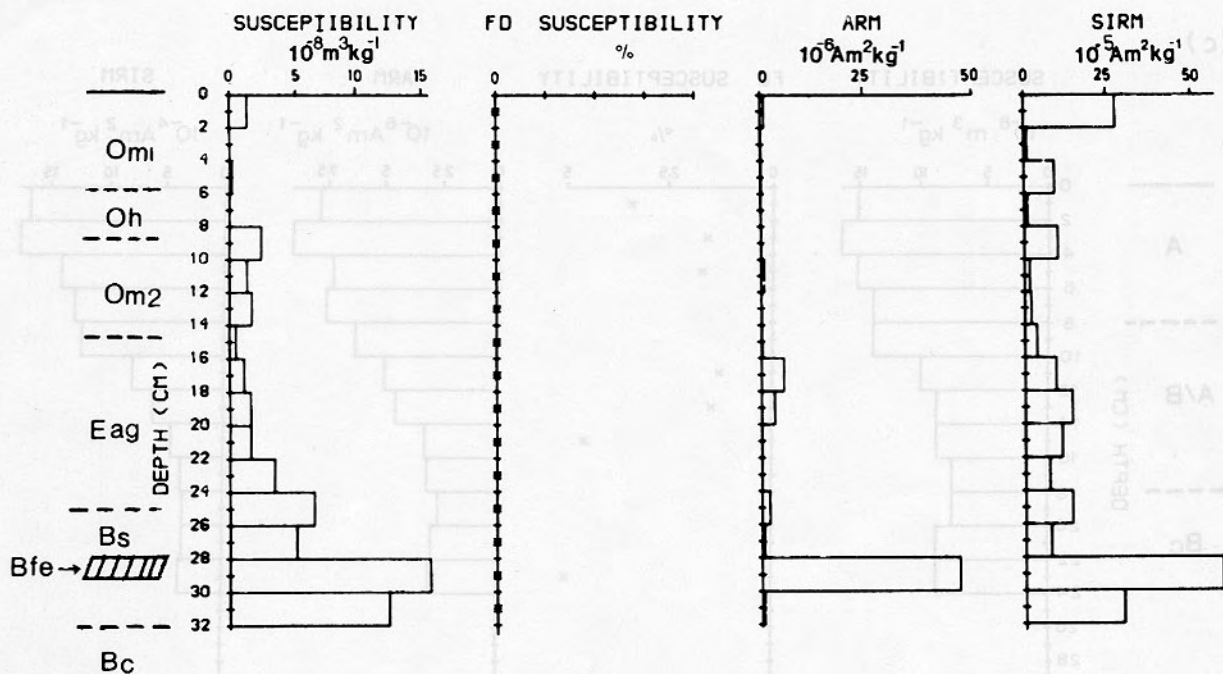


Fig. 4. Stagnopodsol, Exmoor.

ARM and *SIRM*, this parameter displays no significant depth dependence, except that no χ_{fd} was measurable for the parent material. This suggests

that these grains do not derive directly from the parent material, but have been produced during weathering and development of the surficial soil

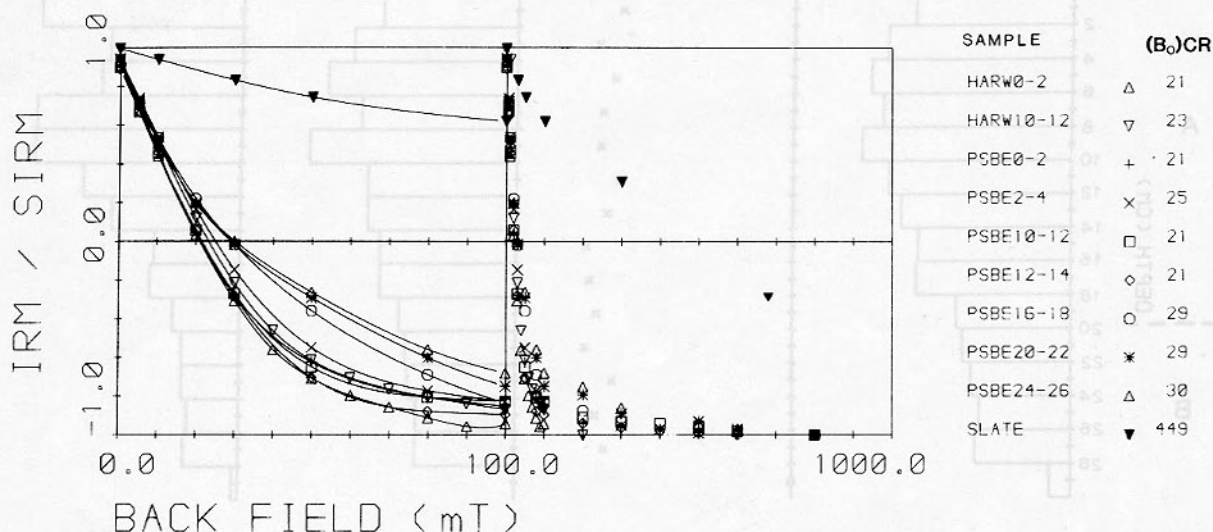


Fig. 5. Coercivity curves for selected samples.

horizons. In addition, there is an apparent correlation between the two notably high profile χ values (at 4–6 cm and 12–14 cm depth) and lower values of χ_{fd} . The inclusion of less weathered granules at these depths within the profile may thus be indicated.

The parent materials of the remaining temperate zone profiles (Fig. 3a–d) range from Triassic sandstone, to Devonian and Silurian slates and shales, soliflucted Devensian till, and chalky loess. The slaty substrate of the Exmoor brown earth profile (Fig. 3d) is notable for its extremely hard magnetic behaviour. It is characterised by very low values of χ and *SIRM* and gives a $(B_0)_{CR}$ value of 449 mT (Fig. 5), indicating the presence of a fine-grained canted antiferromagnetic component. It should be noted that in this, and the other temperate soils, the weathering substrate contributes little if any primary ferromagnetic content to the developing soil horizons, and a generally inverse relationship exists between profile depth and the magnitude of χ , *ARM* and *SIRM*. To use Le Borgne's (1955) original terminology, each of these profiles displays an *enhancement* (section 8) of magnetic properties within their upper horizons.

7. Climate—macroclimatic versus microclimatic control

Table II outlines the reported associations between the various iron oxide forms and different environmental regimes (Schwertmann and Taylor, 1977). From thermodynamic considerations, macroclimatic conditions can be expected to exert some level of systematic control on potential soil iron oxide mineralogies. Earlier, non-magnetic studies have indicated quantitative associations between specific oxide forms and discrete ranges of climatic factors. Kampf and Schwertmann (1983), for example, reported increases in the goethite:haematite ratio in an east–west trending climosequence in S. Brazil. The environmental factors correlating with this sequence comprised: decreasing annual air temperature, increasing excess moisture, increasing soil organic carbon and decreasing soil pH. Conversely, a study of some soils in NW

Tasmania (Taylor and Graley, 1967) observed a decrease in goethite/haematite ratios which correlated with a decrease in altitude from 575 m to sea level, an increase in temperature from 9 to 12 °C and a decrease in rainfall from 1650 to 1080 mm p.a. Within these gross patterns of systematic variation, individual soil characteristics may attenuate the role of general climatic control. Kampf and Schwertmann (1983) additionally noted the paired occurrence of reddish (haematitic) soils on gravels adjacent to yellowish (goethitic) soils on silty parent material. They suggest that the coarser texture of the gravel-based soils allows free drainage and increased heat retention; with respect to haematite formation, these soils thus surmount the limiting factor of temperature. In contrast, the silty textured soils are effectively self-limiting in temperature, due to their poorer drainage and lowered heat retention. Thus, although general control on potential soil iron oxide mineralogy may be exerted by the macroclimate, its actual composition may be finally determined by the micro-environmental pedoclimate.

Insights into such climate:mineralogy associations may also be gained through magnetic analysis. Figure 2a, b illustrates some magnetic data obtained for two highly reddened soils, one from an arid zone environment (the Painted Desert, Arizona, U.S.A.) the other from a semi-arid, vegetated environment (Fredonia, Arizona, U.S.A.). Under its prevailing environment of moisture deficit and elevated temperatures, the Painted Desert soil can be expected to accumulate the dehydrated iron oxide form, haematite ($\alpha\text{Fe}_2\text{O}_3$). Indeed, in comparison with the range of values displayed by the temperate zone profiles, this soil is characterised by very low values of χ and *SIRM*, and by a high ratio between these two parameters. It also displays marked resistance to demagnetisation; even at a backfield of 100 mT, nearly 30% of its initial forward magnetisation is retained (i.e., 'S' values = +0.28). Thus, for this soil, this very hard, typically canted antiferromagnetic behaviour confirms the visual impression of the presence of significant quantities of haematite. In contrast, the similarly reddened Fredonia soil displays values of χ some 20–30 times higher, has much lower *SIRM*/ χ ratios, and strongly negative 'S' ratios

($S' = > -0.5$), indicating not the presence of the quantitatively dominant oxide phase, haematite, but of a magnetically dominant ferrimagnetic phase, of magnetite/maghemite*. Clearly, as with the Painted Desert soil, the haematite present can be attributed to the generally oxidative status of this semi-arid zone soil. The apparently anomalous presence of magnetite (if extraneous origins can be excluded) may reflect the operation of relatively anoxic conditions within localised zones of the soil micro-environment.

8. Fire and fermentation

Natural formation of magnetite is generally related to extreme environmental conditions of high temperature and anaerobia. As noted by Le Borgne (1955), such conditions may be temporarily produced within the soil environment during either natural or man-induced firing of vegetation.

The combustion of organic compounds in the topsoil causes both great temperature elevation (up to 800 °C) and production of a reducing soil pore atmosphere. Under these conditions the non-ferrimagnetic oxides present in the soil as weathering end-products (section 6) are reduced to magnetite, which may itself re-oxidise to maghemite as air re-enters the soil on cooling. In poorly drained soils, the elevated temperatures may cause direct formation of maghemite, without the intermediate magnetite phase, through the dehydration of lepidocrocite (Scheffer et al., 1959).

Oldfield et al. (1981) identified the major controlling variables within the firing process and the variations in magnetic mineralogy which result in response to varying conditions of the system. Analogy may also usefully be made with other magnetic and Mössbauer studies, undertaken in

relation to archaeological finds, of iron oxide alteration induced during the firing of clay pots (for example, Chevalier et al., 1976).

The efficacy of firing as a process of soil magnetite formation is undoubted, the resulting enhancement level depending on site specific factors such as the amounts of organic matter and iron present in the upper soil, its porosity, and the temperature attained.

Figure 3a illustrates the χ and *SIRM* values obtained from a shallow peaty upland soil burnt in an extensive forest fire within the Gwdyr Forest region of N. Wales in 1976. Values of these parameters are very low at the middle and base of the profile indicating there is no primary magnetic input from the parent material of Silurian siltstones and shales. Within the top 5 cm, however, χ values increase dramatically, reaching a maximum at the surface of $36 \mu\text{m}^3 \text{kg}^{-1}$ (corresponding to a ferrimagnetic concentration of 8%). For comparison surface χ values for adjacent unburnt areas vary around $0.13 \mu\text{m}^3 \text{kg}^{-1}$.

Fire is and has been an ecological phenomenon of widespread significance, an observation emphasised by the difficulty presented in attempting to identify totally unburnt areas. It is tempting, therefore, to follow Le Borgne (1960) and ascribe soil magnetite, where present, to production by fire and subsequent distribution within the profile by bioturbation and physical translocation (for example, by lessivage). Schwertmann and Fechter (in press) further emphasised the role of fire in the genesis of soil ferrimagnets through identification of some maghemitic samples with significantly reduced maghemite unit cell size. The reduced d spacings are attributed to the effects of substitution by Al^{3+} of some of the Fe within the maghemite structure. Schwertmann and Fechter (in press) argued that the presence of Al within the maghemite lattice may identify the genesis by fire of this mineral on the basis that:

(1) firstly, lithogenic magnetites usually do not contain Al to any significant extent. It is unlikely, therefore, that the maghemites derive from the oxidation of primary magnetite inherited from the parent rock by weathering;

(2) a second possible mode of formation, the dehydration of lepidocrocite, is excluded as this

* As noted by Longworth et al. (1979), secondary (soil-derived) ferrimagnetic oxides may occupy a range of positions close to the solid solution series between magnetite and maghemite. In addition, precise differentiation between the two mineral phases is extremely difficult. For these reasons, secondary ferrimagnetic minerals will be referred to in this study simply as 'magnetite', with the proviso that a specific mineralogical identification is not thus intended.

mineral does not occur within these soils, nor is it Al-substituted; and

(3) assuming no other source within the soil of Al-substituted magnetite, the presence of structural Al within the maghemites can finally only be attributed to the conversion of goethite or haematite, in which Al substitution seems to be the rule rather than the exception (Norrish and Taylor, 1961) by heating under reducing conditions—that is, under soil firing.

However, despite the postulated ubiquity and efficiency of fire as a mechanism of magnetite production, a number of studies have noted widespread occurrences of generally less dramatic increases of upper soil magnetic content (for example, Le Borgne, 1955; Neumeister and Peschel, 1968; Mullins and Tite, 1973; Oldfield and Maher, 1984). This type of widespread enhancement may perhaps be distinguished from fire effects by its very evenness of distribution, as fire in contrast tends to produce optimum levels of enhancement in a highly localised, almost point specific way, depending on the factors of soil iron content, litter layer depth and soil conductivity. (For example, highest enhancement levels are often found around burnt tree trunks, where organic matter concentration is locally increased.) To account for the more extensive occurrences of low concentrations of soil magnetite, operation of another type of enhancement mechanism is envisaged. Mullins (1977) followed Le Borgne in suggesting that a 'fermentation' process, consisting of oxidation/reduction oscillations incurred during normal pedogenesis through wetting and drying cycles, is responsible for upper soil mineralogy change. More precise definition of the processes involved in this type of 'natural enhancement' may possibly be gained from integration of empirical magnetic data with laboratory synthesis experiments and observations.

Of the four magnetically enhanced profiles illustrated in this paper (Fig. 3a–d), the Exmoor brown earth (Fig. 3d) and the Hardwick Wood pelosol (Fig. 3c) are distinct in that, compared to the burnt soil, they display intermediate to low levels of enhancement, with χ , *SIRM* and *ARM* each demonstrating a steady increase in magnitude away from the poorly or non-magnetic parent

material (of slate and chalk, respectively). Further, peak values are not restricted to the surface soil but (particularly in the Exmoor brown earth) are distributed throughout the A and upper part of the B horizons. The higher level of enhancement shown by the well-mixed Exmoor brown earth is also characterised by consistently high χ_{fd} , indicating the presence throughout this profile of grains of superparamagnetic dimensions. No measurable χ_{fd} was obtained for samples of the parent material of this soil. The heavier textured Hardwick Wood pelosol profile also displays measurable values of χ_{fd} , up to a maximum of 5%, but with a more erratic within-profile distribution. Coercivity curves have been compiled for samples from both profiles (Fig. 5); $(B_0)_{cr}$ values vary within a narrow range of values between 21 and 25 mT.

9. Atmospheric input

Extraneous production and input of ferromagnetic iron to topsoils may be derived from atmospheric fall-out of particulates of either natural or anthropogenic origin. Both volcanic dust and ash falls and industrially-derived particulates may contain significant concentrations of ferromagnetic minerals and thus constitute a potential and previously unconsidered source of magnetic input to soils.

Pyroclastic supply of magnetite to soils has, as yet, received little attention but may validly be excluded as a significant source for many soils. However, a possibly widespread supply of magnetic minerals to the atmosphere is currently generated through urban and industrial activity, by production of magnetic spherules during fossil fuel combustion (Hunt et al., 1984). Spherules appear to be characterised by the presence both of haematite and magnetite phases (together with some trace metal associations), and by a relatively large ($> SP/SD$) magnetite grain size.

Referring again to the four enhanced profiles illustrated in this paper, Fig. 3b illustrates the magnetic variation with depth of a brown sand soil, developed on fluvioglacial sands in the Cheshire basin. As with the burnt soil (Fig. 3a), this profile exhibits a distinct surface layer of enhance-

ment above a relatively poorly magnetic subsoil. High values of χ , *SIRM* and *ARM* (relative to the underlying soil) characterise the enhanced layer with a maximum χ value of $1.5 \mu\text{m}^3 \text{kg}^{-1}$. However, this layer is further characterised by very low values of $\chi_{\text{rd}}\%$, relatively low *ARM*/ χ and high *SIRM*/*ARM* ratios. Immediately below the layer of enhancement, χ , *SIRM* and *ARM* all decline to uniformly low levels throughout the remainder of the profile, implying negligible concentrations of magnetite. $\chi_{\text{rd}}\%$ is consistently measurable for this poorly magnetic part of the profile, reaching a maximum of 5% at 16–22 cm depth. Thus, in contrast to the major part of the profile, superparamagnetic grains are absent from the magnetic assemblage of the surface enhanced layer. Also, its lowered *ARM*/ χ ratios may reflect a relative paucity of grains of single domain dimensions, to which *ARM* is reported to be particularly sensitive (Banerjee et al., 1981).

Recent studies (Oldfield et al., in press; Dearing et al. 1985) have shown that specific particle size fractions of soil may dominantly contribute to the bulk magnetic signal. Mullins (1977) and Oades and Townsend (1953) reported the preferential presence of secondary ('pedogenic') magnetite within the clay fraction ($< 2 \mu\text{m}$) of soils. Figure 6 illustrates the distribution of *SIRM* and *ARM* values with respect to the individual particle size fractions of the magnetically distinct enhanced layer. Highest values of these parameters are clearly associated with the silt-sized fractions, and with the medium-coarse silt (16–63 μm) in particular. For comparison, Fig. 7 illustrates some results of particle size-specific measurements performed on the Exmoor brown earth soil. Here, the highest values of χ , *SIRM* and *ARM* correlate with the $< 2 \mu\text{m}$ fraction; intermediate and progressively decreasing values are obtained for the silt fractions; and lowest values were recorded for the coarse silt and sand.

Thus, although this Cheshire brown sand soil and the Exmoor brown earth profile (section 8) display similar maximum levels of magnetic concentration, their enhanced horizons have distinctly different magnetic characteristics. On the basis of its very restricted vertical extent, its low χ_{rd} and *ARM*, and the dissociation of its magnetic content

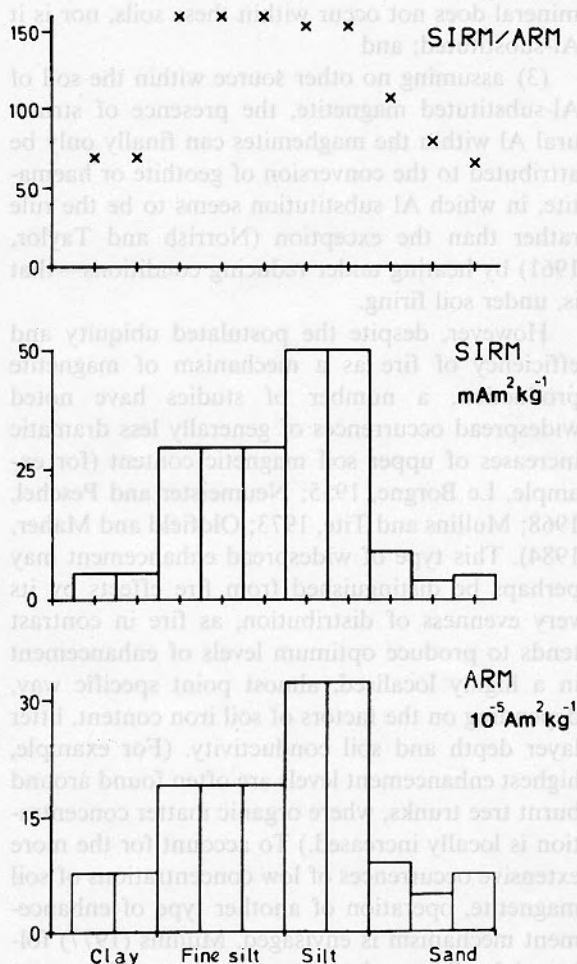


Fig. 6. Particle size-specific magnetic measurements, Sandiway brown sand profile.

from the clay-sized fraction of the soil, it is suggested that the enhancement of the Cheshire soil is attributable not to pedogenic formation of magnetite but to reception at the soil surface of atmospherically-supplied, magnetic, particulate pollution.

10. Podsolisation and gleying

Whereas evidence of natural enhancement seems to be significantly associated with brown earth type soils (Maher, 1984), not the formation but the

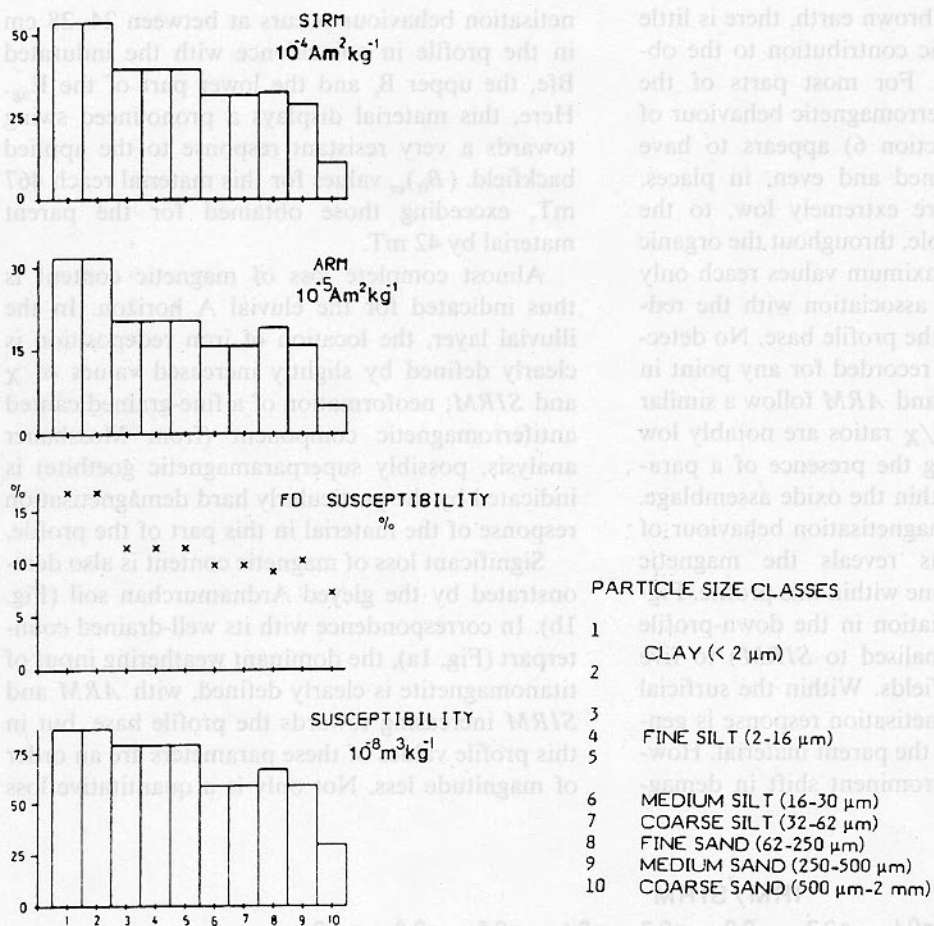


Fig. 7. Particle size-specific magnetic measurements, Exmoor brown earth.

active dissolution of ferrimagnetic minerals is indicated for soils affected by the processes of gleying and podsolisation. In contrast to the stabilising brown earth regime, formation of mobile, organometallic complexes is of major importance in the development of podsolised profiles, effecting the eluviation of iron and aluminium from the upper soil layers. Similarly major transformation and redistribution of iron is incurred under gleying (waterlogged) soil regimes. Iron oxides comprise a large fraction of the reducible components in soils and thus, in the absence of oxygen, provide a sink for the electrons produced by the metabolic reactions of plants and both aerobic and anaerobic microorganisms (Ottow and Munch, 1978). Thus,

dissolution of iron compounds by reduction is generally thought to be rapid and intense in the presence of organic matter in anaerobic conditions. However, by definition, drainage is poor in gleyed soils, and the mobilized iron may not be lost but may remain within the profile in its reduced form. As Moore (1973) noted, levels of total iron in gleys were often only very slightly less than those in their non-gleyed counterparts.

Figures 1a and 4 illustrate the gleyed and podsolised counterparts, respectively, of the previously described Ardnamurchan and Exmoor brown earth profiles. Magnetic differentiation both within and between each pair of profiles is readily apparent. In the podsolised Exmoor profile (Fig. 4),

in major contrast to the brown earth, there is little evidence of ferrimagnetic contribution to the observed magnetic signal. For most parts of the profile, the canted antiferromagnetic behaviour of the parent material (section 6) appears to have been inherited, maintained and even, in places, intensified. χ values are extremely low, to the point of being undetectable, throughout the organic and eluvial horizons. Maximum values reach only $5\text{--}16 \cdot 10^{-8} \text{ m}^3 \text{ kg}^{-1}$, in association with the reddened B_s layer towards the profile base. No detectable levels of χ_{fd} were recorded for any point in the profile. Both *SIRM* and *ARM* follow a similar pattern to χ but *SIRM*/ χ ratios are notably low (c. 2 kAm^{-1}), indicating the presence of a paramagnetic component within the oxide assemblage. Investigation of the demagnetisation behaviour of the individual horizons reveals the magnetic transformations undergone within this profile. Figure 8 illustrates the variation in the down-profile response of *IRM* (normalised to *SIRM*) to five selected demagnetising fields. Within the surficial soil layers, *IRM* demagnetisation response is generally softer than that of the parent material. However, by far the most prominent shift in demag-

netisation behaviour occurs at between 24–28 cm in the profile in coincidence with the indurated *Bfe*, the upper B_s and the lower part of the E_{ag} . Here, this material displays a pronounced swing towards a very resistant response to the applied backfield. $(B_0)_{cr}$ values for this material reach 467 mT, exceeding those obtained for the parent material by 42 mT.

Almost complete loss of magnetic content is thus indicated for the eluvial A horizon. In the illuvial layer, the location of iron redeposition is clearly defined by slightly increased values of χ and *SIRM*; neoformation of a fine-grained canted antiferromagnetic component (from Mossbauer analysis, possibly superparamagnetic goethite) is indicated by the particularly hard demagnetisation response of the material in this part of the profile.

Significant loss of magnetic content is also demonstrated by the gleyed Ardnamurchan soil (Fig. 1b). In correspondence with its well-drained counterpart (Fig. 1a), the dominant weathering input of titanomagnetite is clearly defined, with *ARM* and *SIRM* increasing towards the profile base, but in this profile values of these parameters are an order of magnitude less. Not only is a quantitative loss

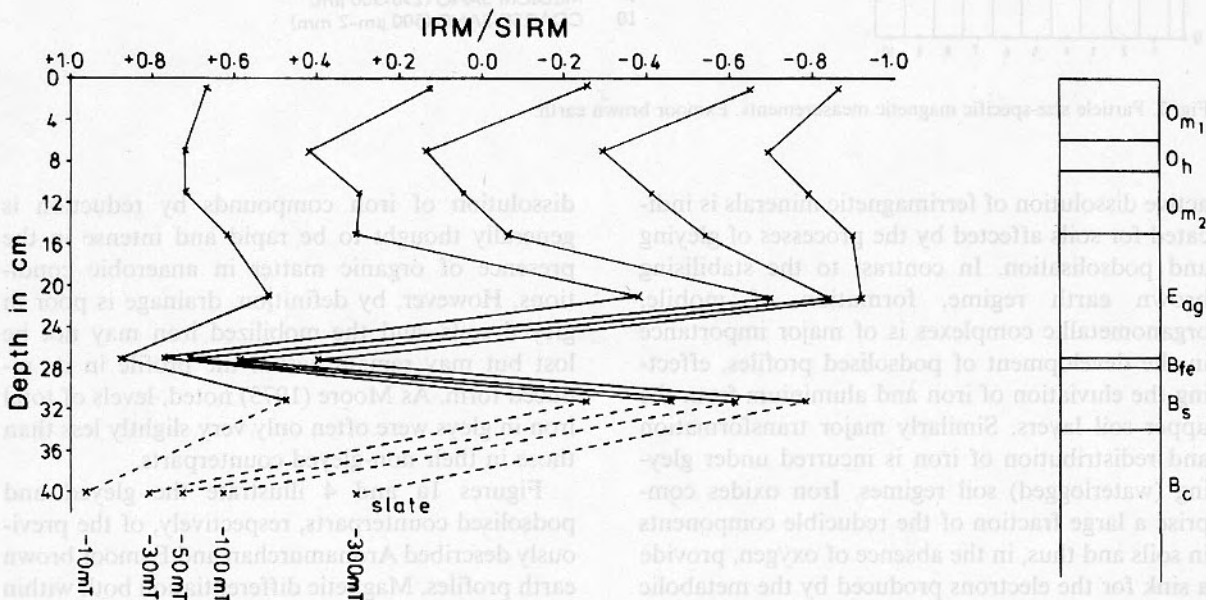


Fig. 8. Demagnetisation response to five selected d.c. demagnetising fields, Exmoor podsol.

of magnetite apparent; from measurement of χ_{fd} , grains of superparamagnetic dimensions appear to be absent from the assemblage in the gleyed soil.

11. Summary

Magnetic characterisation of the soils described in this study has been based upon the isothermal measurement of a range of rapidly and easily obtained mineral magnetic parameters. These parameters do not quantitatively define the magnetic assemblages present but appear to be of sufficient resolution to discriminate and characterise the magnetic variation inherent to these materials. Where extraneous sources of magnetic input can be excluded, the distribution, mineralogy and granulometry of soil magnetic oxides appear to show a coherent response to variations in ambient pedological regime. This is despite the fact that within many soils, the range of parameters measured may reflect the characteristics of only a very small part of the entire soil iron system. As noted by Belozerskiy et al. (1978), c. 90% of soil iron minerals consist of non- or weakly magnetic iron phases. Mineral magnetic measurements are thus highly discriminatory, and can operate at levels of detection well below those of X-ray diffraction and Mossbauer analysis. Further, the technique is relatively rapid, economic and non-destructive, enabling detailed, pre-analysis soil profile characterisation based on high resolutions of profile sampling.

12. Conclusions

(1) Characterisation of diverse soil materials by mineral magnetic measurements has indicated the existence of clear relationships between magnetic differentiation and discrete types of soil environment. Contrasts in soil magnetic assemblage composition, concentration and granulometry thus present the opportunity for characterisation of different soil types and of individual horizons, and, to some extent, of processes operative within them.

(2) The presence of low concentrations ($\ll 1\%$) of magnetite within soils is a widespread phenom-

enon; its neoformation within the soil micro-environment is inferred. However, depending on locality, some soils may receive an extraneous input of magnetite from atmospheric fallout of anthropogenic particulate pollution. Identification of such material appears possible upon the basis of distinctive characteristics of grain size and specific soil particle size associations.

(3) The empirical evidence gained indicates that the iron phases dominantly contributing to the magnetic properties of the soil constitute an environmentally sensitive, conservative and therefore diagnostic part of the soil iron system.

Acknowledgements

The author is especially grateful to Professor F. Oldfield for the provision of the American soil samples and G. Yates for allowing inclusion of as yet unpublished data. This work was carried out during the tenure of a N.E.R.C. studentship.

References

- Banerjee, S.K., King, J. and Marvin, J., 1981. A rapid method for magnetic granulometry with applications to environmental studies. *Geophys. Res. Lett.*, 8: 333-336.
- Belozerskiy, G.N., Kazakov, M.I. Gagarina, E.I. and Khantulev, A.A., 1978. Use of Mössbauer spectroscopy for studying the forms of Fe in forest soils. *Sov. Soil Sci.*, 10: 534.
- Bingham, J.M., Golden, D.C., Bowen, L.H., Buol, S.W. and Weed, S.B., 1978. Iron oxide mineralogy of well-drained vertisols and oxisols. I. Characterisation of iron oxides in soil clays by Mössbauer spectroscopy, X-ray diffractometry, and selected chemical techniques. *Soil Sci. Soc. Am. J.*, 42: 816-825.
- Chevalier, R., Coey, J.M.D. and Bouchez, R., 1976. A study of iron in fired clay; Mössbauer and magnetic measurements. *J. Phys.*, 37: 860-864.
- Dearing, J.A., Maher, B.A. and Oldfield, F., 1985. Geomorphological linkages between soils and sediments: the role of magnetic measurements. In: K. Richards, R. Arnett, S. Ellis (Editors), *Geomorphology and Soils*. George Allen and Unwin, pp. 245-266.
- Goodman, B.A., 1980. Introduction of Mössbauer spectroscopy. In: *Advanced Chemical Methods for Soil and Clay Minerals Research*. NATO Advanced Study Institute, University of Illinois.
- Hunt, A., Jones, J.M. and Oldfield, F., 1984. Magnetic measurements and heavy metals in atmospheric particulates of anthropogenic origin. *Sci. Total Environ.*, 33: 129-139.

- Kampf, N. and Schwertmann, U., 1983. Goethite and haematite in a climosequence in S. Brazil. *Geoderma*, 29: 27-41.
- Kodama, H., McKeague, J.A., Tremblay, R.J., Gosselin, J.R. and Townsend, M.G., 1977. Characterisation of iron oxide compounds and soils by Mössbauer and other methods. *Can. J. Earth Sci.*, 14: 1-15.
- Le Borgne, E., 1955. Susceptibilité magnétique anormale du sol superficiel. *Ann. Geophys.*, 16: 159-195.
- Le Borgne, E., 1960. Influence du feu sur les propriétés magnétiques du sol de du granite. *Ann. Geophys.*, 16: 159-195.
- Longworth, G. and Tite, M.S., 1977. Mössbauer and magnetic susceptibility studies of iron oxides in soils from archaeological sites. *Archaeometry*, 19: 3-14.
- Longworth, G., Becker, L.W., Thompson, R., Oldfield, F., Dearing, J.A. and Rummery, T.A., 1979. Mössbauer effect and magnetic studies of secondary iron oxides in soils. *J. Soil Sci.*, 30: 93-110.
- Maher, B.A., 1984. Origins and Transformations of Magnetic Minerals in Soils. Ph.D. Thesis, University of Liverpool (unpublished).
- Moore, T.R., 1973. The distribution of iron, manganese and aluminium in some soils from N.E. Scotland. *J. Soil Sci.*, 24: 162.
- Mullins, C.E., 1977. Magnetic susceptibility of the soil and its significance in soil science: a review. *J. Soil Sci.*, 28: 223-246.
- Mullins, C.E. and Tite, M.S., 1973. Magnetic viscosity, quadrature susceptibility and frequency dependence of susceptibility in single domain assemblies of magnetite and maghemite. *J. Geophys. Res.*, 78: 804-809.
- Neumeister, H. and Peschel, G., 1968. Magnetic susceptibility of soils and Pleistocene sediments in the neighbourhood of Leipzig. *Albrecht-Thaer-Arch.*, 12: 1055-1072.
- Norrish, K. and Taylor, R.M., 1961. The isomorphous replacement of iron by aluminium in soil goethites. *J. Soil Sci.*, 12: 294-306.
- Oades, J.M. and Townsend, W.N., 1963. The detection of ferromagnetic minerals in soils and clays. *J. Soil Sci.*, 14: 179-187.
- Oldfield, F. and Maher, B.A., 1984. A mineral magnetic approach to erosion studies. *Proceedings of Conference on Drainage Basin Erosion and Sedimentation*, R. Loughran (Editor), A.N.U. Press.
- Oldfield, F., Thompson, R. and Dickson, D.P.E., 1981. Artificial enhancement of stream bedload: a hydrological application of superparamagnetism. *Phys. Earth Planet. Inter.*, 26: 107-124.
- Oldfield, F., Maher, B.A., Donoghue, J. and Pierce, J. in press. Particle-size related mineral magnetic source-sediment linkages in the Rhode River catchment, Maryland, U.S.A. *J. Geol. Soc.*
- Ottow, J.G. and Munch, J.V., 1978. Mechanisms of reductive transformations in the anaerobic micro-environment of hydromorphic soils. In: W.E. Krambein (Editor), *Environmental Biogeochemistry and Geomicrobiology*, vol. 2. The terrestrial environment. Ann Arbor Science Publishers, pp. 483-491.
- Ozdemir, O. and Banerjee, S.K., 1982. A preliminary magnetic study of soil samples in west-central Minnesota. *Earth Planet. Sci. Lett.*, 59: 393-403.
- Scheffer, F., Meyer, B. and Babel, U., 1959. Magnetic measurements as aids in the determination of iron oxides on the soil. *Beitr. Mineral. Petr.*, 6: 371-387.
- Schulze, D.G., 1981. Identification of soil iron oxide minerals by DXRD. *Soil Sci. Soc. Am. J.*, 45: 437-440.
- Schwertmann, U. and Fechter, H., in press. The influence of aluminium on iron oxides. XI. Aluminium-substituted maghemite ($\gamma\text{Fe}_2\text{O}_3$) in soils from burning Al substituted goethite. *Clays Clay Min.*
- Schwertmann, U. and Taylor, R.M., 1977. Iron oxides in Minerals in Soil Environments. J.B. Dixon and S.B. Weed (Editors), *Soil Sci. Soc. Am.*, Madison, WI, pp. 145-180.
- Taylor, R.M. and Gracey, A.M., 1967. The influence of ionic environment on the nature of iron oxides in soils. *J. Soil Sci.*, 18: 341-348.
- Taylor, R.M., McKenzie, R.M., Fordham, A.W. and Gillman, G.P., 1983. Oxide minerals. In: *Soils an Australian Viewpoint*. Division of Soils, CSIRO (CSIRO Melbourne/Academic Press: London) pp. 309-335.