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Magnetic properties of modern soils and Quaternary loessic paleosols: paleoclimatic implications

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Abstract

The magnetic properties of paleosols developed in Quaternary sequences of loess have been used for: stratigraphic definition; correlation with other terrestrial and deep-sea sequences; and paleoclimatic (paleorainfall) reconstruction. In some loess/paleosol sequences, including those of the Chinese Loess Plateau, Tajikistan and the Czech Republic, maxima in magnetic susceptibility values correspond with the paleosol horizons, and minima with the least-weathered loess layers. In other loess/soil sequences, including those of Siberia, Alaska and Argentina, the relationship is completely opposite, with susceptibility minima associated with the most developed paleosols. To account for these opposite relationships, the respective roles of: (1) magnetic enhancement and (2) magnetic depletion and/or dilution in determining soil magnetic properties are investigated for a range of modern soil types. Most magnetic enhancement is seen in the upper horizons of well drained cambisols. Absence or loss of magnetic iron oxides is apparent in acid, podsol profiles and waterlogged soils. For the cambisol profiles, significant correlation is found between susceptibility and organic carbon, cation exchange capacity and clay content. The mineralogy, morphology and grain size of soil magnetic carriers, extracted from three modern enhanced soils and a paleosol from the Chinese Loess Plateau, are also identified by independent petrographic means (microscopy and X-ray diffraction of magnetic extracts). Magnetite and maghemite of ultrafine grain size (from ~ 0.4 to $< \sim 0.001$ μm) are the major contributors to the magnetically enhanced soils. Weathering can concentrate detrital magnetic grains, especially in the fine silt size fractions of soils. The magnetic data from the modern soils indicate that interpretation of paleosol magnetic properties must be done on a site-specific basis, taking into account the possibilities of pedogenic enhancement, pedogenic dilution or depletion, and allochthonous inputs of magnetic minerals. Excessively arid, wet or acid soils are unable to form significant amounts of pedogenic ferrimagnets. Well drained, intermittently wet/dry soils, with reasonable buffering capacity and a substrate source of Fe, show most magnetic enhancement. For those soils which favour magnetic enhancement processes, correlation has been found between the maximum value of the pedogenic susceptibility and the annual rainfall. The almost unique pedogenic system in the Chinese loess plateau, where variation in soil-forming factors other than climate is reduced to a global minimum, allows use of the paleo-susceptibility values as proxy paleorainfall values. To identify the mechanism of any link between magnetic properties, for example, susceptibility, and climate change, the mineralogy and grain size of soil magnetic carriers, requires detailed investigation. Given the prospect of: (1) quantitative paleorainfall records from continental loess records; (2) predictions of present and future climate change; and (3) the value of paleoclimate data for testing of numerical climate models; such magnetic investigations can contribute significantly to our understanding of past and future environmental change. © 1998 Elsevier Science B.V.

Keywords: soil magnetism; paleoclimate; loess; paleosols

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1. Introduction

1.1. Significance of soil magnetic properties for paleoclimatic reconstruction

Paleosols potentially constitute natural archives of paleoclimatic information. However, the integrity, accuracy and retrieval of this information depend on: (1) the degree of development and preservation of diagnostic, soil-formed properties; and (2) whether these properties can be interpreted via modern-day analogues. Multiple buried paleosols are preserved within long sequences (up to ~350 m) of Quaternary loess, most notably in the Loess Plateau of north-central China. Other, often shorter, loess/paleosol sequences occur in disparate locations such as Tajikistan (Forster and Heller, 1994), Alaska (Beget et al., 1990), central North America (Rousseau and Kukla, 1994), Siberia (Rutter and Chlachula, 1995), the Pampas of Argentina (Nabel, 1993), Tunisia (Dearing et al., 1996b), France (Rousseau et al., 1994), Poland (Nawrocki, 1992), the Czech Republic (Kukla, 1975) and India (Gupta et al., 1991). For all of the above locations, mineral magnetic data have been obtained from the paleosols and their less weathered loess substrates. Mineral magnetic measurements are quantitative and relatively easily and rapidly made. Magnetic susceptibility, for example, can be measured in the field using a hand-held probe, at high resolution (e.g. at 5 cm intervals over >150 m stratigraphic thickness at the Chinese Loess Plateau sites). In all cases, the magnetic properties provide sensitive discrimination between the loess units and the interbedded paleosols, and often form the basis for stratigraphic correlation and matching with other climate records, in particular the deep-sea oxygen isotope record. However, as for any sediment, variations in magnetic properties can reflect changes in any of the following: allogenic inputs; authigenic inputs; and post-depositional diagenesis. Thus, the nature of any causal links between climate and magnetic properties is likely to be *site-specific*, as demonstrated, for example, by the inverse relationship between magnetic susceptibility in the Alaskan, Argentinian and Siberian paleosols and the Chinese paleosols. In China the paleosols have higher susceptibilities than their less weathered loess counterparts; in the other three cases, the completely opposite pattern is found, with susceptibility minima corresponding to the most developed pedogenic horizons. To account for these opposite relationships, the mineralogy of the susceptibility carriers, their sources, and their causal links with climate, need to be identified. Identification of such sources and links is greatly assisted by knowledge of the magnetic properties of modern soils, especially if we can understand which climatic and soil-forming conditions favour the in situ formation of strongly magnetic ferrimagnets, and resulting net magnetic enhancement, and which are likely to promote either loss of soil iron or accumulation of non-ferrimagnetic iron oxides, with net magnetic depletion or dilution.

Here, proposed processes of enhancement and depletion or dilution of soil magnetic susceptibility are first reviewed. Then, to investigate the relationship between soil type and degree of magnetic enhancement or depletion, soil magnetic properties in a variety of modern soil-forming environments are investigated. To identify the magnetic carriers in magnetically enhanced soils, the mineralogy, morphology and grain size of magnetically concentrated extracts have also been examined. Finally, the links between magnetic enhancement and climate, soil age and soil type are discussed with reference to paleosol magnetic properties and paleoclimate.

1.2. Rock magnetic studies of soils

Measurements of soils, and paleosols, by mineral magnetic techniques are highly specific to Fe, and very sensitive to particular minerals, especially strong ferrimagnets like magnetite — $(Fe^{3+})_t[Fe^{2+}, Fe^{3+}]_oO_4$, where t = tetrahedral site and o = octahedral site. Current instrumentation is sufficiently sensitive to measure the remanent magnetisation from less than 1 ppb of magnetite. Magnetic measurements measure the in-field and remanent responses of samples to a series of externally applied magnetic fields. In well drained soils, these responses reflect the magnetic properties which arise from the mineralogy and grain size of their constituent iron oxides. In waterlogged soils, iron sulphides, rather than oxides, may dominate the soil magnetic properties (Stanjek et al., 1994). In soils lacking any significant ferrimagnetic content, susceptibility may be carried by paramagnetic components (such as Fe-rich clays, or the iron oxides, ferrihydrite and lepidocrocite). Table 1 summarises the magnetic status of the major iron oxides and their measured magnetic susceptibility. The susceptibility data were obtained from oxide powders kindly provided by Prof. U. Schwertmann, *Institut für Bodenkunde*, Freising.

Processes of iron mineral authigenesis, diagenesis, transport and dissolution, in interaction with weathering inputs of iron, produce vertical differentiation in soil magnetic properties (Babanin et al., 1975; Maher, 1984; Singer and Fine, 1989). Re-distribution of soils on slopes, by erosion and transport processes, can also produce measurable magnetic patterns (Maher, 1984; Dearing et al., 1985). Thus, magnetic minerals can both respond to and reflect soil-forming processes.

Le Borgne (Le Borgne, 1955, 1960) first observed the variation in soil susceptibility values, noting increased magnetic content ('enhancement') within the surface layers of burnt soil. He also observed, however, that susceptibility values could increase in the absence of soil burning, during the drying phase of soil wetting/drying cycles. Russian soil physicists (for example, Babanin, 1973; Babanin et al., 1975; Vadyunina and Smirnov, 1976) attempted large-scale application of susceptibility measurements to characterise the morphology and genesis of major soil groups within the USSR. Mullins (1974) and Mullins and Tite (1973) focused detailed attention on soil magnetic properties from the viewpoint of archaeological prospecting. Tite and Linington (1975) were the first to speculate on the effects of climate on soil magnetic susceptibility. Mullins' (Mullins, 1977) review of magnetic susceptibility of the soil provides a summary of soil magnetic studies at this time.

Recent advances in soil magnetic studies were prompted by magnetically based environmental studies of sediment provenance and soil–sediment linkages (Thompson and Oldfield, 1986). Associations between different soil regimes and observed magnetic characteristics are reported in Dearing (1979), Maher (1984) and Singer and Fine (1989).

Quantitative identification of soil magnetic mineralogies was sought by Longworth and Tite (1977) and Longworth et al. (1979), using Mössbauer analysis to analyse (1) burnt and (2) pedogenically enhanced soil material. Conversely, Coey (1988) has used the distinctive magnetic properties of natural materials to spur theoretical progress in the field of magnetism.

1.3. Magnetic differentiation in soils: magnetic enhancement versus magnetic 'depletion'

The iron oxides, together with amorphous, organically linked iron complexes, constitute the major forms of non-silicate iron in soils. Soil iron oxides are weakly magnetic, in magnetic susceptibility terms, with the significant exception of the ferrimagnets, magnetite and maghemite (Table 1). Weakly magnetic oxides such as hematite and goethite may occur in soils in amounts detectable by X-ray diffraction of bulk samples (~5–10%).

Table 1
Iron oxides in soils and their magnetic susceptibilities

Mineral	Formula	Magnetic Status	Magnetic susceptibility (10^{-8} m^3 kg^{-1})
Hematite	αFe_2O_3	Canted antiferromagnetic	40
Goethite	$\alpha FeOOH$	Canted antiferromagnetic	70
Maghemite	γFe_2O_3	Ferrimagnetic	26000
Lepidocrocite	$\gamma FeOOH$	Paramagnetic	70
Ferrihydrite	$5Fe_2O_3 \cdot 9H_2O$[a]	Paramagnetic	40
Magnetite	Fe_3O_4	Ferrimagnetic	56500

[a]After Schwertmann and Taylor (1977).

The ferrimagnetic minerals most often occur in trace amounts but often dominate measured soil magnetic properties. Soil iron oxides were originally thought to occur in amorphous form, as surface coatings on minerals or voids; increased analytical power can now resolve the cryptocrystalline and sub-micrometre grains that either make up such features, or occur singly with the soil matrix.

1.3.1. Magnetic enhancement

A soil may become magnetically enhanced if there is: (1) conversion of some of the weakly magnetic iron oxides (Table 1) or other Fe source into the strongly magnetic ferrimagnets, magnetite and maghemite; (2) subsequent persistence of these ferrimagnets in the soil profile; and (3) selective concentration of any weathering-resistant detrital ferrimagnets. Iron is released by weathering from primary Fe^{2+}-bearing minerals by oxidation at mineral surfaces. The Fe^{3+} ions produced may be incorporated into an iron oxide phase in situ, or be reduced and mobilised by the soil solution and subsequently re-oxidise and precipitate elsewhere in the profile. Iron oxides can also be actively dissolved, with conversion to free or organically linked iron forms. These processes of: (1) authigenesis, (2) diagenesis, (3) dissolution and (4) redistribution, in interaction with any detrital magnetic inputs, can be expected to produce differentiation of soil magnetic properties, under the constraints set by the biogeochemical conditions of the developing profile. Included within these conditions, which govern the operation of the (bio)chemical reactions within the soil, are the factors of temperature, moisture availability, redox status, organic matter content, bacterial activity, and the initial proportions of the chemical compounds of the system.

Within temperate soils, magnetic enhancement of upper soil layers, as evidenced by increased susceptibility values, has been widely reported (e.g. Le Borgne, 1955 in France; Neumeister and Peschel, 1968 in Germany; Mullins and Tite, 1973; Longworth et al., 1979; Maher, 1984 in the U.K.; Tite and Linington, 1975 in the U.K., Mediterranean and the tropics; Singer and Fine, 1989 in the U.S.A.). Susceptibility values can especially be enhanced by the presence of minor concentrations ($<0.1\%$) of ultrafine-grained ($<\sim 20$ nm) ferrimagnets (Fig. 1). Proposed processes and products of enhancement (Table 2) were summarised by Mullins (1977). New information on specific pathways that may be involved in the 'fermentation' process, during soil wetting/drying cycles, has come from studies of magnetotactic bacteria (e.g., Fassbinder et al., 1990), Fe-reducing bacteria (Lovley et al., 1987) and low-temperature magnetite synthesis (Tamaura et al., 1983; Taylor et al., 1987). Magnetotactic bacteria form distinctive chains of unidimensional, sub-micrometre magnetite crystals intracellularly (Fig. 2a,b) and have been suggested as a source of pedogenic magnetite by Fassbinder et al. (1990), who first reported the presence of magnetotactic bacteria in a (gley) soil in Southern Germany. Maher and Thompson (Maher and Thompson, 1991, Maher and Thompson, 1992) found fossil magnetosomes in paleosol S_1 (Fig. 2c) from Luochuan in the Chinese Loess Plateau, but in very small numbers ($<1\%$ of extracted magnetic grains). Similarly, living soil magnetotactic populations have so far only been found in low numbers, <100 bacteria/ml of soil solution (Fassbinder et al., 1990). However, these authors suggest exponential increases in these populations might occur under episodically favourable soil conditions. Lovley et al. (1987) isolated an Fe-reducing bacterium, GS-15 (now named *Geobacter metalloreducens*), from surface sediments of the Potomac estuary, U.S.A. Fe-reducing bacteria use Fe^{3+} either as a source of Fe atoms for metabolism, or, more significantly, as an electron sink during anaerobic respiration. Whilst *Geobacter m.* itself has not yet been isolated in soils, more than 30 species of Fe-reducing soil bacteria have been identified (Fischer, 1988; Rossellomora et al., 1995). Such bacteria may play a key role in pedogenic formation of ultrafine-grained magnetite (Fig. 2e), by their production and extracellular excretion of Fe^{2+} ions (Maher, 1991). Once in the extracellular environment, the interaction between the excreted Fe^{2+} and ambient Fe^{3+} ions may, under certain conditions, result in the inorganic precipitation of hundreds of ultrafine magnetite crystals around each bacterium

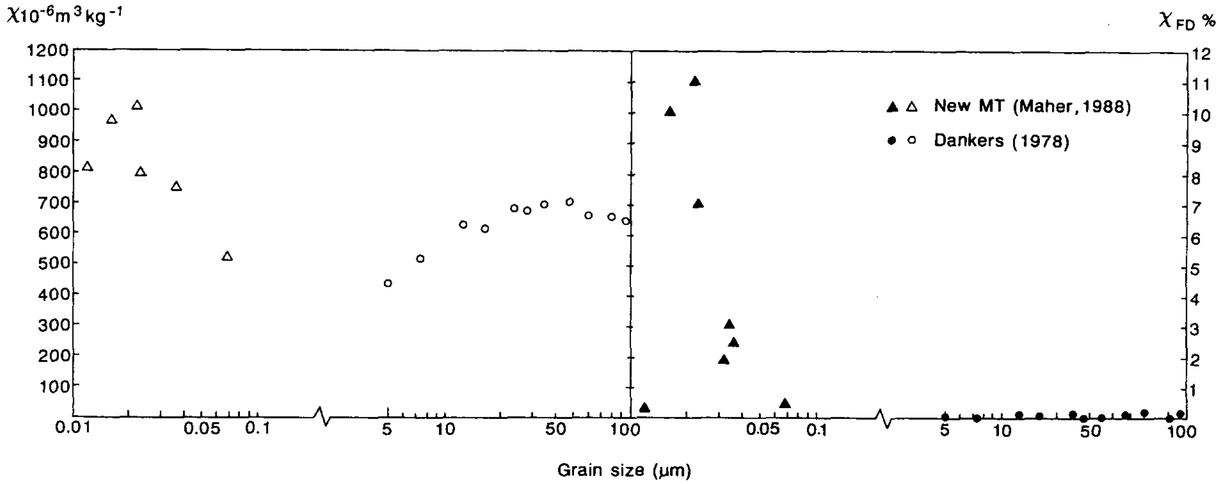

Fig. 1. Magnetic susceptibility and frequency-dependent susceptibility versus grain size for Maher's (Maher, 1988) synthetic magnetites and Dankers' (Dankers, 1978) crushed and sieved natural magnetites.

(Lovley et al., 1987). The conditions in the extracellular, soil micro-environment which favour precipitation of magnetite, rather than the other, poorly magnetic iron oxides, might be inferred from Taylor et al.'s (Taylor et al., 1987) laboratory experiments on low-temperature magnetite synthesis. Rapid and easy synthesis of magnetite was achieved through controlled oxidation of mixed Fe^{2+}/Fe^{3+} solutions at room temperature and near-neutral pH values. The synthetic products were found to range in size from 0.01 to 0.07 μm (Fig. 2d). Conversely, other iron oxyhydroxides, especially lepidocrocite and goethite, were formed in preference to magnetite when the pH was reduced, and/or when the oxidation rate was increased. The specific process by which magnetite was formed in Taylor et al.'s experiments may be that of 'induced hydrolysis' (Tamaura et al., 1983), whereby Fe^{2+} ions are adsorbed onto the surface of poorly crystalline Fe^{3+} phases, such as ferrihydrite. This adsorption promotes dissolution of the oxide phase, due to the resulting surface charge imbalance, and formation of an intermediate Fe^{2+}/Fe^{3+} compound which then, under the appropriate pH and oxidation regime, may precipitate as magnetite. Because of the small size of many of the precipitated crystals, surface oxidation of the magnetite to maghemite is likely to occur subsequently, over periods of months to years (Murad and Schwertmann, 1993 and Maher, unpubl. data). Some grains may exist as cores of magnetite with surface maghemitised coatings. Mössbauer analysis of synthetic magnetite powders (Maher, 1988), stored in air for 10 years, identified a small percentage (<5%) of surviving magnetite amongst otherwise maghemitised grains. Maghemitisation may play an important role in the persistence of the fine-grained ferrimagnets in the soil profile, protecting the inner magnetite core from dissolution.

Using Lowenstam's (Lowenstam, 1981) terminology, *extracellular* formation of magnetite via the mediation of Fe-reducing bacteria may be termed a 'Biologically Induced Mineralisation' (BIM) process; *intracellular* magnetite production by magnetotactic bacteria constitutes a 'Biologically Organised Mineralisation' (BOM) process. BOM processes involve construction by the organism of an intracellular organic framework, into which the required ions are actively transported and induced to crystallise and grow at controlled rates. Control over the size and shape of the crystals formed is thus highly precise. Bacterial magnetosomes are often cubo-octahedral, and 50 nm in diameter; sometimes they adopt the unique crystal habit of elongated prisms (Fig. 2b). BIM processes, in contrast, result in mineral formation by spontaneous interaction

Table 2
Processes of magnetic enhancement

Enhancement: increased (pedogenic) magnetic content, often observed in upper soil layers.

Mechanism	Notes
[1,'] **Fermentation'** Poorly-crystalline Fe oxides reduction/oxidation -----------------------> $Fe_3O_4/\gamma Fe_2O_3$	Probably the most significant pathway, mediated by Fe^{2+} production by Fe^{3+}-reducing bacteria. Produces ultrafine magnetite, grain sizes varying from ~40 - 10nm, subsequently prone to oxidation towards maghemite.
Biogenic contributions Bacterial Fe_3O_4 in magnetotactic bacteria	Bacterial magnetosomes present in many soils but significance of contribution minor compared to the fermentation process.
[1,2]**Burning** reduction oxidation αFe_2O_3 --------> Fe_3O_4 --------> γFe_2O_3 αFeOOH --------> Fe_3O_4 --------> γFe_2O_3 Weathering end-products	Point-specific in effect, the degree of enhancement at each point varying with iron content, organic matter, temperature of burn, soil porosity etc. (Oldfield et al. 1981).
[2]**Dehydration of lepidocrocite** γFeOOH -----------------------> Fe_3O_4 Common in mottles in gley soils	Occurs at elevated temperatures only (>200°C), i.e. also related to burning.
Atmospheric fallout of magnetic spherules Industrially-generated spherules of αFe_2O_3 and Fe_3O_4	Characterised by spherical morphology (fig. 2b) and dissociation from clay fraction of soils (Maher, 1984).

[a]Mullins (1977).
[b]Le Borgne (1955)

between biologically produced metabolites and cations present in the external environment. Control over the size and shape of the crystals formed is thus very low. Magnetite crystals formed around *Geobacter* (Lovley et al., 1987) were very variable in crystal size, with many tiny, superparamagnetic crystals, due to their rapid, uncontrolled precipitation. Lovley et al. (1987) suggest some organic control on mineralisation is exerted by *Geobacter m.*; it is possible that the rate of excretion of Fe^{2+} favours formation of magnetite over other iron oxides. Given the narrow range of conditions suitable for activity by Fe-reducing bacteria (i.e., in locally anoxic micro-zones, with suitable pH and organic supply) and the likely presence of interfering mineral grains, the grain size of the precipitating magnetite can be expected to be uncontrolled but biased to the ultrafine size range ($< \sim 0.03$ µm). Such ultrafine ferrimagnetic grains are easily identified by measurements of frequency-dependent magnetic susceptibility, which are especially sensitive to the presence of grains ~ 0.016–0.023 µm in size (Fig. 1). Under a susceptibility frequency range of 0.47 and 4.7 kHz

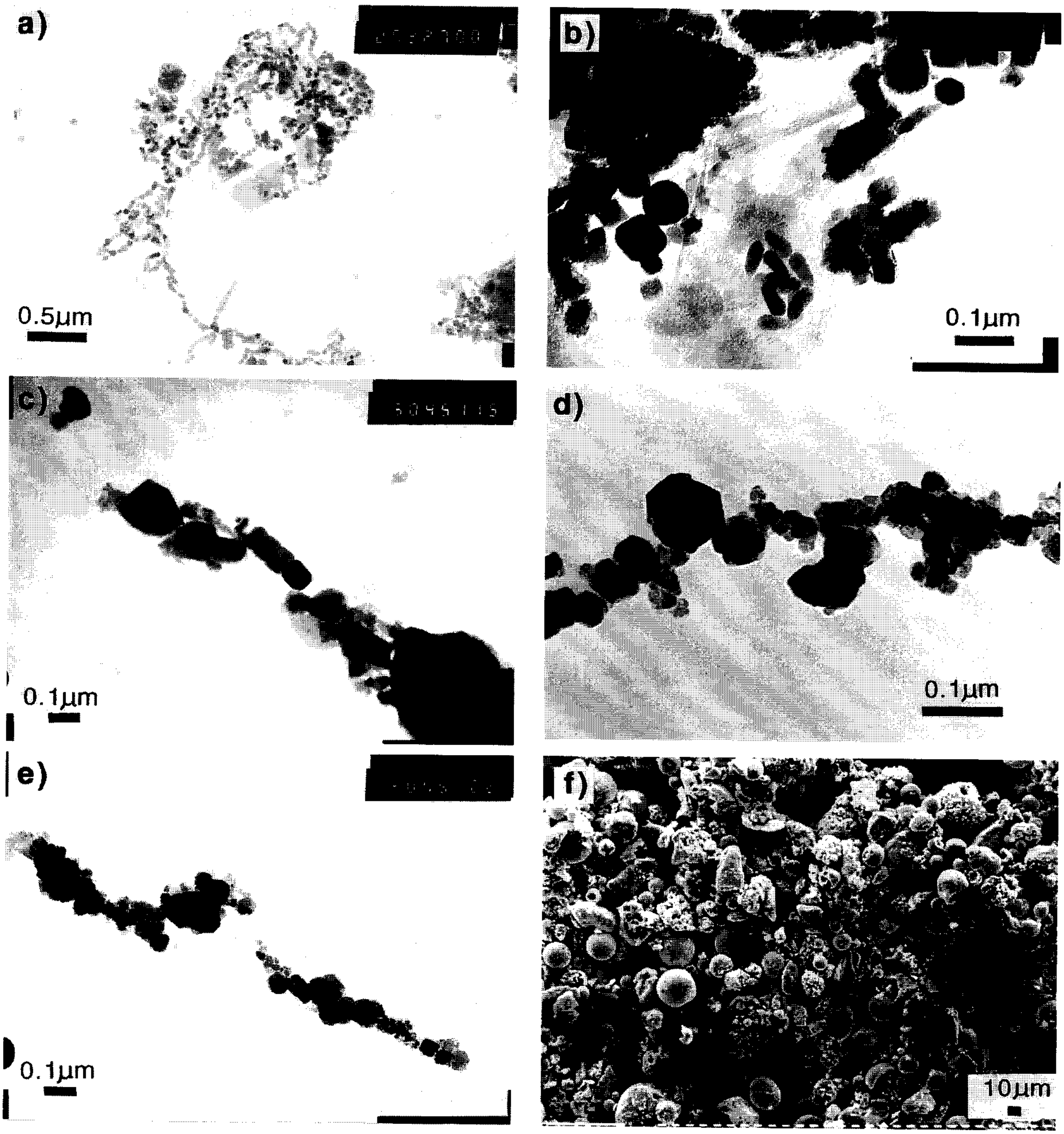

Fig. 2. (a)–(f) Electron micrographs of magnetic particles: (a) magnetosomes formed intracellularly by magnetotactic bacteria, from Indian Ocean deep-sea sediments; (b) magnetosomes with the unique 'bullet'-shaped crystals of definitively direct bacterial origin; (c) a rare chain of bacterial magnetosomes, from palaeosol S_1 in the Chinese loess plateau; (d) synthetic ultrafine magnetite, formed at room temperature (Taylor et al., 1987); (e) ultrafine ferrimagnets of variable grain size, from modern UK soil; (f) magnetic spherules, from deposition of pollutants on soil surface.

(as in the Bartington susceptibility system), grains smaller than ~0.016 μm do not block in at the higher frequency. Thus, frequency-dependent susceptibility measurements respond to a specific, narrow proportion of the ultrafine grain size spectrum (Maher, 1988).

1.3.2. Magnetic 'depletion' and/or dilution

In soil horizons dominated by mobilisation and/or loss of iron by processes of weathering and subsequent reduction or chelation by organic compounds, neither accumulation of iron oxides nor conversion to ferrimagnetic forms is likely to occur. Rather, net depletion of iron may proceed during soil formation under such conditions. However, even in soils which *are* accumulating iron oxides, low magnetic values can arise, through dominant formation (by oxidation) of weakly magnetic Fe^{3+} oxides (i.e., little conversion to ferrimagnets). The poorly magnetic iron oxides nearly always occur in much higher concentrations than the ferrimagnetic forms; iron oxides may typically total between 2 and 5 wt%, but the ferrimagnetic content is typically less than 0.1%. Thus, there is often little direct correlation between soil iron content and measured magnetic susceptibilities, as may be seen from Fig. 3a (data drawn from Fine et al., 1995) and Fig. 3b, from Dearing et al. (1996a). Fine et al.'s (Fine et al., 1995) data demonstrate total absence of correlation between susceptibility and total iron for a number of Chinese loess and paleosol samples (susceptibility varying from a minimum of 18×10^{-8} m^3 kg^{-1} in a loess sample to 199×10^{-8} m^3 kg^{-1} in a paleosol sample). Dearing et al. (1996a) report positive, albeit weak, correlation between total Fe and soil magnetic susceptibility (0.32 at a significance level of $p = 0.0001$) and argue that Fe supply, via the formation of ferrihydrite, is the major limiting factor on the concentration of pedogenically formed ferrimagnets. However, an alternative view is that two distinct populations appear in this data set. The low-susceptibility, almost linear, grouping is probably dominated by Fe present within the weakly magnetic oxides, hematite and/or goethite and paramagnetic minerals, such as Fe-silicates and iron oxyhydroxides (e.g., lepidocrocite). The more scattered, higher susceptibility group almost resembles a normal distribution; it identifies a minimum Fe content of ~10 g/kg, below which susceptibility enhancement, by formation of ferrimagnets, is unlikely. Conversely, high susceptibilities do not associate with high total Fe contents. Thus, an alternative interpretation of this data set would be that, given a minimum amount of available weathered iron, Fe content will rarely be a limiting factor for magnetic enhancement; rather, opportunities for ferrimagnetic conversion and preservation may be the key constraint. The interplay between formation of ferrimagnets (e.g., magnetite) and non-ferrimagnets (e.g., hematite), respectively, is probably competitive and may thus determine the degree of magnetic enhancement (Maher and Thompson, 1995). Oxidation favours formation and accumulation of the non-ferrimagnets, intermittent reduction is required for formation of the ferrimagnets.

Soils which accumulate relatively large concentrations of weakly magnetic components, such as organic matter, quartz and clay minerals, may also display apparent magnetic depletion, through dilution effects.

The interplay between weathering and formation of non-ferrimagnets and ferrimagnets will thus determine the magnetic content of a soil, in terms of magnetic concentration, mineralogy and grain size. Fig. 4, for instance, shows the variation in magnetic properties with soil particle size for a cambisol (brown earth) on dolerite in northwest Scotland. The magnetic properties of this soil are dominated by weathering inputs of igneous magnetite particles from the substrate; thus, the highest concentrations of magnetic material are found in the sand and silt size fractions. Fig. 5 shows the changes in: (1) particle size distribution and (2) the susceptibility of each particle size fraction, from the lower soil (16–22 cm) to the upper soil (0–4 cm) horizons. It is clear that weathering of the detrital ferrimagnetic particles has diminished the susceptibility of the sand and coarse silt fractions, whilst magnetic enrichment has occurred in the fine silt and clay fractions. Comminution of magnetic particles will contribute some of this finer fraction enrichment; measurements of frequency-dependent susceptibility suggest that there has also been some neoformation of ultrafine magnetic

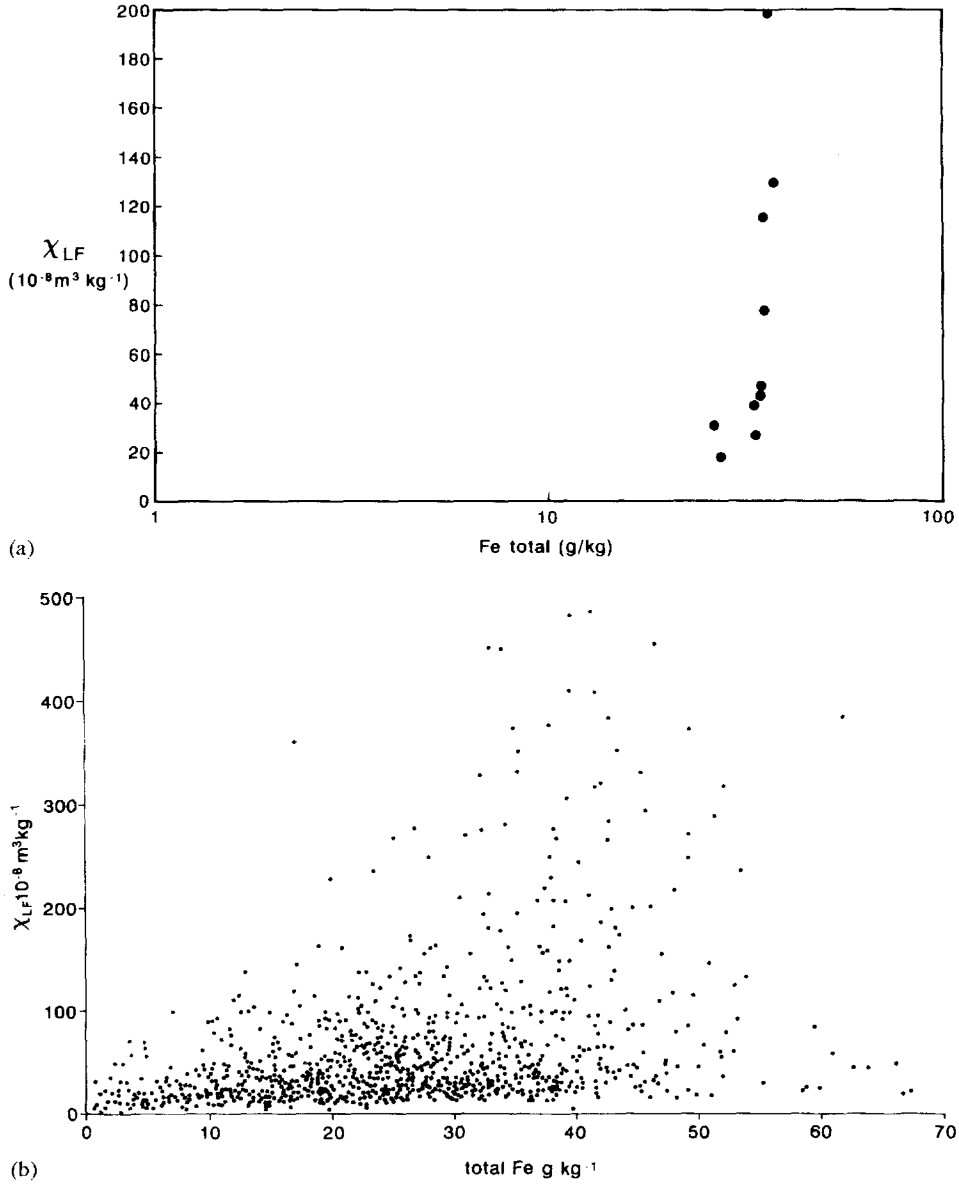

Fig. 3. Fe concentration versus magnetic susceptibility in: (a) Chinese loess and paleosol samples (Fine et al., 1995) and (b) soils in England (from Dearing et al., 1996a).

grains. The net effect of soil formation at this site, however, is to lower the susceptibility from the substrate value, due to weathering of the detrital ferrimagnets and relatively little neoformation of pedogenic ferrimagnets. A few metres down-slope from this cambisol occurs a gleyed soil. As shown by Fig. 6, while similar changes in particle size distribution exist, loss of ferrimagnets has been incurred in every size fraction, with no countering neoformation. Dissolution of ferrimagnets clearly dominates under the waterlogged regime of this soil.

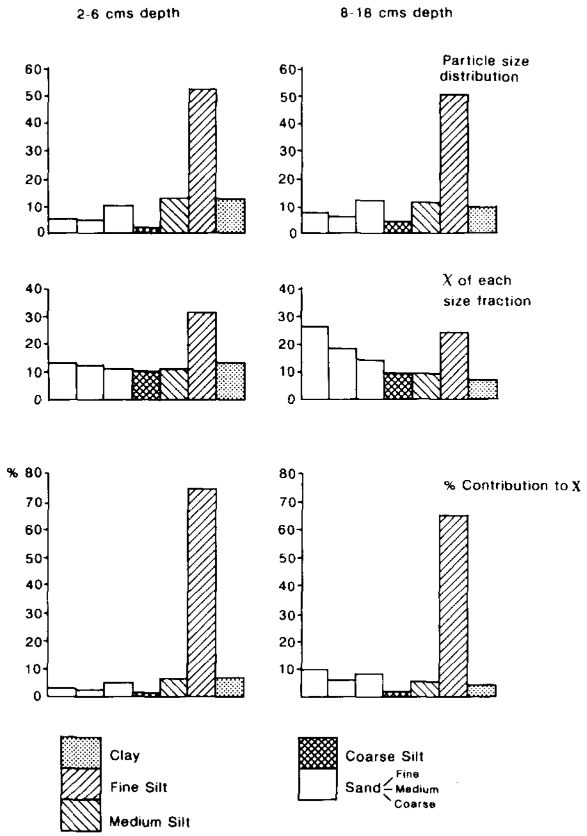

Fig. 4. Magnetic properties and particle size, well drained cambisol on dolerite, Ardnamurchan, Scotland.

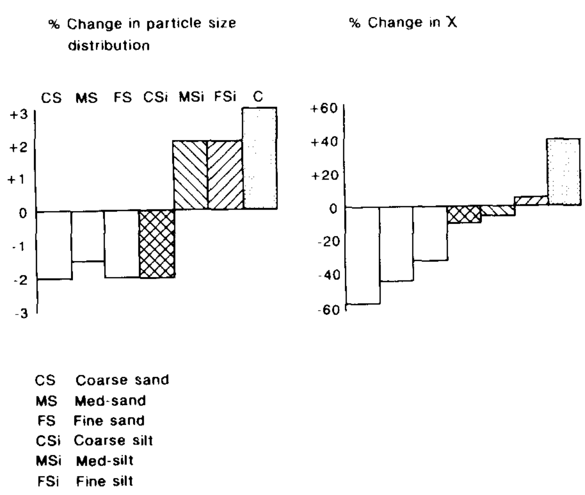

Fig. 5. Changes in magnetic properties and particle size from subsoil to topsoil, Ardnamurchan cambisol.

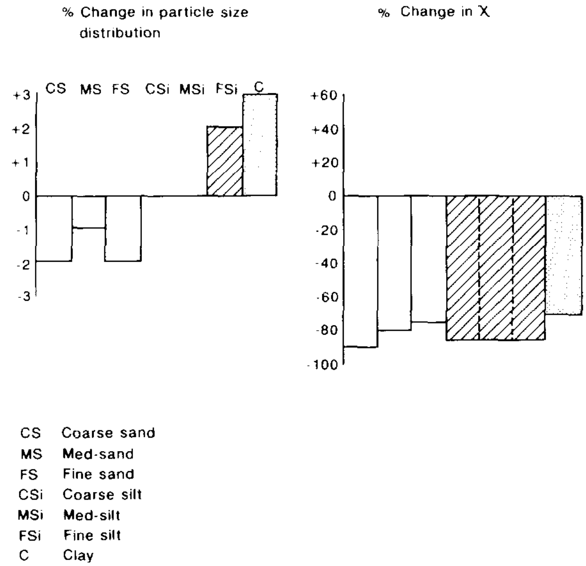

Fig. 6. Changes in magnetic properties and particle size from subsoil to topsoil, Ardnamurchan gley.

2. Sites and methods

To examine the relationships between soil type, and degree and distribution of magnetic enhancement, a range of soil profiles was sampled, first from a toposequence in southwest England, and then from archived material at the Soil Survey of England and Wales (Appendix A). Analytical data for the latter soils were available in published *Memoirs*. The range of samples was designed to include representatives of the major temperate zone soil types, encompassing cambisols, podsols, intergrades between them and gleysols. For each horizon in each profile, samples were subjected to measurements of magnetic susceptibility (at low and high frequencies), anhysteretic remanence (ARM) and selected isothermal remanences (IRMs, at 40, 100 and 300 mT). Definition of these magnetic parameters can be found in Thompson and Oldfield (1986). The toposequence samples were taken from a south-facing slope in Exmoor National Park, U.K., underlain by Devonian slate. Over a 500 m transect, descending from the moorland plateau at ~450 m, four soil types were identified: a humic stagnogley, a stagnopodsol, a dystric cambisol and an imperfectly drained valley gleysol. The cambisol and podsol members of this sequence were investigated previously (Maher, 1984). Each was sampled from excavated soil pits or soil cores. For the Soil Survey samples, the degree of correlation between the magnetic parameters and available soil analytical data was examined by calculating Pearson product correlation coefficients from a correlation matrix including susceptibility, saturation remanence (SIRM), sample depth, clay (<2 μm) content, organic carbon, cation exchange capacity and, where available, pyrophosphate-, oxalate-, and dithionite-extractable iron.

To examine the mineralogy, grain size and morphology of the magnetic material formed by enhancement, an additional, smaller number of enhanced soils was sampled, for magnetic and petrographic analysis of both bulk samples and magnetic extracts obtained from them. These samples (Table 3) included three modern soil profiles developed on 'non-magnetic' parent materials (namely, calcium carbonate and slate), and a last glacial/interglacial, loess/paleosol couplet (L_1 and S_1) from Luochuan in the Chinese Loess Plateau. All of the soils are characterised by much higher values of magnetic susceptibility, frequency-dependent susceptibility and ARM in their mineral horizons than in their parent substrates.

For magnetic measurements, soil samples were individually sealed in labelled polythene bags for transport to the laboratory, where they were oven dried overnight at 40°C. Between 10 and 15 g of the dried soil were gently disaggregated and sieved through a 2 mm sieve, with the <2 mm fraction then packed into pre-weighed 10 cm^3 plastic cylinders, sealed with plastic caps. To avoid particle movement during measurement cycles, clean plastic foam was used to 'bed-down' the samples. Magnetic measurements were then made on each sample.

For extraction of the magnetic minerals, the bulk samples were first separated into two particle size fractions by dispersion and wet sieving through a 38 μm sieve. The magnetic properties of the >38 μm fractions were measured to identify the proportion of magnetic material they contained. The <38 μm fractions were re-dispersed (with Calgon and ultrasonics) and then subjected to a high-gradient magnetic extraction procedure (Petersen et al., 1986; Hounslow and Maher, 1996). This procedure, designed to extract even submicrometre ferrimagnetic grains, produces two extracts. One extract concentrates the ultrafine, submicrometre fraction; the other, the fine ($\sim$2–38 μm) fraction. The non-extracted residues were recovered from suspension by centrifuging, and their magnetic properties measured to determine the amounts of magnetic material removed. For the >38 μm fractions, magnetic extraction by the magnetic edge method (Hounslow and Maher, 1996) was applied. The non-extracted residues of the >38 μm fractions were also recovered from suspension, dried and re-measured for susceptibility, ARM and SIRM. These before- and after-extraction magnetic measurements enable quantification of the amount of magnetic material extracted from the soil fractions at each extraction stage.

The magnetic extracts were analysed by scanning and transmission electron microscopy (S/TEM), energy-dispersive X-ray analysis (EDXA) and X-ray diffraction.

Table 3
Magnetic properties of enhanced soils used for magnetic extraction

Sample	χ (10^{-8} m^3 kg^{-1})	χ_{fd} (10^{-8} m^3 kg^{-1})	χ_{fd} (%)	χ_{ARM} (10^{-6} m^3 kg^{-1})	SIRM (10^{-3} Am^2 kg^{-1})	χ_{ARM}/SIRM (10^{-5} Am^{-1})
PSBE Exmoor cambisol	91	9	9.9	3.9	4.71	82.8
BY Cotswold rendzina	450	41.6	9.2	21.7	16.6	131
CY Norfolk rendzina	87	7.2	8.3	10.4	6.3	166
QJS1 Luochuan palaeosol	200	21.3	10.7	14.2	10.3	138
QJL1 Luochuan loess	70.4	4.8	6.8	3.4	7.4	45.8

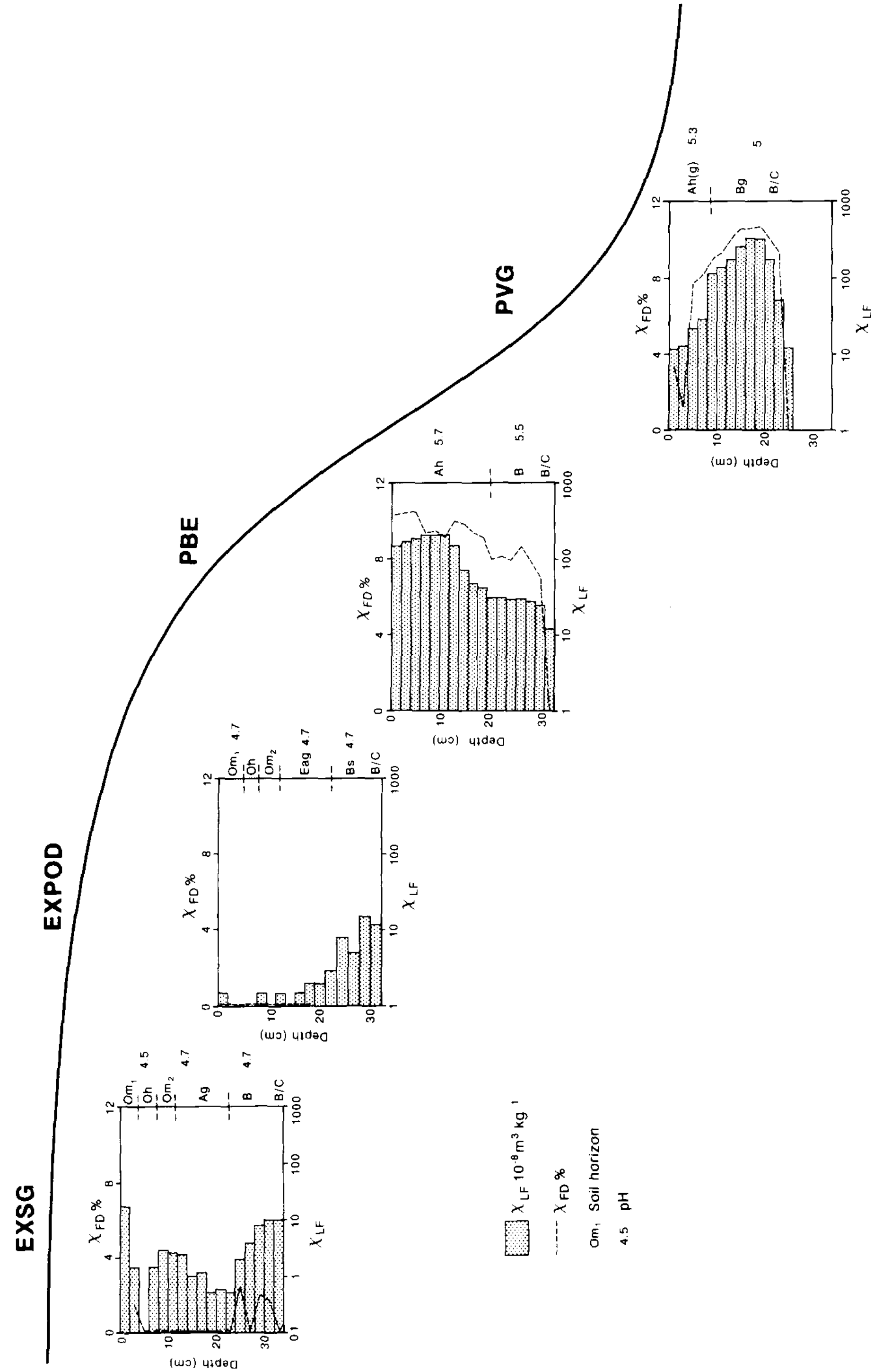

Fig. 7. Magnetic toposequence of soils, Exmoor, UK.

3. Results

3.1. Exmoor toposequence

Fig. 7 shows for the Exmoor toposequence (the stagnogley, the podsol, the cambisol and the valley gley) the variations in their magnetic properties with depth. The slate substrate has very low values of susceptibility ($<10\times10^{-8}$ m^3 kg^{-1}), <1% frequency-dependent susceptibility, unmeasurable ARM, and a low SIRM/susceptibility ratio (~1 k Am^{-1}). Its coercivity of remanence is very high, >400 mT (Fig. 8). These data indicate that this substrate contains low concentrations of a very hard (canted antiferromagnetic) magnetic component, such as hematite or goethite, and also, given the low SIRM/susceptibility value, some paramagnetic minerals, such as Fe-rich clays. The four profiles developed from this magnetically distinctive parent material display quite different magnetic signatures. The podsol and the plateau stagnogley soils are both characterised by very low values of susceptibility ($<20\times10^{-8}$ m^3 kg^{-1}), and barely detectable frequency-dependent susceptibility (<1%). They display slight peaks in susceptibility and SIRM at the surface of the organic peat; the underlying peat layers have extremely low susceptibility and SIRM values. Even within the mineral soil layers, the magnetic content is very low. The higher values of susceptibility and SIRM in these profiles occur towards the C horizon; in the podsol, highest values occur in association with the iron pan (B_{fe}) and the spodic (iron-rich) B_s horizon. The iron pan sample is also characterised by a very high remanent coercivity value (467 mT), as shown in Fig. 8b. The B horizon of

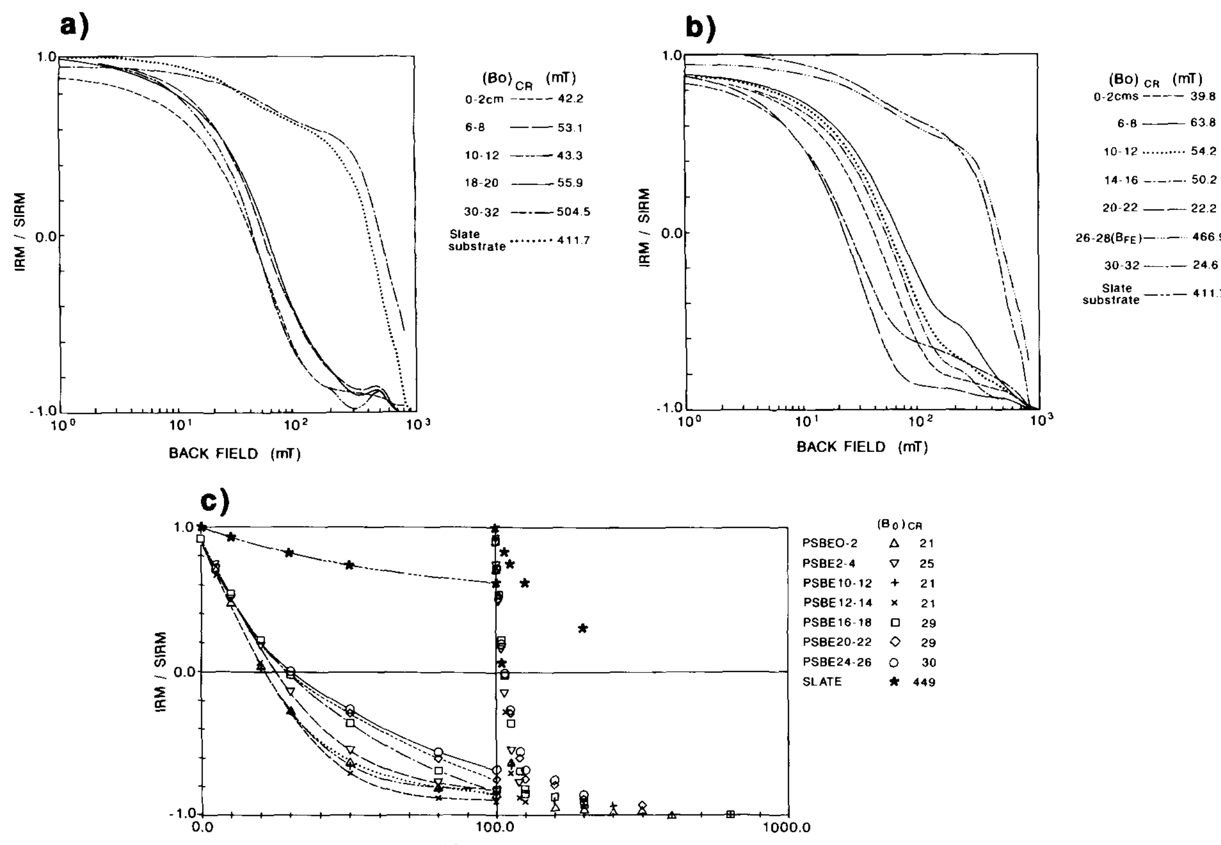

Fig. 8. Coercivity curves for the Exmoor soils: (a) stagnogley; (b) podsol; (c) cambisol.

the plateau stagnogley is slightly more magnetic than the mottled A horizon. Within the surficial soil layers, coercivity values are generally slightly lower than those of the substrate (Fig. 8a). In contrast to these two soils, the cambisol profile displays relatively high values of susceptibility ($\sim 100 \times 10^{-8}$ m^3 kg^{-1}), frequency-dependent susceptibility ($\sim 10\%$) and SIRM (up to 10×10^{-3} Am^2 kg^{-1}). The magnetic content increases with decreasing soil depth, reaching a peak within the middle of the A horizon ($\sim$4–10 cm depth). Upon demagnetisation, samples from this profile display much softer behaviour, with coercivity values of between 21 and 30 mT (Fig. 8c). The imperfectly drained soil, prone to seasonal wetness, displays low values of susceptibility and ARM down to $\sim$8 cm depth. This soil displays yellow mottles of oxidised iron, and an accumulation ($\sim$4 cm) of slowly decomposing organic matter at its surface. Below $\sim$8 cm, susceptibility and ARM values begin to rise steeply, reaching maxima in the B horizon, at $\sim$18 cm depth. Susceptibility values reach 339×10^{-8} m^3 kg^{-1}, and frequency-dependent susceptibility values are typically between 9% and 11%. This profile is unlike other imperfectly drained soils, which have been reported to be deficient in pedogenic magnetite (Maher, 1984; Singer and Fine, 1989). It was sampled at the end of an exceptionally warm, dry summer (September, 1995).

These results show that disparate development of magnetic properties occurs under different soil-forming conditions, even in soils developed on the same parent material and within 500 m distance of each other. Within the cambisol and the subsoil of the valley 'gley', net formation of ferrimagnets has occurred. In the cambisol, either uniformity of process and/or effective mixing is suggested by the similarity of susceptibility values down to a depth of $\sim$18 cm; in the valley gley, magnetite formation seems to have occurred preferentially in the subsoil. Although this soil could be influenced by colluvial inputs, there is little evidence of soil erosion on this slope, which is under permanent grassland pasture. In the plateau gley and the podsol, absence or loss of iron is indicated for the organic, eluvial and gleyed horizons. Accumulation of magnetically very stable material is identified at 24 cm in the podsol, at the iron pan-capped B_s horizon. Processes of iron oxide dissolution dominate in these latter soils, resulting in net magnetic depletion.

These magnetic results can be complemented by use of differential iron extractions, dissolution techniques routinely used by soil scientists to infer the distribution and transformation of iron minerals. Following the methods of McKeague et al. (1971) and Schwertmann (1973), pyrophosphate-extractable iron (reported to represent organically complexed iron) and dithionite-extractable iron (representing crystalline, inorganic iron) were determined for the podsol and cambisol profiles. These extractions were performed by Prof. E. Maltby, at Exeter University. Fig. 9 shows the data obtained. Correlation between the chemical data and the magnetic data is striking. For the podsol, the lack of dithionite-extractable iron in the upper part of the profile indicates that mobilisation of iron has occurred, counteracting the supply of organically linked iron from the surface organic mat. Re-deposition of the mobilised iron is clearly shown below $\sim$25 cm depth, by increased values of both dithionite- and pyrophosphate-extractable iron. For the cambisol, the extraction data indicate homogeneity, especially within the A horizon. Dithionite values are higher in the A, showing accumulation and increased crystallisation of iron oxides. The slightly raised Fe_p/Fe_{dcb} ratio at the surface suggests some leaching and translocation, but this effect is countered by 4 cm depth.

3.2. UK soil survey samples

Statistical analysis of magnetic data obtained for a range of soils from the Soil Survey of England was done with two aims: first, to examine further the relationships between soil and horizon types, and the degree of magnetic enhancement; second, to identify any correlation between soil magnetic properties and other chemical and physical soil properties. A cluster analysis procedure from the SPSS-X computing library was used to classify the

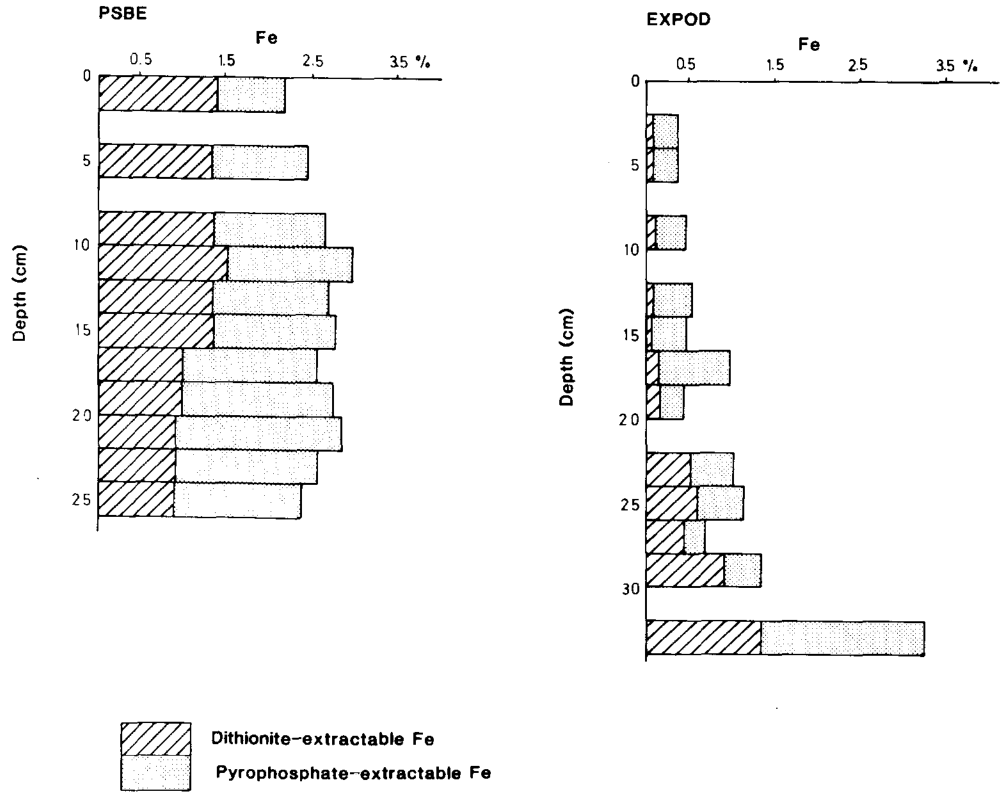

Fig. 9. Chemical extraction data (dithionite-extractables and pyrophosphate-extractable) for (a) the Exmoor cambisol and (b) the Exmoor podsol.

data magnetically. Whilst they cover a wider spatial scale, the number of samples is quite small and sampling was done at much coarser depth resolutions than the Exmoor set. Also, many of the cambisol profiles are, by their nature, of agricultural value and use, and subject to disturbance. Notwithstanding these caveats, these samples, as with the Exmoor set, also exhibit distinct association between soil and horizon type, and soil magnetic properties. Fig. 10 shows the classification obtained and its relationship with the Soil Survey horizon classification. The horizon types most commonly associated with low magnetic contributions to the profile are weathering B/Cs, B horizons and gleyed horizons. Horizons most commonly showing magnetic enhancement are the well drained A and Ap horizons of cambisols. Using the magnetic data from: (1) the cambisol horizons, and (2) the podsol horizons, Pearson product correlation coefficients were calculated from a correlation matrix including susceptibility and SIRM, and other, more conventional soil analyses (Tables 4 and 5). For the cambisol profiles, susceptibility and SIRM showed small but significant, positive correlation with organic carbon, cation exchange capacity and clay content. Neumeister and Peschel (1968) and Woodward et al. (1994) also report positive correlation between magnetic susceptibility and organic carbon. Susceptibility also showed some correlation ($\rho = 0.55$) with pyrophosphate-extractable iron, but not with dithionite-extractable iron. SIRM showed no significant correlation with either pyrophosphate- or dithionite-extractable iron. For the podsol profiles, susceptibility and SIRM showed correlation with cation exchange capacity; susceptibility was also strongly correlated ($\rho = 0.93$) with pyrophosphate-extractable iron.

Classification Clusters

Cluster	χ	ARM	SIRM
4	85	84	85
1	54	51	56
6	46	51	42
2	32	34	36
3	17	16	16
5	7	5	7

					C	
					Bsg	
					Eag	
					Oh	
					Bg	
					C	
					Bc	
					Bt	
					B	
					Bs	
				B/C	B	Ah
				B	Bw	BC
				Bg	Bw	Bt
			Bs	Bw	Bs	B
			A	C	Bs	BCt
		Ae	Ap	A	Ea	Eg
		A	Ap	Ap	Eg	Cu
		Ap	B	Bw	Ea	C
	Ap	Ap	Bw	BhS	Ae	Bc
CLUSTER	4	1	6	2	3	5

Fig. 10. Classification of UK Soil Survey soils by cluster analysis of magnetic data. Clustering was initially based on the values of all the measured data (susceptibility, SIRM, ARM, inter-parametric ratios and demagnetisation parameters). However, highest discrimination was afforded by just three parameters: susceptibility, SIRM and ARM. Classification was also aided if proportional, rather than absolute, data values were used. (The large range in absolute values produced clustering biased towards those few samples with very high values, with consequently poor discrimination for the majority of samples with intermediate or low values). The proportional values were calculated as percentages of the profile totals for each parameter.

3.3. Magnetic extractions from enhanced profiles

Table 3 shows some magnetic data for some modern enhanced soils, and a Chinese loess/paleosol couplet, prior to quantitative magnetic extraction. The sample from Broadway has the highest susceptibility value (450×10^{-8} $m^3\,kg^{-1}$). Fig. 11 plots the χ_{fd} and ARM data for these samples, and for some ferrimagnets of known grain size. Fig. 12 shows the χ, ARM and SIRM of each of the <38 μm and the >38 μm size fractions, and their respective contribution (given the particle size distribution) to the bulk sample magnetic value. All the samples display higher values of χ, ARM and SIRM in their <38 μm size fractions than their >38 μm fractions, with the exception of the Exmoor cambisol (PSBE); the χ of the two size fractions is nearly equal. Measurement of susceptibility, ARM and SIRM at each magnetic extraction step allows calculation of: (1) the absolute extraction efficiency of the procedures, and (2) the percentage of the total measured magnetisation removed by extraction. Fig. 13 shows the extraction data obtained. For the individual size fractions, the susceptibility extraction efficiency (χ_{eff}) is very variable, from as low as 15% to as high as 88%. In terms of total sample susceptibility (i.e., taking into account the particle size distributions and their respective contributions to susceptibility), the magnetic extracts contain between 24% and 49% (mean = 36%) of the susceptibility carriers. In terms of ARM, the absolute extraction efficiencies vary between 34% and 83%; as percentages of the total remanence, the extracts contain between 53% and 83% (mean = 70%) of the ARM carriers. Similarly, for SIRM, absolute extraction efficiencies are between 28% and 88%; as percentages of the total SIRM, the extracts contain between 34% and 78% (mean = 58%) of the SIRM-carrying material.

Lower proportions of the susceptibility carriers (29–49%) are extracted compared with the remanence carriers; significant quantities of the susceptibility-carrying grains remain in the 'non-magnetic' residues. Thus, although the ARM-carriers (grains around the SD/SP boundary, ~0.03 μm in magnetite and maghemite) are efficiently extracted, the ultrafine, SP grains, contributing significantly to susceptibility, are poorly extracted. In fact, frequency-dependent susceptibility data show that the <38 μm residues are significantly *enriched*, post-extraction, in their superparamagnetic (SP) content. For both ARM and SIRM, in excess of 50% of the remanence carriers were extracted for all the samples, with the exception of the highly magnetic Broadway sample, for which only 34.4% of the SIRM carriers was obtained. This anomalously low extraction rate may indicate the presence of significant numbers of interacting SP grains

Table 4
Correlation coefficients for Soil Survey samples, magnetic and conventional soil analyses: Podsol profiles

	ORGC	Fep	Fed	CEC	CLAY	χ	SIRM
ORGC				0.7835(6) $p=0.029$	0.8121(9) $p=0.003$		
Fep			0.7408(10) $p=0.007$	0.9751(6) $p=0.001$	0.6175(10) $p=0.028$	0.9320(10) $p=0.001$	
Fed		0.7408(10) $p=0.007$		0.5299(6) $p=0.136$	0.7813(10) $p=0.003$		
CEC	0.7835(6) $p=0.029$	0.9751(6) $p=0.001$			0.9489(6) $p=0.001$		
CLAY	0.8121(9) $p=0.003$						
χ		0.9320(10) $p=0.001$		0.9521(6) $p=0.001$			0.6478(11) $p=0.015$
SIRM				0.9738(6) $p=0.001$		00.6478(11) $p=0.015$	

Blank squares indicate no significant correlation exists between the variables.
Values given are: Coefficient/(Cases)/Significance.

Table 5
Correlation coefficients for Soil Survey samples, magnetic and conventional soil analyses: Cambisol profiles

	ORGC	Fep	Fed	CEC	CLAY	χ	SIRM
ORGC		0.5307(14) $p=0.025$		0.8620(19) $p=0.001$	0.5314(23) $p=0.004$	0.5383(23) $p=0.004$	0.7238(23) $p=0.001$
Fep	0.5307(14) $p=0.025$		0.5413(15) $p=0.018$		0.7411(15) $p=0.001$	0.5509(15) $p=0.016$	
Fed		0.5413(15) $p=0.018$		0.7588(16) $p=0.001$			
CEC	0.8620(19) $p=0.001$		0.7588(16) $p=0.001$		0.8832(21) $p=0.001$	0.7328(21) $p=0.001$	0.6857(21) $p=0.001$
CLAY	0.5314(23) $p=0.004$	0.7411(15) $p=0.001$		0.8832(21) $p=0.001$		0.6315(29) $p=0.001$	0.5429(29) $p=0.001$
χ	0.5383(23) $p=0.004$	0.5509(15) $p=0.016$		0.7328(21) $p=0.001$	0.6315(29) $p=0.001$		0.6844(29) $p=0.001$
SIRM	0.7238(23) $p=0.001$			0.6857(21) $p=0.001$	0.5429(29) $p=0.001$	0.6844(29) $p=0.001$	

Blank squares indicate no significant correlation exists between the variables.
Values given are: Coefficient/(Cases)/Significance.

(Maher, 1988), which may contribute to the sample remanence but be poorly extracted because of their ultrafine size. Alternatively, some of the SIRM may reside in ferrimagnetic inclusions within host mineral grains, which may also be inefficiently extracted.

3.3.1. *X-ray diffraction*

Fig. 14a–c summarises the minerals identified by X-ray diffraction in the magnetic extracts. For the ultrafine (<2 μm) magnetic extracts, the major minerals present were the ferrimagnets, maghemite and magnetite, the canted antiferromagnets, hematite and goethite, and the diamagnetic mineral, quartz. The latter mineral is extracted magnetically due to the presence of magnetic inclusions within the host quartz grains (Hounslow and Maher, 1996). For the fine-grained ferrimagnets, compositions intermediate between magnetite and maghemite are apparent; superstructure peaks expected

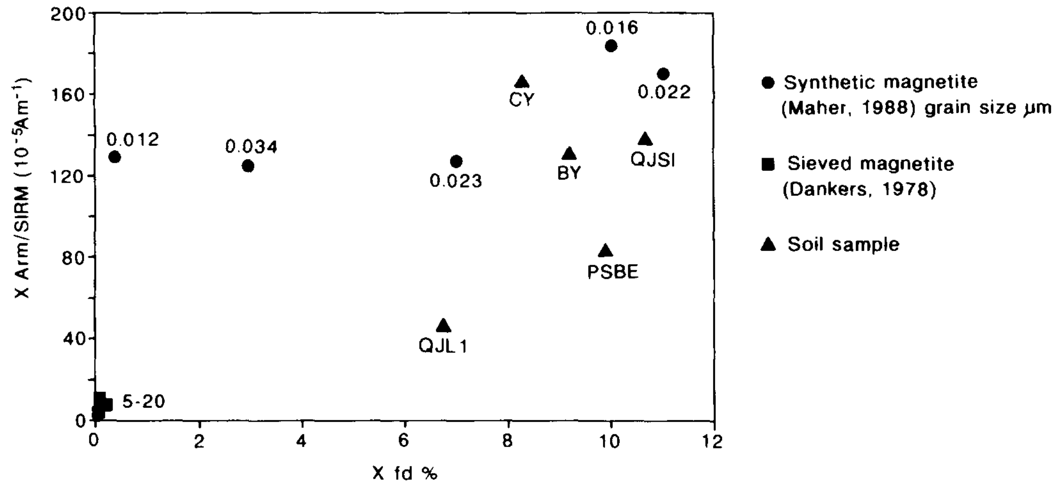

Fig. 11. χ_{fd}% and χ_{ARM}/SIRM data for the magnetically extracted soils (Broadway rendzina, Norfolk rendzina, Exmoor cambisol, Luochuan palaeosol S_1 and Luochuan loess L_1) and some grain-sized ferrimagnets.

for pure maghemite are only seen occasionally but the main magnetite peak (at 2.967 Å) is significantly shifted towards the maghemite peak (at 2.95 Å). Similar mineral assemblages dominate the 2–38 μm and >38 μm extracts, with quartz, spinels and hematite being the major components. Other minerals, carrying no magnetic remanence, but appearing as minor components of the >2 μm magnetic extracts are Fe-rich clays and silicates. In the Broadway sample, carbonate appears in the >2 μm magnetic extract. This is a diamagnetic mineral; its extraction by magnetic means may indicate the presence of magnetic inclusions, such as the bacterially produced magnetosomes seen in Cretaceous chalk samples, or binding of magnetic particles to the carbonate (Hounslow and Maher, 1996). It is not possible, however, for the observed level of magnetic enhancement in the Broadway soil to result solely from chalk dissolution and concentration of magnetic detritus. Susceptibility values for bulk chalk samples are not measurable (due to the diamagnetic nature of chalk), but SIRM values are typically $0.01–0.1 \times 10^{-5}$ $Am^2\,kg^{-1}$. After dissolution of the carbonate, SIRM values for the remaining detrital fraction are around $0.05–0.15 \times 10^{-3}\,Am^2\,kg^{-1}$. In contrast, SIRMs for the Broadway rendzina are $\sim 16 \times 10^{-3}\,Am^2\,kg^{-1}$.

3.3.2. *Electron microscopy*

Transmission electron microscopy of the <2 μm extracts reveals the dominant presence of reasonably well crystalline, submicrometre magnetic grains, of very variable grain size (Fig. 15a–e). The largest grains are ~0.4 μm; the smallest, which often occur as clusters around larger grains (Fig. 15c), are <0.001 μm. Grain size distributions can be estimated from micrographs; Fig. 16 shows the grain size distribution obtained from Fig. 15b. However, given that only 30–50% of the susceptibility carriers were extracted and the additional difficulty in microscopically resolving the finest grain sizes, these grain size data probably significantly over-estimate the actual grain size mean and mode. Only rarely are chains or groups of unidimensional particles observed (Fig. 15e). As previously observed for paleosol S_5 from the Chinese loess plateau, these crystals, presumably formed by magnetotactic bacteria, make up less than 1% of the total extracted assemblages. Magnetotactic bacteria therefore make an insignificant contribution to the single domain/superparamagnetic ferrimagnets found in enhanced soils and paleosols.

Scanning electron microscopy of the ~2–38 μm magnetic fractions identifies the morphology and elemental range of the detrital magnetic compo-

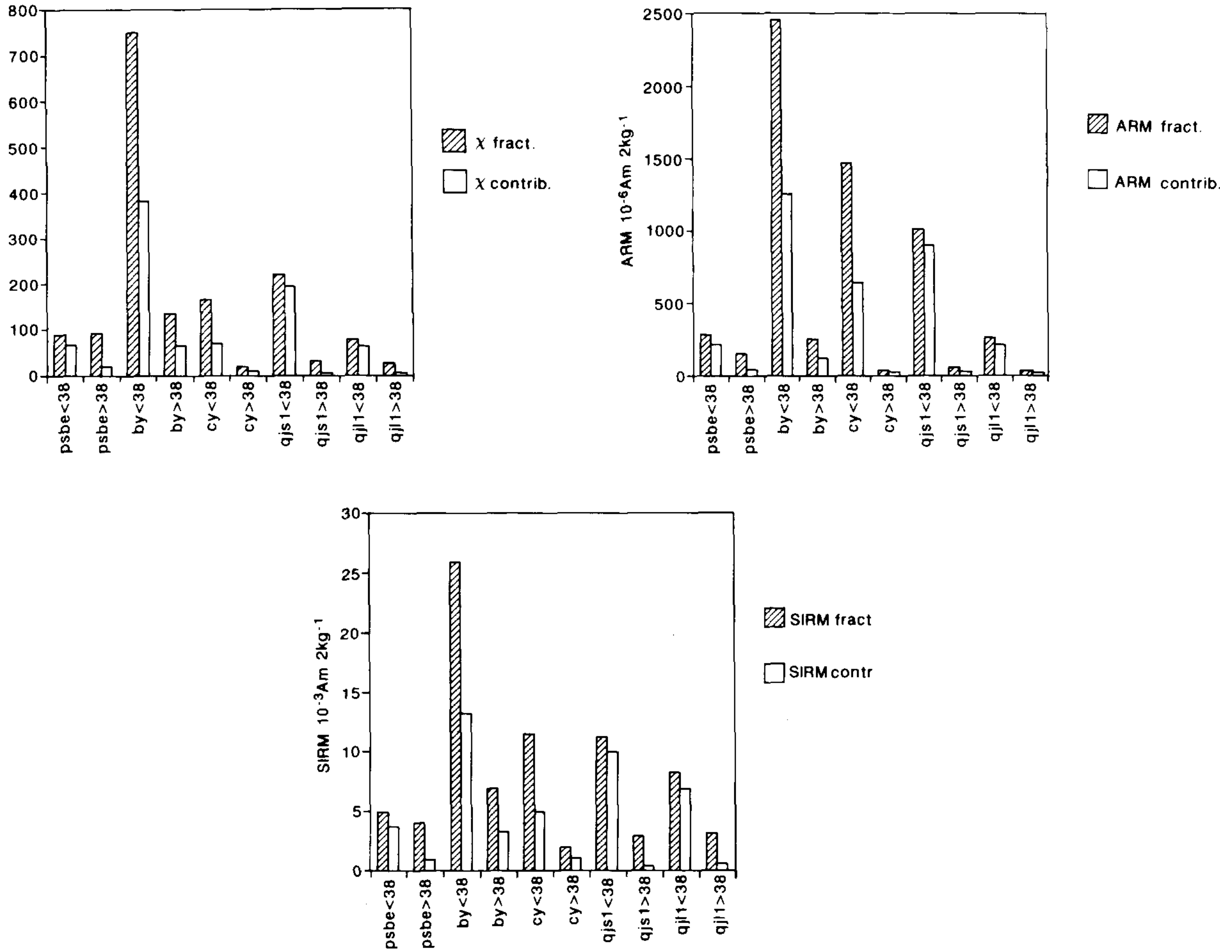

Fig. 12. χ, ARM and SIRM values of the < and >38 μm size fractions and their respective contributions to the bulk magnetic measurement, taking into account the particle size distribution.

nents in these soils. Many of the larger grains (up to ~10 μm) are geometric and well crystallized, consisting of minerals resistant to weathering; they include quartz, a range of Fe-silicates and chromites. Crystals dominantly composed of Fe, presumably representing the spinels identified by XRD, are commonly the smaller grains (~2 μm) in the extract. The 2–38 μm extract from the Norfolk rendzina is notable for its concentration of carbonate fragments, which, upon elemental analysis, contain both calcium and iron. This may reflect a ferroan calcite composition, or the presence of magnetic inclusions. A pre-extraction dissolution step (Hounslow and Maher, 1996), with removal of the carbonate by acetic acid, would be required to identify the source of the Fe content.

Detrital grains (>2 μm) constitute up to 98% of the weight of the magnetic extracts, but display between 13% and 48% of the measured susceptibility of the <2 μm fraction. (The susceptibility of the <2 μm fraction is itself likely to be a significant under-estimate, since there is serious under-extraction of the superparamagnetic grains). The sedimentary substrates of these soils were previously described (e.g. Maher and Taylor, 1988) as 'non-magnetic', in that their bulk susceptibility values were very low. In fact, for the Exmoor cambisol, detrital grains (and any poorly dispersed finer

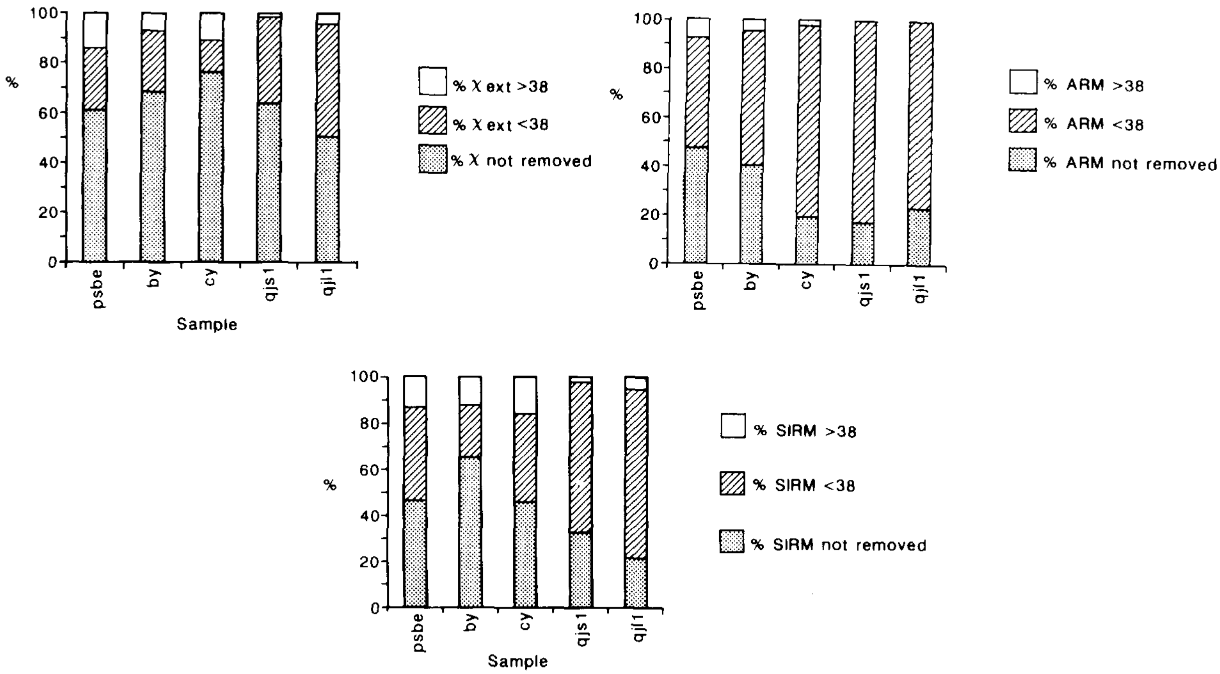

Fig. 13. Extraction efficiency data for χ, ARM and SIRM.

grains) in the fine silt fraction (~2–4 μm) contribute to the susceptibility as much, if not more than, the authigenic grains of the clay-sized fraction (Maher, 1986). Given the presence of ferrimagnetic detrital particles (>2 μm) in each of the substrates examined here, to describe them as 'non-magnetic' is thus, sensu stricto, inaccurate. However, for all but the Exmoor cambisol, the fine-grained, pedogenic magnetic component is the dominant contributor to the enhanced susceptibility and remanence values.

3.3.3. Thermomagnetic data

Interpretation of changes in magnetic behaviour upon heating of soils is often difficult, due to transformations during heating of the iron oxide phases and also Fe-rich clay minerals, under reducing conditions caused by combustion of organic matter. However, thermomagnetic analyses can be used to exclude the possibility of fire as an enhancement mechanism at the Exmoor sites. Soil firing can cause temperatures in the surface layer of soils to reach as high as 800°C and result in formation of ferrimagnets by reduction of other, weakly magnetic iron oxides and Fe-bearing clays. Upon laboratory heating, the two enhanced Exmoor soils both show large increases in magnetisation at ~210°C (Fig. 17), attributable to the conversion of lepidocrocite to maghemite (Van der Marel, 1951). This behaviour is exhibited throughout the mineral horizons of these soils. If these soils had previously been burnt, any lepidocrocite would already have been converted, and further increases in magnetisation would not be seen in the laboratory heating. Lepidocrocite is a weakly magnetic (paramagnetic) oxide, previously reported only in gleyed soils (Brown, 1953; Schwertmann and Taylor, 1977), often occurring together with goethite. It is likely that this restricted reported occurrence of lepidocrocite is an artifact, reflecting the use of bulk X-ray diffraction to identify its presence or absence. Such analysis would fail to identify the presence of this mineral in trace amounts (as is commonly the case for the ferrimagnets also). It seems likely that any of the iron oxide species may occur in any soil, depending on conditions at the micro-environmental scale.

It is also interesting to note that, of the soils

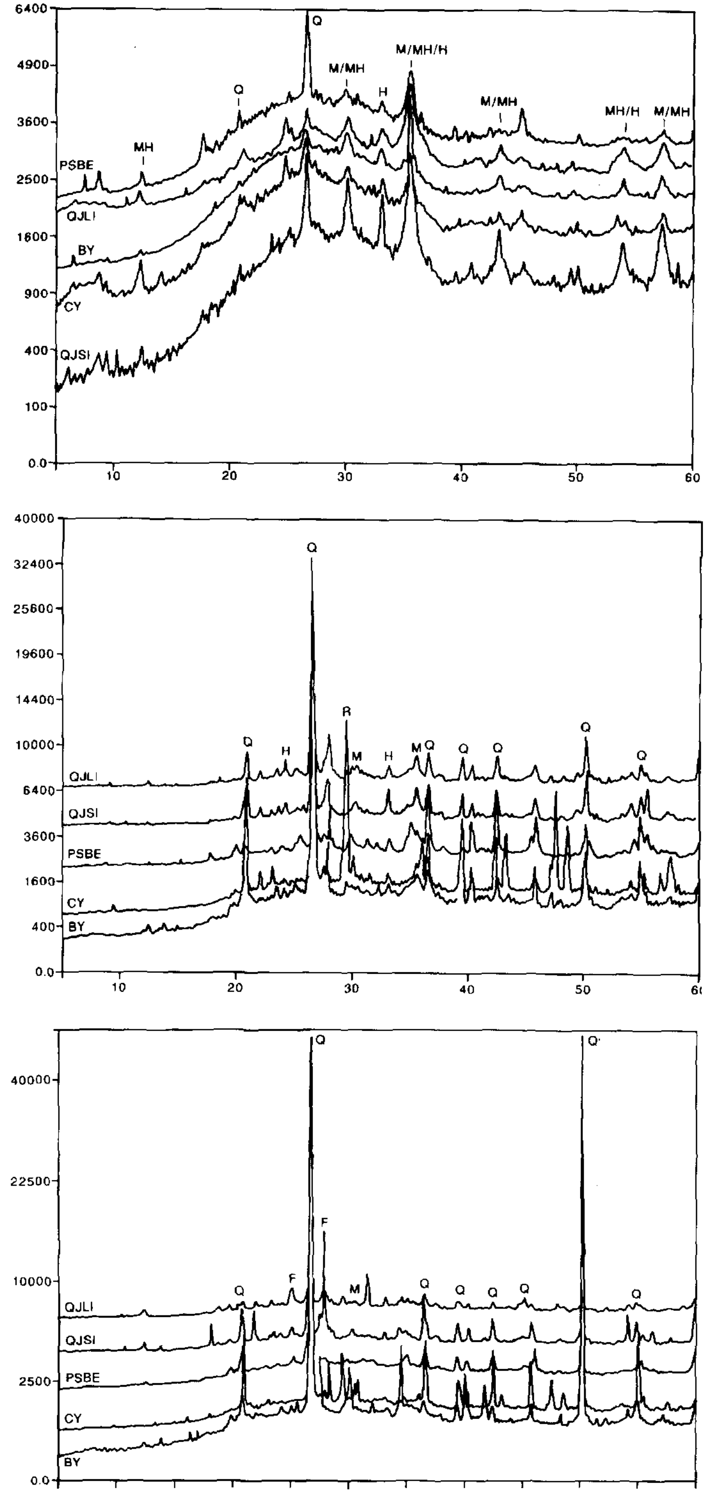

Fig. 14. X-ray diffraction spectra for the three sets of magnetic extracts: (a) $<\sim 2$ μm fraction; (b) ~ 2–38 μm fraction; (c) >38 μm fraction. Q = Quartz; F = Feldspar; MH = Maghemite; M = Magnetite; R = Rutile; H = Haematite.

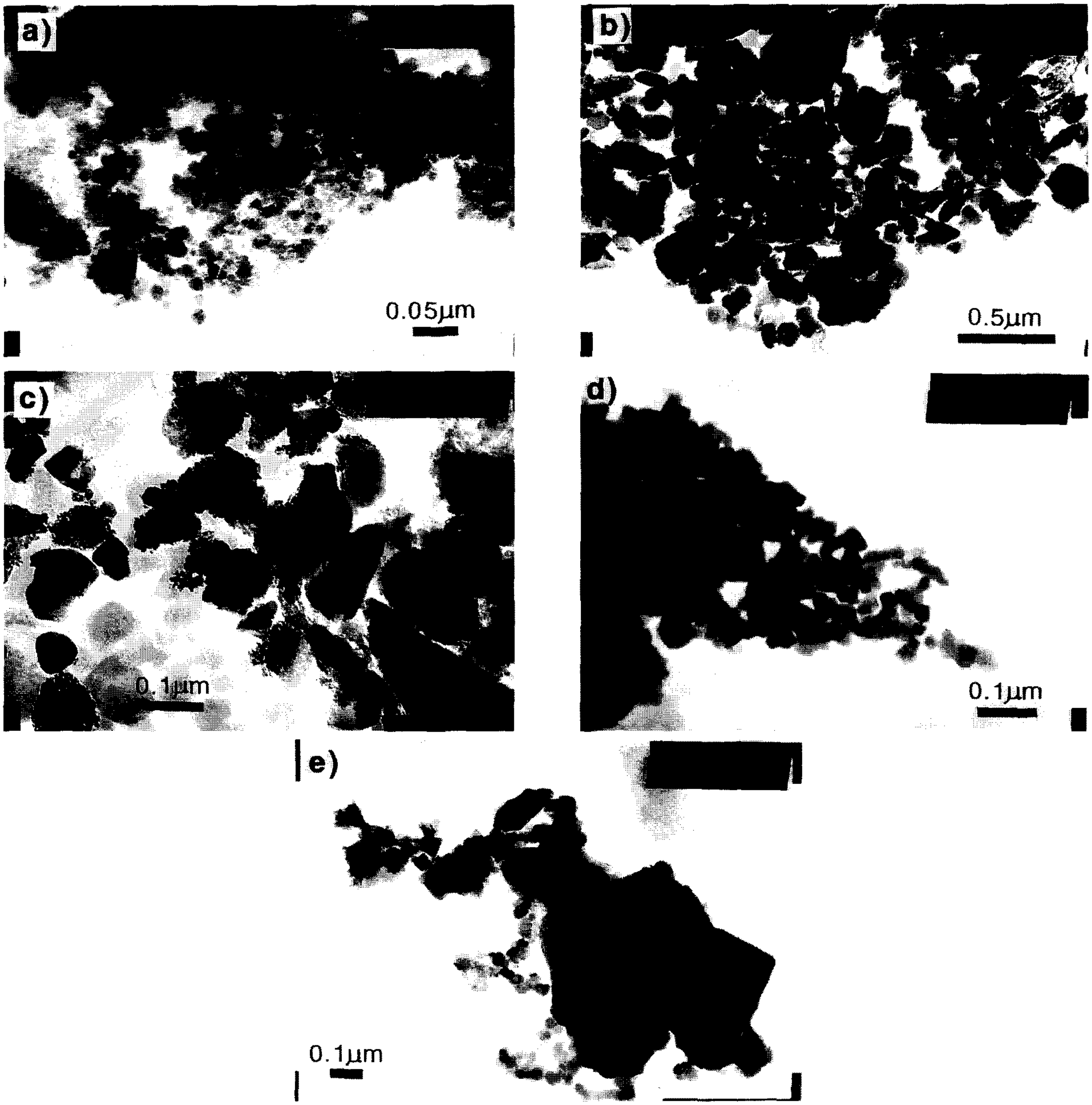

Fig. 15. Transmission electron micrographs of <2 μm soil magnetic extracts: (a) cluster of ultrafine grains, many <0.01 μm, from the Exmoor cambisol; b) Chinese palaeosol, S_1 (see Fig. 16 for the grain size distribution obtained from this micrograph); (c) Chinese palaeosol, S_1, note the large numbers of ultrafine (presumably superparamagnetic) grains attached to the surfaces of larger grains; (d) euhedral grains from the Broadway rendzina; (e) unidimensional, concatenated grains (bacterial magnetosomes) from Chinese loess, L_1.

sampled for magnetic extractions, three (the Exmoor cambisol, and the Chinese loess/paleosol couplet) display XRD peaks characteristic of kaolinite (7 Å), while the remaining two soils (the Norfolk and the Broadway rendzinas) do not. Since kaolinite decomposes at ~550°C (Brindley

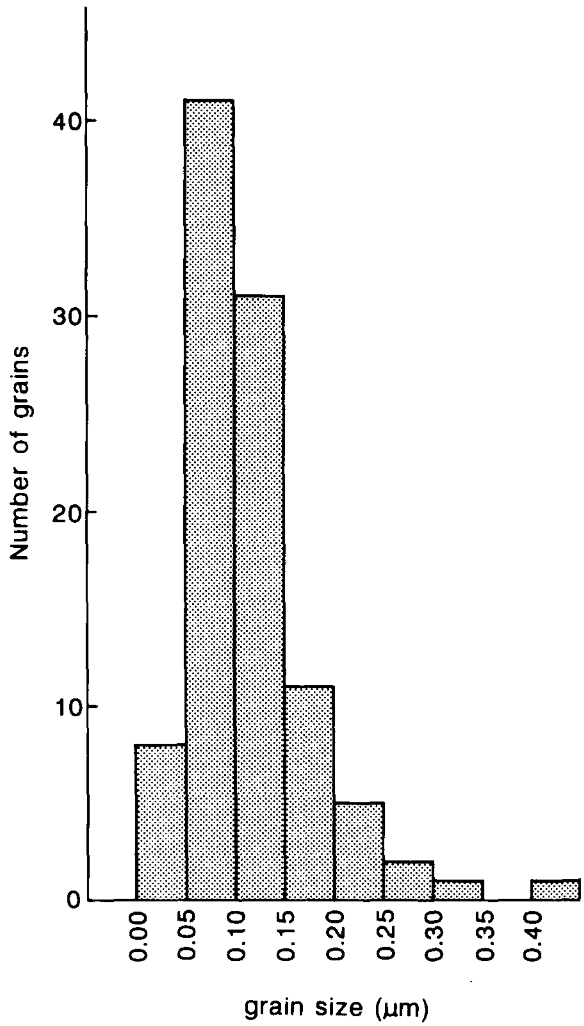

Fig. 16. Grain size distribution estimated from micrograph (Fig. 15b) for Chinese palaeosol S_1.

and Brown, 1980), its presence in the Exmoor soil and the Chinese loess and soil samples indicates that burning to this temperature has not occurred at these locations.

4. Discussion

Pedogenic formation of ferrimagnets appears to be favoured in well drained, not very acidic soils (pH ~5.5–7), on weatherable, Fe-bearing (but often *not* Fe-rich) substrates. The amount of magnetic enhancement often shows little correlation with other soil parameters, with the exception of some positive correlation with soil organic carbon and cation exchange capacity. The minerals formed by enhancement are magnetite and, by subsequent oxidation, maghemite. Maghemite is thus a common component of enhanced soils; it is not formed directly, but as an alteration product of the original mixed Fe^{2+}/Fe^{3+} spinel, magnetite. Oxidation of the smallest magnetite grains to maghemite may promote their subsequent survival in the soil. Ultrafine magnetite may be dissolved even in non-reducing conditions, due to its structural Fe^{2+} content; in contrast, the Fe^{3+} oxides require reduction for their dissolution (Taylor, pers. commun.). This may explain the observed link between susceptibility enhancement and a seasonally wet/dry climate regime (Tite and Linington, 1975), with magnetite formation during periods of intermittent soil wetness and its oxidation to maghemite in subsequent dry periods.

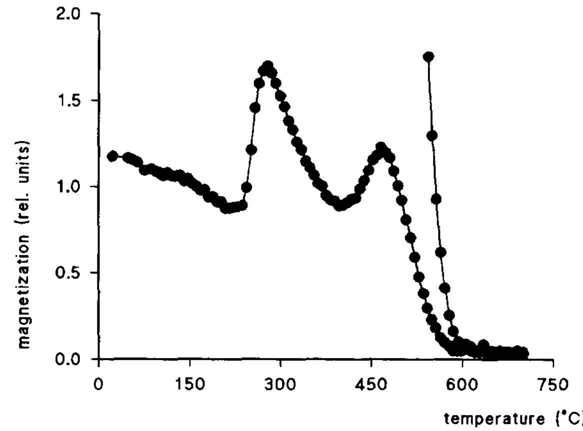

Fig. 17. Thermomagnetic curve for Exmoor cambisol.

A large proportion of the susceptibility increases seen in enhanced soils is due to the superparamagnetic grain size of the authigenic magnetite and maghemite. These empirical observations show interesting correlation with laboratory experiments on magnetite synthesis, where slow oxidation of an Fe^{2+} system at near-neutral pH resulted in rapid formation of ultrafine magnetite (Taylor et al., 1987).

In contrast, rates of magnetic depletion (i.e., from loss of iron and/or conversion to non-ferrimagnetic forms) seem to be highest in permanently wet soils, very acidic podsols and in areas where rainfall exceeds ~2000 mm p.a. From these data, significant enhancement would be predicted for brunisol-type soils undergoing wetting/drying cycles on buffered Fe-bearing parent materials, such as occur on the Cretaceous chalk in the U.K. or on the carbonate-rich loess of China.

These observations appear contradictory to the generally held view that pedogenic formation of iron oxides is extremely slow in well drained calcareous soils, because of slow rates of dissolution of parent, Fe^2-containing minerals in equilibrium with $CaCO_3$ (e.g., Loeppert, 1988). However, as noted by Loeppert (op. cit.), rates of Fe release within such soils may be greatly increased in microsites of active microbial metabolism. Just as the supply of Fe can be controlled by bacterial activity, so the precipitation product of Fe^{2+} oxidation appears to be similarly controlled. In the case of magnetite formation by magnetotactic bacteria, these organisms require the presence of nitrate in micro-aerophilic conditions (Blakemore et al., 1985). Such conditions would be expected in A horizons but not in deeper soil horizons (Fassbinder and Stanjek, 1993). For dissimilatory magnetite production by Fe^{3+}-reducing bacteria, Fe^{2+} production will occur upon (temporary) wetting of parts of the soil and subsequent respiratory depletion of oxygen. The correlation between magnetic content and organic matter suggests efficient Fe^{3+} reduction and magnetite formation, given an adequate supply of oxidisable organic matter. Fischer (1988) notes that the percentage of Fe^{3+}-reducing bacteria is often at a maximum in the lower part of Ah horizons, where enough organic matter exists but where supply of oxygen is lowered due to the higher soil water content. Even in lower horizons, sufficient organic matter exists to support significant numbers of Fe-reducing bacteria; Ottow (1969) reported their presence even at 1 m soil depth. The presence of pedogenic magnetite, of very variable grain size, in the A and B horizons of the enhanced soils investigated here, suggests that the extracellular, BIM pathway is more significant than the intracellular, BOM pathway for pedogenic magnetite formation.

5. Significance for paleoclimate reconstructions from paleosols

It is clear that the magnetic properties of modern soils are sensitive indicators of soil-forming processes and directions. The relationship between soil magnetic properties and ambient climate must be evaluated within the context of other soil-forming factors, which include slope, parent material, organic activity and time. As shown here, even where soils have developed on the same substrate, over the same timescale, great differences in magnetic properties can result over short distances due to changing relief and (soil) climate. These observations, however, serve to emphasise the unique nature of the Quaternary record held by the paleosol sequences of the Chinese loess plateau. Here, between-site variability in pedogenic factors is reduced to an unparalleled minimum (Maher et al., 1994). The parent material is a rapidly weathering, porous, iron-bearing medium of exceptionally uniform composition. Topography is insignificant, with the loess and paleosol units stretching horizontally across hundreds of kilometres of the region. Vegetation can be assumed to co-vary with climate. Thus, the soil system equation (Jenny, 1941) can be reduced in this unique region to a function of climate and time (Maher et al., 1994). On the basis of the modern soil data, and the oxic, well drained, near-neutral pH characteristics of the Chinese loess, efficient pedogenic enhancement of susceptibility would be expected throughout past interstadial and interglacial cycles. Conversely, Kletetschka and Banerjee (1995) suggest fire has played a key role in magnetic enhancement of the Chinese paleosols. As shown here, soils can become magnetically enhanced without being burnt. It would also be difficult to produce the even and gradational distribution of soil susceptibility values seen across the Loess Plateau by firing, which tends to cause efficient enhancement in localised zones (e.g., Maher, 1986).

If the enhancement of the Chinese paleosols is assumed to be pedogenic in origin, the paleosusceptibility variations may be used to reconstruct paleoclimate in the following way. First, it is necessary to identify the relative roles of climate and time. For susceptibility to reflect individual

Quaternary climate stages, it needs to be a rapidly developing soil property, reaching near steady-state with regard to ambient climate in no more than a few thousand years. A continually developing soil property, reaching a maximum only over a timespan of thousands to millions of years, may predominantly reflect the duration of soil formation. Identification of the relative roles of time and climate in soil magnetic enhancement is problematic. For example, Woodward et al. (1994) report susceptibility values for a sequence of Quaternary profiles developed in alluvial terrace sediments in northwest Greece. The youngest soil (<30 yr B.P.) shows no magnetic enhancement. Three profiles, one of late Holocene age (~1000 yr B.P.), the others of late Pleistocene age (~20–28,000 yr B.P.), show similar levels of enhancement in their B horizons (20–40 cm depth). The deepest soil profile, assumed to be the oldest in the sequence, has the highest enhancement. These authors suggest the magnetic data thus demonstrate time dependence, but the question of climate versus time is in fact unresolved. Three of the four soils, spanning an age range of 1000–28,000 yr B.P., display similar magnetic values. The profile assumed to be oldest does have the highest enhancement but is this due to its longer soil-forming duration, or does it reflect an earlier and different soil-forming climate? Similarly, 'chronofunctions' of pedogenic susceptibility over periods of up to 1 million years (Singer et al., 1992) may not be true chronofunctions because climate will also certainly have changed over this timescale.

To identify rates of magnetic enhancement, good age control is required, together with a dense spectrum of soils spanning the established timescale. So far, only circumstantial evidence exists to suggest rapid enhancement of susceptibility in 'suitable' soils. Maher et al. (1994) show that susceptibility values of recent soils in the Loess Plateau area of China are within the same range as the paleosols, some of which have had longer soil-forming durations. Also, strong correlation exists between the pedogenic susceptibility of the young soils and present-day rainfall (Maher et al., 1994; Han et al., 1996). Maher and Thompson (1995) compiled susceptibility and rainfall data for a number of northern hemisphere temperate zone sites, and also found good correlation between pedogenic susceptibility and rainfall (Fig. 18). Such a relationship would not be expected if soil-forming duration was a more dominant factor than climate. Other indications of rapid rates of soil enhancement include the *annually increasing* soil susceptibility at a reclaimed mine site in the Northern Territories of Australia, where no fires have occurred (Milnes, pers. commun.). Similarly, Johnson (pers. commun.) reports localised soil magnetic enhancement, resulting from a farmer's construction of a subsoil drainage ditch, lined with branches. Enhancement has occurred over just 50 years as the wood lining has decomposed.

It is likely that when Fe-reducing bacteria have access to organic matter and a weathering source of reactive (e.g. poorly crystalline) iron, they will, upon activation by the onset of locally anoxic conditions, induce enhancement. Maximum enhancement may occur in the profile where: (1) organic matter is available (for bacterial metabolism and also retardation of crystallisation of Fe to, e.g., hematite); and (2) oxygen levels are locally and temporarily decreased, so that the Fe-reducing bacteria are favoured. Following the initially rapid rise in susceptibility, a near steady-state value may evolve for that ambient (soil) climate, due to competitive equilibrium between: (1) formation and persistence of the pedogenic ferrimagnets; and (2) oxidation to weakly magnetic oxides like goethite or hematite. Thus, intermittent wetting and drying of soils favours magnetite formation and Fe^{3+}-oxide dissolution, whilst drying favours Fe^{3+}-oxide formation at the expense of the neoformed ultrafine magnetites. Without this competitive feedback, magnetically enhancing soils would continue to enhance through time, as long as iron and organic matter were available. Susceptibility values would therefore show time dependence (Singer et al., 1992), rather than climate dependence (Maher and Thompson, 1995).

As soil profiles continue to weather and deepen, it is likely that the *cumulative* susceptibility will increase through time, whilst the maximum pedogenic susceptibility value may maintain a climatically determined equilibrium. Paleorainfall reconstructions from the Chinese loess sequences have yet to take into account the profile- and depth-distribution of pedogenic susceptibility.

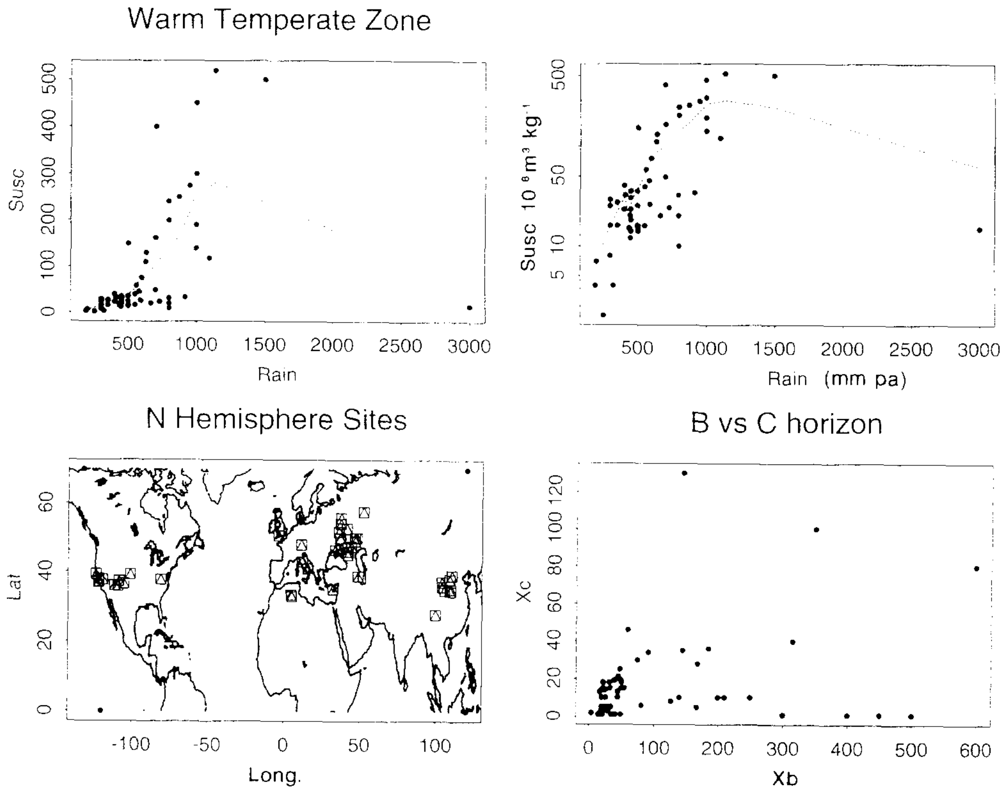

Fig. 18. Pedogenic magnetic susceptibility versus rainfall for a range of Northern hemisphere sites in the temperate zone (from Maher and Thompson, 1995): (a) a linear plot of susceptibility and rainfall; (b) a log–linear plot of susceptibility and rainfall; (c) the geographic distribution of the sites providing the data in (a) and (b); (d) a linear plot of the C horizon and B horizon susceptibility values, the lack of correlation indicating lack of influence of parent material on the degree of pedogenic enhancement.

Problems also remain in determining sufficiently accurately the rate of dust inputs during pedogenesis, and hence their significance for rates of pedogenic enhancement. Calculated accumulation rates for the paleosols may be significantly overestimated, given that the soils are *not* essentially a deposit but are superimposed on the previously deposited glacial loess. Improved time control is required, which may then significantly add to the value of multi-factorial modelling approaches, as described by Anderson and Hallet (1996). However, it is possible that the loess and paleosol units remain within the weathering zone (within ~1 m of the ground surface) for approximately equivalent periods of time (~10 ka), constrained, respectively, by burial rates during glacial periods and by the duration of interglacial periods. For example, given a loess accumulation rate of 10 cm/ka during a glacial period, the residence time of that loess within the weathering zone will be ~10 ka. Given an accumulation rate of 4 cm/ka during an interglacial period, the residence time for weathering will potentially be much longer (~25 ka) but most interglacial periods do not persist beyond 10 ka. Thus, there may be convergence and relative constancy between the weathering durations of both loess sedimentary packets and paleosols.

It is clear from the modern soils that a rainfall-specific enhancement signal will *not* be seen in soils prone to net loss or reduction of iron, such as podsols, gleysols and soils subjected to excessive rainfall (> ~2000 mm). If any of the Chinese paleosols have been subjected to such high rainfall, their pedogenic susceptibility values may appear anomalously low as a result. Deserts, either cold or warm, would also be expected to form soils with low concentrations of pedogenic ferrimagnets. Schwertmann et al. (1982) point out that excessively drained soils may preferentially accumulate hematite, even in temperate climates, due to their enhanced aridity and oxidation, relative to adjacent finer textured soils. In this context, it is interesting to note the complete absence of pedogenic magnetite in the Valley Farm paleosol, a rubified paleosol developed in sands and gravels of early Pleistocene age, in the East Anglian region of the UK.

Pedogenic enhancement of susceptibility may also be difficult to identify in soils dominated by aeolian and weathering inputs of detrital magnetic particles. Superimposed on any pedogenic controls, aeolian input of detrital magnetic particles may be amplified under conditions of local aridity and increased wind intensity (Beget et al., 1990). Conversely, aeolian supply of sand and silt-sized detrital grains is likely to be reduced given more humid conditions, increased ground vegetation cover and decreased wind speeds. Under such conditions, aeolian inputs may be restricted to finer, relatively low-susceptibility, particles. Susceptibility values may also change if the source of the aeolian supply itself varies. In such situations, the susceptibility signal may show lower values in the soils than in the unweathered loess, as in the Alaskan sequences (Beget et al., 1990), and those in Poland (Nawrocki et al., 1995) and Siberia (Rutter and Chlachula, 1995). The latter authors report evidence for pedogenic formation of ultrafine magnetic grains in some of the Siberian and Polish paleosols (e.g., as shown by measurable values of frequency-dependent susceptibility), but net magnetic depletion is apparent in the gleyed interglacial soils and even in the brunisols. From the modern data, magnetite formation would be predicted for the brunisols, unless the climate was either too dry ($< \sim 350$ mm p.a.) or too wet ($> \sim 2000$ mm p.a.) for enhancement to proceed.

6. Conclusions

From the above the following conclusions can be drawn:

(1) Measured variations in magnetic susceptibility values of loess/paleosol sequences may arise from a variety of site-specific sources, including changes in allochthonous and authigenic magnetic inputs.

(2) Allochthonous magnetic inputs to soils can vary by source, rate of input and grain size; in paleosols, such variations may reflect past changes in wind speed, direction and aridity.

(3) Authigenic magnetic inputs vary with the relative rates of magnetic depletion (loss of iron and/or conversion of iron to non-ferrimagnetic forms) and magnetic enhancement, which are sensitive to soil type, especially with regard to opportunities for iron reduction/oxidation cycles. Excessively arid, wet or acidic soils display little magnetic enhancement; intermittently wet/dry soils show most enhancement.

(4) For those soils which are liable to be magnetically enhanced (as above), correlation has been found between the maximum value of pedogenic susceptibility and the annual rainfall. The almost unique pedogenic system in the Chinese loess area, where variation in soil-forming factors other than climate is reduced to a global minimum, allows use of the paleo-susceptibility values as proxy paleorainfall values. Annual rainfall may be an insensitive measure of soil moisture (Derbyshire et al., 1995), and degree of pedogenesis may, in turn, not be a simple function of rainfall, but the strength of the rainfall/susceptibility correlation suggests it may validly be used as a means of proxy paleorainfall reconstruction in this region.

(5) To identify the mechanism and source of any link between magnetic properties, for example, susceptibility and climate change, the mineralogy and grain size of soil magnetic carriers require detailed investigation. Broecker (1992) has stated that indicators of paleorainfall are at best qualitative. Given: (a) the prospect of quantitative reconstruction of past rainfall rates from continental loess records; (b) predicted future climate changes; and (c) the value of paleoclimate data for testing of General Circulation Models, such detailed magnetic investigations constitute an important scientific task.

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Appendix A

Soil Survey Sample Set

Profile No.	Sample No.	Horizon	Depth (cm)	Subgroup	Parent Material	Series
SK66/0312	1	Ae	3–10	Humo-ferric podsol	Bunter sandstone	Shirrel Heath
	2	Ea	10–20			
	3	Bhs	25–29			
	4	Bs	27–50			
	5	Bc	57–90			
	6	Cu	110–140			
SU06/2008	7	Ap_1	0–13	Brown earth (gleyic)	Glauconitic sandstone (Upper Greensand)	Urchfont
	8	Ap_2	13–38			
	9	$E(g)_1$	38–42			
	10	$E(g)_2$	62–86			
SK90/1304	11	Ap	0–31	Ferritic brown earth	Ferruginous sandstone	Banbury
	12	Bw	31–52			
	13	BCt	80–95			
SS63/2208	14	A	3–20	Brown earth	Devonian silt and mudstones	Denbigh
	15	Bw	25–50			
SK66/3791	16	Ea	2–4	Brown sand	Bunter sandstone	Howard
	17	Ea	5–20			
	18	Bs	25–45			
	19	B	40–57			
	20	Bt	60–80			
	21	Cu	135–145			
SK56/6696	22	Ap	0–26	Brown sand	Triassic sandstone	Cuckney
	23	Bw_1	26–52			
	24	Bw_2	52–80			
	25	Bc_1	82–100			
	26	Bc_2	100–150			
SS63/9482	27	Ap	0–23	Brown podsolic	Devonian slates	Manod
	28	Bs	27–42			
SO74/4308	29	–	0–20	Brown earth	Silurian siltstone	Barton
	30	–	20–62			
	31		62–76			
SK78/6175	32	Ap	0–30	Argillic pelosol	Red clay	Worcester
	33	Bt	30–50			
	34	Bc	50–80			
	35	Cr	95–150			
TM12/8729	36	Ap	0–29	Stagnogleyic pelosol	London clay (pyritic)	Althorne
	37	B(g)	29–65			
	38	Cg	65-			
SW71/4166	39	Bw	21–45	Brown earth	Serpentine	Black Head
SS74/6513	40	Oh	0–4	Stagnopodsol	Slate	Hafren
	41	Ah	4–10			
	42	Eag	10–20			
	43	Bsg	21–28			
	44	Bs	28–71			
SO95/8928	45	Bwg	19–46	Calcareous pelosol	Calcareous clay	Evesham
	46	BG	46–80			
	47		80–110			
SO74/3456	48	A	0–22	Brown earth	Devonian sandstone and marl	Eardiston
	49	B	22–35			
	50	B/C	35–48			

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