Magnetic susceptibility of soil: an evaluation of conflicting theories using a national data set

J. A. Dearing,1,* K. L. Hay,1 S. M. J. Baban,1 A. S. Huddleston,1 E. M. H. Wellington2 and P. J. Loveland3

1 School of Natural and Environmental Sciences, Coventry University, Coventry CV1 5FB, UK
2 School of Biological Sciences, University of Warwick, Coventry, CV4 7AL, UK
3 Soil Survey and Land Research Centre, Cranfield University, Silsoe College, Silsoe, Bedford, MK45 4DT, UK

Accepted 1996 August 12. Received 1996 July 31; in original form 1996 April 10

SUMMARY
Magnetic susceptibility values for topsoils across England are combined with data for soil type, geochemistry and concentrations of magnetotactic bacteria in order to evaluate different theories for explaining soil magnetism. Strongly magnetic soils in unpolluted areas are found over weakly magnetic substrates and are dominated by ultrafine superparamagnetic grains. Magnetotactic bacteria are present in insufficient concentrations to account for strongly magnetic soils, and crop burning is discounted as a major factor. A small number of samples show high values associated with either airborne magnetic particulates from pollution or residual primary ferrimagnetic minerals from igneous substrates. The results are used to construct a new mechanism for the formation of secondary ferrimagnetic minerals that links abiological weathering and biological fermentation processes. The fundamental driving force in the mechanism is Fe supply, which may be linked to climate. Observed causative associations between climate and the magnetic susceptibility of loess–palaeosol sequences are supported by the findings.

Key words: climate, magnetic susceptibility, soils.

INTRODUCTION
Magnetic susceptibility measurements are widely used to detect the presence of pedogenic ferrimagnetic minerals (Thompson & Oldfield 1986), particularly in loess–palaeosol sequences where measurements are used as proxy indicators of climatic change (Heller & Liu 1984; Maher, Thompson & Zhou 1994; Liu et al. 1995; Dearing, Livingstone & Zhou 1996). However, there is neither a consensus about the mechanism by which soils are enriched with fine-grained ferrimagnetic minerals, nor a complete elucidation of the links between climate and soil magnetism. During the past 40 years, several theories have been invoked to explain the presence or enrichment of ferrimagnetic minerals in soils:

(1) long-term weathering and pedogenesis that concentrate residual primary ferrimagnetic minerals (Singer & Fine 1989);
(2) accumulation of relatively coarse (> 1 μm) airborne magnetic particulates from mainly pollution sources (Thompson & Oldfield 1986);
(3) strictly anaerobic dissimilatory bacteria (GS-15 type) that produce uncontrolled sizes of single-domain magnetite (Fe₃O₄) grains with diameters < 50 nm (Lovley et al. 1987; Lovley 1991);
(4) anaerobic formation of greigite (Fe₃S₄) linked to microbial reduction (Stanjek et al. 1994);
(5) microaerophilic assimilatory bacteria (magnetotactic bacteria) that produce chains of single-domain magnetite magnetosomes with diameters 20–100 nm (Fassbinder, Stanjek & Vali 1990; Fassbinder & Stanjek 1993);
(6) thermal transformation of weakly magnetic iron oxides and hydroxides to ferrimagnetic magnetite or maghemite by natural fires or crop burning in the presence of organic matter (Le Borgne 1960; Kletetschka & Banerjee 1995);
(7) anaerobic microbial Fe reduction followed by uncontrolled formation of single-domain magnetite or maghemite (γFe₂O₃) grains with diameters < 100 nm, the so-called fermentation mechanism (Le Borgne 1955; Mullins 1977);
(8) abiological weathering of mineral Fe(II) followed by autoxidation leading to magnetite or maghemite, as demonstrated in synthetic experiments (Taylor, Maher & Self 1987; Maher & Taylor 1988).

* Now at: Department of Geography, University of Liverpool, Liverpool L69 3BX, UK.
We evaluate these theories at a regional scale by analysing the pattern of magnetic susceptibility values in topsoils sampled across the whole of England, site and geochemical data for each sample, and genetic screening of soil DNA for magnetotactic bacteria. Frequency-dependent susceptibility (Maher 1988; Dearing et al. 1996) is used to detect the presence of superparamagnetic (SP) secondary ferrimagnetic minerals (SFM).

**METHODS**

Samples were obtained from the National Soil Inventory collection held at the Soil Survey and Land Research Centre, Silsoe, which was used to produce the Soil Geochemical Atlas of England and Wales (McGrath & Loveland 1992). Field sampling was carried out between 1978 and 1982 on a 10 km x 10 km grid across England and Wales. At each sampling site the surveyor took 25 soil cores to a depth of 15 cm (excluding litter, fermentation and humus layers) within a 20 m x 20 m grid, which were bulked in the field. A soil-pit section and the site were described using standard Soil Survey procedures (Hodgson 1976). Samples were air dried, milled to pass a 2 mm sieve, and stored in plastic bags at room temperature. No detectable chemical contamination by any element was observed (McGrath & Loveland 1992), and magnetic measurements on milled and unmilled topsoils showed no statistically significant differences. Total elemental analyses were made on aqua regia digests (4:1 hydrochloric:nitric acids by volume) by ICP, and this paper uses the data published in the Soil Geochemical Atlas. Magnetic susceptibility measurements were made on 10 ml samples at low (470 Hz) and high (4700 Hz) frequencies in a Bartington Instruments dual-frequency MS2B sensor and expressed as mass-specific magnetic susceptibility ($\chi_{\text{LF}}$), mass-specific frequency-dependent susceptibility ($\chi_{\text{FD}}$) and percentage frequency-dependent susceptibility ($\chi_{\text{FD \%}}$) (Dearing et al. 1996). Weak samples with volume susceptibilities $<20 \times 10^{-8}$ SI units were excluded from the calculation of $\chi_{\text{FD \%}}$. Mass-specific susceptibilities were corrected for organic carbon using the Soil Inventory data for loss on ignition and dichromate digestion. A selection of soils at $\sim$ 30 grid sites were resampled in 1995. Differences between the magnetic susceptibility values of the old and new samples have detectable concentrations of SFMs (Table 1) and reach values ($>10^{-9} \text{ m}^3 \text{ kg}^{-1}$) that exceed most published values for soils and palaeosols worldwide (Dearing 1994). About 80 per cent of samples have detectable concentrations of SP grains ($\chi_{\text{FD \%}}$ per cent $>2$); $\sim$ 30 per cent of samples have $\chi_{\text{LF}}$ values controlled by the presence of SP grains ($\chi_{\text{FD \%}}$ per cent $>5$; $\chi_{\text{LF}} > 10^{-8} \text{ m}^3 \text{ kg}^{-1}$; $\chi_{\text{FD}} > 50 \times 10^{-9} \text{ m}^3 \text{ kg}^{-1}$); and $<5$ per cent of samples appear to have magnetic assemblages dominated by SP grains ($\chi_{\text{FD \%}}$ per cent $>8$ per cent; $\chi_{\text{LF}} > 5 \times 10^{-6} \text{ m}^3 \text{ kg}^{-1}$; $\chi_{\text{FD}} > 240 \times 10^{-9} \text{ m}^3 \text{ kg}^{-1}$). Strongly magnetic soils occur mainly in the south, southwest and central parts of England (Fig. 1a, b) over sedimentary and low-grade metamorphic substrates, such as Cretaceous chalk, Jurassic oolitic limestone and Devonian slate (Fig. 1c), which have negligible concentrations of primary ferrimagnetic minerals. These areas also lie south of the maximum extent of the Devensian and Anglian glaciations and can be considered to be free of igneous erratics contained in drift deposits. High values of $\chi_{\text{LF}}$ are also associated with industrial areas (Fig. 1a), especially around the cities of Liverpool, Manchester, Sheffield Leeds and Newcastle-upon-Tyne, but in these samples $\chi_{\text{FD \%}}$ per cent values are generally low (Fig. 1b), indicating the dominance of non-SP ferrimagnetic minerals.

If we assume that SP grains, as detected by frequency-dependence susceptibility, can be used quantitatively to represent the whole SFM component (cf. Hunt et al. 1995), two important results emerge. First, SFMs are produced in virtually all topsoils in England, and second, the total volume of ferrimagnetic minerals ($\chi_{\text{LF}}$) in strongly magnetic soils is largely composed of SFMs of which SP grains are the dominant size (cf. Mullins & Tite 1973; Maher 1986; Dearing et al. 1996).

**HYPOTHESIS TESTING**

The area of igneous rocks in England is small but where outcrops exist, for instance in the Lake District area of northwest England (Fig. 1c), some individual samples show high $\chi_{\text{LF}}$ values reflecting the presence of primary ferrimagnetic minerals. In the majority of areas in which high values of $\chi_{\text{LF}}$ coincide with low values of $\chi_{\text{FD \%}}$ per cent there is evidence for heavy-metal pollution derived from atmospheric emissions (McGrath & Loveland 1992). These samples most likely contain industrially derived fly-ash and related particles containing significant proportions of coarse multidomain (MD) or stable single-domain (SSD) grains of magnetic iron oxides (Hunt 1986). These two groups of samples represent only $\sim$ 12 per cent of the data set, showing that the overall pattern of magnetic variability cannot be explained by the presence of residual primary minerals (theory 1) from parent material, nor the widespread accumulation of pollution particles (theory 2).

Theories (3) and (4) require strongly anaerobic conditions. Ranking the mean $\chi_{\text{FD \%}}$ per cent of major soil types (Table 2) shows that high values ($>5$ per cent) are linked to relatively free-draining profiles with lower values in periodically waterlogged soils (glesys) and strongly podzolized humic-iron podzols. High concentrations of SP grains are not found in soils where strongly anaerobic processes dominate. Relatively free-draining soils may experience frequent periods of anaerobility but soil-water regimes (Robson & Thomasson 1977) for the top five soil types in Table 2 show that waterlogging to within at least 40 cm of the surface exists for $<5$ days per year, an insufficient time to support either significant populations of strictly anaerobic bacteria or to generate the reducing

| Table 1. Summary of magnetic susceptibility data. |
|---------------- |------ |------ |------ |------ |------ |
| $\chi_{\text{LF}}$ ($10^{-6} \text{ m}^3 \text{ kg}^{-1}$) | $\chi_{\text{FD \%}}$ ($10^{-6} \text{ m}^3 \text{ kg}^{-1}$) | $\chi_{\text{FD \%}}$ ($10^{-6} \text{ m}^3 \text{ kg}^{-1}$) | $\chi_{\text{FD \%}}$ ($10^{-6} \text{ m}^3 \text{ kg}^{-1}$) | $\chi_{\text{FD \%}}$ ($10^{-6} \text{ m}^3 \text{ kg}^{-1}$) |
| 1176 | 17.94 | 0.73 | 1.40 |
| 1176 | 1805.6 | 45.2 | 135.1 |
| 1146 | 13.59 | 4.13 | 2.48 |

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conditions for iron sulphide formation (Fischer 1988). Early observations of susceptibility changes over time (Le Borgne 1955) also showed that $\chi_{LF}$ increased as the soil dried, not while it remained anaerobic. High concentrations of SFMs are therefore not linked to the production of magnetic grains in strongly anaerobic environments.

Periodically anaerobic topsoils meet the conditions for microaerophilic magnetotactic bacteria (theory 5). However, genetic screening on fresh samples gives positive identification of small *Magneto spirillum* spp. populations ($<10^3$ cells per gDW) in only $\sim 25$ per cent of strongly magnetic topsoils (calibrated against known densities), and populations are actually higher in the less well-drained subsoil of the most magnetic soil (cf. Fassbinder & Stanjek 1993). Magnetic cocci have not been detected in any sample. Our calculations show that these population densities in topsoils would not provide sufficient magnetosomes to account for the total ferrimagnetic content of these samples, even when accumulated over 10 kyr. Moreover, the SFM component of these soils is dominated by SP grains and magnetotactic bacteria generally produce coarser SSD grains (Fassbinder et al. 1990). While slow dissolution of SSD grains to SP-sized grains could theoretically explain high $\chi_{FD}$ per cent values, maintenance of these values would mean that the soil was not replenished with SSD grains; the bacteria would have to cease functioning and there is no obvious reason for this.

If crop burning controlled the magnetic patterns (theory 6), we would expect to find the highest values for soils under arable cultivation. However, the highest values of the three parameters occur on ley grassland (Table 3), not on arable land. Field-scale studies also suggest that burning is not a major control on soil susceptibility. Our measurements of topsoils from adjacent burned and control plots in a strawburning experiment at Rothamsted Experimental Station show no significant differences after eight years of annual burning. Also, maps of susceptibility used in archaeological prospecting (10 m x 10 m grids) show that background soil susceptibility values in arable fields that have experienced centuries of crop burning are still far lower than 'hot spots' within the same field associated with sites of historic habitation (A. Johnson, personal communication). Overall, the evidence suggests that burning associated with farming is not normally sufficiently intense to alter soil magnetism.

The main pedogenic ferrimagnetic mineral in free-draining temperate soils is usually quoted as maghemite (Le Borgne 1955; Mullins 1977; Singer & Fine 1989; Singer et al. 1995). Maghemite arises from the slow oxidation of magnetite or by burning (Schwertmann 1988). Since burning is rejected as the major mechanism, we argue that magnetite or a non-stoichiometric form of magnetite is the initial ferrimagnetic mineral (cf. Longworth et al. 1979). This does not exclude the possibility or even likelihood that maghemite is the main ferrimagnetic mineral in most soils, because results of laboratory experiments show that magnetite readily oxidizes to maghemite over years and decades (B. Maher, personal communication; Murad & Schwertmann 1993); it is logical to assume that the oxidation of magnetite to maghemite also takes place in the soil environment.

In evaluating the two remaining theories (7 and 8), we use evidence that tests the theoretical formation of magnetite from ferrihydrite ($5\text{FeO}_{\cdot}2\cdot9\text{H}_2\text{O}$). There are three steps in the process (Schwertmann 1988): (1) formation of ferrihydrite, which, because of its high solubility product, is controlled by the oxidation of critical concentrations of Fe(II) supplied through weathering (hydrolysis) of Fe-bearing minerals; (2) liberation of Fe(II) ions (where $\text{pH}>3$) through Fe-reducing bacteria utilizing iron oxides/hydroxides as a terminal electron acceptor; (3) partial dehydration and oxidation of ferrihydrite to magnetite in the presence of excess Fe(II).

The positive correlations between total Fe and $\chi_{LF}$ and $\chi_{FD}$ values are weak (Table 4) but are the strongest of any correlations between magnetic susceptibility parameters and geochemical variables (Hay, unpublished data) and are highly significant ($p=0.0001$). Measurements of $\chi_{LF}$ (Fig. 2a) and $\chi_{FD}$ both reach optimum values where total Fe lies in the range 3–5 per cent, but values of $\chi_{LF}$ per cent (Fig. 2b) show a near-random scatter with total Fe. These relationships indicate that while SFMs may be present over a wide range of Fe values, the magnitude of their concentration is strongly associated with elevated levels of Fe. Indeed, the highest $\chi_{LF}$ values
Table 4. Coefficients of correlation between mass-specific magnetic parameters ($\chi_{Fe}$ and $\chi_{TD}$) and geochemical (total Fe, pH and C$_{org}$) data (normal and log$_{10}$); total Fe measured on aqua regia digests; C$_{org}$ estimated from loss-on-ignition data in organic-rich soils (and by dichromate digestion in others); underlined coefficients are significant at $p = 0.0001$.

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>pH</th>
<th>C$_{org}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\chi_{Fe}(10^{-6}m^3kg^{-1})$</td>
<td>0.32</td>
<td>0.01</td>
<td>-0.01</td>
</tr>
<tr>
<td>$\chi_{TD}(10^{-9}m^3kg^{-1})$</td>
<td>0.27</td>
<td>-0.00</td>
<td>-0.03</td>
</tr>
<tr>
<td>log$_{10}$Fe</td>
<td>pH</td>
<td>log$<em>{10}$C$</em>{org}$</td>
<td></td>
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<tr>
<td>0.46</td>
<td>0.16</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td>log$_{10}$TD</td>
<td>0.23</td>
<td>0.14</td>
<td>-0.15</td>
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for any given value of total Fe in Fig. 2(a) may define the maximum concentration of SFMs that can be attained under favourable conditions within a temperate climate. Previous deductions (Le Borgne 1955; Mullins 1977) and observations (Neumeister & Peschel 1968) that organic carbon is a major control on the production of SFMs are not confirmed (Table 4) at the regional scale. Taken together, these results provide strong evidence that Fe supply, and therefore the production of ferrhydrite, is the major limiting factor on the concentration of SP grains.

Ferrhydrite is also the most easily reduced iron oxide (Fischer 1988), occurring at relatively high Eh values under short-lived periods of anaerobicity, as in wet but free-draining soils containing micropores. The level of available water is a good estimate for the total volume of micropores (0.2–1.5 μm) and is on average highest (> 20 per cent) in English soils with silt-loam, silty clay-loam, clay-loam, sandy silt-loam and silty clay textures (Hall et al. 1977). English soils with high $\chi_{TD}$ per cent and high $\chi_{Fe}$ values generally fall into these particle-size classes and possess well-developed soil structure, indicating long-term micropore stability. Clays, sandy loam, loamy sand and sand textures have lower volumes (11–20 per cent) of micropores and lower values of $\chi_{TD}$ per cent and $\chi_{Fe}$. Le Borgne (1955) observed that susceptibility increases as soil dries out, presumably by autocatalysis where pH > 5. In the English data set the statistical correlations (Table 4) between susceptibility data and pH are either random or weakly significant, many acid soils with pH < 5 show high values of $\chi_{TD}$ per cent, so the role of microbial oxidation in magnetite formation is unclear. However, there is sufficient evidence to propose a dominant and widespread mechanism of SFM production, which combines theories (7) and (8) to give a sequence (Fig. 3) of weathering and ferrhydrite production, bacterially mediated Fe reduction, reaction of ferrhydrite with Fe(H) to form magnetite, and the partial or slow oxidation of magnetite to maghemite.

**DISCUSSION**

In many soil environments, SFMs are metastable and will eventually weather to provide the Fe supply for new SFMs. Thus Fig. 3 represents the means by which a soil may attain the highest net concentrations of SFMs, a balance between mineral production and destruction. We hypothesize that the fundamental driving force at the regional scale (10$^1$–10$^2$ km) is the Fe supply from weathering within the soil, which is the product of the Fe content of the parent material and the rate or duration of weathering. Relatively low levels of total Fe in many sedimentary rocks, such as chalk (Applied Geochemistry Research Group 1978), are compensated for by rapid weathering rates of up to 0.12 mm yr$^{-1}$ (Atkinson 1957) over long periods (> 10$^4$ years) timescales, which has led to consistently high rates of Fe supply (cf. Moukarika, O'Brien & Coey 1991). The most magnetic soils in England are derived from Devonian slates; these are easily weathered, have high levels of Fe and lie south of the Anglian glacial limit (428 kyr BP).

Variations in soil susceptibility at the local scale (< 10$^{-1}$–10$^1$ km) are less likely to be controlled by the Fe supply and more likely to be controlled by other factors and processes, such as soil drainage and intense leaching, which affect the later stages of SFM formation (Fig. 3). For instance, long periods of anaerobicity and more severe reducing conditions in imperfectly drained soils, such as gleys (Table 2), presumably lead to the reduction of ferrihydrate outstripping production, and a decline in the equilibrium concentration of SFMs. In highly porous and acid sandy soils, low volumes of micropores and low levels of organic matter are likely to give rise to limited Fe reduction and small microbial populations. In podzolized soils, all fine-grained iron oxides are vulnerable to Fe(III) chelation, although high $\chi_{TD}$ per cent values in brown podzolic soils (Table 2) point to mild chelation being a positive factor in the initial Fe supply.

Present climatic differences across England are too small to cause significant differences in weathering rates on the same geology. Across steeper climatic gradients or through periods of major climatic change, however, the magnetic properties of soils, in the absence of strong destructive processes, may be expected to be related to climatic controls on weathering and the supply of Fe to the soil. The extent to which climate will affect other stages in the mechanism is uncertain. For instance, Tite & Linington (1975) argued that limestone soils in Italy are more magnetic than those in England because the fermentation mechanism is more extensively activated in the Mediterranean climate. While this may be correct, an effective fermentation mechanism still requires a strong Fe supply, otherwise the concentration of SFMs will remain low.

In many soil environments the dominant processes of weathering are hydrolysis and solution, which are both driven by the level of effective precipitation. Where the concentration of mineral Fe is relatively uniform, as it is in many loess sequences, the Fe supply and the subsequent accumulation of SFMs in palaeosols are likely to be directly attributable to the effective palaeoprecipitation and the timescale of soil formation. Thus the proposed mechanism of SFM formation is fully compatible with claims that magnetic susceptibility profiles of loess–palaeosol sequences in China (eg. Maher et al. 1994; Liu et al. 1995; Thompson & Maher 1995) and Tunisia (Dearing et al. 1996) are semi-quantitatively linked to palaeoprecipitation. However, the accuracy of palaeoprecipitation proxy data will remain uncertain until the conflicting lines of evidence for the timescales over which ‘steady-state’ levels of SFMs are attained (Singer et al. 1992; Maher & Thompson 1995) are reconciled.
CONCLUSIONS

(1) At a regional scale, variations in soil magnetic susceptibility are linked to geology and soil processes, rather than land-use, burning or pollution, which appear to be local factors. Magnetotactic bacteria are not present in sufficient concentrations to account for the variations. The most strongly magnetic soils are found in moderately well-drained soils developed over easily weathered sedimentary rocks and are rich in SP ferrimagnetic minerals.

(2) Fe supply appears to be the major process controlling the magnitude of SFM concentrations. A new mechanism for the formation of SFMs is proposed which identifies the formation of ferrihydrite in the presence of a strong Fe supply as a major initial component. Bacterial Fe reduction causes ferrihydrite to transform to magnetite, which may oxidize over time to maghemite.

(3) Climatic control on weathering is the major factor controlling Fe supply and regional (possibly global) variations in soil magnetism on similar geologies. This provides a
Figure 1. Magnetic susceptibility of English topsoils, geology and major cities. (a) Low-frequency mass-specific magnetic susceptibility values ($x_{LF}$) for English topsoils; (b) percentage frequency-dependent susceptibility ($x_{FD}$ per cent) values for English topsoils; (c) major cities, geology, and glacial limits (Ballantyne & Harris 1994) for Devensian (dashed line) and Anglian (solid line) glaciations.
theoretical basis on which to explain the observed links between palaeosol magnetism in loess sequences and levels of palaeoprecipitation.

ACKNOWLEDGMENTS

The research has been supported by a Coventry University studentship to KLH, sponsorship by Bartington Instruments Ltd and NERC grant GR9/02003. We thank Professor Catt for permission to work on experimental sites at IACR-Rothamsted, Anthony Johnson (Oxford Archaeotechnics) for access to unpublished field surveys, and Dr Barbara Maher (UEA, Norwich) for useful discussions.

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