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Secondary ferrimagnetic minerals in Welsh soils: a comparison of mineral magnetic detection methods and implications for mineral formation

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SUMMARY

A range of low-temperature and isothermal magnetic measurements are used to identify the secondary ferrimagnetic mineral (SFM) grain sizes in 10 representative soil samples from Wales. A comparison of percentage frequency-dependent susceptibility (χ_{FD} percentage) and low-temperature remanence measurements shows that they are sensitive to different ranges of superparamagnetic (SP) grains. The relative distributions of SP grains and stable single domain (SSD) grains are similar in nine of the samples. Typical distributions for soils dominated by SFMs are $\approx$20–30 per cent SSD and 70–80 per cent SP. Multidomain (MD) grains were not detected in the samples studied. There is evidence that some soils contain significant numbers of ultrafine SP grains <0.010 μm that are not detected by low-temperature remanence measurements at 20 K and which will have the effect of depressing values of low-field susceptibility (χ_{LF}) and χ_{FD} percentage. A mixing model suggests that χ_{FD} percentage may be used semi-quantitatively to estimate the proportion of SP grains in a sample. The positively skewed grain-size distributions strongly suggest a mechanism of SFM formation that is driven by processes at the $<10^{-8}$ m scale, thus supporting weathering and fermentation as controlling processes, rather than the degradation of SSD bacterial magnetosomes and primary minerals.

Key words: frequency-dependent susceptibility, low-temperature remanence, soil magnetism.

INTRODUCTION

The rise in the use of magnetic techniques to characterize iron oxide minerals in soils and palaeosols has highlighted the importance of SFMs, which are often identified as SP grains of magnetite or maghemite. These grains, normally defined as <0.030 μm in diameter (Dunlop 1973), occur in many soil environments and may reach concentrations that effectively mask the properties of other mineral grains in bulk measurements. The importance of SFMs is highlighted in many papers that show the mineral magnetic properties of palaeosols existing in loess sequences as a function of pedogenesis and palaeoclimate (e.g. Zhou *et al.* 1990; Maher & Thompson 1992; Banerjee, Hunt & Liu 1993; Hunt *et al.* 1995; Liu *et al.* 1995; Maher, Thompson & Zhou 1995; Dearing, Livingstone & Zhou 1996; Han *et al.* 1996). The formation and mineralogy of SFMs are still debated, with attention focused on first the importance of two major formation mechanisms, weathering/fermentation processes (Le Borgne 1955; Mullins 1977; Thompson & Oldfield 1986; Maher & Taylor 1988; Taylor, Maher & Self 1987; Eyre & Shaw 1994) and magnetotactic bacteria (Fassbinder, Stanjek & Vali 1990), and second the evidence for maghemite (Taylor & Schwertmann 1974a; Stanjek 1987; Moukarika, O'Brien & Coey 1991; Singer *et al.* 1995; Verosub *et al.* 1993), rather than magnetite (Maher & Taylor 1988), as the dominant pedogenic mineral. Recently, Dearing *et al.* (1996b) proposed that the formation of SFMs in temperate soils may follow the following sequence: weathering and ferrihydrite formation; bacterially mediated Fe reduction; reaction of ferrihydrite with Fe(II) to form magnetite; and the partial or slow oxidation of magnetite to maghemite. This provides a mechanism to explain the observed link between soil magnetism and climate in many loess sequences. They based their conclusions on a large survey of χ_{LF} and χ_{FD} percentage measurements of English topsoils. Frequency-dependent susceptibility is a highly effective and rapid measurement for detecting SP grains within the size range 0–0.035 μm and particularly the narrower range 0.01–0.025 μm (Maher

1988), where grains show a theoretical maximum χ_{FD} per cent value of 14–17 per cent (Dearing *et al.* 1996a). An alternative method for detecting the range of SP grains is low-temperature remanence (20–300 K), which detects the proportion of all grains that block at successively higher temperatures (Banerjee *et al.* 1993), and has the advantage over using χ_{FD} percentage of providing data that may be expressed as grain-size distributions. A clearer idea is needed of which magnetic parameters are the most useful for detecting SP grains and to what extent they offer quantitative measures of SP grain concentrations. This paper compares the χ_{FD} percentage and low-temperature methods of detecting SFMs in 10 representative soils from Wales, and also makes comparison with other isothermal magnetic measurements. Data on SFM grain-size distributions are used to test the alternative theories of SFM formation.

METHODS

Over 600 samples of topsoil (0–20 cm) from Wales have been taken from the Soil Survey and Land Research Centre's National Soil Inventory (McGrath & Loveland 1992) for measurements of magnetic susceptibility (Dearing *et al.* 1996a). Samples were air-dried, passed through a 2 mm sieve and ground in a ceramic ball-mill to provide homogeneous subsamples for measurements. For this study, 10 representative samples (W-series) were chosen from sites overlying sedimentary geologies and distant from pollution centres in order to reduce the probability of MD grains contributing to remanence. In addition, the samples were chosen across the whole range of χ_{FD} percentage values ($\approx$0–12 per cent), which are assumed to represent the variability in SP grain concentration in Welsh soils.

Low-field AC susceptibility was measured on 10 cm^3 samples using a dual-frequency (470 Hz and 4700 Hz) Bartington Instruments MS2 sensor on the 0.1 scale. The difference between low- and high-frequency susceptibility (χ_{LF}–χ_{HF}) is expressed as a mass-specific term (χ_{FD} 10^{-9} m^3 kg^{-1}) and as a percentage of the low-frequency susceptibility (χ_{FD} percentage). Acquisition of isothermal remanent magnetization and saturation magnetization at 1 T were measured on $\approx$0.3 g samples using a Molspin vibrating sample magnetometer. Low-temperature thermal demagnetization was measured on $\approx$0.2 g samples using a Quantum Design MPMS machine. Samples were cooled in zero field to 20 K, subjected to a field of 2.5 T and then heated in zero field to room temperature (300 K) with remanence measured in 5 K steps. Anhysteretic remanence was induced in a steady field of 40 μT with a parallel peak AF of 92 mT using a Molspin AC demagnetizer and measured on a Molspin spinner magnetometer. Measurements are expressed as susceptibility of ARM (χ_{ARM} 10^{-6} m^3 kg^{-1}) by dividing the remanence by the steady field.

FREQUENCY-DEPENDENT SUSCEPTIBILITY AND LOW-TEMPERATURE REMANENCE

Thermal remanence demagnetization curves (Fig. 1) for the W-series show no Verwey transition near 118 K (confirmed in plots of negative slope against temperature), indicating the absence of a significant pure magnetite component larger than SSD. The total SP component is estimated from the difference between remanences at 20 K and 300 K, expressed on a mass-specific basis ($SP_{20\text{–}300\,K}$ 10^{-3} A m^2 kg^{-1}), and as a percentage of the total remanence (Banerjee *et al.* 1993) by dividing the difference by the remanence at 20 K (SP/total percentage). SP/total percentage varies from 68 to 80 per cent in nine of the samples, suggesting that the ferrimagnetic grain content of the samples is predominantly SP size. It appears that sample W24 with a SP/total percentage of 46 per cent and an absence of MD grains contains a large SSD component. The relationship between SP/total percentage and χ_{FD} percentage (Fig. 2a) is non-linear and shows zero χ_{FD} percentage equivalent to a SP/total percentage value of 43 per cent. This suggests that the two parameters are sensitive to different grain-size ranges within the SP range. In contrast, the relationship between $SP_{20\text{–}300\,K}$ and χ_{FD} (Fig. 2b) is positive and linear, indicating that either parameter is a reasonable estimate of SP concentration. With the exception of sample W24, similar strong and positive relationships also exist between $SP_{20\text{–}300\,K}$ and other magnetic concentration parameters, for example χ_{LF}, χ_{ARM}, $SP_{300\,K}$ (or SIRM) and M_s (Fig. 3). This suggests that where soils have reasonably constant proportions of grains in the SP and SSD size ranges, any magnetic concentration parameter may be used to estimate the concentration of 'fine ferrimagnetic' grains.

DETERMINATION OF GRAIN SIZE

Analysis of the significance of different grain-size distributions requires the calculation of the critical grain diameters at each blocking temperature. The relaxation time (τ) formula is given by:

$$\tau^{-1}=f_0 \exp[-(KV_p/kT)],$$

where f_0 is the frequency factor, k the Boltzmann's energy constant, T the absolute temperature, K the anisotropy constant and V_p the grain volume. Assuming f_0 is 10^9 s^{-1} and a relaxation time of 10^2 s, the blocking temperature (T_B) for uniaxial grains of constant size is given by

$$T_B=KVp/25k,$$

which can be rewritten in terms of the critical grain diameter for spherical grains (D_p) at any blocking temperature, where $V_p=(\pi D_p{}^3)/6$:

$$D_p=[25kT_B/0.524K]^{1/3}; \qquad (1)$$

however, there are several uncertainties in the constants used to produce this equation (Dearing *et al.* 1996a). The frequency factor may vary between 10^9 and 10^{12} depending on the iron oxides present, and the anisotropy constant varies according to the type and shape of grains. If we assume that the samples have similar mixtures of iron oxides and grain shapes, an alternative approach is to rewrite eq. (1) as $D_p=C_T(T_B)^{1/3}$, where C_T is a constant expressing τ, f_0, k and K, and to find C_T for an assumed critical diameter of SP grains ($D_{p293\,K}$) at room temperature (293 K). The rewritten equation can then be used to estimate D_p for any value of T_B. Table 1 shows the values of C_T and D_p for a range of values of T_B for three assumed values of $D_{p293\,K}$.

GRAIN-SIZE AND FREQUENCY-DEPENDENT SUSCEPTIBILITY

The proportion of grains in a sample lying between two critical diameters (Table 1) is calculated as the difference between

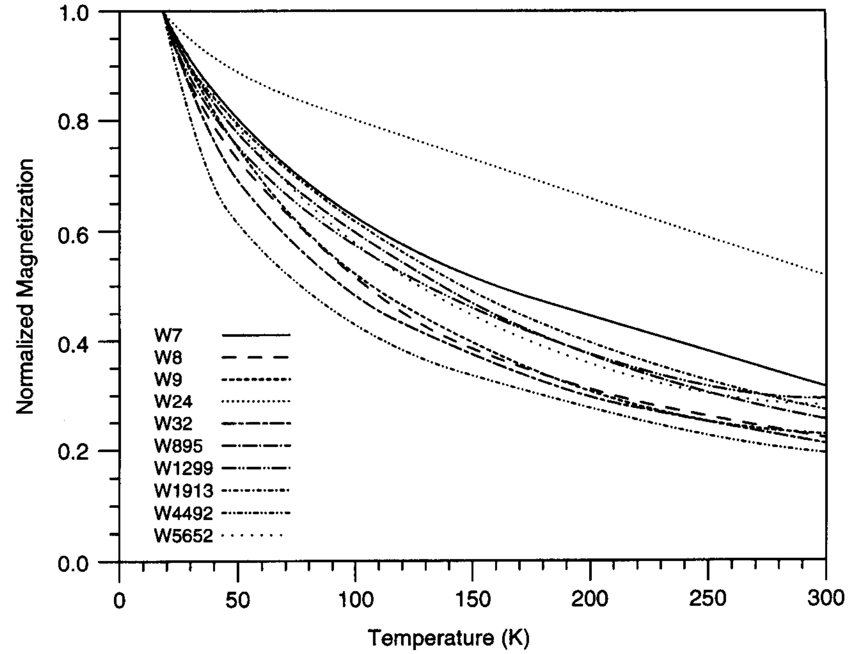


Figure 1. Low-temperature remanence curves (20–300 K) for the W-series normalized to the maximum remanence at 20 K, showing no Verwey transition at ≈118 K.

remanences at the two equivalent blocking temperatures normalized by the maximum remanence at 20 K. However, there are three problems with this approach in calculating grain-size distributions. First, if it is assumed that SP grains block as fine SSD grains on the SP/SSD boundary (≈0.030–0.040 μm), not as coarser SSD (0.040–0.050 μm) or pseudo-single domain (PSD) grains (0.050–8.000 μm) (Dunlop 1973; Hunt *et al.* 1995), then normalization will only give accurate estimates of grain-size distribution where the room-temperature SSD grains are also fine. SIRM values vary from ≈5 to 12.5 $\mathrm{Am^2\,kg^{-1}}$ across the SSD and PSD grain-size ranges (Maher 1988) and normalization of low-temperature remanences will give non-comparable distributions of grains >0.030 μm, except where this fraction contains only fine SSD grains. Second, low-temperature remanences 20–300 K exclude grains smaller than 0.011–0.014 μm (Table 1). Therefore, grain-size distributions will be relative to each other but not absolute. Third, calculated grain sizes depend on the assumed value for $D_{\mathrm{p293\,K}}$, which in the absence of information about mineral type will show errors of ±0.005 μm at 300 K reducing to ±0.002 μm at 20 K (Table 1).

Cumulative frequency curves of grain-size distribution (assuming $D_{\mathrm{p293\,K}} = 0.030$ μm and maximum grain size = 0.040 μm) for the 10 samples (Fig. 4) show that with the exception of W24 the grain-size distributions are similar. In general, the curves are non-linear, with all but sample W24 indicating distributions positively skewed towards fine SP sizes, with ≈30–49 per cent of grains ≈0.012–0.019 μm. Sample W24 shows a distribution skewed towards the coarser grains, with only 16 per cent of grains <0.019 μm.

The effect of small differences in grain-size distribution on χ_{FD} percentage is analysed by plotting bulk χ_{FD} per cent values against losses of remanence between specific temperatures normalized to the maximum $\mathrm{SP_{20\,K}}$. Three sets of remanence loss, $\mathrm{SP_{20\text{–}25\,K}}$, $\mathrm{SP_{35\text{–}70\,K}}$ and $\mathrm{SP_{150\text{–}300\,K}}$, provide estimates of the proportions of grains in the size ranges 0.011–0.015 μm ('fine SP'), 0.012–0.022 μm ('medium SP') and 0.021–0.035 μm ('coarse SP'), respectively (Table 1). $\mathrm{SP_{300\,K}}$ normalized to $\mathrm{SP_{20\,K}}$ is used to estimate the proportion of SSD grains >0.030 μm.

Relationships between χ_{FD} per cent and grain size are indeterminate for 'fine SP' (Fig. 5a), weakly positive for 'medium SP' (Fig. 5b) and weakly negative for 'coarse SP' (Fig. 5c) and SSD (Fig. 5d), suggesting that χ_{FD} percentage is related to the presence of 'medium SP' grains with diameters in the range 0.012–0.022 μm, depending on the assumptions used to produce values of D_{p} (Table 1). These results are consistent with the conclusions of Maher (1988) and Dearing *et al.* (1996a) that χ_{FD} percentage reaches maximum values in the grain-size range 0.013–0.027 μm, and shows lower values in SP grains <0.010 μm and >0.025 μm.

Relationships between bulk mass-specific concentration parameters, such as χ_{LF} or M_{s}, and grain-size contribution are also linear and positive irrespective of grain size or parameter (not shown). As described above, the differences in ferrimagnetic concentrations between samples are significantly larger than the particle-size distributions, and relative proportions of different magnetic grain sizes, for instance SSD and fine SP, are roughly constant in most samples. Consequently, measurements such as χ_{ARM} that peak in the SSD range covary with χ_{FD} percentage, which peaks in the SP range.

GRAIN-SIZE DISTRIBUTIONS OF SECONDARY FERRIMAGNETIC MINERALS

In theory, the cumulative frequency curves (Fig. 4) can be expressed as grain-size distributions. However, as noted above, the calculation of grain-size distributions has to take account of the distribution of both grains within the SSD range and grains <0.010 μm that are not blocked at 20 K. Production of accurate grain-size distributions from low-temperature

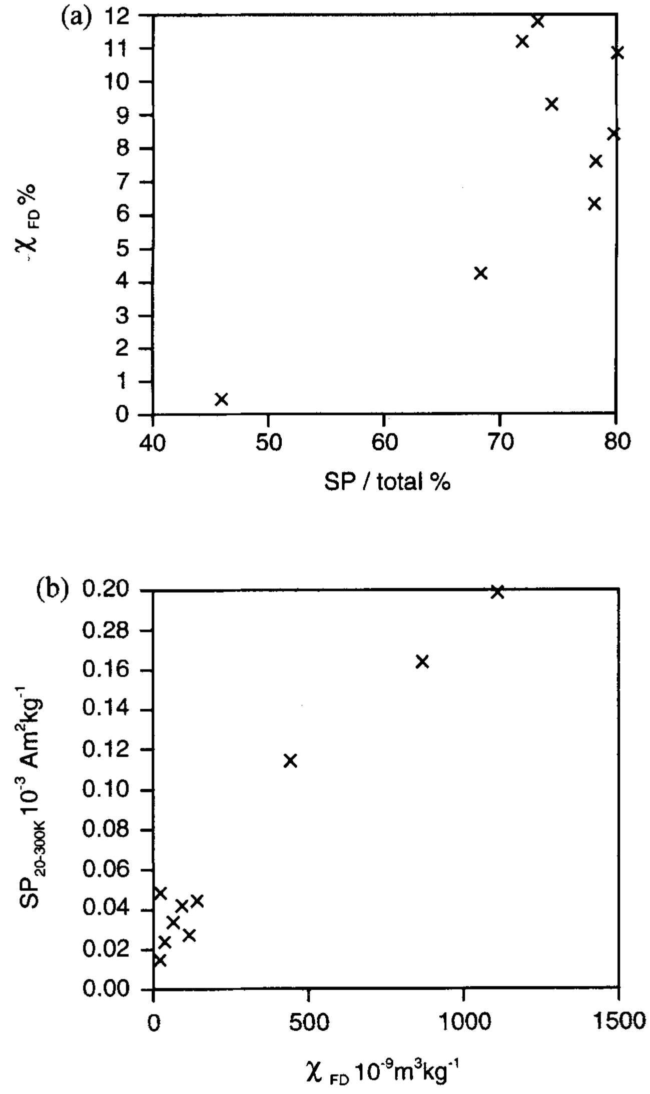


Figure 2. Frequency-dependent susceptibility versus low-temperature remanence estimates of superparamagnetic content. (a) Normalized parameters χ_{FD} percentage and SP/total percentage; (b) mass-specific concentration parameters χ_{FD} (10^{-9} m^3 kg^{-1}) and SP$_{20\text{–}300\ \mathrm{K}}$ (10^{-3} Am^2 kg^{-1}).

remanence is only possible in samples where the SSD grain distribution is constant and fine grained ($\approx$0.030–0.040 µm). Samples with coarse SSD grains (>0.040 µm) will show relatively lower SP$_{300\ \mathrm{K}}$ values and consequently proportions of SSD grains will be underestimated and proportions of SP grains overestimated. Normalizing SIRM with respect to χ_{ARM}, which peaks in the fine SSD grains, may help to distinguish between fine SSD and coarse SSD. Maher's (1988) data for synthetics showed the χ_{ARM}/SIRM ratio varies by a factor of 9–10 in the SSD range. The χ_{ARM}/SIRM ratio for the W-series also varies by a factor of 9, indicating a wide range of grain-size distributions within the SSD range Therefore, grain-size distributions are calculated for only two samples (W9 and W5652), which have similar and high χ_{ARM}/SIRM ratios (Table 2) indicating predominantly fine grains ($\approx$0.030–0.040 µm) in the SSD range.

Both distributions are skewed towards fine SP grain sizes and are generally similar in shape (Fig. 6). The proportion of grains <0.012 µm can be estimated from the difference between M_s values (the whole ferrimagnetic component) and the 20 K remanence (ferrimagnetic grains >0.012 µm). Maher's (1988) maximum SIRM value for SSD magnetite grains is 12.5 Am^2 kg^{-1}, with an average of $\approx$6 Am^2 kg^{-1} for an equal mixture of fine SSD grains (0.030–0.040 µm), and these values are similar in the same samples oxidized to maghemite (Lees 1994). M_s values for ferrimagnetic minerals are 92 Am^2 kg^{-1} and 60 Am^2 kg^{-1} for pure magnetite and maghemite, respectively, but while M_s values for magnetite are generally accepted to be constant across all grain sizes, recent work (Han, Wang & Luo 1994) indicates progressively lower values for maghemite in grain sizes 0.040 µm and smaller. Extrapolation of their data to cover the complete SP grain-size range of maghemite suggests a value of $\approx$45 Am^2 kg^{-1} for equal proportions of fine-grained (<0.030 µm) maghemite. Solving for the fraction of magnetite and maghemite in each sample using these two alternative SIRM values and three alternative M_s values shows that for W5652 all the ferrimagnetic component is accounted for by the 20 K remanence; there are insignificant numbers of grains <0.012 µm. In contrast, calculations for W9 show that SIRM-based estimations of ferrimagnetic minerals <0.012 µm are generally lower than those based on M_s but vary greatly between 0 and 72 per cent depending on the values used for M_s and SIRM. Taking values of $M_s = 60$ Am^2 kg^{-1} and SIRM $= 6 \times 10^{-3}$ Am^2 kg^{-1}, which approximate a mixture of magnetite and maghemite, gives a best estimate of 24 per cent of grains <0.012 µm. On this basis, the greatest difference in ferrimagnetic grain-size distribution (Fig. 6) between the two samples is the proportion of ultrafine grains (<0.012 µm), which is not recorded by low-temperature remanence measurements, but which is apparently reflected in the lower χ_{FD} per cent value of W9 (χ_{FD} per cent = 8.6) compared to W5652 (χ_{FD} per cent = 12.0).

A test of this finding is to recalculate the χ_{FD} per cent values in these samples for the frequency-dependent SP fraction only. From the calculations above, the combined estimated proportions of frequency-independent SSD and frequency-independent SP grains <0.012 µm in W9 and W5652 are 48 per cent (24 per cent SSD + 24 per cent *SP* < 0.012 µm) and 28 per cent (28 per cent SSD + 0 per cent *SP* < 0.012 µm), respectively. Recalculation of the bulk χ_{FD} percentage values taking the whole frequency-independent fraction into account gives values of $\chi_{\mathrm{FD}} = 16.5$ per cent (W9) and $\chi_{\mathrm{FD}} = 16.7$ per cent (W5652), which are not only comparable but also consistent with the theoretical maximum figure of 14–17 per cent (maghemite–magnetite) for spherical frequency-dependent SP grains in the range 0.010–0.025 µm (Dearing *et al.* 1996a).

A SEMI-QUANTITATIVE MODEL FOR IDENTIFYING GRAIN-SIZES

A simple mixing experiment shows how χ_{FD} per cent may be interpreted semi-quantitatively. 12 samples of homogenized SP-rich English chalk (rendzina) soil (χ_{FD} per cent = 10.5) were mixed with known proportions (0.14 per cent–12.1 per cent by mass) of synthetic MD magnetite (χ_{FD} per cent = 0.35). While values of mass-specific χ_{FD} remain roughly constant in all samples ($0.24\text{–}0.37 \times 10^{-9}$ m^3 kg^{-1}), showing that this parameter is a good estimator of the SP concentration in mixed-domain assemblages, the new measurements of χ_{FD} per cent values range between 0.56 and 10.5; the effect of adding

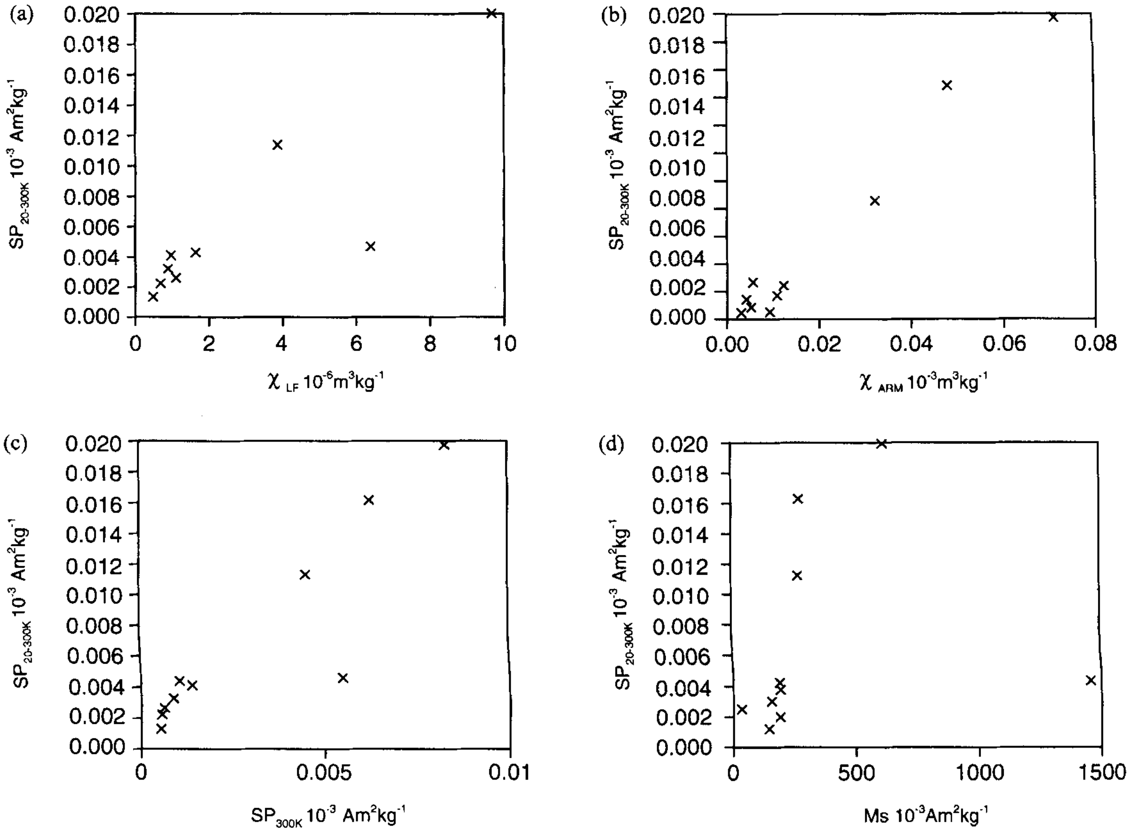


Figure 3. $SP_{20\text{-}300\ K}$ (10^{-3} Am^2 kg^{-1}) versus other mass-specific concentration parameters. (a) χ_{LF} 10^{-6} m^3 kg^{-1}; (b) χ_{ARM} 10^{-6} m^3 kg^{-1}; (c) $SP_{300\ K}$ 10^{-3} Am^2 kg^{-1} equivalent to SIRM; (d) M_s 10^{-3} Am^2 kg^{-1}.

Table 1. Values of C_T at $T = 293$ K, where $D_{p293\ K}$ is 0.025, 0.030 and 0.035 µm, with corresponding calculated D_p values (µm), where T_B varies between 300 and 5 K.

		T_B (K)							
$D_{p293\ K}$	$C_T \times 10^3$	300	250	200	150	100	50	20	5
0.035	5.27	0.035	0.033	0.031	0.028	0.024	0.019	0.014	0.009
0.030	4.52	0.030	0.028	0.026	0.024	0.021	0.017	0.012	0.007
0.025	3.89	0.026	0.024	0.022	0.021	0.018	0.014	0.011	0.007

2 per cent MD magnetite by weight to the initial soil reduces the χ_{FD} per cent value from 10.5 to <2. Assuming that a χ_{FD} percentage value of 10.5 is equivalent to 70–80 per cent frequency-dependent grains (Fig. 5d), proportions of ferrimagnetic grains in the frequency-dependent SP range are then expressed as a percentage of the remeasured bulk M_s value where the initial SSD component lies between 20 and 30 per cent. Fig. 7a shows a curvilinear relationship between χ_{FD} per cent and the percentage of the M_s held by the frequency-dependent SP grains; samples with >50 per cent SP grains as a proportion of total M_s have a χ_{FD} per cent of ≈ 8. The plot may be used to give semi-quantitative estimates of the proportions of frequency-dependent SP grains in the total ferrimagnetic mineral assemblage (as defined by total M_s). In particular, values of χ_{FD} per cent equal to 2, 8 and 11 are equivalent to >10 per cent, >50 per cent and >75 per cent frequency-dependent SP grains. Calibration of these values in terms of magnetite or maghemite is only possible where the mineral assemblage is identified by other means and a suitable M_s for that mineral is chosen.

This semi-quantitative interpretation of χ_{FD} per cent can be linked with other grain-size indicators to increase the range of quantified grain sizes. Most previous attempts at magnetic granulometry studies have utilized χ_{ARM}. King *et al.* (1982) used χ_{ARM}/χ_{LF} ratios to identify fine-grained ferrimagnetics while Maher (1988) and Maher & Taylor (1988) advocated the use of the ratio χ_{ARM}/SIRM because it is particularly sensitive to SSD grain sizes, peaking in the fine SSD range, and it is unaffected by paramagnetic contributions. Oldfield (1994) used the ratios χ_{ARM}/χ_{LF} and χ_{ARM}/χ_{FD} to help distinguish between SSD bacterial magnetosomes and SSD detrital grains in samples of lake and marine sediments. Caution is required when interpreting normalized ratios as 'concentration-independent' parameters indicating mineralogy or domain size, because normalized parameters are only independent of concentration in single-mineral assemblages. In mixed-mineral assemblages, normalized parameters are sensitive to domain size, mineralogy and concentration (Hilton 1986). For the present W-series soil samples, values of χ_{ARM}/SIRM are more grain-size sensitive than other normalized parameters such as χ_{ARM}/M_s and χ_{ARM}/χ_{LF}. With the proviso that confirmation of constant sample mineralogy is required, Maher's (1988)

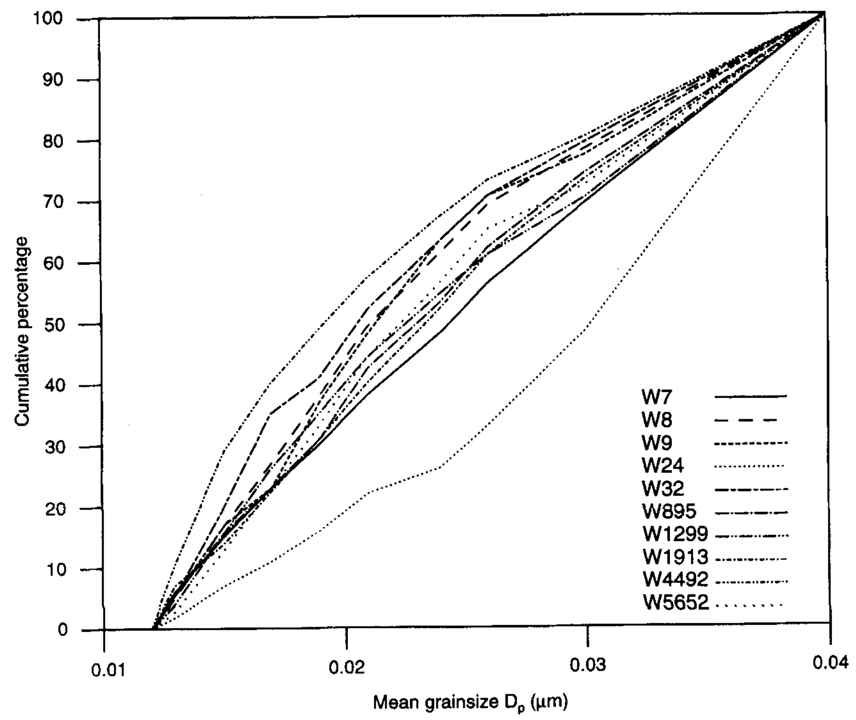


Figure 4. Cumulative frequency curves of grain-size distributions 0.012–0.040 μm calculated from low-temperature remanence curves (Fig. 1) assuming $D_{p293\,K} = 0.030$ μm (Table 1) and maximum grain-size = 0.040 μm.

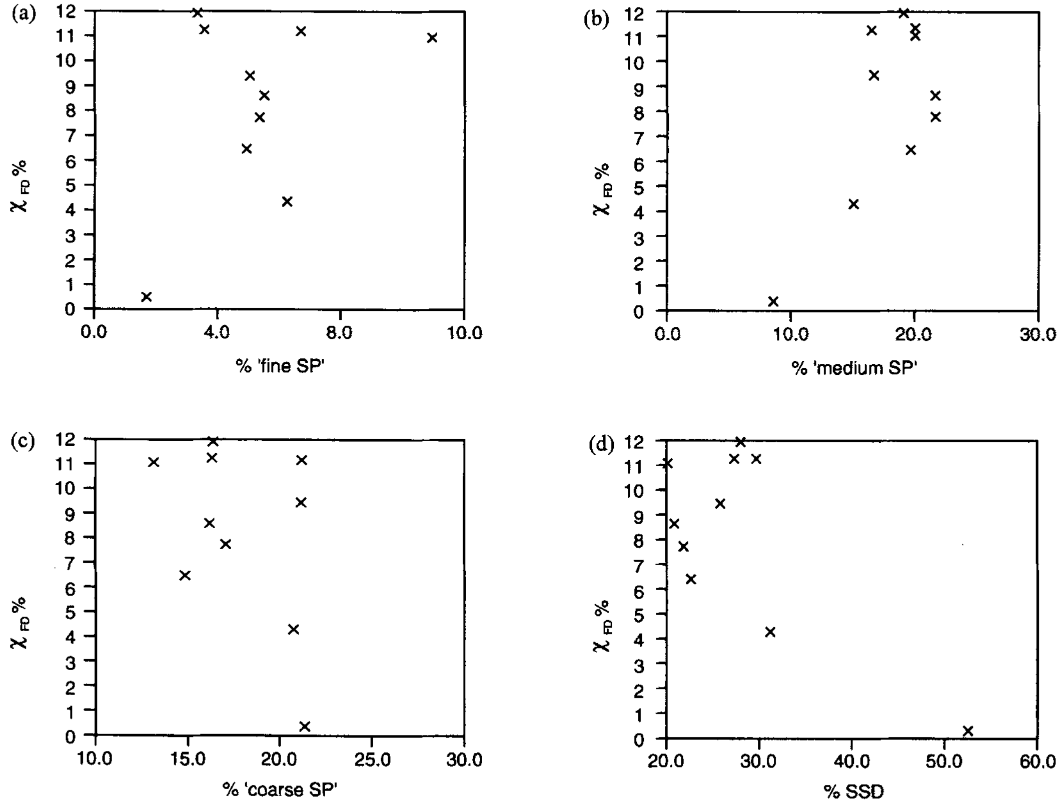


Figure 5. Relationships between bulk χ_{FD} percentage values and percentage grain size of bulk sample in the temperature ranges $SP_{20-25/20\,K}$, $SP_{35-70/20\,K}$, $SP_{150-300/20\,K}$ and $SP_{300/20\,K}$, equivalent to (a) 'fine SP' (≈0.011–0.015 μm); (b) 'medium SP' (≈0.012–0.022 μm); (c) 'coarse SP' (≈0.026–0.035 μm); (d) SSD (>0.026–0.035 μm).

Table 2. Low-temperature and isothermal magnetic measurements for the W-series.

	20 K Am^2 kg^{-1}	300 K Am^2 kg^{-1}	χ_{FD} %	χ_{FD} 10^{-9} m^3 kg^{-1}	χ_{ARM} 10^{-5} m^3 kg^{-1}	χ_{LF} 10^{-6} m^3 kg^{-1}	M_S 10^{-3} Am^2 kg^{-1}
W24	0.0448	0.0235	0.3	20.1	0.009	6.432	1447.7
W7	0.0080	0.0025	4.3	19.8	0.003	0.470	142.8
W9	0.0142	0.0032	6.5	42.6	0.005	0.664	188.2
W8	0.0206	0.0045	7.8	69.6	0.004	0.892	159.6
W32	0.0230	0.0048	8.6	139.0	0.006	1.625	184.3
W895	0.0240	0.0062	9.5	93.2	0.011	0.978	187.9
W1299	0.1420	0.0420	11.3	1093.9	0.072	9.725	608.4
W1913	0.0830	0.0225	11.2	434.5	0.032	3.880	269.0
W4492	0.0175	0.0035	11.1	119.6	0.012	1.082	32.3
W5652	0.1075	0.0300	12.0	850.9	0.048	7.087	269.5

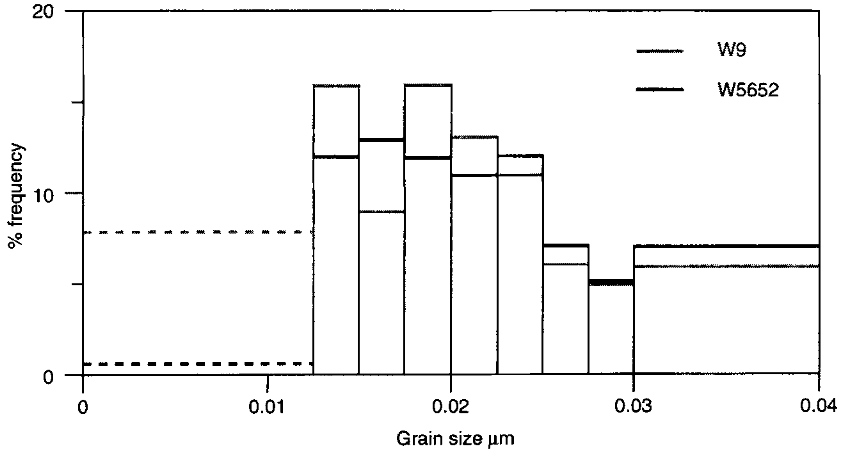


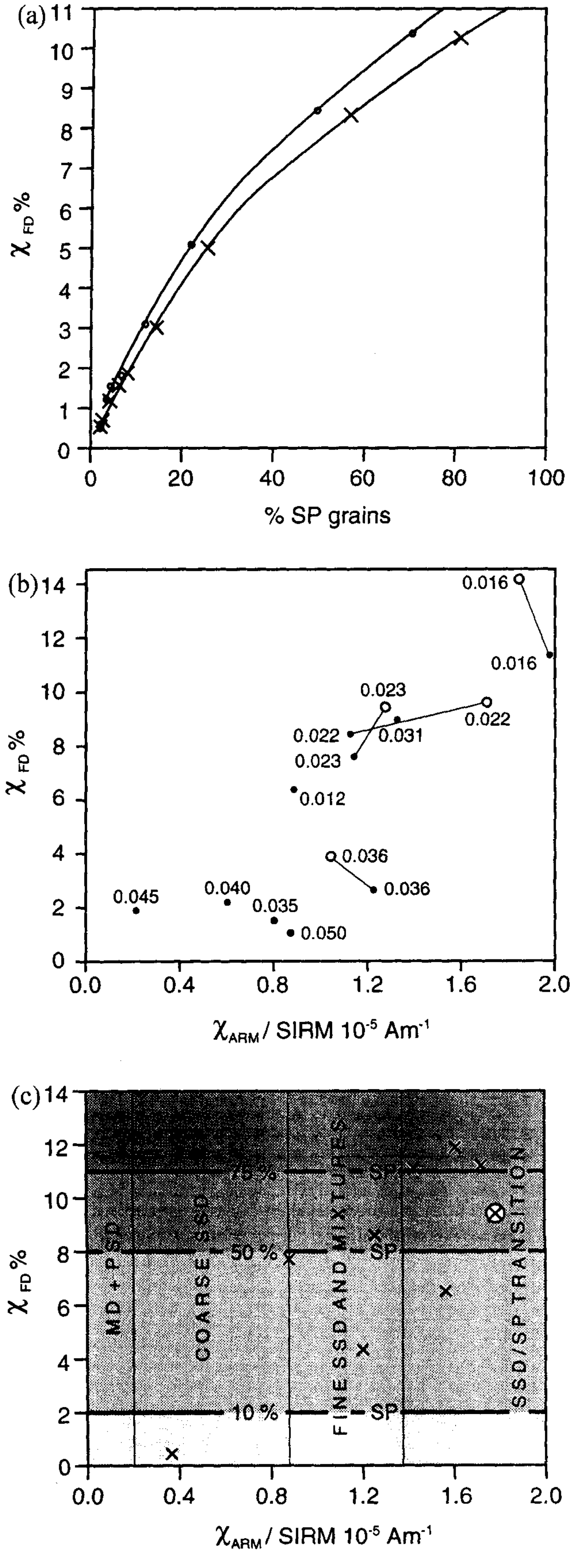
Figure 6. Grain-size distributions for samples W9 and W5652 at 0.0025 μm intervals, where grains >0.030 μm are equally distributed between 0.030 and 0.040 μm. The contributions from grains <0.012 μm (dotted lines), estimated from the differences between M_s and SIRM, are distributed equally between 0 and 0.012 μm and plotted relative to the other data, not to the y-axis scale.

suggestion of combining χ_{ARM}/SIRM with χ_{FD} percentage to identify the SP fraction is applied to the present data set (*cf.* Maher & Taylor 1988). These two *totally independent* normalized parameters increase the degrees of freedom in determining the positioning of assemblages on a bivariate scatter plot, which means that groupings of points give maximum discriminatory power (Hilton 1986).

Fig. 7(b) shows χ_{FD} per cent versus χ_{ARM}/SIRM for Maher's synthetic maghemite samples (Maher 1988; Lees 1994; Dearing *et al.* 1996a). In addition, four data points for original unoxidized magnetite samples are included (Maher 1988) to show the likely variability in mixed magnetite–maghemite systems. There is a broad positive correlation between the two parameters and synthetic grains, confirming that there is either a strong tendency for SP and SSD grains to coexist in similar proportions (*cf.* Taylor, Maher & Self 1987) or for some coarse SP grains to cluster and behave as SSD grains (*cf.* Maher 1988). Thresholds of χ_{ARM}/SIRM for certain modal grain sizes can be estimated from Maher's (1988) new MT data for known grain sizes of magnetite/maghemite (Fig. 7b): values of χ_{ARM}/SIRM $<0.2\times10^{-5}$ Am^{-1} for MD and PSD grains >1000 μm; values of χ_{ARM}/SIRM $<0.9\times10^{-5}$ Am^{-1} for coarse SSD grains ≈0.040–1.000 μm; values $>1.4\times10^{-5}$ Am^{-1} for grains lying at the border of SSD and SP ≈0.030–0.020 μm, including SP grains behaving as SSD grains. Values of χ_{ARM}/SIRM of $0.5–1.4\times10^{-5}$ Am^{-1} represent fine SSD grains 0.030–0.040 μm and mixtures of fine and coarse SSD grains. A plot of χ_{FD} percentage versus χ_{ARM}/SIRM (Fig. 7c) with superimposed threshold values allows estimates to be made of the proportions of frequency-dependent SP grains and non-SP grain sizes in the W-series samples. With the exception of three samples, the W-series contains >50 per cent SP grains, with the remainder in fine SSD or SSD/SP sizes. Samples containing significant concentrations of bacterial magnetosomes should plot in the coarse SSD zone of the diagram where χ_{FD} per cent values vary according to the associated SP fraction. Only sample W24 plots in this zone, and studies are underway to confirm the origin of the SSD grains. The presence of SP grains <0.010 μm, as discussed above, will have the effect of reducing both the bulk χ_{ARM}/SIRM and χ_{FD} percentage values and makes the use of this interpretative plot problematical for extremely fine-grained samples, as demonstrated by the position of Maher's (1988) synthetic sample MT 52 (0.012 μm), which lies in the fine SSD zone. This sample has a long 'tail' of ultrafine grains where ≈ 30 per cent of grains are <0.010 μm (Dearing *et al.* 1996a; Fig. 4). A priority for further research should be determining the size of the ultrafine tail in microscopic studies of magnetic extracts (*cf.* Maher & Taylor 1988; Hounslow & Maher 1996).

PEDOGENIC SECONDARY FERRIMAGNETIC MINERAL FORMATION

The results from different rock magnetic analyses suggest strongly that for a representative set of 10 freely draining



topsoils from Wales the dominant size of ferrimagnetic mineral in all samples is SP, and larger grains make up ≈20–30 per cent of the total. There is also evidence to suggest that in some soils a significant proportion of grains may be extremely fine, with diameters <0.010 μm, as shown in TEM studies of magnetic extracts from Exmoor soils (Maher & Taylor 1988, Fig. 4). Overall, the distributions of magnetic grains in the W-series are similar and positively skewed, with frequencies peaking below 0.020 μm. Comparison of concentration parameters for different grain sizes also reveals that there is a strong covariance between the numbers of grains in different fractions; magnetically enriched soils generally show large concentrations of both SP and SSD grain sizes.

Dearing *et al.*'s (1996b) study of English topsoils included evidence from soil DNA analysis that suggested that magnetotactic bacteria may be present in some soils, especially in less well-drained horizons, but the numbers of bacterial cells and magnetosomes are insufficient to account for the total ferrimagnetic contents in the most magnetic topsoils. TEM studies of magnetic soil extracts (Maher & Taylor 1988) also indicate the rarity of bacterial magnetosomes (M. Hounslow & B. Maher, personal communication). The present evidence of positively skewed grain-size distributions supports the idea of a mechanism driven by pedogenic processes at the $<10^{-8}$ m scale, as implied in the weathering and fermentation hypotheses, rather than by a mechanism driven by the production of 0.040–0.200 μm SSD magnetosomes or the presence of submicron ferrimagnetic inclusions in silicate minerals (*cf.* Morgan & Smith 1981; Hounslow & Maher 1996). The proportions by weight of grain-size fractions 0.030–0.040 μm and 0.012–0.02 μm in W5652 are 26 per cent and 36 per cent, respectively (Fig. 6), an increase from SSD to frequency-dependent SP grains by a factor of 1.4, but this factor increases to 13.9 for the relative difference in the numbers of grains. Degradation or corrosion of magnetosomes and ferrimagnetic inclusions would be expected to reduce the size of the original grains, not to increase the number of fine grains. A further explanation, that both magnetotactic bacteria and pedogenic processes of SFM formation coexist in all the soils sampled, whilst quite plausible, is at variance with the finding that concentrations of SP and SSD grains strongly covary. The only reason why soils should show enhanced levels of both pedogenic SFMs and magnetotactic bacteria is if both are controlled by a single factor or set of factors. The available evidence suggests otherwise: in English soils, the pedogenic mechanism appears to be limited by Fe supply within free-draining topsoils (Dearing

Figure 7. Estimating proportions of SP and non-SP grain-sizes using χ_{FD} percentage and χ_{ARM}/SIRM measurements. (a) Artificial mixing model of soil and synthetic MD magnetite showing threshold values for χ_{FD} percentage of 2, 8 and 11 per cent, equivalent to >10, >50 and >75 per cent frequency-dependent SP grains based on M_s measurements; (b) χ_{FD} percentage versus χ_{ARM}/SIRM for sized synthetic maghemites (solid circles) and magnetites (open circles) from Maher (1988), Lees (1994) and Dearing *et al.* (1996a); (c) semi-quantitative magnetic granulometry plot using χ_{FD} percentage and χ_{ARM}/SIRM, showing the position of W-series samples (x), where the grain-size ranges for zones are defined as >1000 μm (MD+PSD), 0.040–1000 μm (coarse SSD and mixtures), 0.030–0.040 μm (fine SSD) and 0.030–0.020 (SSD/SP transition). Example of use: estimated grain-size proportions for the circled point are 50–75 per cent SP and 50–25 per cent SSD/SP.

et al. 1996b), while magnetotactic bacteria are restricted to microaerophilic soil environments in seasonally waterlogged surface horizons (Fassbinder, Stanjek & Vali 1990) or subsoils (A. Huddleston, personal communication). The present data support the general conclusions of many workers (e.g. Le Borgne 1955; Tite & Linington 1975; Mullins 1977; Maher 1986; Thompson & Oldfield 1986; Maher & Taylor 1988; Zhou *et al.* 1990; Maher & Thompson 1992; Verosub *et al.* 1993; Dearing *et al.* 1996b) that the magnetic properties of free-draining surface soils and palaeosols are often dominated by the presence of SP and SSD ferrimagnetic grains produced by weathering and/or fermentation processes; the contribution by bacterial magnetosomes, if present, is normally of minor importance. Taylor & Schwertmann (1974b) and Taylor, Maher & Self (1987) have demonstrated the ease by which maghemite and SP/SSD grains of magnetite can be synthesized abiologically under laboratory conditions, but in the soil environment the importance of either inorganic or bacterially mediated processes and the precise pathways which lead to the formation of either magnetite or maghemite are still to be established. Extending the findings from studies on English soils (Dearing *et al.* 1996b), we propose that the coexistence of SP and SSD SFM grains in magnetically enhanced Welsh and other temperate topsoils is because the two sets of grains are the products of the *same* combination of inorganic weathering and biological fermentation mechanisms of formation. A reasonably constant proportion of coarse SFMs occurs as either clusters of SP grains (which behave magnetically as SSD grains) or simply as the coarse end of the SFM grain-size spectrum.

CONCLUSIONS

(1) A comparison of χ_{FD} percentage and low-temperature remanence measurements shows that they are sensitive to different ranges of SP grains. Low-temperature remanence measurements (20–300 K) detect the blocking temperatures of grains in the size range ≈ 0.007–$0.035\ \mu$m. Values of χ_{FD} percentage are most sensitive to grains in the size range ≈ 0.012–$0.022\ \mu$m, which is consistent with previously published findings (Maher 1988; Dearing *et al.* 1996a).

(2) Low-temperature remanence measurements may be used to calculate relative grain-size distributions within the SP range, but the calculation of absolute distributions requires the assumptions that SSD grains at room temperature are fine grained and show constant distributions between samples. Values of χ_{ARM}/SIRM seem to offer the best means for assessing these assumptions.

(3) A simple empirical mixing model suggests that χ_{FD} percentage may be used semi-quantitatively where values of 2, 8 and 10 per cent are roughly equivalent to >10, >50 and >75 per cent of frequency-dependent SP grains, respectively. Plots of χ_{FD} percentage versus χ_{ARM}/SIRM represent a strong means for identifying modal grain sizes.

(4) The relative distribution of SP grains and SSD grains is similar in nine out of 10 representative soil samples. Consequently, all magnetic parameters controlled by ferrimagnetic concentrations covary strongly. Typical distributions for soils dominated by SFMs are $\approx$ 20–30 per cent SSD and 70–80 per cent SP. No MD grains were detected in the samples studied. There is evidence that some soils contain significant numbers of ultrafine SP grains $<0.010\ \mu$m that are not detected by low-temperature remanence measurements at 20 K and that will have the effect of depressing values of χ_{LF} and χ_{FD} percentage.

(5) The positively skewed grain-size distributions strongly suggests a mechanism of SFM formation that is driven by processes at the $<10^{-8}$ m scale. This would support hypothesized weathering and fermentation as controlling processes, rather than the degradation of SSD bacterial magnetosomes and primary minerals.

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