

## Formation of ultrafine-grained magnetite in soils

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The magnetic properties of certain soils indicate the widespread presence of ultrafine-grained magnetite, even where there is no detrital input of magnetite<sup>1-3</sup>. This suggests that *in situ* formation of magnetite can occur under soil-forming conditions. Schwertmann and Taylor<sup>4</sup> have stated, however, that magnetite has not been found as a newly formed mineral in soils. Here we report the recovery and identification of pure, ultrafine-grained magnetite from some UK soils that have no apparent external source of magnetite. We consider this magnetite to be of inorganic, *in situ* origin. The identification of magnetite formation during soil development has significance for studies of iron in soils but also has wider environmental implications. Soil-derived magnetite may contribute to the natural remanent magnetism of sediments, and act as a specific indicator of erosional events.

Soil samples were obtained from Exmoor and the south Lake District, UK, from two well-drained, natural brown earth soils developed *in situ*. The soils were selected to exclude any significant detrital input of magnetite; both have weakly magnetic parent materials (Middle Devonian slate and carboniferous limestone, respectively), and no glacial drift is present. Their pH values vary between 5.5-6.0; there was no evidence of charcoal in either profile. Subsamples were taken at 2-cm intervals and were gently crushed and mixed to obtain homogeneity.

The samples were first subjected to a range of mineral (rock) magnetic measurements, to characterize the mineralogy and grain size of the magnetic phases present. Extrinsic magnetic parameters obtained from the air-dried soil samples include low-field magnetic susceptibility ( $\chi$ ), frequency-dependent susceptibility ( $\chi_{FD}$ ), saturation isothermal remanent magnetization (SIRM), anhysteretic susceptibility ( $\chi_{ARM}$ ) and coercivity of remanence ( $(B_0)_{CR}$ ).

In broad mineralogical terms, the magnetic data indicate the predominance of a ferrimagnetic phase. IRM acquisition curves (such as that shown in Fig. 1a) show >90% acquisition of the SIRM at 100 mT, and  $(B_0)_{CR}$  values vary only slightly, between 20-28 mT. The grain size of this ferrimagnetic phase can be inferred from the parameters  $\chi_{FD}$  and  $\chi_{ARM}$ , which are sensitive to the presence of sub-micron-sized grains, especially those spanning the superparamagnetic (SP)/single-domain (SD) boundary ( $\sim 0.01$ - $0.03 \mu\text{m}$ )<sup>6,7</sup>. Figure 1b shows the  $\chi_{FD}$  (%) and  $\chi_{ARM}$  (normalized to SIRM) data obtained from the soils; also shown are published data for synthetic magnetites of controlled grain sizes. The  $\chi_{ARM}/\text{SIRM}$  values for the soils vary within the range occupied by those of the synthetic grains of single-domain size or finer. Their  $\chi_{FD}$  values are closely correlated with the synthetics in the size range  $\sim 0.02 \mu\text{m}$ . A modified Lowrie-Fuller test was performed, in which we compared the stepwise a.c. demagnetization behaviour of the ARM values (acquired in a d.c. field of 0.04 mT, peak a.c. field of 95 mT) with that of the SIRM values. All the soils demonstrate single-domain-type response (that is, Median Destructive Field<sub>ARM</sub> > MDF<sub>IRM</sub>). Figure 2 shows the variation of the magnetic parameters with depth in the Exmoor soil. The magnetic content of the soil increases gradually from the base of the soil to the surface, that is, with age of the soil. The SIRM value would indicate a maximum magnetite concentration of  $\sim 0.1\%$ .

Direct identification of the magnetic mineralogy necessitated extraction and concentration of the magnetic phases (as described below). Curie points were then determined from strong-field thermomagnetic analyses of the magnetic extracts. The thermomagnetic curves (Fig. 3) display Curie temperatures

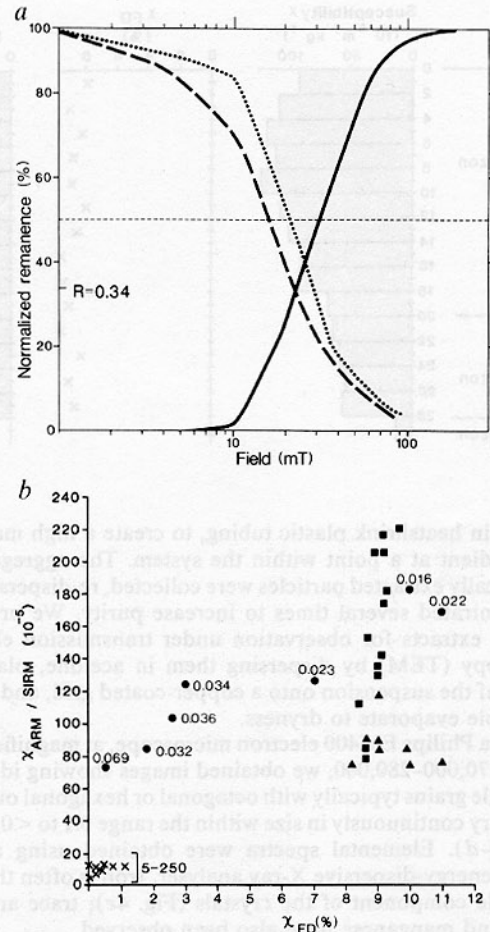


Fig. 1 a, Acquisition of IRM (solid line) and a.c. demagnetization of IRM (dashed line) and ARM (dotted line) for the Exmoor brown earth soil, before magnetic extraction.  $\text{IRM}_{100 \text{ mT}}/\text{SIRM} = 93\%$ , coercivity (at intersection point) = 23 mT, Lowrie-Fuller result ( $\text{MDF}_{\text{ARM}} - \text{MDF}_{\text{IRM}} = +3.5 \text{ mT}$ , Wohlfarth's 'R' = 0.34 (ref. 20). The IRMs were grown in incremental steps, up to a peak magnetic field of 300 mT, the ARMs in a 0.08-mT direct field and 85-mT-peak alternating field. All remanences were measured using a Digico fluxgate magnetometer with a noise level of  $\sim 1 \times 10^{-8} \text{ A m}^2$ . b, Biparametric plot of the ratio,  $\chi_{\text{ARM}}/\text{SIRM}$  versus  $\chi_{\text{FD}}(\%)$  for the untreated soils and for synthetic magnetites of documented grain sizes. Here  $\chi_{\text{FD}}$  is the difference between a low-frequency (0.5 kHz) and a high-frequency (5 kHz) measurement of  $\chi$  expressed as a percentage of the low-frequency measurement. Susceptibility,  $\chi$ , was measured using a Bartington dual frequency sensor, with a noise level of  $\sim 1 \times 10^{-8} \text{ m}^3 \text{ kg}^{-1}$ . Numbers by symbols indicate grain sizes in  $\mu\text{m}$ . ■, Exmoor brown earth; ▲, Lake District brown earth; ●, Maher (ref. 6); ×, Dankers (ref. 19).

of 580-600 °C. This clearly identifies the soil ferrimagnetic phase as magnetite.

Although the magnetic measurements indicate the presence within the soils of magnetite, apparently consisting of SD- and SP-sized grains, they cannot directly identify an authigenic (*in situ*) origin for this material. Ultrafine-grained magnetite can also be formed both lithogenically<sup>8</sup> and biogenically<sup>9,10</sup> within the environment. Other distinguishing properties, notably grain shape characteristics and foreign cation content, must be examined if 'soil' magnetites are to be differentiated from these other known possible sources. This requires direct visual observation and elemental analysis of individual grains of the soil magnetite, extracted from the bulk soil.

We used the extraction technique of Petersen *et al.*<sup>9</sup>. An ultrasonically dispersed soil suspension was circulated around a continuous magnetic extraction system. A rare-earth (iron-neodymium boride) magnet was attached to a soft iron needle,

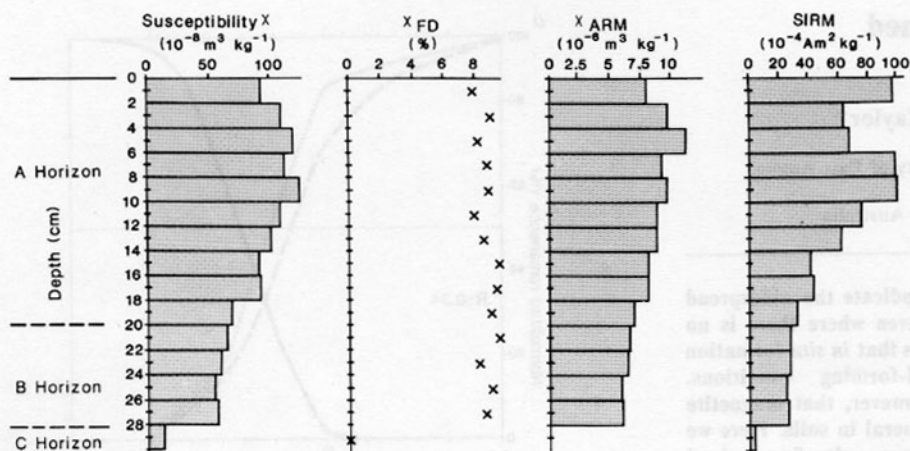


Fig. 2 Variation of magnetic parameters with depth in the Exmoor brown earth soil.

encased in heatshrink plastic tubing, to create a high magnetic field gradient at a point within the system. The aggregates of magnetically extracted particles were collected, re-dispersed and re-concentrated several times to increase purity. We prepared the final extracts for observation under transmission electron microscopy (TEM) by dispersing them in acetone, placing a droplet of the suspension onto a copper-coated grid, and letting the sample evaporate to dryness.

Using a Philips EM400 electron microscope, at magnifications from  $\times 170,000$ – $280,000$ , we obtained images showing idiomorphic single grains typically with octagonal or hexagonal outlines, which vary continuously in size within the range  $0.1$  to  $<0.01 \mu\text{m}$  (Fig. 4a–d). Elemental spectra were obtained using a Link Systems energy-dispersive X-ray analyser. Iron is often the only detectable component of the crystals (Fig. 4e); trace amounts of zinc and manganese have also been observed.

We consider these geometric microcrystals to be of inorganic

authigenic origin, for the following reasons. Their morphology and composition are clearly different from those reported for ultrafine magnetites of lithogenic origin, which occur as elongate inclusions within silicate minerals<sup>8</sup> and are commonly substituted by titanium. Contrasts with the two types of biogenically produced magnetite<sup>11</sup> can also be identified. (Lowenstam<sup>11</sup> distinguishes between boundary-organized biomineralization, where magnetite formation occurs actively and intracellularly, and biologically induced mineralization, where export of metabolic products induces extracellular mineral formation.) Petersen *et al.*<sup>3</sup> showed recently that boundary-organized magnetosomes, formed by magnetotactic bacteria, constitute a significant natural source of ultrafine magnetite. As with the soil magnetite, this bacterial magnetite is commonly substitution-free, but it frequently occurs in chains, occupies a narrow, biologically constrained, SD-grain-size range, and exhibits distinctive hexagonal or teardrop shapes<sup>11</sup>. Lovely *et al.*<sup>13</sup> have reported extracellular production of magnetite by an anaerobic iron-reducing organism, designated GS-15. The magnetite grains thus produced show several similarities to the soil magnetites; they have a broad size distribution (below  $0.05 \mu\text{m}$ ), are substitution-free, and are not arranged in chains. However, whereas the GS-15 cells seem to grow in intimate contact with the precipitated magnetites, we have observed no bacterial cells associating with the soil magnetites. Finally, as noted by Schwertmann<sup>14</sup>, ferrimagnetic phases can be produced in soils through transformation of other soil iron oxides (such as goethite) during burning of the surface soil. Soil goethites and haematites are usually Al-substituted<sup>15</sup>, and hence give rise to similarly substituted ferrimagnetic forms. Thus, although formation of ferrimagnets certainly can occur through soil combustion, this mechanism cannot account for the magnetites documented here. Taylor *et al.*<sup>5</sup> have recently performed a series of laboratory experiments designed to simulate possible pathways of soil magnetite formation. Rapid and easy synthesis of pure, ultrafine-grained magnetites (Fig. 4f) was achieved through controlled oxidation of  $\text{Fe}^{2+}$  solutions at room temperature and near-neutral pH (conditions realistic in terms of the soil environment). These synthetic magnetites appear to be close analogues of the soil magnetites, in terms of their magnetic characteristics<sup>6</sup>, their purity, morphology and their grain size.

Single-domain magnetite is resistant to demagnetization and is capable of efficient acquisition of post-depositional magnetic alignment. Even in low concentrations, it may dominate the magnetization of sediments. Soil magnetite, with its mix of SD- and SP-sized grains, may thus contribute significantly to the ultrafine, remanence-carrying magnetic fraction of sediments. It may constitute the source for the magnetites of demonstrably non-biogenic origin observed both by Petersen *et al.*<sup>9</sup> and by Chang and Kirschvink<sup>16</sup>. Furthermore, where it has been identified in sediments, it is often correlated with independent

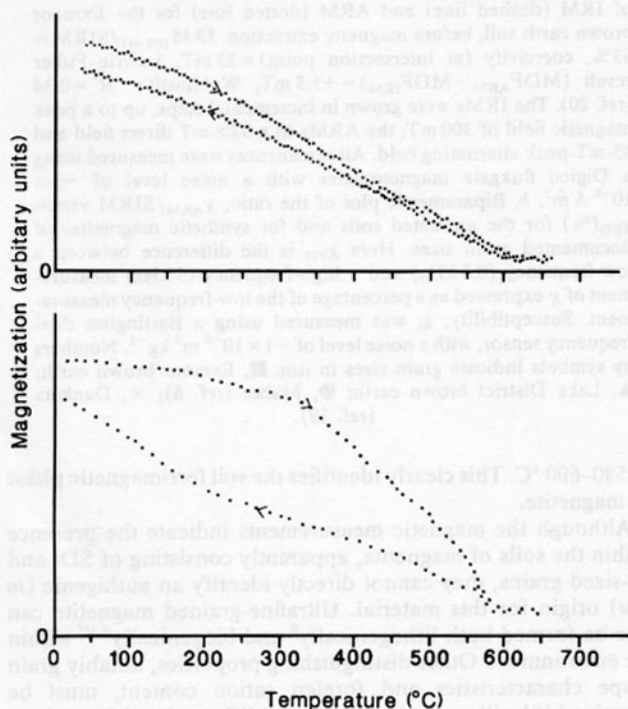
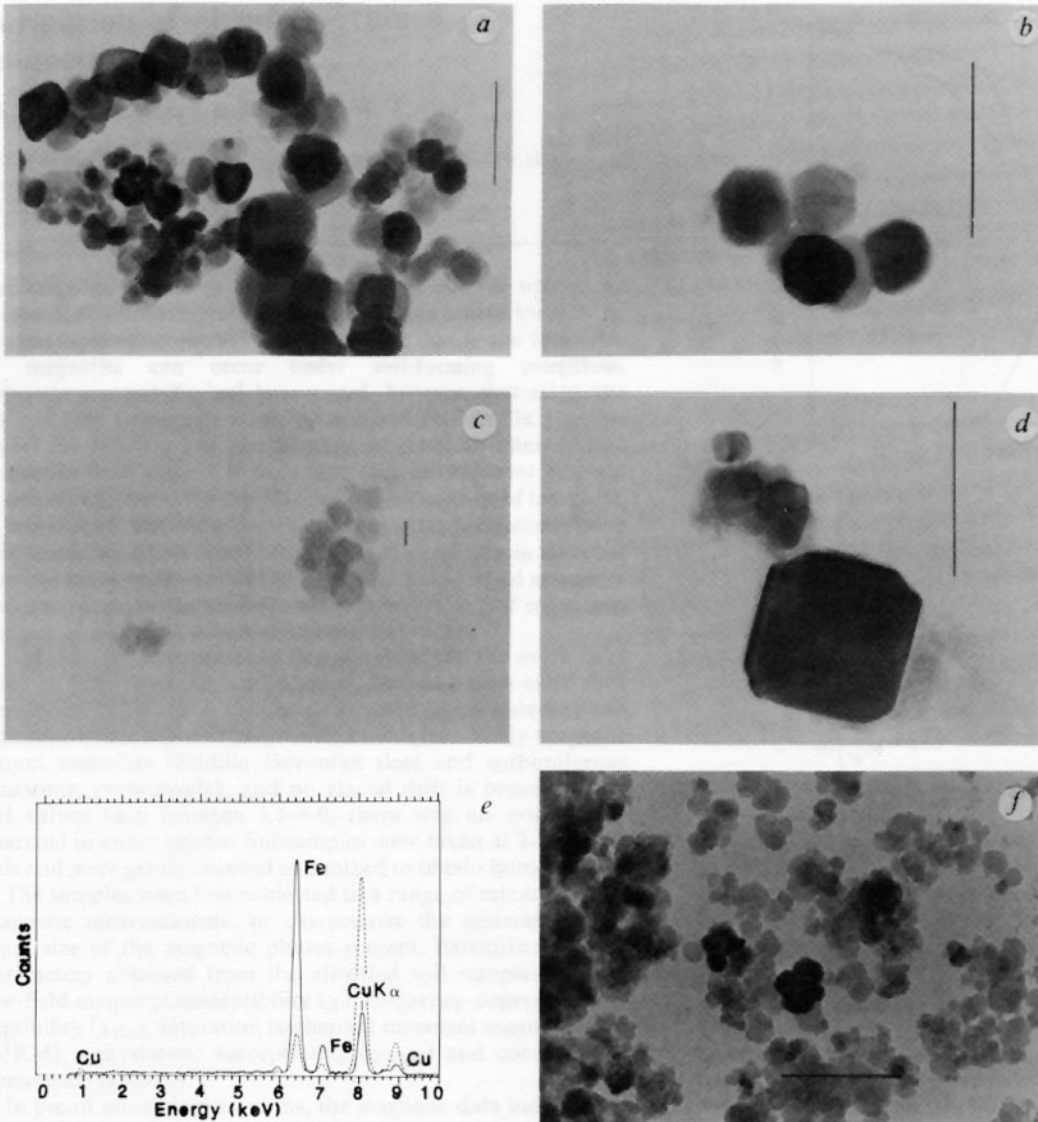


Fig. 3 Curie temperature analyses in air of magnetic minerals extracted by a process of high-gradient magnetic separation from the Exmoor (top) and Lake District (bottom) brown earth soils. Both samples show single-phase Curie points of  $580$ – $600^\circ\text{C}$ . For both soils, but especially for the Lake District soil, magnetization is lower on the return run, probably indicating conversion of some of the finest-grained magnetite to haematite.



**Fig. 4** a-d, TEM images of the mineral grains magnetically extracted from the Exmoor and Lake District soils. a-c are extracts from Exmoor soil (scale bar in a and b indicates 0.1  $\mu\text{m}$ , and in c it represents 0.01  $\mu\text{m}$ ). d shows extracts from Lake District soil (scale bar represents 0.1  $\mu\text{m}$ ). e, Energy-dispersive X-ray analysis of the crystals, obtained in a Philips EM400 with Link Systems analyser (copper peaks are from the support grid). f, TEM image of magnetite crystals synthesized at room temperatures and near-neutral pH (scale bar represents 0.1  $\mu\text{m}$ ).

erosional indicators. For example, cores of Recent sediments from the Potomac estuary show major increases in the concentration of ultrafine-grained magnetite during the past 200 years<sup>17</sup>. These increases occur synchronously with pollen-analytical evidence of land clearance and agricultural intensification. They are also positively correlated with total sedimentation rates and

excess (unsupported) <sup>210</sup>Pb activity. The presence of soil magnetite in these, and other, sediments can therefore be used specifically to infer soil erosional inputs<sup>18</sup>.

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