Identification and paleoclimatic significance of magnetite nanoparticles in soils

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In the world-famous sediments of the Chinese Loess Plateau, fossil soils alternate with windblown dust layers to record monsoonal variations over the last ~3 My. The less-weathered, weakly magnetic dust layers reflect drier, colder glaciations. The fossil soils (paleosols) contain variable concentrations of nanoscale, strongly magnetic iron oxides, formed in situ during the wetter, warmer interglaciations. Mineralogical identification of the magnetic soil oxides is essential for deciphering these key paleoclimatic records. Formation of magnetite, a mixed Fe\(^{2+}/Fe^{3+}\) ferrimagnet, has been linked to soil redox oscillations, and thence to paleorainfall. An opposite hypothesis states that magnetite can only form if the soil is water saturated for significant periods in order for Fe\(^{2+}\) to be reduced to Fe\(^{3+}\), and suggests instead the temperature-dependent formation of maghemite, an Fe\(^{3+}\)-oxide, much of which ages subsequently into hematite, typically aluminum substituted. This latter, oxidizing pathway would have been temperature, but not rainfall dependent. Here, through structural fingerprinting and scanning transmission electron microscopy and electron energy loss spectroscopy analysis, we prove that magnetite is the dominant soil-formed ferrite. Maghemite is present in lower concentrations, and shows no evidence of aluminum substitution, negating its proposed precursor role for the aluminum-substituted hematite prevalent in the paleosols. Magnetite dominance demonstrates that magnetite formation occurs in well-drained, generally oxidizing soils, and that soil wetting/drying oscillations drive the degree of soil magnetic enhancement. The magnetic variations of the Chinese Loess Plateau paleosols thus record changes in monsoonal rainfall, over timescales of millions of years.

Significance

In the famous Chinese Loess Plateau (CLP), weakly magnetic, windblown dust layers alternate with variably magnetic fossil soils, recording monsoonal variations through the last ~3 My. The soils contain strongly magnetic iron oxides, formed in situ, the mineralogy and paleoclimatic significance of which are controversial. Reduction of iron to form Fe\(^{3+}\)-bearing magnetite has been linked to soil wetting/drying. Conversely, oxidation of iron to form Fe\(^{3+}\)-bearing maghemite, which ages into Al-substituted hematite, has been linked to paleotemperature. This study uses structural fingerprinting and electron energy loss spectroscopy to resolve this debate, proving that magnetite is the dominant soil-formed magnet. The magnetic variations of the CLP paleosols thus record changes in monsoonal rainfall, providing a key time series for testing of general circulation climate models.

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by the presence of aluminum, one of the most commonly available metal cations in soils, substituting within some of the vacant sites.

The particle size of soil-formed ferrimagnets is magnetically distinctive, characteristically spanning the superparamagnetic (SP) to stable single domain (SSD) size range (i.e., up to ~50 nm). Curie temperature (\(T_c\)) measurements on soil and paleosol magnetic concentrates (SI Appendix, Fig. S3) indicate the presence in the CLP paleosols of both magnetite (\(T_c \approx 580 \pm 10^3 \text{ K}\)) and maghemite. However, nanoscale magnetite oxidizes at its surface to maghemite, rendering ferrite identification and quantification, whether by magnetic, X-ray diffraction, or chemical dissolution techniques, a challenging task, until now. Torrent and coauthors argue that the coexistence of soils of (trace concentrations) of ferrimagnets with (minor concentrations, up to ~5 wt%) of the highly oxidized hematite can only be explained if the ferrimagnetic phase is Fe\(^{3+}\)-bearing maghemite, not Fe\(^{2+}\)-bearing magnetic (13). They further claim that magnetic data in such cases may be instrumental in identifying the composition of the abiotic ferrites in these paleosols, and hence their causes with climatic factors.

Establishing the causal links between climate and soil magnetism is critically important. Past changes in the East Asian monsoon system preceded subsequent intensification of northern hemisphere glaciations (~2.8 Ma), indicating a possible leading role of monsoonal changes through switches in the poleward distribution of heat and moisture (16). The robustness of paleoclimatic reconstructions from the CLP, and their possible teleconnections, depends on identifying the composition of the abiotic ferrites in these paleosols, and hence their causal links with climatic factors. Although our understanding remains uncertain, arguably the longest and most highly resolved paleoclimate record on the continents remains underused.

To achieve unequivocal identification of the composition of soil nanomagnets, we applied structural fingerprinting from high-resolution transmission electron microscopy (HRTEM) and energy dispersive X-ray analysis (EDXA), to soil magnetic concentrates. The structural fingerprinting approach utilizes crystallographic processing of HRTEM images in which crystal structure factors are obtained using Fourier analysis. The most probable projected crystallographic symmetries for a candidate phase are then obtained, together with geometric information (i.e., reciprocal lattice spacings and interference angles). The combination of geometric information on the reciprocal lattice, plane symmetry, and elemental composition (from EDXA) within a crystal leads to unambiguous identification of the nanoferrite structure.

The soil ferrites were extracted from: a modern, magnetically enhanced soil (a cambisol, from Exmoor, United Kingdom; Fig. 1B and ref. 17); paleosol S\(_1\) (of last interglacial age, ~125,000 y before present [BP]) from the central region of the CLP (Luochuan; Fig. 1A and SI Appendix, Fig. S2); and a paleosol (~5 My BP) from the Mio/Pliocene red clay sequence (at Lintai; ref. 18), which underlies the Quaternary-age loess and paleosols. To examine any possible oxidation effects related to postsampling laboratory storage, we compared recently collected (2011) and “old” (collected in 1990) samples from the Luochuan S\(_1\) paleosol. For independent verification of our structural fingerprinting approach, we additionally used coupled scanning transmission electron microscopy and electron energy loss spectroscopy (STEM/EELS) to quantify the Fe\(^{3+}/\Sigma\text{Fe}\) ratios and to identify the dominant ferrites in the “new” and long-stored Luochuan S\(_1\) paleosol samples.

**Results**

Magnetic concentrates were obtained from the soil and paleosol samples; the extraction efficiency (SI Appendix, Table S1) quantified by before- and after-extraction measurements of magnetic susceptibility, and anhysteretic and saturation remanences (Materials and Methods). For each of the samples, HRTEM imaging (Fig. 2; SI Appendix, Fig. S10) shows agglomerated magnetic nanoparticles with dimensions ranging from ~10 to ~50 nm and mean diameters of 19.9 ± 16.2 nm (measured using a simplified elliptical geometry; SI Appendix, Fig. S7). Some of the larger crystals (Fig. 2C; SI Appendix, Fig. S12A) display euhedral, cubo-octahedral morphologies.

Critically, because reciprocal lattice geometry and plane symmetry information are diagnostic of the dominant crystal structure in the analyzed particles, it is possible to discriminate between nanocrystals of magnetite and maghemite using HRTEM (e.g., refs. 19 and 20). The high-angle reflections (110), (210), and (321), for example, are distinctive, characteristic of the euhedral nanoparticle (Fig. 2C; SI Appendix, Fig. S12A) display euhedral, cubo-octahedral morphologies.

Applying structural fingerprinting to both the modern and fossil soil magnetic concentrates (in total to 210 HRTEM micrographs), demonstrates unequivocally that magnetite is the dominant (>75%) nanocrystalline phase in all but one sample (Fig. 3). Indeed, maghemite was found to be the dominant soil nanomagnet only in the old S\(_1\) paleosol sample (Fig. 4 D–F), which had been collected and stored in the laboratory for >25 y.

![Fig. 1](https://www.pnas.org/content/115/43/11339/DC1/fig1_43.jpg) 
**Fig. 1.** (A) The magnetic susceptibility of the loess/paleosol sequence at Luochuan, central Chinese Loess Plateau (S); (C) the deep-sea oxygen isotope record from site 677 (10) (glacial stages numbered); (C–E) TEM micrographs of nanoscale, low-temperature ferrimagnets formed in the environment, (C) CLP paleosol, (D) United Kingdom modern cambisol (Exmoor), and (E) the unique crystal forms produced intracellularly by magnetotactic bacteria, Cretaceous chalk, United Kingdom.

![Fig. 2](https://www.pnas.org/content/115/43/11339/DC1/fig2_43.jpg) 
**Fig. 2.** (A–C) Magnetic concentrates from Chinese paleosols showing agglomerates of magnetic nanoparticles. The SAED of the euhedral nanoparticle in C identifies a magnetite structure (Inset) along the zone axis (141).
The HRTEM images analyzed show a mixture of aggregated, overlain ferrite grains and 3,226 recognizable single crystals. Magnetite and maghemite were the only ferrites identified by structural fingerprinting; a few (<5) two-line ferrihydrite crystals [based on the Michel et al. (23) model] were additionally identified, occurring in association with magnetite crystals in the modern Exmoor and the Pliocene red clay samples.

The possible presence of Al$^{3+}$ ion substitution could also be examined using structural fingerprinting. Incorporation of the smaller Al$^{3+}$ ions within the magnetite or maghemite unit cell results in modified unit cell dimensions, and accompanying alterations in lattice reflections. None of the samples displayed such modified unit cells; hence, the presence of Al$^{3+}$ substitutions in the soil nanomagnets appears negligible. We additionally checked for Al$^{3+}$ substitutions by elemental analysis using EDXA. The soil ferrimagnets comprise only Fe and O; they display no evidence of substitution by foreign cations (SI Appendix, Fig. S11).

Autocorrelation function analysis was applied to examine periodicity along a single ferrite crystal (e.g., as shown in Fig. 4) and to reveal composite (i.e., overlain) crystals. This approach can also be used to study the crystallinity of the surface layer of the magnetite particles. Areas in the HRTEM images that are dominated by amorphous carbon (from the TEM grid) or poorly crystalline clays associated with the nanoparticles give featureless autocorrelation signals (Fig. 4 C, 1 and 2 and I, 4); whereas, crystalline regions give bright continuous lines matching the orientation of the crystal. A key feature of most of the magnetite particles analyzed is the presence of an amorphous layer near their surface (e.g., compare Fig. 4 C, 1 with C, 2 and Fig. 4 F, 3 with J, 4). EDXA of this 1–4 nm thick amorphous surface layer shows no evidence of elements other than Fe, O, C, or Cu (the latter two associated with the support film and TEM grid, respectively). The autocorrelation function analysis near the magnetite surface provides no evidence of dislocations or discontinuous coverage. These data suggest that the thin surface layer consists of maghemite, rather than clays or any sort of carbonaceous materials.

To make independent verification of our structural fingerprinting approach, we used STEM/EELS analysis to identify the ferrite mineralogy in the newer and long-stored S$_1$ paleosols, from Luochuan, CLP. The EELS data show distinct Fe $L_2$ and $L_3$ peaks arising from excitations of 2$p_{3/2}$ and 2$p_{1/2}$ core electrons to unoccupied $d$-states (3$d_{3/2}$ and 3$d_{5/2}$, respectively) with a consistent Fe $L_2$–$L_3$ energy difference of 13.5 ± 0.2 eV (SI Appendix, Fig. S12). Sample spectra also show weak splitting in the Fe $L_2$ peaks, indicating a weak crystal field around the Fe atom (24). The spectra of the new S$_1$ paleosol samples show slightly wider Fe $L_2$ peaks (3.1–3.9 eV) compared with the old S$_1$ samples (3.0–3.7 eV). Weak preedge peaks at about 708 eV are visible mostly in the old S$_1$ samples, respectively. Assuming that the magnetic exchange parameter $J$ for the new and old paleosol samples is unchanged, the calculated $L_3/L_2$ and the $d$-sub band occupancy H ratios (Materials and Methods) are 4.59–4.74 ($H = 1.78$–2.22) and 5.14–5.86 ($H = 2.43$–2.8) for the new and old paleosol samples, respectively. Assuming that the magnetic exchange parameter $J$ for the new and old paleosol samples is unchanged, the calculated $L_3/L_2$ and the $d$-sub band occupancy H ratios (Materials and Methods) are 4.59–4.74 ($H = 1.78$–2.22) and 5.14–5.86 ($H = 2.43$–2.8) for the new and old paleosol samples, respectively. Assuming that the magnetic exchange parameter $J$ for the new and old paleosol samples is unchanged, the calculated $L_3/L_2$ and the $d$-sub band occupancy H ratios (Materials and Methods) are 4.59–4.74 ($H = 1.78$–2.22) and 5.14–5.86 ($H = 2.43$–2.8) for the new and old paleosol samples, respectively. Assuming that the magnetic exchange parameter $J$ for the new and old paleosol samples is unchanged, the calculated $L_3/L_2$ and the $d$-sub band occupancy H ratios (Materials and Methods) are 4.59–4.74 ($H = 1.78$–2.22) and 5.14–5.86 ($H = 2.43$–2.8) for the new and old paleosol samples, respectively.
observations are thus in agreement with our structural fingerprinting analysis and provide evidence of much greater magnetization in the old compared with the new S₁ paleosol sample.

Discussion

Our new results show that soil-formed, nanoscale ferrimagnets, extracted from magnetically enhanced soils (both modern and paleosol), are dominantly composed of discrete crystals of the mixed Fe²⁺/Fe³⁺ iron oxide, magnetite. This definitive mineralogical identification thus demonstrates that magnetite formation occurs in well-drained, generally oxidizing soils, and substantiates the proposed causal links between the pedogenic formation of magnetite and rainfall-induced changes in soil wetness and microsite redox conditions (7, 18, 26). Conversely, the relatively small proportion of discrete maghemite nanocrystals (with the one exception of the long-stored S₁ paleosol sample) negates the
also highlights the retardation effect on magnetite oxidation as a result of increasing soil pH, with H⁺ solid-state diffusion being the rate-limiting step. Dominant rainfall during the summer monsoon season (wet and warm) results in a reduction of soil pH, but this is accompanied by a sharp depletion of dissolved oxygen, thus retarding the oxidation of soil nanomagnete. During the monsoon winter season (cold and dry), the oxygen diffusion rate increases but soil pH tends to be more alkaline due to reduced bacterial activity, resulting in at least an order of magnitude decline in the rate of magnetite oxidation.

\[ 3\text{Fe}^{2+}\text{Fe}_2^{3+}\text{O}_4 + \frac{1}{2}\text{O}_2 + 2\text{H}^+ \rightarrow 4\text{Fe}^{3+}\text{O}_3 + \text{Fe}^{3+} + \text{H}_2\text{O} \]  

This definitive identification of the Fe\(^{2+}\)-bearing mineral, magnetite as the dominant soil-formed ferrite phase provides a firm basis and rationale for kinetic modeling of magnetite formation processes in soil microsites under wetting and drying cycles. In turn, such modeling will enable improved quantification of East Asian paleoclimate (rainfall, evapotranspiration, temperature) over Quaternary and Mio/Pliocene timescales. Such paleoclimatic data are essential for testing and ground-truthing of general circulation models, whether for hindcasting studies or for robust prediction of future monsoon changes in the populous East Asian region.

**Materials and Methods**

**Magnetic Extraction.** Magnetic concentrates were obtained from the finer solid-state diffusion being the rate-limiting step with increasing time. The topochemical oxidation of magnetite [Eq. 1, after White (27)] involves the migration of Fe\(^{3+}\) ions from the core to the surface (or to the magnetite-magnhemite interface) and electron exchange with dissolved oxygen at the water–mineral interface. The slow rates of solid-state outward diffusion of Fe\(^{3+}\) ions \([10^{-12} - 10^{-20} \text{cm}^2/\text{s} (28-30)]\) and inward diffusion of protons through the magnetite–magnhemite core shell is likely to be self-limiting at low soil temperature and circumneutral pH. Further liberation of core Fe\(^{2+}\) ions is expected to be hindered with increasing time as the oxidized shell becomes thicker (31). We developed an inverse shrinking-core model based on the early work of Wen and others (32-34), to simulate the topotactic oxidation of the soil nanomagnetes. The model, which couples solid-state diffusion of Fe\(^{3+}\) (outward) and H\(^+\) (inward) ions with oxygen gas film and chemical reaction rate-limiting controls, indicates the survival of a \(>20 \text{ nm}\) magnetite core for the order of 1–4 My (Fig. 5). This model simulation

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**Fig. 5.** Shrinking-core model simulation of the soil magnetite oxidation reaction. (A) Schematic representation of a reacting ferrite particle (initial particle radius \(R_0\)) with unreacted magnetite core (\(r_c\)), magnetite oxidation rim and an associated clay film (at \(R_c\)) (B). Shrinking-core model simulation using \(R_0 = 0.001 \text{ atm, } T = 15 ^\circ\text{C, } \text{air-filled porosity } (\theta) = 0.5\), and variable \(R_c\) between 5 and 20 nm. (C) Shrinking-core model simulation using \(R_0 = 10 \text{ nm, } T = 15 ^\circ\text{C, } \text{air-filled porosity } (\theta) = 0.5\), and variable pH between 3.0 and 9.0.
Electron Energy Loss Spectroscopy Analysis (EELS). Samples from the new and the long-stored S paleosol, from Luochuan, CLP, were additionally analyzed using EELS, with a JEOL ARM 200F TEM/STEM operating at 200 kV, equipped with a field emission gun and electron energy loss spectroscopy. STEM-EELS was acquired using a Gatan Gif Quantum ER spectrometer model 965 with a 2.5-mm spectrometer entrance aperture. The camera length was chosen so that Quantum gives a collection half-angle of 38.19 mrad, resulting in high collection efficiency and initial energy resolution of ~1.0 eV (0.1 eV/channel dispersion) determined by measuring the full width at half maximum of the zero-loss peak (ZLP). The exposure time of each EELS spectrum was set to ≤10 s to avoid radiation damage. All data were energy calibrated by aligning the maximum of the ZLP of each EELS spectrum to the same channel. The core-loss EELS spectra were constructed using a curve fitting approach described by ref. 40. The model consisted of a power-law background, Fe L23, O K-edges and their fine structures, multiple scattering, and Hartree–Slater cross-section components. The model was fitted using the Levenberg–Marquardt method and used to determine the d-band occupancy the relative intensity of the white lines (L23/LLM) or the branching ratio Q = (L23)/(LLM + LLM), which was shown to characterize iron oxides (40, 41). A ratio, termed here as H-ratio, developed by Colliex et al. (42) and Morrison et al. (44) is also used here to characterize the occupancy of the d-states. The H ratio is sensitive to increases in populations of higher oxidation states of an ion in the 3d orbital and is defined as: 

\[ H = \frac{h_{3d}}{h_{4d}} = \frac{1}{6/5 \times 2 \times L_2 / L_3 - 1} \] 

where E3 and E4 are the energies of the L2 and L3 peaks determined by fitting Gaussian or Lorentzian function and the determination of the center of the L2 and L3 peaks.

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Supporting Information Appendix for

The identification and paleoclimatic significance of magnetite nanoparticles in soils

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This PDF file includes:

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- Fig. S1: The sediment sequences, and magnetic susceptibility logs, from west to east and south in the Chinese Loess Plateau
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Supplementary Text

Soil and paleosol samples

Fig. S1 illustrates the interleaved stratigraphy of the less-weathered loess layers and variably-developed paleosols across the Chinese Loess Plateau (CLP), together with their magnetic susceptibility variations, from the more arid, high sedimentation rate sites in the west to the increasingly humid, lower sedimentation rate sites in the east and south. For this study, we analysed samples from one modern soil, a magnetically-enhanced cambisol developed on a non-magnetic parent material (slate), from Exmoor, U.K., and from paleosols from the Chinese Loess Plateau (CLP). The latter comprised: samples from the last-interglacial paleosol, S₁ (~125 kyrs age), from Luochuan, in the central region of the CLP; and a sample ~ 5 million years in age (from Lingtai), from the Red Clay, the Mio/Pliocene paleosol sequence which underlies the Quaternary-age loess/paleosol sediments. The locations of the Lingtai (35.0°N, 107.5°E) and classic Luochuan (35.8°N, 109.4°E) sections in the central Loess Plateau are shown in Fig. S2. The Luochuan section is ~135 m thick, and comprises more than 30 loess–paleosol alternations, spanning all of the Quaternary period. The Lingtai sequence consists of ~130 m of Red Clay, of late Miocene/Pliocene age, overlain by ~170 m of interbedded Quaternary loess and paleosols.

We analysed both recently-collected (2011) S₁ samples from Luochuan (kindly provided by Tom Stevens), and samples collected in 1990 (by B. Maher), and subsequently stored in the laboratory. Magnetic and XRD data have previously been reported for the Exmoor modern soil and the Luochuan paleosols (1), and Fig. S3 and Fig. S4. Thermomagnetic analysis of CLP paleosols typically indicates the presence of both magnetite and maghemite (Fig. S3). The majority of the sample magnetisation is lost at ~ 580 °C, the Curie point of magnetite. The inflections in the heating curve at ~300 - 500 °C occur as maghemite (especially the finest-grained particles)
oxidises to hematite. This maghemite-hematite conversion is reflected in the loss of magnetisation (marked by the thick arrow on the y-axis) seen in the cooling curve.

In terms of mineralogy, the bulk soil samples are dominated (~89 wt%) by quartz, clay minerals (including chlorite and illite), and trace (~0.42 wt%) indications of the presence of magnetite and/or maghemite (Fig. S4). Magnetite and maghemite are ferrimagnetic; they have strong positive exchange interactions between their neighbouring atomic magnetic moments, and unequal Fe occupancy in the octahedral and tetrahedral sites, resulting in spontaneous magnetisations and large induced magnetisations, which resist thermal disturbance. Even though these minerals occur in soils typically in trace concentrations (e.g., up to 0.3 % in the CLP paleosols), they account for > 90% of the measured magnetic remanence. In contrast, the weakly-magnetic iron minerals, hematite and goethite, typically occur in minor concentrations (up to ~5%) but contribute very little to soil magnetic susceptibility, anhysteretic remanence (ARM) or saturation isothermal remanent magnetisation (SIRM).

**Magnetic Extraction**

The soil and paleosol samples were subjected to a magnetic extraction procedure using a modified approach based on Petersen *et al.* (2) and Hounslow *et al.* (3, 4). The new modification aimed to protect the ultrafine ferrite particles from oxidation or structural alterations during the magnetic extraction. Briefly, ~1.0 g of dry soil sample was moved to an Ar glovebox and ground gently with an agate pestle and mortar; excessive or forceful grinding that may lead to breaking detrital magnetite particles was avoided. The sample was then dispersed in 50 ml oxygen-free MilliQ water (O$_2$ < 0.1 ppm) containing 0.20 g sodium hexametaphosphate inside the Ar glovebox. The sample was mixed by shaking for 5 min and subjected to ultrasonication for 2 min.
The >40 µm fraction was separated from the fine fraction by centrifugation (2000 rpm for 1.5 min). The above procedure was repeated 10-15 times.

The separated <40 µm soil fraction was then circulated around a magnetic extraction apparatus (Fig. S5) using a peristaltic pump. In this apparatus, an NdFeB (560 milliTesla, mT) magnet is placed on top of a PTFE-coated stainless-steel needle, generating a high-gradient magnetic field (max ~40 mT) around its tip. The magnetic extraction was carried out for 14 days under continuous flow of Ar gas. The magnetic extracts accumulated near the tip of the needle were collected once a day by closing the flushing gate and rinsing the needle with deoxygenated MilliQ water through the rinsing port (Fig. S5). The collected magnetic extracts were transferred immediately to the Ar-glovebox and stored until analysed.

In order to quantify the efficiency of the magnetic extraction procedures, we made before- and after-extraction measurements of magnetic susceptibility, and room-temperature anhysteretic (peak alternating current, ac, field of 80 mT, steady direct current, dc, field 0.1 mT) and saturation remanence (peak dc field 1 T). The magnetic measurements were made at the Centre for Environmental Magnetism and Paleomagnetism, Lancaster University. Room-temperature remanent magnetisations (IRMs) were measured with a Molspin minispin magnetometer (mean background noise level 0.1 x 10^-8 A m^2). To identify magnetic grain sizes and/or magnetic interactions (5, 6), anhysteretic remanence (ARM) was induced in a decaying (80 mT, peak) alternating magnetic field (AF), with a small superimposed direct current (DC) field (0.01 mT), and subsequently AF-demagnetized. Stepwise remanence acquisition was measured with incremental application of DC fields of 10, 20, 30, 50, 75, 100, and 300 mT and 1 T. The extraction efficiency data for each of the three measured magnetic parameters (Table S1) show
that the extraction process removed significant proportions of the susceptibility and remanence carriers in each of the analysed soil and paleosol samples.

**Crystal structure of magnetite and maghemite**

Magnetite (Fe$_3$O$_4$) and maghemite (γ-Fe$_2$O$_3$) are ferrimagnetic at room temperature. Both materials crystallise in a similar close-packed cubic lattice rendering them indistinguishable by standard resolution x-ray diffraction. The key structural differences between magnetite and maghemite lie in the properties of the tetrahedral and octahedral sites.

Magnetite is a mixed Fe$^{2+}$/Fe$^{3+}$ inverse spinel phase with a typical cubic lattice system in which A-sites (tetrahedral with spin down) are occupied by only Fe$^{3+}$ cations whereas B-sites (octahedral with spin up) contain equal numbers of Fe$^{2+}$ and Fe$^{3+}$ cations (Fig. S6). The inverse spinel structure of magnetite can be described as $(Fe^{3+})_8^{\text{tetra}}[Fe_1^{3+}Fe_2^{2+}]_{16}^{\text{octa}}O_{32}$, where tetra and octa denote the tetrahedrally and octahedrally coordinated sites, respectively, of the $Fd\overline{3}m$; ($a = 8.394$ Å) space group. Mössbauer studies of cubic-phase magnetite have shown that at room temperature iron atoms on the B-site behave like Fe$^{2.5+}$ due to electron hopping between the Fe$^{2+}$ and Fe$^{3+}$ sites of the mixed valence octahedral site giving rise to electrical conductivity and a magnetic moment of 4 Bohr magneton ($\mu_B$) per Fe$_3$O$_4$ formula unit ($7$-$10$).

Magnetite is stoichiometric (i.e., $\frac{Fe_A}{Fe_B} = 0.5$) when the moles of vacancies $\delta = 0$ and non-stoichiometric when $0 < \delta < \frac{1}{3}$. When the extreme condition $\delta = \frac{1}{3}$ is reached, the structure becomes depleted in Fe$^{2+}$ and maghemite is formed. The general maghemite cubic-phase
structure can be derived from magnetite by introducing $\frac{8}{3}$ vacancies in the B-site; oxidation of magnetite into maghemite can be schematised as follows:

$$\text{(Fe}^{3+})_{8}^{\text{tetra}} \left[ \text{Fe}^{3+}_{\frac{1}{2}} \text{Fe}^{2+}_{\frac{1}{2}} \right]_{16}^{\text{octa}} O_{32} \rightarrow \text{(Fe}^{3+})_{8}^{\text{tetra}} \left[ \text{Fe}^{3+}_{\frac{5}{6}} \text{□}_{\frac{1}{6}} \right]_{16}^{\text{octa}} O_{32}$$

**magnetite** \hspace{1cm} **maghemite**

Early studies (e.g., (11, 12)) suggested randomly distributed cation vacancies over the octahedral sites in maghemite, with an assumed cubic space group of $Fd\bar{3}m$. However, there is increasing evidence that ageing of soil maghemite leads to ordering of the vacancies, giving rise to superstructure lines (similar to LiFe$_5$O$_8$ (13)) in the x-ray diffraction pattern, and reduces the maghemite cell symmetry to tetragonal space group ($P4_{3}2_{1}2/ P4_{1}2_{1}2; a = 8.322$ Å, $c = 24.996$-25.113 Å) by tripling its basic cubic unit cell along the $c$-axis (14-16). The tetragonal spinel structures of maghemite are most common in synthetic and natural samples although some limited reports have identified primitive cubic maghemite (i.e., $P4_{3}2_{1}2/ P4_{1}32$) in some rock specimens (17, 18). This departure of maghemite from the cubic $Fd\bar{3}m$ symmetry towards the more ordered tetragonal or primitive cubic symmetry in soils allows the elucidation of the ferrite structure using the integrative structural fingerprinting approach described here.

**Ferrite particle size distribution**

The diameters of the ferrite particles were derived by image analysis of >200 HRTEM micrographs ($N = 3090$ individual ferrite crystals) using ImageJ (19) assuming (for measurement purposes) an elliptical geometry for each single grain (Fig. S7). For the major axis distribution, $Q_{1x} = 12.61$ nm, $Q_{2x} = 22.4$ nm, $\mu_x = 19.9$ nm and for the minor axis distribution $Q_{1y} = 10.7$ nm, $Q_{2y} = 17.9$ nm, $\mu_y = 16.2$ nm, where $Q_1$ and $Q_2$ are the first and second quartiles and $\mu$ is the
mean. The particle size distribution indicates that ~25% of the ferrimagnetic particles fall within the superparamagnetic (SP) size range whereas the remaining 75% of the population fall within the stable single domain fraction (SSD) size range. Viscous superparamagnetic particles (VSP) that would saturate in relatively low magnetic fields, and show time- and frequency-dependent magnetic behaviour, are located at the SP-SSD interface (Fig. S7).

Examples of structural ‘fingerprinting’ analysis applied to pedogenic ferrites.

Idealised electron diffraction reflections presented in Fig. S9 of tetragonal maghemite ($P4_32_12$; $c=25.113\,\text{Å}$ (14) and $c=8.322\,\text{Å}$ (20)), primitive cubic maghemite ($P4_132$; $c=8.330\,\text{Å}$ (21)), magnetite ($Fd\overline{3}m$; $c=8.394\,\text{Å}$ (22) and 2L-ferrihydrite ($P6_3mc$ (23)) demonstrate structural differences between these candidate phases in soil magnetic extracts. The data presented in Fig. S10 provide four examples of structural ‘fingerprinting’ analysis, as applied to the soil and paleosol samples analysed here. In the first example (‘old’ $S_1$, Luochuan, CLP paleosol, (a) – (e)), primitive cubic maghemite ($P4_132$; $c=8.330\,\text{Å}$) is found to provide the best fit of the regular lattice of multiple grains (b) along zone-axis ($\langle 251 \rangle$) ($A=3.834$, $B=5.635$, $C=3.797$, $D=5.146\,\text{nm}^{-1}$; d-spacing STDEV = 0.0013, total angular distribution = 3.61). Together with the good fit statistics to the maghemite structure, these data (620 particles analysed) demonstrate that the dominant ferrite phase in this long-stored CLP $S_1$ sample is cubic maghemite. In the second example, from the ‘new’ $S_1$, Luochuan paleosol (Fig. S9 (f) – (j)), magnetite provides the best fit to the magnetic lattice along the zone axis (1̅1̅1) with ($A=3.410$, $B=3.450$, $C=3.408$, $D=5.881\,\text{nm}^{-1}$; $\sigma_d = 0.0020$, total angular distribution = 3.19. If maghemite is the dominant phase then it would be expected to find any of the strong reflections (110), (101), (1̅1̅2) or their symmetry equivalent reflections but all these reflections were absent. In addition, the maghemite
fits ($P4_32_12$ or $P4_132$) produced large $d$-spacing STDEV (0.0089 - 0.0193) and total angular distribution (30.8 -113.11), hence identifying that these crystals are magnetites. In the third example, from the modern Exmoor cambisol (Fig. S10 (k) – (l)), both magnetite and maghemite provided reasonable fit to the structure but the optimal zone axes found allow the differentiation between the two phases based on missing or forbidden reflections. In this case, magnetite provided the best goodness of fit (STDEV and total angular distribution) and hence these crystals are magnetites. Magnetite zone-axis $\langle 1\bar{1}2 \rangle$: $A = 3.447$, $B = 3.941$, $C = 2.074$, $D = 4.103$ nm$^{-1}$, $d$-spacing STDEV = 0.0039, total angular distribution = 12.83. Maghemite ($P4_32_12$) zone-axis $\langle \bar{1}01 \rangle$: $A = 3.941$, $B = 4.480$, $C = 2.112$, $D = 4.462$ nm$^{-1}$, $d$-spacing STDEV = 0.00116, total angular distribution = 224.30. In the fourth example, from the Lingtai Red clay (Fig. S10 (m) – (n)), magnetite provides the best fit to the structure of a single crystallite along the zone-axes $\langle 1\bar{0}1 \rangle$ ($A = 3.645$, $B = 3.801$, $C = 3.148$, $D = 5.651$ nm$^{-1}$; $\sigma_d = 0.0042$). The absence of the 0.170 Å$^{-1}$ reflections (forbidden in magnetite) from the (110), (101) and mirror planes and the presence of strong reflection of the (202) (see Fig. S9) suggests that magnetite is the correct ferrite phase and not any of the maghemite structures or the 2L-ferrihydrite.
Table S1. Magnetic properties of the soil and paleosol samples (< 40 µm), pre- and post-magnetic extraction.

<table>
<thead>
<tr>
<th>Sample</th>
<th>χ&lt;sub&gt;pre&lt;/sub&gt;</th>
<th>χ&lt;sub&gt;post&lt;/sub&gt;</th>
<th>χ% ext. eff.</th>
<th>ARM&lt;sub&gt;pre&lt;/sub&gt;</th>
<th>ARM&lt;sub&gt;post&lt;/sub&gt;</th>
<th>ARM % ext. eff.</th>
<th>SIRM&lt;sub&gt;pre&lt;/sub&gt;</th>
<th>SIRM&lt;sub&gt;post&lt;/sub&gt;</th>
<th>SIRM % ext. eff.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSBE, Exmoor cambisol, Pinkery Farm (20 cm)</td>
<td>26.4</td>
<td>9.9</td>
<td>62</td>
<td>2.0</td>
<td>1.5</td>
<td>21</td>
<td>1.0</td>
<td>0.6</td>
<td>44</td>
</tr>
<tr>
<td>‘OLD’ CLP1 Luochuan paleosol, (collected 1990)</td>
<td>231.5</td>
<td>112.75</td>
<td>52</td>
<td>106.2</td>
<td>55.9</td>
<td>48</td>
<td>12.25</td>
<td>7.8</td>
<td>37</td>
</tr>
<tr>
<td>‘NEW’ CLP1 S1, Luochuan paleosol, 9.1 m depth (collected in 2011)</td>
<td>326.8</td>
<td>125</td>
<td>62</td>
<td>126.1</td>
<td>59.25</td>
<td>53</td>
<td>14.95</td>
<td>8.75</td>
<td>42</td>
</tr>
<tr>
<td>RED CLAY Tertiary Red Clay, Lingtai, 260.94 m, 5.36 Myrs BP</td>
<td>140.0</td>
<td>96.3</td>
<td>31</td>
<td>100.2</td>
<td>70.4</td>
<td>30</td>
<td>9.0</td>
<td>7.0</td>
<td>23</td>
</tr>
</tbody>
</table>

χ = mass-specific magnetic susceptibility (10<sup>-8</sup> m<sup>3</sup> kg<sup>-1</sup>); ARM = mass-specific anhysteretic remanent magnetisation (10<sup>-5</sup> Am<sup>2</sup> kg<sup>-1</sup>); SIRM = mass-specific saturation isothermal remanent magnetisation (10<sup>-3</sup> Am<sup>2</sup> kg<sup>-1</sup>).
Fig. S1. (a) The sediment sequence in the central Chinese Loess Plateau, showing the reddened paleosols (S) interbedded with the lighter-coloured parent loess (L, windblown dust), and (b – d) the varying degrees of magnetic enhancement in the paleosols, lowest in the driest and highest-sedimentation rate sites in the west (b), and increasingly high in the wetter and lower-sedimentation sites to the east (c) and south (d). $S_0 =$ present interglacial soil; $L_1 =$ last-glacial windblown loess; $S_1 =$ last interglacial soil. Sample locations are shown in SI Appendix Fig. S2. Reprinted from ref. 25, with permission from Elsevier.
Fig. S2. Map of the Chinese Loess Plateau, showing the location of the Luochuan and Lingtai sequences. Adapted from Spassov (2002) (24) and reprinted from ref. 25, with permission from Elsevier.
**Fig. S3.** Magnetisation versus temperature for paleosol S₅ from Luochuan, CLP (magnetic susceptibility = $256 \times 10^{-8}$ m$^3$ kg$^{-1}$). Reprinted from ref. 25, with permission from Elsevier.

**Fig. S4.** X-ray (Co-$K_{\alpha}$) diffractograms for the bulk soil and paleosol samples. The samples are dominated by quartz, illite, Fe-chlorite, hematite, goethite, calcite and magnetite/maghemite with average compositions (based on semi-quantitative XRD analysis) of 51.25%, 26.08%, 11.8%, 2.78%, 6.86%, 0.81% and 0.42%, respectively.
**Fig. S5.** Schematic drawing (not to scale) of the experimental set-up used for the magnetic extraction procedure from soil and paleosol samples.
Fig. S6. Crystal structure and spin configuration of magnetite ($Fd\bar{3}m; a = 8.394 \text{ Å}$) and maghemite ($P4_32_12; a = 8.322 \text{ Å}; c = 25.113 \text{ Å}$).
Fig. S7. Particle size distribution of magnetic nanoparticles from the soil and paleosol samples listed in Table S1.
Fig. S8. Lattice fringe ‘fingerprinting’ of: (a) – (c) single phase GaN crystal; (d) - (e) Ag nanoparticles; and (g) – (i) synthetic magnetite. The images (b) and (c), (f) and (i) are power spectra calculated from the HRTEM micrographs (a), (d) and (g), respectively. GaN crystal: Zone axis = ⟨010⟩; A = 3.4947, B = 4.007, C = 1.8804, D = 3.9289 nm⁻¹; Quality of fit: d-spacing STDEV from GaN crystal (space group P6₃mc) = 0.0018. Ag-nanoparticles: Zone axis = ⟨101⟩; A = B = 4.240, C = 4.895 nm⁻¹; d-spacing STDEV from Ag crystal (space group Fm3m) = 0.0035. Magnetite-nanoparticles: Zone axis = ⟨131⟩; A = 3.248, B = 3.801, C =3.090, D = 5.075 nm⁻¹; d-spacing STDEV from magnetite crystal (space group Fd3m) = 0.0107.
**Fig. S9.** Comparison between electron diffraction from ideal structures of tetragonal maghemite ($P4_321_2; c=25.113\,\text{Å}$ (14) and $c=8.322\,\text{Å}$ (20)), cubic maghemite ($P4_132; c=8.330\,\text{Å}$ (21)), magnetite ($Fd\bar{3}m; c=8.394\,\text{Å}$ (22)) and 2L-ferrihydrite ($P6_{3}mc$ (23)). Calculations assume TEM beam voltage of 300 keV, Pseudo-Voigt peak profile and a particle size of 50 nm.
**Fig. S10.** Examples demonstrating the application of the structural ‘fingerprinting’ approach. (a) HRTEM of ‘old’ S₁, Luochuan, CLP paleosol (collected 1990, stored in air for 27 years) and the corresponding FFT power spectra and lattice indexing of (b) a multi-grain area along the tetragonal maghemite (P4₂₃; c = 25.113 Å) along zone-axis (1̅11) (A = 3.775, B = 5.057, C = 3.333, D = 5.013 nm⁻¹; σ₃ = 0.0026); (c) tetragonal maghemite (P4₂₃; c = 8.322 Å) along zone-axis (141) (A = 3.775, B = 5.057, C = 3.333, D = 5.013 nm⁻¹; σ₃ = 0.0065); (d) primitive cubic maghemite (P4₁32; c = 8.33 Å) along zone-axis (2̅13) (A = 3.834, B = 5.635, C = 3.797, D = 5.146 nm⁻¹; σ₃ = 0.0013) and (e) magnetite (Fd̅3m) (2̅2̅3) (A = 3.775, B = 5.057, C = 3.333, D = 5.013 nm⁻¹; σ₃ = 0.0032). (f) HRTEM of ‘New’ paleosol S₁, CLP sample, (g) the corresponding FFT spectrum and lattice indexing of single grain crystal along the magnetite (best fit) zone-axis (1̅11) (A = 3.410, B = 3.450, C = 3.408, D = 5.881 nm⁻¹; σ₃ = 0.0020) and (h) simulated HRTEM diffraction along zone-axis (1̅11) of (h) magnetite (Fd̅3m), (i) tetragonal maghemite (P4₂₃; c
(j) cubic maghemite (P4₁32; c = 8.33 Å). Note the absence of the (110) and related reflections in experimental FFT that are expected for maghemite but not magnetite. (k) HRTEM of modern Exmoor cambisol and (l) the corresponding FFT spectrum and lattice indexing of multi-grain crystals along the magnetite zone-axis \(\{1\bar{1}2\}\) (\(A = 3.447, B = 3.941, C = 2.074, D = 4.103 \text{ nm}^{-1}; \sigma_d = 0.0039\)). (m) HRTEM of Lingtai Red Clay sample and (n) the corresponding FFT spectrum and lattice indexing of a single grain crystal along the magnetite zone-axis \(\{\bar{1}01\}\) (\(A = 3.645, B = 3.801, C = 3.148, D = 5.651 \text{ nm}^{-1}; \sigma_d = 0.0042\)). The black ‘×’ symbols represent overlain lattices that have been fitted to the same candidate phase but details removed for clarity. Note that the modulus of the lattice vectors A, B, C and D are represented by half the lengths of the centred arrows in the FFT images.
**Fig. S11.** Energy-dispersive X-ray spectroscopy analysis (EDXA) data and HRTEM from magnetic extracts of (a) and (b): $S_1$, Luochuan paleosol (‘old’ CLP sample); (c) – (e): $S_i$, Luochuan paleosol (‘new’ CLP sample); (f) and (g): modern Exmoor cambisol; and (h) and (i): Tertiary Red Clay. All the magnetic particles display vanishingly low Al content. Where, in some extracts, the magnetic particles are associated with clay minerals, Si and Al co-occur; in contrast, the Fe-rich particles are notably deficient in Al and Si (e.g., compare (c) with (d)).
Fig. S12. EELS spectra of paleosol magnetic nanoparticles (a) Scanning TEM micrographs from ‘old’ (1-4) and ‘new’ (5-8) paleosol S1, CLP samples with selected areas corresponding to the resulting EELS spectra. (b) Oxygen-K edge and (c) and Fe-L2,3 edge after background subtraction of nanoparticles identified in the selected areas in (a). The solid lines in (b) and (c) represent first model fits of experimental data for O-K or Fe-L2,3. (d) Deconvolution of EELS spectra b1 and c1 showing Gaussian or Lorentzian functions fitted to dominant peaks for determination of their centre, area and FWHM.
References


