New insights into magnetic enhancement mechanism in Chinese paleosols

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Magnetic susceptibility of Chinese loess–paleosol sequences has been extensively used as a reliable paleoclimatic proxy for reconstruction of the Asian summer monsoon system, and its enhancement is usually attributed to neoformation of fine-grained ferrimagnetic particles via pedogenesis, but there is little understanding of either the formation process of such magnetic particles or their actual form and grain sizes. To investigate these problems, scanning electron microscope observations were conducted on magnetic extracts from pristine loess and strongly-pedogenic paleosol samples from Xifeng on the Chinese Loess Plateau. Both magnetic extracts commonly contained coarse-grained detrital magnetite with grain size ranging from a few μm to several tens of μm. However, the magnetic extract from the mature paleosol sample additionally included coarse silicate particles with ultrafine ferrimagnetic inclusions, while that from the pristine loess sample did not. The size of the ferrimagnetic inclusions mainly ranged from tens to hundreds of nanometers. The temperature-dependent susceptibility and hysteresis loops of the paleosol sample, combined with the stratigraphic variations of rock-magnetic parameters, showed that the pedogenic maghemite inclusions should be a potential contributor to magnetic enhancements in Chinese paleosols. The fine-grained ferrimagnetic inclusions have been pedogenically formed by weathering of coarse-grained Fe-bearing silicate minerals. Our proposed magnetic enhancement mechanism is consistent with the accepted rock magnetic result that magnetic enhancement in Chinese paleosols is caused by pedogenic maghemite grains in superparamagnetic and single-domain size regions. The presence of ultrafine ferrimagnetic grains as inclusions within coarse silicate particles is also consistent with Han and Jiang’s (1999) significant experimental result that magnetic enhancement in Chinese paleosols is mainly contributed by the >0.5 μm sediment fractions.

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1. Introduction

Loess–paleosol sequences on the Chinese Loess Plateau (CLP) consist of eolian dust coming from the dry deserts of the north and northwest (Liu, 1985). Loess was mainly deposited under cold and dry conditions of the East Asian winter monsoon system during glacial periods, while paleosols formed by in situ alteration of parent loess under warm and moist summer monsoon conditions during interglacial periods (Liu and Ding, 1998). Previous rock-magnetic studies showed that eolian loess–paleosol sediments on the CLP can provide reliable paleoclimatic records, which include long-term climate change (Heller and Liu, 1984, 1986; Kukla et al., 1988; An et al., 1991, 2001; Ding et al., 1999, 2002; Chen et al., 2002; Deng et al., 2005, 2006; Wang et al., 2007; Nie et al., 2008a, 2010; Han et al., 2011) and short-term climate instability (Porter and An, 1995; Guo et al., 1996; Chen et al., 1997; Heslop et al., 1999; Liu et al., 2005; Wang et al., 2012). Detailed magnetostratigraphic results revealed that Chinese loess–paleosol sequences not only record major magnetozones from the Gauss to the Brunhes (Zheng et al., 1992; Ding et al., 1993; Sun et al., 1998), but also have potential to document geomagnetic excursions such as the Mono Lake, Laschamp, Blake, “Unknown” (11o of Lund et al. (2006)), Santa Rosa, Punaruu, Renion, and so on (Zhu et al., 1994, 1999, 2000; Zheng et al., 1995; Fang et al., 1997; Pan et al., 2002; Yang et al., 2004, 2005, 2007a, 2007b; Jin et al., 2012). Obviously, paleosol units in standard Chinese loess–paleosol sequences always have relatively higher magnetic susceptibility (χ) and relatively larger quartz grain size than adjacent loess units, and a depth-variation curve of χ and quartz grain size is well correlated with marine oxygen isotope stratigraphy (Ding et al., 1994, 2002; Heslop et al., 2000; Sun et al., 2006; Wang et al., 2006; Nie et al., 2008a, 2008b). Therefore, χ is extensively used as a
Various kinds of mechanisms have been proposed to explain magnetic enhancement in Chinese paleosols: (1) a relative enrichment of magnetite in soils due to carbonate leaching and soil compaction processes (Heller and Liu, 1984); (2) a sub-aerial depositional mechanism (Kukla et al., 1988); (3) pedogenesis (Zhou et al., 1990; Maher and Thompson, 1991; Liu et al., 1992; Banerjee et al., 1993; Verosub et al., 1993); (4) decomposition of vegetation (Meng et al., 1997); (5) heating of loess by frequent natural fires (Kletetschka and Banerjee, 1995); and (6) dust dilution (a major cause) and pedogenesis (a minor cause) (Porter et al., 2001). Because of the great progress made over the last three decades in understanding the mineral magnetism of Chinese loess–paleosols, it is now widely accepted that magnetic enhancement is caused by pedogenic neoformation of fine-grained maghemite particles in superparamagnetic (SP) and single-domain (SD) grain size regions (e.g., Liu et al., 2007; Nie et al., 2007, 2008c; Wang et al., 2010). However, the formation process of maghemite from Fe-bearing minerals remains unclear.

Some researchers have proposed that biotic (mineralization by magnetotactic bacteria) or abiotic (inorganic precipitation via iron reduction by iron-reducing bacteria) formation of fine-grained magnetite (e.g., Maher and Thompson, 1995; Jia et al., 1996; Chen et al., 2005) is followed by oxidation to form maghemite, but they should play a minor role in the magnetic enhancement of palaeosols. Either biotic or abiotic formation of fine-grained magnetite requires reducing conditions that lead to an accumulation of Fe$^{3+}$ in the soil solution (Lovley et al., 1987; Maher and Taylor, 1988; Fassbinder et al., 1993). Torrens et al. (2006, 2007) considered that such a strict requirement for magnetite formation did not prevail in well-drained paleosols, and contradicted the coexistence therein of pedogenic magnetite and hematite. Therefore, to interpret magnetic enhancement under aerobic conditions, they proposed a model where ferrihydrite, which is considered to be a primary product of the weathering of Fe-bearing minerals, undergoes transformation to hematite via maghemite as an intermediate product. Some researchers have suggested that maghemite in paleosols could be derived from oxidation of fine-grained magnetite and partial oxidation of coarse-grained magnetite produced a maghemite rim (e.g., Liu et al., 2003; Spassov et al., 2003; Chen et al., 2005). A main effect of low temperature oxidation of magnetite grains is an increase in the coercive force due to enhanced stresses induced by a large gradient in the degree of oxidation from a maghemitized rim to a magnetite core (van Velzen and Zijderveld, 1995). However, this suggested effect is incompatible with the magnetic observation that paleosol units always have a relatively lower coercive force than adjacent loess units (Forster and Heller, 1997; Fukuma and Torii, 1998; Yang et al., 2010). Significantly, Han and Jiang (1999) investigated grain size distribution of magnetic particles from loess L2 and paleosol S1 of Jixian, Xifeng and Xining sections, and confirmed that the enhanced magnetic susceptibility of paleosol S1 is mainly contributed by the >0.5 $\mu$m magnetic particles, not by the <0.1 $\mu$m magnetic particles. This significant result obviously contradicts the widespread acceptance that magnetic enhancement in Chinese paleosols is due to pedogenic neoformation of fine-grained ferrimagnetic particles in superparamagnetic (SP) and single-domain (SD) grain size regions. Therefore, more studies are necessary to better understand the magnetic enhancement mechanism in Chinese paleosols.

Noticeably, Yang et al. (2010) carried out a detailed magnetostratigraphic and rock-magnetic study to decipher the Matuyama–Brunhes polarity transition, and confirmed that both thermal demagnetization (ThD) and alternating field demagnetization (AFD) were effective in isolating characteristic remanent magnetization (ChRM) from weakly pedogenic loess–paleosol sediments, but AFD clearly failed to isolate ChRM from the strong pedogenic S8 paleosol. In this study, we re-collected samples from the original Xifeng section, and carried out scanning electron microscope (SEM) observations with energy dispersive X-ray analyses. In addition, we performed hysteresis loops and thermomagnetic analyses, to elucidate differences in the forms of magnetic minerals between pristine loess and strongly pedogenic paleosols. We used samples from the pristine L8 loess, which has $\chi$ values around 20–30 x 10$^{-8}$ m$^3$ kg$^{-1}$, and from the mature S8 paleosol which has $\chi$ values around 90–110 x 10$^{-8}$ m$^3$ kg$^{-1}$, and the results are discussed in terms of a magnetic enhancement mechanism in Chinese paleosols.

2. Geological setting and laboratory methods

The Xifeng section at Hujiayaoxian village (35°45′ N, 107°49′ E), about 20 km east of Xifeng town in Gansu province, lies in a central part of the CLP (Fig. 1). The mean annual temperature and precipitation in this area are about 8.8 °C and 650 mm, respectively. The eolian sedimentary sequence consists of an upper loess–paleosol section 168 m thick and a lower red clay deposit 55 m thick, underlain by Miocene fluvial–lacustrine strata. Detailed descriptions of the Xifeng loess–paleosol and red clay pedostratigraphies are given by Kukla and An (1989) and Sun et al. (1998), respectively. The present sampling site was the same location sampled by Yang et al. (2010). It was also referred to as XIFENG II (Kukla and An, 1989) and is about 10 km away from the XIFENG I site at Chenjiachuan village (Liu et al., 1988). Although a previous magnetostratigraphy study found the Matuyama–Brunhes transition to be in the lower L8 (Kukla and An, 1989), a recent study of the high-resolution magnetic record revealed it across the L8–S8 boundary (Yang et al., 2010).

$\chi$ was measured using a Kappabridge KLY-4 system. Hysteresis parameters were measured using a MicroMag 2900 Model alternating gradient force magnetometer. Temperature-dependence of $\chi$ ($\chi$–T) was measured using a Kappabridge KLY-3S system. For SEM observations, a SEM (JEOL JSM-6480LVII) equipped with an energy dispersive X-ray spectrometer (EDS) was used. EDS analyses were obtained at 15 kV and 0.6 nA.

3. Results

3.1. Hysteresis loops and thermomagnetic analyses

Hysteresis loops vary significantly with $\chi$ values (Fig. 2). The specimens from the mature S8 paleosol showed the effect of strong pedogenesis with high $\chi$ values >100 x 10$^{-8}$ m$^3$ kg$^{-1}$ and narrower hysteresis loops than those from the pristine loess which had low $\chi$ values around 20 x 10$^{-8}$ m$^3$ kg$^{-1}$. In addition, the loop for the paleosol specimens closes more rapidly than that for the loess specimens. These results, together with higher Ms and Mr and lower Hc and Hcr values in the paleosol than in the loess, support that magnetic enhancement in Chinese paleosols is mainly caused by the in situ produced low coercivity ferrimagnetic minerals.

A $\chi$–T curve is highly sensitive to mineralogical changes during thermal treatments, and has been widely used to identify magnetic minerals in Chinese loess–paleosol studies (e.g., Florindo et al., 1999; Deng et al., 2000, 2006). The $\chi$–T heating curves from the pristine L8 loess and the mature S8 paleosol display a rapid drop in $\chi$ values near 580 °C, and residual $\chi$ values (<5% of their original susceptibility) above 580 °C which continue to decrease slowly up to 680 °C (Fig. 3). These $\chi$–T behaviors indicate that magnetite is a major contributor to the $\chi$ values, and that hematite is a quite minor contributor to the $\chi$ values. Furthermore, the loss in $\chi$ between 300 °C and 450–500 °C, caused by thermal conversion from the pedogenically produced fine-grained maghemite to hematite (Liu et al., 2010), is much larger in the paleosol than in the loess. The result of the $\chi$–T curve, combined with the stratigraphic variations of rock-magnetic parameters (Yang et al., 2010), implies that neoformation of fine-grained maghemite particles accounts for the observed magnetic enhancement in Chinese paleosols.
3.2. SEM observations of magnetic extracts

Magnetic grains were extracted using a neodymium magnet inserted within a glass tube. Preliminary magnetic extractions were conducted using thick solutions of the pristine L8 loess and the strongly pedogenic S8 paleosol dispersed into water. To eliminate adherent nonmagnetic minerals, the extracts were re-dispersed into water, and re-extracted in the same way. The second extracts were used for SEM observations.

The magnetic extracts of the pristine L8 loess tend to be dominated by magnetite grains (Fig. 4a), and have no iron sulfide minerals such as greigite and pyrrhotite which are often observed in lacustrine and marine sediments (e.g., Roberts and Weaver, 2005). The extracted magnetite grains have irregular shapes with different sizes ranging

Fig. 1. A sketch map of loess distribution in central China. The Xifeng section is marked with a star.

Fig. 2. Typical hysteresis loops with correction of paramagnetic contribution for pristine loess L8 (a) and a strongly pedogenic paleosol S8 (b).
from a few μm to several tens of μm. This suggests that they are not pedogenically formed but are of detrital and eolian origin. In addition, these coarse detrital magnetite grains have no obvious oxidized rims (Fig. 4a).

Significantly, the magnetic extracts from the mature S8 paleosol similarly contain eolian coarse-grained detrital magnetite grains that have no obvious oxidized rims, but they unexpectedly also contain coarse-grained silicate minerals (Figs. 4b and c, and 5a and b). Also, the silicate minerals have numerous fine-grained ferrimagnetic inclusions whose grain sizes mainly range from tens to hundreds of nanometers (Figs. 4c and d, and 5c and d). The numerous inclusions of ultrafine ferrimagnetic particles explain why the coarse silicate particles are extracted by a magnet. Such inclusions of ultrafine ferrimagnetic grains within host silicate grains are not observed in the magnetic extracts of the pristine loess (Fig. 4a). Therefore, they were obviously formed by in situ pedogenic processes.

4. Discussion

The Xifeng samples show magnetic parameters such as χ, anhysteretic remanent magnetization (ARM), ARM/saturation isothermal remanent magnetization (SIRM) and natural remanent magnetization (NRM) that are about 4–5 times higher in the strongly pedogenic S8 paleosol than those in the pristine L8 loess (Yang et al., 2010). What causes such magnetic enhancement in paleosols? The results of hysteresis loops (Fig. 2) and χ–T curves (Fig. 3) suggest that magnetic enhancement in the mature S8 paleosol can be attributed to pedogenically formed maghemite grains, which show low coercivity and are thermally decomposed between 300 °C and 450–500 °C. Our SEM observations of magnetic extracts show that the mature paleosol and pristine loess samples both have detrital magnetite grains ranging from a few μm to several tens of μm in size (Fig. 4a and b). However, only the extracts from the mature paleosol contain coarse-grained silicate minerals having inclusions of ultrafine ferrimagnetic grains (Fig. 4c and d). The rock-magnetic results indicate that the inclusions within coarse-grained silicate minerals should be maghemite that has been pedogenically produced (Figs. 2 and 3, and Yang et al. (2010)).
Therefore, the pedogenically formed maghemite inclusions are a potential contributor to the observed magnetic enhancement in the paleosol.

How were the ferrimagnetic inclusions formed within the coarse-grained host silicate minerals? Based on the SEM observations and EDS analyses (Figs. 4 and 5), we propose that they were pedogenically formed by weathering of coarse-grained Fe-bearing paramagnetic silicate minerals, rather than by oxidation of original Fe oxides. The proposed formation mechanism is very consistent with the known weathering process of Fe-bearing silicate minerals such as biotite, chlorite, vermiculite, and amphibole. Murakami et al. (1996) found that chlorite, which is a main silicate mineral in Chinese loess–paleosol sediments (Jeong et al., 2008; Huang et al., 2011), is progressively weathered to vermiculite, and ultimately to kaolinite and fine-grained Fe oxide. Other silicate minerals such as biotite, vermiculite, pyroxene and amphibole, which are also commonly present in Chinese loess–paleosol sediments (e.g., Jeong et al., 2008), usually weather to a variety of clay minerals, admixed with Fe oxide minerals (e.g., Wilson, 2004). The proposed formation mechanism is also consistent with the results of mineralogical investigation of Chinese loess–paleosol sediments. Huang et al. (2011) analyzed the clay mineral transformation of loess from the Wugong section in the southernmost CLP, and showed that the origin of the vermiculite-like minerals in the paleosol S0 could be traced back to both chlorite and illite. Noticeably, Chen et al. (2003) investigated the magnetic extracts of the paleosol S5 from the Luochuan section using transmission electron microscope (TEM), and observed that the ultrafine ferrimagnetic particles, which distribute on the surface of chlorite and contain a small amount of phosphorous and sulfur, originate from the weathering of chlorite. Furthermore, our proposed formation mechanism is consistent with a convincing model of maghemite growth in soils presented by Orgeira et al. (2011). Their model suggests that during the weathering, hydrolysis of primary Fe-bearing minerals could release Fe$^{2+}$ ions which could further oxidate to form poorly crystallized oxyhydroxides (ferrihydrite). During alternating drying/wetting cycles, oxyhydroxides, such as ferrihydrite, could produce ultrafine magnetite and maghemite particles which should lead to magnetic enhancement in soils. Our result together with those reported by Chen et al. (2003) and Huang et al. (2011), as well as the convincing model presented by Orgeira et al. (2011), indicates that the weathering of Fe-bearing silicate releases Fe ions and forms ultrafine Fe oxide minerals during the in situ pedogenic processes, which should be a potential contributor to the magnetic enhancement in Chinese paleosols.

Fine-grained ferrimagnetic inclusions within host silicate minerals as a potential contributor to the magnetic enhancement in Chinese paleosols are also supported by many previous studies that demonstrated that both total $\chi$ (susceptibility of a bulk sample) and magnetic enhancement of Chinese paleosols are mainly contributed by the >0.5 μm sediment fractions (Han and Jiang, 1999; Oldfield et al., 2009). The size of
the sediment fractions should reflect that of the host silicate minerals with the in situ pedogenesis produced fine-grained ferrimagnetic inclusions. Other studies have shown that the coarse sediment fractions of Chinese loess–paleosol sediments contain more detrital magnetite and nonferrous quartz, whereas relatively fine sediment fractions contain more Fe-bearing silicate minerals such as chlorite and amphibole (Zheng et al., 1994). Component differences with differing grain size of the sediment fractions will cause different magnetic enhancement effects, as is confirmed by the mass susceptibility and contribution to the total $\chi$ values of the different fractions in Fig. 6 (data from Han and Jiang (1999)). Quartz particles are nonferrous, and therefore cannot produce ferrimagnets by weathering. Pristine loess sediments undergo only limited pedogenesis and are less affected by magnetic enhancement. Their total $\chi$ values are mainly contributed by detrital magnetite particles which are enriched mainly in the relatively coarser sediment fractions (Fig. 6). On the other hand, in the mature paleosol, the contribution of the >10 $\mu$m sediment fraction to the total $\chi$ value is smaller because the total $\chi$ value was considerably increased by magnetic enhancement in the <10 $\mu$m sediment fractions, as shown by the high mass susceptibility values (170–490 $\times 10^{-8}$ m$^2$ kg$^{-1}$). Obviously, although magnetic enhancement was not small, even in the <0.5 $\mu$m sediment fractions, their contribution to the total $\chi$ value was quite small because the fraction was only a small part of the sediment. These results further support our hypothesis that magnetic enhancement in Chinese paleosols may be attributed to fine-grained ferrimagnetic inclusions within coarse-grained host silicate minerals pedogenically formed from weathering of Fe-bearing paramagnetic silicate minerals.

Finally, we mention the NRM of paleosols, relating to our SEM observation and rock magnetic experiment results. For strongly pedogenic paleosol samples, ThD is useful for isolating a primary remanence component from a NRM, whereas AFD is not (Heller and Liu, 1984; Jin and Liu, 2010; Yang et al., 2010). Because Chinese loess–paleosol sediments include magnetic minerals of eolian and pedogenic origins, their NRM consists of a chemical remanent magnetization (CRM) component mainly carried by pedogenic fine-grained maghemite inclusions and a primary detrital remanent magnetization (DRM) component mainly carried by eolian coarse-grained magnetite. NRMs of strongly-pedogenic paleosols are dominantly contributed by pedogenic fine-grained maghemite. Because pedogenic maghemite particles have coercivities close to or slightly lower than eolian coarse-grained detrital magnetite, AFD is unable to separate the CRM and DRM components. However, a CRM component carried by pedogenic maghemite inclusions can easily be removed by ThD as a result of thermal decomposition between 300 °C and 450–500 °C (Fig. 3, Liu et al. (2010)). After the thermal decomposition, a primary NRM component mainly carried by detrital coarse-grained magnetite (Fig. 4b) remains.

5. Conclusions

$\chi$–T analyses and hysteresis loops, combined with the stratigraphic variations of the rock-magnetic parameters from the Xifeng loess–paleosol sequence (Yang et al., 2010), indicate that magnetic enhancement in Chinese paleosols is mainly caused by the in situ produced fine-grained maghemite minerals.

SEM observations and EDS analyses on magnetic extracts from the pristine L8 loess and the strongly-pedogenic S8 paleosol show that the pedogenic fine-grained ferrimagnetic inclusions within coarse host silicate particles should be a potential contributor to magnetic enhancement in Chinese paleosols. SEM observations also validate that fine-grained ferrimagnetic inclusions mainly range from tens to hundreds of nanometers, and they have been formed by weathering of coarse-grained Fe-bearing host silicate minerals, rather than by oxidation of original Fe oxides.

Our new results are very consistent with the previous rock-magnetic data, the known weathering process of Fe-bearing silicate minerals, and the percentage of different grain-size sediment particles contributing to the total $\chi$ and its enhancement. However, the present data lack the ability to determine quantitatively how the pedogenically produced fine-grained ferrimagnetic inclusions contribute to the total magnetic enhancement. We need further investigations including magnetic extractions, gauging of extraction efficiency, identification of magnetic extractions, quantification of the pedogenically produced fine-grained ferrimagnetic inclusions contributing to the total magnetic enhancement, to justify if the pedogenic fine-grained ferrimagnetic inclusions from weathering of Fe-bearing paramagnetic silicate minerals are responsible for the major magnetic enhancement in Chinese paleosols.

Fig. 6. Mass-normalized $\chi$ of different grain-size sediment fractions, and the percentage contribution of each fraction to the total $\chi$ (susceptibility of a bulk sample) for the loess and paleosol samples. This graph is modified from the results of the Xifeng section reported by Han and Jiang (1999).
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