The different climatic response of pedogenic hematite and ferrimagnetic minerals: Evidence from particle-sized modern soils over the Chinese Loess Plateau

Xinbo Gao a, b, Qingzhen Hao a, b, *, Luo Wang a, b, Frank Oldfield c, Jan Bloemendal c, Chenglong Deng d, b, Yang Song e, Junyi Ge f, b, Haibin Wu a, b, Bing Xu a, b, Fengjiang Li a, b, Long Han a, b, Yu Fu a, b, Zhengtang Guo a, b, g

a Key Laboratory of Cenozoic Geology and Environment, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing, China
b University of Chinese Academy of Sciences, Beijing, China
c School of Environmental Sciences, University of Liverpool, Liverpool, UK
d State Key Laboratory of Lithospheric Evolution, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing, China
e Key Laboratory of Vertebrate Evolution and Human Origins of Chinese Academy of Sciences, Institute of Vertebrate Paleontology and Paleoanthropology, Chinese Academy of Sciences, Beijing, China
g Center for Excellence in Tibetan Earth Sciences, Chinese Academy of Sciences, Beijing, China

ABSTRACT

In recent years, increasing interest in loess studies has focused on qualitative and quantitative paleoclimatic reconstruction using the imperfect antiferromagnetic mineral hematite. However, the linkage between the hematite formation and climatic variables remains controversial. Here we present the results of a comprehensive investigation of the magnetic properties and statistical analysis of a suite of clay and silt fractions of modern soil samples from 179 sites across the Chinese Loess Plateau (CLP) and adjacent regions. Our objective was to clarify the relationships between modern climatic variables and pedogenic hematite, as well as pedogenic ferrimagnetic minerals. First-order reversal curve measurements were also conducted on representative particle-sized subsamples from a N-S transect to understand the differences in magnetic mineralogy between the two fractions. Our results show that pipette extraction separates the fine-grained superparamagnetic (SP) and most of the single-domain (SD) magnetic grains into the clay fraction, and that the remaining silt fraction displays the magnetic properties of coarse pseudo-single domain (PSD) or a mixture of multidomain (MD)/PSD and a few SD particles. Only the pedogenic clay fraction shows a strong correlation with climatic variables. The application of redundancy analysis helps to distinguish the climate variables controlling the formation of ferrimagnetic minerals and hematite during pedogenesis. On the CLP, pedogenic ferrimagnetic minerals are sensitive to mean annual precipitation, while pedogenic hematite formation is preferentially dependent on mean annual temperature. The confirmation of the temperature-dependent nature of hematite on the CLP provides a new possibility for quantitatively reconstructing the paleotemperature history of Chinese loess/paleosol sequences.

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1. Introduction

The direct interaction between soils and climatic conditions makes paleosols an important terrestrial archive of past environmental change, and a potentially powerful resource for quantitative paleoenvironmental and paleoclimatic reconstruction (Sheldon and Tabor, 2009; Tabor and Myers, 2015). On the Chinese Loess Plateau (CLP), the loess/paleosol sequences contain hundreds of paleosol horizons (Liu, 1985; Kukla and An, 1989; Guo et al., 2002; Ding et al., 2002; Hao and Guo, 2007), which are regarded as one of the most important archives of past warm periods (Guo et al., 2009;
Hao et al., 2012b, 2015). Environmental magnetism has played an indispensable role in uncovering the paleoclimatic mysteries recorded in these paleosols (Heller and Evans, 1995; Maher, 2011, 2016), particularly in quantitative paleoclimatic reconstruction (Maher, 1998; Orgeira et al., 2011; Maxbauer et al., 2016, and references therein).

The use of magnetic proxies-based climofunctions in the field of loess research has long focused on ferrimagnetic minerals. Magnetic measurements, in combination with non-magnetic analyses, demonstrated that the neoformation of fine-grained ferrimagnetic minerals during pedogenesis is the fundamental cause of the magnetic enhancement of paleosols intercalated with the loess layers on the CLP (Zhou et al., 1990; Maher and Thompson, 1991; Verosub et al., 1993) and modern soils around the world (Guyodo et al., 2006; Blundell et al., 2009). The positive correlation between magnetic susceptibility ($\chi_m$) of modern soils and mean annual precipitation (MAP) has been observed on the CLP (Lü et al., 1994; Maher et al., 1994). Subsequently, similar relationships between ferrimagnetic proxies of modern soils and MAP have been widely confirmed in the temperate zone of the Northern Hemisphere, such as the CLP (Liu et al., 1995; Han et al., 1996; Xia et al., 2012; Song et al., 2014; Nie et al., 2014), Northern Europe (Maher and Thompson, 1995), the steppe regions of Russia (Maher et al., 2002), the Midwestern United States (Geiss et al., 2008), and North Africa (Lyons et al., 2010; Balsam et al., 2011).

In recent years, there has been increasing interest in exploring the climatic implications of imperfect antiferromagnetic minerals in soils and their quantitative relationships with paleoclimatic conditions (Ji et al., 2001; Balsam et al., 2004; Deng et al., 2006; Hao et al., 2009; Torrent et al., 2010). Hyland et al. (2015) observed a high linear correlation ($R^2 = 0.96$) between the ratio of goethite (G) and hematite (H), $G/H$, and MAP for 70 modern soils worldwide, and suggested that the strong linear relationships can be used to estimate paleoprecipitation values for a wide range of climatic regimes (100–3300 mm/yr). Liu et al. (2013, 2016) established a new climofunction between the precipitation and ratio of frequency-dependent susceptibility ($\chi_{fd}$) and hard isothermal remanence magnetization (HIRM), $\chi_{fd}/\text{HIRM}$, and applied it to reconstruct the temporal variation of the MAP for the last 600 kyr based on the loess/paleosol sequences in Luochuan and Sanmenxia.

Although numerous studies have been carried out on the CLP (Balsam et al., 2011; Maher and Possolo, 2013, and references therein), the dominant climatic factors controlling the formation of ferrimagnetic minerals and hematite during pedogenesis still require further investigation for three reasons. Firstly, although the production of hematite is linked with precipitation in many studies, abundant evidence from in vitro experiments showed that hematite was more temperature-dependent than precipitation-dependent (Schwertmann, 1971, 1985; Torrent and Guzman, 1982; Torrent et al., 1982; Barron and Torrent, 2002; Barrón et al., 2003). Secondly, magnetic signals of the eolian deposits in the CLP region reflect minerals of both pedogenic and detrital origin. It is necessary to further confirm the link between climatic factors and the magnetic properties of the pedogenic minerals. Thirdly, robust statistical approaches need to be introduced in investigations of the relationships between magnetic proxies and climatic variables. As has been demonstrated by Song et al. (2014), it is difficult to discriminate the influence of precipitation and temperature on changes in magnetic properties using the traditional Pearson correlation analysis in the East Asian monsoon region where precipitation and temperature covary.

Various techniques have been employed in isolating the magnetic signals of pedogenic origin. Based on the dust origin of cosmogenic $^{10}$Be, Beer et al. (1993) and Heller et al. (1993) tried to separate detrital and pedogenic contributions to the magnetic susceptibility of Chinese loess. Later, Banerjee et al. (1993) and Liu et al. (1995) applied low-temperature magnetic techniques to quantitative estimation of the superparamagnetic (SP) component of pedogenic origin on the CLP. On the assumption of a constant background value of the detrital component in loess deposits, some studies calculate the absolute differences between magnetic values of magnetically enhanced paleosol and unaltered loess horizons to denote the pedogenic magnetic properties (Maher et al., 1994; Florindo et al., 1999). By contrast, Geiss and Zanner (2007) proposed the ratio $M_{\text{enhanced}}/M_{\text{parent}}$ material named “relative enhancement”, where $M$ represents either anhysteretic remanent magnetization (ARM), isothermal remanent magnetization (IRM) or $\gamma_{IRM}$. Recently, mathematical “unmixing” models (Kruiver et al., 2001; Heslop et al., 2002; Egli, 2003), based on the analysis of the coercivity distribution from IRM acquisition curves or alternating field demagnetization curves, have demonstrated great potential for estimating the pedogenic magnetic component. Other techniques, such as chemical solution (Verosub et al., 1993; Deng et al., 2004) and magnetic extraction (Liu et al., 2003), have also been frequently applied.

In comparison with the above techniques, the pipette method combined with gravitational settling appears to be a powerful tool for separating pedogenic and detrital components in loess/paleosol samples (Zheng et al., 1991; Sartori et al., 2005; Hao et al., 2008, 2009, 2012a,b; Oldfield et al., 2009). The advantage of this approach is that the extracted pedogenic and detrital components can then be subjected to various laboratory measurements. It has been demonstrated that pedogenic ferrimagnets and hematite mainly exist in the clay fraction (Hao et al., 2008, 2009; Oldfield et al., 2009; Torrent et al., 2010). Furthermore, 4 $\mu$m has been suggested as the preferred upper size limit for a more complete representation of the pedogenic component in Chinese loess/paleosol samples (Hao et al., 2008; Oldfield et al., 2009).

In this study, the pipette method was used to separate the clay (<4 $\mu$m) and silt (4–61 $\mu$m) fractions of 179 modern soils from the CLP and adjacent regions. A range of standard environmental magnetic measurements were performed on these two particle-sized fractions. Additionally, first-order reversal curve (FORC) measurements were conducted on 8 representative particle-sized subsamples from a N-S transect to help understand the differences in the magnetic mineralogy of the two fractions. Redundancy analysis (RDA), particularly useful for dealing with variations in biotic communities with varying environmental conditions (Leps and Smilauer, 2003), combined with traditional Pearson correlation analyses, were then used to clarify the relationships between pedogenic ferrimagnetic minerals, hematite and modern climatic factors.

2. Material and methods

2.1. Modern soil samples

Exclusively modern soil samples at 257 sites were taken from the CLP and adjacent regions (Song et al., 2014). Modern soils were typically developed on L0 (the youngest loess layer deposited above Holocene Paleosol S0 on the Chinese Loess Plateau). Every sample site was far away from main roads, farmland, cities, and factories in order to avoid potential contamination. Leaves, roots and small crushed stones were removed in the field. Samples at 2–5 cm beneath the surface in A-horizon (topsoil) were collected. Song et al. (2014) found that 77 bulk samples had abnormal low $\chi_{fd}$, $\gamma_{IRM}$ and S-ratios values. These samples were thought to be affected by contamination from modern human activities or other local factors and were excluded from further statistical analysis. Data from the remaining 180 bulk samples was used for analysis of the
relationships between ferrimagnetic properties and climate parameters.

In this study, we worked on 179 of these 180 bulk samples (Fig. 1), because one sample was not sufficient for particle separation. These samples cover a gradual northwestern to southeastern mean annual rainfall gradient from 150 to 700 mm and a north to south mean annual temperature gradient from 6 to 13 °C.

2.2. Particle separation

We used a diameter of 4 μm as the boundary between pedogenic and detrital components (Hao et al., 2008; Oldfield et al., 2009). Each sample was separated by pipette and wet-sieve methods into three grain-sized fractions: clay (<4 μm), silt (4–61 μm) and sand (>61 μm). I. Before particle separation, the samples were dis-aggregated using excessive buffered acetic acid (2 M, pH 4.5) to remove carbonate. The pretreatment of buffered acetic acid instead of hydrochloric acid avoids significant loss of soft and hard magnetic signals (Hao et al., 2009). II. Each sample was rinsed three times, then transferred to a conical flask and shaken on a recirculating shaker for 24 h after adding 25 mL 0.05 M of Calgon solution. III. The samples were further dispersed ultrasonically for 15 min. IV. Dispersed samples were wet sieved through a 61 μm oxidation-resistant steel sieve and separated into coarse (>61 μm) and fine fractions (<61 μm). V. Fine fractions were transferred to a settling cylinder, and clay and silt particles were separated by the pipette method based on Stokes’ law. More details of the procedures were illustrated in Zheng et al. (1991) and Hao et al. (2009). VI. The pipetted samples were rinsed, centrifuged, and then freeze-dried to avoid any oxidation of iron minerals. The dried separates were weighed and packed for further analysis.

2.3. Magnetic measurements

All of the particle-sized separates in the clay and silt fractions were subject to the following routine magnetic measurements. Material in the size range >61 μm, separated by wet sieve method and mainly composed of sand and plant debris, was not measured, because our main focus was on pedogenic magnetic materials.

Low and high-frequency magnetic susceptibility (χ_{f1} and χ_{f2}) were measured at 470 Hz and 4700 Hz using a Bartington MS2 meter. Frequency-dependent susceptibility, expressed as a mass specific term (χ_{f0}), was obtained from the difference between the measurements at a low and a high frequency and is also expressed as a percentage of χ_{f1}(χ_{f0}%). Note that a summary of the symbols and acronyms used in this paper is given in Table 1.

Anhysteretic Remanent Magnetisation (ARM) was acquired in a peak alternating field of 100 mT with a steady direct biasing field of 0.1 mT using a 2G Enterprises Model 760R cryogenic magnetometer. Values were expressed as ARM susceptibility (χ_{ARM}) after dividing the ARM by the 0.1 mT direct bias field. χ_{ARM} is especially sensitive to the abundance of ferrimagnetic particles within the stable single-domain (SSD) range (~30–50 nm for magnetite) (King et al., 1982; Dunlop and Ozdemir, 1997).

Saturation Isothermal Remanent Magnetization (SIRM) was imparted in a field of 1 T, followed by reverse fields of 40 mT, 100 mT and 300 mT (expressed as −40 mT, −100 mT and −300 mT), using a 2G Enterprises Pulse Magnetizer. All remanence measurements were also made using a 2G Enterprises Model 760R cryogenic magnetometer. Remanence parameters, Soft_{40mT}, Hard_{100mT} and HIRM were calculated following Robinson (1986) and Thompson and Oldfield (1986):

\[
\text{Soft}_{40mT} = 0.5 \times (\text{SIRM} - \text{IRM}_{40mT})
\]

\[
\text{Hard}_{100mT} = 0.5 \times (\text{SIRM} + \text{IRM}_{100mT})
\]

\[
\text{HIRM} = 0.5 \times (\text{SIRM} + \text{IRM}_{300mT})
\]

As with χ_{f1}, χ_{f2} and χ_{ARM}, Soft_{40mT} is often used as an indicator of ferrimagnetic minerals. HIRM is used as a routine parameter and mainly reflects variations in the concentration of hematite with remanence coercivity larger than 300 mT (Robinson, 1986; Thompson and Oldfield, 1986). However, Hu et al. (2013) combining chemical dissolution, diffuse reflectance spectroscopy, and remanence unmixing approaches, stated that pedogenic nanosized hematites exhibit a mean remanence coercivity at about 130 mT in Chinese loess and paleosol samples. Therefore, we also use Hard_{100mT} as an additional parameter for hematite. HIRM and Hard_{100mT} have also been expressed as percentages of SIRM (HIRM % and Hard_{100mT}%). Ratios between individual magnetic parameters: SIRM/χ_{f1}, χ_{ARM}/χ_{f1} and χ_{ARM}/SIRM, have also been used in this study.

First-order reversal curve (FORC) diagrams were measured using a Micromag vibrating sampling magnetometer (VSM 3900). 180 FORCs were measured with a field step of ~0.8 mT for each subsample. FORC diagrams were produced by the FORCinel software (Harrison and Feinberg, 2008).

All of the remanence measurements were made at the Paleomagnetism and Geochronology Laboratory, particle separation and magnetic susceptibility measurements at the Laboratory of Soil Geology and Environment, Institute of Geology and Geophysics, Chinese Academy of Sciences (IGGCAS).

2.4. Meteorological data

Modern meteorological data for a forty-years interval (1951–1990) were obtained from 648 stations of the China Meteorological Administration. Inverse-distance weighting spatial interpolation was used to calculate climatic variables for each sampling site. Five climatic variables were chosen: mean annual precipitation (MAP), mean annual temperature (MAT), mean annual potential evaporation (MAE), mean annual range of temperature (MART) and monthly precipitation variability (MPV). MPV was calculated as

\[
\text{MPV} = \frac{\sum_{i=1}^{12} |X_i - \overline{X}|}{12 \times \overline{X}} \times 100\%.
\]

Song et al. (2014) confirmed that the accuracy of the climatic variables derived from this spatial interpolation was statistically acceptable.

2.5. Statistical analysis

Traditional Pearson correlation analysis and redundancy analysis (RDA), one of the canonical constrained ordination techniques, were employed. Pearson correlation analysis, performed using SPSS statistics 22, provides quantitative estimates of the degree of linear correlation between climatic variables and magnetic properties. RDA was used to investigate multivariate relationships between magnetic properties for the clay and silt fractions and climatic variables.

RDA is essentially a principal component analysis, constrained by the climatic or predictor variables (Legende and Legendre, 1998; ter Braak and Smilauer, 2002). Both of them belong to canonical constrained ordination techniques. RDA allows us to examine the variation in a matrix of response variables (e.g. magnetic proxies) that can be explained by a matrix of predictor variables (e.g. climatic variables) (ter Braak and Prentice, 1988). RDA
Fig. 1. Locations of the 180 modern soil sites on the Chinese Loess Plateau, mean annual precipitation (top) (mm, dashed black line) and mean annual temperature (bottom) (°C, dotted black line) for the interval 1951–1990. Green stars are the selected 8 samples for first-order reversal curve measurements. Green dots are the 6 omitted samples with extremely high HIRM values. The codes of cities are as follows: JB, Jingbian; LC, Luochuan; LZ, Lanzhou; QA, Qinan; SMX, Sanmenxia; TY, Taiyuan; XA, Xi’an; XF, Xifeng; YC, Yinchuan; YL, Yulin; ZZ, Zhengzhou. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
has been widely used in ecology (Leps and Smilauer, 2003), pedology (Ponge et al., 2011; Beaudette and O’geen, 2016), water chemistry (Johnson et al., 1997; Sliva and Williams, 2001) and other geological sciences. RDA was performed on the statistical software CANOCO for Windows 5 (ter Braak and Smilauer, 2002). CANOCO was chosen as it comprises a collection of statistical methods (e.g. linear or unimodal) for data analysis based on the characteristics of the dataset. Prior to analysis, detrended correspondence analysis (DCA) was used to determine the most appropriate analysis method with the longest gradient length (standard deviation units) as the criterion (ter Braak, 1988; ter Braak and Prentice, 1988). Our DCA results for the clay and silt fractions show that the longest gradient lengths are 0.795 and 0.497 respectively, which are less than the critical value of 3.0 (Leps and Smilauer, 2003), and therefore that linear methods (RDA) were appropriate for our datasets.

3. Results and discussion

3.1. Data selection

To remove the effects of possible contamination from modern human activities or local factors, the HIRM values of the clay fraction were evaluated first. HIRM here mainly reflects the variation of hematite. Previous studies demonstrated that the formation of pedogenic ferrimagnetic minerals and hematite is closely related in aerobic soils (Torrent et al., 2006; Hao et al., 2009), and therefore we used a bivariate plot of HIRM versus $\chi_{lf}$ to evaluate the effects of possible contamination or local factors.

Fig. 2 shows the relationship between HIRM and $\chi_{lf}$ in the clay fraction of 179 samples. There is a clear positive correlation between HIRM and $\chi_{lf}$. However, 6 samples show abnormally high HIRM values ($>11 \times 10^{-4}$ Am$^2$/kg). Repeat measurements of these 6 samples excluded the possibility of measurement error. Among these 6 samples, 2 samples were collected from the northeastern margin of the Mu Us desert, and the other 4 samples from the Yellow River valley in the southeastern-most Loess Plateau (Fig. 1). Consequently, additions of local materials to these loessic soils may have made a significant contribution to their high HIRM values. Thus, we excluded these 6 samples from further statistical analysis.

3.2. Spatial patterns of magnetic properties of the clay and silt fractions

Spatial changes in the magnetic properties of the clay and silt fractions for the selected 173 modern soil samples are shown in the form of contour maps in Fig. 3.
Fig. 3. Contour maps of $X_{mf}$,$X_{ARM}$, Soft$_{40mT}$, and HIRM for the clay and silt fractions over the Chinese Loess Plateau. For each magnetic proxy, the consistent scale and color ramp are used for clay and silt fractions, and the color ramp is given in the right side. Black dot curves represent the approximate limits of the Mu Us desert. The codes of cities are as same as Fig. 1.
3.2.1. Ferrimagnetic properties

For ferrimagnetic properties, the clay fraction (Fig. 3a–d) generally exhibits high $\chi_{fr}$, $\lambdaARM$, and $SIRM_{40mT}$ values, with wide variation ranges across the entire region. $\chi_{fr}$ varies from 23.20 to 306.83 $\times 10^{-8}$ m$^3$/kg, $\lambda_{fr}$ from 1.20 to 3187 $\times 10^{-8}$ m$^3$/kg, $\lambda_{ARM}$ from 89.51 to 2351.51 $\times 10^{-8}$ m$^3$/kg and $SIRM_{40mT}$ from 1.37 to 22.58 $\times 10^{-8}$ Am$^2$/kg. Another prominent and consistent feature is the southeastward increasing trend with strong NW-SE gradients. For all the ferrimagnetic properties, steeper gradients are observed in the southernmost part of the Loess Plateau. The steeper gradients are caused by the exponential increase of ferrimagnetic minerals with increasing MAP (e.g., Song et al., 2014).

In contrast, the silt fraction exhibits overall low and somewhat uniform values of ferrimagnetic properties across the CLP (Fig. 3f–i). $\chi_{fr}$ varies from 21.20 to 139.84 $\times 10^{-8}$ m$^3$/kg (mean of 55.03 $\times 10^{-8}$ m$^3$/kg), $\lambda_{fr}$ from 0 to 3.59 $\times 10^{-8}$ m$^3$/kg (mean of 1.32 $\times 10^{-8}$ m$^3$/kg), $\lambda_{ARM}$ from 35.81 to 241.28 $\times 10^{-8}$ m$^3$/kg (mean of 102.18 $\times 10^{-8}$ m$^3$/kg) and $SIRM_{40mT}$ from 1.59 to 10.01 $\times 10^{-8}$ Am$^2$/kg (mean of 3.98 $\times 10^{-8}$ Am$^2$/kg). Contour maps of $\chi_{fr}$ and $SIRM_{40mT}$ even exhibit high values in the margin of the Mu Us desert and the eastern margin of the CLP. 'Bull’s eyes’ in contour maps were commonly the result of extremely high values of ferrimagnetic properties of one or two subsamples. These extreme values in the bull’s eyes and in the eastern margin of the CLP probably reflect the influence of local provenance or geomorphological factors. No obvious increasing trends across the CLP are observed for these ferrimagnetic properties of the silt fraction.

3.2.2. Imperfect antiferromagnetic properties

A bivariate plot of HIRM versus Hard$^{50mT}$ was used to evaluate their validity as indicators of the concentration of hematite in the loessic soils (Fig. 4). In both the clay and silt fractions, the two parameters are near perfectly linearly correlated. This suggests that both parameters yield similar information in reflecting the relative variation of hematite concentration between samples from the Chinese loess deposits.

For imperfect antiferromagnetic properties, the clay fraction exhibits variable HIRM values (Fig. 3e), ranging from 3.89 to 9.97 $\times 10^{-4}$ Am$^2$/kg. Like the ferrimagnetic proxies, the spatial pattern of HIRM is characterized by a generally southeastward increasing trend from NW-SE. The spatial pattern exhibits relatively sparse contour lines in the northern Loess Plateau and dense lines in the southern region. This spatial pattern resembles that of MAT rather MAP with dense contour lines especially in the northwestern region (Fig. 1), which suggests a close relationship between pedogenic hematite reflected by HIRM and MAT over the CLP region.

By contrast, the silt fraction exhibits overall uniform HIRM values across the CLP (Fig. 3j), ranging from 2.44 to 11.83 $\times 10^{-4}$ Am$^2$/kg (4.48 $\times 10^{-4}$ Am$^2$/kg on average). High HIRM values mainly occur in the marginal area of the Mu Us desert, probably as a result of locally derived minerals (Yang et al., 2009; 2011; Hu and Yang, 2016; Zhang et al., 2016).

3.3. Spatial changes in ferrimagnetic grain-size of the clay and silt fractions

To further understand the differences in magnetic mineralogy between the clay and silt fractions, contour maps of frequency percent values and interparametric ratios ($\chi_{fr}$/SIRM, $\lambda_{fr}$/SIRM, $\lambda_{ARM}$/SIRM and $\lambda_{ARM}$/SIRM) are shown in Fig. 5, and FORC diagrams for 8 representative fractioned subsamples on a N-S transect are shown in Fig. 6.

3.3.1. Percentages and interparametric ratios

The percentages and normalized properties used in Fig. 5 eliminate the effects of magnetic concentration variations on magnetic properties and thus provide an effective method of characterizing variations in different magnetic components and in average ferrimagnetic grain size, primarily reflecting the domain status of the magnetic particles (Thompson and Oldfield, 1986; Hunt et al., 1995; Peters and Dekkers, 2003). In practice, the interpretation of these parameters often must be combined with other magnetic parameters because they may be influenced by complex factors. In the present study, the magnetic properties of the clay and silt fractions are mainly controlled by ferrimagnetic minerals, as indicated by their high S-ratio values (0.80–0.95). Consequently, we use these percentages and ratios to evaluate the mean magnetic grain-size.

The clay fraction (Fig. 5a–d) has overall high $\chi_{fr}$% values, low SIRM/SIRM values and high $\lambda_{ARM}$/SIRM and $\lambda_{ARM}$/SIRM values. $\chi_{fr}$% varies from 5% to 10%, SIRM/SIRM from 0.95 to 1.95 $\times 10^4$ A/m, $\lambda_{ARM}$/SIRM from 3.8 to 8.6 and $\lambda_{ARM}$/SIRM from 2.6 to 8.4 $\times 10^{-4}$ m$^3$/kg. The southeastward increasing trend of $\chi_{fr}$% in the northern region (Fig. 5a) implies an increase in the contribution of fine viscous particles around the Single domain (SD)/Superparamagnetic particle (SP) boundary (Dearing et al., 1996). $\lambda_{ARM}$ reaches maximum values in the main area of the CLP implying a relatively uniform grain-size distribution (GSD) of fine viscous particles around the SD/SP boundary (Worm, 1998; Worm and Jackson, 1999). Relatively low SIRM/SIRM ratios (Fig. 5b) in the clay fraction (0.95–1.95 $\times 10^4$ A/m) can also be ascribed to high concentrations of viscous SP particles (Fig. 5a) (Hunt et al., 1995). High values of $\lambda_{ARM}$/SIRM and $\lambda_{ARM}$/SIRM (Fig. 5c and d) in the clay fraction (3.8–8.6 for $\lambda_{ARM}$/SIRM and 2.6–8.4 $\times 10^{-4}$ m$^3$/kg for $\lambda_{ARM}$/SIRM) are indicative of a high concentration of SD particles which are more efficient at acquiring remanence, particularly ARM (Banerjee et al., 1981; King et al., 1982; Maher, 1988). The most prominent feature of the spatial patterns for these properties is that all the percentages and ratios exhibit near uniform values in the area south of 37°–38°N, the main area of the CLP, which indicates almost uniform GSD for the clay fraction in the main area of the CLP.

In comparison with the clay fraction, the silt fraction has overall low $\chi_{fr}$% values, high SIRM/SIRM values and low $\lambda_{ARM}$/SIRM and $\lambda_{ARM}$/SIRM values (Fig. 5e–h). $\chi_{fr}$% varies from 0 to 5%, SIRM/SIRM from 1.15 to 2.1 $\times 10^4$ A/m, $\lambda_{ARM}$/SIRM from 0.9 to 2.9, and $\lambda_{ARM}$/SIRM from 0.8 to 2.3 $\times 10^{-4}$ m$^3$/kg. The spatial patterns of $\chi_{fr}$%, SIRM/SIRM, $\lambda_{ARM}$/SIRM and $\lambda_{ARM}$/SIRM are broadly similar, and all characterized by relatively lower values in the region of the Mu Us desert and generally uniform values in the main area of the CLP. Significantly low $\chi_{fr}$% values (0–5%, mean of 2.39%) indicate the dominant contributions from the nearly frequency-independent coarser particles. In addition, low ratios of $\lambda_{ARM}$/SIRM and $\lambda_{ARM}$/SIRM in the silt fraction (0.9–2.9 for $\lambda_{ARM}$/SIRM and 0.8–2.3 $\times 10^{-4}$ m$^3$/kg for $\lambda_{ARM}$/SIRM) further demonstrate that coarse-grained pseudo-single domain (PSD)/multidomain (MD) ferrimagnetic minerals dominate the magnetic assemblages of the silt fraction.

3.3.2. First-order reversal curves

In recent years, FORC diagrams have been used increasingly as they have significant advantages for discriminating the domain status of magnetic particles, the coercivity, and magnetic interaction field distributions (Roberts et al., 2014, and references therein). Here, FORC measurements were carried out on 8 representative samples selected from the Mu Us desert in the north to the southern margin of the CLP (Fig. 1). This N-S transect covers a gradual annual rainfall gradient from 278.6 to 601.1 mm, and an annual temperature gradient from 7.8 to 12.2°C. Fig. 6 shows the FORC diagrams for 4 of the 8 representative particle–sized samples selected from the N-S transect.

For the clay subsamples (Fig. 6a–d), the tightly closed contours
with a central ridge along the \( H_c \) axis and a negligible vertical spread indicate the presence of magnetically non-interacting SD particles (Carvallo et al., 2004; Egli et al., 2010; Roberts et al., 2014). The appearance of the secondary peaks at the origin of the FORC diagrams (Fig. 6b–d) is interpreted as a hallmark of SP particles, as is further verified by the vertical contours near the \( H_c \) axis in the lower left-hand region of the FORC diagrams (except for MS-77) (Roberts et al., 2000; Pike et al., 2001). These results agree well with the environmental magnetic properties (Fig. 5a–d) and confirm that particle separation procedures successfully isolate the SP and SD particles into the clay fraction.

For the silt subsamples (Fig. 6e–h), the closed inner contours and the divergent outer contours are the characteristics of typical PSD grains, or a mixture of SD + MD grains (Roberts et al., 2000; Muxworthy and Dunlop, 2002; Smirnov, 2006). On the transect, there is a trend with the southern samples containing increased contributions of SD particles, as indicated by narrowed and prolonged closed inner contours. These are essentially consistent with the weakly southward increase in \( \chi_{\text{ARM}}/\mu_0 \) and \( \chi_{\text{ARM}}/\text{SIRM} \) ratios (Fig. 5g and h). Additionally, small peaks at the origin of the FORC diagrams for MS-50 and MS-38 probably result from the influence of fine viscous SP particles. It should be noted that concentration of SD and SP particles is much lower in the silt fraction than in the clay fraction; for example, the values of \( \chi_{\text{ARM}} \) of the silt fraction is one order of magnitude lower of the clay fraction in the main CLP region (Fig. 3c–h). Therefore, we attribute the behavior of SP and SD particles to the effects of low-temperature oxidation (LTO) of coarse magnetite, which has been detected frequently in Chinese loessic soils (Deng et al., 2001; Liu et al., 2003; Chen et al., 2005; Hao et al., 2012a,b). However, the possibility of contamination from finer grades cannot be excluded completely.

In summary, the above magnetic properties indicate that the ferrimagnetic mineral assemblage of the clay fraction mainly consists of fine-grained SD + SP particles, and in contrast, the dominant magnetic component of the silt fraction is coarser PSD and/or a mixture of SD and PSD/MD particles. These lines of evidence confirm that particle separation of loessic samples at a diameter of 4 \( \mu \)m provides a practical means of separating the magnetic minerals of pedogenic and detrital origin (Hao et al., 2008; Oldfield et al., 2009).

3.4. Correlation of magnetic properties of pedogenic and detrital components with those of bulk samples

Successful separation of magnetic minerals of pedogenic and detrital origin in the loessic soils provides an opportunity to evaluate the environmental implications of routine environmental magnetic parameters of bulk samples. In Chinese loess studies, \( \chi_{\text{HI}} \), ARM, IRM, and HIRM are frequently used to reconstruct changes in the East Asian summer monsoon, and it is generally thought that these proxies mainly reflect the products of pedogenic processes. It has been found, however, that the detrital fraction is responsible for a significant proportion of the signals of high-coercivity magnetic minerals (Hao et al., 2009, 2012a). This points to the need to test statistically whether the measurements of bulk samples provide information of clear environmental significance.

Fig. 7 shows the correlation of the magnetic properties of the clay and silt fractions with those of bulk samples of 173 modern soils on the CLP. In all cases, the horizontal axis gives the results of bulk samples (Song et al., 2014), and the vertical axis gives the results of clay and silt fractions.

For ferrimagnetic properties (Fig. 7a–c), both \( \chi_{\text{HI}} \), \( \chi_{\text{ARM}} \), and \( \text{Soft}_{40\text{mT}} \) for the clay fraction exhibit significant and positive linear correlations with those for bulk samples (\( R^2 = 0.90, P < 0.001, n = 173 \) for \( \chi_{\text{HI}} \); \( R^2 = 0.93, P < 0.001, n = 173 \) for \( \chi_{\text{ARM}} \); and \( R^2 = 0.84, P < 0.001, n = 173 \) for \( \text{Soft}_{40\text{mT}} \)), whereas those for the silt fraction exhibit a poor correlation (\( R^2 = 0.05, P < 0.005, n = 173 \) for \( \chi_{\text{HI}} \); \( R^2 = 0.32, P < 0.001, n = 173 \) for \( \chi_{\text{ARM}} \); and \( R^2 = 0.26, P < 0.001, n = 173 \) for \( \text{Soft}_{40\text{mT}} \)). The weak positive correlation of the ferrimagnetic properties for the silt fraction with those for bulk samples may result from the effects of LTO or contamination from the clay fraction during the pipette procedure. In any case, much lower absolute values with small spatial changes (Fig. 3) allow them to be treated as background values. These features further demonstrate that the spatial variations of ferrimagnetic properties for bulk samples are predominantly controlled by the clay fraction, and thus, ferrimagnetic properties of bulk samples can be used to reflect variations in the concentration of pedogenic ferrimagnetic minerals.

For imperfect antiferromagnetic properties (HIRM) (Fig. 7d), the situation is rather different. Both the clay and silt fractions exhibit a poor correlation with bulk samples (\( R^2 = 0.34, P < 0.001, n = 173 \) for...
Fig. 5. Contour maps of the normalized percentages and interparametric ratios for the clay and silt fractions over the Chinese Loess Plateau. For each magnetic proxies, the consistent scale and color ramp are used for clay and silt fractions, and the color ramp is given in the right side. Black dot curves represent the approximate limits of the Mu Us desert. The codes of cities are as same as Fig. 1.
Fig. 6. FORC diagrams for 4 of 8 representative subsamples on a N-S transect (a-d, clay subsamples; e-h, silt subsamples). In all FORC diagrams, 180 FORCs were measured, averaging time is 0.5 s, and field step is 0.8 mT. Please note the different scales of Hu-axis and Hc-axis are used for clay and silt fractions.
3.5. The different climatic response of pedogenic ferrimagnetic minerals and imperfect antiferromagnetic hematite

The clay and silt fractions exhibit a different relationship with climatic variables. Table 2 summarizes the Pearson’s correlation coefficients between magnetic properties and climatic variables (MAP, MAT, MAE, MART, MPV) for the clay and silt fractions. The absolute values of correlation coefficients are much higher for the clay fraction than for silt fraction. For the clay fraction, both MAP and MAT are positively correlated with the magnetic parameters $c_{\text{cl}}$, $c_{\text{fd}}$, $c_{\text{ARM}}$, $\text{Soft}_{40\text{mT}}$, and HIRM, and the correlations are significant at the 0.01 level. However, MAE, MART, and MPV are negatively correlated with these magnetic parameters, except for the positive correlation between HIRM, $c_{\text{ ARM}}$, and MAE. The absolute values of the correlation coefficients are much higher between magnetic parameters and the climatic variables MAP, MAT, and MPV. These results further confirm the dominant role of climate in the production of magnetic minerals in the loess sequences of the CLP.

Additionally, the correlation coefficients between the ferrimagnetic proxies ($\chi_{\text{ARM}}$, $\text{Soft}_{40\text{mT}}$, SIRM) and modern MAP are almost same for the clay fraction and bulk samples (Song et al., 2014), indicating the validity of using the ferrimagnetic proxies of bulk samples in quantitative climate reconstruction.

Unlike the clay fraction, absolute correlation coefficients are much lower for the silt fraction. The correlation for several
parameters, such as $\chi_{ll}$ and Hard$_{100mT}$, is not significant at the 0.01 probability level. For the correlation significant at the 0.01 level, ferrimagnetic parameters are generally positively correlated with MAP, MAT, and negatively correlated with MAE, MART, and MPV. HIRM is negatively correlated with MAP, MART and positively correlated with MAE. The positive correlations of ferrimagnetic properties of silt fraction with climatic variables support the hypothesis that the southward increase of SP and SD particles in the silt fraction may be partly induced by LTO.

Another remarkable result is that for the clay fraction, the antiferromagnetic properties exhibit a different response to MAP and MAT than the ferrimagnetic properties. The ferrimagnetic properties consistently have higher correlation coefficients with MAP than those with MAT (Table 2). In contrast, the antiferromagnetic properties have slightly higher correlation coefficients with MAT than MAP; i.e., for Hard$_{100mT}$ versus MAP and MAT, the correlation coefficients are 0.419 and 0.561, respectively, and for HIRM versus MAP and MAT, they are 0.346 and 0.582, respectively. For the covariance of MAP and MAT over the CLP, it is difficult to judge whether these small differences in correlation coefficients are meaningful. Further statistical analyses are needed to investigate the relationships between different magnetic proxies and climatic variables.

RDA further quantifies the complex and covarying effects of climate on magnetic properties. RDA was performed using 5 climatic variables (MAP, MAT, MAE, MART, and MPV) and 8 magnetic parameters ($\chi_{ll}$, $\chi_{dl}$, ARM, Soft$_{40mT}$, HIRM, Hard$_{100mT}$, HIRM%, and Hard$_{100mT}$%). The two important outputs from RDA are: (1) the correlation matrix of climatic variables with the RDA axes; (2) the fraction of each climatic variable that is explained by the RDA axes (Jongmann et al., 1995). The RDA ordination diagram or RDA ‘Biplot’ is a standard method of presenting results from RDA. The RDA biplot displays the response variables (magnetic proxies) and predictor variables (climatic variables) as arrows. In the present study, all magnetic variables were square-root transformed and centered during RDA analysis. The relative lengths of these arrows are approximately proportional to the rate of change in that direction. The correlation between magnetic proxies and climatic variables is approximately equal to the cosine of the angle between corresponding arrows. An acute angle (<90°) means a positive correlation, and the smaller the angle, the stronger the positive correlation. An obtuse angle (>90°) indicates a negative correlation. A right angle (90 or 270°) means minimum correlation with arrows perpendicular to each other (Leps and Smilauer, 2003).

Table 3 summarizes the results of the RAD analysis for the clay and silt fractions. For the clay fraction, the first two RDA axes (Axis 1 and Axis 2) cumulatively captured 69.1% of the total magnetic data and 86.5% of the total magnetic variation. The absolute values (>0.61) of the inter-set correlation of significant environmental variables with axes indicate that MAP, MAT, MART, and MPV are strongly correlated with RDA Axis 1. In contrast, RDA Axis 2 did not correspond to any interpretable variable. However, three temperature-related variables, MAT, MAE and MART, are most strongly associated with RDA Axis 2, having absolute values varying from 0.15 to 0.27.
For the silt fraction, the first two RDA axes (Axis 1 and Axis 2) collectively captured just 12.6% of the variance of the magnetic data. This poor inter-set correlation between the 8 magnetic variables and the 5 environmental factors rendered it unnecessary for further analysis. However, the RDA biplot for the silt fraction is also given in Fig. 9b.

Table 3
Summary statistics for the first 4 axes of RDA for the clay and silt fractions, with 8 magnetic variables and 5 climatic variables.a

<table>
<thead>
<tr>
<th></th>
<th>Axis 1</th>
<th>Axis 2</th>
<th>Axis 3</th>
<th>Axis 4</th>
<th>Total variance</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Clay fraction,</strong> n = 173</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Eigenvaluesa</td>
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<td>0.001</td>
<td>0.000</td>
<td>0.000</td>
<td>1.000</td>
</tr>
<tr>
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<td>0.395</td>
<td>0.277</td>
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<td></td>
</tr>
<tr>
<td>Cumulative percentage variance of species data</td>
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<td>0.690</td>
<td>0.691</td>
<td>0.691</td>
<td></td>
</tr>
<tr>
<td>of species-environment relation</td>
<td>99.9</td>
<td>99.9</td>
<td>100.0</td>
<td>100.0</td>
<td></td>
</tr>
<tr>
<td>Sum of all eigenvalues</td>
<td>0.0329</td>
<td>0.4911</td>
<td>0.0374</td>
<td>0.0269</td>
<td></td>
</tr>
<tr>
<td>Sum of all canonical eigenvalues</td>
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<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td></td>
</tr>
<tr>
<td>Inter-set correlation of significant environmental variables with axes</td>
<td>−0.0813</td>
<td>0.0157</td>
<td>−0.0475</td>
<td>−0.0464</td>
<td></td>
</tr>
<tr>
<td>MAP</td>
<td>−0.7088</td>
<td>−0.1479</td>
<td>0.0992</td>
<td>−0.0194</td>
<td></td>
</tr>
<tr>
<td>MAT</td>
<td>0.3583</td>
<td>−0.2708</td>
<td>0.0660</td>
<td>−0.0803</td>
<td></td>
</tr>
<tr>
<td>MAE</td>
<td>0.6150</td>
<td>−0.2083</td>
<td>−0.0382</td>
<td>−0.0081</td>
<td></td>
</tr>
<tr>
<td>MPV</td>
<td>0.7098</td>
<td>0.1140</td>
<td>−0.0324</td>
<td>−0.0786</td>
<td></td>
</tr>
<tr>
<td><strong>Silt fraction,</strong> n = 173</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Eigenvaluesa</td>
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<td>0.040</td>
<td>0.001</td>
<td>0.000</td>
<td></td>
</tr>
<tr>
<td>Species-environment Correlations</td>
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<td>0.152</td>
<td>0.166</td>
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<tr>
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<tr>
<td>of species-environment relation</td>
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<td>99.8</td>
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<td></td>
</tr>
<tr>
<td>Sum of all eigenvalues</td>
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<td>0.3583</td>
<td>0.0803</td>
<td>0.0492</td>
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</tr>
<tr>
<td>Sum of all canonical eigenvalues</td>
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<td>0.8013</td>
<td>0.0183</td>
<td>0.0081</td>
<td></td>
</tr>
<tr>
<td>Inter-set correlation of significant environmental variables with axes</td>
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<td>−0.4911</td>
<td>0.0374</td>
<td>−0.0269</td>
<td></td>
</tr>
<tr>
<td>MAP</td>
<td>0.0442</td>
<td>−0.3882</td>
<td>0.0839</td>
<td>0.0462</td>
<td></td>
</tr>
<tr>
<td>MAT</td>
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<td>0.3048</td>
<td>0.1011</td>
<td>0.0505</td>
<td></td>
</tr>
<tr>
<td>MAE</td>
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<td>0.3868</td>
<td>0.0275</td>
<td>−0.0554</td>
<td></td>
</tr>
<tr>
<td>MPV</td>
<td>−0.1018</td>
<td>0.4228</td>
<td>0.0159</td>
<td>−0.0782</td>
<td></td>
</tr>
</tbody>
</table>

a MAP = mean annual precipitation; MAT = mean annual temperature; MAE = mean annual potential evaporation; MART = mean annual range of temperature; MPV = monthly precipitation variability.

For the silt fraction, the first two RDA axes (Axis 1 and Axis 2) collectively captured just 12.6% of the variance of the magnetic data. This poor inter-set correlation between the 8 magnetic variables and the 5 environmental factors rendered it unnecessary for further analysis. However, the RDA biplot for the silt fraction is also given in Fig. 9b.

Fig. 9a shows the RDA ordination diagram for the clay fraction. The concentration-dependent ferrimagnetic proxies (MPV, ARM and Soft40mT) are all clustered in a narrow range, which reflects their similarity in characterizing the variation of ferrimagnetic minerals. Like the case of the ferrimagnetic proxies, the clustering of HIRM and Hard100mT in a narrow range also suggests their similarity in characterizing the variation of hematite.

In the RDA ordination diagram (Fig. 9a), the arrows of ferrimagnetic proxies and MAP have small acute angles, compared with a large angle for MAT. This indicates the strong control of MAP on the ferrimagnetic properties, instead of MAT. Our results further demonstrate that the production of ferrimagnetic minerals during pedogenesis depends mainly on mean annual precipitation (Maher et al., 1994, 2003; Han et al., 1996; Geiss et al., 2008; Song et al., 2014).

In contrast, HIRM and Hard100mT, which mainly reflect the variation of hematite, remain closed to MAT, and away from MAP (Fig. 9a). This indicates that MAT, rather than MAP, is the dominant controlling factor for the production of hematite. Therefore, RDA analysis and Pearson’s correlation analysis both indicate that the production of pedogenic hematite is more dependent on mean annual temperature, while the production of pedogenic ferrimagnetic minerals, is more dependent on mean annual precipitation on the CLP.

The concentration-dependent ferrimagnetic proxies (MPV, ARM and Soft40mT) are all clustered in a narrow range, which reflects their similarity in characterizing the variation of ferrimagnetic minerals. Like the case of the ferrimagnetic proxies, the clustering of HIRM and Hard100mT in a narrow range also suggests their similarity in characterizing the variation of hematite.

However, the remanent magnetization of hematite is two orders of magnitude lower than that of magnetite/maghematite. Consequently, HIRM% and Hard100mT% decrease along with magnetic enhancement of ferrimagnetic minerals, which are mainly controlled by MAP in the CLP region.

Fig. 10 presents the correlation of HIRM and Hard100mT for the clay fraction of 173 samples with modern climatic factors (MAT and MAP). It is evident that the pedogenic hematite content on the CLP is closer linked with MAT than MAP. Overall, a moderate correlation can be observed between HIRM, Hard100mT and MAP (R² = 0.34, P < 0.001, n = 173 for HIRM vs MAT; R² = 0.31, P < 0.001, n = 173 for Hard100mT vs MAT). However, a poor correlation is obtained between HIRM, Hard100mT and MAP (R² = 0.12, P < 0.001, n = 173 for HIRM vs MAP; R² = 0.18, P < 0.001, n = 173 for Hard100mT vs MAP). It is well known that the clay fraction contains hematite of eolian origin, as also indicated by the HIRM values of samples in the northern margin of the CLP (Fig. 3e). However, it appears that the influence of sedimentary sorting on clay-sized sediments during the wind transportation are not significant (Peng et al., 2016), and the concentration of hematite in clay fraction should not exhibit spatial changes caused by sedimentary sorting. This allows the eolian input of hematite to be treated as background values. Therefore, the linear relationship between MAT and HIRM or Hard100mT opens up the new possibility of using these magnetic properties to quantitatively reconstruct paleotemperatures.
3.6. The production and transformation of magnetic minerals during pedogenesis

The mechanism of production and transformation of magnetic minerals in natural environments has been studied for at least half a century (Feitknecht and Michaelis, 1962; Schwertmann, 1966; Chukhrov et al., 1973). Schwertmann (1985) and Cornell and Schwertmann (2003) made detailed reviews of the occurrence and formation of iron oxides in various pedoenvironments. From this previous work, the production under ambient conditions of hematite, mainly from the precursor ferrihydrite, has been clearly demonstrated. However, the origin of ferrimagnetic minerals under natural pedogenesis remains controversial. In loess research, two views regarding the production and transformation route of pedogenic ferrimagnetic minerals and hematite have been widely accepted. Maher (1998) proposed a divergent pathway. This model suggests that a wet season with periodically reducing conditions will lead to the formation of fine-grained ferrimagnetic magnetite, and that a dry season with oxidizing conditions will result in the rapid oxidation of the fine-grained magnetite to maghemite and then to hematite. The iron in the formation of maghemite results, in part, from the dissolution of hematite and goethite, and the initial magnetite is commonly oxidized to maghemite. Later, a completely competitive equilibrium between the formation of pedogenic ferrimagnets and hematite. Intermittent wetting and drying of soils favor magnetite formation and Fe3+-oxide dissolution, whilst drying favors Fe3+-oxide formation at the expense of the neoformed ultrafine maghemite (Maher, 1998). In the CLP region, however, modern soils show a southeastward increase in the concentration of pedogenic hematite (Fig. 3e), with a decrease in dryness as shown by modern meteorology (Fig. 1). It is still an open question whether intermittent drying during the rainy season is sufficient for the transformation of magnetite to hematite.

The statistical analysis of ferrimagnetic properties and climatic variables indicates that precipitation is the primary control on the formation of ferrimagnetic minerals in soils on the CLP. This is in accordance with the above views on the two pathways of ferrimagnetic enhancement. In both pathways, the prerequisite is that free Fe2+ is primarily released by the weathering of iron-containing silicates, such as chlorite (Spassov et al., 2003; Peng et al., 2014) and probably partly by the dissolution of goethite and hematite (Maher, 1998; Cornell and Schwertmann, 2003). The MAP of the CLP region is dominated by summer precipitation, and shows a southeastward increase (Fig. 1). In the southern region, the enhanced soil water caused by the increase in precipitation is not only conducive to the decomposition of iron-bearing silicates, but also to the formation of sufficient absorbing ligands and organic acids. It is generally accepted that the absence or limited presence of absorbing ligands and organic acids may result in the direct crystallization of goethite, which in turn prevents the accumulation of magnetite or maghemite (Schwertmann, 1985; Cornell and Schwertmann, 2003). According to the second pathway of magnetic mineral formation, sufficient absorbing ligands and organic acids may not only accelerate the transformation from ferrihydrite to maghemite (Schwertmann, 1985; Barron and Torrent, 2002; Barrón et al., 2003), but may also strongly impede the direct transformation from ferrihydrite to hematite (Cabello et al., 2009; Michel et al., 2010; Gutiérrez et al., 2016) and thereby favor the accumulation of maghemite in loessic soils on the CLP. Therefore, an increase in precipitation over the CLP mainly leads to the enhancement of ferrimagnetic signals.

More importantly, this study shows that temperature plays the predominant role in the formation of hematite in loessic soils on the CLP in the temperate climate regime. Laboratory conditions with pH at ~7.5 favor the formation of hematite (Maher, 2007). pH values ranging from 6.5 to 8.7 of the modern soils from the CLP are close to this optimum condition. For the production of hematite, the two pathways both emphasize a prolonged dry season favoring the formation of hematite (Maher, 1998; Torrent et al., 2006, 2010). Based on changing concentrations of hematite and goethite in both the Luochuan and Lingtai loess sections of the CLP, Balsam et al. (2004) also suggested that moderate dry conditions with MAP of ~350–450 mm favor the production of hematite. In the first pathway, the variation in magnetic properties is influenced by a competitive equilibrium between the formation of pedogenic ferrimagnets and hematite. Intermittent wetting and drying of soils favor magnetite formation and Fe3+-oxide dissolution, whilst drying favors Fe3+-oxide formation at the expense of the neoformed ultrafine maghemite (Maher, 1998). In the CLP region, however, modern soils show a southeastward increase in the concentration of pedogenic hematite (Fig. 3e), with a decrease in dryness as shown by modern meteorology (Fig. 1). It is still an open question whether intermittent drying during the rainy season is sufficient for the transformation of magnetite to hematite. Statements supporting the temperature-dependent nature of hematite formation mainly come from proponents of the second pathway (Barron and Torrent, 2002; Torrent et al., 2006, 2010). Enhanced soil temperature favors transformation of maghemite to hematite (Torrent et al., 2010), and also promotes the formation of hematite directly by dehydration and rearrangement within ferrihydrite aggregates (Schwertmann, 1985). Therefore, contrary to the case of ferrimagnetic minerals, ambient temperature is the dominant climatic factor influencing the formation of hematite in the loessic soils on the CLP.

The observation of the temperature-dependent nature of pedogenic hematite formation in this study is consistent with previous in vitro experiments and studies of natural materials. In...
earlier in vitro experiments, Torrent et al. (1982) found that with decreasing humidity and increasing temperature relatively more hematite formed. Synthetic experiments of ferrihydrite-hydromaghemite-hematite revealed that transformation of intermediate hydromaghemite to hematite is more dependent on temperature (Barron and Torrent, 2002; Cabello et al., 2009; Michel et al., 2010). In natural soil studies, an overall positive correlation has been observed between the ratio of hematite/(hematite + goethite) and temperature for soils from both south Brazil (Kämpf and Schwertmann, 1983) and southern Germany (Schwertmann et al., 1982). Moreover, Schwertmann (1985) suggested that warm and dry soil environments favor the formation of reddish soils, in which pedogenic nano-sized hematite is usually the major pigment mineral. After comparison of the hematite content of soils from the CLP, southern Spain and the Cerrado region in Brazil, Torrent et al. (2010) found that the ratio of hematite concentration, determined by the diffuse reflectance spectroscopy method, and frequency dependent magnetic susceptibility overall increases with increasing MAT.

Fig. 10. Correlation between antiferromagnetic proxies (HIRM and Hard_{100mT}) of the clay fraction and climatic variables (MAT and MAP).

However, paleotemperature reconstruction has been seriously restricted by the lack of reliable indices. Until now, only biological proxies have been used to shed light on this issue, such as phytoliths (Wu et al., 1994; Lü et al., 1996), lipid molecular fossils (Zeng et al., 2011; Xie et al., 2003) and bacterial tetraethers (Peterse et al., 2011; Jia et al., 2013). Our study convincingly demonstrates that the hematite production during pedogenesis is more dependent on temperature, instead of precipitation on the Chinese Loess Plateau. This finding provides a new way of using pedogenic hematite to quantitatively reconstruct paleotemperature, which has long been a difficult task in paleoclimatic reconstruction based on loess/paleosol studies.

4. Conclusions

This study used the pipette and wet-sieve methods to separate modern soil samples at 179 sites across the Chinese Loess Plateau into three fractions: clay (<4 μm), silt (4–61 μm) and sand (>61 μm). From a comprehensive study of the magnetic properties of the clay and silt fractions, and statistical analysis of modern climatic variables and magnetic properties of 173 subsamples (6 subsamples are excluded for the possible contamination or local
factors), we make the main following conclusions:

1. This study confirms that separation of loess samples at a grain diameter of 4 μm using pipette and gravitational settling methods provides a practical way to separate the magnetic minerals of pedogenic and detrital origin. The magnetic assemblage of the clay fraction of the 173 modern soils is characterized by fine-grained ferrimagnets, i.e., SD + SP maghemitte or magnebite, while the magnetic assemblage of the silt fraction consists of coarser PSD and/or a mixture of SD and PSD/MD magnetite, which has been altered by various degree of low-temperature oxidation.

2. The ferrimagnetic properties of bulk samples are predominantly controlled by the pedogenic clay fraction. For antiferromagnetic properties, however, the detrital silt fraction makes a dominant contribution to the HIRM of bulk samples across the CLP. Thus, great caution must be used in using the HIRM of bulk samples to characterize variations in the concentration of pedogenic hematite.

3. Redundancy analysis together with Pearson correlation analysis indicates different climatic response of pedogenic ferrimagnetic minerals and imperfect antiferromagnetic hematite on the Chinese Loess-Plateau. The formation of ferrimagnetic minerals of pedogenic origin mainly depends on mean annual precipitation. However, the pedogenic hematite is predominantly controlled by mean annual temperature. High ambient temperature favors the production of hematite, probably through promoting the transformation of maghemite to hematite, as well as directly from ferrihydrite to hematite.

4. This study makes clear the temperature-dependent nature of hematite formation during pedogenesis in the CLP region, providing a basis for paleotemperature reconstruction with a sound physico-chemical explanation. The study thus offers the possibility of using pedogenic hematite to quantitatively reconstruct paleotemperature changes recorded in the long loess-soil sequences of the late Cenozoic from the CLP.

Acknowledgments

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