Different Enrichment Patterns of Magnetic Particles Modulated by Primary Iron-Phosphorous Input

Juan Ren1, Xiaoyong Long1, Junfeng Ji2, Vidal Barrón3, José Torrent3, Yong Wang1, and Shiyou Xie1

1School of Geographical Sciences, Southwest University, Chongqing, China, 2Institute of Surface Geochemistry, College of Earth Sciences and Engineering, Nanjing University, Nanjing, China, 3Departamento de Agronomía, Universidad de Córdoba, Córdoba, Spain

Abstract Magnetic particles associated with iron (Fe) oxides are widespread on the surface of Earth and Mars and serve as reasonable climatic indicators. Ferrimagnetic maghemite (Mgh) and antiferromagnetic hematite (Hm), which dominate magnetism and redness, often coexist or compete with each other in soils and sediments. The formation efficiency of Mgh relative to Hm could be modulated by geochemical background besides climate, especially by phosphate (P), which has a high affinity for the surfaces of precursor iron oxides in natural systems. We investigated two Ferralsol sequences around a P mining field with similar climates and contrasting P/Fe ratios. High P/Fe ratios retard iron oxide crystallization, grain growth, and transformation into Hm, thereby promoting more effective accumulation of ferrimagnetic Mgh as an intermediate product. The lack of ligand-protected effects well interprets asynchronous changes in magnetism and redness in soils and sediments across large spatiotemporal scales, especially in highly weathered soils.

Plain Language Summary Iron oxides are critical carriers of magnetism and dyeing agents of soils and sediments. The concentration of pedogenic maghemite (Mgh) and hematite (Hm), which dominate magnetism and redness, is considered to be controlled by the primary iron input and climate conditions. However, phosphate exhibits a high affinity for the surfaces of precursor iron oxides, especially in highly weathered soils. We investigated two Ferralsol sequences around a P mining field with contrasting P/Fe ratios but similar climates. High P/Fe ratios are observed to impede iron oxide crystallization, grain growth, and transformation into Hm, thereby promoting more effective accumulation of ferrimagnetic Mgh as an intermediate product. The presence and absence of ligand-protected effects help explain asynchronous changes in magnetism and color in nature systems across large spatiotemporal scales.

1. Introduction

Magnetic particles associated with pedogenic iron oxides are ubiquitous on the surface of Earth and Mars as the preferential weathering product of Fe-bearing minerals (Christensen et al., 2001). Magnetic particles can be divided into ferrimagnetic (FM) and antiferromagnetic (AFM) particles. The FM particles, mainly maghemite (Mgh, γ-Fe2O3) and magnetite (Mgt, Fe3O4), often dominate magnetism, although they contribute a low weight to the total amount of iron oxides in soils and sediments (Liu et al., 2012). On the other hand, AFM particles include hematite (Hm, α-Fe2O3) and goethite (Gt, α-FeOOH), which are the main red and yellow color agents, respectively, in soils and sediments (Cornell & Schwtermann, 2003).

In past decades, the magnetic properties determined by the content and ratio of FM particles with differing sizes have widely been employed as climatic proxies in paleoclimate reconstruction, especially with Quaternary loess and Tertiary red clay deposited on the Chinese Loess Plateau (CLP) (Liu et al., 2003; Maher, 2011; Nie et al., 2016). Meanwhile, the color indices mainly determined by AFM Hm and Gt have been extensively used in soil taxonomy (Mullins, 1977). Moreover, the ratios of Hm and Gt, which directly reflect the soil moisture and relative humidity of the regional climate (Cornell & Schwtermann, 2003), were proved to be helpful in the interpretation of nonlinear magnetic responses to climate in soils and sediments (Balsam et al., 2004; Gao et al., 2018; Ji et al., 2004; Liu et al., 2013; Nie et al., 2010; Torrent et al., 2006).

To date, the formation mechanisms of FM and AFM particles with pedogenesis are still under debate because field work and laboratory experiments have been conducted under wide climate ranges and...
variable conditions (Barrón & Torrent, 2002; Jiang et al., 2018; Lovley & Phillips, 1986; Maher & Taylor, 1988). Nevertheless, the genetic relation between FM particles and AFM particles has gradually been confirmed by growing evidences (Long et al., 2015, 2016; Torrent et al., 2006), especially after Mgh-like particles with increasing size from superparamagnetic (SP) to single domain (SD) were found to act as an intermediate product of Hm in solution under ambient conditions (Barrón & Torrent, 2002; Jiang et al., 2018). These experiments demonstrate the common positive correlation between magnetism and redness at a large scale. However, the relative formation efficiency of Mgh and Hm seems to be modulated by water activity (Long et al., 2016) and ligand adsorption of precursor iron oxides (Cabello et al., 2009) due to the similar thermodynamic stability of Mgh and Hm in nanometers (Navrotsky et al., 2008). Our previous study found significant grain growth of Mgh particles and their transformation to Hm in tropical Ferralsol, with a high formation efficiency estimated by Hm/(Hm + Gt) above 0.6 (Long et al., 2015). However, in some red soils and sediments with relatively high chemical weathering intensity formed in warm periods (Fang et al., 2003; Guo et al., 2002; Ren et al., 2020), the asynchronous change of redness and magnetism can also be frequently observed (Chen et al., 2019; Jiang et al., 2015; Nie et al., 2016; Walker et al., 1981), although the Hm/(Hm + Gt) fluctuates slightly below 0.6, and the positive correlation between redness and magnetism is still maintained in these soils and sediments (Balsam et al., 2004; Ding et al., 2001; Ji et al., 2004; Torrent et al., 2006). This indicates that the formation pattern of Mgh and Hm in highly weathered soils and sediments may have undergone a major shift, although their genetic relation remains.

Various organic and inorganic ligands have been introduced as additives to modulate the phase and size of the aging product of precursor iron oxides in vitro (Cabello et al., 2009; Gálvez et al., 1999; Jiang et al., 2018). Phosphorus (P), as the major element in most soils and sediments (Tiessen et al., 1984), has higher affinity for iron oxides as a phosphate ligand than other anion ligands due to its specific adsorption (Brady & Weil, 2016), which not only controls the availability of phosphate (Smeck, 1985; Walker & Syers, 1976) but also affects the crystallization and aggregation of iron oxides (Gálvez et al., 1999; Xu et al., 2017). These phenomena can be observed more significant in highly weathered soils in which positive charged iron oxides are enriched (Borggaard, 1983; Chacon et al., 2006; Fink et al., 2016; Vitousek et al., 2010). Nevertheless, the soil phosphate concentration relative to pedogenic iron oxides varies with parent material composition and chemical weathering intensity (Chen & Wang, 2005; Smeck, 1985). To explore the effect of P/Fe ratio on the formation efficiency of Mgh and Hm in natural systems, we focused on two Ferralsol sequences around a P mining area with contrasting P/Fe ratios but comparable degrees of chemical weathering controlled by similar climates. This approach provides us with an opportunity to evaluate the influence of phosphate ligand on the formation efficiency of various magnetic particles and interpret the asynchronous changes in magnetism and redness in soils and sediments at large spatial and temporal scales.

2. Materials and Methods

The two soil sequences were sampled in the Kunyang P mining area, which is located on the Yunnan Plateau in southwestern China. The mining area is derived from lower Cambrian siliceous dolomite strata that contain phosphorite with a P2O5 proportion as high as 36% (Xiao et al., 2019). The mean altitude of the Yunnan Plateau is approximately 2,000 m, and the climate is relatively dry and warm with a mean annual precipitation of 994 mm and a mean annual temperature of 15.1°C due to the foehn effect of the surrounding mountains (Shi et al., 2019). The profile has undergone strong chemical weathering since the uplift of the Yunnan Plateau in the Late Cenozoic (Z. R. R Liu & Zhou, 2017). The uppermost soils can be categorized as Ferralsol, which were considered to have undergone strong chemical weathering since the uplift of the Yunnan Plateau in the Late Cenozoic (Yin, 2010). The soil samples were collected at intervals of 20 or 40 cm depending on the thickness of profiles.

The chemical compositions of soil samples were determined by the X-ray fluorescence method using ARL9800XP + XRF spectrometry. The chemical index of alteration (CIA) was calculated as Al2O3/(Al2O3 + CaO + Na2O + K2O) by the molar ratio. The total P (P2O5) and total Fe (Fe2O3) were calculated from the contents of P2O5 and Fe2O3 and P/Fe by the molar ratio of P2O5 and Fe2O3. Free iron (Fe3+) and amorphous iron (Fe2+) were extracted with citrate-bicarbonate-dithionite and ammonium oxalate, respectively. The Fe3+ reflects the total amount of pedogenic iron oxides, while the Fe2+ reflects the poorly crystallized phases that make a lower weight contribution but have a higher specific surface area than well-
crystallized phases (Jambor & Dutrizac, 1998). The redness was calculated as the ratio of the average reflectance in the red light band (630–700 nm) and visual light band (400–700 nm). The standard Hm and Gt minerals used in the experiment were Pfizer R1599 red and Hoover Color Corporation Synox Hy610 yellow. The Hm was estimated by a working curve established by the deferrated samples mixed with a series of given contents of standard Hm and Gt according to the procedure in our previous study (Long et al., 2011). Finally, the Hm and Gt contents were calculated by the following equations when Fed was assigned as the combination of iron in stoichiometric Hm (Fe2O3), Gt (FeOOH) (Torrent et al., 2007), and Feo:

\[
\text{Hm (\%)} = 10^{-4} \times e^{23.05 \times \text{Redness}}
\]

\[
\text{Gt (\%)} = 1.59 \times (\text{Fed} - \text{Feo} - \text{Hm}/1.43)
\]

Magnetic susceptibility (\(\chi\)) was measured with an MS2 instrument from Bartington. The low-frequency (\(\chi_{lf}\)) and high-frequency (\(\chi_{hf}\)) values were determined at 0.47 and 4.7 kHz, respectively, to estimate the total amount of ferrimagnets. The frequency dependence of the magnetic susceptibility, \(\chi_{lf}\) and \(\chi_{hf}\), usually used to estimate the absolute and relative content of ultrafine (<20 nm) SP particles, was calculated as \(\chi_{lf} - \chi_{hf}\) and \(\chi_{lf}/\chi_{hf} \times 100\), respectively (Dearing et al., 1996). Meanwhile, the anhysteretic remanent magnetization (ARM), which is sensitive to SD particles (Liu et al., 2004), was measured in an alternating field of 100 mT with a superimposed 0.05 mT bias field. The \(\chi_{ARM}\) was calculated by ARM normalized by the bias field. The saturated isothermal remanent magnetization (SIRM) was attained at 1 T with an ASC-10 impulse magnetizer and measured with an AGICO JR6 spinner magnetometer.

3. Results
As illustrated in Table 1 and Figure 1, in the two sequences, \(P_t\) decreased from 0.85% to 0.07%, while \(Fe_t\) increased from 6.3% to 17.7%, which resulted in the wide range of P/Fe from 0.008 to 0.179 (Figures 1a and 1b). According to the P/Fe, these profiles can be divided into HP sequence with a high P/Fe (0.037–0.179) and LP sequence with a low P/Fe (0.008–0.023). These profiles were labeled according to the mean P/Fe in the following order: HP3 > HP2 > HP1 > LP3 > LP2 > LP1 (Table 1). The two sequences have undergone comparable chemical weathering intensity as indicated by the CIA values from 85.2 to 96.5 in the HP sequence and from 87.3 to 99.2 in the LP sequence (Figure 1b).

The total amount of pedogenic iron oxides estimated by the Fed ranging from 4.6% to 10.1% in the HP sequence was only slightly lower than that ranging from 5.7% to 12.7% in the LP sequence (Figure 1c) due to the opposite change in \(Fe_t\) with Fed/Fet (Figures 1a and 1c). In contrast, the \(Fe_o\) and \(Fe_o/Fed\) ratios in the HP sequence were signiﬁcantly higher in the HP sequence than in the LP sequence (Figures 1f–1h). These parameters have demonstrated a common increase in both sequences except that \(P_t\) and \(Fe_o/Fed\) exhibited monotonic deceasing trends as P/Fe decreased (Figure 2).

4. Discussion
4.1. Monotonic Increasing Crystallinity of Iron Oxides With Decreasing P/Fe
Although the P/Fe ratio exhibits different ranges in both sequences, the \(P_t\) and \(Fe_t\) show linear but opposite changes along the two sequences (Figures 2a and 2e), which indicates that the primary Fe and P input derived from the parent materials is competitive. In shallow marine sediments, Fe-bearing minerals usually exist in the form of carbonate and silicate (siderite and glauconite), while the P-bearing minerals in the form of phosphate (apatite) (Zhang et al., 2008). Their proportion fluctuates with the sedimentary environment, which controls the depositing of phosphate, silicate, and carbonate from nearshore to offshore areas (Z. R. R Liu & Zhou, 2017). Thus, a high content of phosphate in the parent material is often accompanied by a low content of Fe silicate and carbonate. Meanwhile, at the profile scale, phosphate tends to be leached
with weathering, whereas the immobile iron oxides tend to concentrate under aerobic conditions (Walker & Syers, 1976). Consequently, both diagenesis and pedogenesis account for the dramatic difference in the wide range of P/Fe between the two sequences. The soils possess lower Fet and higher Fed/Fet in the HP sequence than in the LP sequence, which narrows the differences in Fed, Hm, and Gt between both sequences. This result can be attributed to a high proportion of primary Fe carbonates in the LP sequence, which is easier to weather than the primary Fe silicates in the HP sequence (Zhang et al., 2008). More importantly, the monotonic decrease in Fe o/Fed with P/Fe indicates that the crystallinity of iron oxide increases as P/Fe decreases (Figure 2g). This result confirms that the presence of phosphate can impede the aggregation and crystallization of amorphous iron oxide in soil solution (Barrón & Torrent, 2002; Gálvez et al., 1999).

### 4.2. Comparable Hm and Gt Competition in High and Low P/Fe Sequences

In contrast to the monotonic change in amorphous iron oxide along the two sequences, the competition between crystalline Hm and Gt estimated by Hm/(Hm + Gt) changes comparably as the P/Fe is reduced in each sequence (Figures 2d and 2h). The highest Hm/(Hm + Gt) often appears in the middle of the profile (Figure 1e) and is located at the highest position of the valley (Table 1). Considering that the two sequences were sampled with limited horizontal (<12 km) and vertical space (<300 m), the climatic difference can be neglected, but the water redistribution along a slope or a profile can still cause significant variations in Hm/(Hm + Gt). The high Hm/(Hm + Gt) in the middle of the upslope profile often correlates with good drainage and low water activity. Conversely, the low Hm/(Hm + Gt) in the downslope profiles, especially in the top and bottom of the profile, is often accompanied by poor drainage controlled by surface water and groundwater (Boero & Schwertmann, 1987; Torrent et al., 2010).

Nevertheless, Hm/(Hm + Gt) exhibited a corresponding increase with decreasing P/Fe in each sequence. Previous studies have found that high P/Fe under acidic conditions often favors the formation of Hm rather than Gt, and the effect was found to become more significant with increasing temperature from 25°C to 100°C (Gálvez et al., 1999). In our study, the soil pH variation is limited from 4 to 6, and the mean annual temperature of the study area is approximately 15°C. More importantly, Hm/(Hm + Gt) demonstrates comparable increases in both sequences as P/Fe decreases. Therefore, the change in Hm/(Hm + Gt) in this study was likely mainly controlled by similar climates and pedogenic environment rather than by P/Fe.

### 4.3. Different Magnetic Enhancement Patterns in High and Low P/Fe Sequences

In contrast to the comparable change trends of AFM Hm and Gt, FM particles reveal different change patterns in the two sequences. The FM particles with increasing sizes indicated by $\chi_{fd}$, $\chi_{ARM}$, and SIRM exhibited common enrichment at stable accelerations ($R^2 = 0.90, 0.89,$ and 0.91) in the HP sequence but had unstable even rates ($R^2 = 0.53, 0.71,$ and 0.36) in the LP sequence as P/Fe declined (Figures 3a–3c), which reveals a faster accumulation rate of FM particles in the HP sequence than in the LP sequence. Meanwhile, the relative contents of finer FM particles indicated by $\chi_{fd}/\chi_{ARM}$ and ARM/SIRM were both higher in the HP sequence than those in the LP sequence (Figures 3d and 3f). However, $\chi_{fd}/\chi_{ARM}$ changed comparably but in opposite directions with the decrease in P/Fe (Figure 3e). This result suggests that the FM particles accumulated in the HP sequence are commonly finer than those in the LP sequence, and the FM particles around the boundary of SP and SD particles could have undergone significant growth in the LP sequence.

### Table 1

Mean Values of Chemical Weathering Parameters and Iron Oxides Along Different P/Fe Profiles

| Profile/Sequence | Altitude (m) | $P_t$ (%) | $Fe_t$ (%) | $P/Fe$ | CIA | $Fe_d$ (%) | $Fe_o$ (%) | Hm (%) | Fed/Fet | Feo/Fed | Hm/(Hm + Gt) | $\chi_{ld}$ ($10^{-8}$ m$^3$ kg$^{-1}$) |
|------------------|--------------|-----------|------------|--------|-----|------------|----------|--------|---------|---------|-------------|--------------------------------------|
| HP3 | 2,010 | 0.67 | 10.3 | 0.118 | 88.5 | 7.3 | 0.39 | 2.83 | 0.71 | 0.05 | 0.27 | 244 |
| HP2 | 2,256 | 0.58 | 9.6 | 0.117 | 91.2 | 6.6 | 0.55 | 2.14 | 0.67 | 0.09 | 0.20 | 836 |
| HP1 | 2,266 | 0.26 | 11.0 | 0.042 | 95.4 | 7.8 | 0.72 | 3.52 | 0.71 | 0.09 | 0.33 | 2,140 |
| LP3 | 1,976 | 0.14 | 14.2 | 0.018 | 90.2 | 7.6 | 0.35 | 2.62 | 0.53 | 0.05 | 0.23 | 914 |
| LP2 | 1,976 | 0.12 | 14.2 | 0.015 | 94.5 | 7.8 | 0.41 | 3.82 | 0.55 | 0.06 | 0.33 | 1,345 |
| LP1 | 2,158 | 0.10 | 16.7 | 0.011 | 97.7 | 11.2 | 0.41 | 6.33 | 0.67 | 0.04 | 0.39 | 2,413 |
| HP sequence | 2,177 | 0.51 | 10.3 | 0.095 | 91.6 | 7.2 | 0.56 | 2.76 | 0.69 | 0.08 | 0.26 | 1,050 |
| LP sequence | 2,037 | 0.12 | 15.1 | 0.015 | 94.1 | 9.0 | 0.39 | 4.30 | 0.59 | 0.05 | 0.31 | 1,576 |
Figure 1. $P_t$ and $Fe_t$ change in opposite directions along the two sequences (a). $P/Fe$ is commonly higher in the HP sequence than in the LP sequence with comparable chemical weathering indicated by the CIA (chemical alternation index) (b). $Fe_d$ is slightly lower in the HP sequence than in the LP sequence due to opposite changes in $Fe_t$ and $Fe_d/Fe_t$ (c). Amorphous iron oxides indicated by $Fe_o$ and $Fe_o/Fe_d$ are both higher in the HP sequence, while crystalline iron oxides indicated by $Hm$ and $Hm/(Hm + Gt)$ are slightly higher in the LP sequence (d and e). The absolute magnetic parameters of $\chi_{ ARM}$, $\chi_{ ARM}/SIRM$, and SIRM are slightly lower in the HP sequence, but the relative parameters of $\chi_{ fd}$, $\chi_{ fd}/\chi_{ ARM}$, and $ARM/SIRM$ are commonly higher in the HP sequence (f–h).
sequence. The grain growth of FM particles has also been observed in our previous studies on the climosequence with dramatic changes in Hm/(Hm + Gt) (Long et al., 2015). However, the Hm/(Hm + Gt) values in the two sequences are comparable, and therefore, the difference in the accumulation efficiency of different FM particles should be controlled by the contrasting P/Fe ranges. To further evaluate the amount and size distribution of the FM particles accompanying the formation of Hm and avoid the influence of Hm content difference in both sequences, $\chi_{fd}/Hm$, $\chi_{ARM}/Hm$, and SIRM were normalized by Hm, respectively. As illustrated in Figures 3g–3i, the FM particles accompanying Hm indicated by $\chi_{fd}/Hm$, $\chi_{ARM}/Hm$, and SIRM/Hm exhibited similar change trends as those of $\chi_{fd}$, $\chi_{ARM}$, and SIRM in Figures 3a–3c. $\chi_{fd}/Hm$ and SIRM/Hm were higher in the HP sequence and LP sequence, respectively, while $\chi_{ARM}/Hm$ was comparable in both sequences. This result confirms that SD particles were enriched comparably with Hm in two sequences, while the finer and coarser FM particles were enriched in the HP and LP sequences, respectively. In addition, in order to avoid the little difference of Hm/(Hm + Gt) between two sequences, $\chi_{fd}$%, $\chi_{fd}/\chi_{ARM}$, and ARM/SIRM were normalized by Hm/(Hm + Gt) in Figures 3j–3l to trace the formation efficiency of finer FM particles relative to coarser FM particles under the specific formation efficiency of Hm indicated by Hm/(Hm + Gt); the normalized parameters commonly reveal monotonic decreasing with decreasing P/Fe. These results verify that the coarsening and transformation of FM particles are contributed to the lack of the protection of phosphate ligands (Barrón & Torrent, 2002).

4.4. Mechanism and their Significance in Paleoclimate Reconstruction

Previous experimental studies have found that organic and inorganic ligands play an important role in modulating the aging product of ferrihydrite (Fh) (Cabello et al., 2009). The proper level of phosphate via specific
adsorption or ligand exchange on the surfaces of Fh can favor the dehydration and rearrangement of Fh to form Hm but inhibit the dissolution of Fh to form Gt (Barrón et al., 1997; Gálvez et al., 1999; Xu et al., 2017). Mgh-like FM particles increasing in size from SP to SD particles were observed as an intermediate product (Barrón et al., 2003; Hu et al., 2013; Liu et al., 2008) due to their higher thermodynamic stability than Hm in nanometers (Hiemstra, 2015; Navrotsky et al., 2008). As the experiment was conducted in a wide range of P/Fe, the FM particles were both gradually enriched as P/Fe decreased when the P/Fe was greater than 0.0275 or less than 0.025. The two magnetism enhancement patterns were divided by a dramatic magnetic reduction as P/Fe decreased from 0.0275 to 0.025 (Barrón & Torrent, 2002). Our study verifies the P/Fe-mediated processes by assuming that the ratio of P/Fe in solid soils determines the ratio of phosphate and Fh dispersed in soil solution. Moreover, the two sequences with comparable changes in Hm and Gt verify that the ratio of Hm/(Hm + Gt) can be used as a reasonable climatic and environmental indicator independent of parent materials across a large scale (Cornell & Schwtermann, 2003; Torrent et al., 1980).

Figure 3. Magnetic parameters, including $\chi_{fd}$, $\chi_{ARM}$, and SIRM, increase stably and exponentially in the HP sequence but unstably and linearly in the LP sequence with decreasing P/Fe (a–c). The ratios of finer FM particles, including $\chi_{fd}$, $\chi_{fd}/\chi_{ARM}$, and ARM/SIRM, change slowly in the HP sequence but rapidly in the LP sequence (d–f). The fine and coarse magnetic particles accompanying the formation of Hm indicated by $\chi_{fd}$/Hm and SIRM/Hm are mostly higher and lower, respectively, in the HP sequence than those in the LP sequence, while the intermediate SD particles remain comparable (g–i). The relative change in the grain size of FM particles accompanying Hm indicated by $\chi_{fd}$/Hm, $\chi_{fd}/\chi_{ARM}$/Hm/(Hm + Gt), and (ARM/SIRM)/Hm/(Hm + Gt) decreases monotonically with decreasing P/Fe (j–l).
In natural systems, the change in P/Fe in soils and sediments is controlled by parent material composition and chemical weathering intensity. Carbonates deposited in marine environments often possess a much higher mean P/Fe of approximately 0.219 than that of granites with P/Fe of approximately 0.067, although the Fe content in carbonates is much lower than that of granites (Chen & Wang, 2005). This difference explains the extremely high magnetism of soils in Terra Rossa derived from carbonates (Grison et al., 2011; Lu et al., 2012) when the regional climate favors the formation of Hm. In addition, the soils derived from basalts that have a high Fe content but a lower P/Fe of approximately 0.010 (Chen & Wang, 2005) have high magnetism and frequently observed FM particle growth and transformation into Hm (Camêlo et al., 2018; de Oliveira et al., 2000; Liu et al., 2017). Nevertheless, if the parent material composition is comparable, the change in P/Fe is mainly controlled by chemical weathering that leads to the leaching of phosphate and concentration of immobile iron oxides. This process then results in the decline of P/Fe and causes the formation pattern shift of FM particles and Hm. For the aeolian sediments on the CLP, if their composition is assumed to be homogenous (Guo et al., 2002), the lower P/Fe ratio in red clay and paleosols at extreme stages, such as S5, is accordingly correlated with the higher chemical weathering intensity than in normal loess and paleosols (Chen et al., 2001; Han et al., 2007). Actually, the P/Fe of normal loess and paleosol layers (0.031–0.043) is commonly higher than that of red clay and paleosols in extreme stages (0.019–0.024) (Chen et al., 2001; Han et al., 2007), and these two ranges are divided by the inflection range at approximately 0.0275–0.025 as indicated by this study and a previous laboratory study (Barrón & Torrent, 2002). Thus, when climate changed gradually from the Tertiary to the Quaternary, the shift in magnetic enhancement pattern leads to the decoupling of magnetism and redness in the long term, although the magnetism and redness mostly changed in phase in loess or in red clay (Balsam et al., 2004; Ji et al., 2004; Nie et al., 2016; Torrent et al., 2006). In addition, the warmer climate and the longer burial time of aeolian sediments can also promote more FM particle transformation into Hm (Barrón & Torrent, 2002; Jiang et al., 2018) in Tertiary red clay than in Quaternary loess (Nie et al., 2014, 2018), even though these factors are expected to exert a gradual influence rather than an abrupt shift in the change in color and magnetism.

Additionally, some other inorganic and organic ligands often concur in soils and sediments (Cabello et al., 2009), which also change with parent material composition, chemical weathering intensity, and biological recycling (Vitousek et al., 2010), and could influence the formation efficiency of Mgh and Hm especially for soils adjacent to rock and ground with high inorganic and organic ligand content despite their lower affinity for iron oxides than phosphate. Therefore, the ligand-protected effect usually masked by chemical weathering intensity could better explain the mechanism of different magnetic enhancement patterns in soils and sediments in addition to climate, which is of great significance in soil taxonomy, paleoenvironment reconstruction, and spatial exploration.

5. Conclusions

The formation efficiency of FM particles and AFM Hm in soils and sediments can be modulated by primary iron and phosphorous. The FM particles accompanying the formation of Hm stably accelerated in high P/Fe sequence but unstably increased at even rates in low P/Fe sequence. The Mgh particles relative to Hm became less abundant and coarser under a low P/Fe. This result is attributed to the more rapid grain growth of FM particles and transformation into Hm without enough P ligand protection to retard the crystallization of iron oxides.

Data Availability Statement

The original data presented in this paper can be accessed through the public domain repository Zenodo (https://doi.org/10.5281/zenodo.3932444).

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