Different enrichment patterns of pedogenic magnetic particles modulated by primary iron-phosphorous input

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Abstract

Magnetic particles including ferrimagnetic (FM) and antiferromagnetic (AFM) particles are ubiquitous in the surface of Earth and Mars. The FM particles dominating soil magnetism usually coexist or compete with AFM hematite due to their comparable thermodynamic stability. The uncertain correlation can be modulated by phosphorous (P) absorption during aging of precursor amorphous iron (Fe) oxides. We investigated two Ferralsol sequences around a P mining field with comparable content of hematite but contrasting P/Fe ratio. The FM particles accompanying the formation of hematite are enriched stably at accelerating rates under high P/Fe but at unstably even rates under low P/Fe. The FM particles became less abundant and coarser while the iron oxide crystallinity increased monotonically as P/Fe decreased. We attribute it to more rapid grain growth of FM particles and transformation into hematite without P retarding the crystallization of iron oxides.

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11	Key Points:
12	• Iron oxide crystallinity increases monotonically as soil P/Fe decreases
13	• Ferrimagnets accompanying hematite enrich with acceleration under high P/Fe
14	• Rapid grain growth of ferrimagnets and transformation into hematite without
15	the protection of proper amount of P

17 Abstract

Magnetic particles including ferrimagnetic (FM) and antiferromagnetic (AFM) 18 particles are ubiquitous in the surface of Earth and Mars. The FM particles 19 dominating soil magnetism usually coexist or compete with AFM hematite due to 20 21 their comparable thermodynamic stability. The uncertain correlation can be modulated by phosphorous (P) absorption during aging of precursor amorphous iron (Fe) oxides. 22 We investigated two Ferralsol sequences around a P mining field with comparable 23 content of hematite but contrasting P/Fe ratio. The FM particles accompanying the 24 formation of hematite are enriched stably at accelerating rates under high P/Fe but at 25 unstably even rates under low P/Fe. The FM particles became less abundant and 26 coarser while the iron oxide crystallinity increased monotonically as P/Fe decreased. 27 We attribute it to more rapid grain growth of FM particles and transformation into 28 29 hematite without P retarding the crystallization of iron oxides.

30

Plain Language Summary

Iron (Fe) oxide is an important carrier of soil magnetism. On account of the high 31 affinity of phosphate (P) for iron oxides the relationship between them has been 32 highly concerned. We investigated soil samples from a P mining field and its 33 34 surrounding with significant variation of P/Fe ratio. It indicates the grain sizes and contents of magnetic particles change with the P/Fe and exhibits different growth and 35 enrichment patterns in different P/Fe ranges. Our results reveal P can affect the 36 37 aggregation and transformation of iron oxides and related magnetic minerals in soils, which is of great significance for understanding the causes of soil magnetism. 38

39 **1 Introduction**

Magnetic particles derived from pedogenic iron oxides are ubiquitous on the 40 surface of Earth and Mars as the weathering product of Fe-bearing minerals 41 [Christensen et al., 2001]. The magnetic particles can be divided into ferrimagnetic 42 (FM) and antiferromagnetic (AFM) particles according to magnetic properties. The 43 FM particles mainly including maghemite (Mgh, γ -Fe₂O₃) and magnetite (Mgt, Fe₃O₄) 44 often dominate soil and sediment magnetism although they make little weight 45 contribution to total amount of iron oxides [Liu et al., 2012]. The contents and ratios 46 of FM particles with differing sizes have widely been employed as pedogenic 47 indicators in soil survey and paleoclimate reconstruction, especially in the aeolian 48 49 sediments of Quaternary loess and Tertiary red clay deposited in Chinese Loess Plateau (CLP) [Mullins, 1977; Liu et al., 2003; Maher, 2011; Maxbauer et al., 2016; 50 51 *Nie et al.*, 2016]. On the other, the AFM particles including hematite (Hm, α -Fe₂O₃) and goethite (Gt, α -FeOOH), which are main red-yellow color agents in soils and 52 sediments, can reflect soil moisture and relative humidity of regional climate [Cornell 53 and Schwtermann, 2003]. The Hm/(Hm+Gt) ratio has also been extensively referred 54 55 in soil taxonomy and assisted in the interpretation of nonlinear magnetic response to climate reconstructed by the loess and red clay in past decades [Xiong and Li, 1987; 56 Balsam et al., 2004; Ji et al., 2004; Liu et al., 2006; Torrent et al., 2006; Nie et al., 57 58 2010; Liu et al., 2013; Gao et al., 2018].

However, the type, genesis and grain size distribution of FM particles withpedogenesis are still under debate due to field work and laboratory synthesis

conducted under contrast climates and variable conditions [Lovley and Phillips, 1986; 61 Gálvez et al., 1999; Barrón and Torrent, 2002; Liu et al., 2003]. Nevertheless, the 62 genetic relation between FM and AFM particles has been gradually confirmed with a 63 growing evidence [Torrent et al., 2006; Long et al., 2015, 2016], especially after the 64 nanometer FM particles with growing size from superparamagnetic (SP) to single 65 domain (SD) were found to act as intermediate products of Hm in the solution under 66 ambient conditions [Barrón and Torrent, 2002; Liu et al., 2008; Gutiérrez et al., 2016; 67 Jiang et al., 2018]. The process has been evidenced by the common positive relation 68 69 between SP particles and Hm in soils and sediments derived from different parent materials and wide climate range at a large scale, even in the soils with low Hm 70 formation efficiency in high rainfall regions [Torrent et al., 2006; Long et al., 2015, 71 72 2016]. Moreover, the accumulating rate of fine FM particles accompanying the formation Hm decreases with the formation efficiency of Hm estimated by 73 Hm/(Hm+Gt) due to their grain growth and transformation into Hm [Long et al., 74 75 2015]. However, the negative correlation between SP particles and Hm can be only found in the tropical soils with extremely high Hm/(Hm+Gt) above 0.6, which 76 suggests the more rapid transformation from FM to AFM particles than the 77 accumulation of FM particles [Long et al., 2015]. Furthermore, at a large spatial and 78 temporal scale, the change of FM particles and Hm, which determine magnetism and 79 redness of soils and sediments, change out of phase. For example, the surface soils in 80 south tropical China are characterized by lower magnetism and higher redness than 81 those in north temperate China [Han et al., 1996; Yang et al., 2001; Hu et al., 2014]. 82

Similar phenomenon can also be found in the comparison between Tertiary red clay
and Quaternary loess on CLP [*Nie et al., 2010, 2016*]. Considering the Hm/(Hm+Gt)
of soils and sediments is too low to favor the transformation from FM particles to Hm,
the uncertain relation between them at a large scale could be affected by other factors
besides climate.

Theoretically, the presence of FM particles as the intermediate product of Hm in 88 solution is attributed to their higher thermodynamic stability relative to Hm at 89 nanometer [Chernyshova et al., 2007; Navrotsky et al., 2008; Hiemstra, 2015]. The 90 91 size-dependent stability can be maintained with anion absorption or ligand exchange to retard grain growth and transformation of FM particles [Cabello et al., 2009; Jiang 92 93 et al., 2018]. Phosphate (P) is widespread in the natural environment and has high 94 affinity for the surface of iron oxides, thereby influencing the crystallization and aggregation of amorphous iron oxide [Gálvez et al., 1999; Barrón and Torrent, 2002; 95 Wang et al., 2017; Xu et al., 2017; Wang et al., 2018]. The FM particles can 96 accumulate effectively under a proper P/Fe ratio between 0.025 and 0.0275 during the 97 aging process of Fh in solution with the presence of phosphate [Barrón and Torrent, 98 99 2002].

However, the effect of P/Fe on the neoformation of FM particles and Hm has not been independently investigated in natural system because the change of P/Fe is often accompanied by chemical weathering that results in the leaching of P and the enrichment of Fe. The competition between Hm and Gt, which occurs extensively in different spatial scale, could also affect the FM particles with Hm [*Cornell and* 105 *Schwtermann, 2003*]. In this study, we focused on two soil sequences around a P 106 mining area under subtropical climate. Each sequence consisting of 3 saprolitic 107 Ferralsol profiles possesses changes of comparable chemical weathering intensity and 108 Hm/(Hm+Gt) but contrast ratio of P/Fe (0.008 ~ 0.179). They provide us an 109 opportunity to explore magnetic enrichment patterns of FM particles accompanying 110 the formation of Hm under different primary Fe and P input from parent material.

111

2 Materials and Methods

The two soil sequences were sampled around the Kunyang P mining area, which 112 is located at Yunnan Plateau in southwestern China and is one of the largest P mining 113 114 areas in the world. This mining area is derived from Paleozoic siliceous dolomite strata and contains phosphorite with a P₂O₅ proportion of up to 36% [Xiao et al., 115 2019]. The mean altitude of the Yunnan Plateau is around 2000 m, and the climate is 116 relatively dry and warm with a mean annual precipitation of 994 mm and a mean 117 annual temperature of 15.1 °C. All profiles were sampled on a highland with well 118 drainage on both sides. The uppermost soils can be categorized as Ferralsol, which 119 120 was considered to have undergone strong chemical weathering since the uplift of Yunnan Plateau in Late Cenozoic [Yin, 2010]. The soil profiles covered by natural 121 woodlands and grasslands were focused, and the samples were collected from the 122 surface to the bottom of outcrops covering horizons with the intervals of 20 cm or 40 123 cm depending on the thickness of profile. 124

125 The air-dried soil samples were sieved to < 2 mm and ground into powders to 126 conduct chemical analysis. The chemical compositions were determined by

X-ray fluorescence method using ARL9800XP + XRF spectrometry. The Chemical 127 Index of Alteration (CIA) was calculated as $Al_2O_3/(Al_2O_3 + CaO + Na_2O + K_2O)$. The 128 total Fe (Fe_t) and total P (P_t) were separately calculated by Fe₂O₃ and P₂O₅ expressed 129 as percentage. The P/Fe was calculated by molar ratio of P and Fe. The free iron (Fed) 130 and amorphous iron (Fe_o) were extracted with citrate-bicarbonate-dithionite (CBD) 131 and ammonium oxalate, respectively. Diffuse reflectance spectra (DRS) was measured 132 on a Perkin-Elimer Lambda 900 spectrophotometer at 2 nm intervals. The redness 133 was calculated as the ratio of average reflectance in the red light band (630 ~ 700 nm) 134 135 and visual light band (400 ~ 700 nm). Standard Hm and Gt minerals used in the experiment were Pfizer R1599 red and Hoover Color Corporation Synox Hy610 136 yellow. The Hm was estimated by a working curve established by the deferrated 137 138 samples mixed with a series of given content of standard Hm and Gt according to the procedure in our previous study [Long et al., 2011]. Finally, the Hm and Gt content 139 were calculated by the following equation when we assign free iron oxides (Fe_d) to 140 141 the combination of iron in stoichiometric Hm (Fe₂O₃), Gt (FeOOH) [Torrent et al., 2007] and Fe_o: 142

- 143 Hm (%) = $10^{-4} \times e^{23.03 * \text{Redness}}$
- 144 $Gt (\%) = 1.59 \times (Fe_d Fe_o Hm/1.43)$

Magnetic susceptibility (χ) was measured with a MS2 instrument from Bartington. The low-frequency (χ_{lf}) and high-frequency (χ_{hf}) were determined at 0.47 and 4.7 kHz to estimate the total ferrimagnet content. The frequency dependence of the magnetic susceptibility, χ_{fd} and χ_{fd} %, usually used to estimate the absolute and relative content of ultra-fine (<20 nm) SP particles, was defined as $\chi_{\rm lf} - \chi_{\rm hf}$ and ($\chi_{\rm lf} - \chi_{\rm hf}$) / $\chi_{\rm lf} \times 100\%$ 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 $\chi_{\rm ARM}$ was calculated by ARM normalized by the basing field. The saturation isothermal remanent magnetization (SIRM) was attained at 1T with the ASC-10 impulse magnetizer and measured with an AGICO JR6 spinner magnetometer.

156 **3 Results**

As illustrated in **Table 1 and Figure 1**, the P_t reveals a significant change from 157 0.07% to 0.85% while the Fe_t changes from 6.3% to 17.7%, which results in the wide 158 range of P/Fe from 0.008 to 0.179 (Figures 1a and 1b). According to the P/Fe, the 159 profiles can be divided into HP sequence with high P/Fe (0.037 ~ 0.179) and LP 160 sequence with low P/Fe (0.008 ~ 0.023). These profiles were labeled according to the 161 mean P/Fe following the order HP3 > HP2 > HP1 > LP3 > LP2 > LP1. The ranges of 162 P/Fe in HP and LP sequences are divided by the P/Fe ratio of 0.025 ~ 0.0275 163 164 proposed to control the FM particle transformation in solution [Barrón and Torrent, 2002; Cabello et al., 2009]. However, the two sequences have undergone comparable 165 chemical weathering as indicated by the CIA from 85.2 to 96.5 in HP sequence, and 166 from 87.3 to 99.2 in LP sequences (Figure 1b). 167

As for the iron oxides, the total amount of pedogenic iron oxides estimated by Fe_d ranging from 4.6% to 10.1% in HP sequence is only slightly lower than that from 5.7% to 12.7% in LP sequence (**Figure 1c**) due to the opposite change of Fe_t and

Fe_d/Fe_t (Figures 1a and 1c). In contrast, the Fe_o and Fe_o/Fe_d in HP sequence are 171 commonly higher than those in LP sequence (Figure 1d). However, the Hm changes 172 from 0.57% to 5.59% in HP sequence and from 0.56% to 8.3% in LP sequence, while 173 Hm/(Hm+Gt) in HP sequence ranging from 0.07 to 0.44 is similar to that from 0.06 to 174 0.49 in LP sequence (Figure 1e). Besides, the absolute contents of FM particles 175 indicated by χ_{fd} , χ_{ARM} and SIRM are mostly lower in HP sequence than those of in LP 176 sequence, which accords with the change trend of Fe_d and Hm, but the relative 177 proportions of finer FM particles indicated by χ_{fd} %, χ_{fd}/χ_{ARM} , and ARM/SIRM are 178 179 significantly higher in HP sequence than in LP sequence (Figures 1f-1h).

To explore the P/Fe effect on the enrichment of iron oxides and related FM particles, the above parameters were plotted versus P/Fe (**Figure 2**). Note that the P/Fe was plotted in reverse order from high to low indicating chemical weathering from weak to strong in each sequence. These parameters have demonstrated common increase in each sequence except that the P_t and Fe_o/Fe_d reveal monotonic deceasing as P/Fe decreases.

186 **4 Discussion**

187 4.1 Monotonic increasing crystallinity of iron oxides with the decreasing of P/Fe

The P_t and Fe_t show opposite liner change along two sequences (**Figures 2a and 2e**), which indicates the loss of P mainly derived from primary P-bearing minerals (mostly apatite) accompanied by the enrichment of immobile iron oxides with enhanced chemical weathering [*Ruttenberg, 2003*]. However, the soils possess lower Fe_t and higher Fe_d/Fe_t in HP sequence than those in LP sequence, which thus narrows the difference of Fe_d, Hm and Gt between both sequences. It could be attributed to the more primary Fe carbonate in LP sequence, which is easier to be weathered than primary Fe silicates in dolomite strata [*Veizer and Mackenzie, 2003*]. Meanwhile, the monotonical decreasing of Fe_o/Fe_d with P/Fe indicates that the crystallinity of iron oxide increases as P/Fe reduces (**Figure 2g**). It confirms the conclusion that presence of phosphate can retard the crystallization or aggregation of amorphous iron oxide in soil solution [*Gálvez et al., 1999; Barrón and Torrent, 2002*].

4.2 Comparable Hm and Gt competition in high and low P/Fe sequences

In contrast to the monotonic change of amorphous iron oxide along two sequences, 201 202 the competition between crystalline Hm and Gt estimated by Hm/(Hm+Gt) changes comparably as the P/Fe reduces in each sequence (Figures 2d and 2h). The highest 203 Hm/(Hm+Gt) often appears in the middle of profile (Figure 1e) locating at the 204 highest position of upslope bedside the valley (Table 1). Normally, Hm often forms 205 under dry and warm condition with low water actively while Gt forms under wet and 206 cold condition with high water activity, and the competition between them can be 207 208 observed in natural systems at different scales [Cornell and Schwtermann, 2003]. Considering two sequences were sampled with limited horizontal (< 12 km) and 209 vertical space (< 400 m), the climatic difference can be neglected but the water 210 redistribution along a slope and a profile can still make significant variations of 211 Hm/(Hm+Gt). The high Hm/(Hm+Gt) in the middle of upslope profile often 212 correlates with well drainage and low water activity. Reversely, the low Hm/(Hm+Gt) 213 in the downslope profiles, especially in the top and bottom, is often accompanied by 214

the poor drainage controlled by surface water and groundwater [*Boero and Schwertmann, 1987; Torrent et al., 2010*]. In addition, the high organic matters and rapid biological process on the surface could also lead to the preferential dissolution of Hm but favor the formation of Gt [*Schwertmann, 1971*].

Nevertheless, the Hm/(Hm+Gt) exhibits a correspond increasing with the 219 decreasing of P/Fe in the two sequences. Previous studies have found that the P/Fe of 220 $0 \sim 0.030$ under acid condition often favors the formation of Hm rather than Gt, and 221 the effect become more significant with the increasing temperature from 25°C to 222 223 100°C [Gálvez et al., 1999]. In this study, the soil pH variation is limited from 4 to 6 (not included in this paper) and the mean annual temperature is around 15°C. 224 Meanwhile, the Hm/(Hm+Gt) demonstrates comparable increases as the P/Fe 225 226 decreases. Therefore, The change of Hm/(Hm+Gt) and P/Fe in both sequence seems to be both controlled by comparable chemical weathering under similar pedogenic 227 environment. In other words, the variation of Hm/(Hm+Gt) in both sequences is 228 mainly controlled by the exterior factor of soil moisture rather than interior factor of 229 parent material composition. 230

4.3 Different magnetic enhancement patterns in high and low P/Fe sequences

Contrary the comparable change trend of Hm and Gt, the FM particles reveal different change pattern in the two sequences. The FM particles with growing sizes indicated by χ_{fd} , χ_{ARM} and SIRM exhibit common enrichment at stable accelerations ($R^2 = 0.90$, 0.89 and 0.91) in HP sequence but at unstable even rates ($R^2 = 0.53$, 0.71 and 0.36) in LP sequence as P/Fe reduces (**Figures 3a-3c**). Meanwhile, the relative contents of finer FM particles indicated by χ_{fd} % and ARM/SIRM are both higher in HP sequence than those in LP sequence (**Figures 3d and 3f**). However, The χ_{fd}/χ_{ARM} changes comparably but in opposite directions with the decrease of P/Fe. It can be inferred that FM particles accumulated in HP sequence are commonly finer than in LP sequence, but the FM particles around the boundary of SP and SD particles could have undergone significant growth in LP sequence.

4.4 Coordination and Competition between Hm and FM particles in high and low

244 **P/Fe sequences**

245 To evaluate the amount and size distribution of FM particles accompanying Hm with the decreasing of P/Fe, the magnetic parameters were normalized by Hm and 246 replotted versus P/Fe. As illustrated in Figures 3g-3i, the FM particles accompanying 247 248 Hm indicated by χ_{fd} /Hm, χ_{ARM} /Hm and SIRM/Hm exhibit similar change trend as χ_{fd} , χ_{ARM} and SIRM in Figures 3a-3c. However, the χ_{ARM} /Hm is comparable in both 249 sequences but the χ_{fd} /Hm is mostly higher and the SIRM/Hm is lower in LP sequence. 250 251 It suggests SD particles are enriched comparably with Hm in two sequences, while the 252 finer and coarser FM particles are enriched in HP and LP sequence, respectively. In addition, the γ_{fd} %/Hm, (γ_{fd} / γ_{ARM})/Hm and (ARM/SIRM)/Hm, which are calculated to 253 trace the relative change of FM in size with the formation of Hm in Figures 3j-3l, 254 255 commonly reveal monotonic decreasing with the decreasing of P/Fe. It reflects the coarsening of FM particles accompanying Hm with lowering interference of 256 257 phosphate.

4.5 Mechanism and their significance in paleoclimate reconstruction

Previous experimental studies have found that the organic and inorganic ligands 259 play an important role in modulating the aging product of Fh [Cabello et al., 2009]. 260 The proper amount of phosphate via specific adsorption or ligand exchange on the 261 surface of Fh can favor the dehydration and rearrangement of Fh to form Hm but 262 inhibit the dissolution of Fh to form Gt [Barrón et al., 1997; Gálvez et al., 1999; Xu et 263 al., 2017]. The Mgh-like FM particles with growing size from SP to SD particles were 264 observed as intermediate products [Liu et al., 2008] due to their higher 265 thermodynamic stability than Hm in nanometer [Navrotsky et al., 2008]. As the 266 Barrón and Torrent [2002]'s experiment conducted in wide range of P/Fe, the FM 267 particles are both gradual enrichment as P/Fe decreases above 0.0275 or below 0.025. 268 The magnetism enhancement patterns are divided by a dramatic magnetic reduction as 269 270 the P/Fe decrease from 0.0275 to 0.025. Our study verifies the P/Fe-mediated processes by assuming that the ratio of P/Fe in solid soils determines the ratio of 271 phosphate and Fh dispersed in soil solution. Although the formation path of Hm is 272 described by three successive steps as Fh $\xrightarrow{1}$ SP Mgh $\xrightarrow{2}$ SD Mgh $\xrightarrow{3}$ Hm in 273 274 laboratorial experiments [Barrón and Torrent, 2002], we believe that the three steps concur in natural systems but develop to different extent under specific condition. The 275 gradual magnetic enhancement with the decreasing P/Fe is determined by Step 1 and 276 277 Step 2, two steps by promoting the crystallization and aggregation of Fh to form FM particles, thus the decreasing of phosphate favors the crystallization of Fh to Mgh. 278 However, the abrupt magnetic reduction with the decrease of P/Fe from 0.0275 to 279

0.025 is dominated by Step 2 and Step 3 after a large amount of FM particles havebeen accumulated through Step 1.

Generally, the two sequences with comparable change of Hm and Gt but contrast 282 range of P/Fe verified that the ratio of Hm/(Hm+Gt) can be used as a reasonable 283 pedogenic environment and paleoclimatic proxy independent of parent materials in a 284 wide spatio-temporal range. It is noteworthy that the P/Fe plays an important role in 285 modulating the FM particles accompanying Hm in formation rate, accumulation and 286 size distribution. In natural system, the change of P/Fe is often controlled by the 287 288 parent material composition and chemical weathering intensity. The carbonate protolith deposited in marine environment often possesses much higher mean P/Fe 289 around 0.170 than granitic protolith around $0.043 \sim 0.059$ although the Fe content in 290 291 carbonates is much lower than that of granites [Chen and Wang, 2005]. It explains the extremely high magnetism of soils in Terra Rossa derived from carbonate [Grison et 292 al., 2011; Lu et al., 2012]. In addition, the soils derived from basaltic rocks, which 293 294 often have a fairly low P/Fe about 0.010 [Long et al., 2011] but have the highest Fe [Chen and Wang, 2005], can also cause high magnetism as well as the frequently 295 observed FM particle growth and transformation into Hm [Da Costa et al., 1999; Lu 296 et al., 2008; Long et al., 2015; Liu et al., 2017]. However, the sedimentary rocks and 297 sediments possess higher variation of P/Fe depending on the depositing environment 298 and chemical weathering intensity. As for the aeolian sediments of loess and red clay 299 300 on CLP, the P/Fe of loess and paleosol around 0.031 is commonly higher than that of red clay and paleosol in extreme stages like S5 around 0.019 [Chen et al., 2001], 301

which can also be divided by the inflection range around $0.0275 \sim 0.025$. Since the 302 composition of aeolian sediments is usually homogeneous [Guo et al., 2002], the 303 lower P/Fe is correlated with higher chemical weathering intensity of red clay than 304 loess and paleosol. Thus, when the climate changed gradually from Tertiary to 305 Quaternary, the shift of magnetic enhancement patterns from low P/Fe to high P/Fe 306 mode can lead to the decoupling of magnetism and redness form loess to red clay 307 although the magnetism and redness mostly change in phase in loess or in red clay. 308 Meanwhile, the warmer Tertiary climate and the longer depositing time could also 309 310 possibly promote more FM particles transformation into Hm [Barrón and Torrent, 2002; Jiang et al., 2018], although these factors should exert a gradual rather than 311 abrupt influence on the change of color and magnetism of loess and red clay. 312 313 Nevertheless, in addition to phosphate, some other inorganic and organic ligands often concur in soils and sediments despite their lower affinity for iron oxides than 314 phosphate [Cabello et al., 2009]. These ligands dominating the formation of 315 crystalline iron oxides and related FM particles can change with parent materials, 316 chemical weathering intensity and biological recycling. The P/Fe-modulated magnetic 317 enhancement patterns would help understand the potential influence of parent 318 materials on magnetic particles besides climatic conditions. Conversely, magnetic 319 particles are proved to be the pedogenic sensitive indicators involving in more 320 comprehensive information about pedogenic environment, which is of great 321 322 significance in paleoenvironment reconstruction and planet exploration.

323 **5** Conclusion

To unravel the role of P/Fe on the geneses and fate of FM particles in associated 324 with AFM Hm in natural systems, two saprolitic soil sequences around a P mining 325 field are examined. The crystallinity of iron oxide increases monotonically with the 326 327 decreasing of P/Fe while the Hm and Hm/(Hm+Gt) change comparably in HP and LP sequence under similar regional climate and local water activity variation. More 328 importantly, the enrichment of FM particles accompanying Hm stably accelerates as 329 the P/Fe reduces from $0.179 \sim 0.037$ in HP sequence, especially for the finer FM 330 particles. However, the enrichment of FM particles accompanying Hm unstably 331 increases at comparable even rates as the P/Fe reduces from 0.023 to 0.008 in LP 332 333 sequence. The FM particles accompanying Hm became less and coarser in LP sequence than HP sequence. We attributed it to more rapid grain growth of FM 334 335 particles and transformation into Hm without enough P protection to retard the crystallization of iron oxides. 336

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Profile/Sequence	Altitude (m)	P _t (%)	Fe _t (%)	P/Fe	CIA	Fe _d (%)	Fe ₀ (%)	Hm (%)	Fe _d /Fe _t	Fe _o /Fe _d	Hm/(Hm+Gt)	$\chi_{\rm lf}(10^{-8}~m^3~kg^{-1})$
HP3	2010	0.67	10.3	0.118	88.5	7.3	0.39	2.83	0.71	0.05	0.27	244
HP2	2256	0.58	9.6	0.117	91.2	6.6	0.55	2.14	0.67	0.09	0.20	836
HP1	2266	0.26	11.0	0.042	95.4	7.8	0.72	3.52	0.71	0.09	0.33	2140
LP3	1976	0.14	14.2	0.018	90.2	7.6	0.35	2.62	0.53	0.05	0.23	914
LP2	1976	0.12	14.2	0.015	94.5	7.8	0.41	3.82	0.55	0.06	0.33	1345
LP1	2158	0.10	16.7	0.011	97.7	11.2	0.41	6.33	0.67	0.04	0.39	2413
HP sequence	2177	0.51	10.3	0.095	91.6	7.2	0.56	2.76	0.69	0.08	0.26	1050
LP sequence	2037	0.12	15.1	0.015	94.1	9.0	0.39	4.30	0.59	0.05	0.31	1576

Table 1. Averages of chemical weathering parameters and iron oxides along different P/Fe profiles

Figure 1. (a) P_t and Fe_t change in opposite direction along the two sequences. (b) 348 P/Fe is common higher in HP sequence than LP sequences with comparable chemical 349 350 weathering indicated by CIA (Chemical Alternation of Index). (c) Fe_d is slightly lower in HP sequence than that in LP sequence due to opposite change of Fet and 351 Fe_d/Fe_t. (d and e) Amorphous iron oxides indicated by Fe_o and Fe_o/Fe_d are both 352 higher in HP sequence while crystalline iron oxides indicated by Hm and 353 Hm/(Hm+Gt) are a little higher in LP sequence. (f-h) The absolute magnetic 354 parameters of χ_{If} , χ_{ARM} and SIRM are a little lower in HP sequence but the relative 355 356 parameters of χ_{fd} %, χ_{fd} / χ_{ARM} and ARM/SIRM are commonly higher in HP sequence.



Figure 2. (a and e) P_t and Fe_t monotonously decrease and increase, respectively, with the deceasing of P/Fe in both sequences. (b-d, f-h) The Fe_d, Fe_o, Hm and their ratio parameters increase comparably as the P/Fe reduces in two sequences except that the Fe_o/Fe_d decreases monotonously. Note that the x-axis of P/Fe is illustrated in reverse order to indicate chemical weathering from weak to strong. The LP sequence with low P/Fe below 0.025 was shadowed and enlarged independently on the right.



365	Figure 3. (a-c) The magnetic parameters including χ_{fd} , χ_{ARM} and SIRM increase
366	stably and exponentially in HP sequence but increase unstably and linearly in LP
367	sequence with the decreasing of P/Fe. (d-f) The ratios of finer FM particles including
368	$\chi_{fd}\%,~\chi_{fd}/\chi_{ARM}$ and ARM/SIRM change slowly in HP sequence but rapidly in LP
369	sequence. (g-i) The finer and coarser magnetic particles accompanying the formation
370	of Hm indicated by χ_{fd}/Hm and SIRM/Hm are mostly higher and lower, respectively,
371	in HP sequence than those in LP sequence while the intermediate SD particles are
372	kept comparable. (j-l) The relative change of grain size of FM particles accompanying
373	Hm indicated by χ_{fd} %/Hm, (χ_{fd}/χ_{ARM})/Hm and (ARM/SIRM)/Hm decrease
374	monotonously with the decreasing of P/Fe.
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