



Release of iron from chlorite weathering and links to magnetic enhancement in Chinese loess deposits



Shuzhen Peng^{a,b,*}, Qingzhen Hao^b, Frank Oldfield^c, Zhengtang Guo^b

^a Key Laboratory of tourism and resources environment in Universities of Shandong, Taishan University, Taian 271021, China

^b Key Laboratory of Cenozoic Geology and Environment, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing 100029, China

^c School of Environmental Sciences, University of Liverpool, Liverpool L69 7ZT, UK

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ABSTRACT

Chlorite weathering is potentially useful as an indicator of *in situ* weathering related to the strength of the East Asian summer monsoon in Chinese loess deposits. The chlorite ratio (the integral area ratio of chlorite diffraction peaks at 0.47 nm and 0.7 nm) is a new proxy for evaluating the release of free iron from chlorite weathering. This ratio was measured using X-ray diffraction (XRD) on the <2 μm fraction of samples from four loess sections spanning the last 130 ka across the eastern Chinese Loess Plateau. The variations in the chlorite ratio in the four loess sections indicate that the release of free iron from chlorite weathering had taken place in all four last Interglacial S1 soils and also, with the exception of the northernmost Huanxian section, in the middle Holocene S0 soils. In contrast, the illite/chlorite (I/C) ratio measurements point to a reduction in chlorite content only in the southernmost Weinan section. This comparison suggests that chlorite weathering was initially characterized by Fe²⁺ leaching rather than by conversion of chlorite to another mineral phase during the incipient weathering stage. The southward increase in the chlorite ratio along the four sections is entirely consistent with the weathering gradient resulting from the present-day summer monsoon climate pattern. Thus, the chlorite ratio provides a more quantitative and sensitive tool for evaluating chlorite weathering. The results also suggest that chlorite weathering may be responsible for supplying free Fe for the formation of fine-grained secondary ferrimagnets in most, if not all, of the eastern Loess Plateau region.

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1. Introduction

The wind-blown loess deposits on the Chinese Loess Plateau (CLP) provide an unparalleled continuous terrestrial record of changes in the East Asian monsoon (An et al., 1991; Ding et al., 1995; Guo et al., 2002; Hao et al., 2012; Kukla and An, 1989; Liu, 1985). Post-depositional chemical weathering and pedogenesis show a close link with the intensity of the East Asian summer monsoon in the region. Up to now, elemental and isotopic ratios, for example, the chemical index of alteration (CIA) (Liu et al., 1995), Rb/Sr (Chen et al., 1999) and ⁸⁷Sr/⁸⁶Sr (Yang et al., 2001), have been widely used to quantify *in situ* weathering signals. However, some studies show that eolian sorting can affect these proxies because the mineralogical and geochemical components are partly dependent on particle size (e.g., Eden et al., 1994; Peng and Guo, 2001). The uncertainties in applying geochemical weathering indices to the loess deposits have also been evaluated recently (Bugge et al., 2011). Therefore, alternative approaches are still

important for characterizing the *in situ* weathering of loess deposits in northern China.

Numerous studies have explored the clay mineral assemblages of Chinese loess deposits and their links to past climate change (Bronger and Heinkele, 1990; Gylesjö and Arnold, 2006; Jeong et al., 2011; Ji et al., 1999; Liu, 1985; Zhao et al., 2005). Clay minerals (<2 μm) in Chinese loess primarily consist of illite and chlorite (e.g., Liu, 1985). However, the climatic significance of clay minerals is somewhat controversial because some authors regard them as primarily of detrital origin (e.g., Gylesjö and Arnold, 2006; Ji et al., 1999; Liu, 1985). Recent studies have suggested that significant weathering of chlorite has occurred in the contemporary soils and paleosols of the southern CLP (Jeong et al., 2011; Zhao et al., 2005). It has also been suggested that illite can form in paleosols due to feldspar weathering (Bronger and Heinkele, 1990). These studies provide a basis for exploring the use of clay minerals in reconstructing past climate changes.

Chlorite weathering has often been suggested as the primary free Fe supply for the formation of secondary ferrimagnetic minerals with strong magnetic signals (e.g., Spassov et al., 2003; Torrent et al., 2007). The extent to which free Fe is released by chlorite weathering in the northern part of the CLP is in doubt, as previous studies suggest that significant chlorite weathering has been restricted to the southern part (Jeong et al., 2011; Zhao et al., 2005). In this study, the clay mineralogy

* Corresponding author at: Key Laboratory of tourism and resources environment in Universities of Shandong, Taishan University, Taian 271021, China. Tel./fax: +86 538 6715208.

E-mail address: shuzhenpeng@gmail.com (S. Peng).

of samples from four loess sections spanning the last 130 ka on a NW–SE transect is investigated, with the primary aim of assessing chlorite weathering across the CLP. The contribution of chlorite weathering to the iron supply for secondary ferrimagnetic mineral formation is also considered.

2. Material and methods

The four studied sections, Huanxian (HX, 36°37' N, 107°19' E), Xifeng (XF, 35°53' N, 107°58'E), Changwu (CW, 35°12' N, 107°48'E) and Weinan (WN, 34°18'N, 109°30'E) lie along a NW–SE transect across the eastern CLP (Fig. 1). The mean annual temperature (MAT) and mean annual precipitation (MAP) of these sections are 8 °C and 400 mm, 8.3 °C and 550 mm, 9.1 °C and 584 mm, and 13.6 °C and 691 mm, respectively. The upper parts of the sections span the last 130 ka and contain Holocene (S0), Last Interglacial (S1) soils and Last Glacial loess (L1). The unit L1 can be subdivided into three parts: loess horizons (L1LL1 and L1LL2) and a weakly developed soil complex (L1SS1). All samples were collected at 10-cm intervals.

Magnetic susceptibility (MS) was measured on air-dried samples using a Bartington Instruments MS2 susceptibility meter. Clay minerals were measured by X-ray diffraction (XRD) on oriented mounts of clay-sized particles (<2 μm). The samples were pretreated to remove organic matter using a 10% H₂O₂ solution. Oriented specimens were prepared on glass slides using the pipette method at room temperature. XRD analysis was carried out using a PANalytical X'Pert PRO X-ray diffractometer with CuKα radiation, operating at 40 kV, 40 mA. Slides were scanned from 3 to 28 °2θ with a step size of 0.0167°2θ and a scan speed of 0.0711°/s under the air-dried and ethylene-glycol saturated condition for Mg-saturated samples, and the air-dried and heated to 400 °C condition for K-saturated samples. To distinguish chlorite (0.354 nm) from kaolinite (0.358 nm), the range 24–26°2θ was also measured with a step size of 0.004 °2θ and a scan speed of 0.006°/s.

The identification of clay minerals was made primarily based on the position of the (001) series of basal reflections on the XRD diagrams (Moore and Reynolds, 1989). Peak identification was performed graphically using the Macintosh program MacDiff (version 4.2.5) (Petschick, 2000). The chlorite chemistry was calculated based on the integral

area ratios of the 1.4 nm, 0.7 nm (minus the kaolinite portion) and 0.47 nm peaks (John et al., 2006; Oinuma et al., 1972). The integral areas of chlorite (0.7 nm) were separated by relative proportions given by a ratio of the kaolinite (0.358 nm) and chlorite (0.354 nm) complex peak areas (Biscaye, 1965). The chlorite ratio was calculated as the integral area ratio of the chlorite diffraction peak at 0.47 and 0.7 nm. The illite/chlorite ratio (I/C ratio), an index for characterizing the weathering of chlorite (Zhao et al., 2005), was calculated as the ratio of the areas of the (002) peak of illite at 0.5 nm and the (003) peak of chlorite at 0.47 nm.

3. Results

The typical XRD patterns of the <2 μm fraction from the studied loess sections are illustrated in Fig. 2. The reflections of chlorite are identified at 1.4, 0.7 and 0.47 nm based on a comprehensive comparison of four multiple XRD diagrams obtained under different measurement conditions (Fig. 2). A ternary diagram of the relative percentages of chlorite at the 1.4, 0.7 and 0.47 nm peaks of all samples from the four sections is shown in Fig. 3. This diagram was proposed by Oinuma et al. (1972) to characterize chlorite chemistry. The 1.4, 0.7 and 0.47 nm peaks reflect Mg-, Fe- and Al-chlorites, respectively. Fig. 3 clearly indicates that the chlorite composition oscillates between Fe- and Mg-chlorites in the trioctahedral sheet of the silicate layer (John et al., 2006; Oinuma et al., 1972). This is in good agreement with earlier results obtained using an electron microprobe (Ji et al., 2006). The remarkable feature is that the percentages of Fe- and Mg-chlorites vary widely, whereas the Al-chlorite percentage remains relatively constant among all the loess and soil samples. All loess samples lie within a fairly narrow range of Fe- and Mg-chlorite content, while the paleosol samples show a much wider range for these two chlorites, with a trend towards the Fe-chlorite end-members decreasing from the Huanxian to Weinan sections.

Because the Al-chlorite percentage remains relatively unchanged in response to weathering, we use the chlorite ratio (0.47/0.7 nm) to indicate the Fe-chlorite loss relative to Al-chlorite, with high values corresponding to higher levels of loss of Fe-chlorite. Fig. 4 shows that the chlorite ratio in the Xifeng, Changwu and Weinan sections is higher in

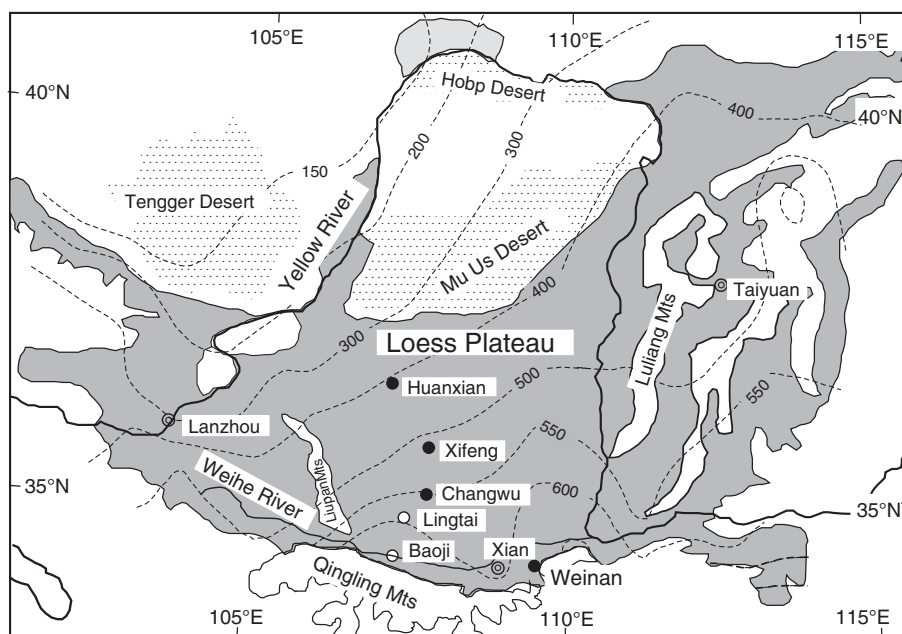


Fig. 1. Schematic map showing the Chinese Loess Plateau (gray color), the locations of the sections in this study (solid circle) and other mentioned sections in this text (open circle), and the modern mean annual precipitation isolines (mm, dashed line) (after Hao and Guo, 2005).

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