



# Elimination and evaluation of grain size's effect in analysis of chemical weathering of loess–paleosol sequences

Xiaoguang Qin\*, Yan Mu<sup>1</sup>

Key Laboratory of Cenozoic Geology and Environment, Institute of Geology and Geophysics, Chinese Academy of Sciences, No.19 Beitucheng Xi Rd., Beijing 100029, China

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## ABSTRACT

The elimination of grain size's effect is vital to analyze the chemical weathering history of eolian deposits. In this study, the relationship between chemical weathering and grain-size distribution of eolian deposits are analyzed and a new approach was developed to eliminate the effect of grain size in evaluation of chemical weathering. It was concluded (1) the effect of grain size to major elemental abundances (MEA) can be eliminated by deducting the grain size-led offset from measured major elemental abundances. (2) The effect of grain size to MEA intensified from south to north in Chinese loess plateau as chemical weathering weakened. The effect of grain size to MEA did not change the whole evolution trend of MEA in time series. (3) The similarity between median size and MMEA indicated the effect level of grain size to MEA. (4) The effect of chemical weathering to grain-size distribution is neglectable for loess–paleosol formation. (5) Usually, the effect of grain size to chemical weathering index is more remarkable in interglacial periods than in glacial period.

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## 1. Introduction

Loess is widely distributed on the Earth's surface, especially, in the northern China (Liu, 1985; Eitel et al., 2004; Sinha et al., 2006). Loess deposited during cold periods when northwesterly monsoons prevailed, whereas paleosols developed on the loess and coupled with dust deposition during warm periods when southeasterly winds of summer monsoons dominated (Liu, 1985). Loess–paleosol sequences in Chinese loess plateau recorded the history of chemical weathering in arid and semiarid regions of Asia. The studies of elemental behaviors of loess during pedogenesis demonstrated that systemic variation of element abundances indicated variations of pedogenetic intensity (Gallet et al., 1996). Various dimensionless weathering indexes, such as Chemical Index of Alteration (CIA) and Chemical Index of Weathering (CIW), have been widely employed to quantify the relative weathering intensity of loess deposits (Liu et al., 1995a,b; Chen et al., 2001). However, chemical weathering intensity was largely influenced by three factors: chemical weathering in source regions, post-depositional weathering and grain size that is related to depositional processes (Yang et al., 2006). Because elemental concentrations of dust deposits are partially dependent on grain-size changes (Wen et al., 1989), those proxies of chem-

ical weathering intensity of loess may be different prior to any post-depositional weathering processes. It strongly suggests that elemental concentrations free of grain-size effects are important to reveal the chemical weathering history of the region. Yang et al. (2006) invested elemental depletion characteristics in Chinese and Tajik loess and elemental ratios in different size fractions for a north–south transect on the Chinese loess plateau. They developed a proxy of chemical weathering intensity,  $(\text{CaO} + \text{Na}_2\text{O} + \text{MgO})/\text{TiO}_2$  of decarbonated residue that was believed to suffer little grain-size influence. In this paper, we developed a new approach to eliminate grain size's effect of chemical weathering by deducting directly the grain size-led offset from measured major elemental abundances.

## 2. Studied sections and measurement

We choose two loess–paleosol sections respectively located at the north and south of Chinese loess plateau to evaluate the approach eliminating grain size's effect of chemical weathering. Weinan loess–paleosol section (34°34'N, 109°32'E) located at Yangge town of Weinan, Shanxi province in the southern part of the Loess Plateau. Xifeng loess–paleosol section (35°44.8'N, 107°39.7'E) located at Gansu province, the northern part of the loess plateau (Fig. 1).

The two S<sub>0</sub>–L<sub>2</sub> loess–paleosol sections were sampled at the interval of 10 cm. Magnetic susceptibility (MS) of samples was measured by a Bartington MS2 susceptibility meter. Grain-size distribution was determined with a Malvern Mastersizer 2000 particle analyzer. Measurement procedures are same as methods of Qin et

\* Corresponding author. Tel.: +86 10 82998392.

E-mail addresses: [xiaoguangqin@mail.iggcas.ac.cn](mailto:xiaoguangqin@mail.iggcas.ac.cn) (X. Qin), [muyan@mail.iggcas.ac.cn](mailto:muyan@mail.iggcas.ac.cn) (Y. Mu).

<sup>1</sup> Tel.: +86 10 82998392.

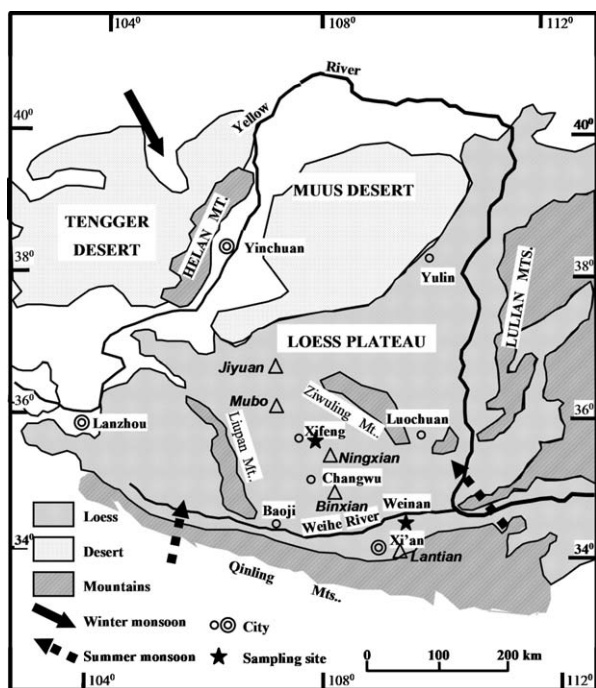


Fig. 1. Location of Weinan and Xifeng sections in Chinese Loess Plateau. Triangle: sampling sites of Yang et al. (2006).

al. (2005). For measurement of major elemental abundances (MEA), samples were finely ground in agate mortar. MEA were determined by X-ray fluorescence spectrometry (XRF). Analytical precisions are  $\pm 0.1\%$  for all major elements except for  $P_2O_5$ ,  $MnO$  ( $\pm 0.01\%$ ),  $SiO_2$  ( $\pm 0.2\%$ ) and  $K_2O$  ( $\pm 0.05\%$ ). The formations of two sections were determined by comparing the MS sequences published by Liu et al. (1994, 1995a,b).

### 3. Method eliminating grain size's effect of chemical weathering intensity

Yang et al. (2006) studied the impact of grain-size distribution to MEA of decarbonated loess–paleosol samples from different locations of Chinese Loess Plateau (Fig. 1). In their study, all samples for carbonate-free analysis were treated with 1 M acetic acid for 12 h at room temperature to remove carbonate after finely ground in agate mortar. The residue was rinsed and dried up in an oven at  $105^\circ C$ . Then, samples were sent to X-ray fluorescence analysis again. They found that most MEA of different grain-size fractions vary considerably for both loess and/or paleosols. However, MEA of loess–paleosol samples in a grain-size fraction are close but obviously different from MEA of other grain-size fractions. From their results, the average major elemental abundances (AMEA) of different grain-size fractions of decarbonated loess–paleosol samples were summarized in Table 1. Abundances of  $Al_2O_3$ ,  $Fe_2O_3$ ,  $K_2O$ ,  $MnO$ ,  $P_2O_5$  and  $MgO$  in fine grain fractions are larger than those in coarse grain fractions and  $SiO_2$ ,  $Na_2O$ , and  $CaO$  in fine grain fractions are lower than in coarse grain fractions.

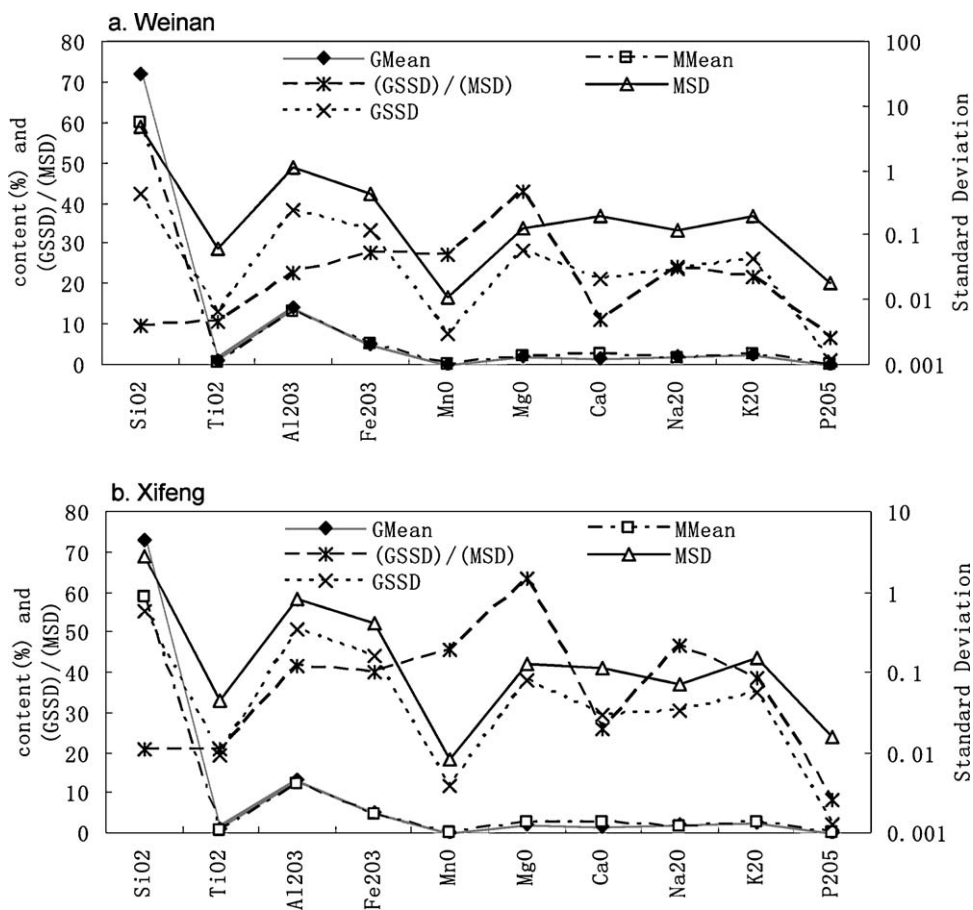


Fig. 2. Comparisons of mean and standard deviation (SD) of GSMEAs and MEAs. (a) Weinan section and (b) Xifeng section. GMean, GSD: the mean and the standard deviation of GSMEA. MMean, MSD: the mean and the standard deviation of MMEA. (GSD)/(MSD): the ratio ( $\times 100\%$ ) of SD of GSMEA and MMEA. MMEA of CaO is the value estimated from NaO and the ionic molar ratio Ca/Na of loess silicate because measured samples were not decarbonated.

**Table 1**  
Average major elemental abundances of 6 grain-size fractions (based on Yang et al., 2006).

Grain-size range	<2 $\mu\text{m}$	2–5 $\mu\text{m}$	5–16 $\mu\text{m}$	16–32 $\mu\text{m}$	32–64 $\mu\text{m}$	>64 $\mu\text{m}$
SiO <sub>2</sub>	56.21	64.92	72.48	75.85	77.96	79.75
TiO <sub>2</sub>	0.72	0.93	0.84	0.73	0.71	0.65
Al <sub>2</sub> O <sub>3</sub>	23.59	17.78	13.27	11.61	10.26	9.32
Fe <sub>2</sub> O <sub>3</sub>	9.74	7.19	4.90	3.97	3.39	3.11
MnO	0.17	0.16	0.09	0.05	0.05	0.05
MgO	3.8	3.20	2.25	1.63	1.44	1.14
CaO	1.00	1.00	1.33	1.73	1.74	1.66
Na <sub>2</sub> O	0.41	1.20	1.94	2.14	2.15	2.07
K <sub>2</sub> O	4.12	3.50	2.76	2.14	2.15	2.12
P <sub>2</sub> O <sub>5</sub>	0.24	0.14	0.19	0.16	0.15	0.13

MEA completely led by grain-size distribution can be estimated from the grain-size distribution (GSD) of samples and AMEA of 6 grain fractions in Table 1:

$$S_i = \sum_{j=1}^6 a_{i,j} c_j \quad (1)$$

where  $i$  means  $i$ th oxide (SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, etc.).  $j$  ( $=1, 2, \dots, 6$ ) means  $j$ th of six grain-size fractions.  $a_{i,j}$  is AMEA of  $i$ th oxide in  $j$ th grain-size fraction.  $c_j$ , the percentage content of  $j$ th grain-size fraction gotten from GSD of a studied sample.  $S_i$  is the estimated major elemental abundance of  $i$ th oxide for the studied sample and was called as the grain size-led major elemental abundances (GZMEA).

It is known that chemical weathering intensity of loess–paleosol samples should be evaluated on a uniform GSD. Therefore, we can choose any one loess sample as a standard sample of GSD. The

difference of GZMEA between the standard sample and a studied sample can be seen as the grain size-led MEA offset of the studied sample. Grain size-free MEA (GZFMEA),  $H_{i,j}$ , is gotten from the following formula for the  $i$ th oxide of the  $j$ th studied sample:

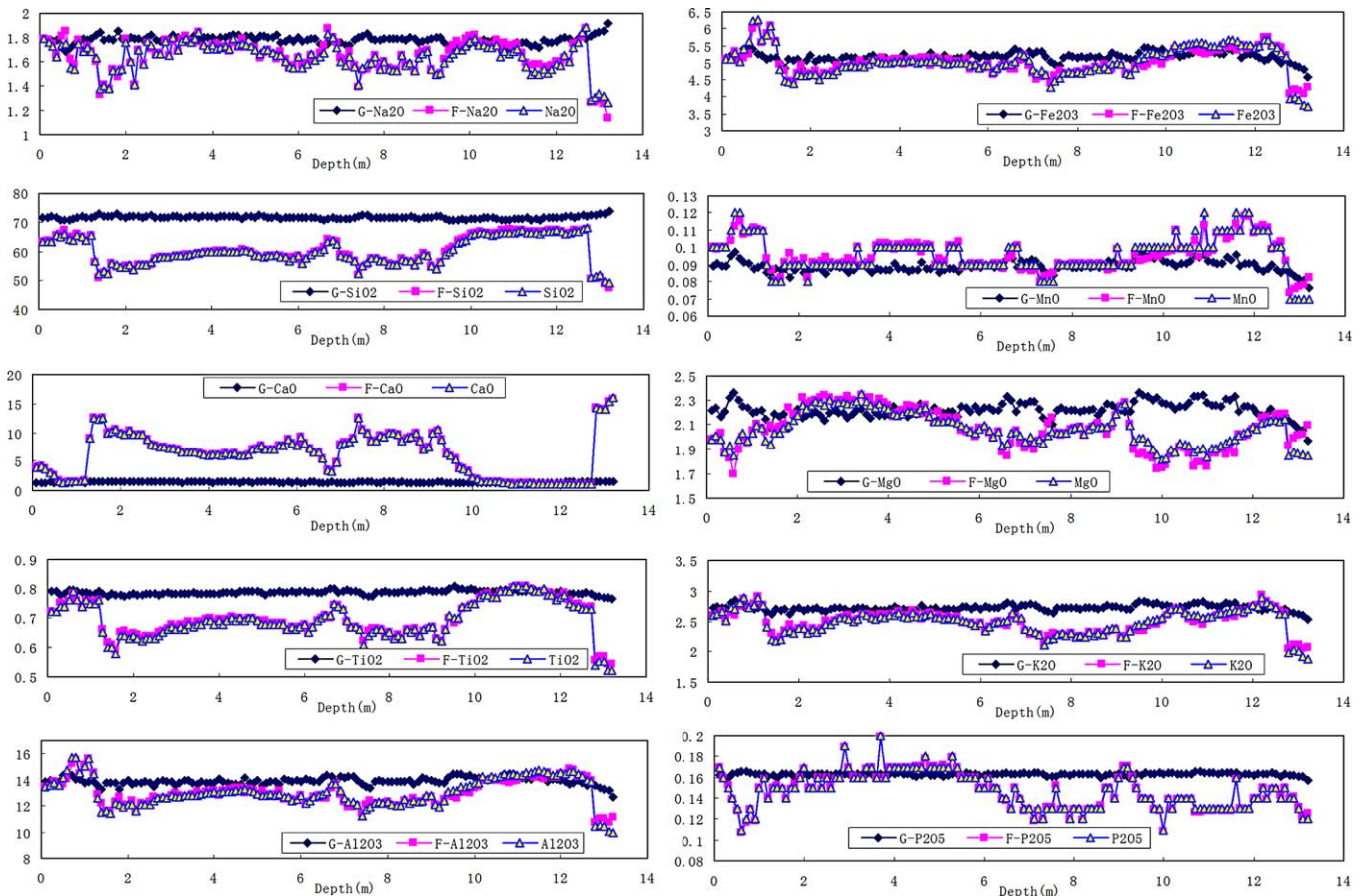
$$H_{i,k} = M_{i,k} - (S_{i,k} - B_i) \quad (2)$$

where  $B_i$  is GZMEA of the  $i$ th oxide of the standard sample.  $S_{i,k}$  is GZMEA of the  $i$ th oxide of the  $k$ th sample.  $M_{i,k}$  is the measured major elemental abundance (MMEA) of the  $i$ th oxide of the  $k$ th sample.

#### 4. Analysis

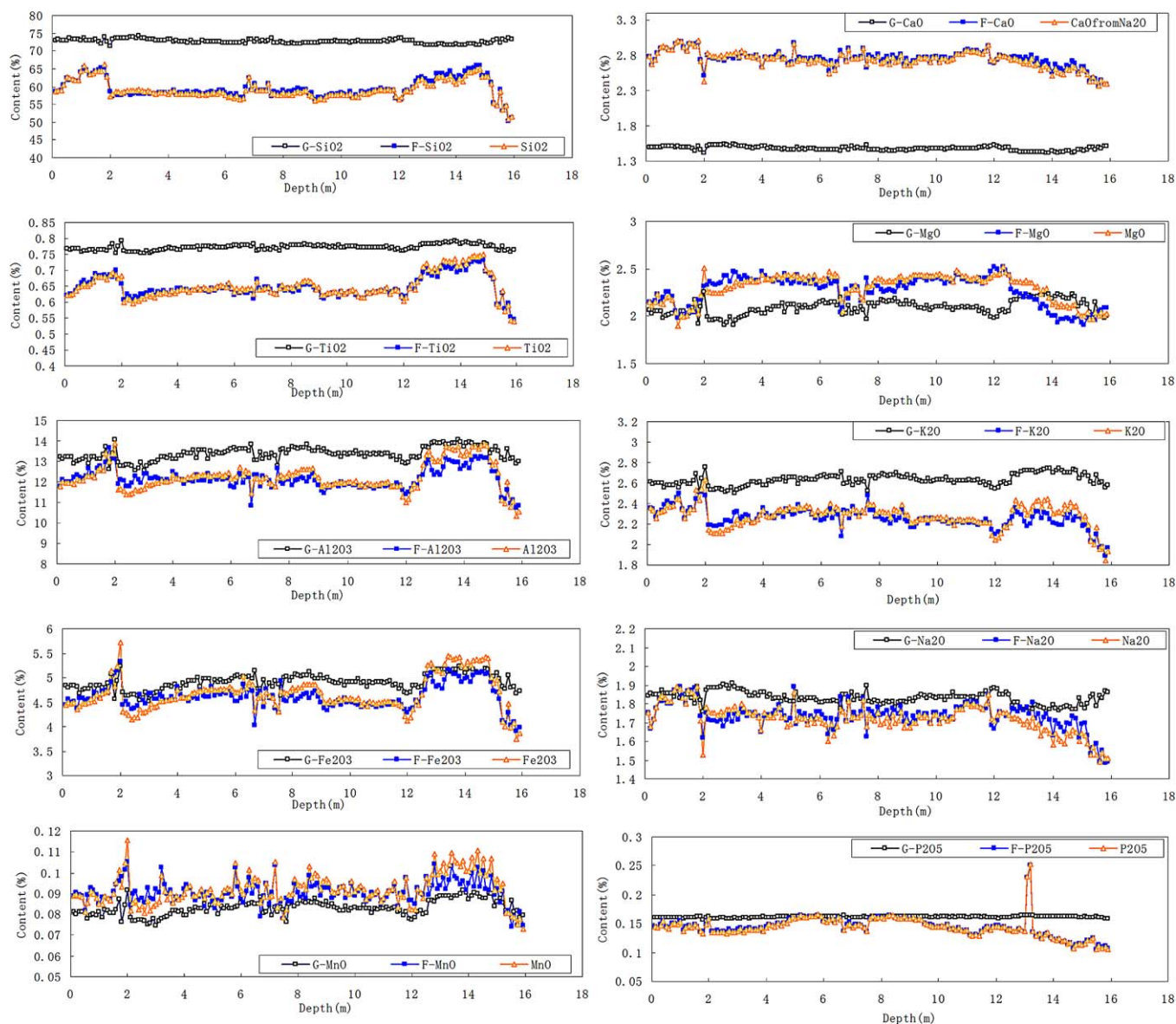
##### 4.1. The effect of grain size to MEA of loess recorded by time series

In Fig. 2, the mean and the standard deviation (SD) of GSMEA and MMEA of Weinan and Xifeng loess–paleosol sections were shown.



**Fig. 3.** Comparison of measured major elemental abundances (MMEA), grain size-led major elemental abundances (GZMEA) and grain size-free major elemental abundances (GZFMEA) of Weinan S<sub>0</sub>–L<sub>2</sub> loess–paleosol section. Dark blue diamond (G-oxide): GZMEA. Pink square (F-oxide): GZFMEA. Blue triangle (oxide): MMEA. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)





**Fig. 4.** Comparison of measured major elemental abundances (MMEA), grain size-led major elemental abundances (GZMEA) and grain size-free major elemental abundances (GZFMEA) of Xifeng  $S_0$ – $L_2$  loess–paleosol section. Dark black square (G-oxide); GZMEA. Blue square (F-oxide); GZFMEA. Orange triangle (oxide); MMEA. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

It was found that means of GSMEA and MMEA of each oxide are very close for most oxides, suggesting that MEA estimated from grain-size distribution are acceptable.  $SiO_2$  and CaO was an exception. It is because the measurement of MEA in our study is not decarbonated, thus to lead the larger CaO abundance and the lower  $SiO_2$  abundance. Due to the similarity of MEA between loess and granite (Liu, 1985; Gallet et al., 1996), we use the approximate average ionic molar ratio Ca/Na (=0.88) of albite and Ca-plagioclase in granites of China (Wuhan Collage of Geology, 1980) as the ionic molar ratio Ca/Na of loess silicate to estimate CaO abundance of carbonate-free loess samples. In this case, the means of GSMEA and MMEA of CaO are very close and the grain size-led offset is too low to change the abundance of CaO carbonate-free loess samples.

The time series of MMEA, GZMEA and GZFMEA of Weinan and Xifeng loess–paleosol sections were shown in Figs. 3 and 4, respectively. The curves of MMEA and GZFMEA are almost identical except for a few minor differences for most oxides. The amplitude of glacial–interglacial fluctuation of GZMEA is far less than that of MMEA. Therefore, the effect of grain size to the abundance of most

oxides is slight. It is concluded that the grain size's effect of MEA of loess and paleosol is existent but not enough to change the whole evolution trend of chemical weathering of loess–paleosol formation.

#### 4.2. The relationship between MEA and Md

GSD of loess and paleosol is similar but the proportion of  $<10 \mu m$  particles of loess samples is remarkably different from that of paleosol samples (Qin et al., 2005). Table 2 lists correlation coefficients between GZMEA of oxides and the proportion of each grain-size fraction, Md, and MS. Larger value of correlation coefficients indicates that coarse particles play a major role for Md and fine particles ( $<16 \mu m$ ) are major contributors of MS.

It was noted that GZMEA of  $SiO_2$ , CaO and  $Na_2O$  significant positively correlated with Md but GZMEA of  $Al_2O_3$ ,  $Fe_2O_3$ ,  $P_2O_5$ ,  $K_2O$ ,  $TiO_2$ , MgO, and MnO are negatively correlation with Md. Obviously, coarse particles ( $>16 \mu m$ ) are former's major contributors and fine particles (especially  $<5 \mu m$ ) are latter's major contributors. Abso-

**Table 2**

Correlation coefficients between GZMEA, Md, MS, and the proportion of grain-size fractions of Weinan section (black boxes indicate these negative correlation coefficients with larger absolute value).

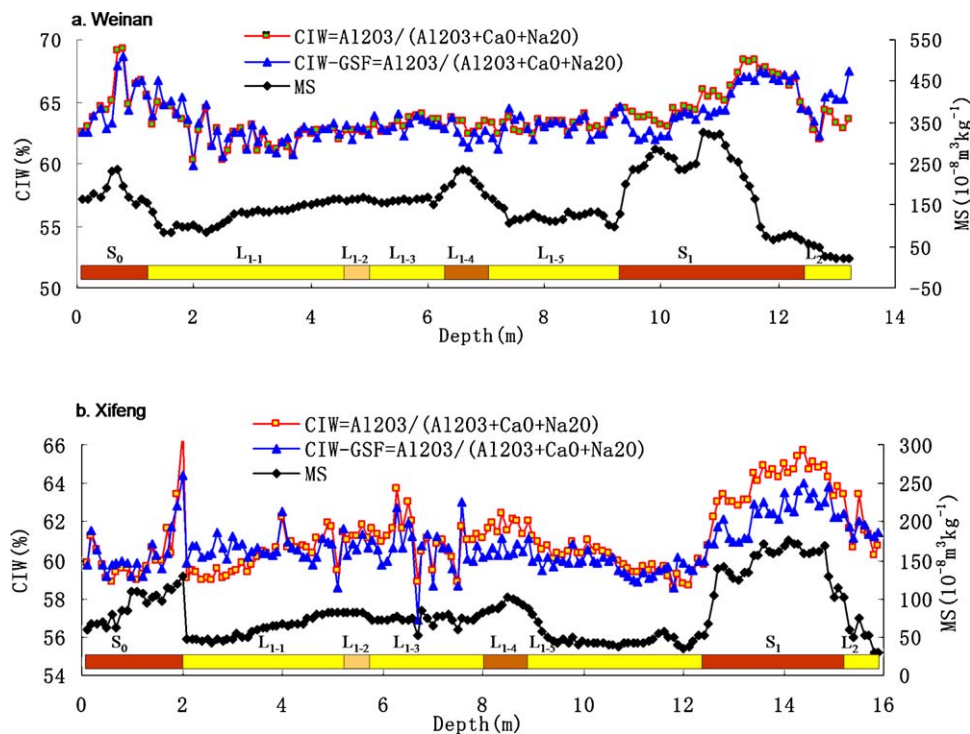
	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	MS	Md
Md	0.95	-0.96	-0.94	-0.95	-0.96	-0.97	0.98	0.88	-0.96	-0.66	-0.69	1
<2μm	-0.79	0.38	0.81	0.80	0.75	0.73	-0.65	-0.87	0.77	0.89	0.47	-0.58
2–5μm	-0.87	0.87	0.86	0.87	0.93	0.89	-0.94	-0.86	0.91	0.48	0.60	-0.92
5–16μm	-0.67	0.92	0.65	0.65	0.67	0.73	-0.76	-0.50	0.67	0.35	0.62	-0.83
16–32μm	0.38	-0.22	-0.38	-0.40	-0.50	-0.37	0.48	0.53	-0.47	-0.04	-0.14	0.39
32–64μm	0.75	-0.83	-0.74	-0.75	-0.77	-0.77	0.84	0.68	-0.77	-0.39	-0.76	0.85
>64μm	0.66	-0.73	-0.65	-0.63	-0.56	-0.68	0.56	0.48	-0.59	-0.72	-0.40	0.64
MS	-0.70	0.67	0.69	0.70	0.69	0.70	-0.71	-0.65	0.70	0.51	1	-0.69

lute values of correlative coefficient between GZMEA and Md are significantly larger than those between GZMEA and MS. Thus, the similarity between MEA and Md can be regarded as a proxy indicating the effect level of grain size to MEA.

#### 4.3. The effect of grain size to MEA of loess recorded by the standard deviation

Comparing the standard deviation of GSMEA (GSSD) with the standard deviation of MMEA (MSD), a GSSD close to MSD means that the changes of GSMEA may significantly dominate the fluctuation of MEA. Thus, the ratio (GSSD/MSD) is an indicator of effect

level of GSD to MEA. In Weinan section, most of GSSD are about 10–30% of MSD (Fig. 2a). The ratio (48%) of MgO is the largest. However, the whole trend of MgO was not changed after removing the grain size-led offset except for a few slight changes (Fig. 3). Similar characteristics were also found in Xifeng section (Fig. 2b). Because Xifeng section is located at the north of Weinan section and is closer to dust sources, chemical weathering intensity of Xifeng loess was weaker than Weinan loess. Thus, the Xifeng's ratio (GSSD/MSD) larger than Weinan's suggests that the effect of grain size to MEA in Xifeng was more prominent than in Weinan. It is concluded that the effect of grain size to MEA increased from south to north as dust source distance decreased and chemical weathering intensity



**Fig. 5.** Paleoclimatic change recorded by Chemical Index of Weathering (CIW) of Weinan and Xifeng loess-paleosol section since the last interglacial period. a. Weinan section and b. Xifeng section. CIW, Chemical Index of Weathering calculated from MMEA based on the formula  $CIW = 100 \times Al_2O_3 / (Al_2O_3 + CaO + Na_2O)$ , CaO is estimated from Na<sub>2</sub>O because analyzed samples were not decarbonated; CIW-GSF, grain size-free Chemical Index of Weathering gotten from GSFMEA; MS, magnetic susceptibility; S<sub>0</sub>, Holocene paleosol; L<sub>1-1</sub>, L<sub>1-3</sub>, L<sub>1-5</sub>, loess of the last glacial period; L<sub>1-2</sub>, L<sub>1-4</sub>, paleosols of the last glacial period (L<sub>1-2</sub> is not clear in two sections); S<sub>1</sub>, paleosol of the last interglacial period; L<sub>2</sub>, loess of the penultimate glacial period

weakened. Usually, the grain size's influence was weak enough to be ignored for most oxides in most cases.

#### 4.4. The effect of chemical weathering to grain size of loess recorded by the standard deviation

On the other hand, chemical and physical weathering may result in coarse mineral particles broken into fine grains, thus changing GSD of loess and paleosol. Clearly, GSSD would be close to MSD if weathering was strong and remarkably dominated GSD. A GSSD value much larger than MSD suggests that GSD may be dominated by wind deposition process and there might be other factors impacting MMEA. The effect of weathering to GSD would be slight and negligible if the GSSD value is far less than MSD in loess records and the fluctuation trends of GSMEA and MMEA are different. Thus, the ratio (GSSD/MSD) also indicates the effect of weathering to GSD. In both Weinan and Xifeng loess sections, GSSD is lower than MSD and GSMEAs fluctuations differed from MMEA's. Especially, the ratio GSSD/MSD (20–60%) of Xifeng is larger than that of Weinan. It is known that chemical weathering in Xifeng should be weaker than that in Weinan because the summer monsoon comes from southeast to northwest and dust source was nearer to Xifeng than to Weinan (Liu, 1985). Thus, the effect of weathering to GSD is unimportant and negligible in loess–paleosol formations.

### 5. Chemical weathering from last interglacial period

Chemical Index of Weathering ( $CIW = 100 \times Al_2O_3 / (Al_2O_3 + CaO + Na_2O)$ ) of loess–paleosol section is a useful proxy of paleoclimatic change (Liu and Ding, 1998). Fig. 5 shows depth sequences of CIW gotten from MMEA, grain size-free CIW (CIW-GSF) calculated from GZFMEA and magnetic susceptibility (MS) in Weinan and Xifeng loess–paleosol formations, respectively. It was noted that the glacial–interglacial scale fluctuation between CIW and CIW-GSF was similar except for a few short stages in two sections. In interglacial periods, CIW was often overestimated, especially during the last interglacial period  $S_1$ . Chemical weathering of Weinan recorded by CIW-GSF was usually less than that of Xifeng. Grain-sizes' impact to CIW in the north of Loess Plateau was stronger than in the south. In poorly developed paleosol  $L_{1-4}$ , chemical weathering (CIW-GSF) did not strengthen significantly in two sites. It was noted that the fluctuation of MS was obviously different from CIW-GSF during the last interglacial period in Weinan section, implied that there may be special environmental forcings.

### 6. Conclusion

From above analysis, several important conclusions can be summarized.

(1) The effect of grain size to MEA is existent and can be eliminated by deducting the grain size-led offset from MMEA. The approach allows all oxides to be useable for sequential analysis. Thus, all former chemical weathering indices, such as CIA and CIW, still can be used to study the behavior of chemical weathering.

- (2) The effect of grain size to MEA intensified from south to north as chemical weathering weakened in Chinese loess plateau. The effect of grain size to MEA did not change the whole fluctuation trend of MEA in most cases.
- (3) The similarity level between Md and MMEA can be used as a proxy of effect level of grain size to MEA.
- (4) The effect of chemical weathering to grain-size distribution is neglectable for loess–paleosol formation in most cases although chemical weathering may be overestimated during interglacial periods.

The premise of the above approach is that AMEA of each grain-size fraction is relatively steady. It is impossible to completely eliminate grain size's effect of chemical weathering because MEA of every grain-size fraction varies slightly from loess to paleosol. However, It is the simplest and most efficient approach to eliminate grain size's effect of chemical weathering of eolian deposits.

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