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

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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) The effect of grain size to chemical weathering of loess–paleosol sequences is analyzed and a new approach was developed to eliminate the effect of grain size in evaluation of chemical weathering intensity. It was concluded that elemental 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.

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 deposits 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 chemical 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.

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, Shaanxi 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 S0–L2 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 al.
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 ±0.1% for all major elements except for P₂O₅, MnO (±0.01%), SiO₂ (±0.2%) and K₂O (±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 °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 Al₂O₃, Fe₂O₃, K₂O, MnO, P₂O₅ and MgO in fine grain fractions are larger than those in coarse grain fractions and SiO₂, Na₂O, and CaO in fine grain fractions are lower than in coarse grain fractions.
Table 1

<table>
<thead>
<tr>
<th>Grain-size range</th>
<th>&lt;2 μm</th>
<th>2–5 μm</th>
<th>5–16 μm</th>
<th>16–32 μm</th>
<th>32–64 μm</th>
<th>&gt;64 μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>56.21</td>
<td>64.92</td>
<td>72.48</td>
<td>75.85</td>
<td>77.96</td>
<td>79.75</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.72</td>
<td>0.93</td>
<td>0.84</td>
<td>0.73</td>
<td>0.71</td>
<td>0.65</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>23.59</td>
<td>17.78</td>
<td>13.27</td>
<td>11.61</td>
<td>10.26</td>
<td>9.32</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>9.74</td>
<td>7.19</td>
<td>4.90</td>
<td>3.97</td>
<td>3.39</td>
<td>3.11</td>
</tr>
<tr>
<td>MnO</td>
<td>0.17</td>
<td>0.16</td>
<td>0.09</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>MgO</td>
<td>3.8</td>
<td>3.20</td>
<td>2.25</td>
<td>1.63</td>
<td>1.44</td>
<td>1.14</td>
</tr>
<tr>
<td>CaO</td>
<td>1.00</td>
<td>1.00</td>
<td>1.33</td>
<td>1.73</td>
<td>1.74</td>
<td>1.66</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.41</td>
<td>1.20</td>
<td>1.94</td>
<td>2.14</td>
<td>2.15</td>
<td>2.07</td>
</tr>
<tr>
<td>K₂O</td>
<td>4.12</td>
<td>3.50</td>
<td>2.76</td>
<td>2.14</td>
<td>2.15</td>
<td>2.12</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.24</td>
<td>0.14</td>
<td>0.19</td>
<td>0.16</td>
<td>0.15</td>
<td>0.13</td>
</tr>
</tbody>
</table>

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:

\[ S_i = \sum_{j=1}^{6} a_{ij} c_j \]  (1)

where \( i \) means \( i \)th oxide (SiO₂, Al₂O₃, etc.), \( j (=1,2,\ldots,6) \) means \( j \)th of six grain-size fractions. \( a_{ij} \) 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), \( H_{i,k} \), is gotten from the following formula for the \( i \)th oxide of the \( j \)th studied sample:

\[ H_{i,k} = M_{i,k} - (S_{i,k} - B_i) \]  (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 S₀–L₂ 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.)
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. \( \text{SiO}_2 \) and \( \text{CaO} \) was an exception. It is because the measurement of MEA in our study is not decarbonated, thus to lead the larger \( \text{CaO} \) abundance and the lower \( \text{SiO}_2 \) 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 \( \text{Ca}/\text{Na} = 0.88 \) of albite and Ca-plagioclase in granites of China (Wuhan Collage of Geology, 1980) as the ionic molar ratio \( \text{Ca}/\text{Na} \) of loess silicate to estimate \( \text{CaO} \) abundance of carbonate-free loess samples. In this case, the means of GSMEA and MMEA of \( \text{CaO} \) are very close and the grain size-led offset is too low to change the abundance of \( \text{CaO} \) carbonate-free loess samples.

The time series of MMEA, GSMEA 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 \( \mu \text{m} \) 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 \( \mu \text{m} \)) are major contributors of MS.

It was noted that GZMEA of \( \text{SiO}_2 \), \( \text{CaO} \) and \( \text{Na}_2\text{O} \) significant positively correlated with Md but GZMEA of \( \text{Al}_2\text{O}_3 \), \( \text{Fe}_2\text{O}_3 \), \( \text{P}_2\text{O}_5 \), \( \text{K}_2\text{O} \), \( \text{TiO}_2 \), \( \text{MgO} \), and \( \text{MnO} \) are negatively correlation with Md. Obviously, coarse particles (>16 \( \mu \text{m} \)) are former’s major contributors and fine particles (especially <5 \( \mu \text{m} \)) 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).

<table>
<thead>
<tr>
<th></th>
<th>SiO₂</th>
<th>TiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>MnO</th>
<th>MgO</th>
<th>CaO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>P₂O₅</th>
<th>MS</th>
<th>Md</th>
</tr>
</thead>
<tbody>
<tr>
<td>Md</td>
<td>0.95</td>
<td>-0.96</td>
<td>-0.94</td>
<td>-0.95</td>
<td>-0.96</td>
<td>-0.97</td>
<td>0.98</td>
<td>0.88</td>
<td>-0.96</td>
<td>-0.66</td>
<td>-0.69</td>
<td>1</td>
</tr>
<tr>
<td>&lt;2μm</td>
<td>-0.79</td>
<td>0.38</td>
<td>0.81</td>
<td>0.80</td>
<td>0.75</td>
<td>0.73</td>
<td>-0.65</td>
<td>-0.87</td>
<td>0.77</td>
<td>0.89</td>
<td>0.47</td>
<td>-0.58</td>
</tr>
<tr>
<td>2.5μm</td>
<td>-0.87</td>
<td>0.87</td>
<td>0.86</td>
<td>0.87</td>
<td>0.93</td>
<td>0.89</td>
<td>-0.94</td>
<td>-0.86</td>
<td>0.91</td>
<td>0.48</td>
<td>0.60</td>
<td>-0.92</td>
</tr>
<tr>
<td>5–16μm</td>
<td>-0.67</td>
<td>0.92</td>
<td>0.65</td>
<td>0.65</td>
<td>0.67</td>
<td>0.73</td>
<td>-0.76</td>
<td>-0.50</td>
<td>0.67</td>
<td>0.35</td>
<td>0.62</td>
<td>-0.83</td>
</tr>
<tr>
<td>16–32μm</td>
<td>0.38</td>
<td>-0.22</td>
<td>-0.38</td>
<td>-0.40</td>
<td>-0.50</td>
<td>-0.37</td>
<td>0.48</td>
<td>0.53</td>
<td>-0.47</td>
<td>-0.04</td>
<td>-0.14</td>
<td>0.39</td>
</tr>
<tr>
<td>32–64μm</td>
<td>0.75</td>
<td>-0.83</td>
<td>-0.74</td>
<td>-0.75</td>
<td>-0.77</td>
<td>-0.77</td>
<td>0.84</td>
<td>0.68</td>
<td>-0.77</td>
<td>-0.39</td>
<td>-0.76</td>
<td>0.85</td>
</tr>
<tr>
<td>&gt;64μm</td>
<td>0.66</td>
<td>-0.73</td>
<td>-0.65</td>
<td>-0.63</td>
<td>-0.56</td>
<td>-0.68</td>
<td>0.56</td>
<td>0.56</td>
<td>-0.59</td>
<td>-0.72</td>
<td>-0.90</td>
<td>0.64</td>
</tr>
<tr>
<td>MS</td>
<td>-0.70</td>
<td>0.67</td>
<td>0.69</td>
<td>0.70</td>
<td>0.69</td>
<td>0.70</td>
<td>-0.71</td>
<td>-0.65</td>
<td>0.70</td>
<td>0.51</td>
<td>1</td>
<td>-0.69</td>
</tr>
</tbody>
</table>

Lute values of correlation 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.
5. Chemical weathering from last interglacial period

Chemical Index of Weathering (CIW = 100 \times \frac{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 S1. 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 L1-4, 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 usable 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 negligible 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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References