Effectiveness of rare earth elements constrain on different materials: a case study in central Asia

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Effectiveness of rare earth elements constrain on different materials: a case study in central Asia

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Abstract Rare earth elements (REE) have been extensively used to indicate for material provenance since they behave conservatively and mainly transport in particulate form during earth surface processes. Nevertheless, the application of REE for material provenance study has to be cautious because grain size and mineral fractionations can alter bulk compositions of weathered sediments. Central Asia is one of the most important dust source regions globally and numerous studies on REE compositions of surface materials have been conducted. In this study, REE compositions of various materials from this area are summarized to explore the existing REE-related problems. Overall, chondrite-normalized REE patterns for many surface materials are so uniform that they cannot serve as reliable approaches in tracing material source regions. In contrast, great variations of REE compositions occur among different materials that are derived even from the same parent rock due to influences of grain-size distributions and heavy minerals. For the same reason, small-scale loess around the Tibetan Plateau has different upper continental crust (UCC)-normalized REE patterns compared to those of typical loess. Therefore, great cautions should be made when UCC-normalized REE patterns and REE ratios are utilized to investigate material provenance. Finally, some suggestions are proposed for such studies in future.

Keywords Rare earth elements · Material provenance · Upper continental crust · Central Asia

Introduction

Rare earth elements (REE) are a series of typical immobile elements that do not readily fractionate during earth surface processes (Taylor and McLennan 1985). This set of elements is widely used as robust evidence to determine source regions of dust aerosols (Svensson et al. 2000; Yang et al. 2007a; Zdanowicz et al. 2006; Zhang et al. 2009), loess (Honda et al. 2004; Sun 2002a), fluvial and marine sediments (Nakai et al. 1993; Yang et al. 2002), especially after the publication of a classic book by Taylor and McLennan (1985). The theories proposed in this book provide fundamental principles for subsequent geochemical studies. However, some theories on REE mentioned in the book sometimes are partially understood and misused. Among them the commonly misused two theories are “there is no significant difference in the REE patterns between the finest fractions (<1 μm) and the silt-sized (<20 μm) fraction (P37)” and “the nature of the Europium (Eu)-anomalies is similar in all of the size fractions considered (P38)”. Based on these two theories it is sometimes even considered that REE compositions are constant in all size fractions of the same material. Consequently, REE compositions and Eu anomalies were simply compared among different grain sizes in material provenance studies (Chang et al. 2000; Sun et al. 2007; Wu et al. 2009; Yang et al. 2007a), ignoring those cautions noted by the authors in the same book. Many of these cautions are related to the...
influence of heavy minerals such as: “heavy minerals reside most in silt fraction is generally HREE-enriched and high in total REE, and may significantly affect REE patterns of the sediments when clay fractions are minor (P31)””. Additionally, all of these theories are inferred mainly from studies of fine-grained clayey sediments and chondrite-normalized REE patterns, hence cannot be generalized to other materials directly and are not totally fit for the upper continental crust (UCC) normalized REE patterns and REE ratios. Therefore, great cautions should be made when these theories are applied directly to provenance studies of fine clay-lacked materials.

Central Asia is one of the largest dust source regions in the world (Prospero et al. 2002), and dust derived from this area is of particular interest in research areas such as paleoclimate (Ding et al. 2001), atmospheric circulation (Aloys et al. 2003; Kang et al. 2002; Prospero et al. 2002; Rea et al. 1998), and even tectonic activities (An et al. 2001). The Loess Plateau (LP) and the Taklimakan Desert (TAK) are the two most important dust source areas in this region. It has been proposed that loess is contributed from deserts, materials of which are initially derived from various processes such as glacial grinding and frost weathering in high mountain areas (Sun 2002a, 2007). Meanwhile, the TAK and its surrounding areas possess various materials from primary weathered material (e.g., moraine) to highly weathered materials (e.g., loess and dust), serving as an ideal place to deeply discuss variations of REE compositions among different materials. To date, numerous studies on REE compositions have been conducted around this area (Fig. 1) (Chang et al. 2000; Honda et al. 2004; Liu et al. 1993; Sun 2002a; Wu et al. 2008; Yang et al. 2007b), while lots of researchers only performed direct comparison of REE values among materials with totally different grain-size distributions and mineral compositions (Chang et al. 2000; Liu et al. 1993; Wu et al. 2008, 2009; Yang et al. 2007a), which is unrigorous and may result in false conclusions. A sophisticated analysis is required to evaluate interrelations among REEs and corresponding control factors of REE compositions of these materials. With this as motivation, we performed a critical analysis of variations in REE compositions among different materials from central Asia by integrating data from former studies. Two examples of small-scale loess and ice core dust relating to the TAK and the Tibetan Plateau (TP) are particularly discussed to illustrate factors that deserve attention in future REE-related studies. As influences of grain-size distributions and heavy minerals on REE compositions are major topics of this study, Cerium (Ce) anomalies are not discussed since they are generally closely related to redox conditions of samples (Brookins 1989; Rankin and Childs 1976) and kept constant among different grain sizes. In addition, although redox system may change during transport and sedimentation, Ce anomalies keep almost constant among different materials due to relatively cold and dry environments of studied area (Fig. 2).

Materials

Published REE concentrations from central Asia are listed in Table 1. Materials of bulk and fine fractions for the TAK

![Fig. 1 Study location of central Asia](image-url)
sand, loess accumulated around the TP, the typical loess, sediment, and dust deposited on the Dunde glacier (Fig. 1) are adopted to investigate variations of REE concentrations and compositions.

**Results and discussion**

**Chondrite-normalized REE patterns**

Generally, chondrite-normalized REE patterns, UCC-normalized REE patterns and REE ratios are three effective approaches for describing and comparing REE compositions among different materials. However, ratios of REE concentrations between normal surface materials and chondrite usually vary so widely that some detailed characteristics cannot easily be detected (Marx et al. 2005), especially for those materials with uniform REE compositions due to multiple recycle processes. For example, chondrite-normalized REE patterns of all materials listed in Table 1 are uniform with steep LREE, fairly flat HREE profiles and moderate Eu depletion (Fig. 3). This phenomenon is in accordance with those theories suggested by Taylor and McLennan (1985). However, significant differences appear for UCC-normalized REE patterns (Fig. 4). Despite chondrite-normalized REE patterns have been successfully used in distinguishing material provenance in some studies (Nakai et al. 1993; Taylor and McLennan 1985), UCC-normalized REE patterns and REE ratios are another two prevalent approaches in source tracing studies (Wu et al. 2009; Yang et al. 2007a). Therefore, the effectiveness and potential inaccuracy in practical use of these two methods are evaluated in the following parts.

**Table 1** REE concentrations (mg/kg) in different materials and grain sizes from the TP and central Asia

<table>
<thead>
<tr>
<th>Sample sites</th>
<th>La</th>
<th>Ce</th>
<th>Pr</th>
<th>Nd</th>
<th>Sm</th>
<th>Eu</th>
<th>Gd</th>
<th>Tb</th>
<th>Dy</th>
<th>Ho</th>
<th>Er</th>
<th>Tm</th>
<th>Yb</th>
<th>Lu</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (n = 9)</td>
<td>68.54</td>
<td>140.32</td>
<td>15.69</td>
<td>57.39</td>
<td>10.84</td>
<td>1.45</td>
<td>8.28</td>
<td>1.27</td>
<td>7.55</td>
<td>1.41</td>
<td>4.1</td>
<td>0.61</td>
<td>4</td>
<td>0.61</td>
</tr>
<tr>
<td>2 (n = 35)</td>
<td>88.84</td>
<td>179.13</td>
<td>20.24</td>
<td>73.55</td>
<td>14.19</td>
<td>2.16</td>
<td>13.27</td>
<td>2.25</td>
<td>10.35</td>
<td>1.86</td>
<td>6.11</td>
<td>0.79</td>
<td>5.47</td>
<td>0.82</td>
</tr>
<tr>
<td>3 (n = 8)</td>
<td>33.66</td>
<td>67.61</td>
<td>7.5</td>
<td>26.98</td>
<td>4.88</td>
<td>0.86</td>
<td>3.92</td>
<td>0.63</td>
<td>3.54</td>
<td>0.75</td>
<td>1.98</td>
<td>0.29</td>
<td>1.91</td>
<td>0.28</td>
</tr>
<tr>
<td>4 (n = 10)</td>
<td>44.26</td>
<td>85.64</td>
<td>10.08</td>
<td>37.69</td>
<td>7.2</td>
<td>1.27</td>
<td>5.58</td>
<td>0.86</td>
<td>5.05</td>
<td>1.03</td>
<td>2.75</td>
<td>0.41</td>
<td>2.55</td>
<td>0.39</td>
</tr>
<tr>
<td>5 (n = 39)</td>
<td>32.6</td>
<td>68.9</td>
<td>7.7</td>
<td>29.5</td>
<td>5.9</td>
<td>1.2</td>
<td>5.4</td>
<td>0.8</td>
<td>4.7</td>
<td>1</td>
<td>2.9</td>
<td>0.4</td>
<td>2.9</td>
<td>0.4</td>
</tr>
<tr>
<td>6 (n = 15)</td>
<td>31.83</td>
<td>68.48</td>
<td>7.59</td>
<td>27.91</td>
<td>5.63</td>
<td>0.87</td>
<td>4.89</td>
<td>0.83</td>
<td>4.73</td>
<td>0.95</td>
<td>2.77</td>
<td>0.41</td>
<td>2.67</td>
<td>0.39</td>
</tr>
<tr>
<td>7 (n = 18)</td>
<td>70.11</td>
<td>135.52</td>
<td>15.47</td>
<td>52.95</td>
<td>9.75</td>
<td>1.68</td>
<td>8.28</td>
<td>1.31</td>
<td>7.02</td>
<td>1.53</td>
<td>4.01</td>
<td>0.6</td>
<td>3.84</td>
<td>0.6</td>
</tr>
<tr>
<td>8 (n = 17)</td>
<td>32.91</td>
<td>66.31</td>
<td>7.52</td>
<td>28.01</td>
<td>5.57</td>
<td>1.1</td>
<td>5.44</td>
<td>0.76</td>
<td>4.56</td>
<td>0.92</td>
<td>2.68</td>
<td>0.38</td>
<td>2.47</td>
<td>0.37</td>
</tr>
<tr>
<td>9 (n = 8)</td>
<td>32.58</td>
<td>67.91</td>
<td>7.77</td>
<td>28.54</td>
<td>5.52</td>
<td>1.02</td>
<td>4.87</td>
<td>0.75</td>
<td>4.34</td>
<td>0.83</td>
<td>2.42</td>
<td>0.36</td>
<td>2.32</td>
<td>0.35</td>
</tr>
</tbody>
</table>

1: <45 μm fraction of the TAK sand (Honda et al. 2004); 2: <53 μm fraction of TAK (Yang et al. 2007b); 3: bulk sand samples of TAK (Honda et al. 2004); 4: loess of the south TP (from Sun JM, personal communication); 5: loess of the LP (Ding et al. 2001); 6: moraine of high mountains around TAK (Chang et al. 2000); 7: <63 μm fraction of the Yarlung Tsangbo sediment (Li et al. 2009); 8: dust trapped in Dunde ice core (Wu et al. 2009); 9: loess of the TAK (Honda et al. 2004)
UCC-normalized REE patterns from materials of the TAK

UCC-normalized REE patterns from moraine to dust of the TAK are plotted in Fig. 4. It has been suggested that these materials are closely connected with each other (Chang et al. 2000; Sun 2002a; Yang et al. 2007b) and the processes can be described briefly as follows: first, large amount of clastic materials such as moraine are produced by high mountain weathering processes in the TP and the Tianshan surround the TAK. Second, weathered clastic materials are transported to the Tarim basin by ephemeral glacial river to form the TAK sand. Finally, fine fractions of TAK sands are entrained to high altitude during dust storm periods and transported to distant areas by the westerlies. During this process some dust materials are accumulated on slope of mountains facing the TAK to form small-scale loess (Sun 2002a). However, REE patterns among some of these materials vary greatly due mainly to grain size and mineral sorting (Fig. 4). For example, both the <45 and the <53 μm fractions of the TAK sand exhibit higher REE concentrations, totally different REE patterns and strong negative Eu anomalies compared to those of other materials. These characteristics are different from the general opinion that the finer fraction holds the higher REE concentrations (Taylor and McLennan 1985); and it is attributed mainly to the influence of REE-enriched heavy minerals that are generally resided in coarse silt fraction (Liu et al. 1993; Taylor and McLennan 1985; Yang et al. 2007b). Meanwhile, study on grain-size distributions has shown that the TAK sand lacks fine clay fractions (Wang et al. 2003), supporting the argument that heavy minerals significantly affect REE concentrations and patterns when clay fractions are minor (Taylor and McLennan 1985). Thus, it is the lack of fine clay fraction in the <45 and the <53 μm fractions of the TAK sand that leads to heavy mineral-affected REE patterns. It is proposed that some high field elements such as Zirconium (Zr) and Hafnium (Hf) reside especially in REE-enriched heavy minerals (e.g., Zircon) (McLennan 1989; Taylor and McLennan 1985). Correspondingly, Zr concentration within the <53 μm fraction for the TAK sand is abnormally high (446.92 mg/kg) (Yang et al. 2007b), exceeding the threshold of 300 mg/kg (Taylor and McLennan 1995), further indicating the contribution of heavy minerals to REE concentrations and compositions. For the same reason, moraines at high altitude mountain areas generally experience immature weathering process and almost all the fine clay fractions are removed away by wind and water, resulting in abnormal REE patterns.

Virtually, a distinct influence of heavy minerals on REE compositions was widely observed for many weathered materials in the TP. In southern TP, similar to those of the <45 and <53 μm fractions for the TAK sand, the <63 μm fraction of the Yarlung Tsangbo (YT) sediment also exhibited higher REE concentrations and different REE patterns when compared with those of the bulk sediment (Li et al. 2009). In addition, some bulk sand samples from the TAK and bulk river sediments from the eastern TP exhibited heavy mineral-related REE patterns (Borges et al. 2008; Honda et al. 2004). It has been proposed that some critical elemental ratios (e.g., Lanthanum (La)/Ytterbium (Yb), Eu/Eu*) are not greatly affected by sedimentary process (Taylor and McLennan 1985). However, our analysis indicated that these two ratios vary with a great range (Fig. 4), which should inevitably exert significant influence on material provenance related studies.

The TP is the youngest and highest plateau in the world, its dry and cold environments result in extremely immature weathered surface soil with relatively low concentrations of fine clay fractions. Therefore influence of heavy minerals on the REE patterns can easily be unveiled out. This phenomenon is clear in the TAK sand because fine clay fractions are constantly transported out of the TAK by dust storms, resulting in intense abnormal REE patterns for materials (e.g., the <53 μm fraction of the TAK sand).

Distinct REE patterns for small-scale loess around the TP

It has been suggested that REE compositions of loess are uniform all over the world, even for loess with small-scale source regions based on chondrite-normalized REE patterns (Gallet et al. 1996; Taylor and McLennan 1985). In addition, heavy minerals exert minor influence on loess REE compositions (Gallet et al. 1996; Liu 1985) despite
concentrations of some typical heavy mineral-related elements (e.g., Zr and Hf) of loess are higher than those of UCC (Taylor and McLennan 1985). However, this is not the case for the loess accumulated around the TP.

Large quantities of small-scale loess sediments are distributed around the TP and other high mountains in China besides the famous LP (Fang et al. 1999; Sun 2002b; Sun et al. 2007) (Fig. 1). REE compositions of small-scale loess have been reported and attributed to local provenance (Fang 1995; Honda et al. 2004; Sun 2002b; Sun et al. 2007). Honda et al. (2004) measured eight bulk loess samples around the TAK. These samples can be easily divided into two groups based on REE concentrations and compositions. The first group includes five samples (samples 49, 105, 124, 134, 142) having uniform REE patterns (hereafter called the “TAK1”) resemble to that of the LP loess; whereas the other group includes three samples (samples 128, 129, 132) clearly having higher REE concentrations and stronger Eu depletion (hereafter called the “TAK2”) (Fig. 5a). Interestingly, REE patterns of the TAK2 are significantly inherited from that of the <45 µm fraction of the TAK sand. In addition, these three samples were collected from the same site, indicating that it is the same wind regime transporting the heavy mineral-enriched coarse fraction of the TAK sand to this place. Meanwhile, REE patterns of the total TAK loess and the YT loess accumulated in the southern TP (Sun et al. 2007) (Fig. 5a) are similar, resulting from their similar grain-size distributions (Fig. 5b). Generally, loess in the LP are transported from areas hundreds of kilometers away, whereas loess accumulated around the TP are subjected to relatively short-distance transport (Sun et al. 2007), resulting in totally different grain-size distributions between loess of the LP and the TP (e.g., the Kunlun Mts. and the YT) (Fig. 5b). It is clear that grain size of the <30 µm fraction accounts for most parts of the LP loess, whereas this fraction accounts for small parts of the Kunlun and YT loess. Therefore, the lack of fine clay fractions of the Kunlun and YT loess causes a clear influence on the heavy minerals REE patterns. In summary, unlike conclusions proposed by other study (Gallet et al. 1996), the UCC-normalized REE patterns of small-scale loess accumulated around the TP are distinct, resulting mainly from their unique grain-size distributions and special mineral compositions.

REE ratios

Similar to fine-grained sedimentary rocks, long-range transported dust materials generally are sufficiently mixed because they are derived from various kinds of material rocks, resulting in quite uniform UCC-normalized REE patterns. In this case REE patterns are not effective for distinguishing provenance, and REE ratios are adopted and proved as effective approaches (Sun 2002a; Taylor and McLennan 1985; Wu et al. 2008). However, this method tends to achieve unilateral or wrong results because it is produced from fewer elements compared to REE patterns. To address this issue, a provenance study on dust trapped within the Dunde ice core (Fig. 1) over the northeastern TP is adopted and discussed (Wu et al. 2009). In that study REE ratios (Ce/Yb vs. Eu/Yb) of ice core dust and “fine” particle (the <53 µm fraction) of the TAK sand were compared to demonstrate the contribution of material of the TAK to the ice core dust. From Fig. 6a it can be found that the REE ratios of the ice core dust fall within those of the fine particles. Thus, it seems that dust derived from the TAK is transported onto the Dunde glacier. However, totally opposite conclusion can be achieved from plot of other REE ratios (La/Gadolinium (Gd) vs. Terbium (Tb)/Yb) (Fig. 6b), implying no connection between sand of the TAK and the ice core dust. Actually, the <53 µm fraction of the sand is not fit for the
comparison. Firstly, only particles finer than 20 μm can be entrained into air and transported over long distances, whereas particles with size range of 20–70 μm can be suspended in air and transported only for short distances (Pye 1987). However, the distance between the Dunde glacier and the TAK is about 1,000 km. Thus the <53 μm fraction of the sand is unlikely to be transported onto the Dunde glacier. Secondly, as discussed previously, the <53 μm fraction contained relatively large amount of heavy minerals, which greatly influence its REE compositions. Virtually, distinct differences of REE compositions between the <53 μm fraction and the ice core dust can be discovered from their UCC-normalized REE patterns (Fig. 4), making consequent comparison between REE ratios useless. Thus, only those fine particles (e.g., the <20 μm fraction) potentially being transported for long distances are fit for comparison of REE ratios with long-range transported dust. In summary, great cautions should be made when REE ratios are used for provenance study if either grain size or UCC-normalized REE patterns among various materials are clearly different.

Conclusions

Several conclusions can be drawn based on the above discussion:

1. Some REE-related theories proposed by Taylor and McLennan are based on chondrite-normalized REE patterns, which cannot simply be applied to material provenance study. Generally, chondrite-normalized REE patterns for almost all the surface materials from central Asia are uniform and not vigorous in tracing material source regions.

2. Heavy minerals can affect REE compositions of materials that lack of fine clay fractions, especially for moraine and some “fine” fractions (such as the <45 μm fraction and the <53 μm fraction) of the TAK sand. Therefore, REE compositions of these materials cannot simply be used as effective tracing proxies in dust and loess provenance studies.

3. Small-scale loess around the TP derived from local regions has different UCC-normalized REE patterns compared with that of typical loess, resulting from their abnormal grain-size distribution characteristics and relatively high heavy mineral concentrations. Thus, if grain-size distributions of loess are greatly different, it is not effective to compare their REE compositions when performing provenance analysis.

4. Great care must be made when REE ratios are utilized to distinguish provenance. If the target dust and its potential source material have different grain-size distributions or clear different UCC-normalized REE patterns, the utilization of REE ratios is almost worthless.

5. Finally, as REE compositions are closely connected with grain-size distributions and mineral compositions of the material, and it is generally hard to find same fraction of the target material and potential provenance material, REE compositions may hardly provide robust evidence in material provenance studies. Therefore, other approaches such as atmospheric circulation patterns and isotopic compositions should also be utilized as supporting evidences.

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