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Rare earth elements in the surface sediments of the Yarlung Tsangbo (Upper Brahmaputra River) sediments, southern Tibetan Plateau

Chaoliu Li [a], Shichang Kang [a,b,*], Qianggong Zhang [a,c], Feiyue Wang [d]

[a] Key Laboratory of Tibetan Environment Changes and Land Surface Processes, Institute of Tibetan Plateau Research, CAS, Beijing 100085, China
[b] State Key Laboratory of Cryospheric Sciences, CAS, Lanzhou 730000, China
[c] Graduate School of Chinese Academy of Sciences, Beijing 100039, China
[d] Department of Chemistry, University of Manitoba, Winnipeg, Canada MB R3T 2N2

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ABSTRACT

The Yarlung Tsangbo (YT) is the Tibetan portion of the Brahmaputra River. It transports a large amount of sediment annually to the Indo-Gangetic Plain and thus contributes significantly to the Quaternary evolution of the Plain. Eighteen surface sediment samples were collected from the YT, and the compositions of rare earth elements (REEs) were analyzed for the bulk sediments, <63 μm and <20 μm fractions. Results show that the YT sediments originated mainly from the Lhasa Terrane. The REE compositions in the YT sediments are similar along the river, with the light and middle REEs enriched relative to the upper continental crust, but the REE concentrations are higher than its lower reaches – the Brahmaputra River. The average grain size of the sediments is in the coarse range (123.8 μm). Grain size influences the REE concentrations of the YT sediment significantly. The <63 μm fraction of the sediment has higher REE concentrations and different REE patterns when compared with those in the bulk sample and <20 μm fraction, due to the presence of REE-enriched heavy minerals of zircon, monazite and allanite in this fraction. The relatively low REE concentrations in acid-leachable fractions of the sediments suggest most REEs in the sediments occur in the stable minerals due to the dominance of physical weathering in this region.

1. Introduction

The Ganges–Brahmaputra River currently transports ~1×10^9 t/yr of sediment to the ocean, ranking it first among the world's rivers (Milliman and Syvitski, 1992; Ramesh et al., 2000). These sediments contribute material for the formation of the Indo-Gangetic Plain, which is one of the world's largest areas of Quaternary alluvial sedimentation (Benn and Owen, 2002) and represent important archives of changes in climate and tectonics.

Rare earth elements (REEs) in river sediments have been widely used as valuable indicators of petrogenetic processes in the aquatic environments such as chemical evolution of the continental crust, weathering processes in drainage basins and sediment sources (e.g. Goldstein and Jacobsen, 1988; Holser, 1997; Nesbitt et al., 1990; Vital et al., 1999; Kumar et al., 2007). Numerous studies have been carried out on the sedimentary environment of Ganges–Brahmaputra River (e.g. Martin and Meybeck, 1979; Ramesh et al., 2000; Egashira et al., 2004; Tripathi et al., 2007). However, most of them were focused on its lower reaches south of the Himalayas. Few data are available for the REE compositions of the sediments from the upper reaches of the Brahmaputra River (e.g. Singh and France-Lanord, 2002; Garzanti et al., 2004; Hren et al., 2007), known as the Yarlung Tsangbo (YT) in the Tibetan Plateau. The YT flows across the southern Tibetan Plateau and is a major source of water and sediment to the Ganges–Brahmaputra (Singh and France-Lanord, 2002), discharging about 150 km^3 of water and 2.4×10^7 t of sediments to the Ganges–Brahmaputra basin annually (Ding et al., 2001).

Here we report the concentration, speciation and distribution patterns of REEs in the surface sediments of the YT. We believe the background information on the behaviors of REEs in the YT sediments are of significant importance for a better understanding of the weathering processes in the YT basin and for the evolution history of the Ganges–Brahmaputra basin.

2. Regional setting

The YT originates from the Chamyungdung glacier at an elevation of 5200 m a.s.l. in the Tibet–Himalayas (Fig. 1). It generally

* Corresponding author. Institute of Tibetan Plateau Research, CAS, No.18, Shuangqing Rd, Beijing 100085, China. Tel./fax: +86 10 6284 9681.
E-mail address: shichang.kang@itpcas.ac.cn (S. Kang).

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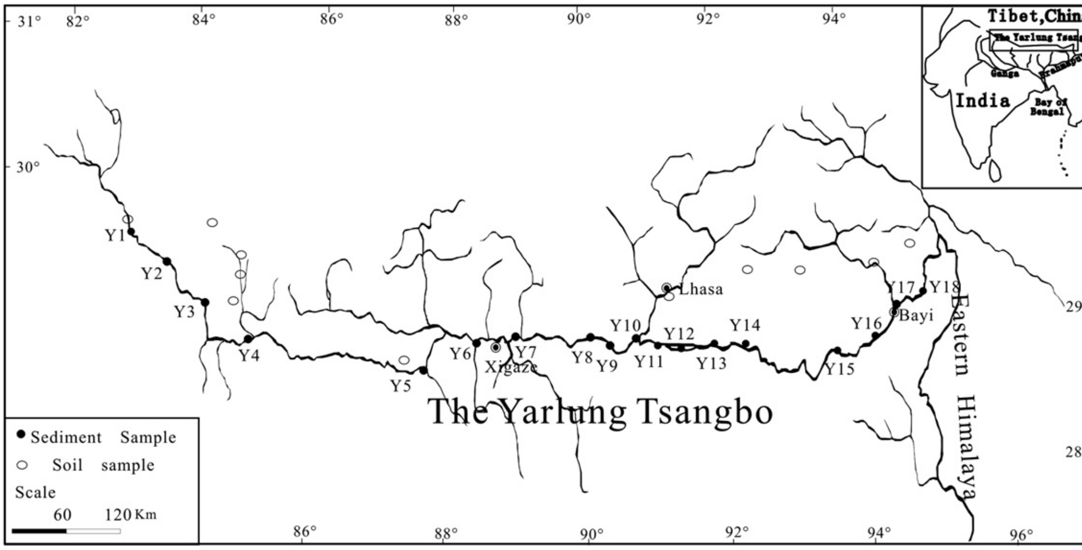

Fig. 1. The map of the Yarlung Tsangbo showing the sampling sites.

flows southeastward in southern Tibetan Plateau of China, but makes an abrupt turn near Mt. Namchabarwa (7782 m a.s.l.) and flows south to India from where it is known as the Brahmaputra. The length from the source to the China–India border is 2057 km, with an average equilibrium slope of 2.6‰ and a drainage area of 2.4×10^5 km^2 (Guan et al., 1984). The YT drains ~1300 km along the Indus–Tsangpo Suture (Fig. 2), and erodes through Paleozoic to Eocene sedimentary rock along with the plutonic and volcanic rock of the suture. The plutonic rocks are the Trans-Himalayan batholith (gabbros and diorites), lying adjacent to the Indus–Tsangpo Suture zone and the granitic belts farther north (Lhasa Terrane) (Taylor and McLennan, 1985; Xu, 1985; Debon, 1986). The precipitation in the YT basin occurs mostly from June to September induced by the Indian monsoon. From its lower reaches upwards, the annual rainfall decreases dramatically from more than 5000 mm to 310 mm due to the weakening of the monsoon (Ding et al., 2001) and the strong rain-shadow effect of the Himalayas (Hren et al., 2007). The combined effects of the heavy monsoonal precipitation, rapid rock uplift of the syntaxis between the Indian and Eurasian plates (Burg et al., 1998) and glacial abrasion (Zeitler et al., 2001) result in intense weathering in the YT basin (Sarin et al., 1989; Galy and France-Lanord, 2001), especially at the eastern syntaxis of the Himalayas (Hren et al., 2007).

3. Materials and methods

A total of 18 surface sediment samples were collected in October 2006 and June 2007, respectively, along the 1587 km section of the YT from upstream to the YT canyon (Fig. 1). The sediments were scooped up by plastic spade from the upper 3 to 5 cm of the river bed where the water depth was less than 50 cm. The sampling sites were selected carefully to minimize possible effects of human activities. The unevenly distributed sampling sites were mainly due to the geomorphologic obstacles (e.g. deep gorges). The samples were kept in plastic sacks and transported to the laboratory within days and air dried prior to the analysis. For the purpose of studying source material of the YT sediment, eleven surface soil samples were also collected along the north bank of the YT (Fig. 1).

The grain-size distribution of the sediments was measured by a laser particle sizer (S3500, Microtrac, USA) after being pretreated with 10% H_2O_2 and 0.1 M HCl (Yang et al., 2002).

REE Concentrations in the sediments were determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) (X-7; Thermo-elemental, USA) at the Institute of Tibetan Plateau Research. The air dried bulk samples were well ground and sieved through a 200 mesh nylon sieve. In order to investigate the grain-size dependency of element concentrations, the grain-size fractions of <20 μm and <63 μm were separated by pipetting and sieving, respectively. All the samples were heated at 105 °C for less than 24 h before being processed. Approximately 20 mg of the heated samples were initially placed in a high-pressure Teflon digestion vessel with 1 ml concentrated HNO_3 (CMOS, JT. Baker, USA) and 1 ml concentrated HF (BVIII, Beijing Institute of Chemical Reagent Research, P.R. China). Subsequently, the vessels were treated in an ultrasonic bath for 20 min. The samples were then digested in an oven at 190 °C for less than 24 h. After cooling, the solutions were dried on a hot plate at 150 °C, and HNO_3 was added into the residue and heated at 150 °C for another 24 h. Finally, indium and rhodium were added as internal standards and the digestant was diluted to 50 ml using Milli-Q® water. Since no residual particles (dark minerals) were visible after the dissolution produce, the sampling and analytical methods used in this study represented the total REE concentrations in the samples. In each digestion batch, a reagent blank was also used to check the sample handing processes. The reference sample GSS-1 (P.R. China) was used for quality control of the analyses, and the recoveries ranged from 90% for Tb to 106% for Ce. The RSD of the values measured by ICP-MS were less than $\pm 5\%$ in all analyzed elements. The concentrations of trace elements other than REEs were also analyzed which will be reported elsewhere.

In addition, separate bulk sample aliquots were leached with 2 M HCl and 0.5 M HNO_3 for 24 h under the room temperature to extract the leachable fraction (Yang et al., 2002). REEs in the leachable fraction were also analyzed by ICP-MS following a similar procedure as described above.

4. Results

4.1. Grain-size distribution

The mean grain sizes of the YT sediments vary between 30.5 and 234.5 μm with average value of 123.8 μm, which is much coarser than those from other larger rivers (Yang et al., 2002). Most

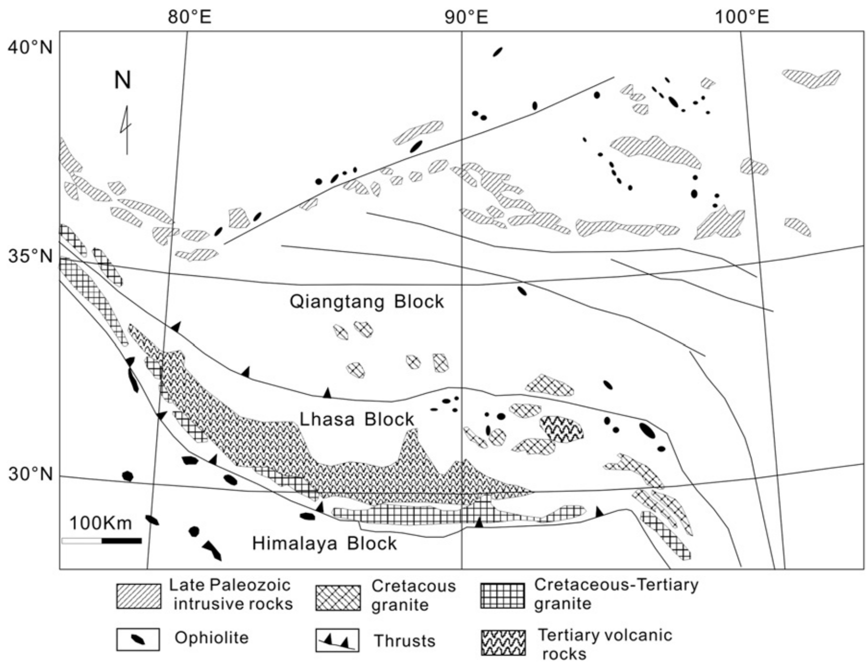

Fig. 2. Geologic map of the tectonic units and main rock types in the Yarlung Tsangbo basin and in Tibet (modified from the Sino-UK Geological Expedition Team, 1990).

sediment samples show similar grain-size distribution patterns (listed in the Supplementary material). Among them the coarsest sediments are found at samples Y9 and Y14 with larger mean grain sizes than others and depletion in fine grains less than 20 μm. According to the field observation recorded during collecting samples, the water flow rate at these two sites is high, which could wash much of the fine grains away.

4.2. REE compositions

Except for the most upstream site Y1, the sediments from the YT appear to have a relatively uniform REE compositions (Fig. 3a), likely due to the well mixing of the sediments and the limited time available for preferential absorption (Murray et al., 1992). The distinctive REE pattern of Y1 might be due to its headwater location, which reflects the geology and hydrology of local small drainage basins as suggested by others (Goldstein and Jacobsen, 1988; Ramesh et al., 2000).

REE concentrations of the bulk sediments from the YT are listed in the Supplementary material, which follow the same order as their average abundances in the Earth's crust, but vary over a wide range due to the grain-size effect. For example, La and Yb vary from 16.5 to 58.6 μg/g and from 1.11 to 3.73 μg/g, respectively. The average values of Light REEs (LREEs, La–Eu) and Heavy REEs (HREEs, Gd–Lu) in bulk sediments are 159 μg/g and 15.5 μg/g, respectively. The ratios of LREE/HREE in sediments vary from 8.03 to 14.9, suggesting that LREEs are enriched in the bulk sediments when compared with HREEs. Average Ce/Ce* and Eu/Eu* ratios are 1.07 and 0.66, respectively (formula of Ce/Ce* and Eu/Eu* are shown in the Supplementary material). The upper continental crust (UCC)-normalized pattern of the river sediments is nearly linear with the enrichment of both LREEs and Middle REEs (MREEs, Sm–Dy) (Fig. 4).

The REE distribution patterns for the <20 μm and <63 μm fractions normalized to the UCC are shown in Fig. 3b and c, respectively. The REE patterns within each fraction are generally similar due to the efficient mixing mechanism of source lithologies during sedimentary processes (McLennan, 1989). However, the REE concentrations in the <63 μm fraction are higher than the <20 μm fraction and the bulk sediment, and show different LREE patterns and negative Eu anomalies (Fig. 3c). The distinctive REE pattern for Y1 in the <20 μm fraction (Fig. 3b) agree with that in the bulk sediment and is due to the same reason mentioned above. Sites Y9 and Y14 have higher REE concentrations and extreme negative Eu anomalies in the <63 μm fraction, which may be induced by the few grains less than 20 μm of these two sites in this fraction.

4.3. Acid-leachable REEs

The acid-leachable REEs account for 13.8–24.9% of the total REE concentrations, with MREEs more prone to acid leaching than LREEs and HREEs (Figs. 5 and 6). The leachable fraction of REEs in the YT sediments is much lower than that of the Yangtze (20–43%) (Yang et al., 2002). This is not surprising due to the dominant role of physical weathering process in the YT sediments and most REEs in the YT sediments are present as resistant minerals (Caggianelli et al., 1992). Therefore, as same as sediments of other rivers over the Tibetan Plateau (Borges et al., 2008), the YT sediments strongly inherit the REE characteristics from the weathering products of source areas.

5. Discussion

5.1. Controls of the REEs in the YT sediments

5.1.1. Grain-size effect

Generally, the REE concentrations are closely related to grain sizes. REEs are enriched in clay and silt fractions, but depleted in the sand fraction (Vital et al., 1999). Our study shows that the mean grain size and REE concentrations are closely negative correlated (Fig. 7), indicating that smaller grain-size fraction in the sediments contains higher REE concentrations. Therefore, the grain size appears to be one of the major factors controlling the REE concentrations in the YT sediments.

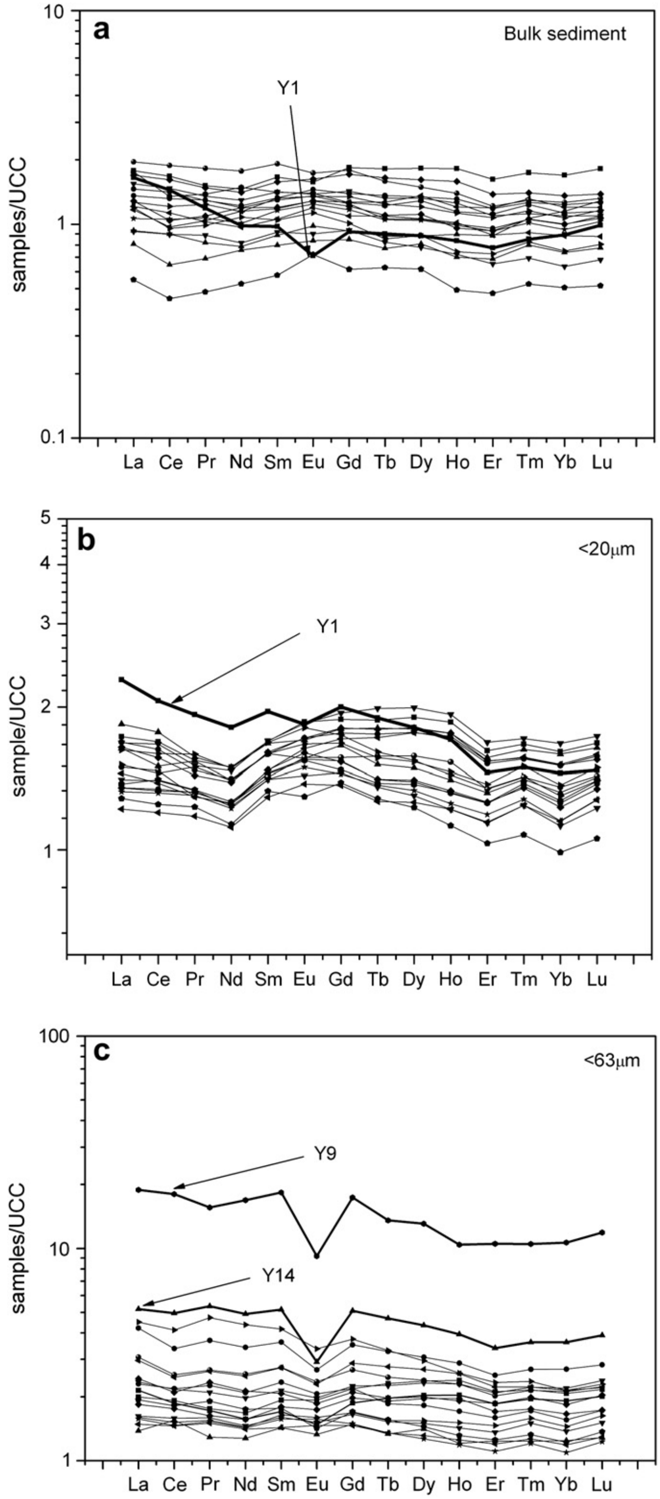

Fig. 3. The upper continental crust (UCC) normalized distribution patterns for REEs in a) the YT bulk sediments; b) <20 μm and c) <63 μm fractions of the sediments from the YT.

5.1.2. Heavy mineral effect

An interesting finding in this study is that <63 μm fraction in the YT sediments contains higher REE concentrations than <20 μm fraction (Fig. 8). We hypothesize that this "abnormal" grain-size effect is mainly resulted from the presence of REE-enriched heavy minerals since some heavy minerals account for a considerable fraction of REEs despite their low abundance in the river sediments (Yang et al., 2002). Therefore, more heavy minerals present in the <63 μm fraction than in the <20 μm fraction in the YT sediments. Such minerals include zircon, apatite, monazite and allanite, among which monazite, allanite and zircon may be the most possible candidates because of their high REE concentrations (Gromet and Silver, 1983). This phenomenon also exists in other rivers on the Tibetan Plateau. During previous study on eastern Tibetan river sediments some samples with LREE enriched and significant Eu negative anomalies were also found, and was explained as the contribution of REE-rich minerals like zircon, monzonite, and allanite (Borges et al., 2008).

To test this hypothesis, comparisons among the three fractions of the YT sediment are shown by multi-element diagrams (Fig. 9). Generally, elements such as Cu, Zn, Rb, Cs and Sn are associated with clay minerals, while elements such as Y, Zr, Hf and Th are associated with heavy minerals (Vital et al., 1999). Furthermore, some elements exclusively reside in specific types of minerals. For instance, large part of Th is incorporated in monazite (Gromet and Silver, 1983) and allanite (Hermann, 2002). Zr is predominantly

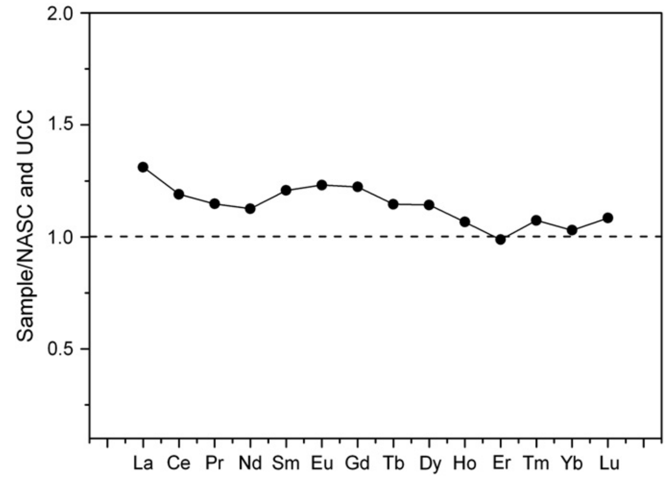

Fig. 4. UCC normalized distribution patterns for average REE concentrations of the YT bulk sediments.

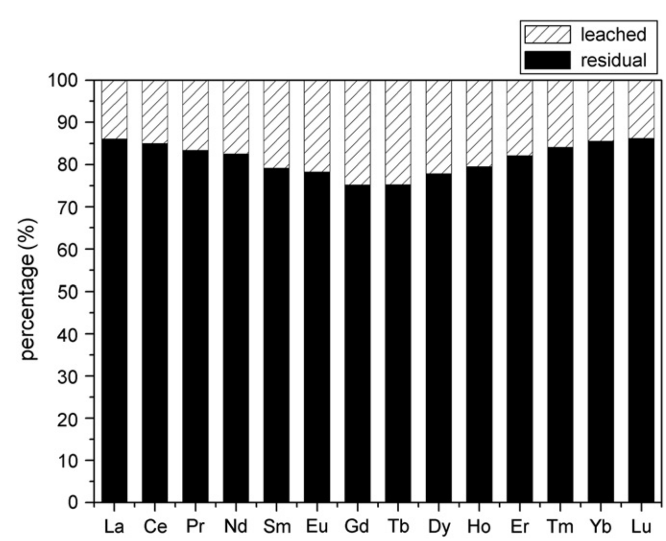

Fig. 5. Average concentration rations of acid-leachable and residual fractions of REEs of all the YT sediments.

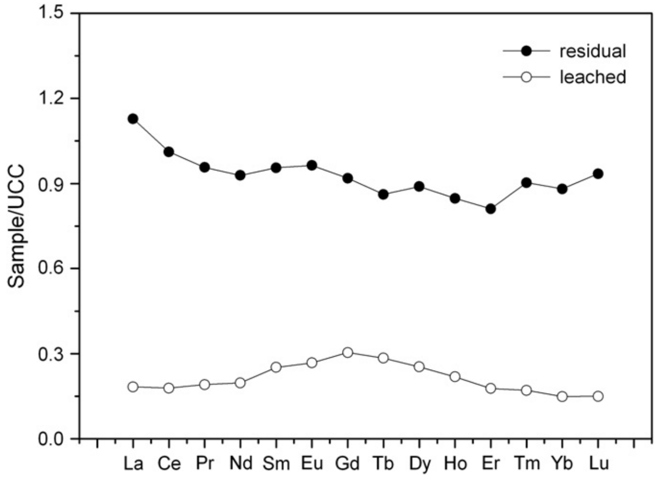

Fig. 6. UCC normalized leachable and residual distribution patterns for average concentration. Note that MREEs are enriched in the leachable fraction.

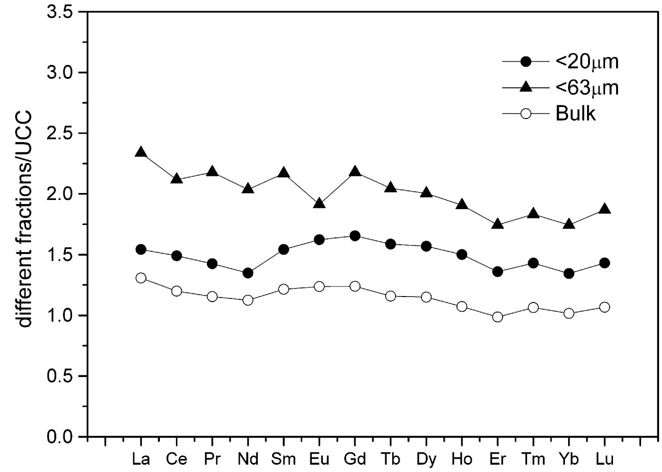

Fig. 8. UCC normalized REE distribution patterns of different grain sizes in the YT sediments. Note the samples from Y9 and Y14 are excluded due to their unusual grain-size distribution.

resided in zircon (Hermann, 2002). Therefore, the concentrations of these elements are easily explained by the presence of relevant heavy minerals. It is clearly that concentrations of many trace elements have an increasing trend with decreasing grain size except for Y, Zr, Hf, Ta, Th and U (Fig. 9), which mainly exist in coarse primary minerals resistant to weathering (Zhang et al., 2002). Among them Zr, Hf and Th have far higher relative concentrations in the <63 μm fraction than other fractions, demonstrating high abundances of the zircon, monazite and allanite. To further prove this idea, Zr/Sc against Th/Sc and La against Th are presented in Fig. 10a and b. Study has shown the Zr/Sc ratio is a useful index of zircon enrichment, and the Th/Sc ratio is a sensitive index of the bulk composition of the provenance (McLennan et al., 1993). Therefore enrichment in zircon can be easily observed in <63 μm fraction and least in <20 μm fraction (Fig. 10a), reflecting zircon is mostly enriched in <63 μm fraction. Due to zircon has a considerable HREEs (McLennan, 1989), LREE-enriched heavy minerals must be presented in <63 μm fraction. The highest La concentration and its close relationship with Th in <63 μm fraction reveals the enrichment of monazite and allanite (Fig. 10b), which are LREEs dominant (Yang et al., 2002). Thus these relationships support the above suggestion that heavy minerals zircon, monazite and allanite contribute much to the high REE concentrations and abnormal REE distribution patterns of <63 μm fraction.

5.1.3. *Weathering process*

The leachable fraction of REEs is unstable and can be bioavailable upon changes in pH and redox potential. These fractions of REEs can be released from particles to water and removed from water back to particles (Zhang et al., 1998). The dissolved-colloidal REEs, especially LREEs, may be scavenged/adsorbed onto the surface of Fe-Mn oxides/hydroxides, and then coagulated and transferred into the particulate forms (Byrne and Kim, 1990; Elderfield et al., 1990). The Himalayan rivers are characterized by dominating physical erosion due to high elevation and relative low temperature (Galy and France-Lanord, 1999). Therefore, the dissolved REE and reactive Fe-Mn oxide concentrations should be lower than those of the Yangtze, which has relatively strong chemical weathering process (Yang et al., 2002). Consequently, the particle–water reaction processes are weak and most part of REEs is still stable in the YT sediments.

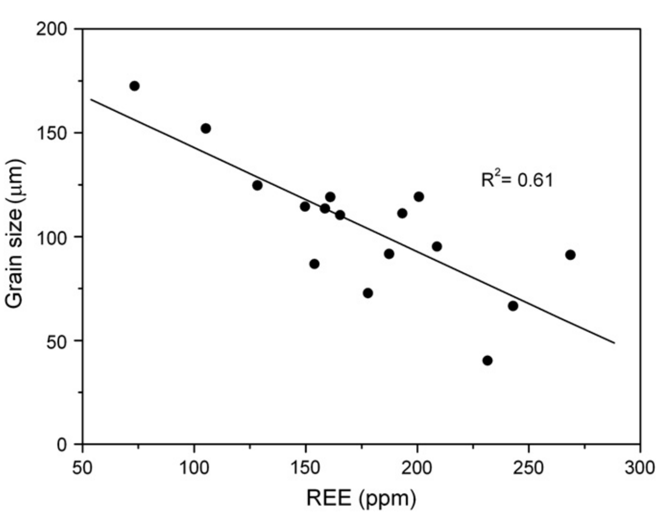

Fig. 7. Relationship between the average REE concentrations of the YT bulk sediments and the grain-size distribution. Note the samples from Y9 and Y14 are excluded during linear fit.

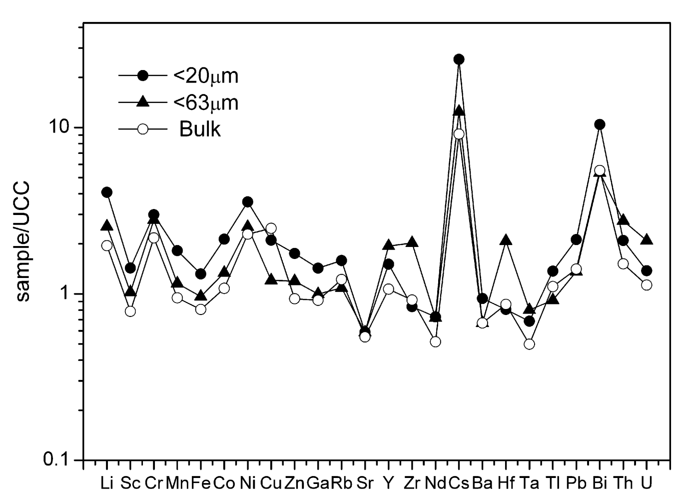

Fig. 9. UCC normalized distribution patterns for average trace element concentrations of different grain sizes in the YT sediments (Y9 and Y14 are also excluded).

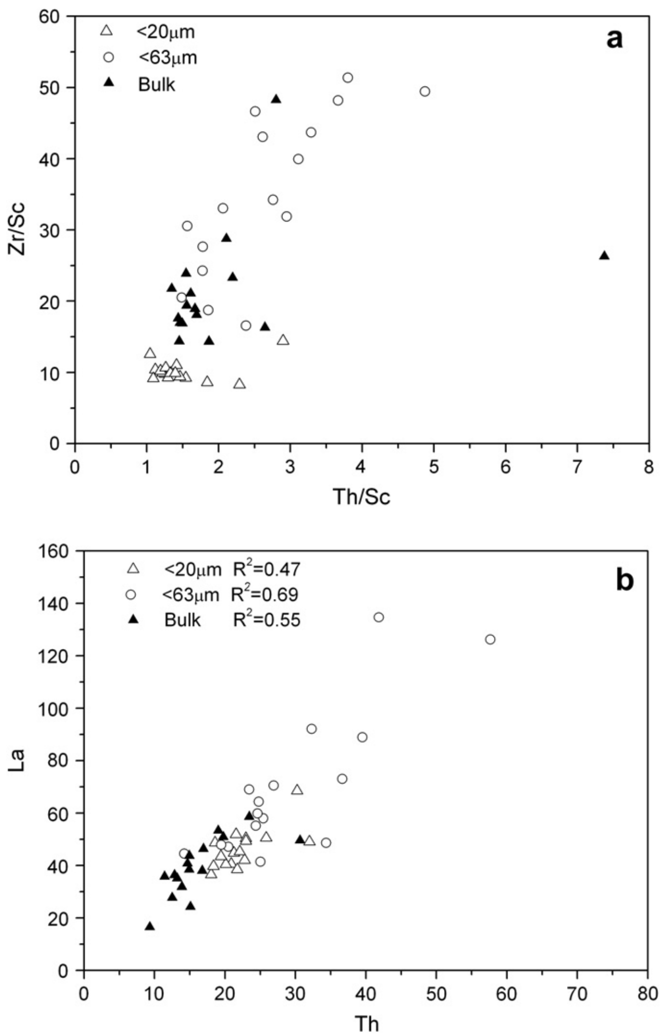

Fig. 10. Correlations between a) Zr/Sc and Th/Sc; b) La and Th.

5.2. Comparison with other rivers originated from the Tibetan Plateau

The UCC normalized REE distribution patterns of the YT sediments and other rivers originated from the Tibetan Plateau are given in Fig. 11. All these river sediments have a similar REE pattern of MREE enrichment relative to UCC despite of the difference in weathering mechanisms and intensities (Condie, 1991; Zhang et al., 1998). REE distribution pattern of the YT sediment is much similar to the upstream of the Yellow River and the Yangtze River on the east Tibetan Plateau, though LREEs in the YT sediments are slightly enriched due to the contribution of heavy minerals. The YT sediment has higher REE concentrations and relatively smooth REE distribution patterns compared with its lower reaches – Brahmaputra River, which is a result from the effect of enormous sediment produced from Eastern Himalaya part of the YT (Singh et al., 2005; Hren et al., 2007). This trait can also be derived from the differences between REE compositions of the upper and lower reaches of the Yellow River and Yangtze River. For example, both the Yellow River and the Yangtze River has the higher REE concentrations and different REE distribution patterns compared with their upstream. Research showed that downstream of the Yellow River and the Yangtze River reflect the material characteristic of the Loess Plateau and the Jinshajiang River, respectively (Yang et al., 2002). Therefore,

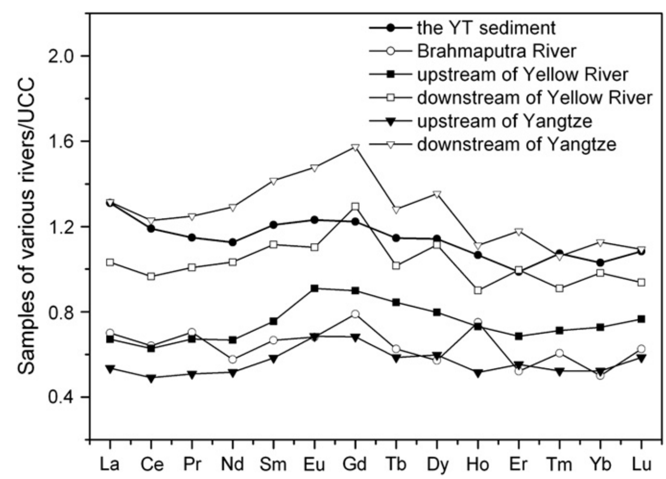

Fig. 11. Comparison of the REE patterns between the YT and other rivers from the Tibetan Plateau. Data for downstream of Yangtze and Yellow River from (Yang et al., 2002); data for upstream of Yangtze and Yellow River from (Borges et al., 2008); and data for the Brahmaputra River from (Ramesh et al., 2000).

REE compositions of the rivers on the Tibetan Plateau are similar and usually differ with their lower reaches.

5.3. Provenance of the YT sediment

Geologically, the YT is located between the Lhasa Terrane and the Himalaya Terrane (Fig. 2). However it is suggested that YT sediments are derived mostly from the Lhasa Terrane due to most of its tributaries located at its north part during loess study of the YT basin (Sun et al., 2007). Therefore REE compositions of loess and surface soil of north bank in the YT basin are select to compare with the sediments. The similarity between REE distribution patterns of the YT sediments and the loess indicate their same origins and slight differences in REE concentrations and LREE distribution patterns are due to their different grain-size distributions (Fig. 12). In the same way, supreme similar REE concentrations and distribution patterns between the YT sediments and the surface soil (Fig. 12) suggest that almost all the YT sediments are derived directly from the surface soil.

Therefore, the following processes can be inferred for the production of the YT sediments and its relationship with soil and loess: Firstly, a large amount of clastic, silt-sized materials

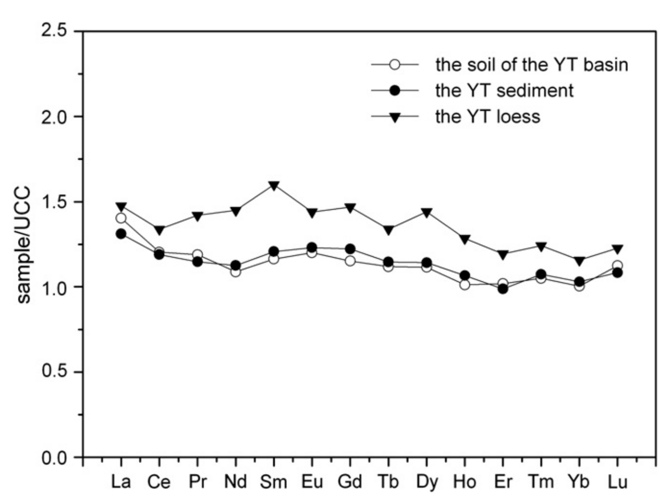

Fig. 12. UCC normalized REE distribution pattern of the YT sediment, surface soil of the YT basin and YT loess.

produced through glacier erosion and weathering in the high mountains of Lhasa Terrane to form the surface soil (Sun et al., 2007). Secondly, the soil is delivered to the YT by outwash of glacial meltwaters during the monsoon period. Finally, some of the sediments are then transported out of the river channel by strong near surface wind during non-monsoon period and become loess deposits (Sun et al., 2007).

6. Conclusions

The YT sediments are derived mainly from glaciers erosion and physical weathering in the Lhasa Terrane. REEs of the bulk sediments display LREE and MREE enrichment relative to UCC. The acid-leachable REE fractions show MREE enrichment, and account for 20% of the bulk REE concentrations, which is in agreement with the dominance of physical processes in the YT basin. In addition, the REE compositions of the YT sediments are much similar with the surface soil of the YT basin. Therefore REE compositions of the YT sediment inherit mostly from the surface soil and the source rocks. REE patterns of the YT sediments are similar with other rivers over the Tibetan Plateau but different with its lower reaches – Brahmaputra River.

Different from the general rule that REE concentrations in sediments increases with decreasing grain sizes, REE concentrations in the <63 μm fraction of the YT sediments are higher than those of <20 μm fraction due to the contribution of some REE-enriched heavy minerals such as zircon, monazite and allanite. However, grain size is still the dominating factor of the bulk sediment.

Acknowledgements

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Appendix. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi: 10.1016/j.quaint.2009.05.003.

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