Acta Geochim (2017) 36(3):552–555
DOI 10.1007/s11631-017-0234-7

ORIGINAL ARTICLE

# Behavior of rare earth elements in granitic profiles, eastern Tibetan Plateau, China

**Lifeng Cui[1] · Zhiqi Zhao[1] · Congqiang Liu[1] · Sheng Xu[2] · Taoze Liu[1] · Chenglong Tu[1] · Hu Ding[1]**

Received: 27 April 2017 / Revised: 1 June 2017 / Accepted: 16 August 2017 / Published online: 30 August 2017

**Abstract** Rare earth elements (REEs) can record geologic and geochemical processes. We studied two granitic regolith profiles from different climatic zones in eastern Tibetan Plateau and found that (1) ΣREEs ranged from 119.65 to 275.33 mg/kg in profile ND and 5.11–474.55 mg/kg in profile GTC, with average values of 205.79 and 161 mg/kg, respectively. ΣREEs was higher in accumulation horizon and semi-regolith; (2) Influenced by climate, the fractionation of light and heavy REEs (LREEs and HREEs) varied during weathering. The ratio of LREEs/HREEs in pedosphere was higher than semi-regolith in tropical profile; (3) A negative Eu anomaly in both profiles was the result of bedrock weathering. A positive Ce anomaly was observed in all layers of profile ND, and only in the upper 100 cm of profile GTC. This indicates that redox conditions along the regolith profile varied considerably with climate. (4) Normalized by chondrite, LREEs accumulated much more than HREEs; REE distribution curves were right-leaning with a V-type Eu anomaly in both profiles.

**Keywords** Chemical weathering · Eu anomaly · Critical zone · Soil weathering

## 1 Introduction

Regolith is the layer of physically, chemically, or biologically altered material that overlies non-weathered rock (Brantley and Lebedeva 2011). Granitic regolith plays a key role in climate change, soil management, and geomorphology evolution. The process of granite weathering is a $CO_2$-consuming reaction with a long-term impact on the global carbon cycle. Rare earth elements (REEs) are active in weathering process. Their activities are controlled by the stability of primary minerals and by weathering conditions (pH, Eh, redox, etc.) (Nesbitt 1979). In weathering processes, REEs record paleoclimatic data, including rainfall, groundwater, and atmospheric evolution. Research on REEs in weathered profiles has theoretical and practical significance in some human-related environmental problems, such as finding and developing residual weathered deposits, studying trace elements in the supergene geochemical cycle, and atmospheric composition evolution.

In this paper, we selected a continental climate profile (ND) in northeastern Tibetan Plateau and a subtropical monsoon profile (GTC) in southeastern Tibetan Plateau. We analyzed the geochemistry of REEs in both granitic profiles to understand elemental behavior and evolution affected by different climate.

## 2 Method and materials

### 2.1 Geologic and geographic parameters

The Guyong pluton, containing profile GTC, is a Himalayan monzonitic granite that formed 63 million years ago. The pluton below profile ND is an Indosinian granite of

---

11th International Symposium on Geochemistry of the Earth's Surface.

✉ Lifeng Cui
clfbest@126.com

[1] State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550081, China

[2] Scottish Universities of Environmental Research Centre, Glasgow G75 0QF, UK

235 million years of age. The altitudes of the sites are 1538 m and 3302 m, respectively.

Profile ND is near the border region of monsoon zone and westerly belt with mean annual precipitation, temperature, and evaporation of 300 mm, 3.3 °C, and 1500–1900 mm, respectively. Profile GTC belongs to a subtropical humid monsoon climate. The mean annual precipitation, temperature, and evaporation there are 1481 mm, 14.8 °C, and 1600 mm, respectively (Fig. 1).

### 2.2 Sampling strategy

Samples were continuously collected along profiles. In profile GTC, 53 samples were collected. From 0 to 50 cm, one sample was collected every 5 cm; from 50 to 300 cm, one sample every 10 cm; and below 300 cm, every 20 cm. Unlike profile GTC, profile ND did not display a thick regolith. In ND, a total of 25 samples were collected, with one sample every 5 cm above 100 cm, and one per 10 cm below 100 cm.

### 2.3 Analytical methods

Powder samples were dried in an oven at 60 °C. Each 50-mg sample was weighed and placed in a Teflon container to be digested in 5 mL mixed $HNO_3$, HF, and $HClO_4$ concentrated acid (volume ratio of 2:1:1). After the samples were dissolved and dried, they were diluted with 2% nitric acid to be analyzed. Blank sample and standard reference materials were processed simultaneously. Trace element and REE concentrations were analyzed by inductively coupled plasma mass spectrometry in State Key Laboratory of Environmental Geochemistry.

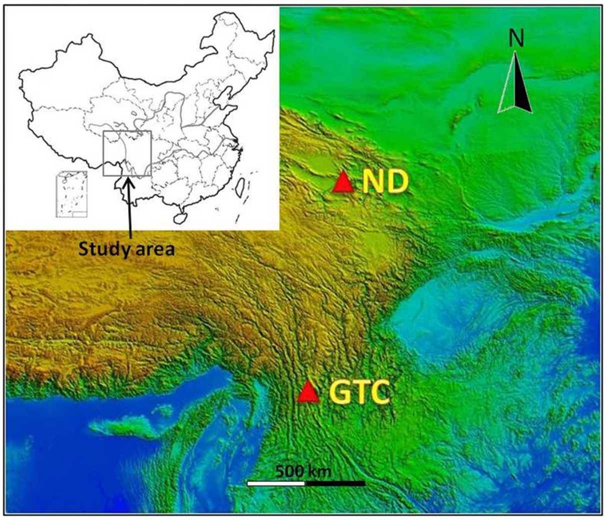

**Fig. 1** Diagram of geomorphology and profile location

## 3 Results and discussion

### 3.1 Profile ND

ΣREEs in profile ND ranged from 119.65 to 275.33 mg/kg, with an average value of 205.79 mg/kg. Except for the deepest sample, all had higher REEs than bedrock (140.29 mg/kg, Zhang et al. 2006). From top to bottom, REEs decreased little with depth. LREEs were much higher than HREEs; thus, the distribution pattern of REEs is a decreasing curve from LREEs to HREEs. The ratio of LREEs/HREEs were little changed above 120 cm, but decreased below this layer. The surface 20 cm was unique in its contribution of dry deposition and not influenced by weathering and pedogenesis process. We assume that the dry deposition accounted for this phenomenon; scattered losses kilometers away from the sampling site support this explanation well.

Normalized by chondrite, the ratio of La/Yb revealed that LREEs accumulated more than HREEs, and the LREEs/HREEs value was about 10 and almost constant. Below 120 cm (weathering front), ΣREE, LREEs, HREEs, and LREEs/HREEs decreased. Normalized by chondrite, the negative anomaly of Eu ($Eu/Eu^* < 1$) generally decreased with depth. Otherwise, a positive $Ce/Ce^*$ anomaly was maintained, indicating that all layers are weathering under an oxidation environment. The lack of precipitation should account for the lack of a reduction environment. The values of Y/Ho and Sm/Nd are discussed below (Fig. 2, 3).

### 3.2 Profile GTC

The REE concentrations in profile GTC yielded larger variances than profile ND, ranging from 5.11 to 474.55 mg/kg (163.72 mg/kg on average). The REEs in bedrock is 313 mg/kg (Zhou et al. 2015). Unlike profile ND, REEs were enriched in parts of the semi-regolith and depleted in the upper half of the profile. Except for a few layers, ΣREEs generally increased with depth and were enriched in the middle–lower part, like other granite profiles (Yang et al. 2016). Between 150 and 200 cm, relatively high REEs might have been the result of deposition of migrated REEs. Quartz veins might have caused the lack of REEs below the illuvial horizon. The ratio of LREEs/HREEs was in the range of 3.72–17.15, with an average value of 7.79. The semi-regolith below 150 cm had a lower ratio than the upper profile.

The strong weathering conditions under a tropical climate may account for the higher REE fractionation than in other studied profiles (Yang et al. 2016). Under long-term weathering and biogeochemistry reactions, REEs can

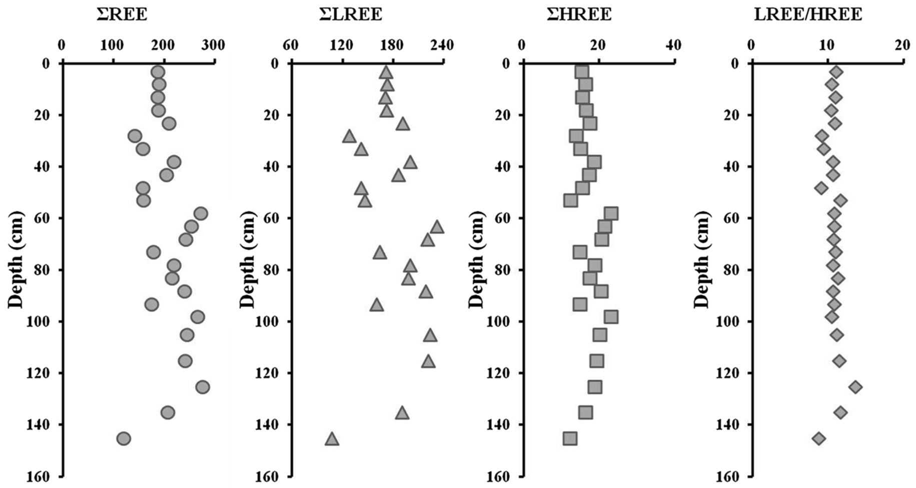

**Fig. 2** Distribution of ΣREE, ΣLREE, ΣHREE, and LREE/HREE in profile ND

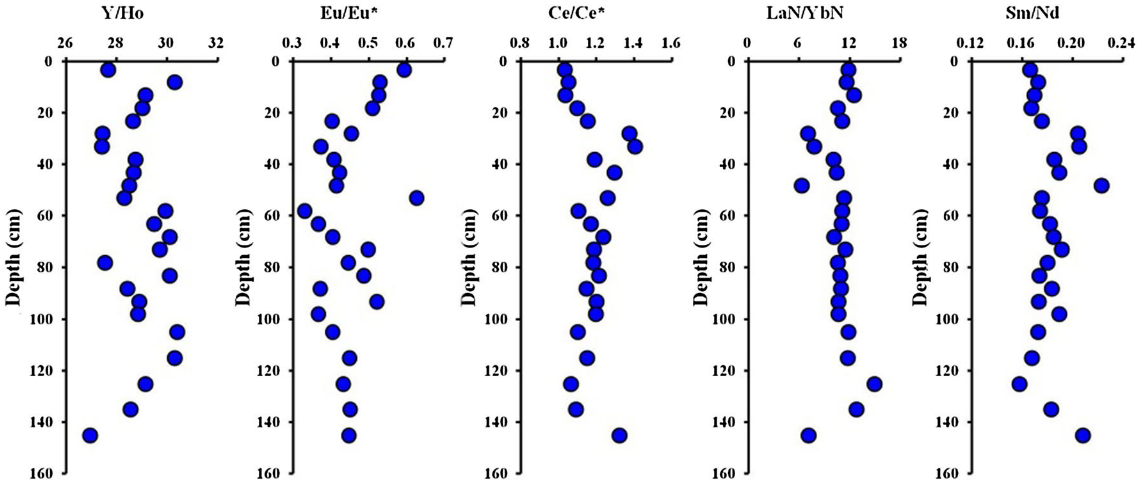

**Fig. 3** Geochemistry indicators in profile ND

activate and redistribute, even eroding into runoff. Hydrolysis activities and absorption rates of LREEs are stronger than HREEs. Thus, LREEs tend to stick in the surface while HREEs are dissolved to bicarbonate and organic complexes and migrate to the sublayer. In profile ND's weak weathered district, there was no obvious fractionation in LREEs/HREEs.

In chondrite-normalized REE plots, the curves lean to the right with a V-type Eu anomaly. The negative anomaly of Eu (Eu/Eu* $< 1$) was conspicuous in profile GTC. Eu/Eu* ranged from 0.13 to 0.56. As plagioclase is the main host of Eu, plagioclase weathering may account for the negative Eu anomaly below illuvial horizon.

The range of Ce/Ce* was 0.33–3.56, with a positive anomaly (Ce/Ce* $> 1$) in soil and in illuvial horizon and negative (Ce/Ce* $< 1$) in semi-regolith. Redox conditions are the key factor that affect Ce distribution. $Ce^{3+}$ is stable in water solutions and can be oxidized to insoluble $Ce^{4+}$ (Nesbitt 1979). In regolith surface, $Ce^{4+}$ can be enriched by clay minerals or Fe–Mn oxides (Ohta and Kawabe 2001).

Elements Sm, Nd, Y, and Ho have similar geochemical character. Their fractionation has special meaning to geologic processes (mineralization, diagenesis, ocean evolution, etc.). Sm/Nd ranged from 0.14 to 0.25, and Y/Ho from 16.91 to 24.90 in profile GTC; in profile ND, Sm/Nd and Y/Ho were 0.16–0.22 and 26.93–30.37, respectively. In bedrock, Sm/Nd and Y/Ho were 0.18 and 29.76 for ND and 0.22 and 27.4 for GTC, both respectively. In contrast to other geologic processes, there was no clear fractionation of Sm/Nd and Y/Ho in either profile during weathering (Fig. 4, 5).

## 4 Conclusions

Based on REE concentrations of two typical granitic regoliths in different climates, we summarize that:

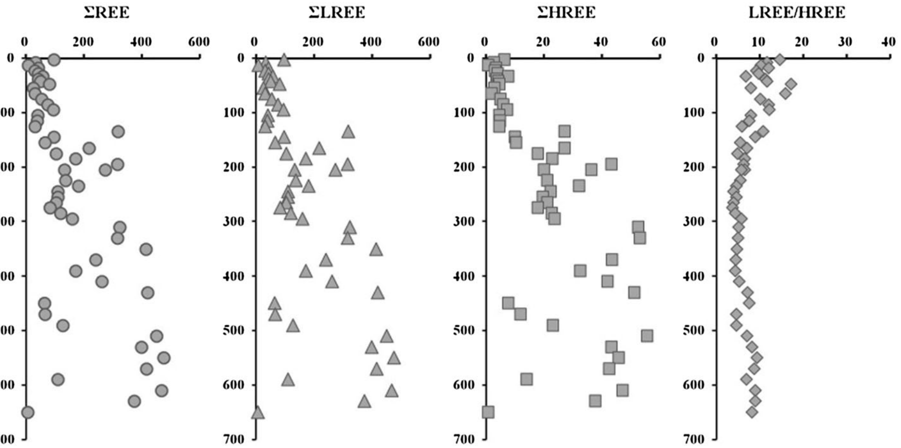

**Fig. 4** Distribution of ΣREE, ΣLREE, ΣHREE, and LREE/HREE in profile GTC

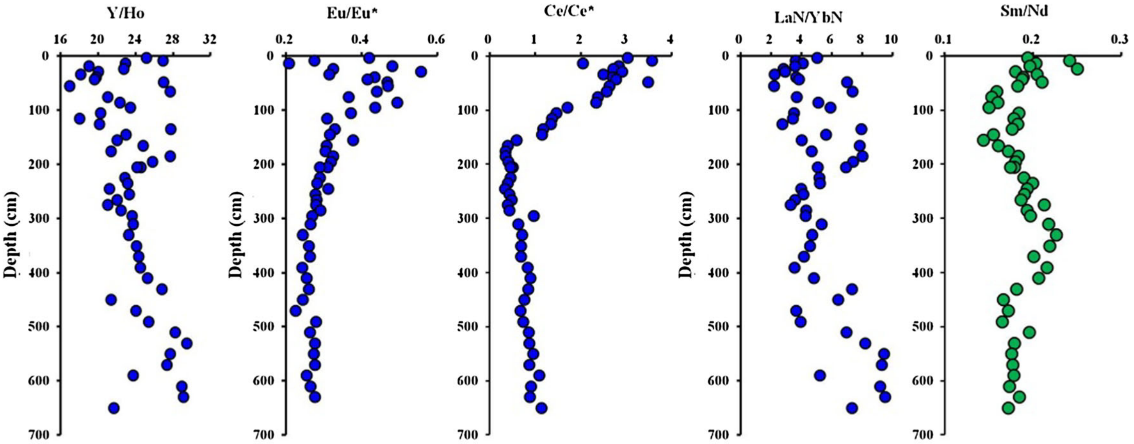

**Fig. 5** Geochemistry indicators in profile GTC

(1) In tropical profile GTC, REEs concentrated in semi-regolith and were lost to weathering in pedosphere, and even in part layers of illuvial horizon. Under continental climate, REEs were variably enriched in all layers.

(2) Normalized by chondrite, LREEs accumulate much more than HREEs, the distribution curves of REEs were typically right-leaning with V-type Eu anomaly in both profiles. The fractionation of HREEs and LREEs was not obvious in continental profile ND. LREEs were more detained in pedosphere of tropical profile GTC.

(3) Eu and Ce anomalies indicated that tropical profile GTC developed in a reduction environment below the pedosphere. However, all layers in continental profile ND weathered under oxidation conditions.

**Acknowledgements** This study was funded by National Natural Science Foundation of China (41210004, 41603018, 41673124 and 2013CB956401), ministry of water resources of People's Republic of China (201401050).

## References

Brantley SL, Lebedeva M (2011) Learning to read the chemistry of regolith to understand the critical zone. Annu Rev Earth Planet Sci 39:387–416. doi:10.1146/annurev-earth-040809-152321

Nesbitt HW (1979) Mobility and fractionation of rare earth elements during weathering of a granodiorite. Nature 279:206–210

Ohta A, Kawabe I (2001) REE(III) adsorption onto Mn dioxide (δ-$MnO_2$) and Fe oxyhydroxide: Ce(III) oxidation by δ-$MnO_2$. Geochim Cosmochim Acta 65:695–703

Yang JX, Liu CQ, Zhao ZQ et al (2016) Geochemical behavior of rare-earth element during the weathering of granite under different climatic conditions. Acta Mineral Sinic 36:125–137 **(In Chinese)**

Zhang HF, Chen YL, Xu WC et al (2006) Granitoids around Gonghe Basin in Qinghai Province: petrogenesis and tectonic implications. Acta Petrol Sinic 22:2910–2922 **(In Chinese)**

Zhou XP, Qi HW, Hu RZ et al (2015) Geochronology and geochemistry of granites in the Tengchong Xinqi area western Yunnan and their tectonic implications. Bull Mineral Petrol Geochem 34:139–148 **(In Chinese)**