

Rare earth element chemistry indicates chemical alteration of zircons during the evolution of weathering profile

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Abstract Although rare earth elements (REEs) in magmatic zircons have been widely used to identify the type and compositional evolution of host rocks, REE distribution patterns during the chemical alteration of zircons need clarification. We investigated REE characteristics in zircons with different degrees of chemical weathering through systematic observation of a granodiorite-weathering profile in southeast China. Despite the relatively stable provenance of the studied profile (zircon U–Pb ages are 95.2 ± 4.8 Ma), the zircon REEs exhibited systematic differences in abundance and fractionation patterns from the bedrock to upper layers, e.g. $\sum\text{REE}$, $(\text{LREE}/\text{HREE})_{\text{CN}}$, and Ce/Ce^* . This evidence suggests chemical alteration of zircons during intensive chemical weathering and an expected influence on REE variability in the weathered products due to the presence of REE-bearing minerals.

Keywords Weathering profile · Rare earth elements · Zircon

1 Introduction

The rare earth elements (REEs) are a coherent group of elements that have been used extensively to trace low-temperature geological and biogeochemical processes in a range of rocks, soils, sediments, and aquatic environments (Taylor et al. 1986; Yang et al. 2002; Tanaka et al. 2007; Lim et al. 2014). Typically, the light REEs (La to Eu, LREEs) reside in trace minerals such as apatite, epidote, and allanite, whereas the heavy REEs (Gd to Lu, HREEs) are associated with minerals such as zircon. Zircon (ZrSiO_4) may withstand mechanical and chemical breakdown over billions of years. Thus, the concentration and distribution of REEs in zircons are of great importance to the potential use of zircon REE characteristics as indicators of host rocks (Belousova et al. 2002). However, some studies have found that zircon REE patterns and abundances are generally not useful as indicators of provenance in that zircon REEs exhibit a narrow abundance range with no systematic pattern differences (Hoskin and Ireland 2000; Hoskin and Schaltegger 2003). Hanchar and Westrenen (2007) suggested that the content and distribution pattern of zircon REEs can indicate growth environment and chemical composition of the melt or fluid. For many years, zircon was believed to be chemically resistant under surface pressure–temperature (P–T) conditions. In this study, we present zircon REE features as an indicator of chemical alteration of zircons during intensive chemical weathering in southeast China.

2 Samples and methods

Thirty-two samples were collected from a granodiorite weathering profile located in Xianyou County of Fujian Province ($118^\circ44.694'E$, $25^\circ21.853'N$). We analyzed REE

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contents in separate minerals of one granodiorite bedrock and six weathered products for heavy mineral separation using standard procedures described by Mange and Maurer (1992). The separated detrital zircon grains were identified using an Electron Probe Micro-Analyzer (JEOL JXA-8230, EPMA with EDS and CL), and then measured for REE content and U–Pb age using RESOLUTION in situ laser ablation inductively coupled plasma-mass spectrometer (ICP–MS) (Agilent 7900, LA-ICPMS) in the State Key Laboratory of Marine Geology at Tongji University (Su et al. 2017). Synthetic silicate glass (NIST SRM 610) was used to calibrate REE concentration, and results were obtained in $\mu\text{g/g}$. U to Pb ratios and ages were corrected through replicate analyses of standard zircons 91,500 and Plesovice. $^{207}\text{Pb}/^{238}\text{U}$ ages and $^{206}\text{Pb}/^{238}\text{U}$ ages were calculated using ICP-MS DaTaCal9.2 (Liu et al. 2010a, b) separately for older (>1 Ga) and younger (<1 Ga) zircons (Compston et al. 1992).

3 Results and discussion

Detrital zircons from the weathering profile returned relatively stable $^{206}\text{Pb}/^{238}\text{U}$ ages of 95.2 ± 4.8 Ma, which agree with the Cretaceous age of local granite bedrock. The average total REE ($\sum\text{REE}$) concentrations in zircons were 750 and 1500 $\mu\text{g/g}$ for the bedrock and weathering products, respectively. Chondrite-normalized REE patterns in all the zircon grains indicate a significant enrichment of HREE (contribution of $>90\%$) relative to LREE (Fig. 1a), with chondrite-normalized $(\text{LREE}/\text{HREE})_{\text{CN}}$ ratios of 0.018 ± 0.005 on average. This is consistent with previous observations by Garzanti et al. (2011). In comparison, the granodiorite bedrock-normalized REE patterns of zircons from the weathered products were discernably different, especially for LREEs (Fig. 1b). We note that the concentrations of some LREEs may have been underestimated by the LA-ICP-MS method.

Ce and Eu anomalies in zircons were observed in the profile. The ratios Ce/Ce^* and Eu/Eu^* were used to describe Ce and Eu anomalies, calculated as $\text{Ce}/\text{Ce}^* = \text{Ce}_{\text{CN}}/(\text{La}_{\text{CN}}^{0.5} \times \text{Pr}_{\text{CN}}^{0.5})$ and $\text{Eu}/\text{Eu}^* = \text{Ce}_{\text{CN}}/(\text{Sm}_{\text{CN}}^{0.5} \times \text{Gd}_{\text{CN}}^{0.5})$; the subscript CN indicates chondrite-normalized. The average Ce/Ce^* and Eu/Eu^* ranged from 2.4 to 15.1 and 0.33 to 0.48, respectively, showing a strong positive Ce anomaly and a slight negative Eu anomaly. This reflects the higher trace element abundance of crust-affinity zircons, with REE patterns exhibiting a steeply-rising slope from LREEs to HREEs, and with enriched Ce values relative to La and Pr, and depleted Eu values relative to Sm and Gd (Belousova et al. 2002).

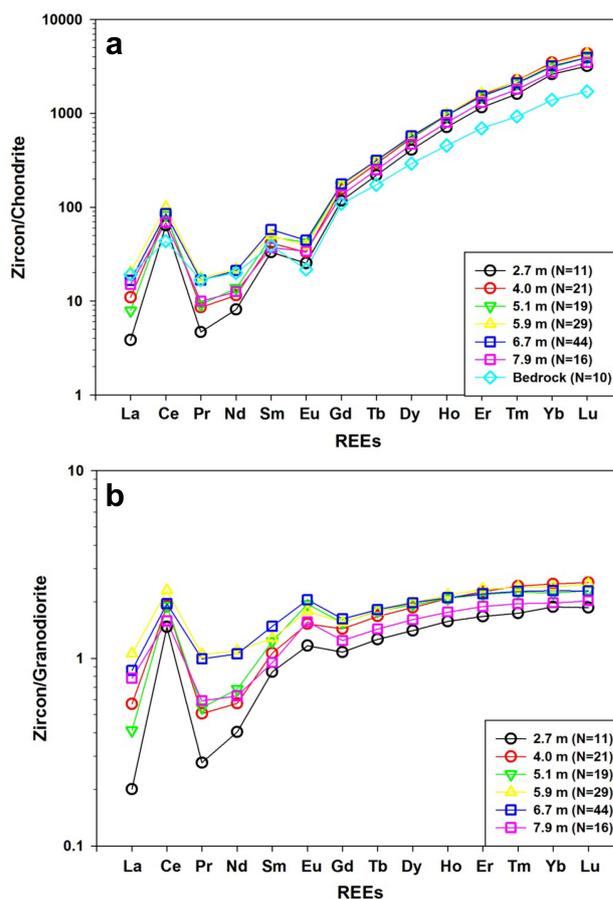


Fig. 1 **a** Chondrite-normalized REE patterns of zircons in the granodiorite bedrock and weathered products; **b** granodiorite bedrock-normalized REE patterns of zircons in the weathered products. Note that N is the number of zircon grains measured

To compare zircon REE patterns with chemical weathering intensity, depth variations of REEs are illustrated in Fig. 2. The chemical index of alteration (CIA) is widely used as a proxy for chemical weathering in sediment source areas. CIA is derived from the molecular weights of the oxides, i.e., $\text{CIA} = \text{Al}_2\text{O}_3/(\text{Al}_2\text{O}_3 + \text{CaO}^* + \text{Na}_2\text{O} + \text{K}_2\text{O}) \times 100$ (Nesbitt and Young 1982). CaO^* represents the calcium content in the silicate fraction of the sediments. In general, CIA values of 50–65, 65–85, and >85 represent weak, intermediate, and strong silicate weathering, respectively. In this case, the whole profile was highly-weathered between 4.3 and 7.9 m depth and completely-weathered in the top 4.3 m (Fig. 2).

Zircon grain percentage generally increased from the granodiorite bedrock to the upper layers (saprolite). $\sum\text{REE}$ concentration in zircon initially increased (below 4 m, $\text{CIA} < 90$) and then decreased (above 4 m, $\text{CIA} > 90$), which is nearly opposite to the trend of ZrO_2 in the profile. This indicates that REEs may be replaced by Zr^{4+} in the

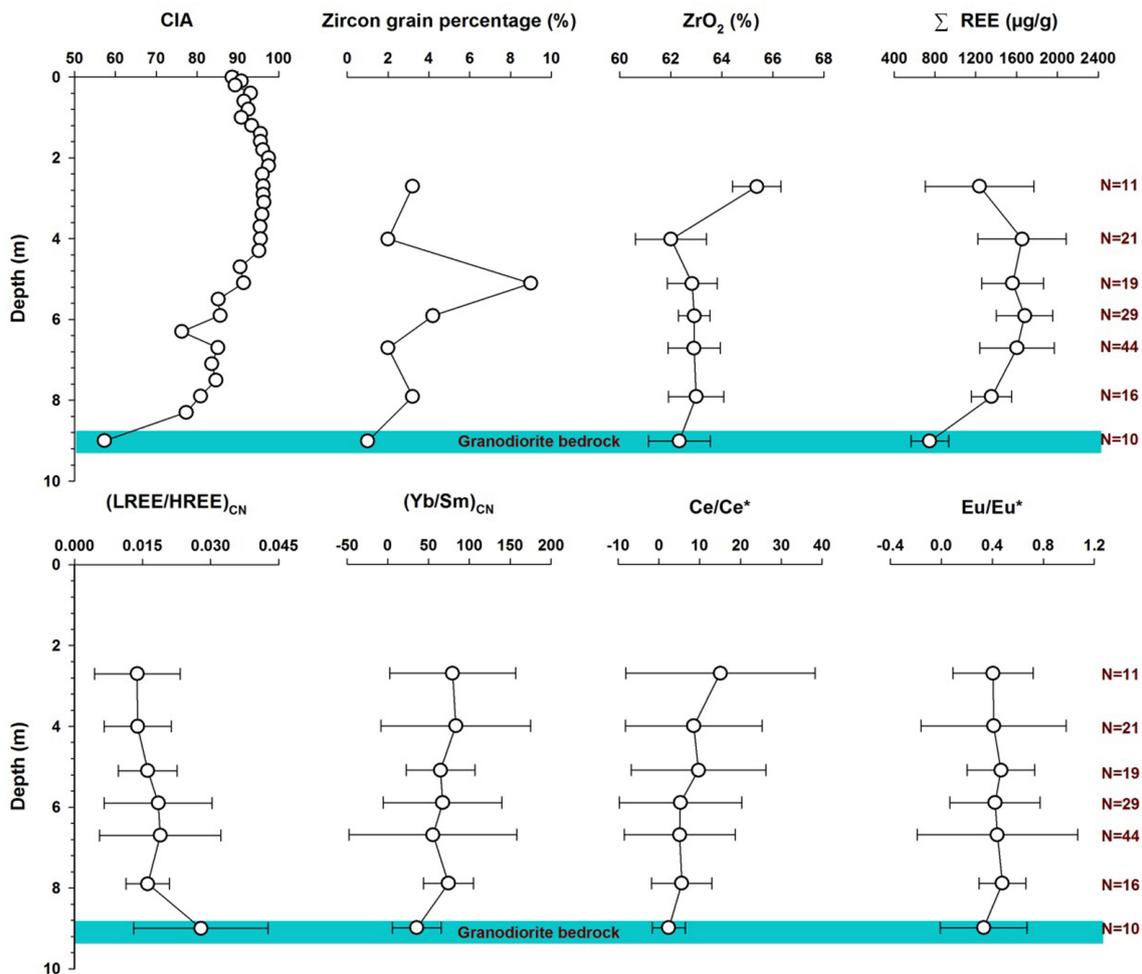


Fig. 2 Depth variations of CIA, zircon grain percentage in the total heavy mineral fractions, ZrO_2 content, total REE* concentration (ΣREE), chondrite-normalized $(LREE/HREE)_{CN}$ and $(Yb/Sm)_{CN}$, Ce/Ce^* and Eu/Eu^* in zircon grains of the weathering profile. Note that N is the number of zircon grains measured

chemical alteration of zircons. The $(LREE/HREE)_{CN}$ ratios decreased upward [that is increasing for $(Yb/Sm)_{CN}$], implying that the most important impact of enhanced chemical weathering on geochemistry of zircons is the accumulation of HREEs.

Meanwhile, Ce/Ce^* values increased gradually from the granodiorite bedrock to the upper layers, while a relatively stable trend was noted for Eu/Eu^* . It has been reported that Ce anomaly is caused by the change of melting oxygen fugacity during zircon crystallization (Trail et al. 2012). However, this is contrary to the negative Eu anomaly since Zr^{4+} tends to be replaced by Eu^{3+} instead of Eu^{2+} . Negative Eu anomalies could also be related to fractional crystallization of plagioclase in the magma or to remaining plagioclase at the source, which removes most Eu (Cullers and Graf 1984). In this study, it was difficult to ascertain the role chemical weathering has played thus far, but the changes in the value of the anomaly could be related to

redox conditions in the sediments during chemical weathering.

4 Conclusions

This study analyzed zircon REE composition from a relatively stable provenance granodiorite-weathering profile in southeast China. Systematic differences were observed in zircon REE abundances and differentiation (diffusion–reaction) between light and heavy REEs [e.g. ΣREE , $(LREE/HREE)_{CN}$ and Ce/Ce^*] in the profile. Our REE data suggest the existence of some process, likely chemical weathering, that took place after zircons had formed and changed the geochemistry of zircons in the weathered products. These findings will help to further elucidate the constraints of mineralogy on REE compositions in sediments using zircon REE data.

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