American Mineralogist, Volume 105, pages 848–859, 2020

REE redistributions during granite weathering: Implications for Ce anomaly as a proxy for paleoredox states

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Abstract

Different responses of Ce to the redox state from those of the other light rare earth elements (LREEs) can be used to understand paleoredox states. To establish the possibility of using the Ce anomaly as a proxy for paleo-environments, we examined the mineralogical and chemical characteristics of bulk samples and REE-bearing minerals of a modern weathering profile developed on granite, by X-ray fluorescence analysis, laser-ablation inductively coupled plasma mass spectrometry, field emission electron microprobe analysis, field emission scanning electron microscopy, and X-ray diffractometry. Bulk samples showed no significant Ce-anomalies except for the topmost layer that had a positive Ce-anomaly reflecting significant loss of LREEs except for Ce. Allanite-(Ce), primary REE-bearing mineral, contributed to ~100% of La, Ce, Pr, and Nd in the parent rock, and gradually decreased in amount toward the topmost layer. Secondary cerianite-(Ce) [$Ce(IV)O_2$] was observed in the weathering profile, especially at shallower depths. Secondary rhabdophane-(La), -(Ce), -(Nd), and -(Y) were also observed in the weathering profile but in less amounts in the topmost layer. The occurrences of rhabdophane-(La) and -(Nd) in contact with halloysite, a secondary clay mineral, suggest probable adsorption of REEs onto halloysite prior to their formation. Similar formation mechanisms are likely for rhabdophane-(Ce) that commonly occurred in grain boundaries and was usually formed in contact with halloysite. Rhabdophane-(Y) occurred in association with fluorapatite. The ratios of La, Pr, and Nd of rhabdophane-(La), -(Ce), and -(Nd) were similar to that of allanite-(Ce), suggesting that these LREEs are inherited from allanite-(Ce) and behave similarly before the formation of rhabdophane. Different negative Ce-anomaly values of rhabdophane [i.e., ~0.03–0.34 for rhabdophane-(La), -(Nd), and -(Y), and ~0.6 for rhabdophane-(Ce)] can result from a difference in intensity of the formation of cerianite-(Ce) prior to the precipitation of rhabdophane. We have classified LREE redistributions in both secondary minerals and bulk weathered samples during oxic weathering and suggested that Ce anomaly can provide useful information on anoxic weathering and thus atmospheric oxygen evolution in the Precambrian if Ce anomalies of both bulk samples and secondary REE-bearing minerals are determined.

Keywords: REE, weathering, Ce anomaly, paleoredox, phosphate