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

KOJI ICHIMURA¹, KENZO SANEMATSU², YOSHIKI KON², TETSUICHI TAKAGI², and TAKASHI MURAKAMI¹,*

¹Department of Earth and Planetary Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan
²Geological Survey of Japan, National Institute of Advanced Industrial Science and Technology, Central 7, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8567, Japan

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)O₂] 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)] 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

INTRODUCTION

Because weathering is mineral-water-atmosphere interaction, geological records of paleoweathering provide useful information on paleo-environments, especially atmospheric oxygen and carbon dioxide concentrations (Holland 1984; Rye and Holland 1998; and references therein). Chemical analyses of rare earth elements (REEs) have been applied to paleosols, ancient weathering soils, to understand paleo-environments (e.g., Wiggering and Beukes 1990; Macfarlane et al. 1994; Pan and Staufler 2000; Parnaï et al. 2000; Murakami et al. 2001; Yang et al. 2002; Yang and Holland 2003; Utsunomiya et al. 2003; Ichimura and Murakami 2009), using Ce anomaly [Ce/Ce* = Ce₀/(La₀×Pr₀)½, where Ce = Ce₀, Ce* = (La₀×Pr₀)½ and REEs is the REE concentration normalized by CI chondrite (McDonough and Sun 1995)].

Earlier studies (Sawka et al. 1986; Banfield and Eggleton 1989; Braun et al. 1990, 1993; Cotten et al. 1995) have reported that Ce fractionation occurs in modern, oxic weathering as follows: cerianite-(Ce) [Ce(IV)O₂] is formed through Ce(III) oxidation and subsequently rhabdophane with negative Ce-anomalies is formed, utilizing dissolved P and REEs from primary minerals such as apatite and allanite. Such Ce fractionation has been considered to result from a difference in mobility between Ce(IV) and other trivalent LREE, including Ce(III) and to be evidence of the presence of a significant amount of atmospheric oxygen. Then the absence or presence of Ce anomaly has been applied to paleosols to determine whether the paleosols were formed under oxic or anoxic conditions (e.g., Wiggering and Beukes 1990; Macfarlane et al. 1994).

On the other hand, the above Ce fractionation processes under oxic conditions may be further complicated by (1) Ce(III) oxidation by oxyhydroxide-assisted scavenging (e.g., Janots