Natural isotopic variation of europium among geological samples

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Significant mass-dependent isotope fractionation of ^{146}Nd/^{144}Nd was recently reported for marine carbonates [1,2]. In this study, degree of natural isotopic variation of Eu among carbonates and many kinds of igneous rocks was evaluated to understand the isotopic variation observed in rare earth elements (REE).

Europium was extracted and purified by conventional cation-exchange chromatography. Precise ^{153}Eu/^{151}Eu isotope ratios were determined by multiple collector ICP-MS with a Sm doping technique to correct its mass discrimination effect, and discussed in the epsilon scale relative to an in-house standard reagent (Alfa Aeser 99.999% Eu_2O_3).

The ε^{153}Eu values of three basalts are identical within analytical uncertainty and the average is -0.8 ± 0.5 (2SD). The ε^{153}Eu value of a manganese nodule is –0.3 and indistinguishable from those of the basalts. On the other hand, the ε^{153}Eu values of the marine limestones and dolomites are significantly higher than basalts. The ε^{153}Eu values of marine carbonate rocks are correlated with their ε^{146}Nd values [1]. The correlation between Eu and Nd isotopic compositions indicates that the mass-dependent isotope fractionation of Eu and Nd was produced when the marine carbonates were formed. It is consistent with the correlation between Ce and Nd isotopic compositions reported previously [2]. Europium is stable as both trivalent and divalent whereas Nd and other REE are generally stable only as trivalent. The observed correlation indicates that Eu and Nd behaved similarly as trivalent species in seawater and in the marine carbonates, and the isotope fractionation is produced by non-redox reactions such as precipitation and/or dissolution.

The ε^{153}Eu values of felsic igneous rocks are also determined, and an isotopic variation is observed beyond analytical uncertainty among some of the felsic rocks. Possible isotope fractionation processes will be discussed.

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Ce oxidation by Mn oxide produced by *Acremonium* sp. strain KR21-2

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Biogenic Mn oxide has attracted many geochemists in terms of the ability to highly adsorb and oxidize various trace elements. In this study, we focused on rare earth element (REE), and especially studied change in chemical states of Ce by Mn oxide produced by a Mn-oxidizing fungus.

We used *Acremonium* sp. strain KR21-2 as a model of Mn-oxidizing fungi [1]. Strain KR21-2 was cultured in HEPES-buffered AY medium with and without 1 mM Mn^{2+}, respectively. Manganese oxide was formed around hyphae in the cultivation in the medium containing Mn^{2+}. Partitioning experiments of REEs between hyphae plus Mn oxide and 10 mM NaCl solution were carried out under different pH conditions. Oxidation states of Ce adsorbed on the hyphae and Mn oxide were determined using XANES.

The REE partitioning pattern between hyphae without biogenic Mn oxide and 10 mM NaCl solution showed no Ce anomaly. The observation without Ce anomaly is consistent with the results of XANES analyses, which indicated that Ce adsorbed on the hyphae was trivalent. The partitioning patterns between biogenic Mn oxide plus hyphae and 10 mM NaCl solution show variation with increasing pH. At pH4.5, fairly large positive Ce anomaly was observed, which is consistent with previous works using synthetic Mn oxide [2,3]. The presence of Ce(IV) on the biogenic Mn oxide was shown by XANES analysis. In contarst, no Ce anomaly was observed at pH 5.96, and negative Ce anomaly appeared at pH6.51. XANES analyses showed the presence of Ce(IV) on the biogenic Mn oxides even at pHs 5.96 and 6.51. This suggests that Ce(IV) was probably stabilized in solution under higher pH conditions due to complexation with organic ligand excreted by hyphae.

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