

Change of host phase of REE and preservation of REE pattern during the diagenesis of marine sediments

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Relative abundances of rare earth elements (REE) in geological materials are used widely to investigate geochemical problems such as the origins of sedimentary rocks and REE behavior during processes such as weathering and diagenesis. One of the REE, cerium (Ce), can exist in either trivalent or tetravalent form depending on the redox condition. Thus, knowledge of the oxidation state of Ce in rocks and minerals could potentially be used to constrain the redox states of past and present geological environments. In this study, we examined validity of REE pattern as geochemical indicators reflecting sedimentary paleoenvironment.

For this aim, we discussed the behavior of REE under diagenetic environment by using Ce and Mn distributions in sediments, and oxidation states of Ce and Mn determined in X-ray absorption near edge structure (XANES). Sediment core samples used in this study were recovered from North Pacific at Site 1179, ODP Leg 191. Sediment at these core sites consists of siliceous ooze, clay, and thin volcanic ash layer. According to XRF data, the concentration depth profiles of Fe and Mn show that they have high concentration peaks. Manganese is accumulated at 0.20 m, and then decreases toward deep due to reductive dissolution of MnO₂. The oxidation state of Mn from 0.60 m to 7.18 m is mostly divalent, which is consistent with the low concentration of Mn layer. Marine ferromanganese nodule is known to have a high absorption capacity for REE. Among the REE, Ce tends to accumulate in Mn oxide due to oxidation from soluble Ce^{III} to insoluble Ce^{IV}. Cerium concentration in sediments is relatively constant from top to bottom of the core, but Mn concentration is not. These results imply that the host phase of Ce changed from Mn-oxides to the other phase.

We confirmed that host phase of Ce changed from Mn oxide to phosphate based on the chemical leaching experiments. Additionally, positive Ce anomaly were observed in both Mn and P phases determined by laser ablation (LA)-ICP-MS, suggesting that the anomaly was conserved during change in the host phase of Ce. Micro-XANES study also showed that Ce in Mn oxides is tetravalent, but trivalent in apatite found at the depths of 0.70 m and 0.80 m.

Overall, the shapes of REE patterns were similar from the surface to the depths studied here, though the host phase of REE changed from Mn oxides to phosphate. Thus, the phosphate having high affinity for REE is important to keep the initial REE pattern during the diagenesis.