Formation process of Ce(IV) phase in the redox gradient in weathered granite

Yoshio Takahashi[1]; Masaharu Tanimizu[2]

[1] Earth and Planetary Systems Sci., Hiroshima University; [2] KOCHI, JAMSTEC

Cerium can behave differently from other rare earth elements (REE) at earth's surface due to the stability of tetravalent state, Ce(IV), which is highly insoluble. Since trivalent states are exclusively found for other REE (except for Eu(II) under reducing condition such as magmas and hydrothermal water in deep underground), relative abundance of REE in natural samples, namely REE pattern, can show anomalous data for Ce, which we call Ce anomaly. For the formation of Ce anomaly, there needs oxidant for Ce(III) to be oxidized to Ce(IV). In our previous studies for Ce in weathered granite and marine ferromanganese oxides, it has been suggested that Ce is effectively oxidized by Mn oxides, which is a powerful oxidant in natural systems. However, it was found in the redox gradient of weathered granite that there is not high correlation between the abundances of Ce and Mn. In the sample, there are Fe (hydr)oxide and Mn oxide bands, suggesting that there was a gradient of redox condition during the weathering processes. In the profile, micro-XRF for the sample conducted at beamline 10.3.2 in Advanced Light Source (ALS) showed that Ce was enriched between the two bands. In addition, Ce was enriched as homogeneous Ce oxide, CeO_2, or Ce hydroxide, $Ce(OH)_4$. These results suggest that (i) Ce can be oxidized possibly by oxygen without contribution of Mn oxide as the oxidant and (ii) Ce is oxidized under the intermediate redox condition between the redox conditions where $Fe(OH)_3$ and MnO_2 can precipitate. This result, which can be actually predicted by Eh-pH diagrams, show that Mn oxide is not essential for the formation of CeO_2 in natural water-rock systems. This fact, in turn, can be a constraint on the estimation of paleoredox condition based on the formation of Ce anomaly in geological samples. For example, it was not clear whether Mn oxide is needed for the formation of Ce anomaly in banded iron formation (BIF), the redox condition of which is more oxic than the condition needed for the formation of CeO_2. Based on the present data, it is suggested that the redox condition, or oxygen fugacity in the atmosphere, can be lower than that needed for Mn oxidation in the paleomarine system.