9A, 12C/2004G334

Determination of the Eu(II)/Eu(III) ratios in minerals by X-ray absorption near-edge structure (XANES) and its application to hydrothermal deposits

Yoshio TAKAHASHI[1*], German R. KOLONIN,[2] Galina P. SHIRONOSOVA,[3]
Irina I. KUPRIYANOVA,[3] and Hiroshi SHIMIZU[1]

[1]Dept. Earth and Planetary Systems Science, Hiroshima University, Hiroshima 739-8526, Japan
[2]Institute of Mineralogy and Petrography, SB RAS, Prosp. Koptyuga 3, Novosibirsk, 630090, Russia
[3]Fedorovskii All-Russia Research Institute of Mineral Resources, Staromonetnyi per. 31, Moscow, 119017, Russia

Abundances of rare earth elements (REE) have provided useful information for characterizing various geochemical samples such as rocks, minerals, and water samples, with the purpose of estimating the source materials of the sample and environment where the sample was formed. Among various features involved in REE patterns (= relative abundances of REE normalized by proper reference materials), an anomalous abundance of Eu, called Eu anomaly, can be used as an indicator of redox conditions, origin of the materials, and REE fractionation during crystallization differentiation. The Eu anomaly is presumably caused by the formation of Eu(II) in reducing environment, which induces the fractionation of Eu from other trivalent REEs. The extent of Eu anomaly is often expressed as $Eu_N/Eu_N^* = Eu_N/\{(Sm_N)^{1/2}(Gd_N)^{1/2}\}$, where N indicates normalized abundances. Although there have been many studies discussing Eu anomaly with the Eu_N/Eu_N^* ratio assuming the presence of Eu(II), few studies have identified Eu(II) in rocks and minerals. X-ray absorption near-edge structure (XANES) is a promising tool for the speciation of trace elements, which was employed in this study to determine Eu(II)/Eu(III) ratios in apatite and fluocerite in hydrothermal vein deposits, Malyshevskoe and Katuginskoe deposites, respectively, in Russia. It is expected that the Eu(II)/Eu(III) ratio determined for the minerals can be used to estimate the Eu(II)/Eu(III) ratio in hydrothermal solutions where the minerals have formed, which in turn can be used to estimate f_{O_2} in the hydrothermal solution, based on the relationship between the Eu(II)/Eu(III) ratio and f_{O_2}.

Europium L_{III}-edge XANES was measured in synchrotron radiation facilities in both BL-12C of Photon Factory (PF) in KEK, Tsukuba, Japan. The fluorescence yield was measured using a 19-element Ge semiconductor detector (SSD).

It was found that the Eu(II)/Eu(III) ratios in minerals can be determined based on the peak area ratio of white lines, resonance peak, in normalized XANES spectra for Eu(II) and Eu(III) species. For precise determination of the Eu(II)/Eu(III) ratios, however, it was revealed that the transition probabilities for each individual Eu(II) and Eu(III) species in the system must be quantified, because we found that the peak area in normalized XANES spectra is clearly different in each Eu(II) and Eu(III) species, as exemplified in the Fig. 1. Despite this ambiguity, the method was applied to Eu in natural hydrothermal apatites (Eu = 39 and 64 ppm) and fluocerite (Eu = 282 ppm). The relation between the Eu(II)/Eu(III) ratio in these hydrothermal minerals, and the distribution coefficients of Eu(II) and Eu(III) were discussed, taking into account Eu anomalies in their REE patterns. It is considered that by combining the Eu(II)/Eu(III) ratios determined by XANES and the degree of Eu anomaly in REE patterns, we can provide new information on the distribution of Eu(II) and Eu(III) in various geochemical studies.

References

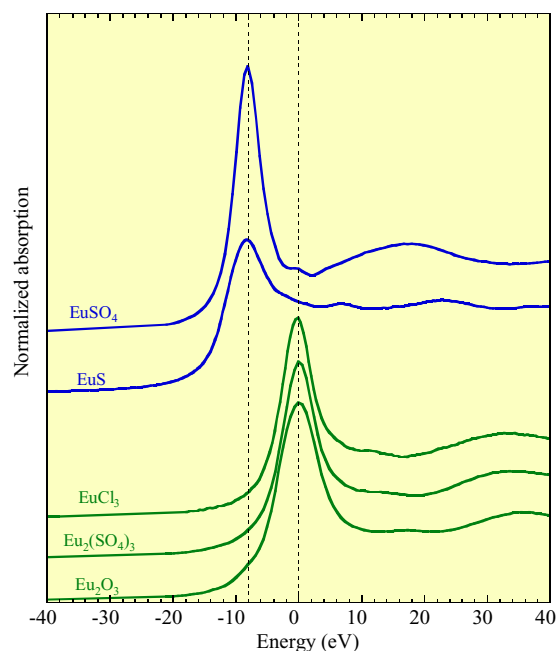[1] Y. Takahashi et al., Min. Mag. 69 (2005) 177-188.

* ytakaha@hiroshima-u.ac.jp

Fig. 1. Europium L_{III}-edge XANES spectra for various Eu(III) and Eu(II) species: Eu_2O_3, $Eu_2(SO_4)_3$, $EuCl_3$, EuS and $EuSO_4$.