High-sensitivity analysis of fluorescence XANES at Eu $L_{\rm III}$-edge for the determination of oxidation state for trace amount of Eu in natural samples using Bragg-type crystal analyzer system

In natural samples, relative concentrations of rare-earth elements (REEs) normalized by the concentration of appropriate materials such as chondrite are frequently employed to discuss the migration of REEs in various natural systems. Europium (Eu), one of the REEs, has been an important REE in geochemistry, since Eu can be present both as Eu(II) and Eu(III) under physicochemical conditions of the Earth [1]. The results of many studies have suggested that an anomalous abundance of Eu compared with neighboring REEs such as Sm and Gd (= Eu anomaly) is observed presumably because of the presence of Eu(II), which behaves similarly to divalent cations such as Ca(II) but distinctively different from other REES present exclusively as the trivalent form, except for Ce that can be present as Ce(IV) and which can be directly detected in natural samples such as by XANES [2]. However, it is difficult to detect Eu(II) in natural samples directly by such spectroscopic methods, except for several instances of minerals with high concentrations of Eu (20–700 ppm), such as apatite [1]. The Eu(II)/Eu(III) ratio has been utilized to estimate the redox condition in the aqueous environment in which these minerals were formed. However, Eu contents in normal crustal materials are typically lower than 1 ppm, which cannot be measured by the normal fluorescence XAFS technique. In particular, the detection limit is not determined by the Eu concentration itself, but by the interference of Mn $K\alpha$ emissions ($K\alpha_1$ and $K\alpha_2$: 5.900 and 5.889 keV, respectively) on Eu $L\alpha$ emissions ($L\alpha_1$: 5.849.5 keV) for the fluorescence XAFS measurement at the $L_{\rm III}$-edge [3]. Thus, the separation of Mn $K\alpha$ and Eu $L\alpha$ is essential for the high-sensitivity measurement of Eu $L_{\rm III}$-edge fluorescence XANES.

In high-sensitivity XANES analysis, high-energy-resolution fluorescence detection (HERFD)-XANES [4] is important not only for reducing interference fluorescence X-rays from coexisting elements, but also for sharpening the XANES peak, which enables us to separate peaks otherwise overlapped in normal XANES spectra, owing to the suppression of inner-shell lifetime broadening related to the core-hole lifetime effect, as shown in this study. Consequently, it is possible to identify peaks corresponding to minor species such as Eu(II) in natural samples.

In this study, we employed HERFD-XANES to investigate trace amounts of Eu in feldspar by developing a technique of fluorescence XANES measurement using a crystal analyzer in the Bragg geometry [3]. We previously conducted sensitive fluorescence XANES measurement using a bent crystal Laue-type analyzer (BCLA) for osmium-187 produced by the decay of rhenium-187 in molybdenite mineral [5]. However, this method in the Laue geometry is not effective for measuring Eu $L\alpha$ emissions around 5.8 keV, since the thickness of the Si crystal employed for BCLA is typically 0.2 mm, which absorbs more than 99.9% of fluorescence X-rays at 5.8 keV. Thus, we applied the Bragg-type crystal analyzer for the sensitive measurement of Eu $L_{\rm III}$-edge fluorescence XANES in natural samples [3]. Wavelength-dispersive fluorescence XANES at the Eu $L_{\rm III}$-edge was measured at SPring-8 **BL39XU**. For this analysis, Eu $L\alpha_1$ emission was measured during the scan of the incident photon energy from 6.95 to 7.05 keV using 13 Ge 333 spherically bent crystals (diameter of 40 mm) and the PILATUS 100 K detector mounted on a Rowland circle of a diameter of 820 mm [6].

Natural samples JF-1, a standard rock issued by Geological Society of Japan (GSJ) prepared from natural feldspar (Ohira Feldspar) from Nagiso, Nagano, Japan, were employed. In addition, raw feldspar was also collected in the study area in Nagiso (JF-1-raw). REE patterns of JF-1 and JF-1-raw normalized by that of CI chondrite in Fig. 1 showed a distinct Eu positive anomaly, which suggests the presence of Eu(II) in the sample. Concentrations of Eu and Mn measured for JF-1 were 0.64 and 3.4 mg/kg, while those for JF-1-raw were 0.42 and 5.2 mg/kg, respectively. In addition to the very low concentration of Eu, a Mn/Eu ratio larger than 5 can make it difficult to measure Eu $L_{\rm III}$-edge XANES. In this study, however, the effective separation

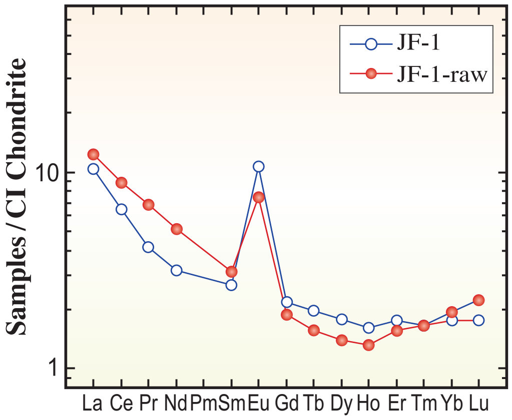

Fig. 1. Chondrite-normalized REE patterns for JF-1 (recommended and measured values).

of Eu Lα_1 from Mn Kα was attained by high-energy-resolution detection using the crystal analyzer system (Fig. 2). Consequently, the measurement of Eu L_{III}-edge XANES was possible for Eu at a concentration lower than 1 mg/kg in natural feldspar samples (Fig. 3).

The spectra of natural samples exhibit an intense peak at 6.983 keV assigned to Eu(III) with a small peak at 6.974 keV that can be assigned to Eu(II) [1]. The ratio of Eu(II) to Eu(III) was determined by fitting the Eu(II) and Eu(III) peaks in the spectra with a combination of Lorentzian and arctangent functions. As a result, the Eu(II)/Eu(III) ratios determined from the peak area ratio of the Lorentzian function were 0.010 and 0.015 for JF-1 and JF-1-raw, respectively. If we assume that (i) $\mathrm{Eu_N}^*$ (subscript N means the normalized value in Fig. 1) defined as $\mathrm{Eu_N}^* = \mathrm{Sm_N}^{0.5} \times \mathrm{Gd_N}^{0.5}$ corresponds to Eu(II) and (ii) ($\mathrm{Eu_N}$ - $\mathrm{Eu_N}^*$) to Eu(III), it is possible to estimate Eu(II)/Eu(III) from the REE pattern. The values were 4.0 and 2.1 for JF-1 and JF-1-raw, respectively, which are much higher than the 0.010 and 0.015 values determined by XANES. We suggest that the high Eu content in the feldspar relative to other REEs is caused by the (i) melting/dissolution of primary plagioclase with a positive Eu anomaly under the oxic condition and (ii) incorporation of Eu as Eu(III) into the feldspar samples during its crystallization/precipitation processes. Further study is needed to clarify the geochemical processes, but the high-sensitivity XANES analysis technique developed here is highly important for understanding the behavior of Eu in such natural systems.

HEFRD is effective for high-sensitivity XANES analysis based on (i) the decrease of the background level to measure the targeted fluorescence X-ray, such as a decrease of the interference of Mn in this study and (ii) the separation of independent peaks in XANES corresponding to different species owing to the sharpening of the XANES peak. HERFD-XANES spectra measured for Eu_2O_3 clearly reflected the sharpening effect, which makes it possible to observe clearly the Eu(II) peak in the XANES spectrum in Fig. 3, although the Eu(II) peak intensity is ca. 2% relative to that of Eu(III). The low detection limit of XANES analysis for trace amounts of Eu established in this study will contribute to a better understanding of the geochemical behavior of Eu, an important element among REEs.

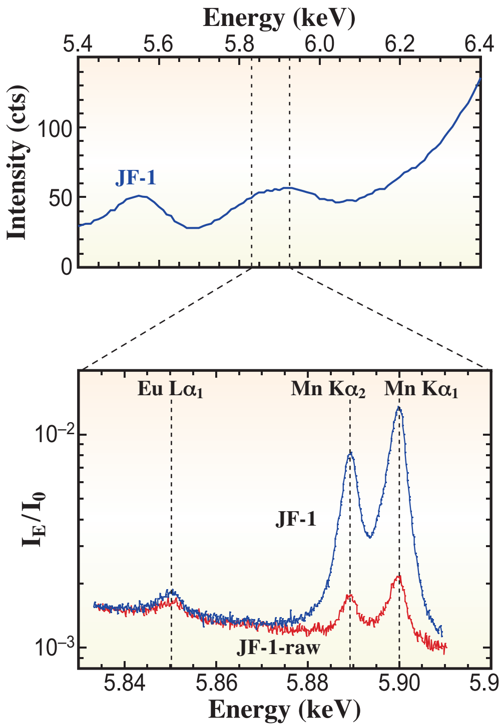

Fig. 2. X-ray fluorescence spectra (energy range from 5.83 to 5.91 keV) shown as I_E/I_0 (I_E: X-ray intensity determined by the PILATUS detector; I_0: intensity of incident X-ray) when irradiated at 7.05 keV.

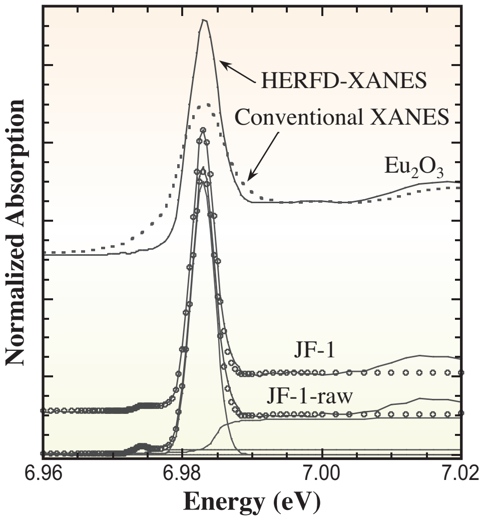

Fig. 3. Europium L_{III}-edge HERFD-XANES for Eu in Eu_2O_3, Eu in JF-1, and Eu in FJ-1-raw, and conventional XANES for Eu_2O_3 (dotted curve). Peak fitting results are shown as small circles for JF-1.

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