The determination of oxidation state for trace amount of europium in natural samples using high-sensitive analysis of fluorescence XANES by Bragg-type crystal analyzer system

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Europium (Eu), one of rare earth elements (REEs), has been an important element among REE in geochemistry, since Eu can be present both as Eu(II) and Eu(III) under physico-chemical condition of the earth (Henderson, 1983; Taylor and McLennan, 1995). On the Earth, Eu(II) is selectively incorporated into magma and feldspars in hot water (especially Ca feldspars), and the REE pattern shows positive Eu anomalies. As a result, negative Eu anomalies are often found in the REE pattern of the entire rock, which doesn’t contain other minerals or Ca feldspars (Taylor and McLennan, 1995). In general, the Eu concentration in cosmo-geochemical samples is low, and it’s difficult to experimentally determine the Eu(II)/ Eu(III) ratio. In this study, the Eu(II)/ Eu(III) ratio was obtained by the XANES method using high-sensitivity X-ray fluorescence analysis, and compared with the Eu(II)/ Eu(III) ratio estimated from the REE pattern. I aimed to analyze the cosmo-geochemical behavior of Eu, which is an index of the oxidation-reduction state.
Geochemical (rock) standard samples JF-1, JF-2 (potassium feldspar) and Ohira feldspar, which is the original rock of JF-1 (Imai et al., 1995; Janovszky et al., 2021; Tanaka et al., 2018), and synthesized meteorite samples (Ingrao et al., 2019) were used as samples. In particular, the Eu concentration in feldspar is as low as 1 ppm or less (Ando et al., 1989; Imai et al., 1995), while the Eu fluorescent X-rays (Lα rays) are close to the high-concentration Mn Kα rays within 50 eV during fluorescent XAFS analysis and are subject to serious interference. Since the energy resolution of the SDD detector is about 130 eV, it’s impossible to separate Eu Lα lines. Therefore, in this study, XANES analysis (HERFD-XANES: High Energy Resolution Fluorescence Detected XANES) was performed by high energy resolution fluorescence detection using a Bragg-type spectroscope.
Separation of Eu Lα rays from Mn Kα rays by a Bragg-type spectroscope and its high-energy resolution analysis show that the peak of XANES becomes sharper by taking only the maximum intensity part of fluorescent X-rays. It has become possible to detect trace amounts of Eu(II). From the obtained results, the Eu(II)/ Eu(III) ratio in the feldspar is 2% or less, which is significantly lower than the Eu(II)/ Eu(III) ratio expected from the REE pattern. This is because the solid phase (plagioclase, etc.) enriched with Eu(II) dissolves (or melts) to become Eu(III) in a more oxidative environment, and potassium feldspar was generated from the melt or fluid that took in the Eu(III). On the other hand, Eu(II)/ Eu(III) in oldhamite (CaS) in meteorite samples is 43% or less, which is almost the same as the Eu(II)/ Eu(III) ratio expected from the REE pattern. This is because the synthesized meteorite sample hasn’t undergone thermal metamorphism in the past. In other words, it was clarified that the combination of the Eu anomaly appearing in the REE pattern and the Eu(II)/ Eu(III) ratio obtained from XANES is an indicator of whether the sample has undergone thermal metamorphism in the past. In the future, new cosmic- geochemical findings will be obtained by applying this method to actual meteorites with Eu anomalies and determining the Eu(II)/ Eu(III) ratio.

Keywords: europium, XANES, oxidation state