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Direct observation of Ce(III)/Ce(IV) ratios in rocks by XANES

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Introduction

Relative abundances of rare earth elements (REE) in geological materials, REE patterns, are useful to investigate various geochemical processes. In the REE patterns, cerium has been of particular interest due to its active redox chemistry at earth's surface. It has been believed that the appearance of Ce anomaly in the REE patterns of geochemical samples is due to the redox transformations of Ce during the sample formation. However, in most cases, the oxidation state of Ce has not been measured directly by appropriate method due to the lack of sufficient sensitivity and elemental selectivity of the methods. In that sense, fluorescent XAFS has elemental selectivity and high sensitivity. Previously, we observed the presence of Ce(IV) species in natural rocks based on XANES technique [1]. In this report, we show the application of XANES for the direct measurement of Ce(III)/Ce(IV) ratios in natural rocks. It is expected that the combination of REE patterns and the oxidation state of Ce given by XANES provides a new perspective on Ce and REE behavior during various geochemical processes.

Experimental

As examples of natural rocks, weathered and fresh Toki granites (ML1 and DH3, respectively) were obtained from outcrops in the Tono district, Gifu, Japan. Mixtures having different ratios of Ce(III) and Ce(IV) reagents diluted with silica sand were prepared in order to obtain the relationship between the molar ratio of Ce(III)/Ce(IV) and the area ratio of Ce(III) and Ce(IV) peaks in XANES spectra. The Ce L_{III} edge XANES spectra for these samples were recorded in fluorescence at BL-12C of KEK-PF using a 19 element pure-Ge solid-state detector (SSD) [2, 3].

Results and Discussion

XANES spectra determined for the standard samples with various Ce(III)/Ce(IV) ratios were deconvoluted to obtain contributions of Ce(III) and Ce(IV) species in the spectra. The calibration obtained was used to estimate the percentage of Ce(III) and Ce(IV) in the natural specimens.

In the bulk of fresh granite (DH3) without Ce anomaly (Fig. 1), we could not find any signal from Ce(IV) in the XANES spectra. In the weathered granitic rock showing positive Ce anomaly (ML1), both Ce(III) and Ce(IV) were detected and the amount of Ce(III) estimated from XANES was estimated to be 30% (Fig. 2). This abundance corresponds to that of Ce(III) estimated from REE pattern as an interpolated value from La and Pr abundances (Open circle in Fig. 1). This shows that Ce(III) is contained in the bulk that has not reacted with water and that Ce(IV) was formed by oxidation in the aqueous phase and redistributed to the granite after being dissolved initially as Ce(III) [4].

This study shows that the determination of Ce(III)/Ce(IV) ratios by XANES is a promising tool to provide various information for REE behavior in natural systems. Further study applying the similar technique to various natural samples is proceeding.

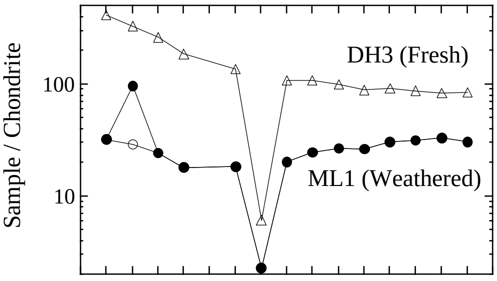

Fig. 1 REE patterns of fresh and weathered granite.

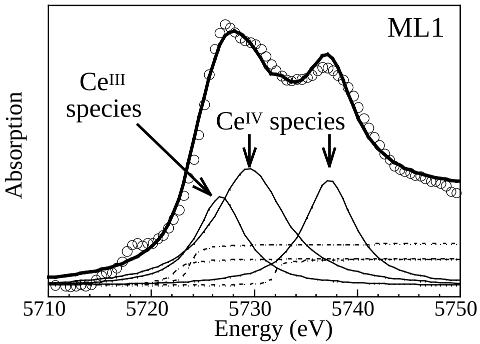

Fig. 2 Ce L_{III} edge XANES spectrum for wethered granite ML1.

References

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