

A New Method for the Determination of Ce(III)/Ce(IV) Ratios in Rocks; Application to Weathering, Sedimentary, and Diagenetic Processes

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In the REE (rare earth element) 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 physico-chemical method. This is because the method requires high sensitivity and high selectivity for the element to prevent other elements in natural samples from interfering the Ce signal. In this contribution, we report the new method for the direct measurement of Ce(III)/Ce(IV) ratios in rocks by X-ray absorption near-edge structure (XANES). It is shown that the combination of REE patterns and the oxidation state of Ce given by XANES provides a new perspective on Ce and REE behaviour during various geochemical processes such as weathering, sedimentary, and diagenetic processes.

The oxidation state of Ce in weathered granitic rocks, manganese nodules, and cherts were determined by XANES at Ce LIII edge (5.73 keV). Their REE abundances range from 15 ppm to 1200 ppm. The spectra were obtained at beam line 12C of KEK-Photon Factory in Tsukuba, Japan, by the fluorescence yield from Ce using a 19 element pure-Ge solid-state detectors having high energy-resolution to separate Ce signals from the scattering one and fluorescent X-ray of other elements. Small chips were directly used for manganese nodules and cherts, while powder sample was used for the granite. Areal ratio for Ce(III) and Ce(IV) peaks in XANES spectra was calibrated to molar ratio of Ce(III) and Ce(IV) in the mechanical mixtures of Ce(III) (chloride or acetate) and Ce(IV) (sulphate) species diluted by silica sand. The calibration was used to estimate the percentage of Ce(III) and Ce(IV) in the natural specimens.

In the bulk of fresh granite with no Ce anomaly, we could not find any signal from Ce(IV) in the XANES spectra. In the weathered granitic rock showing positive Ce anomaly, both Ce(III) and Ce(IV) were detected and the amount of Ce(III) estimated from XANES corresponds to that of Ce(III) estimated from REE pattern as an interpolated value from La and Pr abundances. 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)

Although the degrees of the positive Ce anomalies in hydro-genetic manganese nodules were similar to that found in the weathered granites when normalized by chondrite, Ce in the nodules were exclusively tetravalent. The predominance of Ce(IV) species is independent of the degrees of Ce anomalies found in four manganese nodules employed in this study. Similar results were also obtained for Ce sorbed on manganese oxide prepared in laboratory experiments. These results show that manganese oxide plays an important role for the redox chemistry of Ce in the ocean (Takahashi et al., in press).

In cherts that we studied, little contribution of Ce(IV) was found irrespective of various Ce anomalies in their REE patterns (both positive and negative when normalized by chondrite). This suggests that Ce(IV) has been reduced to Ce(III) during diagenetic processes. The fact that REE patterns show various Ce anomalies in spite of possible homogenisation by diagenesis shows that REE patterns more or less preserve the information of Ce anomalies formed at its deposition. As seen from this example, if we can find such a difference between the results of REE pattern and XANES, the discrepancy will give us precious knowledge about the initial condition and the subsequent change of Ce during geological processes such as diagenesis and alteration.

The present study shows a promising method to provide new knowledge on the behaviour of Ce and other REE by the combination of Ce anomaly and its oxidation state given by XANES. Used together with the degrees of Ce anomalies appeared in the REE patterns, this information has promise for refining our knowledge of various geochemical processes such as weathering, sedimentary, and diagenetic processes that control the REE behaviour. Such a refinement should in turn improve geological interpretations based upon REE data.

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