

Geochemical implications from oxidation states of trace elements in geological materials

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Compared with abundances and isotope ratios of trace elements, chemical-state of trace element, another feature of chemical element in geological materials, has not been widely used to extract geochemical information. Recently, analytical technique for chemical-state such as fluorescent XANES has been established, which can be applied to trace elements of ppm order in geological materials. In this paper, oxidation states of Mn, Co, and Ce in weathered granite, manganese nodules, siliceous sediments, cherts, and zircons are reported by using XANES technique. In particular, oxidation state of Ce is of great interest, since comparison of Ce(III)/Ce(IV) ratio and Ce anomaly in REE pattern will provide valuable information to investigate diverse geochemical issues.

Introduction: Compared with abundances and isotope ratios of trace elements, chemical-state of trace element, another feature of chemical element in geological materials, has not been widely used to extract geochemical information. Recently, analytical technique for chemical-state such as fluorescent XAFS has been established, which can be applied to trace elements of ppm order in geological materials. In this paper, oxidation states of Mn, Co, and Ce in various geological materials are reported. In particular, oxidation state of Ce is of great interest, since comparison of Ce(III)/Ce(IV) ratio and Ce anomaly in REE pattern will provide valuable information to investigate diverse geochemical issues such as the origins of geological materials formed in marine environment etc.

Experimental: The XANES spectra of Ce LIII edge, Co K edge, and Mn K edge were obtained by using beam line 12C at KEK-PF. The fluorescence yield from Mn, Co, or Ce was measured using a 19 element SSD. We applied this technique to weathered granite, manganese nodules, siliceous sediments, cherts, and zircons.

Results and Discussion

Granitic rocks: Granitic rocks (fresh: DH3; weathered: ML1) were obtained from Toki area, Gifu, Japan. Chondrite-normalized REE pattern for DH3 shows no Ce anomaly, while a large positive Ce anomaly was found in ML1. This shows that some weathering processes, including redox reactions, have altered the original REE patterns of ML1. From XANES technique, the percentages of Ce(III) were estimated to be 30% and 100% for ML1 and DH3, respectively. For DH3, Ce is exclusively trivalent, which agrees with the fact that the REE pattern of DH3 has no Ce anomaly. For the ML1 having an intense positive Ce anomaly, Ce(III) is still involved in the sample whose percentage is estimated to be ca. 30%. When the Ce(III) abundance is plotted in the REE pattern of ML1, a smooth pattern through the other REE and Ce(III) is obtained. This means that we can obtain the Ce(III) abundance in the sample by interpolating normalized values of La and Pr for the ML1 granite.

Manganese nodules: The manganese nodules employed in this study is of hydrogenetic or diagenetic origin, estimated from their occurrences, mineralogy, and chemistry. When normalized by chondrite or shale, fractions of Ce(III) in these samples were estimated to be 20-100%. However, their XANES spectra show that in all the samples more than 90% of Ce are found to be Ce(IV). This is possibly due to the oxidative sorption of dissolved Ce(III) in the seawater by the surface of manganese oxide. The existence of Ce(IV) in manganese nodules can be explained reasonably by normalizing the REE patterns by seawater, which produce large positive Ce anomalies for REE patterns of all manganese nodules examined in this study.

Cherts: Among the cherts employed in this study, we can find both positive and negative chondrite-normalized Ce anomalies. These anomalies are related to the depositional environments of the cherts. The various magnitudes of the Ce anomalies should be caused by the redox reactions that have affected Ce(IV) concentrations in the marine environment. However, the cherts' XANES spectra reveal that Ce(IV) contributes less than 5% of the total Ce in spite of the various Ce anomalies. If we assume that Ce was incorporated into the cherts as Ce(IV) during their formation, the present results show that diagenetic processes with reductive reaction of Ce(IV) to Ce(III) have occurred in the cherts. This suggests that the bulk REE pattern of the chert is rather conservative and resistant to diagenesis, while the Ce valence is more sensitive to the diagenetic processes.

The combination of REE patterns and the oxidation state of Ce revealed by XANES provides a new perspective on Ce and REE behavior during processes such as weathering and diagenesis. More results on Ce oxidation states in siliceous sediments and zircons will be also reported in the presentation.