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Chemical processes in marine system of various elements in ferromanganese crusts and nodules based on speciation by XAFS

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We have conducted speciation of various elements in ferromanganese crusts and nodules by X-ray absorption spectroscopy such as X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS). In the presentation, we would like to introduce geochemical information we can get through the speciation of various elements in the ferromanganese oxides.

Cerium (Ce) anomaly has been suggested to include redox condition of the depositional environment where the crust or nodule grows. It is true that the degree of Ce anomaly varies from positive to negative for ferromanganese nodules with three main origins: hydrogenetic, diagenetic, and hydrothermal nodules have positive, medium and negative anomalies if their REE patterns are normalized by shale. However, XANES results showed that more than 90% of Ce in any crust and nodule samples are tetravalent, suggesting that Ce is completely oxidized to Ce(IV) when adsorbed on ferromanganese oxides, or in particular by manganese oxides. This oxidation is unique to Ce(III) among all REE, which results in the anomalous behavior of Ce. If we assume that the adsorption of trace elements on manganese oxide is terminated once after certain layer of manganese oxide is closed from the oxide-seawater interface by the growth, the degree of Ce anomaly can be regulated by the growth rate, because enrichment of Ce relative to other REE must increase as adsorption reaction proceeds for longer time. Thus, as has been suggested in the case of Co, the degree of Ce anomaly can be a signature of growth rate ferromanganese oxides.

A series of speciation and adsorption studies for oxyanions on ferromanganese oxides showed that some ions forms outer-sphere complexes (selenate and chromate), but other inner-sphere complexes (selenite and molybdate). When they form inner-sphere complex, most of them take bidentate-binuclear surface complex. It has been suggested that the affinity of oxyanions to ferromanganese oxides (= logKsc; Ksc: surface complex stability constant) is proportional to second dissociation constant of the oxyacids (pKa2). The order of pKa2 is also correlated with the structure of surface complex: oxyanions with lower and higher pKa2 form outer and inner surface complexes, respectively. In this relationship, however, we could not explain low affinity of chromate by pKa2. Similar shortcomings are also found if we employ pKa1 for this discussion. We here found that average of pKa1 and pKa2 (= (pKa1 + pKa2)/2) can explain explicitly the variation of the affinities and surface structures. This is reinforced by the fact that the inner-sphere complex is mainly bidentate formed via two OH groups in the oxyanions, which must be related to the pKa of the two proton dissociation reactions. Systematic understanding of the affinities by (pKa1 + pKa2)/2 will be useful to predict the solid-water distributions of these ions in ocean.

More studies on the speciation of other elements such as zirconium and implications obtained will be given in the presentation.