

Concentration mechanisms of trace elements on ferromanganese nodule : Arsenic(As) and Antimony(Sb)

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Ferromanganese nodules and crusts (marine manganese deposits) are typical chemical deposition at sea floor, and has been focused as metal resource in the world. Marine manganese deposit was known to grow after adsorption and formation of surface complex with trace or useful elements. Thus, marine manganese deposit was considered as a key to reveal geochemical environment since they retain information of the environment when they have formed. Genetic process of marine manganese deposit can be divided into three origins, which are hydrogenetic, diagenetic, and hydrothermal origins.

In this study, we focused on the mechanism of enrichment of arsenic (As) and antimony (Sb) of the trace elements in marine manganese deposit. Antimony has been used as the products such as flame retardant agents of textiles and plastic products, catalysts, and pigments. However, Sb has very high supply risk all over the world (British Geological Survey, 2012). Arsenic and Sb belong to same group in the periodic table. However, it is possible that chemical processes of their incorporation into marine manganese deposit are different, because coordination environment of As and Sb can be very different: As prefers tetrahedral symmetry, while Sb octahedral. Thus, it is possible to clarify the enrichment mechanism of trace elements to the marine manganese deposits based on the the coordination number and surface complex structure for Sb and As.

Therefore, we studied distributions of As and Sb to natural marine manganese deposits and also to synthetic iron hydroxides and manganese oxides in laboratory experiments via adsorption or coprecipitation process. Moreover, extraction rates of As and Sb by phosphoric acid after their adsorption/coprecipitation into iron hydroxides or manganese oxides. Similar experiments were also conducted for natural Fe-Mn nodules. The concentration of As and Sb in natural marine manganese deposits were also measured by ICP-MS after acid decomposition.

From these results, the macroscopic distribution of As and Sb on iron hydroxides and manganese oxides were determined. In addition, X-ray absorption fine structure (XAFS) of these samples were measured at SPring-8 to clarify the chemical species of As and Sb on the surface of the marine manganese deposit. Furthermore, the adsorption forms of As and Sb to marine manganese deposit were also estimated by quantum chemical calculation. From these results, we discuss the enrichment mechanism of As and Sb into marine manganese deposits.

Keywords: marine manganese deposits, antimony, arsenic, concentration mechanism, X-ray absorption fine structure