

## Enrichment mechanisms of tellurium in ferromanganese crusts

Toshiki Sugiyama<sup>1</sup>, SAKAGUCHI, Aya<sup>1\*</sup>, KASHIWABARA, Teruhiko<sup>2</sup>, USUI, Akira<sup>3</sup>, TAKAHASHI, Yoshio<sup>1</sup>

<sup>1</sup>Department of Earth and Planetary Systems Science, Hiroshima University, <sup>2</sup>Japan Agency for Marine-Earth Science and Technology, <sup>3</sup>Department of Natural Environmental Science, Faculty of Science, Kochi University

Marine ferromanganese crusts (FMCs) consist of iron (Fe) hydroxides and manganese (Mn) oxides with various minor and trace elements. Especially for tellurium (Te), which is recognized as one of the rare metals, it has been reported that this element is concentrated about 105 times in FMCs compared with earth's crust, and the host phase might be Fe (oxy)hydroxide (Hein et al., 2003). Actually, in our previous study, the high concentration of Te in very surface layers of FMCs was found from the top to halfway down of a seamount in the Pacific Ocean. However, the concentration of Te in surface layers through the seamount showed good correlation with that of Mn instead of Fe. In this study, we attempted to clarify the enrichment mechanism of Te in FMCs with some methods including X-ray absorption fine structure (XAFS) technique for synthesised/natural samples.

Seventeen FMC samples were collected from the Takuyo-Daigo seamount, from 950 m (summit) to 3000 m in water depth, with hyper-dolphin (remotely operated vehicle) equipped with live video camera and manipulators. The growth rates of all FMC samples were estimated to be about 3 mm/Ma. Very surface layer (less than 1 mm) of all FMC was analyzed with XRD and XAFS to confirm the mineral composition and speciation of Te. Furthermore, to serve as an aid to clarify the adsorption mechanism of Te on FMCs, distribution coefficients (Kd) and oxidation states were determined through the adsorption experiments of Te(IV) and Te(VI) on ferrihydrite and delta-MnO<sub>2</sub>. In all the experiments, pH and ionic strength were adjusted to pH 7.5 and 0.7 M, respectively. The oxidation state of Te in water phase was determined with HPLC-ICP-MS. As for the analysis of oxidation and adsorption states on the solid phase, XAFS was employed.

The major mineral composition of Fe and Mn had no significant variation through the water depth of Takuyo-Daigo seamount. The oxidation state of Te in all samples showed hexavalent, and there was no significant difference of adsorption state independent of the DO, salinity and temperature in water. It has been reported that Te exists as tetravalent and hexavalent in sea water of the Pacific Ocean (Lee and Edmond, 1985). Thus, it can be said that the Te in sea water is oxidised and incorporated into FMCs. As a result of the adsorption experiments in laboratory, the Kd of Te on ferrihydrite was larger than that of delta-MnO<sub>2</sub>, and Te(IV) was adsorbed to a larger degree than Te(VI) on both minerals (Fig.1 a). The adsorption experiments of Te(IV) on delta-MnO<sub>2</sub> showed that the solid phase has only hexavalent Te (Fig.1 b), although the water phase has both tetra and hexavalent species of Te. Te(IV) on ferrihydrite was not oxidized to Te(VI). From these results, it can be suggested that Te(IV) was oxidized by delta-MnO<sub>2</sub> and would be adsorbed onto ferrihydrite. Actually, the results of double-cell adsorption experiments support this hypothesis. The detail of our results and discussion will be given in the presentation.

Keywords: ferromanganese crusts, tellurium, XAFS

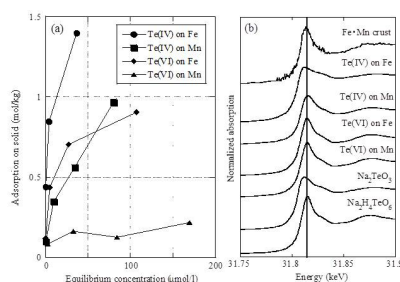


Fig.1 (a) The adsorption isotherm for Te on synthesized ferrihydrite and  $\delta$ -MnO<sub>2</sub>, and (b) the chemical species of Te in adsorbed oxides and natural ferromanganese crust