Water column profile around Takuyo-Daigo Seamount and monitoring of seawater chemistry in the excavating test of cobalt-rich ferromanganese crusts

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Future development of cobalt-rich ferromanganese crusts requires proper environmental impact assessment and monitoring of the plume of suspended particles on seawater chemistry and ecological processes. Such assessment requires an environmental baseline obtained by measuring parameters including alkalinity, dissolved oxygen, total organic carbon, nutrients (PO_4, NO_3, NO_2, and SiO_2), and metals (Cu, Zn, Cd, Pb, and Hg). However, the concentration of these metals in the pelagic ocean is extremely low (ng/L level), and the effects of interference due to salinity are significant, making difficult to measure even with highly sensitive instruments such as ICP-MS. Although these metals can be concentrated and measured by solid-phase extraction, such methods are not yet generally used. These metals are not a sensitive indicator for monitoring of dissolved element because they show little elution from manganese oxides in oxidative seawater.
We conducted an environmental baseline survey in 2018 around Takuyo-Daigo Seamount, with CTD observations and analysis of water samples collected at the flat top (900 m water depth) and base (5,300 m water depth). The pH fell from 8.2 at the surface to a minimum of 7.5 near the seamount top. Dissolved oxygen also decreased downward from the surface, reaching a minimum near the seamount top, then gradually increased until the base depth. In contrast, nutrient concentrations increased with depth from the surface layer (nmol/L level) to the near-peak depth. The levels of Cr, Mn, Fe, Ni, Cu, Zn, and Pb were below detection limits at all depths, whereas reasonable results were obtained for Li, B, Mg, Ca, V, As, Rb, Sr, Mo, Cd, Ba, and U. Cadmium and Ba showed a nutrient-type distribution with decreasing concentrations in the surface layer; other elements exhibited a conservative-type distribution with constant concentrations at depth.
To investigate metal leaching from ferromanganese crusts, crust samples collected from Takuyo-Daigo Seamount were subjected to shaking tests with seawater (solid/liquid ratio of 1:100), and the elements that showed clear elution were Mo, Cd, and Ba. As for nutrients, significant elution of PO_4 and SiO_2 was observed. We propose that Mo and Ba should additionally be included in the environmental baseline. Molybdenum shows a conservative distribution, and so reactions of seawater with crusts can be readily detected regardless of water depth. Barium, which exhibits a nutrient-type distribution, could be a sensitive indicator in the surface water. Another important point is the pH-regulating effect of manganese oxides. Our previous study showed that addition of manganese nodule to artificial seawater with pH regulated by CO_2 causes a pH decrease when the initial pH is high and an increase when the initial pH is low. The charge zero point was estimated to be around pH 7.4 (Wang et al., 2018). In the seawater shaking tests, the initial pH of 8.0 was found to decrease to 7.5; therefore, pH is possibly important monitoring parameter in surface water with high pH, although the effect would be minimal in mid-deep water with low pH.
An excavating test of cobalt-rich ferromanganese crusts was conducted in 2020 at Takuyo-Daigo Seamount. We analyzed water samples collected by a ROV and excavator tank water during the test, as

well as ROV water samples before and after the test. Although the amount of suspended solids in the ROV water samples increased during the test, no changes in nutrient and metal concentrations were observed, and we concluded that the chemical composition of seawater in its dissolved state was not affected. In contrast, there was a slight increase in the concentration of Mo in the excavator tank water, suggesting an influence of leaching from crust fragments. This is consistent with the fact that the suspended solids in the ROV sampling water during the test were 0.04 to 85 mg/L, whereas the concentrations in the excavator tank water were as high as 12 to 313 mg/L.

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