Micro X-ray fluorescence mapping to charactarize layers of Fe–Mn nodules in the western North Pacific

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A dense field of hydrogenous ferromanganese nodules was discovered in the region southeast of Minamitorishima (Marcus) Island, the western North Pacific [1, 2]. Previous study [1] defined two fundamental features on structure and geochemistry of nodules, as follows. The large nodules generally consist of three concentric layers: the outermost mottled (sediment-filled) layer L0; the massive black layer L1; and the innermost porous layer L2. Elements including Fe, Ti, and Co are concentrated in the nodule rim rather than the center. In contrast, Mn, Al, P, Ca, Ni, and Zn are concentrated in the center, and decrease toward the rim.

To further investigate the relationship between structure of oxide layers and features on compositions of Si, Al, P, Ca, K, Mn, Fe, Ti, Ni, Cu, and Y, we conducted mapping analysis for vertically half-cut and polished surface of nodules including nuclei by a microfocus X-ray fluorescence analytical microscope (XGT-7000; HORIBA) at Kyoto University. Analysis was conducted in vacuo, by an energy-dispersive spectrometer, and at an accelerating voltage of 50 kV, 100 μm beam, and intervals of 90-194 μm.

We identified that L2 is further sub-divided into three layers, which correspond to layers obtained by X-ray CT [3]. The most inner part of L2 (around nuclei) is characterized by high intensity of Ti and Fe. In contrast, outer part of L2 is characterized by higher intensity of Mn than that of the inner part. Many spots of high intensity of P, Ca, and Y, indicating particles of calcium phosphate including highly amount of Y (and probably rare-earth elements), are observed in the entire area of L2. L1 is clearly characterized by low Si. Furthermore, we observed thin layers showing high intensity of Cu and Ni at the sediment-filled boundaries between L1 and L2, and L1 and L0. Existence of such thin layers suggests that nodules in southeast of Minamitorishima Island were covered by pelagic sediment at the intervals before formation of L1 and L0.

[1] Machida et al. (2016) *Geochem. J.* **50**, 539-555.
[2] JAMSTEC press release, August 26, 2016.
[3] Shimomura et al. (2018) *Goldschmidt Conference 2018*.