Chemostratigraphy of ferromanganese crusts based on Independent Component Analysis

*Keishiro Azami[1], Qing Chang[2], Jun-Ichi Kimura[2], Kazutaka Yasukawa[1,3], Kentaro Nakamura[1], Yasuhiro Kato[1,3]

1. Department of System Innovation, Graduate School of Engineering, The University of Tokyo, 2. Japan Agency for Marine-Earth Science and Technology, 3. Chiba Institute of Technology

Ferromanganese (Fe-Mn) crusts are chemical sedimentary rocks that occur in submarine environment and are composed mainly of Fe-Mn (oxyhydr)oxides[1]. Due to a slow growth rate (1-10 mm/Myr), Fe-Mn crusts are expected to record long-term changes in ocean environments. Therefore, many studies have tried to discuss paleoceanographic environments from chemostratigraphy of Fe-Mn crusts. However, previous approaches by using bulk chemical analysis and EPMA have been severely limited in a spatial (and thus temporal) resolution and number of measurable elements, respectively. In addition, the criteria for sectioning stratigraphy based on chemical composition and growth structure proposed in previous studies are not objective sufficiently.

Here, we show the elemental maps of Fe-Mn crusts analyzed by using femto-second laser ablation (LA)-ICP-MS (iCAP Q). The laser beam was approximately 30 μm in diameter and 10 Hz repetition rate which scanned over sample surface along the growth direction at 70 μm/s, and space between adjacent scan lines was 80 μm. Concentrations of major and trace elements were calculated from standard materials of JMn-1 and Nod-P-1 (issued by GSJ and USGS, respectively) and normalized into 100% of major element oxides. The LA-ICP-MS analysis enables us to discuss the chemostratigraphy of Fe-Mn crusts with a time resolution approximately two orders of magnitude higher than previous works.

Based on the elemental mapping images, distribution patterns of almost all the elements are classified into three types: (1) Mn-oxide type showing the clear column structures, (2) Fe-oxyhydroxide type enriched in the space between the columns and (3) debris type showing spotty high contents between the columns. Several elements (e.g. Ti, Ce, Th) show the compositional changes irrespective of the boundaries of the growth structure, indicating that the sectioning of Fe-Mn crusts' stratigraphy merely based on the growth structure is insufficient. In addition, because the compositional changes are sometimes observed as the layer of submillimeter-scale, it would not be detected by the previous low-resolution bulk chemical analysis.

We also performed independent component analysis (ICA) on the elemental mapping data to section the stratigraphy of Fe-Mn crusts objectively and systematically. Based on the influence of the extracted ICs to each data point (IC scores), we systematically sectioned the chemostratigraphy of Fe-Mn crusts for the first time. In addition, we interpreted the geological meanings of each IC based on the geochemical features of the ICs (IC loadings). The results show that the boundaries of the chemostratigraphy generally coincide with that of the growth structure, but some of the layers showing the same structural character were divided into multiple layers based on geochemical features. Systematic sectioning based on multi-elemental features by using ICA will be a powerful tool to reconstruct paleoceanographic changes from Fe-Mn crusts.

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