# A rapid and precise determination of rare metals in various types of deep-sea mineral resources by ICP-MS

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The rare metals are key materials for high-tech industries such as automotive, aerospace, and electronics. Rare metal resources, however, are extremely unevenly distributed in the world, resulting in an unstable supply of rare metals. Recently, the deep-sea mineral resources have received renewed attention as future metal resources. Toward the exploitation of deep-sea mineral resources, it is necessary to accumulate comprehensive data about rare metal compositions of deep-sea minerals. In this study, therefore, a simple method for precise simultaneous determination was developed using ICP-MS in order to assess the distribution and potential of rare metals in deep-sea mineral resources.

ICP-MS has been widely used for determination of trace metal concentrations in geological samples because of its great sensitivity, wide dynamic range, and high sample throughput. In this study, this analytical technique is used for determination of rare metals in high matrix ore samples. A combination of an improved low temperature HF-$HNO_3$-$HClO_4$ digestion followed by $HNO_3$-HCl-HF treatment and a systematic interference correction is developed for simultaneous determination of 61 elements in ore samples. The method developed in this study offers three advantages: (1) suppression of evaporation loss of volatile elements (e.g., Ge, Se, Sb, Te, Re, Au) by low temperature (below 90 $^{o}$C) digestion, (2) high sample throughput by complete simultaneous determination of 61 elements without any time-consuming pre-concentration and/or separation techniques, and (3) precise and accurate determination by applying an appropriate method for interference corrections.

The developed method is applied to four types of deep-sea mineral resources: ferromanganese (Fe-Mn) nodules, Fe-Mn crusts, mid-ocean ridge type hydrothermal sulfide deposits, and arc/back-arc type hydrothermal sulfide deposits. In Fe-Mn nodules/crusts, most metals are enriched significantly compared to their crustal abundances. Among the Fe-Mn crust samples, the concentrations of some rare metals (such as V, Rh, Te, W, Ir, and Pt) decrease with increasing water depth, and no local differences are recognizable in ore samples. Compared to Fe-Mn crusts, the Fe-Mn nodules are slightly depleted in V, Co, As, Y, REE and W and strongly depleted in Rh, Sn, Te, Pt, Pb and Bi. On the other hand, the nodules are enriched in some metals including Mn, Ni, Cu, Zn, Cd and Tl, due to diagenetic remobilization from ambient sediments.

The chemical composition of sulfide ores shows the conspicuous enrichment of specific metals such as Cu, Zn As, Se, Rh, Pd, Ad, Cd, Sb, Te, Re, Ir, Au, Pb, and Bi, whereas noticeable depletion of other elements. The metals in seafloor hydrothermal deposits are derived from leaching of the host rocks and magmatic fluids. Only some metals (Cu, Te, Se, In and Mo) are enriched in mid-ocean ridge basalt-hosted sulfide ores. On the other hand, variety of metals, such as Pb, Sb, As, Tl, Bi, Cd, Au, Zn, Ag and Sn, are enriched in hydrothermal deposits in back-arc basin, reflecting acidic volcanic host rocks and/or Pb-rich sedimentary rocks. Interestingly, it is found that the ultramafic rock-hosted ores from mid-ocean ridge hydrothermal field contains much higher Au content than normal MORB-hosted ores, although no other metals show significant differences.