Determination of highly siderophile element concentrations and ¹⁸⁷Os/¹⁸⁸Os ratio for ferromanganese nodule reference materials

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Highly siderophile element concentrations (HSEs: Re, Au, Ir, Os, Ru, Rh, Pt and Pd) and the Re-Os isotope systems are recognized as important tracers in ferromanganese (Fe-Mn) nodule and crust, because their stratigraphic layers record the history of regional and global paleo-oceanic conditions [e.g. 1, 2]. In general, HSEs determination requires large quantities (0.5-2 g) of sample powders [e.g. 3]. However, geochemical studies on the Fe-Mn nodules and crusts demand more restricted and detailed sampling [e.g. 4]. A renewed analytical protocol that is suitable for small quantities for milligram order of sample powder is a prerequisite to obtain the comprehensive geochemical features of their major, trace elements and isotopic compositions. In addition, there are few standard materials of Fe-Mn nodules and crusts with certified or reference values for HSEs and ¹⁸⁷Os/¹⁸⁸Os ratio.

Here, in order to evaluate a homogeneity of the HSEs (Re, Ir, Os, Ru, Pt and Pd) and ¹⁸⁷Os/¹⁸⁸Os ratio in reference Fe-Mn nodules (JMn-1, Nod-A-1 and Nod-P-1), we carried out replicate analyses for their reference powders (ca. 100 mg) by using isotope dilution mass spectrometery (ID-MS) applying high-temprerature inverse aqua regia digestion in Carius tubes [3]. Relatively large variations for the HSE abundances and ¹⁸⁷Os/¹⁸⁸Os ratios observed in multiple analyses of JMn-1 and Nod-P-1 likely reflect sample powder heterogeneities at the 100 mg level. By contrast, triplicate analyses of Nod-A-1 show excellent reproducibilities (0.2% for ¹⁸⁷Os/¹⁸⁸Os, 0.5% Os, 2.4% Ir, 0.2% Ru, 0.8% Pt, 1.8% Pd and 9.0% Re, RSDs). This observation indicates that Nod-A-1 can be useful candidate reference material to obtain certified values with small mesurement uncertainties for the Fe-Mn hydroxideoxide samples.

[1] Hein et al. (2003) *Geochim. Cosmochim. Acta* **67**, 1117-1127. [2] Klemm et al. (2005) *Earth Planet. Sci. Lett.* **238**, 42-48. [3] Ishikawa et al. (2014). *Chem. Geol.* **384**, 27-46. [4] Usui et al. (2007) *Island Arc* **16**, 420-430.