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Using Nickel as a New Isotope Tracer of Oceanic Processes

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The study of "non-traditional" stable isotopes (e.g., Fe, Mo, Zn, Cr, and Cu) has blossomed in the past decade as analytical techniques have improved, particularly with the development of high-precision MC-ICPMS. The application of Ni isotopes, however, remains largely unexplored. Because Ni has a complex chemistry, both in geological and biological systems and Ni isotopes encompass a wide mass range ($\sim$10%), the potential for Ni isotope fractionation is significant. In particular, recent Ni isotope analysis (Cameron et al., 2009, PNAS v106, 10944–10948) have shown that methanogens fractionate Ni isotopes toward lighter isotopes which contrasts with the apparent Ni-isotope homogeneity in rocks. However, the variation of Ni isotopes in altered volcanic rock, hydrogeneous marine sediments and ore deposits remains unknown.

Here, we present chemical separation and mass spectrometric procedures necessary for measuring natural mass-dependent variations of Ni isotopes in terrestrial silicates, ferromanganese crusts as well as sedimentary, magmatic and hydrothermal sulfides. Ni isotope ratios are determined using a high-resolution multicollector ICP-MS *Neptune* (Thermo Fisher Scientific Inc.) at WHOI and IFREMER. Instrumental mass bias is corrected using Cu NIST *SRM* 976 as internal standard and all analyses are reported in delta notation relative to Ni NIST *SRM* 986. Internal reproducibility of $\delta^{62/58}$Ni, $\delta^{60/58}$Ni, and $\delta^{62/60}$Ni averages $\pm$0.07‰ $\pm$0.04‰ and $\pm$0.04‰ respectively (2σ). Ni from silicate and oxide matrices is purified using a combination of anion exchange chemistry and DMG complexation using Eichrom Technologies Ni Resin while Ni from sulfides is purified using standard procedures for anion and cation exchange chromatography. Although incomplete yield has prevented measurement of Ni isotopes in silicates without using the double-spike method, we collected preliminary data for modern hydrothermal sulfides, pyrite from Archean black shales and Ni-ore sulfides. We observed a preliminary range of $\sim$2‰ variation for $\delta^{62/58}$Ni. We also found significant inorganic Ni-isotope fractionation onto cation-exchange chromatography resins indicating that the initial eluent is isotopically light (e.g. -0.4‰ for 45% yield). Although the mechanisms of Ni-isotope fractionation remains unclear, our preliminary data suggest significant abiotic Ni isotope fractionation that is comparable to those seen during Ni uptake by methanogens. Hence, the use Ni isotopes as direct biomarker for methanogens should be used with caution.