Nickel isotope variations in natural systems and implications for their use as a geochemical tracer
Bleuenn Gueguen\textsuperscript{1,2}, Olivier Rouxel\textsuperscript{1,2}, Emmanuel Ponzevera\textsuperscript{2}, Jeffry Sorensen\textsuperscript{3}, Brandy Toner\textsuperscript{4}, Andrey Bekker\textsuperscript{4}, and Yves Fouquet\textsuperscript{7}
\textsuperscript{1}Université de Brest, IUEM, UMR 6538, BP 80 F- 29280 Plouzané, France.
\textsuperscript{2}IFREMER, Département Géosciences Marines, 29280 Plouzané, France.
\textsuperscript{3}University of Minnesota, Department of Soil Water & Climate, St Paul, MN 55108 USA.
\textsuperscript{4}University of Manitoba, Department of Geological Sciences, Winnipeg, MB R3T 2N2, Canada.

Due to the importance of Ni in biological processes and its ubiquitous distribution in Earth geochemical reservoirs such as ore deposits, Ni isotopes are now receiving a growing interest as a potential biogeochemical tracer [1], [2]. Ni is particularly interesting for oceanographic studies such as the investigation of oceanic metalliferous deposits (rocks that precipitated in deep-sea oceans) in order to shed light on their metals enrichments sources. However, it is crucial to know the composition of Earth’s major reservoirs, including mantle-derived rocks and marine sediments, which to date remains poorly known.

In this study we report Ni isotopic composition of a range of key terrestrial rocks comprising geological reference materials of mantle-derived and sedimentary rocks as well as selected samples of Ni-rich ore deposits, iron meteorites and oceanic metalliferous deposits. Samples were measured by MC-ICP-MS (Neptune) and data were subsequently corrected for instrumental mass bias using the double-spike correction method (i.e. mixed \textsuperscript{61}Ni and \textsuperscript{62}Ni isotopes). Results are reported according to \( \delta^{60/58}\text{Ni} \).

We determined the Bulk Silicate Earth (BSE) at 0.05 \( \pm 0.05\% \) (based on silicate rocks analyses), whereas iron meteorites are enriched in heavy isotopes by 0.30-0.35\% consistent with the available literature values [1], [3]. In contrast negative values ranging from -0.67\% to -0.35\% have been measured in magmatic Ni-rich sulfides (pentlandite). Strikingly, oceanic metalliferous deposits (deep-sea Mn-nodules and various Fe-Mn crusts) show systematically positive values ranging from 0.30 to 1.80 \( \pm 0.04\% \). As the main sources of Ni to the oceans are continental erosion and atmospheric inputs and its oceanic residence time is \( \sim 10,000 \) years, we would expect the BSE isotopic composition to govern Ni isotope composition in ocean waters. Experimental results of Ni isotope fractionation during Ni sorption onto Fe and Mn oxyhydroxides (i.e. ferrihydrite, goethite and birnessite) reveal a maximum fractionation factor of -1.00 \( \pm 0.03\% \). Natural isotopic variations of crusts cannot be simply explained by adsorption processes and indicate that modern seawater is probably highly enriched in heavy isotopes. These variations could be partly due to local ocean sources with different Ni isotope composition (including hydrogenous and diagenetic sources) or to fractionations between chemical species [2]. Moreover, since Ni has a nutrient-type profile in oceans (albeit non biolimiting) and that negative fractionations were measured in methanogens [1], interactions with the biosphere might play a major role in the regulation of Ni isotope composition in seawater.

Despite small mass difference between Ni isotopes, our results prove that measurable variations in Ni isotope fractionations occur under both low and high temperature conditions and that Ni is a promising tool for investigating metals cycling in oceans.
