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Nickel isotope variations in natural systems and implications for their use as a geochemical tracer

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Due to the importance of nickel in biological processes and its ubiquitous distribution in Earth geochemical reservoirs such as ore deposits, nickel isotopes are now receiving a growing interest as a potential biogeochemical tracer [1,2,3]. Although initial studies have demonstrated the utility of Ni isotopes as a tracer for a range of cosmochemical, geochemical and microbiological processes, Ni isotope composition of Earth's major reservoirs, including mantle-derived rocks and marine sediments remains poorly known. In addition, given the novelty of the investigation field, detailed procedure of analytical techniques for high-precision Ni isotope analysis is currently needed to further develop Ni isotopes as a robust geochemical tracer.

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 nickel-rich ore deposits [4,5] and iron meteorites. Samples were measured by MC-ICP-MS (Neptune) in a medium resolution mode and data were subsequently corrected for instrumental mass bias using the double-spike correction method (i.e. mixed ^{61}Ni and ^{62}Ni isotopes). Ni isotopic ratios are reported relative to the nickel NIST SRM 986 standard according to the conventional delta notation used for stable isotopes, i.e. $\delta^{60/58}$Ni, and 2σ standard deviation determined by repeated analyses of NIST SRM 986 is 0.04‰Ṡilicate rocks display a small range of values between 0.00 and 0.15‰ but negative values ranging from -0.67‰ to -0.35‰ have been measured in magmatic nickel-rich sulfides (pentlandite). In contrast, iron meteorites with $\delta^{60/58}$Ni values of 0.30-0.35‰ are enriched in heavy isotopes compared with terrestrial rocks, which is consistent with the available literature values [1,3,6].

USGS geological reference materials of deep-sea manganese nodules show positive values, but marked distinction appears between the one from the Atlantic Ocean with a $\delta^{60/58}$Ni value of 1.06‰ and the one from the Pacific Ocean with a value of 0.38‰Ȧlthough Ni isotope composition of seawater is still unknown, these preliminary data suggest that hydrogeneous record of Ni isotopes in the oceans is a promising field of investigation. Ni isotope variations in Fe-Mn nodules and crusts could be due to either ocean sources with different Ni isotope composition (including hydrogenous and diagenetic sources) or different mechanisms involved during precipitation of Fe-Mn nodules and crusts. Experimental results of Ni isotope fractionation during Ni sorption onto Fe and Mn oxyhydroxides such as ferrihydrite, goethite and birnessite will be presented to provide a new insight on the potential use of Ni isotopes as a useful paleo-oceanographic proxy. Despite small mass difference between Ni isotopes, our results indicate that measurable Ni isotope fractionations occur under both low and high temperature conditions with more than 2‰ range for the analyzed set of samples and that distinct Ni isotope compositions are typical for different rocks, thus corroborating the use of nickel isotopes as a geochemical tracer. In conclusion, the observed natural variability in Ni isotopes undermines their use as a unique signature of ancient metabolism such as methanogenesis as was earlier proposed [1].

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