

# Report for the Joint Use/Research of the Institute for Planetary Materials, Okayama University

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**Category:** International Joint Research

**Name of the research project:** Ni isotope fractionation during Fe-oxide formation: implications for using Ni isotopes as a biomarker

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**Research report:**

*This project is described in great detail in the 2019 End Report, and a brief summary of the new results from 2020 is given here. For more in-depth information please refer to the 2019 report.*

## 1. Research purpose

The isotopic composition of nickel (Ni) has great potential as a biogeochemical tracer in natural samples, as it is a transition metal involved in the major marine redox cycles, as well as being a vital micronutrient used by both marine and terrestrial life. Nickel isotopes are therefore being developed as a geochemical fingerprint for both biological and abiotic processes in both terrestrial and extraterrestrial environments. The ongoing project “Ni isotope fractionation during Fe-oxide formation: implications for using Ni isotopes as a biomarker” aims at constraining fundamental isotopic fractionation mechanisms and pathways during the abiotic formation of ferrihydrite, one of the most ubiquitous Fe-oxides on Earth. Previous experimental studies have shown limited Ni isotopic fractionation during incorporation of Ni into, or adsorption onto, the ferrihydrite crystal structure (e.g. Wasylenki et al., 2015; Wang and Wasylenki, 2017), with ferrihydrite solids being ~0.3‰ lighter than the experimental fluids. Fractionation caused by methanogenic archaea (the most primitive form of life more likely to be present in extraterrestrial environments), on the other hand, fractionate Ni isotopes by -0.44 to -1.5‰ (Cameron et al., 2009), suggesting that Ni isotopes

have a clear “biological fingerprint”. However, our results obtained thus far show that abiotic fractionation of Ni isotopes start overlapping with the suggested biological fingerprint when Ni is adsorbed to ferrihydrite in solutions containing dissolved silicon (Si). This has implications for the use of Ni as a biomarker in both extraterrestrial rocks, as the search for extra-terrestrial life has found Earth-analogues in Si-rich hydrothermal sinter deposits (Ruff and Farmer, 2016), as well as in ancient terrestrial rocks as much of the work on the earliest life on Earth has involved structures found in silica rich rocks (e.g. Djokic et al., 2017).

## **2. Conducted research**

Ferrihydrite was synthesized through a series of bench-top experiments in 2019 (yielding 125 unique experimental conditions), with focus on Ni incorporation mechanism (adsorption and/or incorporation), varying Ni concentration, pH, equilibration time and varying Si concentration (as Si is hypothesized to act as an inhibitor during Ni incorporation). The precipitated ferrihydrite and experimental fluids were subsequently analyzed for Ni elemental partitioning behavior and a fraction of the samples could be analyzed for their Ni isotopic composition. The results from the project has great potential to increase our understanding of the Ni isotopic system and help determine the capabilities of Ni isotopes as a geochemical tracer and biomarker. However, due to the global travel restrictions imposed by the COVID-19 pandemic several samples remain to be analyzed for their isotopic composition. During 2020 a visit by the primary applicant was not possible, but analyzes were continued by IPM graduate student Dilan Ratnayake and professor Ryoji Tanaka. A further 21 solid ferrihydrite samples were analyzed for their Ni isotopic composition, almost doubling the solid data set. These results confirm the initial results obtained in 2019, and highlight the increased fractionation observed during adsorption of Ni onto ferrihydrite when Si is present (Figure 1). Further, new data showing the dependency of pH on Ni sorption mechanism and associated isotopic fractionation suggests that previous theories of greatly differing fractionation factors between adsorbed and incorporated Ni is wrong or may be over-simplified.

## **3. Research outcomes**

The data obtained in 2020 support the hypothesis that was developed following the 2019 results; the addition of Si greatly changes the Ni isotopic fractionation factor during adsorption of Ni. However, during coprecipitation, Si does not affect the fractionation. Although the exact fractionation factors cannot be calculated until data is obtained from the fluid samples, the compositions of the solid ferrihydrite samples suggest that Ni adsorbed to ferrihydrite with 2.2mM Si present in the experimental fluid have up to twice as large fractionation as when no Si is present or during coprecipitation (Figure 1). Our coprecipitation experiments show similarly low Ni isotopic fractionations of  $\sim -0.3\text{‰}$  as found in previous experimental studies (e.g. Wasylenki et al., 2015), including samples with higher Si concentrations, whereas the adsorbed Ni with higher Si content

show fractionations of  $<-0.8\%$ . These differences provide clues to fractionation mechanisms, and supports the hypothesis that Si outcompetes Ni for adsorption sites, altering the fractionation factor. However, the full dataset is needed in order to properly and accurately model the experiments.

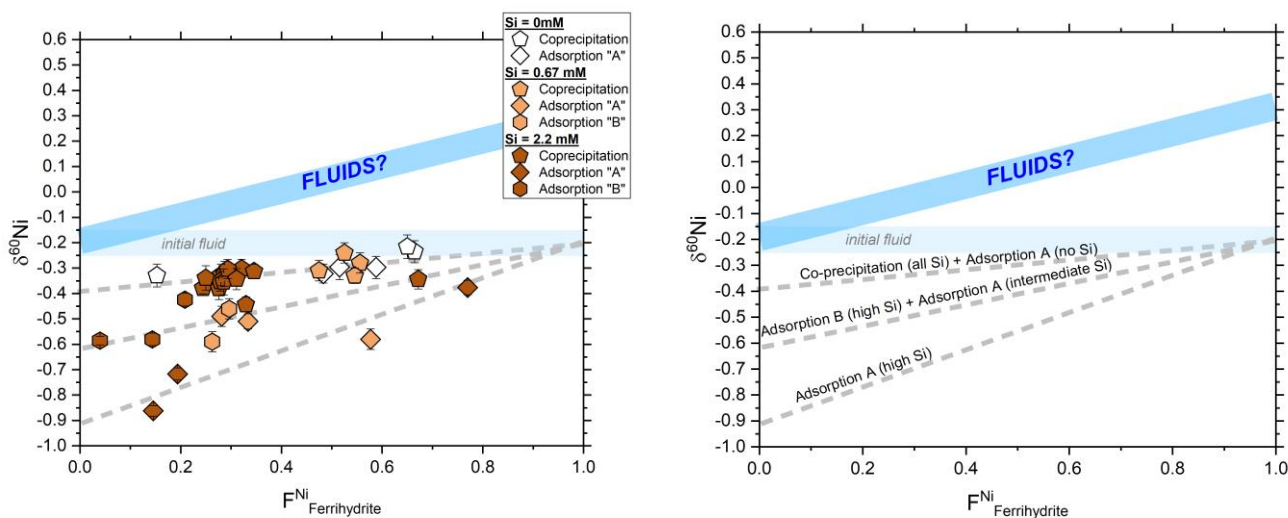


Figure 1. a) The Ni isotopic composition of solid ferrihydrite samples against the fraction of Ni sorbed to ferrihydrite solids ( $F^{\text{Ni}}_{\text{Ferrihydrite}}$ ), and b) schematic showing the separate trends of the experimental conditions. Coprecipitated samples have lower isotopic fractionation regardless of Si content, whereas the fractionation factor progressively increases for adsorption experiments as more Si is added. Samples in beige color were analyzed during 2020.

Twelve solid samples from “Experiment 4” (pH dependency experiment - please refer to 2019 report for experiment details) were analyzed during 2020 (Figure 2). Experiment 4 tests the dependency of pH on Ni incorporation mechanism, and hence the control of incorporation mechanism of isotopic fractionation. The experiment was designed to test and separate the effects of Ni incorporation vs surface adsorption, as more Ni is adsorbed at high pH ( $<7$ ), increasing the proportion of structurally incorporated Ni at lower pH ranges (Wang and Wasylenki, 2017). A previous study showed that the Ni isotopic fractionation associated with incorporation of Ni was distinctly different from that of adsorption, with the fractionation factor even being positive, generating a “U-shaped” trend between the Ni isotopic composition and pH, and the fraction of Ni being sorbed to the ferrihydrite,  $F^{\text{Ni}}_{\text{Ferrihydrite}}$  (Wang and Wasylenki, 2017). However, these experiments were conducted as coprecipitation experiments only, and a three-endmember mixing model (fluid, adsorbed and incorporated Ni) was necessarily invoked to describe the trend. Our extended experiments, however, which included both coprecipitation as well as pure adsorption show that the observed trends persists regardless of incorporation mechanism (Figure 2). Although the adsorbed Ni seem to be associated with a more negative fractionation factor at mid-range pH values, the trends cannot be explained by a simple three-endmember mixing scenario. It is possible instead that the observed trends are caused by reaction kinetics which overwrite the effects of

incorporation mechanism. The working hypothesis (in lieu of the rest of the data that needs to be collected) is that reaction kinetics differ between early stages of adsorption/incorporation, where solids take on the composition of the initial experimental fluid, and later stages when ferrihydrite crystals become more saturated and isotopic exchange reactions approach equilibrium. At the latest stages when 90-100% of Ni is sorbed to the solid it will naturally have the same composition as the initial experimental solution. The remaining experiments to be analyzed were conducted with varying Si concentrations, and these have great potential to decipher the effect of Si at different equilibrium conditions.

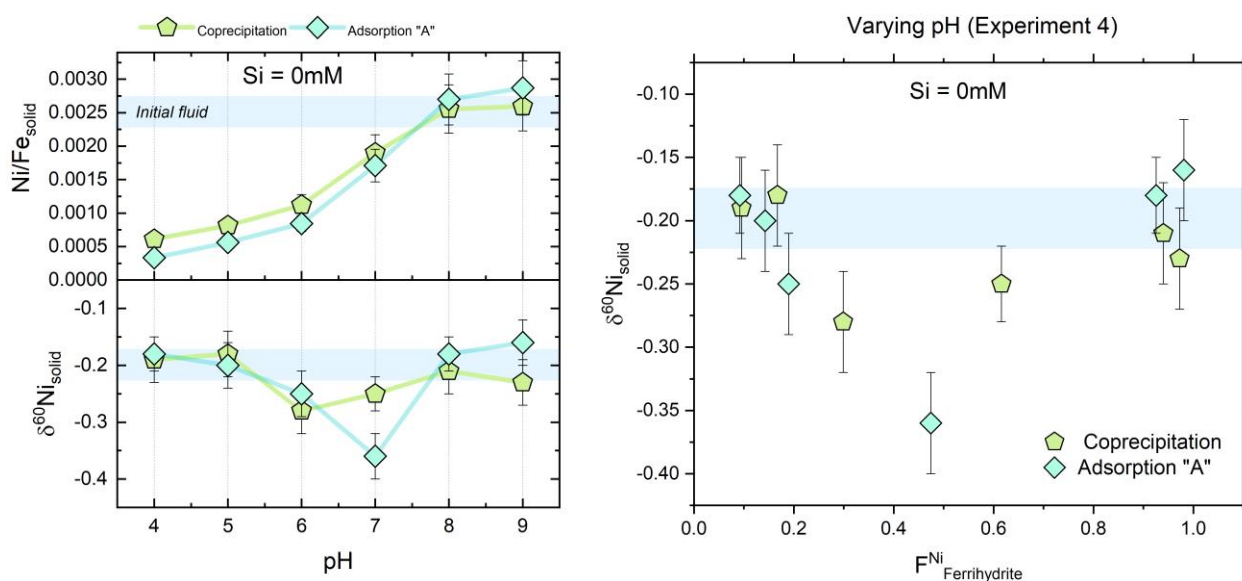


Figure 2. Results from “Experiment 4” where pH was varied between 4 and 9 for a) Ni/Fe molar ratios, b) Ni isotopic composition and c) Ni isotopic composition against fraction Ni sorbed to the ferrihydrite solids ( $F^{Ni}_{Ferrihydrite}$ ). Coprecipitation experiments yield ferrihydrite solids with higher Ni/Fe ratios compared to pure adsorption experiments, as some Ni is adsorbed as well as incorporated into the solid structure during crystal growth. However, both experiments yield the same Ni isotopic compositions at low pH and low  $F^{Ni}_{Ferrihydrite}$ , suggesting a more complicated explanation than simple three-endmember mixing between fluid, incorporated and adsorbed Ni.

#### 4. Continued collaboration during 2021

A further 10 solid samples from experiment 4 (containing Si), and ~48 fluid samples remain to be analyzed in this project. Especially the fluid samples are crucial in order to calculate isotopic fractionation factors used to determine the mechanism of fractionation. Due to the continued effects of the COVID-19 pandemic the chief collaborators (Dilan Ratnayake and Prof Ryoji Tanaka) at IPM will continue to analyze these samples during 2021.

## References

- Wang, S-J. and Wasylenki, L. E. (2017) Experimental constraints on reconstruction of Archean seawater Ni isotopic composition from banded iron formations, *Geochimica et Cosmochimica Acta* 206, 137-150
- Wasylenki, L. E., Howe, H., D., Spivak-Birndorf, L. J. and Bish, D. L. (2015) Ni isotope fractionation during sorption to ferrihydrite: Implications for Ni in banded iron formations, *Chemical Geology* 400, 56-64