Ni isotope fractionation during coprecipitation of Fe(III)(oxyhydr)oxides in Si solutions

Neubeck Anna 1,*, Hemmingsson Christoffer 2, Boosman Arjen 3, Rouxel Olivier 4, Bohlin Madeleine 1

1 Department of Earth Sciences, Uppsala University, Sweden
2 Department of Geological Sciences, Stockholm University, Sweden
3 Department of Earth Sciences, Utrecht University, The Netherlands
4 Ifremer, Unit of Marine Geosciences, Brest, France

* Corresponding author : Anna Neubeck, email address : anna.neubeck@geo.uu.se

Abstract :

The dramatic decline in aqueous Ni concentrations in the Archean oceans during the Great Oxygenation Event is evident in declining solid phase Ni concentrations in Banded Iron Formations (BIFs) at the time. Several experiments have been performed to identify the main removal mechanisms of Ni from seawater into BIFs, whereby adsorption of Ni onto ferrihydrites has shown to be an efficient process. Ni isotopic measurements have shown limited isotopic fraction during this process, however, most experiments have been conducted in simple solutions containing varying proportions of dissolved Fe and Ni as NO3 salts, as opposed to Cl salts which are dominant in seawater. Further, Archean oceans were, before the advent of siliceous eukaryotes, likely saturated with a morphous Si as seen in the interlayered chert layers within BIFs. Despite Si being shown to greatly affect the Ni elemental partitioning onto ferrihydrite solids, no studies have been made on the effects of Si on the Ni isotope fractionation. Here we report results of multiple coprecipitation experiments where ferrihydrite precipitated in mixed solutions with Ni and Si. Ni concentrations in the experiments ranged between 200 and 4000 nM for fixed concentrations of Si at either 0, 0.67 or 2.2 mM. The results show that Si at these concentrations has a limited effect on the Ni isotope fractionation during coprecipitation of ferrihydrite. At 0.67 mM, the saturation concentration of cristobalite, the isotopic fractionation factors between the precipitating solid and experimental fluid are identical to experiments not containing Si (0.34 ± 0.17‰). At 2.2 mM Si, and the saturation concentration of amorphous silica, however, the Ni isotopic composition of the ferrihydrite solids deviate to more negative values and show a larger variation than at low or no Si, and some samples show fractionation of up to 0.5‰. Despite this seemingly more unstable fractionation behaviour, the combined results indicate that even at high concentrations of Si as 2.2 mM, the δ60Ni values of the forming ferrihydrites does not change much. The results of our study implicate that Si may not be a major factor in fractionating stable Ni isotopes, which would make it easier to interpret future BIF record and reconstruct Archean ocean chemistry.

Keywords : Stable Ni isotopes, Ferrihydrite precipitation, Co-precipitation experiment, Banded, Iron Formation, Silica
1. Introduction

Prior to the onset of large-scale global mantle convection after the Archean to Proterozoic Transition, low vertical mixing of the mantle restricted the capture and burial of elements (Andrault et al., 2017), resulting in higher elemental concentrations in the Archean oceans. It has been hypothesized that the depletion of nickel (Ni) in early Earth oceans, as a result of the onset of global mantle convection, had a direct negative influence on the strongly nickel-dependent methanogenic biosphere, indirectly leading to the onset of the ‘great oxygenation event’ (GOE) (Konhauser et al., 2015, 2009). It was suggested that successive removal of essential trace elements led to a dramatic decline in abundance of methanogens, paving the way for oxygen-producing cyanobacteria and the concomitant onset of atmospheric oxygenation. Although valuable clues can be found in Ni/Fe variability in banded iron formations (BIFs) which may have formed as a consequence of a gradual atmospheric oxygenation, anoxygenic photosynthesis or C-P-O-Fe cycling, both the source of the early Earth atmosphere and its composition is highly debated (Andrault et al., 2017; Bekker et al., 2010; Holland et al., 1986; Konhauser et al., 2017; Marakushev and Belonogova, 2019; Ozaki et al., 2019; Thibon et al., 2019). BIFs are chemical sedimentary deposits (usually of Archean and Paleoproterozoic age) characterized by layers of iron oxides alternating with chert layers. The mechanisms of formation of these deposits are still debated and several explanations have been put forward, such as the formation through oxidation of dissolved Fe as a consequence of photosynthetic, cyanobacterial production of molecular oxygen (Cloud, 1973). Other, purely abiotic explanations have been suggested, such as the oxidation of ferrous iron to ferricydrite or magnetite through UV oxidation or by reduction of carbon dioxide to methane (Thibon et al., 2019). Several abiotic processes show a preferential uptake of light Ni isotopes, such as the adsorption and coprecipitation of Ni with ferricydrites (Eusterhues et al., 2011; Twidwell and Leonhard, 2008; Wasylenki et al., 2015). Ferricydrite, a primary Fe(III)-oxide, was likely the first Fe-oxide phase to form as the ferrous ocean oxidised and produced the extraordinary BIF deposits (Posth et al., 2013; Wasylenki et al., 2015). The large specific surface area of ferricydrites promote adsorption of trace elements and possibly the fractionation of their stable isotopes. Several experiments have been conducted to evaluate the magnitude of abiotic fractionation of Ni isotopes in ferricydrites, through adsorption and coprecipitation experiments (Gueguen et al., 2018; Wang and Wasylenki, 2017; Wasylenki et al., 2015). The studies demonstrated a strong coupling between iron oxide precipitation and light Ni, with fractionation factors between the experimental solution and ferricydrite of ~+0.35‰. However, these fractionation factors were determined from experiments conducted in solutions containing only Fe and Ni dissolved in water or dilute NaNO₃. The Archean
ocean is hypothesised to have had dissolved silicon, Si, concentrations as high as 2.2 mM (Konhauser et al., 2009; Jones et al., 2015), evidenced by the microcrystalline quartz layers alternating with the iron bands within BIF deposits. The presence of Si has been shown to have a large effect on the partitioning of Ni into ferrihydrites (Konhauser et al., 2009), but no studies have yet been made on the effects on Ni isotopes during this process. Therefore, as a first step to investigate the effects of Si on Ni isotope fractionation, we conducted multiple coprecipitation experiments to investigate the isotopic fractionation of Ni sorption when ferrihydrite forms in mixed solutions with Si and Ni.

2. Experimental and analytical methods

2.1 Mineral synthesis

All coprecipitation experiments were conducted in a clean lab at the Swedish Museum of Natural History in Stockholm, Sweden. The experiments were performed at room temperature (~24°C) in acid cleaned plastic beakers (PP) with constant agitation by a Teflon coated magnetic stirrer. Stock solutions of FeCl₂, NiCl₂ and Si (as sodium metasilicate nonahydrate) were prepared by diluting concentrated solutions and powders with Milli-Q (18.2 MΩ) water. The stock solutions were diluted further with Milli-Q for each experiment to a final experimental volume of 100 ml. The final solutions had an Fe concentration of 180 µM, Si concentrations of either 0, 0.67 or 2.2 mM and Ni concentrations ranging between 100 and 4000 nM, that covers the suggested Archean oceanic dissolved Ni concentrations ranging from approx. 200-400 nM (Konhauser et al. 2009, Table 1).

Ferrihydrite was synthesised through rapid hydrolysis of Fe²⁺ by raising the solution pH by dropwise addition of 1M NaOH to a pH of 7. The pH was monitored throughout the experiment with a pH meter (Orion model 250A). Once the pH was stable, the solution was left to equilibrate for 30 minutes. The pH of the solution was not allowed to deviate more than ±0.1 from pH 7 and was controlled by adding small amounts (generally 5 to 10 µl) of 0.1 M HCl or NaOH. Following 30 minutes of equilibration, the experiments were stopped and the contents were split into two ~50 ml fractions and immediately centrifuged to separate the ferrihydrite precipitates from the supernatant. One of the ferrihydrite fractions was kept as a solid for mineral determination using X-ray diffraction, and the other was dissolved in 20 ml 0.5M HNO₃ for elemental and Ni isotopic analyses.
2.2 X-Ray diffraction methods

Single crystal X-ray diffraction (XRD) was used to verify phase identities of ferrihydrites synthesised in the experiments. The XRD analyses were conducted on the same day as the precipitation experiments to avoid possible aging or alteration of the minerals. The analyses were performed on a Bruker D8 diffractometer using CuKα radiation, incident- and diffracted-beam Soller slits, and a Bruker Sol-XE detector. The samples were mounted on thin glass fibres attached to brass pins and mounted onto goniometer heads. Data were analysed using Bruker’s EVA program.

2.3 Ni isotope analyses

Chemical purification of Ni and subsequent Ni isotope measurements were conducted at the Ifremer Centre de Bretagne in Brest, France, and follow the methods of Gueguen et al. (2013). A double spike method was used where a $^{61}$Ni-$^{62}$Ni spike (containing equal proportions of $^{61}$Ni and $^{62}$Ni) was added to all samples prior to chemical processing. The double spike allows correction of instrumental mass bias occurring during analysis as well as possible fractionation arising from less than 100% yields during column chromatography.

Samples and standards (NIST SRM 986) containing Ni concentrations of 0.5 to 1 μg Ni were evaporated on a hotplate. The spike was then added at a Ni$_{sample}$/Ni$_{spike}$ ratio of 1 and re-evaporated to dryness, ready to be taken up by the column elution matrix. Procedural blank measurements yielded Ni concentrations of 3-4 ng and are considered negligible compared to the high Ni concentrations of the processed samples.

2.3.2 Sample purification

The relatively simple matrix of ferrihydrite solids and experimental fluids allowed for a single step column procedure to be used, utilizing the Eichrome Ni specific resin (second column step in Gueguen et al., 2013). The Ni-spec resin contains a dimethylglyoxime (DMG) molecule, which at pH >8 forms a Ni-DMG complex which is retained in the resin. The dry sample-spike residues were dissolved in 1 ml 0.24M HCl, after which the pH was increased by the addition of 0.3 ml 1M ammonium citrate and 125μl concentrated ammonia. Between each addition step, 15 minutes were allowed for homogenization of the solution.

Approximately 0.5 ml wet Ni-spec resin was loaded into polypropylene columns. The resin was washed with 6.5 ml MilliQ and 4.5 ml of 0.2M ammonium citrate+0.45M ammonia. The
columns were then capped and an additional 0.5 ml of the 0.2M ammonium citrate +0.45M ammonia solution was added to buffer the resin pH to ~9. The prepared sample and NIST standard solutions were then loaded onto the column and the resin was resuspended, increasing the active surface area and rate of complexation. The suspension was then left for 1 hour. The Ni yields through the column were close to 100% implying that the 1-hour equilibration time was sufficient. After 1 hour the columns were left to drain, and 2.2 ml of the 0.2M ammonium citrate+0.45M ammonia solution was added twice, in intervals of 15 minutes. This step washes out Fe and other matrix elements. Thereafter, 2.2 ml of MilliQ was added three times in intervals of 15 minutes, to wash out excess ammonium citrate and ammonia salts. Ni was then collected in 6.6 ml of 3M HNO3, which was added three times as 2.2 ml with 15 minutes between each time. The collected Ni cuts were then dried down on a hot plate at ~95°C overnight, and then refluxed in concentrated HNO3 for 24 hours to fully oxidise and break down the Ni-DMG complex. Following evaporation, the sample residue was then dissolved in 1 ml of 0.3M HNO3 ready for isotopic analysis.

2.3.3 Isotopic measurements

Ni isotopes were measured on the Thermo Scientific Neptune multi-collector inductively coupled mass spectrometer (MC-ICP-MS) at the Ifremer Centre de Bretagne in Brest, France. The analyses were made in medium resolution with simultaneous measurements of $^{58}$Ni, $^{60}$Ni, $^{61}$Ni and $^{62}$Ni, as well as $^{57}$Fe to monitor the isobaric interference of $^{58}$Fe on $^{58}$Ni. Each sample was measured with 50 cycles of 4 seconds integration time, separated by acid blank measurements of 10 cycles with 4 seconds integration time. Samples were introduced using an ApexQ MicroFlow PFA-50 self-aspirating nebulizer at an injection rate of ~60µl/min. The sample and skimmer cones are made of Ni, but $^{58}$Ni intensities of the blanks indicate no Ni is contributed from the cones, as demonstrated previously (Fujii et al., 2011; Gueguen et al., 2013; Moynier et al., 2007).

2.3.4 Ni isotope data reduction

Nickel isotope compositions of samples are expressed using the delta (δ) notation where the isotopic ratio of the sample is normalised to that of the NIST SRM 986 standard, following:

$$\delta^{X}\text{Ni}_{\text{sample}} (\%) = \left( \frac{X_{\text{Ni}^{58}}^{\text{Sample}}}{X_{\text{Ni}^{58}}^{\text{NIST SRM 986}}} - 1 \right) \times 1000$$

(1)
where X denotes either the $^{60}$Ni, $^{61}$Ni or $^{62}$Ni isotope ($^{64}$Ni was not considered in this study). The data presented in this study is described using the $^{60}$Ni/$^{58}$Ni ratio given as $\delta^{60}$Ni.

Prior to double spike calculation, the $^{58}$Ni intensity was corrected for interference of $^{58}$Fe following:

$$^{58}\text{Fe} = ^{57}\text{Fe}_{\text{Measured}} \times \left( \frac{^{58}\text{Fe}}{^{57}\text{Fe}} \right)_{\text{Natural}}$$

(2)

where $^{58}\text{Fe}/^{57}\text{Fe}_{\text{Natural}}$ is the ratio of the natural abundances of the $^{58}$Fe and $^{57}$Fe isotopes. The intensity of $^{58}$Fe is then subtracted from the measured $^{58}$Ni signal.

The nickel isotopic compositions of samples were then calculated using the double spike calculation template from Gueguen et al., 2013.

NIST SRM 986 was passed through columns four separate times yielding an average value and external reproducibility of the method of $-0.01 \pm 0.08\%o$.

3. Results

3.1 X-Ray diffraction

Powder X-ray diffraction of the solid phase showed two peaks around 36 degrees and 63 degrees characteristic for and assigned to the (110) and (115) planes of 2-line ferrihydrite (Figure 1), showing that the addition of Si up to 2.2 mM did not affect the formation of ferrihydrite in our experiments. No aging minerals such as goethite or hematite were detected in the spectra.

3.2 Ni isotopic composition of coprecipitated solids and fluids

The Ni isotopic compositions of the ferrihydrite solids ranged from $-0.37$ to $+0.02\%o$, while fluids were isotopically heavier with $\delta^{60}$Ni values ranging from $-0.08$ to $+0.26\%o$. The isotopic composition of both fluids and solids increase with increasing fraction of Ni incorporated in the solids (Figure 2). The fraction of Ni sorbed to ferrihydrite in our experiments ranged from 0.32 to 0.86, however there was no systematic distinction between the varying Si concentrations (Table 1, Figure 2).
The apparent fractionation factor between the residual fluid and forming ferrihydrite solids, \( \Delta^{60}\text{Ni}_{\text{solution-solid}} \) (where \( \Delta^{60}\text{Ni}_{\text{solution-solid}} = \delta^{60}\text{Ni}_{\text{solution}} - \delta^{60}\text{Ni}_{\text{solid}} \)), ranges from -0.08 to +0.52‰, with an average of +0.28±0.33‰ (2 stdev, n=14). The variability is caused by two sets of samples which show the opposite sense of fractionation with solids being slightly heavier than fluids (Table 1, Figure 2). The mechanism of fractionation of these particular samples is discussed in section 4.2. Excluding these samples, the mean value is +0.34 ± 0.17‰, in good agreement with previous coprecipitation and adsorption experiments not containing Si (Wasylenki et al., 2015; Wang and Wasylenki, 2017; Gueguen et al., 2018).

The average \( \Delta^{60}\text{Ni}_{\text{solution-solid}} \) of samples not containing any Si, and those containing 0.67 mM Si are within error of each other at +0.28±0.02 and +0.29±0.10‰ respectively, while the samples containing the highest concentrations of Si at 2.2 mM have higher and more varied \( \Delta^{60}\text{Ni}_{\text{solution-solid}} \) at +0.41±0.16‰. While two of the high Si samples have similar apparent fractionation factors as the no and low Si samples, three samples have significantly higher apparent fractionation of +0.43 to +0.52‰ (Figure 3).

4. Discussion

4.1 Ferrihydrite precipitation in the presence of Cl

The main results of this study agree with the aggregated conclusions of previous coprecipitation and adsorption experiments (Gueguen et al., 2018; Wang and Wasylenki, 2017; Wasylenki et al., 2015), despite our experiments differing in two important ways: i) FeCl₂ was used instead of Fe(NO₃)₃ for the ferrihydrite synthesis and ii) Si was added to the experiments, to be present in solution throughout mineral formation. Using FeCl₂ instead of Fe(NO₃)₃ could theoretically have an impact on the uptake and fractionation of Ni due to differences in particle size of the synthesized ferrihydrite (Hiemstra et al., 2019), or due to the formation of akaganéite (β-FeOOH·xHCl) in the Cl environment. Our data does not suggest any formation of akaganéite in our samples, however, as XRD spectra show the formation of 2-line ferrihydrite regardless of the added Cl (Figure 1). It has been shown that the particle size of ferrihydrite changes considerably depending on the reagents that are used for the synthesis, where FeCl₂ result in larger particles with a smaller specific surface area (approx. 1000 m² g⁻¹) and Fe(NO₃)₃ result in smaller particles and a concomitant larger specific surface area (approx. 1100 m² g⁻¹). The aging of ferrihydrite (the number of Fe atoms per particle volume as a function of time) has been shown to be non-linear and slow in nitrate solutions, whereas in Cl⁻ based solutions uptake of Fe is fast and linear (Hiemstra et al., 2019). In a Cl⁻ based solution, the number of Fe atoms incorporated into the ferrihydrites reach
approximately 600 after 25 hours and in a nitrate solution this number is only 160. Ferrihydrates from nitrate does not reach the same amount of Fe incorporated into the ferrihydrates even after 200 hours (Hiemstra et al., 2019). Since these reaction pathways are different in terms of uptake, the Ni fractionation factor could as well be influenced by this process, since it is commonly dependent of the Ni concentration (Hiemstra et al., 2019). However, the similarities of our results and those of previously conducted experiments in nitrate environments suggest that either the resulting particle sizes were similar in the different environments, or that potential differences had little impact in the resulting Ni uptake and Ni isotopic fractionation. Aqueous Ni speciation may have an influence on Ni incorporation into ferrihydrates in an ancient ocean due to putative ligand-controlled isotopic fractionation. According to Fuji et al. (2011), equilibrium exchange of Ni between different aqueous species (hydrated Ni$^{2+}$, hydroxides, chlorides, sulfides, sulfate, and carbonates) and organic ligands showed that the isotopic effect can be as high as 2.5‰, which is in the same magnitude as biologic fractionation of Ni by methanogens (Cameron et al. 2009). Moreover, Fuji et al. (2011) could show that the isotopic fractionation coupled to abiotic speciation between the different Ni species was approximately 1.7‰, which may have a strong effect on the isotopic signature of the geologic rock record such as the BIFs. However, in our system, the dominating Ni species are Ni$^{2+}$ and NiCl$^+$ and the speciation between those two species would, according to Fuji et al. (2011), have an isotopic effect of approximately 0.1‰ if considering a pH close to modern oceans (~8) and a log $\mu$CO$_2$ of approximately -3.5. In an Archaean ocean, the effect would likely have been even less due low concentrations of Cl$^-$ (Fuji et al. 2011) and therefore, we consider these effects as negligible. The same fractionation value is found between Ni$^{2+}$ and NiCl$^+$ as a function of pH, where the maximum fractionation between these two species is estimated to be approximately 0.1‰ (Fuji et al. 2014).

4.2 Ni isotopic fractionation mechanism in the presence of Si

To test which fractionation mechanism best explains the distribution of our coprecipitation data we fit the fluid and solid isotopic compositions against the fraction of Ni in the ferrhydrite solid ($F_{\text{Ferrihydrite}} = 1 - Ni_0/Ni$) to three fractionation models; a Rayleigh model which describes kinetic fractionation of Ni between the fluid and solid phase, a linear equilibrium model assuming isotopic fractionation occurs at equilibrium between the fluid and solid, and a model describing equilibrium fractionation between three pools of Ni
assuming Ni is both adsorbed and incorporated into the solid ferrihydrite structure (Figure 2). All models use -0.05‰ as the starting composition of the experimental fluid. Wang and Wasylenki (2017) showed that coprecipitated ferrihydrite consists of both surface adsorbed and incorporated Ni and that these pools have distinct isotopic compositions with $\delta^{60}$Ni values increasing in the order adsorbed < solution < incorporated. They determined that the fractionation factors between the solution and adsorbed Ni ($\Delta_{\text{solution-adsorbed}}$) is ~+0.3 to +0.44‰ based on pure adsorption experiment from Wasylenki et al. (2015) and that the fractionation factor between the solution and incorporated Ni ($\Delta_{\text{solution-incorporated}}$) is -0.18‰ (Wang and Wasylenki, 2017). The data is fitted using global models where fluid and solid data are regressed simultaneously. For the linear and Rayleigh models, the best-fit fractionation factor is modelled against measured $\delta^{60}$Ni and $F_{\text{Ferrihydrite}}$ values. The linear model gives best-fit $\Delta^{60}$Ni$_{\text{solution-solid}}$ of +0.32 ± 0.02‰ (1se) with a global $R^2$ of 0.90, while the Rayleigh model (following Wasylenki et al, 2015) gives +0.17 ± 0.02 ‰ (1se) and $R^2$ of 0.86. For the three-pool Ni model the fractionation factors given by Wang and Wasylenki (2017) are used in the first instance but do not fit our dataset as well as the simpler models. Using $\Delta_{\text{solution-adsorption}}$ of +0.44‰ and $\Delta_{\text{solution-incorporated}}$ of -0.18‰ gives a global $R^2$ value of 0.8 (but significantly worse individual fits to fluid and solids, Figure 2). Modelling the two fractionation factors provide best-fit values which are both positive (+0.57 and +0.29‰ respectively) i.e. mimicking the simpler linear two-pool Ni fractionation model. However, the regression is mainly driven by the samples containing Si, especially the 2.2mM sample with $F_{\text{Ferrihydrite}}$ of 0.32. It is possible that the presence of Si affects the fractionation factors, or the distribution of Ni between the adsorbed, incorporated and fluid fractions. Conclusions regarding this cannot be drawn from our current dataset. Although providing a poorer fit to the entire data set, the partitioning of Ni between an isotopically lighter adsorbed phase, and an isotopically heavy incorporated phase may describe the two sets of samples where the ferrihydrite solids are isotopically heavier than their respective fluids (Figure 2). The reason these particular experiments yielded solids with higher proportion of Ni incorporated compared to other samples are unknown. Adsorption is heavily influenced by pH where higher pH promotes more adsorption of Ni onto the ferrihydrite particles (e.g. Gueguen et al., 2018). However, all samples in this study were synthesised at the same pH (7±0.1). Wang and Wasylenki (2017) show that pH, and in extension the Ni/Fe ratio of the solid have the largest effect on the ratio of adsorbed and incorporated Ni. However, the Ni/Fe ratio of these two sets of samples do not explain why they may have relatively more Ni incorporated. Overall, the simpler linear equilibrium isotope fractionation model best fit our dataset as a whole, yielding
a best-fit value of $\Delta_{\text{solution-solid}}$ of $+0.32\%$, and we cannot systematically distinguish between adsorbed or incorporated Ni. Although Si may influence the relative proportions of Ni being adsorbed and incorporated into the solid ferrihydrite structure, our data and modelling suggest that addition of Si did not appear to significantly change the Ni isotopic fractionation mechanism during ferrihydrite coprecipitation.

4.3 Implications for Archean seawater reconstruction using BIF record

Although previous studies have investigated the influence of Fe oxide precipitation on the fractionation of Ni in order to understand the formation environment of BIFs (Gueguen et al., 2018; Wang and Wasylenki, 2017; Wasylenki et al., 2015), the combined influence of Si and Fe precipitation on the Ni isotope fractionation has not previously been investigated. Konhauser et al. (2009) demonstrated that the presence of Si greatly reduced the partitioning behaviour of Ni into precipitating ferrihydrite particles, but no isotopic analyses were made. The rationale for our added Si concentrations are, as in Konhauser et al. (2009), based on the assumption that Si was not readily removed from the seawater in the Precambrian oceans, due to the absence of Si-precipitating organisms. The source and sinks of Si to the oceans were therefore purely abiotic and thus, coprecipitation and adsorption may have had a much larger impact on the global Si cycle (Siever, 1992, 1957). We used Si concentration saturations with respect to cristobalite (0.67 mM) and amorphous Si (2.2 mM) (Jones et al., 2015; Konhauser et al., 2009). The higher Si concentration (2.2mM) represents the highest suggested Si concentration for the Precambrian ocean. Coprecipitation of Ni with ferrihydrite in solutions containing variable amounts of Si shows a preferential uptake of the light Ni isotopes into the solid phase, with an average fractionation of $\Delta^{60}_{\text{Ni}_{\text{solution-solid}}}$ of 0.34±0.17‰ (Figure 2). The magnitude of isotope fractionation agrees with previous studies that do not contain Si, where both coprecipitation and adsorption of Ni onto 2-line ferrihydrite have the same fractionation factor of 0.35±0.08‰ (adsorption, Gueguen et al., 2018) and 0.35±0.10‰ (adsorption and coprecipitation, Wasylenki et al., 2015). However, 3 data points in our experiments which contain the highest concentration of Si, have significantly higher $\Delta^{60}_{\text{Ni}_{\text{solution-solid}}}$ at 0.43 to 0.52‰. It is unclear at present why this is, but since coprecipitation involves Ni being both incorporated into the structure and surface adsorption it could be due to changing ratios of these processes. Wang and Wasylenki (2017) hypothesise that the fractionation factors are
significantly different between adsorbed and incorporated Ni, and a more detailed study is currently undertaken to study this under the influence of Si.

The possible <0.2‰ increase and large variation observed in $\Delta^{66}$Ni of high Si samples suggest that temporal variations in Archean seawater chemistry may exert secondary controls on Ni isotope fractionation. It will be important to constrain these in order to accurately interpret a future Ni isotope record of BIFs. Our data suggests that the recorded stable Ni isotopic composition of a high-Si Archean ocean may have been different from an ocean with a low Si content. Thus, the stable Ni isotopic signatures in the BIF record would show a larger fractionation factor than the younger oceans with less available Si. It is yet unknown however, how significant the <0.2‰ difference in, as it depends entirely upon the overall variation of the future BIF record. Further, although +0.2‰ is a fairly large number in Ni isotope-space, and significantly larger than typical analytical uncertainties of ~0.05‰, a possible biological signal superimposed on this abiotic signal is expected to be significantly larger (<1.5‰, Cameron et al., 2009). These results indicate that despite this relatively large offset, abiotic processes have a limited fractionation compared to known methanogenic-derived Ni isotope fractionations. However, as of yet, such methanogenic signatures have not been preserved in the geological rock record. Furthermore, experimental and theoretical investigations on equilibrium exchange between aqueous Ni species and ligands have shown a relatively strong isotopic effect (2.5‰), which would overprint any biological or co-precipitation signal in a BIF with our results. Thus, more studies need to be undertaken to understand the mechanisms behind these results. Importantly, Ni isotopic fractionation factors during coprecipitation of ferrihydrite with Si concentrations as high as 0.67mM, and even 2.2mM for some samples, show no observable differences to when Si is not present in fluid. A combined effect of these potential influencing factors on the Ni isotope fractionation simplifies the interpretation of the BIF record, as the contemporary seawater would have been ~0.3-0.5‰ heavier than the BIF composition. However, it is still unknown how a biological signature superimposed on this would affect the composition. So far, only one biologic experimental study has been undertaken (Cameron et al. 2009), to show the biological effect on Ni isotope fractionation but if the general biological fractionation of Ni is in that isotopic range (~1.5 ‰), ferrihydrite precipitates with or without Si would be overprinted by biological fractionation. On the other hand, if the sink of light Ni is concentrated to organic-rich shales, the isotopic fractionation would be as large as 2.5‰ (Fuji et al. 2011) and thus be visible in the geological rock record if preserved through time.
5. Conclusions

The aggregated results from this study show that Ni isotope fractionation during coprecipitation of Fe(III)(oxyhydr)oxides in Si solutions show best fit lines for equilibrium fractionation for fluids as shown also by previous studies. The presence of Si seemed to influence the fractionation factor so that higher concentrations of Si resulted in a larger fractionation factor. However, the explanation for this result requires a more extensive study that is currently underway. The use of FeCl₂ rather than Fe(NO₃)₃ did not seem to have an effect on the fractionation factor or amount of Ni being incorporated into solids, even though using different reactants have been shown to have an impact on the particle surface area and thus the possible adsorption potential. Our experiments show that Si has no consistently resolvable influence on Ni isotope fractionation when coprecipitated by Fe(III)(oxyhydr)oxides and further experiments needs to be undertaken to explore the influence of Si.

Credit Author Statement
A.N. came up with the idea and drafted the article. A.B. and C.H. did the laboratory experiments. M.B. helped with crucial interpretations and writing of the article. O.R. was responsible for laboratory used for the experiments. All authors has read and approved the article.

Declaration of interests
The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments
This research was funded by Swedish research council (contract 2017-05018 to A.N.) and the European Union’s Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 844529 (to M.B.)

References
Andrault, D., Muñoz, M., Pesce, G., Cerantola, V., Chumakov, A., Kantor, I., Pascarelli, S., Rüffer, R., Hennet, L., 2017. Large oxygen excess in the primitive mantle could be the source of the Great Oxygenation Event. Geochemical Perspect. Lett. 6, 5–10.
Azeez, P.A., Banerjee, D.K., 1991. Nickel uptake and toxicity in cyanobacteria. Toxicol. Environ. Chem. 30, 43–50. https://doi.org/10.1080/02772249109357639

Bekker, A., Slack, J.F., Planavsky, N., Krapež, B., Hofmann, A., Konhauser, K.O., Rouxel, O.J., 2010. Iron formation: The sedimentary product of a complex interplay among mantle, tectonic, oceanic, and biospheric processes. Econ. Geol. https://doi.org/10.2113/gsecongeo.105.3.467

Cameron, V., Vance, D., Archer, C., House, C.H., 2009. A biomarker based on the stable isotopes of nickel. Proc. Natl. Acad. Sci. 106, 10944–10948. https://doi.org/10.1073/pnas.0900726106

Cloud, P., 1973. Paleoecological significance of the banded iron-formation. Econ. Geol. 68, 1135–1143. https://doi.org/10.2113/gsecongeo.68.7.1135

Eusterhues, K., Rennert, T., Knicker, H., Kögel-Knabner, I., Totsche, K.U., Schwertmann, U., 2011. Fractionation of organic matter due to reaction with ferrihydrite: Coprecipitation versus adsorption. Environ. Sci. Technol. 45, 527–533. https://doi.org/10.1021/es1023898

Fujii, T., Moynier, F., Dauphas, N., Abe, M., 2011. Theoretical and experimental investigation of nickel isotopic fractionation in species relevant to modern and ancient oceans. Geochim. Cosmochim. Acta. https://doi.org/10.1016/j.gca.2010.11.003

Gueguen, B., Rouxel, O., Ponzevera, E., Bekker, A., Fouquet, Y., 2013. Nickel isotope variations in terrestrial silicate rocks and geological reference materials measured by MC-ICP-MS. Geostand. Geoanalytical Res. 37, 297–317. https://doi.org/10.1111/j.1751-908X.2013.00209.x

Gueguen, B., Sorensen, J. V., Lalonde, S. V., Peña, J., Toner, B.M., Rouxel, O., 2018. Variable Ni isotope fractionation between Fe-oxyhydroxides and implications for the use of Ni isotopes as geochemical tracers. Chem. Geol. 481, 38–52. https://doi.org/10.1016/j.chemgeo.2018.01.023

Hiemstra, T., Mendez, J.C., Li, J., 2019. Evolution of the reactive surface area of ferricydrite: Time, pH, and temperature dependency of growth by Ostwald ripening. Environ. Sci. Nano. https://doi.org/10.1039/c8en01198b

Holland, H.D., Lazar, B., McCaffrey, M., 1986. Evolution of the atmosphere and oceans. Nature 320, 27–33. https://doi.org/10.1038/320027a0

Huertas, M.J., López-Maury, L., Giner-Lamia, J., Sánchez-Riego, A.M., Florencio, F.J., 2014. Metals in cyanobacteria: Analysis of the copper, nickel, cobalt and arsenic homeostasis
mechanisms. Life. https://doi.org/10.3390/life4040865
Jones, C., Nomosatryo, S., Crowe, S.A., Bjerrum, C.J., Canfield, D.E., 2015. Iron oxides,
divalent cations, silica, and the early earth phosphorus crisis. Geology 43, 135–138.
https://doi.org/10.1130/G36044.1
Konhauser, K.O., Pecoits, E., Lalonde, S. V., Papineau, D., Nisbet, E.G., Barley, M.E., Arndt,
N.T., Zahnle, K., Kamber, B.S., 2009. Oceanic nickel depletion and a methanogen famine before the Great Oxidation Event. Nature 458, 750–753.
https://doi.org/10.1038/nature07858
Konhauser, K.O., Planavsky, N.J., Hardisty, D.S., Robbins, L.J., Warchola, T.J., Haugaaard,
R., Lalonde, S. V., Partin, C.A., Oonk, P.B.H., Tsikos, H., Lyons, T.W., Bekker, A.,
Johnson, C.M., 2017. Iron formations: A global record of Neoarchaean to Paleoproterozoic environmental history. Earth-Science Rev. https://doi.org/10.1016/j.earscirev.2017.06.012
Konhauser, K.O., Robbins, L.J., Pecoits, E., Peacock, C., Kappler, A., Lalonde, S. V., 2015.
The Archean Nickel Famine Revisited. Astrobiology 15, 804–815.
https://doi.org/10.1089/ast.2015.1301
Marakushev, S.A., Belonogova, O. V., 2019. Ideas and perspectives: Development of nascent autotrophic carbon fixation systems in various redox conditions of the fluid degassing on early Earth. Biogeosciences. https://doi.org/10.5194/bg-16-1817-2019
Moynier, F., Blichert-Toft, J., Telouk, P., Luck, J.M., Albarède, F., 2007. Comparative stable isotope geochemistry of Ni, Cu, Zn, and Fe in chondrites and iron meteorites. Geochim. Cosmochim. Acta 71, 4365–4379. https://doi.org/10.1016/j.gca.2007.06.049
Ozaki, K., Thompson, K.J., Simister, R.L., Crowe, S.A., Reinhard, C.T., 2019. Anoxygenic photosynthesis and the delayed oxygenation of Earth’s atmosphere. Nat. Commun. 10.
https://doi.org/10.1038/s41467-019-10872-z
Posth, N.R., Köhler, I., D. Swanner, E., Schröder, C., Wellmann, E., Binder, B., Konhauser, K.O., Neumann, U., Berthold, C., Nowak, M., Kappler, A., 2013. Simulating Precambrian banded iron formation diagenesis. Chem. Geol. 362, 66–73.
https://doi.org/10.1016/j.chemgeo.2013.05.031
Siever, R., 1992. The silica cycle in the Precambrian. Geochim. Cosmochim. Acta 56, 3265–3272. https://doi.org/10.1016/0016-7037(92)90303-Z
Siever, R., 1957. The silica budget in the sedimentary cycle. Am. Mineral. 42, 821–841.
Thauer, R.K., Kaster, A.-K., Goenrich, M., Schick, M., Hiromoto, T., Shima, S., 2010. Hydrogenases from Methanogenic Archaea, Nickel, a Novel Cofactor, and H₂ Storage.
Annu. Rev. Biochem. 79, 507–536. https://doi.org/10.1146/annurev.biochem.030508.152103

Thibon, F., Blichert-Toft, J., Tsikos, H., Foden, J., Albalat, E., Albarede, F., 2019. Dynamics of oceanic iron prior to the Great Oxygenation Event. Earth Planet. Sci. Lett. 506, 360–370. https://doi.org/10.1016/j.epsl.2018.11.016

Twidwell, L.G., Leonhard, J.D., 2008. Removal of cadmium, copper, nickel and zinc from aqueous solution by adsorption on ferrihydrite and long-term storage stability of the metal loaded product, in: Hydrometallurgy 2008: Proceedings of the 6th International Symposium. pp. 149–161.

Wang, S.J., Wasylenki, L.E., 2017. Experimental constraints on reconstruction of Archean seawater Ni isotopic composition from banded iron formations. Geochim. Cosmochim. Acta 206, 137–150. https://doi.org/10.1016/j.gca.2017.02.023

Wasylenki, L.E., Howe, H.D., Spivak-Birndorf, L.J., Bish, D.L., 2015. Ni isotope fractionation during sorption to ferrihydrite: Implications for Ni in banded iron formations. Chem. Geol. 400, 56–64. https://doi.org/10.1016/j.chemgeo.2015.02.007
**Figure and table captions**

**Figure 1** – X-Ray diffraction patterns of three representative solid samples, with no Si (red), 0.67 mM Si (green) and 2.2 mM Si (blue) all showing the characteristic pattern of 2-line ferrihydrite.

**Figure 2** – Ni isotopic compositions of ferrihydrite solids (brown) and supernatant fluids (blue) against fraction of Ni sorbed (F{subscript: Ferrihydrite}) to the solid phase during coprecipitation. Experiments not containing Si are given as circles, 0.67mM Si as triangles and 2.2mM Si as squares. Modelled best fit lines for three isotopic fractionation models are given: linear equilibrium fractionation (solid line), Rayleigh fractionation (dashed line) and a three-pool equilibrium Ni model (dotted line). See section 4.2 for discussion. Two sample pairs with
opposite fractionation behaviour are not included in the fit (greyed out symbols). The error bars represent the external reproducibility (2 standard deviations) of ±0.08‰. Reference data from adsorption and coprecipitation experiments from Wasylenki et al., 2015 and Wang and Wasylenki, 2017.

Figure 3 – Comparison of apparent fractionation factors between ferrihydrite solids and supernatant fluids (Δ60Ni_solution-solid) for the different Si concentrations used in the experiments. The error bars are propagated errors using the external reproducibility of fluid and solid isotopic measurements of ±0.08‰, yielding a propagated error on Δ60Ni_solution-solid of ±0.11‰. The blue circles represent experiments with no added Si, green triangles 0.67 mM Si and orange squares 2.2 mM Si. Most samples have the same fractionation of ~0.29‰, but three of the highest Si samples have more fractionated samples with up to 0.52‰.
Table 1 - Experiment setup and compositions of ferrihydrite solids and solutions. The 2 standard deviations of isotopic measurements are the internal error (the external 2 standard deviation is ±0.08‰).

| Experiment ID | [Si]_{init} | [Ni]_{init} | [Fe]_{Sol} | [Ni]_{Sol} | F_{Sol}^{Ni} | δ^{60}Ni_{Sol} | 2 stdev | [Fe]_{Flu} | [Ni]_{Flu} | F_{Flu}^{Ni} | δ^{60}Ni_{Flu} | 2 stdev | Δ^{60}Ni_{solution-solid} | 2 stdev | Isotopic mass balance |
|---------------|-------------|-------------|------------|------------|-------------|----------------|---------|------------|-------------|----------------|----------------|---------|------------------------|---------|----------------------|
|               | mM          | nM          | μmol       | nM         | %           | %              |         | μmol       | nM          | %           | %              |         | %                      |         | %                    |
| 0.200         | 0.200       | 0           | 200        | 200        | 353.7       | 229           | 0.70    | 0.09       | 0.07        | 2.9          | 0.30          | nd      | nd                     | nd      | nd                   |
| 0.2000        | 0.2000      | 0           | 2000       | 2000       | 327.6       | 1710          | 0.52    | -0.20      | 0.03        | 3.2          | 0.48          | 0.08    | 0.02                    | 0.28    | 0.03                 |
| 0.4000        | 0.4000      | 0           | 4000       | 4000       | 380.4       | 3678          | 0.49    | -0.20      | 0.06        | 3.8          | 2028          | 0.51    | 0.07                    | 0.27    | 0.06                 |
| 1.200         | 1.200       | 0.67        | 200        | 200        | 229.3       | 140           | 0.50    | -0.27      | 0.03        | 66.8         | 99            | 0.50    | 0.04                    | 0.05    | 0.31                 |
| 1.4000        | 1.4000      | 0.67        | 400        | 400        | 242.6       | 408           | 0.56    | -0.01      | 0.03        | 62.2         | 176           | 0.44    | -0.06                   | 0.06    | -0.05                |
| 1.600         | 1.600       | 0.67        | 600        | 600        | 281.4       | 1092          | 0.84    | -0.08      | 0.05        | 49.7         | 94            | 0.16    | 0.22                    | 0.06    | 0.30                 |
| 1.1000        | 1.1000      | 0.67        | 1000       | 1000       | 310.3       | 1032          | 0.66    | -0.23      | 0.04        | 37.4         | 344           | 0.34    | 0.08                    | 0.05    | 0.31                 |
| 1.2000        | 1.2000      | 0.67        | 2000       | 2000       | 196.2       | 3091          | 0.74    | -0.16      | 0.05        | 76.6         | 513           | 0.26    | 0.17                    | 0.04    | 0.34                 |
| 1.4000        | 1.4000      | 0.67        | 4000       | 4000       | 283.6       | 8353          | 0.86    | -0.08      | 0.05        | 44.6         | 562           | 0.14    | 0.13                    | 0.06    | 0.21                 |
| 2.200         | 2.200       | 2.2         | 200        | 200        | 280.8       | 237           | 0.72    | -0.31      | 0.04        | 21.7         | 56            | 0.28    | 0.21                    | 0.17    | 0.52                 |
| 2.400         | 2.400       | 2.2         | 400        | 400        | 178.3       | 405           | 0.39    | 0.02       | 0.05        | 83.9         | 244           | 0.61    | -0.06                   | 0.05    | -0.08                |
| 2.600         | 2.600       | 2.2         | 600        | 600        | 106.8       | 736           | 0.56    | -0.26      | 0.03        | 104.7        | 264           | 0.44    | 0.17                    | 0.04    | 0.43                 |
| 2.1000        | 2.1000      | 2.2         | 1000       | 1000       | 257.2       | 1309          | 0.61    | -0.17      | 0.04        | 33.1         | 385           | 0.39    | 0.13                    | 0.02    | 0.30                 |
| 2.2000        | 2.2000      | 2.2         | 2000       | 2000       | 213.2       | 1018          | 0.32    | -0.37      | 0.04        | 48.5         | 1361          | 0.68    | 0.07                    | 0.05    | 0.43                 |
| 2.4000        | 2.4000      | 2.2         | 4000       | 4000       | 163.0       | 7597          | 0.85    | -0.10      | 0.05        | 84.2         | 583           | 0.15    | 0.26                    | 0.04    | 0.36                 |

Journal Pre-proof