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Variable Ni isotope fractionation between Fe-oxyhydroxides and implications for the use of Ni isotopes as geochemical tracers

Gueguen Bleuenn^{1, 2, *}, Sorensen Jeffry V. ³, Lalonde Stefan¹, Pena Jasquelin⁴, Toner Brandy M. ³, Rouxel Olivier²

¹ Univ Brest, Lab Geosci Ocean, Inst Univ Europeen Mer, UMR 6538, F-29280 Plouzane, France.

² IFREMER, Ctr Brest, Unite Geosci Marines, F-29280 Plouzane, France.

³ Univ Minnesota, Dept Soil Water & Climate, St Paul, MN 55108 USA.

⁴ Univ Lausanne, Inst Earth Surface Dynam, CH-1015 Lausanne, Switzerland.

* Corresponding author : Bleuenn Gueguen, email address : bleuenn.gueguen@univ-brest.fr

Abstract :

Nickel (Ni) isotopes have recently emerged as a new biogeochemical tracer in marine environments, but our understanding of the mechanisms of Ni isotope fractionation in natural systems with regards to its fractionation by mineral surfaces is incomplete. This study aims to provide experimental constraints on Ni isotope fractionation during adsorption to goethite and 2-line ferrihydrite, two Fe minerals that vary in terms of distinct crystalline properties. We conducted two types of adsorption experiments: one with variable pH (5.0 to 8.0) and constant initial Ni concentration, one at a constant pH of 7.7 and variable initial Ni concentrations. Isotopic measurements were made on both the solid phase and the supernatant solutions in order to determine the Ni isotope fractionation factors ($\Delta 60/58$ Nimin-aq = $\delta 60/58$ Nimin - $\delta 60/58$ Niaq) between the mineral and aqueous phases. Our results show preferential adsorption of lighter Ni isotopes during adsorption of Ni to Fe oxyhydroxides presumably under conditions of near equilibrium conditions. Adsorption to goethite generates the greatest fractionation, with $\Delta 60/58$ Nimin-ag = -0.77 ± 0.23 % (n = 14, 2sd), whereas adsorption to 2-line ferrihydrite samples yield $\Delta 60/58$ Nimin-aq = -0.35 ± 0.08 % (n = 16, 2sd). Using Ni K-edge extended X-ray absorption fine structure (EXAFS) spectroscopy, we found that Ni forms an inner-sphere complex and that its coordination environment does not vary significantly with pH nor with surface loading. In addition, we found no evidence of Ni incorporation into the mineral. We suggest that the more than two-fold increase in Ni isotope fractionation in goethite relative to 2-line ferrihydrite is due to the lower Ni-Fe coordination number in the second shell, which results in the formation of a weaker surface complex and thus favors the adsorption of lighter Ni isotopes. These results show that Ni isotope fractionation during sorption by Fe-oxyhydroxides is dependent on mineralogy, which has important implications for the use of Ni isotopes as environmental tracers and the interpretation of their record in sedimentary rocks.

Keywords : Fe-oxyhydroxides, Sorption experiments, Nickel isotopes

26

27 **1. Introduction**

28

Nickel is a micro-nutrient in modern oceans and displays a nutrient-type profile in 29 seawater, where it is depleted in surface waters due to biological uptake (Bruland, 1980; Price 30 and Morel, 1991; Morel and Price, 2003). The evolution of marine biogeochemical Ni cycling 31 has become a topic of much interest as ancient metalliferous deposits because Banded Iron 32 Formations (BIF) appear to record a dramatic decrease in marine Ni concentrations through 33 geological time (Konhauser et al., 2009; Konhauser et al., 2015), attributed to a shift from 34 35 ultramafic volcanism and eruption of Ni-rich komatiites to basaltic volcanism as the Earth's 36 crust cooled. Iron-rich sedimentary rocks such as Granular Iron Formations (GIF) and BIF were deposited from seawater throughout much of the Precambrian and have been widely 37 used as an archive to reconstruct the geochemical composition of seawater in Precambrian 38 marine environments, in which Fe-oxyhydroxides were the carriers of trace metals (e.g., 39 Bekker et al., 2010). Hence, Ni isotope systematics of Iron Formations hold great promise for 40 the study of ancient biogeochemical cycles and paleo-environments. But first, the mechanisms 41 42 of Ni isotope fractionation during Fe-oxyhydroxide precipitation and burial need to be well 43 constrained.

The geochemical cycling of Ni in modern oceans is largely controlled by input from
continental weathering and riverine transport and removal from seawater through
precipitation in authigenic Mn-rich sediments (Sclater et al., 1976; Gall et al., 2013; Cameron
and Vance, 2014). Preliminary investigations have shown that seawater is characterized by an
average δ^{60/58}Ni value of 1.44 ±0.15‰ (2sd, n=29) relative to the NIST SRM 986
international standard, which is heavier than the average crustal value (estimated at 0.05
±0.05‰; Gueguen et al., 2013). The riverine input flux is estimated at a δ^{60/58}Ni value of

0.80% with a range of values from 0.29 % to 1.34% (Cameron and Vance, 2014). The 51 52 oceanic output flux, dominated by authigenic Mn-oxyhydroxides (Krishnaswami, 1976; Leinen, 1987; Koschinsky and Halbach, 1995; Manceau et al., 2002; Peacock and Sherman, 53 2007b), has a $\delta^{60/58}$ Ni value of ~1.7‰ (i.e., the average Ni isotope composition of 54 hydrogenetic ferromanganese crusts as reported by Gall et al. (2013) and Gueguen et al. 55 (2016)). The isotopically heavy signature of rivers relative to the bulk crust implies that a 56 light Ni isotopic reservoir should be retained in the continental crust, probably during soil 57 formation (Ratié et al., 2015). Based on isotopic mass balance considerations, Cameron and 58 Vance (2014) identified a missing source of isotopically heavy Ni in modern oceans. 59 Alternatively, the heavy Ni isotopic composition of seawater could be balanced by an oceanic 60 61 sink enriched in light Ni isotopes, perhaps in sulfides (Gueguen et al., 2013; Hofmann et al., 2014) associated with anoxic or suboxic marine sediments enriched in organic matter that 62 accumulate in reducing environments (e.g., continental margins with strong upwelling 63 regimes, restricted anoxic basins, fjords). However, the role of organic-rich sediments in the 64 Ni isotope mass balance is unclear as bulk $\delta^{60/58}$ Ni of organic-rich sediments display a large 65 range from 0.28‰ to 2.5‰ (Porter et al., 2014). 66

Large terrestrial Ni reservoirs exist in ultramafic complexes (Manceau and Calas, 67 68 1985; Valeton et al., 1987; Butt and Cluzel, 2013), and weathering of these complexes can 69 lead to significant Ni enrichment in laterites. While Ni released during weathering of ultramafic complexes will have a greater affinity for Mn-oxides (Manceau et al., 1987), a 70 71 significant portion of Ni is in fact sequestered in the abundant Fe-oxides (mostly goethite) formed during lateritization (Manceau et al., 2000; Quantin et al., 2008; Dublet et al., 2012; 72 Dublet et al., 2014; Ratié et al., 2015). In a recent study, Ratié et al. (2015) demonstrated that 73 weathering of ultramafic complexes leads to the enrichment of light Ni isotopes (by -0.47 ‰) 74 in Ni-rich laterites relative to unweathered bedrock, consistent with the preferential loss of 75

heavy Ni isotopes to the mobile phase and eventually to the riverine flux. Nickel in these
laterites is either incorporated into the mineral lattice or sorbed onto the mineral surface.
Nickel sorption on Fe-oxyhydroxides may therefore influence the isotope signature of Ni in
weathering environments, and in turn, the riverine flux of Ni to the oceans.

The use of Ni isotopes as biosignatures has also garnered attention in the recent 80 literature and the evolution of Ni biogeochemical cycling in the ancient oceans may be 81 recorded in the Ni isotope composition of coeval authigenic sediments. However, 82 understanding the isotope fractionation of metals such as Ni during adsorption to Fe-oxides 83 and other authigenic minerals is paramount to accurately reconstruct the biogeochemical 84 85 cycling of nutrients using the sedimentary record. Wasylenki et al. (2015) reported the 86 equilibrium Ni isotope fractionation factor during Ni sorption to ferrihydrite (experiments done at room temperature), showing an enrichment of the light Ni isotopes on the solid phase 87 by -0.35 ± 0.10 ‰ (1 sd). However, further studies are needed in order to evaluate in more 88 detail the mechanisms and range of parameters controlling Ni isotope fractionation during 89 adsorption onto mineral phases, including the effects of coordination environment or the type 90 of mineral phase (e.g., poorly crystalline versus more crystalline phases). For instance, 91 92 different Ni isotope fractionation could be expected among different Fe-oxyhydroxides based 93 on coordination chemistry considerations, because this effect has been observed for other metal/metalloid isotope systems such as Cu, Ge, Mo and Zn (Pokrovsky et al., 2008; Li and 94 Liu, 2010; Wasylenki et al., 2011; Pokrovsky et al., 2014). These experimental data are 95 96 crucial to interpret the trace metal isotopic records in Iron Formations, where the mechanism of formation of Fe-oxyhydroxides- precursor mineral phases and scavenging of trace metals 97 are poorly known, and to evaluate the preservation of the isotopic signal during 98 recrystallization. The role of iron oxides recrystallization on the Ni cycling is also important 99

to consider as it could have impacted the Ni signal preserved in Iron Formations (Frierdich etal., 2011).

To address this problem, we conducted Ni adsorption experiments on two synthetic 102 Fe-oxyhydroxides, 2-line ferrihydrite and goethite, as a function of pH, variable Ni loading to 103 104 pre-formed minerals, (i.e., no co-precipitation) and duration of experiments. Our goal is to mechanistically understand the isotope fractionation during Ni adsorption to Fe-phases with 105 106 different crystallinity, with special consideration to Ni speciation, coordination, and structure of adsorbent. The local coordination environment of Ni at the mineral surface was evaluated 107 by Ni K-edge EXAFS spectroscopy, while the isotopic fractionation of Ni between solid and 108 109 aqueous phases were measured by Multi Collector-Inductively Coupled Plasma-Mass Spectrometer (MC-ICP-MS) using double-spike (⁶¹Ni-⁶²Ni) correction of instrumental mass 110 bias. Our results build on the results of Wasylenki et al. (2015) regarding the causes for Ni 111 isotope fractionation. We expand on the role of Fe-oxides in the transfer of continental Ni to 112 the oceans and in the biogeochemical cycling of Ni isotopes, furthering the development of Ni 113 isotopes as a geochemical tracer in surface environments. 114

115

116 **2. Materials and methods**

117

118 We used synthetic mineral phases to investigate surface driven Ni isotope 119 fractionation. The use of synthetic mineral phases allowed for Ni K-edge EXAFS 120 spectroscopy on samples with low Ni concentration without interference from significant 121 amounts of incorporated Ni. Goethite (α -FeOOH) and 2-line ferrihydrite were synthesized by 122 raising the pH of a Fe(NO₃)₃ solution with KOH at 25°C. Goethite was formed by heating the 123 solid precipitate at 70°C for 60 hours following the protocol of Cornell and Schwertmann 124 (2003). The precipitates were washed three times with ultrapure water and centrifuged at

125	7,000 rpm for 30 minutes. The goethite was stored freeze-dried while the 2-line ferrihydrite
126	was synthesized within 48 hours of each experiment and stored at -30°C. The synthetic
127	minerals were characterized by BET (Brunauer-Emmett-Teller) surface area, powder X-ray
128	diffraction, and electrophoretic mobility. For BET, samples were dried and degassed at 150°C
129	before specific surface area was measured by N_2 adsorption (Micromeritics Tristar II 3020).
130	The specific surface areas for goethite and 2-line ferrihydrite were 25.5 and $119 \pm 3 \text{ m}^2/\text{g}$,
131	respectively. Bulk powder X-ray diffraction was performed using a Pananalytical X'Pert Pro
132	diffractometer (Characterization Facility, University of Minnesota). Mineral surface charge,
133	which is reflected in surface electrokinetic potential, was determined using a ZetaPALS
134	analyzer (Brookhaven Instruments Corp.) for 0.98 - 1.44 g/L of mineral suspended in
135	ultrapure water. Instrumental settings consisted of an applied voltage of 7.54V and electric
136	field of 9.29 V/cm. Data were acquired over 3 cycles of 5 measurements per mineral
137	(Electronic Annex, Table A1).

138

139 2.1. Nickel sorption experiments

140

For the Ni sorption experiments, a stock solution of 17 mmol/L Ni (1000 mg/L Ni) 141 142 was made with a Ni(NO₃)₂·H₂O(aq) salt (Fischer Scientific). Aqueous suspensions were prepared with 0.15 g of goethite or 2-line ferrihydrite in 150 mL of 0.05 mol/L NaNO₃ in 250 143 mL Teflon bottles. The Fe-oxyhydroxides were allowed to equilibrate for 24 hours at the 144 145 target experimental pH before the addition of an aliquot of Ni from the stock solution. Nickel was added slowly using a micropipette over a 15 minutes' period, with continuous mixing 146 with a Teflon-coated stir bar to reduce changes to the pH of the suspension. A control 147 consisting of the mineral in 0.05 mol/L NaNO₃ solution with no Ni added was included with 148 each set of experiments and Ni in the blank did not exceed 0.1% of the total amount of Ni 149

measured during Ni sorption experiments. Samples were named according to the adsorbent
(i.e., "Fh" for 2-line ferrihydrite and "Goe" for goethite) and the type of experiment (i.e.,
"pH" for pH-dependent experiments, "C" for varying initial Ni concentration experiments and
"T" for time-dependent experiments).

Nickel sorption experiments (Table 1) were performed as a function of pH (pH 5.0, 154 6.0, 7.0, 7.7 and 8.0) with an initial Ni concentration of 170 µmol/L Ni (10 mg/L Ni). A 155 156 separate set of Ni sorption experiments were also performed at pH 7.7 as a function of initial Ni concentration (17, 85, 170, 341, and 426 µmol/L Ni). The suspension pH was maintained 157 constant within ± 0.2 pH units with a custom-built pH control system consisting of 6 Hanna 158 159 Instruments HI 504 controllers, each equipped with a Thermo Scientific Orion 9110 pH electrode. Adjustments of the pH were made with additions of 0.05 mol/L HCl and 0.05 160 mol/L NaOH using two 3-way General ValveTM solenoid valves and a Manostat Carter 161 peristaltic cassette pump. The pH electrodes were calibrated using pH 4 and pH 7 commercial 162 buffers before each experiment. After the addition of Ni, the suspension was allowed to react 163 for 24 hours before the solution was separated from the solids by vacuum filtration (0.22 µm 164 polycarbonate filter, Millipore). The solids were not rinsed prior to storage or analysis. After 165 166 filtration, the supernatant solution was refrigerated at 2°C until analysis by ICP-MS and the solid material on filter was stored at -20° C. The solid-phase samples on the filter membranes 167 were cut in half and reserved for Ni K-edge EXAFS spectroscopy and isotopic analysis. 168 Time-dependent experiments were done to check whether kinetic isotopic effects are 169 170 affecting our experiments (Table 2). They were performed at a fixed pH of 7.7 and at two

171 different initial Ni concentrations of 170 μ mol/L and 426 μ mol/L, in order to assess the

172 potential effect of dissolved Ni concentration (i.e., Ni loading) on Ni isotope fractionation

173 factor. Four different batches were prepared for each initial Ni concentration and were

allowed to react for 18 (or 19 hours for 2-line ferrihydrite), 20, 22, and 23 hours, respectively.

A maximum equilibration time of 24 hours was chosen based on our initial test time-175 176 dependent experiments with goethite and ferrihydrite in which the aqueous Ni concentration stabilized after 18 to 23 hours of reaction, consistent with experimental design implemented 177 by Wasylenki et al. (2015). These findings are consistent with bulk chemical equilibrium and 178 were used to choose the reaction time for the adsorption experiments. This also prevents the 179 potential effect of diffusion-controlled penetration of Ni into Fe (oxy)hydroxides on Ni 180 isotope fractionation, since this process has been shown to occur over long (week to month) 181 timescales, while surface adsorption reaches completion within a few hours (Bruemmer et al., 182 1988). As discussed below, at bulk chemical equilibrium the mineral continues to exchange 183 184 Ni with the aqueous phase, so isotopic changes are still possible. By contrast, no net change in 185 loading to the mineral occurs, implying that the Ni concentration in the mineral is constant. 186

- 187 2.2. Nickel K-edge EXAFS spectroscopy
- 188

Nickel K-edge EXAFS spectroscopy measurements were conducted at the Advanced 189 Photon Source (Argonne National Laboratory) at beamline 20-BM in fluorescence mode 190 191 using a 12-element Canberra germanium detector. The Ni-sorbed minerals were prepared for 192 Ni K-edge EXAFS analysis by thawing to room temperature and transferring from the filter to a mylar adhesive with a microspatula. Multiple mylar layers were stacked (6-8 layers) and the 193 edges sealed to form an envelope around the sample. Measurements were conducted at room 194 195 temperature and individual scans were examined for systematic changes in peak-position or 196 shape to detect photon-induced sample alteration; none was observed. Multiple scans were 197 averaged to improve the signal to noise ratio. The Athena program was used for averaging replicate scans and energy calibration (Ni foil with inflection point set to 8334.5 eV), and the 198 Artemis program was used to generate phase and amplitude paths for Ni K-edge EXAFS 199

fitting (Ravel and Newville, 2005). Data reduction, including background subtraction and 200 conversion to k-space, and shell-by-shell fitting were performed using the SixPack software 201 package (Webb, 2005) with the following settings: $E_0=8347 \text{ eV}$, Rbkg=1.0 Å (Kelly et al., 202 2008), a Gaussian pre-edge function, quadratic post-edge function, no clamping, default 203 spline knots value, a Kaiser-Bessel window function, and a k-weight =3. The amplitude 204 reduction factor, $S_0^2 = 0.96$, was determined by fitting the first coordination shell of aqueous 205 206 published standards (NiCl₂ and Ni-EDTA) (Peña et al., 2010). Fits were evaluated using the calculated R-factor with a value of 0.05 or less representing a reasonable fit (Kelly et al., 207 2008). 208

X-ray absorption spectra were collected from 8130 to 9300 eV. Models for the
adsorption geometry of Ni were based on the assumption that Ni coordinates to Fe octahedra
via edge-sharing or corner-sharing linkages. First, the Ni-O shell was fit with all parameters
varied. The optimized parameters for the first shell were constrained in subsequent fits, which
included second-shell Ni-Fe paths.

The Ni-Fe second shell was modeled assuming to the occurrence of short and long 214 bond distances, following the model used for Ni/Zn sorption on ferrihydrite (Arai, 2008; 215 216 Cismasu et al., 2013). Specifically, two types of bond orientations between Fe and Ni 217 octahedral were modeled. Type 1 is comprised of a Ni octahedron that shares an edge, two 218 bond via two shared oxygen molecules, with an Fe octahedra (mineral surface). Type 2 is comprised of a Ni octahedron that shares a corner, or one bond via a shared oxygen, with an 219 220 Fe octahedra (mineral surface). Type 1 bond distances are shorter and share more bonds with the mineral surface than Type 2. Distortion of the Ni-O coordination sphere can be influenced 221 by either the number of bonds with the mineral surface, or geometric strain introduced due to 222 the type of surface site (e.g., number/type of Fe octahedra) to which the Ni binds. 223

224	The Ni K-edge EXAFS model was based on published coordination number (CN)
225	ratios of a short and long Ni-Fe and Zn-Fe paths in the second shell of Ni K-edge EXAFS
226	data from Ni/Zn-adsorbed 2-line ferrihydrite samples (Table 3) (Manceau and Gates, 1997;
227	Carvalho-E-Silva et al., 2003; Arai, 2008; Dublet et al., 2012; Cismasu et al., 2013). Reported
228	CN ratios for Ni-sorbed 2-line ferrihydrite ranged from 0.4 :0.7 (CN _{short} :CN _{long}) with a
229	maximum total second-shell CN of 5 (Arai, 2008). Thus, CN _{short} :CN _{long} ratios of 1:1 to 4:5
230	were tested in the model. A ratio of 2:3 best described the Ni K-edge EXAFS data in both fit
231	statistics and uncertainty of varied parameters. In the final model, two type 1 Ni-Fe paths
232	were modeled for every three type 2 Ni-Fe paths. The uncertainties on the CN values are
233	between 0.144 and 0.931 (estimated to be ~25% of the CN value) and the uncertainties on the
234	interatomic distances are between 0.0078 and 0.0618 Å.
235	
236	2.3. Aqueous speciation of Ni
237	
238	The aqueous speciation of Ni was calculated for the initial experimental conditions
239	using the MINEQL+ v.4.6 software program (Environmental Research Softaware) with
240	default stability constants. The calculations used the initial Ni concentrations (17, 85, 170,
241	341, and 426 μmol Ni/L), pH range (5.0 to 8.0 in 20 steps), ionic strength (0.05 mol/L
242	NaNO ₃), and partial pressure of CO ₂ g (0.03943 vol%) for a system in contact with the
243	atmosphere and showed that no Ni precipitation is predicted for our experimental conditions.
244	We used Ni surface complexation values for bidentate adsorption on goethite [$2 = SOH + Ni^{2+1}$
245	$\Rightarrow = 2(SOH)Ni + 2H^+$, log K = -2.45] from Xu et al. (2006), and for ferrihydrite, monodentate
246	adsorption per Dzombak and Morel (1990) (their classic two-site ferrihydrite model, strong
247	and weak sites, as already included in vMINTEQ). For aqueous speciation calculations during
248	adsorption modeling, the default vMINTEQ thermo.vdb database was used, which is an

expanded version of the MINTEQA2 database. Between pH 5.0 and 7.0, the dominant Ni 249 250 species in aqueous solution, under the initial experimental conditions considered here, is the Ni²⁺ (hexaquo) (> 88 %). In addition to Ni²⁺ (hexaquo), NiNO₃⁺ is present and accounts for > 251 11% of the Ni in solution. For the experiments with a pH value greater than 7.0, the aqueous 252 Ni species include minor contributions from NiHCO₃⁺ and NiCO₃⁰. Slow addition of Ni 253 during the experiments over a 15-minutes period reduced the risk of precipitation of Ni above 254 pH 7.8. For the experiments at pH 7.7, Ni occurs as: (1) 83.7% Ni²⁺ (hexaquo); (2) 10.7 % 255 NiNO₃⁺; (3) 4.1 % NiHCO₃⁺; and (4) 1.5 % NiCO₃⁰ for initial Ni concentrations ranging from 256 17 to 426 μ mol/L. 257

258

259 2.4. Concentration determinations and column chromatographic purification of Ni

260

All manipulations were performed in a class 1000 clean room and exclusively used 261 acid-cleaned plasticware and teflonware. Solid samples were digested in 6 mol/L HCl at room 262 temperature for 72 hours. The total concentrations of Ni and Fe in the solids were determined 263 by quadrupole ICP-MS (X-series2, Thermo Scientific) at the Pôle Spectrométrie Océan (PSO, 264 Brest, France). Nickel concentrations in the filtrates were first estimated by mass balance 265 266 using the initial concentrations in solutions used at the start of each experiment and the Ni concentrations in the solids determined by quadrupole ICP-MS at the end of the experiment. 267 Nickel concentrations were then recalculated by isotope dilution after isotope measurements. 268 269 For the separation of Ni onto chromatographic columns, an aliquot of each filtrate was evaporated to dryness at 80°C prior to redissolution in 1 ml of 6 mol/L HCl. A full description 270 of the purification method can be found in Gueguen et al. (2013). Briefly, our two-step 271 separation procedure involved: (1) separation of Fe onto an anion exchange chromatographic 272 resin (BioRad AG1-X8, 100-200 mesh); (2) separation of Ni from the remaining matrix using 273

274	a Ni-specific resin (Ni-Spec by Eichrom). This Ni-resin contains dimethylglyoxime (DMG)
275	functional groups, which complexes Ni in ammonium citrate solutions at pH 8-9. Nickel is
276	then eluted with 3 mol/L HNO ₃ after breakdown of the Ni-DMG complex.
277	
278	2.5. Ni isotope mass spectrometry and double-spike correction scheme
279	
280	Nickel isotope compositions were measured by MC-ICP-MS (Neptune, Thermo
281	Scientific) at the PSO (Brest, France) using a double spike for mass bias correction following
282	the method described in Gueguen et al. (2013). The double spike is a mixture of ⁶¹ Ni and ⁶² Ni
283	that was added to samples at spike/natural ratio of 1 prior to the chromatographic separation
284	on Ni-specific resin. Corrected ratios were calculated using an iterative scheme following the
285	method described by Siebert et al. (2001). An ESI (Elemental Scientific Inc., USA)
286	desolvating introduction system (ApexQ) was employed for all measurements. The nine
287	Faraday cups of the instrument allowed simultaneous measurement of Ni isotopes ⁵⁸ Ni, ⁶⁰ Ni,
288	⁶¹ Ni, ⁶² Ni, ⁶⁴ Ni, and potential isobaric interferences from Zn (measured on ⁶⁶ Zn) and Fe
289	(measured on ⁵⁷ Fe). Argon oxide interferences (e.g., ⁴⁰ Ar ¹⁸ O ⁺ on ⁵⁸ Ni ⁺ and ⁴⁰ Ar ¹⁷ O on ⁵⁷ Fe)
290	were resolved using the medium resolution mode of the MC-ICP-MS.
291	Nickel isotope values were reported according to the conventional delta notation
292	(equation 1) relative to the Ni international isotopic standard NIST SRM 986 :
293	$\delta^{60/58} \text{Ni} (\%) = (^{60/58} \text{Ni}_{\text{sample}} / ^{60/58} \text{Ni}_{\text{NIST986}} - 1) \times 1000 $ (1)
294	For each sample, 50 measurement cycles were performed, resulting in an internal standard
295	error (2se) value typically between 0.02 and 0.04 ‰. The external precision was evaluated
296	through the duplicated measurements of geostandards (USGS Nod-P-1, $\delta^{60/58}$ Ni=0.33‰; and
297	USGS Nod-A-1, $\delta^{60/58}$ Ni=1.04‰) and was found to be ~0.06 ‰ (2sd).

- 299 **3. Results**
- 300
- 301 *3.1. Nickel sorption by Fe oxyhydroxides*
- 302

The loadings of Ni onto both 2-line ferrihydrite and goethite expressed in terms of the 303 304 percent of Ni sorbed for pH-dependent and varying initial [Ni] experiments are displayed in Table 1. The sorption of Ni onto 2-line ferrihydrite for pH ranging from 5.0 to 8.0 (i.e., pH-305 dependent experiments, with initial Ni concentration of 170 µmol/L) resulted in Ni uptake 306 between < 1% and 45% translating into 0.02 to 0.62 µmol Ni/m² mineral (Figure 1a). At pH 307 7.7 (varying initial Ni concentrations experiments, 17 to 426 µmol/L Ni), final Ni loadings on 308 2-line ferrihydrite ranged from 0.11 to 1.71 µmol Ni/m² mineral (Figure 1), which correspond 309 310 to a percentage of sorbed Ni between 25% and 78%. Nickel sorption to goethite at pH 5.0, 6.0, and 8.0 resulted in Ni uptake between < 1% 311 and 4.3% of the initial 170 µmol/L aqueous Ni (Figure 1), corresponding to Ni loadings 312 ranging from 0.04 and 0.28 µmol Ni/m². At pH 7.7, Ni uptake from solutions with initial 313

concentrations of 17, 170, and 426 µmol/L Ni yielded final Ni loadings onto the mineral
between 0.63 to 1.33 µmol Ni/m², corresponding to percentage of sorbed Ni between 8% and

316 19%.

Zeta potential measurements at pH 7 indicated that 2-line ferrihydrite exhibits a net
negative surface charge with a value of -3.44 mV (Electronic Annex, Table A1). Zeta
potential measurements at pH 7 indicated that goethite exhibits a net positive surface charge
with a value of +3.46 mV. 2-line ferrihydrite has more Ni-sorbed at pH 7 than goethite, which
is consistent with the more negative surface charge of 2-line ferrihydrite relative to goethite.

323 *3.2. Surface complexation modeling*

324

325	Constant capacitance surface complexation modeling (CCM) for Ni adsorption to 2-
326	line ferrihydrite and goethite (Figure 2) was implemented using adsorption parameters
327	provided by Dzombak and Morel (1990), Xu et al. (2006) and Davis and Kent (1990), in order
328	to verify that sorption processes control Ni behavior in our experiments. Our experimental
329	data for 2-line ferrihydrite were in good agreement with the surface complexation model
330	calculated with parameters from Dzombak and Morel (1990) (Figure 2). The best fit of our
331	data for Ni adsorption to goethite was obtained with a constant capacitance model (Figure 2)
332	generated using adsorption constants from Xu et al. (2006) for bidentate adsorption in the Ni-
333	goethite system, our BET-measured surface area of 25.5 m^2/g , solid concentrations close to 1
334	g/L, and a goethite site density of 1 site per nm ² . Adopting higher literature values for the
335	latter (e.g., 2.3 sites per nm ² (Davis and Kent, 1990) or 6 sites per nm ² (Xu et al., 2006))
336	results in model adsorption values significantly higher than what was observed. Finally, it is
337	important to point out that the CCM is a simple surface complexation model that integrates a
338	smaller number of parameters in comparison to the diffuse-layer model and the triple-layer
339	models (Hayes et al., 1991) and thus may not approximate natural conditions as closely.
340	

341 3.3. Nickel K-edge EXAFS Spectroscopy

342

Nickel K-edge EXAFS spectra were collected for six Ni-sorbed 2-line ferrihydrite
samples (Fh-pH-05, Fh-C-07, Fh-C-08, Fh-C-09, and Fh-C-10) and one Ni-sorbed goethite
sample (Goe-C-06) as indicated in Table 1. The Ni K-edge EXAFS spectra collected for the
2-line ferrihydrite samples at pH 7.7 and 8.0 are similar in phase and amplitude despite
different Ni-loadings and pH values (displayed in k-space with best fits; Figure 3). All Ni Kedge EXAFS spectra were fit with ~ 6 Ni-O atom pairs in the first-shell at a distance of 2.05 ±

3490.01 Å (Table 3). For the Ni-Fe second-shell atom pairs, two sub-shells were required to350describe the data: ~ 1.5 Ni-Fe (type 1) at 3.10 ± 0.02 Å and ~ 0.6 Ni-Fe (type 2) at 3.56-3.60351 ± 0.06 Å. Errors in the second shell coordination numbers were estimated using the fractional352parameter error as an indicator. As these error values were low we estimated CN error to be353~25% of the value.

The magnitude and imaginary portion of the Fourier transformed Ni K-edge EXAFS 354 spectra and fits are displayed in Figure 4. The only notable difference in the Ni K-edge 355 EXAFS derived fit parameters obtained for 2-line ferrihydrite and goethite was a lower Ni-Fe 356 coordination number in the type 1 second shell for Ni-sorbed goethite. Nickel sorbed to 357 358 goethite had on average 1.0 ± 0.4 Fe in its second shell, while Ni-sorbed to 2-line ferrihydrite 359 had an average of 2.2 ± 0.56 Fe atoms in its second shell (Table 3). This difference can be viewed by comparing peak amplitudes of the two minerals whereby 2-line ferrihydrite 360 samples have greater peak amplitudes than goethite. The Ni K-edge EXAFS data are also 361 consistent with the formation of inner-sphere complexes with no evidence for a separate Ni 362 phase. 363

364

365 *3.4. The Ni isotope composition of sorbed Ni and supernatant solutions*

366

The Ni isotope composition of the initial Ni stock solution was determined at $\delta^{60/58}$ Ni = -0.33 ± 0.05 ‰ (2sd, n=4, Table 1). The Ni isotope compositions of mineral-associated Ni (i.e, sorbed onto 2-line ferrihydrite and goethite) and solution are reported in Table 1. The difference in Ni isotopic composition between the mineral sorbed-Ni and Ni remaining in solution, which we define as the fractionation factor, is expressed as $\Delta^{60/58}$ Ni_{minaq} (equation 2) according to:

374
$$\Delta^{60/58} \text{Ni}_{\text{min-aq}} = \delta^{60/58} \text{Ni}_{\text{mineral}} - \delta^{60/58} \text{Ni}_{\text{aqueous}}$$
(2)

375

Figure 5 presents $\delta^{60/58}$ Ni values of the mineral and the associated filtrate versus corresponding percent Ni sorbed in pH-dependent, variable initial Ni concentration and timedependent experiments. The results show a systematic enrichment in light Ni isotope compared to the starting solution during Ni sorption to the mineral surface, which is accompanied by enrichment of the residual aqueous Ni in heavy isotopes. Isotopic mass balance (equation 3), was verified for each sample and was consistent within uncertainty with the Ni isotope composition of the original stock solution (Table 1).

383

384
$$\delta^{60/58}$$
Ni_{bulk} = (%Ni_{sorbed}/100 x $\delta^{60/58}$ Ni_{mineral}) + ((1 - %Ni_{sorbed}/100) x $\delta^{60/58}$ Ni_{aqueous}) (3)

385

The magnitude of the Ni isotope fractionation factor $\Delta^{60/58}$ Ni_{min-aq} (equation 2) between the solid phase and aqueous phase is larger for goethite (-0.77 ±0.23 ‰) than for 2-line ferrihydrite (-0.32 ±0.20 ‰), with no significant correlation with the percentage of adsorption (Figures 5 and 7). We observe consistent and similar $\Delta^{60/58}$ Ni_{min-aq} values for pH-dependent and variable Ni concentration experiments for 2-line ferrihydrite on the one hand, and for goethite on the other hand.

The pH-dependent adsorption experiments on 2-line ferrihydrite yielded surface loadings from 0.02 to 0.62 µmol Ni/m² mineral with $\Delta^{60/58}$ Ni_{min-aq} values ranging from -0.37 to -0.03 ‰ (Figure 6). At low loadings of Ni onto 2-line ferrihydrite, i.e., 0.02 – 0.04 µmol Ni/m² mineral which correspond to 1 and 3% percent of to the total added Ni sorbed in the pH 5.0 and 6.0 experiments, Ni isotopes were not fractionated ($\Delta^{60/58}$ Ni_{min-aq} = -0.03‰) or weakly fractionated ($\Delta^{60/58}$ Ni_{min-aq} = -0.12 ‰) respectively. Although Figure 6 seems to indicate that decreasing $\Delta^{60/58}$ Ni_{min-aq} values are correlated with increasing pH for 2-line ferrihydrite, we think these data are an artifact since low pH values (5.0 and 6.0) also correspond to very low Ni loadings (see discussion). For this reason, we decided to not include these data when discussing average Ni isotope fractionation factors. In contrast, at pH 7.7, the percent Ni sorbed was generally higher and Ni loadings of $0.32 - 1.71 \mu mol Ni/m^2$ mineral were achieved, which represent between 23 and 78% Ni-sorbed on 2-line ferrihydrite. This gave a range of $\Delta^{60/58}Ni_{min-aq}$ values between -0.40 and -0.24 ‰ (Figures 6 and 7).

405 Nickel sorption by goethite for the pH-dependent experiment was minimal, ranging 406 from 0.6 to 4% of the initial Ni (corresponding to loadings of $0.04 - 0.28 \,\mu$ mol Ni/m²

407 mineral), and Ni isotope fractionation was characterized by $\Delta^{60/58}$ Ni_{min-aq} values between -0.96

and -0.70 % (Figure 6). At pH 7.7 and for different initial Ni concentrations, final loadings of

409 Ni of 0.63 to 1.33 μ mol Ni/m² mineral yielded $\Delta^{60/58}$ Ni min-aq values between -1.03 and -0.78

410 % (Figure 6). Goethite with the lowest loading of Ni (also corresponding to the lowest pH)

411 displayed the smallest Ni isotope fractionation factor relative to other samples, with

412 $\Delta^{60/58}$ Ni_{min-aq} = -0.70 ‰ and -0.88 ‰ for pH 5.0 and 6.0, respectively. The largest $\Delta^{60/58}$ Ni_{min-}

413 aq value of -1.03 ‰ was measured at pH 7.7 for goethite with the highest Ni loading.

Time-dependent experiments were performed in order to identify potential kinetic effects (i.e., non-equilibrium Ni fractionation) in our experiments. Experiments were conducted for four different durations, i.e., 18 or 19, 20, 22, and 23 hours and for two different initial Ni concentrations of 170 µmol/L and 426 µmol/L (Table 2). The Ni isotope fractionation factor $\Delta^{60/58}$ Ni_{min-aq} is between -0.77 and -0.72 ‰ (average $\Delta^{60/58}$ Ni_{min-aq} = -0.75 ± 0.05 ‰; 2sd, n=4) and $\Delta^{60/58}$ Ni_{min-aq} values are between -0.73 to -0.62 ‰ (average $\Delta^{60/58}$ Ni_{min-aq} = -0.67 ± 0.09 ‰; 2sd, n=4) for the two experiments respectively.

421

422 **4. Discussion**

424	Previous work on non-traditional isotope systems, such as Mo (Barling and Anbar,
425	2004; Goldberg et al., 2009; Kashiwabara et al., 2009; Wasylenki et al., 2011), Zn (Pokrovsky
426	et al., 2005; Juillot et al., 2008), Cu (Balistrieri et al., 2008; Pokrovsky et al., 2008), Tl
427	(Rehkämper et al., 2002), Cd (Wasylenki et al., 2014), Hg (Jiskra et al., 2012), Fe (Icopini et
428	al., 2004; Mikutta et al., 2009; Beard et al., 2010; Wu et al., 2011; Wu et al., 2012; Frierdich
429	et al., 2014), Ge (Li and Liu, 2010; Pokrovsky et al., 2014), and Se (Mitchell et al., 2013)
430	have shown that adsorption reactions are often accompanied by significant isotope
431	fractionation processes that may vary according to sorbent composition and sorbate structure.
432	By contrast, sorption of Cr(VI) to Fe-oxyhydroxides is not accompanied by significant isotope
433	fractionation (Ellis et al., 2004). Hence, the combination of spectroscopic and isotopic
434	measurements is essential for understanding isotopic fractionation processes. Here, we discuss
435	the result of both approaches to address the mechanisms and significance of Ni isotope
436	fractionation during Ni sorption to Fe-oxyhydroxides.
437	

438 *4.1. Surface coordination of Ni at the mineral surface*

439

440 Coordination chemistry (i.e., coordination number, bond length) correlates with the 441 extent of isotope fractionation because shorter bond lengths (i.e., stiffer bonds) or lower coordination numbers favor enrichment of heavier isotopes (e.g., Schauble, 2004; Pokrovsky 442 et al., 2005). The first coordination shell of a metal is comprised of oxygen atoms. Variations 443 of the coordination number of the metal (e.g., between the aqueous phase and the solid phase) 444 during adsorption of a transition metal to the surface of any given Fe-oxyhydroxide mineral is 445 a common cause for isotope fractionation. For instance, heavy isotope enrichment during Zn 446 sorption on ferrihydrite was accounted for by a decrease in the coordination number of the 447 aqueous species relative to the adsorbed species. According to EXAFS data, the adsorption of 448

Zn onto ferrihydrite produces a significant shift in Zn coordination number, from 6 in the 449 450 solution to 4 in the solid, while Zn sorbed on goethite occurs in octahedral coordination, i.e., similar to aqueous Zn. The larger isotope fractionation factor measured for ferrihydrite 451 relative to goethite can thus be explained by a different coordination environment of the 452 sorbed Zn (i.e., 4 for ferrihydrite and 6 for goethite) and differences in Zn-O bond stiffness 453 (i.e., 1.96 Å for ferrihydrite and 2.11 Å for goethite; Juillot et al., 2008). For Ni, isotopic 454 fractionation cannot be related to changes in the coordination number between aqueous Ni 455 and sorbed Ni because Ni exclusively occurs in coordination 6 in the natural environment. 456 The length of Ni – O bonds in water is 2.1 Å compared to the 2.05 Å observed when Ni is 457 458 sorbed to the mineral surface (Soper et al., 1977), therefore, heavier Ni isotopes enrichment 459 should be expected during sorption to the mineral surface. The systematic enrichment in lighter Ni isotopes on the mineral phase found in this study and in Wasylenki et al. (2015) 460 precludes this option. 461

Wasylenki et al. (2015) suggest that distortion of the coordination environment after 462 Ni sorption to ferrihydrite could explain light Ni isotopes enrichment of the mineral surface. 463 Given our Ni K-edge EXAFS data quality it was not possible to support or refute this 464 hypothesis because we could not achieve fitting multiple Ni-O paths to the Ni-O shell (first 465 466 coordination shell). However, the number of bonds between Ni and surface oxygens, which is reflected in the second shell parameters (i.e., surface complex geometry), may cause slight 467 distortion or distribution of the electron density in the first coordination shell, even if they 468 469 cannot be captured by the Ni K-edge EXAFS data. Thus, we argue that the number of bonds between Ni and surface oxygens could distort the first coordination shell. 470

471 Consistent with previous studies (Manceau et al., 2000; Carvalho-E-Silva et al., 2003;
472 Arai, 2008; Dublet et al., 2012) adsorbed Ni displayed octahedral coordination (Electronic
473 Annex, Table A2). For an inner-sphere surface complex of Ni on Fe oxyhydroxides, the

second major coordination shell is composed of Fe atoms. The interatomic distances between 474 475 Ni and Fe, as measured by Ni K-edge EXAFS spectroscopy, define the local coordination environment of the Ni surface species and Ni sorbed on ferrihydrite and goethite have been 476 studied in detail (Waychunas et al., 2002; Arai, 2008; Juillot et al., 2008; Dublet et al., 2012; 477 Cismasu et al., 2013). It was demonstrated that Ni sorbed on ferrihydrite occurs in octahedral 478 coordination between Ni-O₆ and Fe-O₆ polyhedra with interatomic distances in the range of 479 3.05-3.08 Å for edge-sharing type 1 surface complexes, 3.19-3.12 Å for edge-sharing type 2, 480 and 4.03-4.07 Å for corner-sharing (Arai, 2008). Type 1 edge sharing is between Ni and Fe 481 octahedra in the chains and type 2 surface complexes is between Ni and Fe octahedra in the 482 483 rows (Arai, 2008). The interatomic distances modeled here for goethite samples reflect the 484 three Fe-Fe second-shell interatomic distances for edge-sharing coordination between Ni and a chain of Fe-O₆ octahedra (i.e., type 1), edge-sharing between chains of Fe-O₆ octahedra (i.e., 485 type 2), and corner-sharing Fe-O₆ octahedra between double chains (Manceau and Drits, 486 1993). 487

Incorporation of Ni into Fe-oxyhydroxides lattices is possible, but our Ni K-edge 488 EXAFS data shows the absence of Ni incorporation in the minerals. Cornell et al. (1992) 489 reported Ni incorporation into synthetic goethite at ~5% of the total molar fraction and several 490 491 studies showed that incorporation of Ni in goethite occurs via diffusion into the mineral lattice 492 where Ni can occupy vacant Fe positions in synthetic goethite (Barrow et al., 2012; Brümmer et al., 2013). Fischer et al. (2007) showed that Ni reaction with the goethite surface is 493 494 continuous with time and that Ni is incorporated via diffusion in the lattice structure of the mineral. Wasylenki et al. (2015) reported nearly identical isotopic signatures for surface 495 sorbed Ni and incorporated Ni, suggesting that the influence of incorporated Ni is negligible 496 in the isotopic budget and that potential Ni isotope fractionation during diffusion can be 497 precluded. 498

499	The best Ni K-edge EXAFS model for Ni sorbed to 2-line ferrihydrite data, with two
500	Ni-Fe distances in the second shell, is consistent with a short Ni-Fe distance produced by
501	edge-sharing polyhedra (3.10 \pm 0.02 Å) in addition to a longer Ni-Fe distance produced by a
502	combination of edge-sharing and corner-sharing polyhedra not resolved by our Ni K-edge
503	EXAFS data (3.57 \pm 0.06 Å). The data quality for the Ni-sorbed goethite prevented a robust
504	second-shell fit to the Ni K-edge EXAFS. However, the fit results were consistent with a Ni-
505	Fe atom pair at 3.07 \pm 0.03 Å and revealed a difference relative between goethite and 2-line
506	ferrihydrite in the Ni-Fe coordination number. The Ni K-edge EXAFS measurements on
507	goethite and 2-line ferrihydrite from this study also indicate that the Ni coordination
508	environment was similar among all samples. Therefore, the difference in Ni isotope
509	fractionation between the two minerals may be due to minor differences in surface site density
510	and distribution. Since no detectable difference in surface speciation was observed as a
511	function of Ni loading to the 2-line ferrihydrite surface at pH 7.7 or as a function of pH (7.7
512	versus 8.0), alternative variable parameters such as protonation state of the mineral, surface
513	complex geometry (e.g., number of bonds between Ni and mineral surface), surface coverage
514	or bond lengths between the two minerals might have influenced Ni isotope fractionation.
515	
516	4.2. Nickel isotope fractionation factors during Ni adsorption to Fe-oxyhydroxides

517

In the case of equilibrium isotopic fractionation, the fractionation factor between mineral and solution, the α_{min-aq} value (related to $\Delta^{60/58}$ Ni_{min-aq} values as $\approx 10^3$.ln α_{min-aq}), ultimately depends on the difference in bond stiffness between two species involved in the reaction. In a closed system, the Ni isotope composition of the solution and mineral-bound Ni are related to the proportion of Ni sorption to the mineral (Figure 5). If equilibrium isotope fractionation is maintained during the experiment, the fractionation factor, $\Delta^{60/58}$ Ni_{min-aq},

should remain constant regardless of the percentage of Ni adsorption and duration of the 524 experiments. We recognize that equilibrium isotope fractionation is best demonstrated using 525 the 3-isotopes method (Wu et al., 2011), which allows the determination of the rate of isotopic 526 exchange and extrapolate the isotope fractionation factors during incomplete isotope 527 exchange. Here, we mainly relied on the constant Ni isotope fractionation factor between 528 solution and mineral during the reaction progress in order to derive equilibrium $\Delta^{60/58}$ Ni_{min-aq} 529 values. Results obtained for 2-line ferrihydrite and goethite (i.e., pH dependent, concentration 530 dependent, and time dependent) are for the most part consistent with isotopic equilibrium in a 531 closed system (i.e., constant $\Delta^{60/58}$ Ni_{min-aq} values), although significant departure from this 532 relationship is observed at low percentage of Ni sorption (Figure 7) and in one goethite 533 534 sample (i.e., the variable initial Ni concentrations experiments with 19.3% Ni-sorbed (Figure 535 5)).

In order to derive meaningful Ni isotope fractionation factors from the experimental data, the % of Ni adsorption should be generally comprised between 5% to 95%, i.e., too low or too high values may pose problem in the determination of $\delta^{60/58}$ Ni of the mineral and solution, respectively. Using this more restricted dataset, we determine an average $\Delta^{60/58}$ Ni_{minaq} = -0.32 ±0.20 ‰ for the 2-line ferrihydrite and $\Delta^{60/58}$ Ni_{min-aq} = -0.77 ±0.23 ‰ for goethite.

For time-dependent experiments, we determine a range of $\Delta^{60/58}$ Ni_{min-aq} values for the 541 2-line ferrihydrite between -0.32 ± 0.04 and $-0.38 \pm 0.06\%$, and for goethite between -0.65542 ± 0.07 and -0.77 ± 0.07 %. Therefore, $\Delta^{60/58}$ Ni_{min-aq} values do not vary within uncertainties over 543 the course of the experiments. This is in agreement with previous results of Wasylenki et al. 544 (2015) showing no variations in $\Delta^{60/58}$ Ni_{min-aq} values for 2-line ferrihydrite for experiment 545 duration between a few hours to 30 days. There is also no appreciable difference in the 546 magnitude of Ni isotope fractionation factor depending on the initial Ni concentration and 547 sorption %, i.e., $\Delta^{60/58}$ Ni_{min-aq} = -0.35 ±0.01 ‰ (2sd, n=4) for an initial Ni concentration of 548

170 μ mol/L and $\Delta^{60/58}$ Ni_{min-aq} = -0.36 ± 0.05 ‰ (2sd, n=4) for an initial Ni concentration of 549 426 μ mol/L (Table 2). Average $\Delta^{60/58}$ Ni_{min-aq} values for 2-line ferrihydrite and goethite time-550 dependent experiments are also similar to the average value calculated for the pH-dependent 551 and varying initial Ni concentrations experiments suggesting that our experiments are at 552 isotopic equilibrium. The duration of experiments is the same for low Ni-sorbed samples than 553 for high Ni-sorbed samples. Therefore, if there were any kinetic effects we would expect them 554 to be similar whatever the amount of sorbed Ni or that larger isotope fractionation would 555 556 occur for low Ni-sorbed samples compared to high Ni-sorbed samples which is not the case in our experiments. Although these experiments did not allow the determination of isotopic 557 558 exchange rates between the solution and the mineral, which would have required shorter 559 experiment duration, we suggest that isotopic equilibrium was likely achieved in our experiments. This assumption is also consistent with previous goethite adsorption experiments 560 561 for Cu and Zn isotopes systematics (Pokrovsky et al., 2005; Pokrovsky et al., 2008) for which isotope fractionation factors were similar for short duration experiments (~20 hours) than for 562 long duration experiments (~ 100 days). 563

The smaller Ni isotope fractionation factors for goethite and 2-line ferrihydrite at low 564 % (Figure 7) can be explained in several ways: (1) non-equilibrium fractionation (i.e., kinetic 565 566 fractionation processes) due to partially irreversible reaction between sorbed Ni on the 567 mineral and Ni in solution; (2) a change in coordination chemistry in the mineral with pH and/or Ni loading; and (3) retention of aqueous Ni on the mineral during filtration, leading to 568 569 incomplete separation of Ni in mineral and Ni in solution. As explained above, timedependent experiments suggest that isotopic equilibrium is achieved which, thus, discounts 570 hypothesis (1). Hypothesis (2) can also be ruled out since no change in coordination 571 chemistry as a function of pH was observed in the Ni K-edge EXAFS measurements. We 572 propose that the low $\Delta^{60/58}$ Ni_{min-aq} values measured in samples prepared at low pH may be due 573

574	to the presence of a small fraction of the supernatant solution that remained trapped in the
575	mineral even after filtering, which would mute Ni isotope fractionation during adsorption.
576	Using the final Ni concentration measured in supernatant solutions and the estimated volume
577	of water present in the mineral, we calculated that the supernatant solution should contribute
578	between 0.0002 and 0.0070 $\mu mol~Ni/m^2$ for 2-line ferrihydrite. Hence, for low Ni-loading in
579	the 2-line ferrihydrite experiments, Ni in solution may account for between 13 % and 44 % of
580	the total Ni in the sorbed fraction. This mixing effect is the most plausible explanation
581	(hypothesis 3) for the variation in $\Delta^{60/58}$ Ni _{min-aq} values (i.e., decrease) at low Ni-loading.

582

583 4.3. Differences in Ni isotope fractionation between goethite and 2-line ferrihydrite

584

Our experiments showed that Ni sorbed to goethite is twice more fractionated towards 585 lighter $\Delta^{60/58}$ Ni_{min-aq} values (~ -0.77 ‰) than Ni sorbed to 2-line ferrihydrite (~ -0.35 ‰). 586 Nickel species in solution that are likely to be adsorbed onto minerals are the Ni²⁺ 587 (hexaquo) species (Peacock and Sherman, 2007a). The surface complexation model reported 588 in Figure 2 predicts that under the experimental conditions used in our study Ni should sorb to 589 590 goethite to a greater extent than we observed in our experiments. At pH values less than ~ 8.0 , 591 the expected point of zero net charge for goethite is such that it should be positively charged. 592 In contrast, the zeta potential measurements for 2-line ferrihydrite indicate a net negatively charged surface. The net negative surface charge of 2-line ferrihydrite tends to attract 593 594 dissolved cations to its surface while the net positive surface charge of goethite tends to repel dissolved cations and ferrihydrite has a higher surface area than goethite. This is in agreement 595 596 with the strong uptake of Ni from solution by 2-line ferrihydrite observed in our experiments and predicted by our surface complexation model (Figure 2). 597

Two different modes of isotope fractionation are then possible during Ni adsorption to 598 Fe-oxyhydroxides. One involves isotopic exchange among aqueous species in solution 599 followed by preferential adsorption of one of these species onto the mineral phase. This 600 mechanism may lead to contrasting isotope composition between the fluid and mineral, as 601 602 previously observed for the Mo isotope system (Siebert et al., 2003; Barling and Anbar, 2004). An alternative mechanism of fractionation may take place directly during metal 603 adsorption and involves the preferential adsorption of one isotope from the aqueous phase 604 onto the solid phase because of, for instance, differences in coordination chemistry or kinetic 605 effects. These two mechanisms are not mutually exclusive and combination of the two is 606 607 likely to occur in natural systems. Pokrovsky et al. (2014) identified five mechanisms that 608 could be responsible for equilibrium isotope fractionation during sorption reactions: (1) protonation of metal species in solution or on the mineral surface; (2) mineral surface 609 610 coverage and distribution of weak sites versus strong sites; (3) bond distances between the metal and oxygen atoms and the presence of other atoms in the mineral structure; (4) change 611 in coordination between the fluid and the solid phase; and (5) binding mode of the metal. 612 Below we evaluate each of these mechanisms in light of the results from our study. 613

Mechanism (1) : Protonation of aqueous or sorbed Ni. As a divalent cation, Ni has a relatively low ionic potential, e.g., in contrast to Fe^{3+} and Al^{3+} . Hence, $Ni(H_2O)6^{2+}$ does not readily undergo hydrolysis and Ni tends to form relatively weak aqueous complexes with ligands when compared to trivalent cations. In addition, because we expect the presence of a single aqueous Ni species, $Ni(H_2O)6^{2+}$, in our experiments there should be no isotopic fractionation occurring in solution.

Mechanism (2): Mineral surface coverage and distribution of weak and strong sites.
Villalobos et al. (2003) demonstrated that goethite synthesized with variable NaOH addition
rates yield variable site densities that are in turn reflected in adsorption behavior. The goethite

minerals synthesized in our study appear to fall on the low end of surface site concentrations 623 reported in literature for goethite. Our Ni K-edge EXAFS data and fits revealed no detectable 624 differences between low and high Ni loadings onto 2-line ferrihydrite. Therefore, we have no 625 evidence to support a fractionation mechanism based on discrimination between weak and 626 strong sorption sites. The Ni loading data when normalized to mineral surface area show no 627 distinct differences between 2-line ferrihydrite and goethite in terms of range or magnitude of 628 Ni surface coverage (Figure 1 and Table 1). This suggests that mineral surface loading does 629 not explain the Ni isotope fractionation observed in our experiments. 630

Mechanism (3): Bond distances between the metal and oxygen atoms and the presence of other atoms in the mineral structure. The minerals studied here were synthesized in the laboratory and are free of impurities. In addition, as discussed above, the Ni-O firstshell interatomic distances are indistinguishable among our 2-line ferrihydrite and goethite sorbents.

636 Mechanism (4): Change in coordination between the fluid and the solid phase. Based 637 on thermodynamic modeling, we expect the aqueous Ni speciation is > 80% Ni²⁺ (hexaquo), 638 Ni(H₂O)₆²⁺, and in octahedral coordination with O. Based on our Ni K-edge EXAFS data, the 639 Ni sorbed to 2-line ferrihydrite and goethite is also in octahedral coordination with O.

640 Mechanism (5): Metal bonding environment. The Ni K-edge EXAFS data and fit results indicate that the local coordination environment for Ni at the mineral surface is similar 641 for all Ni loadings and pH values for 2-line ferrihydrite. To determine whether we can extend 642 643 this finding to goethite, we compared two samples for which Ni K-edge EXAFS data were collected : (1) Goe-C-06 (1.33 µmol Ni/m²) and Fh-C-10 (1.71 µmol Ni/m²). These two 644 samples have similar Ni loadings when the amount of adsorbed Ni is normalized by specific 645 surface area (Table 1) and the Ni K-edge EXAFS-derived fit parameters for the Ni-O shell are 646 identical within errors. In other words, the Ni species have the same coordination number and 647

the same bond lengths for Ni-O (recall some of the coordinating oxygens are contributed by 648 the mineral and waters of hydration). The only difference in Ni speciation between the two 649 samples is a lower Ni-Fe coordination number in the second shell for Ni-sorbed goethite. On 650 average, the Ni sorbed to goethite has only 1.0 Fe (range 0.6-1.5) in its second shell, while Ni-651 sorbed to 2-line ferrihydrite has 2.2 Fe (range 1.8-2.7) (Table 3). This difference in surface 652 complex geometry, which may originate from the structure of goethite as discussed below, 653 suggest that the number of bonds formed between Ni and surface oxygen atoms, as indicated 654 by the number of Ni-Fe near neighbors, may influence the distribution of electron density in 655 the first coordination shell of Ni and thus influence its isotopic fractionation. 656

657 Of these possible mechanisms, only mechanism (5) 'binding mode of the metal' 658 provides a good explanation for our data. Specifically, we observe a subtle difference between the Ni-Fe second-shell coordination environment when comparing two Ni-sorbed mineral 659 660 samples having similar Ni loading when expressed in terms of surface area rather than total mass. Nickel sorbed to goethite has fewer Fe atoms in the second-shell than Ni sorbed to 2-661 line ferrihydrite. The goethite structure is known to generate three different surface functional 662 groups based on the number of Fe atoms bonded to a surface oxygen (Essington, 2003) : type 663 (1) \equiv Fe₃-O^{1/2-}, type (2) \equiv Fe₂-O¹⁻, and type (3) \equiv Fe-O^{3/2-}. In our experiments, sorption of 664 $Ni(H_2O)_6^{2+}$ by site type (3) is most consistent with the results. In addition, fewer Fe atoms in 665 the second coordination shell is consistent with weaker surface complexes and the observed 666 enrichment of light Ni isotopes in the Ni-sorbed to goethite sample leading to larger isotopic 667 fractionation (i.e., larger fractionation factor $\Delta \delta^{60/58}$ Ni_{min-aq}) than for 2-line ferrihydrite. 668

669

670 4.4. Implications for Ni isotope biogeochemical cycling in modern and ancient surface671 environments

674

In modern Earth surface environments, Fe-oxyhydroxides are likely an important 675 carrier of Ni in riverine suspended sediments (Turekian, 1977; Snodgrass, 1980; Callender, 676 2014) and in soils (Dublet et al., 2012; Ratié et al., 2015). Snodgrass (1980) showed that Ni 677 occurs in solution (0.5% only), as adsorbed species (3.1%), as precipitated inorganic phases or 678 particle coatings (47%), as organic matter-bound complexes (14.9%) and as crystalline 679 material (34.4%). Martin and Meybeck (1979) showed that Ni occurs mainly in the truly 680 dissolved phase. However, a proportion of the total dissolved pool consists of Ni sorbed to Fe 681 682 and Mn-oxides colloids and particles (Mouvet and Bourg, 1983; Gaillardet et al., 2014) while 683 a significant proportion of Ni is associated with colloidal organic matter and organic compounds (Vasyukova et al., 2010). Considering that the proportion of each of these Ni 684 pools in rivers may vary depending on environmental and geological settings, Ni speciation 685 may exert a strong influence on the Ni isotope composition of rivers. Bedrock lithology, rock 686 alteration processes and soil formation may be also important. For example, the Ni isotope 687 composition of Ni-rich laterites forming through weathering of ultramafic complexes 688 indicates an enrichment in light Ni isotopes by -0.47 ‰ compared to the bedrock composition 689 690 (Ratié et al., 2015). Nickel isotope fractionation during adsorption to Fe-oxyhydroxides might 691 explain the observed light isotopes enrichment in weathering environment, and by isotopic mass balance, the overall enrichment in heavy isotopes in rivers (Cameron and Vance, 2014). 692 693 This would indicate a significant role for Fe in Ni isotopic cycling on continental surfaces and more specifically in the delivery of Ni to the oceans both in terms of elemental flux and 694 isotopic composition. 695

696 In natural environments, the reaction rate for the transformation of ferrihydrite to 697 goethite can be relatively rapid (< 500 days) and does not depend on pH (Schwertmann et al.,

2004), but ferrihydrite can be metastable in some environments (Navrotsky et al., 2008; Toner 698 699 et al., 2012). The presence of large amounts of Ni incorporated in Fe-oxyhydroxides has been shown to slow the transformation of poorly crystalline Fe-oxyhydroxides to more crystalline 700 phases (Cornell et al., 1992; Cornell and Schwertmann, 2003). During dissolution of Fe(III)-701 702 oxyhydroxides, Ni is released more slowly than Fe, which leads to enrichment in Ni in the residual solid phase (Cornell et al., 1992). The presence of organic ligands in seawater may 703 704 also affect the crystallization of ferrihydrite and its transformation to goethite (Cornell and 705 Schwertmann, 1979). Therefore, in the case of differential Ni isotope fractionation between the two mineral phases as observed in this study, the overall Ni isotope composition of Fe-706 707 oxyhydroxides may be controlled by the nature of the initial mineral phase precipitated. 708 Based on our results, we propose that Ni adsorption on Fe-oxyhydroxides is likely to be a major mechanism for explaining the enrichment in heavy Ni isotopes in river water 709 710 compared to the Bulk Silicate Earth by ~ 0.6-0.7 ‰ (Cameron and Vance, 2014). However, 711 one should also consider the possibility that the present-day main river discharges (e.g., Amazon river) may contain some anthropogenic Ni as a by-product of fossil fuel burning, 712 which may alter both the natural concentration of Ni in rivers and its isotopic composition. 713 For instance, Gueguen et al. (2013) report a $\delta^{60/58}$ Ni value of 0.5 ‰ in coal, which is heavier 714 than the Bulk Silicate Earth isotopic composition. Such anthropogenic input could also 715 explain the apparent Ni isotopic imbalance in the ocean (Cameron and Vance, 2014), thereby 716 implying that Ni delivery to the ocean occurs under non steady-state conditions. 717

718

*4.4.2. Application to Precambrian seawater chemistry and ancient Ni biogeochemical cycling*720

The marine biogeochemical cycle of Ni experienced major perturbations during the
Precambrian (Konhauser et al., 2009; Konhauser et al., 2015), including an apparent sharp

decrease in the Ni delivery to the ocean at the onset of the Great Oxidation Event, at ca. 2.5 723 724 Ga. Under the overall anoxic conditions and high Ni bioavailability of the Archean oceans, microorganisms such as methanogens may have been important primary producers. Given 725 that methanogens fractionate light Ni isotopes by up to ~ -1.5 % (Cameron et al., 2009), such 726 727 a shift in Ni utilization in the oceans should have left characteristic imprints in the Ni isotopic composition of Precambrian seawater. Because Fe-oxyhydroxides were probably an important 728 729 host phase for Ni in ancient marine environments (Konhauser et al., 2009), an understanding 730 of Ni isotope fractionation during sorption to ferrihydrite or goethite is critical for inferring the Ni isotopic composition of Precambrian seawater from the Precambrian sediment record 731 732 (Wasylenki et al., 2015). Tracing the evolution of Ni isotopic composition in Precambrian 733 seawater by investigating BIFs could provide meaningful insights into the coevolution of the chemical composition of seawater with biological evolution and diversification (Bekker et al., 734 735 2010). However, Fe-oxides such as hematite and magnetite are the predominant carrier of Ni in these deposits, although accessory minerals such as silicates (e.g., stilpnomelane) and 736 carbonates may be also important. Because the nature and origin of the Fe-oxyhydroxide 737 precursor in BIF remain poorly known, interpretations based on the Ni isotope composition in 738 739 BIF should be made with significant caution given the range of possible fractionation factors 740 for different mineral types (e.g., ferrihydrite vs. goethite) and adsorption mechanisms. Our results show that Ni isotope fractionation during abiotic reactions involving 741 adsorption on Fe-oxides are of the same order of magnitude as for biotic reactions (i.e., 742 743 Cameron et al., 2009) and vary between different mineral surfaces i.e., from ~ -0.35 ‰ (2-line ferrihydrite) to ~ -0.77 ‰ (goethite). Hence, the use of Ni isotopes as biosignatures should be 744 approached with caution, as Ni isotope fractionation produced by abiotic processes may mask 745 any isotope signals related to biotic processes. This issue is critical for BIF studies because 746 the large extent of Fe precipitation in seawater, leading to the accumulation of freshly formed 747

Fe-oxyhydroxides at the seafloor as likely BIF precursors, may also shift the isotopiccomposition Ni remaining in seawater.

In a previous study, Wasylenki et al. (2015) suggested that Ni isotopes in BIF should 750 be offset by ~ -0.35 ‰ relatively to seawater. We further propose that such an offset is likely 751 a minimum value, considering that fractionation up to ~ -0.77 ‰ is observed during sorption 752 to goethite, regardless of potential kinetic isotope effects. Clearly, further study investigating 753 754 the preservation of Ni isotope signatures during Fe-oxyhydroxide recrystallization to hematite and magnetite is warranted in order to directly apply Ni isotope systematics to the BIF record. 755 Although Wasylenki et al. (2015) showed that there was apparently no isotope fractionation 756 757 during aging of ferrihydrite and recrystallization to goethite and hematite, they did not 758 determine the proportion of ferrihydrite that has recrystallized, and longer experimental durations as well as heating of the system should be explored to better evaluate the effect of 759 760 ferrihydrite aging on Ni isotopes. The effect of silica (Eickhoff et al., 2014) and the possibility that it could affect the Ni isotope fractionation factor during BIF formation, has also to be 761 considered when investigating the BIF record. 762

763

764 5. Summary

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Consistent with previous studies (Wasylenki et al., 2015), we found that Ni isotopes are readily fractionated towards light Ni isotopes during adsorption to Fe-oxyhydroxide minerals. Building on that work, we have demonstrated that Ni sorbed to 2-line ferrihydrite is less fractionated than Ni sorbed to goethite with average $\Delta^{60/58}$ Ni_{min-aq} values of -0.35 ±0.08 % and -0.77 ±0.23 %, respectively. No difference in $\Delta^{60/58}$ Ni_{min-aq} values was observed either as a function of Ni loading or as a function of pH in both 2-line ferrihydrite and goethite. For both 2-line ferrihydrite and goethite, Ni K-edge EXAFS results indicate that there are no

measurable changes in Ni coordination as a function of pH or final Ni loading to the mineral. 773 774 In addition, on the timescale of our experiments there is no evidence that Ni is structurally incorporated into either mineral. The only difference we found between the two minerals is 775 the lower Ni-Fe coordination number in the second shell of goethite, and we argue that this 776 may account for a larger Ni isotope fractionation factor (~ -0.77 ‰) to goethite in comparison 777 to 2-line ferrihydrite (~ -0.35 ‰). Although additional data are required to strengthen the 778 779 conclusions on kinetic experiments, first results suggest that Ni concentrations and $\Delta^{60/58}$ Ni_{min}aq values do not vary with time, as it would be expected for suspensions at equilibrium. In 780 addition, the $\Delta^{60/58}$ Ni_{min-aq} values for 2-line ferrihydrite and goethite in the kinetic experiments 781 on average are similar to the $\Delta^{60/58}$ Ni_{min-aq} values calculated for the pH-dependent and varying 782 initial Ni concentrations experiments suggesting that our experiments are at isotopic 783 equilibrium over a duration of ~24 hours. 784

785

The magnitude of isotope fractionation suggests that Ni adsorption to Fe-786 oxyhydroxides is a significant process controlling Ni isotope abundances in the natural 787 environment. Our study also shows that such Ni isotope fractionation factors during Ni 788 789 adsorption on Fe-oxides are in the same direction and extent as for biological uptake of Ni by 790 methanogens. Hence, these findings provide important insights into the mechanisms of Ni 791 isotope fractionation in natural environments, as well as cautionary guidelines for interpreting Ni isotope (bio)signatures in ancient sedimentary rocks. This study underpins the need to 792 793 further investigate the influence of weathering and soil processes, as well as anthropogenic 794 inputs, on the Ni isotopic composition of rivers and, in turn, on the mass balance of Ni 795 isotopes in seawater.

796

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816	

Figure captions:

Figure 1: Nickel loading to minerals (µmol/m² mineral) as a function of (a) pH (data from
pH-dependent experiments) and (b) initial aqueous concentration of Ni (µmol/L) (data from
varying initial Ni concentration experiments).

Figure 2: Surface complexation modeling (SCM) using a Constant Capacitance Model
(CCM) and experimental data from this study showing percent of Ni sorbed versus solution
pH for (a) 2-line ferrihydrite and (b) goethite. The SCM (bold line) fits the experimental data
well (filled circles) for 2-line ferrihydrite (a) while experimental data (filled stars) for goethite
deviates from the SCM (dashed line) (b). A possible explanation for this discrepancy was that
very little Ni was adsorbed (< 5 %) on the goethite surface, contributing non-negligible
uncertainty to the determination of percent Ni sorbed.

830

Figure 3: Summary of Ni K-edge EXAFS spectra in k-space for Ni-sorbed 2-line ferrihydrite
at pH 7.7 and 8.0. Data are displayed as solid lines, while fits to data are displayed as dashed
lines.

834

Figure 4: Summary of Fourier transformed data (magnitude and imaginary part) and fits for
Ni-sorbed 2-line ferrihydrite at pH 7.7 and 8.0. Data are displayed as solid lines, while fits to
data are displayed as dashed lines.

838

Figure 5: Nickel isotope composition (‰) of minerals (circles) and supernatant solutions 839 840 (squares) for pH-dependent (pink symbols), variable initial Ni concentration in solution (brown symbols) and time-dependent experiments (blue symbols) for (a) 2-line ferrihydrite 841 and (b) goethite. The straight black line in the two plots represents the Ni isotope composition 842 of the starting Ni solution ($\delta^{60/58}$ Ni = -0.33 ‰). The error bar (2sd) corresponds the 843 reproducibility of the geostandards (~ ± 0.06 %; see section 2.5 for explanation). Values are 844 consistent between each experiment according to the type of mineral, i.e., -0.35 ± 0.08 % for 845 2-line ferrihydrite and -0.77 ± 0.23 ‰ for goethite. The average $\delta^{60/58}$ Ni value for 2-line 846 ferrihydrite does not take into account the very low Ni-sorbed samples (unfilled datapoints on 847

the figure, see main text for explanation). Note also that the x-axis is different for 2-line
ferrihydrite and goethite because the range of %-adsorption is lower for goethite than for 2line ferrihydrite.

851

Figure 6: Ni isotope fractionation factors ($\Delta^{60/58}$ Ni_{min-aq} = $\delta^{60/58}$ Ni_{mineral} - $\delta^{60/58}$ Ni_{aqueous}) versus (a) pH using results from pH-dependent experiments and (b) final Ni loading to the mineral (µmol/g mineral) for goethite (diamonds) and 2-line ferrihydrite (circles). The error bar (2se) corresponds to the value of ±0.05 ‰ as the highest value determined by error propagation on samples (see section 3.4 for more explanation). The unfilled datapoints in plot (a) correspond to very low Ni-sorbed to 2-line ferrihydrite (see main text for explanation).

858

Figure 7: Ni isotope fractionation factors ($\Delta^{60/58}$ Ni_{min-aq} = $\delta^{60/58}$ Ni_{mineral} - $\delta^{60/58}$ Ni_{aqueous}) versus %-adsorption for (a) 2-line ferrihydrite and (b) goethite for each type of experiment. Pink dots are for pH-dependent experiments, brown dots for the variable initial Ni concentration experiments and blue dots are for the time-dependent experiments. The unfilled red datapoints in plot (a) (2-line ferrihydrite) correspond to very low Ni-sorbed samples (see main text for explanation).

865

866 <u>Table captions:</u>

867

Table 1: Sample information, summary of experimental conditions, Ni loading to the mineral
and Ni isotope composition (‰) of mineral phases and supernatant solutions for pH-

870 dependent experiments, variable Ni concentration experiments. Non-filled symbols

871 correspond to the very low sorbed Ni samples (see text for discussion).

- **Table 2:** Sample information, summary of experimental conditions, Ni loading to the mineral
- and Ni isotope composition (‰) of mineral phases and supernatant solutions for time-
- 875 dependent experiments.
- 876
- **Table 3**: Summary of Ni K-edge EXAFS fit parameters.
- 878
- 879

880 **<u>References:</u>**

- Arai, Y., 2008. Spectroscopic Evidence for Ni(II) Surface Speciation at the Iron
- 882 Oxyhydroxides–Water Interface. Environmental Science & Technology, 42(4): 1151-1156.

883 Balistrieri, L.S., Borrok, D.M., Wanty, R.B., Ridley, W.I., 2008. Fractionation of Cu and Zn

- isotopes during adsorption onto amorphous Fe(III) oxyhydroxide: Experimental mixing of
 acid rock drainage and ambient river water. Geochimica Et Cosmochimica Acta, 72(2): 311-
- 886 328.
- Barling, J., Anbar, A.D., 2004. Molybdenum isotope fractionation during adsorption by
 manganese oxides. Earth and Planetary Science Letters, 217(3-4): 315-329.

Barrow, N.J., Brümmer, G.W., Fischer, L., 2012. Rate of desorption of eight heavy metals
from goethite and its implications for understanding the pathways for penetration. European
Journal of Soil Science, 63(3): 389-398.

- Beard, B.L. et al., 2010. Iron isotope fractionation between aqueous ferrous iron and goethite.
 Earth and Planetary Science Letters, 295(1-2): 241-250.
- Bekker, A. et al., 2010. Iron Formation: The Sedimentary Product of a Complex Interplay
 among Mantle, Tectonic, Oceanic, and Biospheric Processes. Economic Geology, 105(3):
 467-508.
- Bruemmer, G.W., Gerth, J., Tiller, K.G., 1988. Reaction kinetics of the adsorption and
 desorption of nickel, zinc and cadmium by goethite. I. Adsorption and diffusion of metals.
 Journal of Soil Science, 39(1): 37-52.
- Bruland, K.W., 1980. Oceanographic distributions of Cadmium, Zinc, Nickel, and Copper in
 the North Pacific. Earth and Planetary Science Letters, 47(2): 176-198.
- Brümmer, G.W., Barrow, N.J., Fischer, L., 2013. Effect of porosity of goethite on the sorption
 of six heavy metal ions. European Journal of Soil Science, 64(6): 805-813.
- Butt, C.R.M., Cluzel, D., 2013. Nickel Laterite Ore Deposits: Weathered Serpentinites.
 Elements, 9(2): 123-128.
- 906 Callender, E., 2014. Heavy Metals in the Environment Historical Trends A2 Holland,
- Heinrich D. In: Turekian, K.K. (Ed.), Treatise on Geochemistry (Second Edition). Elsevier,
 Oxford, pp. 59-89.
- Cameron, V., Vance, D., 2014. Heavy nickel isotope compositions in rivers and the oceans.
 Geochimica Et Cosmochimica Acta, 128(0): 195-211.
- 911 Cameron, V., Vance, D., Archer, C., House, C.H., 2009. A biomarker based on the stable
- 912 isotopes of nickel. Proceedings of the National Academy of Sciences of the United States of
- 913 America, 106(27): 10944-10948.
- 914 Carvalho-E-Silva, M.L. et al., 2003. Incorporation of Ni into natural goethite: An
- 915 investigation by X-ray absorption spectroscopy. American Mineralogist, 88(5): 876-882.

- 916 Cismasu, A.C., Levard, C., Michel, F.M., Brown Jr, G.E., 2013. Properties of impurity-
- 917 bearing ferrihydrite II: Insights into the surface structure and composition of pure, Al- and Si-
- 918 bearing ferrihydrite from Zn(II) sorption experiments and Zn K-edge X-ray absorption
- 919 spectroscopy. Geochimica et Cosmochimica Acta, 119(0): 46-60.
- 920 Cornell, R.M., Giovanoli, R., Schneider, W., 1992. The effect of Nickel on the conversion of
- 921 amorphous iron(III) hydroxide into more crystalline iron-oxides in alkaline media. Journal of
- 922 Chemical Technology and Biotechnology, 53(1): 73-79.
- 923 Cornell, R.M., Schwertmann, U., 1979. Influence of organic-anions on the crystallization of
 924 ferrihydrite. Clays and Clay Minerals, 27(6): 402-410.
- 925 Cornell, R.M., Schwertmann, U., 2003. The Iron Oxides: Structure, Properties, Reactions,
 926 Occurrences and Uses. Wiley, New York, 603 pp.
- Davis, J.A., Kent, D.B., 1990. Surface complexation modeling in aqueous geochemistry.
 Mineral-Water Interface Geochemistry, 23.
- Dublet, G. et al., 2012. Ni speciation in a New Caledonian lateritic regolith: A quantitative Xray absorption spectroscopy investigation. Geochimica et Cosmochimica Acta, 95(0): 119133.
- Dublet, G. et al., 2014. XAS evidence for Ni sequestration by siderite in a lateritic Ni-deposit
 from New Caledonia, American Mineralogist, pp. 225.
- Dzombak, D.A., Morel, F.M.M., 1990. Surface complexation modeling : hydrous ferric oxide.
 Wiley, New York.
- Bickhoff, M. et al., 2014. Nickel partitioning in biogenic and abiogenic ferrihydrite: The
 influence of silica and implications for ancient environments. Geochimica et Cosmochimica
 Acta, 140(0): 65-79.
- Ellis, A.S., Johnson, T.M., Bullen, T.D., 2004. Using Chromium Stable Isotope Ratios To
 Quantify Cr(VI) Reduction: Lack of Sorption Effects. Environmental Science & Technology,
 38(13): 3604-3607.
- 942 Essington, M.E., 2003. Surface chemistry and adsorption reactions, Soil and water chemistry.
 943 CRC Press LLC, Boca Raton, FL.
- 944 Fischer, L., Brümmer, G.W., Barrow, N.J., 2007. Observations and modelling of the reactions
- of 10 metals with goethite: adsorption and diffusion processes. European journal of soil
 science, 58(6): 1304-1315.
- Frierdich, A.J., Beard, B.L., Reddy, T.R., Scherer, M.M., Johnson, C.M., 2014. Iron isotope
 fractionation between aqueous Fe(II) and goethite revisited: New insights based on a multidirection approach to equilibrium and isotopic exchange rate modification. Geochimica et
 Cosmochimica Acta, 139(0): 383-398.
- Frierdich, A.J., Luo, Y., Catalano, J.G., 2011. Trace element cycling through iron oxide
 minerals during redox-driven dynamic recrystallization. Geology, 39(11): 1083-1086.

- Gaillardet, J., Viers, J., Dupré, B., 2014. Trace Elements in River Waters. In: Turekian,
 H.D.H.K. (Ed.), Treatise on Geochemistry (Second Edition). Elsevier, Oxford, pp. 195-235.
- Gall, L. et al., 2013. Nickel isotopic compositions of ferromanganese crusts and the constancy
 of deep ocean inputs and continental weathering effects over the Cenozoic. Earth and
 Planetary Science Letters, 375(0): 148-155.
- Goldberg, T., Archer, C., Vance, D., Poulton, S.W., 2009. Mo isotope fractionation during
 adsorption to Fe (oxyhydr)oxides. Geochimica et Cosmochimica Acta, 73(21): 6502-6516.
- 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. Geostandards and Geoanalytical Research, 37(3): 297-317.
- Gueguen, B. et al., 2016. Comparative geochemistry of four ferromanganese crusts from the
 Pacific Ocean and significance for the use of Ni isotopes as paleoceanographic tracers.
 Geochimica et Cosmochimica Acta.
- Hayes, K.F., Redden, G., Ela, W., Leckie, J.O., 1991. Surface complexation models: An
 evaluation of model parameter estimation using FITEQL and oxide mineral titration data.
 Journal of Colloid and Interface Science, 142(2): 448-469.
- Hofmann, A. et al., 2014. Comparing orthomagmatic and hydrothermal mineralization models
 for komatiite-hosted nickel deposits in Zimbabwe using multiple-sulfur, iron, and nickel
 isotope data. Mineralium Deposita, 49(1): 75-100.
- Icopini, G.A., Anbar, A.D., Ruebush, S.S., Tien, M., Brantley, S.L., 2004. Iron isotope
 fractionation during microbial reduction of iron: The importance of adsorption. Geology,
 32(3): 205-208.
- Jiskra, M., Wiederhold, J.G., Bourdon, B., Kretzschmar, R., 2012. Solution Speciation
- 976 Controls Mercury Isotope Fractionation of Hg(II) Sorption to Goethite. Environmental
- 977 Science & Technology, 46(12): 6654-6662.
- Juillot, F. et al., 2008. Zn isotopic fractionation caused by sorption on goethite and 2-Lines
 ferrihydrite. Geochimica Et Cosmochimica Acta, 72(19): 4886-4900.
- Kashiwabara, T., Takahashi, Y., Tanimizu, M., 2009. A XAFS study on the mechanism of
 isotopic fractionation of molybdenum during its adsorption on ferromanganese oxides.
 GEOCHEMICAL JOURNAL, 43(6): e31-e36.
- Kelly, S.D., Hesterberg, D., Ravel, B., 2008. Analysis of Soils and Minerals Using X-ray
 Absorption Spectroscopy, Methods of Soil Analysis. Soil Science Society of America,
- 985 Madison, WI.
- Konhauser, K.O. et al., 2009. Oceanic nickel depletion and a methanogen famine before the
 Great Oxidation Event. Nature, 458(7239): 750-754.
- Konhauser, K.O. et al., 2015. The Archean Nickel Famine Revisited. Astrobiology, 15(10):
 804-815.

- Koschinsky, A., Halbach, P., 1995. Sequential leaching of marine ferromanganese
 precipitates: Genetic implications. Geochimica et Cosmochimica Acta, 59(24): 5113-5132.
- Krishnaswami, S., 1976. Authigenic transition elements in Pacific pelagic clays. Geochimica
 Et Cosmochimica Acta, 40(4): 425-434.
- Leinen, M., 1987. The origin of paleochemical signatures in North Pacific pelagic clays:
 Partitioning experiments. Geochimica et Cosmochimica Acta, 51(2): 305-319.
- Li, X.F., Liu, Y., 2010. First-principles study of Ge isotope fractionation during adsorption
 onto Fe(III)-oxyhydroxide surfaces. Chemical Geology, 278(1–2): 15-22.
- Manceau, A., Calas, G., 1985. Heterogeneous distribution of nickel in hydrous silicates from
 New Caledonia ore deposits. American Mineralogist, 70(5-6): 549-558.
- Manceau, A., Drits, V.A., 1993. Local structure of ferrihydrite and feroxyhite by EXAFS
 spectroscopy. Clay Minerals, 28(2): 165-184.
- Manceau, A., Gates, W.P., 1997. Surface structural model for ferrihydrite. Clays and ClayMinerals, 45(3): 448-460.
- Manceau, A., Llorca, S., Calas, G., 1987. Crystal chemistry of cobalt and nickel in
 lithiophorite and asbolane from New Caledonia. Geochimica Et Cosmochimica Acta, 51(1):
 1006 105-113.
- Manceau, A. et al., 2000. Crystal chemistry of trace elements in natural and syntheticgoethite. Geochimica et Cosmochimica Acta, 64(21): 3643-3661.
- Manceau, A. et al., 2002. Deciphering Ni sequestration in soil ferromanganese nodules by
 combining X-ray fluorescence, absorption, and diffraction at micrometer scales of resolution.
 American Mineralogist, 87(10): 1494-1499.
- Martin, J.M., Meybeck, M., 1979. Elemental mass-balance of material carried by major world
 rivers. Marine Chemistry, 7(3): 173-206.
- Mikutta, C. et al., 2009. Iron isotope fractionation and atom exchange during sorption of
 ferrous iron to mineral surfaces. Geochimica et Cosmochimica Acta, 73(7): 1795-1812.
- 1016 Mitchell, K., Couture, R.-M., Johnson, T.M., Mason, P.R.D., Van Cappellen, P., 2013.
- Selenium sorption and isotope fractionation: Iron(III) oxides versus iron(II) sulfides.
 Chemical Geology, 342: 21-28.
- Morel, F.M.M., Price, N.M., 2003. The Biogeochemical Cycles of Trace Metals in theOceans. Science, 300(5621): 944.
- 1021 Mouvet, C., Bourg, A.C.M., 1983. Speciation (including adsorbed species) of copper, lead,
- 1022 nickel and zinc in the Meuse River: Observed results compared to values calculated with a
- 1023 chemical equilibrium computer program. Water Research, 17(6): 641-649.
- Navrotsky, A., Mazeina, L., Majzlan, J., 2008. Size-Driven Structural and Thermodynamic
 Complexity in Iron Oxides. Science, 319(5870): 1635-1638.

- Peacock, C.L., Sherman, D.M., 2007a. Sorption of Ni by birnessite: Equilibrium controls on
 Ni in seawater. Chemical Geology, 238(1-2): 94-106.
- Peacock, C.L., Sherman, D.M., 2007b. Crystal-chemistry of Ni in marine ferromanganesecrusts and nodules. American Mineralogist, 92(7): 1087-1092.
- Peña, J., Kwon, K.D., Refson, K., Bargar, J.R., Sposito, G., 2010. Mechanisms of nickel
 sorption by a bacteriogenic birnessite. Geochimica et Cosmochimica Acta, 74(11): 30763089.
- Pokrovsky, O.S., Galy, A., Schott, J., Pokrovski, G.S., Mantoura, S., 2014. Germanium
 isotope fractionation during Ge adsorption on goethite and its coprecipitation with Fe
 oxy(hydr)oxides. Geochimica et Cosmochimica Acta, 131(0): 138-149.
- Pokrovsky, O.S., Viers, J., Emnova, E.E., Kompantseva, E.I., Freydier, R., 2008. Copper
 isotope fractionation during its interaction with soil and aquatic microorganisms and metal
 oxy(hydr)oxides: Possible structural control. Geochimica et Cosmochimica Acta, 72(7): 17421757.
- Pokrovsky, O.S., Viers, J., Freydier, R., 2005. Zinc stable isotope fractionation during its
 adsorption on oxides and hydroxides. Journal of Colloid and Interface Science, 291(1): 192200.
- Porter, S.J., Selby, D., Cameron, V., 2014. Characterising the nickel isotopic composition of
 organic-rich marine sediments. Chemical Geology, 387(0): 12-21.
- Price, N.M., Morel, F.M.M., 1991. Colimitation of phytoplankton growth by Nickel andNitrogen. Limnology and Oceanography, 36(6): 1071-1077.
- 1047 Quantin, C., Ettler, V., Garnier, J., Šebek, O., 2008. Sources and extractibility of chromium
 1048 and nickel in soil profiles developed on Czech serpentinites. Comptes Rendus Geoscience,
 1049 340(12): 872-882.
- 1050 Ratié, G. et al., 2015. Nickel isotope fractionation during tropical weathering of ultramafic
 1051 rocks. Chemical Geology, 402(0): 68-76.
- Ravel, B., Newville, M., 2005. ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X ray absorption spectroscopy using IFEFFIT. Journal of Synchrotron Radiation, 12: 537-541.
- 1054 Rehkämper, M. et al., 2002. Thallium isotope variations in seawater and hydrogenetic,
 1055 diagenetic, and hydrothermal ferromanganese deposits. Earth and Planetary Science Letters,
 1056 197(1-2): 65-81.
- Schauble, E.A., 2004. Applying Stable Isotope Fractionation Theory to New Systems.
 Reviews in Mineralogy and Geochemistry, 55(1): 65-111.
- Schwertmann, U., Stanjek, H., Becher, H.-H., 2004. Long-term in vitro transformation of 2line ferrihydrite to goethite/hematite at 4, 10, 15 and 25°C. Clay Minerals, 39(4): 433-438.
- Sclater, F.R., Boyle, E., Edmond, J.M., 1976. On the marine geochemistry of nickel. Earthand Planetary Science Letters, 31(1): 119-128.

- 1063 Siebert, C., Nagler, T.F., Kramers, J.D., 2001. Determination of molybdenum isotope
- 1064 fractionation by double-spike multicollector inductively coupled plasma mass spectrometry.1065 Geochemistry Geophysics Geosystems, 2: 1032.
- Siebert, C., Nagler, T.F., von Blanckenburg, F., Kramers, J.D., 2003. Molybdenum isotope
 records as a potential new proxy for paleoceanography. Earth and Planetary Science Letters,
 211(1-2): 159-171.
- Snodgrass, W.J., 1980. Distribution and behavior of nickel in the aquatic environment. NewYork, John Wiley & Sons, pp. 203-274.
- Soper, A.K., Neilson, G.W., Enderby, J.E., Howe, R.A., 1977. A neutron diffraction study of
 hydration effects in aqueous solutions. Journal of Physics C: Solid State Physics, 10(11):
 1793.
- Toner, B.M. et al., 2012. Mineralogy of iron microbial mats from loihi seamount. Frontiers inmicrobiology, 3.
- 1076 Turekian, K.K., 1977. The fate of metals in oceans. Geochimica Et Cosmochimica Acta,1077 41(8): 1139-1144.
- Valeton, I., Biermann, M., Reche, R., Rosenberg, F., 1987. Genesis of nickel laterites and
 bauxites in greece during the jurassic and cretaceous, and their relation to ultrabasic parent
 rocks. Ore Geology Reviews, 2(4): 359-404.
- 1081 Vasyukova, E.V. et al., 2010. Trace elements in organic- and iron-rich surficial fluids of the
 1082 boreal zone: Assessing colloidal forms via dialysis and ultrafiltration. Geochimica et
 1083 Cosmochimica Acta, 74(2): 449-468.
- 1084 Villalobos, M., Trotz, M.A., Leckie, J.O., 2003. Variability in goethite surface site density:
 1085 evidence from proton and carbonate sorption. Journal of Colloid and Interface Science,
 1086 268(2): 273-287.
- 1087 Wasylenki, L.E., Howe, H.D., Spivak-Birndorf, L.J., Bish, D.L., 2015. Ni isotope
 1088 fractionation during sorption to ferrihydrite: Implications for Ni in banded iron formations.
 1089 Chemical Geology, 400(0): 56-64.
- Wasylenki, L.E., Swihart, J.W., Romaniello, S.J., 2014. Cadmium isotope fractionation
 during adsorption to Mn oxyhydroxide at low and high ionic strength. Geochimica et
 Cosmochimica Acta, 140(0): 212-226.
- Wasylenki, L.E. et al., 2011. The molecular mechanism of Mo isotope fractionation during
 adsorption to birnessite. Geochimica Et Cosmochimica Acta, 75(17): 5019-5031.
- 1095 Waychunas, G.A., Fuller, C.C., Davis, J.A., 2002. Surface complexation and precipitate
- geometry for aqueous Zn(II) sorption on ferrihydrite I: X-ray absorption extended fine
 structure spectroscopy analysis. Geochimica et Cosmochimica Acta, 66(7): 1119-1137.
- Webb, S.M., 2005. SIXpack: a graphical user interface for XAS analysis using IFEFFIT.
 Physica Scripta, 2005(T115): 1011.

- Wu, L., Percak-Dennett, E.M., Beard, B.L., Roden, E.E., Johnson, C.M., 2012. Stable iron
 isotope fractionation between aqueous Fe(II) and model Archean ocean Fe–Si coprecipitates
 and implications for iron isotope variations in the ancient rock record. Geochimica Et
- 1103 Cosmochimica Acta, 84(0): 14-28.
- Wu, L.L., Beard, B.L., Roden, E.E., Johnson, C.M., 2011. Stable Iron Isotope Fractionation
 Between Aqueous Fe(II) and Hydrous Ferric Oxide. Environmental Science & Technology,
 45(5): 1847-1852.
- Xu, Y., Axe, L., Yee, N., Dyer, J.A., 2006. Bidentate Complexation Modeling of Heavy
 Metal Adsorption and Competition on Goethite. Environmental Science & Technology, 40(7):
 2213-2218.
- 1110

Mineral	Sample name	Type of experiment	рН	[Ni] _{aq} ^{initial} (µmol/L)	Final loading to mineral (μmol Ni/g) ^c	Final loading to mineral (μmol Ni/m ²) ^c	% of Ni sorption ^d	δ ^{60/58} Ni _{mineral}	2se ^e	δ ^{60/58} Ni _{aqueous}	2se	Δ ^{60/58} Ni _{min-aq} ^f	2se ^g	Mass balance (‰)
2-line Ferrihydrite ^a	Fh-pH-01	pH dependent	5.0	170	1.99	0.02	1.2	-0.36	0.02	-0.32	0.03	-0.03	0.03	-0.32
2-line Ferrihydrite	Fh-pH-02	pH dependent	6.0	170	4.77	0.04	2.9	-0.47	0.02	-0.35	0.03	-0.12	0.04	-0.35
2-line Ferrihydrite	Fh-pH-03	pH dependent	7.0	170	38.21	0.32	23.4	-0.57	0.02	-0.30	0.03	-0.27	0.04	-0.36
2-line Ferrihydrite	Fh-pH-04	pH dependent	7.7	170	66.61	0.56	41.7	-0.52	0.02	-0.15	0.03	-0.37	0.04	-0.31
2-line Ferrihydrite	Fh-pH-05*	pH dependent	8.0	170	73.81	0.62	45.3	-0.55	0.02	-0.17	0.04	-0.38	0.05	-0.34
2-line Ferrihydrite	Fh-C-06	Varying initial [Ni]	7.7	17	12.97	0.11	78.1	-0.41	0.02	-0.02	0.04	-0.39	0.04	-0.33
2-line Ferrihydrite	Fh-C-07*	Varying initial [Ni]	7.7	85	38.64	0.32	46.8	-0.51	0.02	-0.18	0.04	-0.32	0.04	-0.34
2-line Ferrihydrite	Fh-C-08*	Varying initial [Ni]	7.7	170	41.31	0.35	24.8	-0.56	0.02	-0.22	0.04	-0.34	0.04	-0.30
2-line Ferrihydrite	Fh-C-09*	Varying initial [Ni]	7.7	341	131.24	1.10	39.2	-0.54	0.03	-0.13	0.04	-0.40	0.05	-0.29
2-line Ferrihydrite	Fh-C-10*	Varying initial [Ni]	7.7	426	203.14	1.71	49.8	-0.53	0.03	-0.28	0.04	-0.24	0.05	-0.40
Goethite ^b	Goe-pH-01	pH dependent	5.0	170	1.00	0.04	0.6	-1.00	0.03	-0.30	0.03	-0.70	0.04	-0.31
Goethite	Goe-pH-02	pH dependent	6.0	170	1.33	0.05	0.8	-1.13	0.03	-0.25	0.04	-0.88	0.05	-0.25
Goethite	Goe-pH-03	pH dependent	8.0	170	7.17	0.28	4.3	-1.19	0.03	-0.23	0.03	-0.96	0.05	-0.27
Goethite	Goe-C-04	Varying initial [Ni]	7.7	170	15.96	0.63	9.5	-1.08	0.02	-0.27	0.04	-0.80	0.04	-0.35
Goethite	Goe-C-05	Varying initial [Ni]	7.7	341	17.56	0.69	19.3	-1.15	0.02	-0.12	0.04	-1.03	0.04	-0.35
Goethite	Goe-C-06*	Varying initial [Ni]	7.7	426	33.86	1.33	7.9	-1.07	0.02	-0.29	0.03	-0.78	0.04	-0.35
Ni standard solution	-	-	-	-	-	-	-	-	-	-0.32	0.03	-	-	-
Ni standard solution	-	-	-	-	-	-	-	-	-	-0.34	0.03	-	-	-
Ni standard solution	-	-	-	-	-	-	-	-	-	-0.30	0.03	-	-	-
Ni standard solution	-	-	-	-	-	-	-	-	-	-0.35	0.06	-	-	-
Average Ni	_	_	_	_	_	_	_	_	-	-0.33	0 05 (2sd)	_	-	-
standard solution ^h										0.00	0.00 (200)			
Nod-A-1 ⁱ	-	-	-	-	-	-	-	-	-	1.06	0.02	-	-	-
Nod-A-1 ⁱ	-	-	-	-	-	-	-	-	-	1.01	0.03	-	-	-
Nod-A-1 ⁱ	-	-	-	-	-	-	-	-	-	1.05	0.04	-	-	-
Nod-P-1 ⁱ	-	-	-	-	-	-	-	-	-	0.30	0.03	-	-	-
Nod-P-1 ⁱ	-	-	-	-	-	-	-	-	-	0.35	0.04	-	-	-
Nod-P-1 ⁱ	_	_	_	l _	_	_	_	_	-	0.34	0.03		-	
Nod-P-1 ⁱ	_	_	-	_	_	_	-	_	-	0.32	0.03	-	-	-

Table 1: Sample information, summary of experimental conditions, Ni loading to the mineral and Ni isotope composition (‰) of mineral phases and supernatant solutions for pH-dependent and variable Ni experiments.

* Samples for which Ni K-edge EXAFS data were collected.

^a 2-line ferrihydrite (0.014 mol Fe/g dry mineral)

^b Goethite (0.015 mol Fe/g dry mineral)

^c Final loading corresponds to the amount of Ni per gram or m² of mineral in the reactor. The amount of mineral added per reactor measured was ~ 0.15 g.

^d Ni sorbed fractions (%) were determined by mass balance using measured amount of Ni in solution and adsorbed onto minerals.

^e 2se corresponds to the two standard error of the mean determined on the 50 measurement cycles on the MC-ICP-MS for each sample (see text for explanation).

^f The difference in isotopic composition between the mineral and the supernatant solution is expressed as $\Delta^{60/68}$ Ni_{min-aq} = $\delta^{60/68}$ Ni_{min}

^g '2se' corresponds to error propagation of the $\Delta^{60/58}$ Ni_{min/aq} values (2se = $\sqrt{((2se_{mineral})^2 + (2se_{aqueous})^2))}$.

^h The initial Ni standard solution used for experiments was processed several times through chromatography columns. The two standard deviation (2sd, n=4) was calculated on these duplicates.

¹Nod-A-1 and Nod-P-1 are duplicates of USGS geostandards measured for monitoring the reproducibility of the data.

Mineral*	Sample name	Duration of experiment (hours)	рН	[Ni] _{aq} ^{initial} (µmol/L)	Final Ioading to mineral (µmol Ni/g)	Final loading to mineral (µmol Ni/m ²)	% of Ni sorption	δ ^{60/58} Ni _{mineral}	2se	δ ^{60/58} Ni _{aqueous}	2se	$\Delta^{60/58} Ni_{min-aq}$	2se	Mass balance (‰)
Goethite	Goe-T-07	18	7.7	170	41.0	1.6	22.3	-0.98	0.05	-0.21	0.06	-0.77	0.07	-0.38
Goethite	Goe-T-08	20	7.7	170	41.7	1.6	22.0	-0.96	0.05	-0.19	0.05	-0.77	0.07	-0.36
Goethite	Goe-T-09	22	7.7	170	42.2	1.7	22.6	-0.98	0.08	-0.26	0.03	-0.72	0.08	-0.42
Goethite	Goe-T-10	23	7.7	170	42.5	1.7	22.0	-0.98	0.04	-0.24	0.04	-0.74	0.05	-0.41
Goethite	Goe-T-11	18	7.7	426	65.3	2.6	17.2	-0.88	0.06	-0.25	0.04	-0.62	0.07	-0.36
Goethite	Goe-T-12	20	7.7	426	50.6	2.0	14.4	-0.99	0.06	-0.27	0.03	-0.73	0.07	-0.37
Goethite	Goe-T-13	22	7.7	426	56.7	2.2	15.6	-0.94	0.03	-0.29	0.06	-0.65	0.07	-0.39
Goethite	Goe-T-14	23	7.7	426	51.6	2.0	12.9	-0.97	0.05	-0.29	0.07	-0.68	0.08	-0.38
2-line Ferrihydrite	Fh-T-11	19	7.7	170	225.2	1.9	92.4	-0.36	0.04	0.00	0.05	-0.36	0.06	-0.33
2-line Ferrihydrite	Fh-T-12	20	7.7	170	224.5	1.9	92.9	-0.37	0.04	-0.02	0.03	-0.35	0.05	-0.35
2-line Ferrihydrite	Fh-T-13	22	7.7	170	223.5	1.9	93.2	-0.36	0.02	-0.01	0.04	-0.35	0.04	-0.34
2-line Ferrihydrite	Fh-T-14	23	7.7	170	322.7	2.7	95.0	-0.39	0.05	-0.05	0.03	-0.34	0.05	-0.38
2-line Ferrihydrite	Fh-T-15	19	7.7	426	444.4	3.7	91.5	-0.41	0.04	-0.03	0.05	-0.37	0.06	-0.37
2-line Ferrihydrite	Fh-T-16	20	7.7	426	443.1	3.7	91.5	-0.43	0.04	-0.05	0.05	-0.38	0.06	-0.40
2-line Ferrihydrite	Fh-T-17	22	7.7	426	392.9	3.3	85.7	-0.37	0.02	-0.05	0.04	-0.32	0.04	-0.33
2-line Ferrihydrite	Fh-T-18	23	7.7	426	443.1	3.7	91.3	-0.42	0.06	-0.06	0.01	-0.36	0.06	-0.39

Table 2: Sample information, summary of experimental conditions, Ni loading to the mineral and Ni isotope composition (‰) of mineral phases and supernatant solutions for the time-dependent experiments.

*See Table 1 for footnotes.

Sample Name	Path	CN	R (Å)	σ ² (Å ²)	$\Delta E_0 (eV)$	x	Red χ^2	R-factor
Fh-C-10	Ni-O	5.945 ± 0.644	2.050 ± 0.0078	0.0069 ± 0.0011	-5.273 ± 1.233	0.8088 ± 0.1304	23.39	0.0145
	Ni-Fe	1.618 ± 0.405	3.102 ± 0.0159	0.0079 ± 0.0017				
	Ni-Fe	0.574 ± 0.144	3.561 ± 0.0488	0.0079 ± 0.0017				
Fh-C-09	Ni-O	6.543 ± .0760	2.052 ± 0.0087	0.0082 ± 0.0013	-4.844 ± 1.275	0.7022 ± 0.1250	10.69	0.0166
	Ni-Fe	1.404 ± 0.351	3.096 ± 0.0187	0.0079 ± 0.0020				
	Ni-Fe	0.894 ± 0.224	3.596 ± 0.0347	0.0079 ± 0.0020				
Fh-C-08	Ni-O	6.507 ± 0.754	2.050 ± 0.0087	0.0084 ± 0.0013	-4.972 ± 1.275	0.8407 ± 0.1340	10.09	0.0162
	Ni-Fe	1.681 ± 0.420	3.102 ± 0.0161	0.0080 ± 0.0019				
	Ni-Fe	0.478 ± 0.120	3.593 ± 0.0618	0.0080 ± 0.0019				
Fh-C-07	Ni-O	6.441 ± 0.931	2.046 ± 0.0105	0.0068 ± 0.0015	-5.312 ± 1.666	0.7678 ± 0.1814	8.29	0.0261
	Ni-Fe	1.536 ± 0.384	3.112 ± 0.0239	0.0078 ± 0.0021				
	Ni-Fe	0.696 ± 0.174	3.524 ± 0.0583	0.0078 ± 0.0021				
Fh-pH-05	Ni-O	5.846 ± 0.767	2.046 ± 0.0092	0.0061 ± 0.0013	-5.446 ± 1.516	0.7287 ± 0.1532	11.31	0.0215
	Ni-Fe	1.457 ± 0.364	3.103 ± 0.0212	0.0076 ± 0.0021				
	Ni-Fe	0.814 ± 0.204	3.567 ± 0.0430	0.0076 ± 0.0021				
Goe-C-06	Ni-O	7.404 ± 0.861	2.045 ± 0.0092	0.0102 ± 0.0015	-6.092 ± 1.250	-	3.23	0.0100
	Ni-Fe	1.040 ± 0.445	3.070 ± 0.0277	0.0102 ± 0.0015				

Table 3: Summary of Ni EXAFS fit parameters.

CN: coordination number

R: interatomic distance

 σ^2 : Debye-Waller factor

 ΔE_0 : energy shift

Red χ^2 : reduced chi squared statistic

S₀²: 0.96

K-range: 3-1

R-range: 1-4





Figure 2



Figure 3



Figure 4









Electronic Annex

Variable Ni isotope fractionation between Fe-oxyhydroxides and implications for the use of Ni isotopes as geochemical tracers

Bleuenn Gueguen^{1,2*}, Jeffry V. Sorensen³, Stefan V. Lalonde¹, Jasquelin Peña⁴, Brandy M. Toner³, and Olivier Rouxel²

¹Institut Universitaire Européen de la Mer, Laboratoire Domaines Océaniques UMR 6538, Université de Brest, 29280 Plouzané, France
²IFREMER, Centre de Brest, Unité Géosciences Marines, 29280 Plouzané, France
³Department of Soil, Water, and Climate, University of Minnesota, St. Paul, MN 55108, USA
⁴Institute of Earth Surface Dynamics, University of Lausanne, CH-1015 Lausanne, Switzerland

Submitted to Chemical Geology

*Corresponding author:

E-mail address: bleuenn.gueguen@univ-brest.fr

Current address: Institut Universitaire Européen de la Mer, CNRS UMS 3113, Université de Brest, 29280 Plouzané, France

Supplementary Figures :



Figure A1: Nickel speciation modeling (logarithm of molal concentrations of different Ni species) versus pH of solution for 170 μ mol/L of Ni in starting solution. The curves represent the different Ni species present in the system, i.e., Ni²⁺, Ni(OH)_{2aq}, Ni(OH)₃⁻, NiCO_{3aq}, NiHCO₃⁺, NiNO₃⁺, NiOH⁺.





Figure A3: Nickel speciation versus pH of the solution for different initial Ni (aq), (a) 17 μ mol Ni /L, (b) 85 μ mol Ni /L, (c) 170 μ mol Ni /L, (d) 341 μ mol Ni /L, and (e) 426 μ mol Ni /L.



^{1:} Ni(2+) \triangle 2: NiOH+ 2: Ni(0H)2 (\diamond 2: Ni(0H)3- 2: NiHCO3+ 2: NiCO3 (aq \bigcirc 2: NiNO3+ \bigcirc 5: BUNSENITE \diamond 5: Ni(0H)2 \bigcirc 7: TOTAL Ni(*



1: Ni(2+) \triangle 2: NiOH+ 2: Ni(OH)2 (\Diamond 2: Ni(OH)3- 2: NiHCO3+ 2: NiCO3 (aq \bigcirc 2: NiNO3+ \bigcirc 5: BUNSENITE \diamond 5: Ni(OH)2 \bigcirc 7: TOTAL NI(*



(c)

1: Ni(2+) \triangle 2: NiOH+ 2: Ni(OH)2 (\Diamond 2: Ni(OH)3- 2: NiHCO3+ 2: NiCO3 (aq \bigcirc 2: NiNO3+ \bigcirc 5: BUNSENITE \diamond 5: Ni(OH)2 \bigcirc 7: TOTAL NI(*



1: Ni(2+) \triangle 2: NiOH+ 2: Ni(OH)2 (\Diamond 2: Ni(OH)3- 2: NiHCO3+ 2: NiCO3 (aq \bigcirc 2: NiNO3+ \bigcirc 5: BUNSENITE \diamond 5: Ni(OH)2 \bigcirc 7: TOTAL NI(*



1: Ni(2+) \triangle 2: NiOH+ 2: Ni(OH)2 (\Diamond 2: Ni(OH)3- 2: NiHCO3+ 2: NiCO3 (aq \bigcirc 2: NiNO3+ \bigcirc 5: BUNSENITE \diamond 5: Ni(OH)2 \bigcirc 7: TOTAL Ni(*

Supplementary Tables :

Mineral type	Amount of mineral in solution	Conductance	Current	Applied Voltage	Zeta potential	Mobility	Relative Residual	
2-line Ferrihydrite	1.44 g/L	344 µS	2.56 mA	7.54 V	-3.44 mV	-0.027	0.0093	
Goethite	0.984 g/L	81 µS	0.712 mA	7.54 V	3.46 mV	0.27	0.0151	

 Table S1: Zeta potential measurement parameters.

Table S2: Summary of EXAFS fit parameters for previous Ni-sorption and -incorporation experiments. Data for Zn are shown for comparison. Literature data is from (Manceau et al., 2000; Waychunas et al., 2002; Arai, 2008; Juillot et al., 2008; Dublet et al., 2012; Cismasu et al., 2013).

Sample type	Atom Pair	CN ¹	R (Å) ²	$\sigma^2 (\text{\AA}^2)^3$	Reference
Ni-sorbed goethite	Ni-O	5.1	2.10	0.0049	Dublet et al. 2012
	Ni-Fe	1.5	3.00	0.0049	
	Ni-Fe	2.4	3.14	-	
Ni-sorbed goethite	Ni-O	5.7	2.06	0.0051	Arai, 2008
	Ni-Fe	1.2	3.03	0.0050	
	Ni-Fe	1.1	3.18	0.0050	
	Ni-Fe	1.7	4.06	0.0080	
Zn-sorbed goethite	Zn-O	4.6	2.06	0.0081	Juillot et al. 2008
	Zn-Fe	0.9	3.07	0.0081	
	Zn-Fe	0.8	3.26	-	
Zn-sorbed ferrihydrite	Zn-O	3.6	1.98	0.006	Cismasu et al. 2013
	Zn-Fe	0.9	3.21	0.011	
	Zn-Fe	1.9	3.44	0.01	
Zn-sorbed ferrihydrite	Zn-O	5.05	1.96	0.007	Waychunas et al. 2002
	Zn-Fe	1.93	3.43	0.012	
Zn-sorbed ferrihydrite	Zn-O	3.2	1.96	0.0049	Juillot et al. 2008
	Zn-Fe	1	3.47	0.01	
Ni-sorbed ferrihydrite	Ni-O	5.9	2.05	0.0054	Arai, 2008
	Ni-Fe	1.0	3.08	0.0050	
	Ni-Fe	1.8	3.21	0.0050	
	Ni-Fe	1.0	4.03	0.0080	
Ni-sorbed ferrihydrite	Ni-O	5.7	2.06	0.0060	Arai, 2008
	Ni-Fe	1.4	3.05	0.0050	
	Ni-Fe	1.9	3.21	0.0050	
	Ni-Fe	1.1	4.05	0.0080	
Ni-sorbed ferrihydrite	Ni-O	5.8	2.06	0.006	Arai 2008
	Ni-Fe	1.5	3.06	0.0050	
	Ni-Fe	1.3	3.19	0.0050	
	Ni-Fe	0.9	4.07	0.0080	
Ni-bearing goethite	Ni-O	5.3	2.07	0.0036	Manceau et al. 2000
	Ni-Fe	2.1	3.00	0.0064	
	Ni-Fe	1.4	3.18	0.0064	
	Ni-Fe	2.5	3.62	0.0064	
Ni-bearing goethite	Ni-O	5.7	2.05	0.0049	Dublet et al. 2012
	Ni-Fe	2.0	2.98	0.0049	
	Ni-Fe	2.0	3.16	-	
	Ni-Fe	1.2	3.57	-	

^{1,2,3} See Table 2 and main text.

References :

Arai, Y., 2008. Spectroscopic Evidence for Ni(II) Surface Speciation at the Iron Oxyhydroxides–Water Interface. Environmental Science & Technology, 42(4): 1151-1156.

Cismasu, A.C., Levard, C., Michel, F.M., Brown Jr, G.E., 2013. Properties of impurity-bearing ferrihydrite II: Insights into the surface structure and composition of pure, Al- and Si-bearing ferrihydrite from Zn(II) sorption experiments and Zn K-edge X-ray absorption spectroscopy. Geochimica et Cosmochimica Acta, 119(0): 46-60.

Dublet, G. et al., 2012. Ni speciation in a New Caledonian lateritic regolith: A quantitative X-ray absorption spectroscopy investigation. Geochimica et Cosmochimica Acta, 95(0): 119-133.

Juillot, F. et al., 2008. Zn isotopic fractionation caused by sorption on goethite and 2-Lines ferrihydrite. Geochimica Et Cosmochimica Acta, 72(19): 4886-4900.

Manceau, A. et al., 2000. Crystal chemistry of trace elements in natural and synthetic goethite. Geochimica et Cosmochimica Acta, 64(21): 3643-3661.

Waychunas, G.A., Fuller, C.C., Davis, J.A., 2002. Surface complexation and precipitate geometry for aqueous Zn(II) sorption on ferrihydrite I: X-ray absorption extended fine structure spectroscopy analysis. Geochimica et Cosmochimica Acta, 66(7): 1119-1137.