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

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### 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 ( $\Delta_{60/58}\text{Nimin-aq} = \delta_{60/58}\text{Nimin} - \delta_{60/58}\text{Niaq}$ ) 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  $\Delta_{60/58}\text{Nimin-aq} = -0.77 \pm 0.23\text{‰}$  ( $n = 14$ , 2sd), whereas adsorption to 2-line ferrihydrite samples yield  $\Delta_{60/58}\text{Nimin-aq} = -0.35 \pm 0.08\text{‰}$  ( $n = 16$ , 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

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

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

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

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

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

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

100 to consider as it could have impacted the Ni signal preserved in Iron Formations (Friedrich et  
101 al., 2011).

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

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 ( $\alpha$ -FeOOH) and 2-line ferrihydrite were synthesized by  
122 raising the pH of a  $\text{Fe}(\text{NO}_3)_3$  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<sub>2</sub> adsorption (Micromeritics Tristar II 3020).  
130 The specific surface areas for goethite and 2-line ferrihydrite were 25.5 and 119 ± 3 m<sup>2</sup>/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

141 For the Ni sorption experiments, a stock solution of 17 mmol/L Ni (1000 mg/L Ni)  
142 was made with a Ni(NO<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O(aq) salt (Fischer Scientific). Aqueous suspensions were  
143 prepared with 0.15 g of goethite or 2-line ferrihydrite in 150 mL of 0.05 mol/L NaNO<sub>3</sub> in 250  
144 mL Teflon bottles. The Fe-oxyhydroxides were allowed to equilibrate for 24 hours at the  
145 target experimental pH before the addition of an aliquot of Ni from the stock solution. Nickel  
146 was added slowly using a micropipette over a 15 minutes' period, with continuous mixing  
147 with a Teflon-coated stir bar to reduce changes to the pH of the suspension. A control  
148 consisting of the mineral in 0.05 mol/L NaNO<sub>3</sub> solution with no Ni added was included with  
149 each set of experiments and Ni in the blank did not exceed 0.1% of the total amount of Ni

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

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

169 Time-dependent experiments were done to check whether kinetic isotopic effects are  
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  $\mu\text{mol/L}$  and 426  $\mu\text{mol/L}$ , 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  
174 allowed to react for 18 (or 19 hours for 2-line ferrihydrite), 20, 22, and 23 hours, respectively.



175 A maximum equilibration time of 24 hours was chosen based on our initial test time-  
176 dependent experiments with goethite and ferrihydrite in which the aqueous Ni concentration  
177 stabilized after 18 to 23 hours of reaction, consistent with experimental design implemented  
178 by Wasylenki et al. (2015). These findings are consistent with bulk chemical equilibrium and  
179 were used to choose the reaction time for the adsorption experiments. This also prevents the  
180 potential effect of diffusion-controlled penetration of Ni into Fe (oxy)hydroxides on Ni  
181 isotope fractionation, since this process has been shown to occur over long (week to month)  
182 timescales, while surface adsorption reaches completion within a few hours (Bruemmer et al.,  
183 1988). As discussed below, at bulk chemical equilibrium the mineral continues to exchange  
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

189 Nickel K-edge EXAFS spectroscopy measurements were conducted at the Advanced  
190 Photon Source (Argonne National Laboratory) at beamline 20-BM in fluorescence mode  
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  
193 a mylar adhesive with a microspatula. Multiple mylar layers were stacked (6-8 layers) and the  
194 edges sealed to form an envelope around the sample. Measurements were conducted at room  
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  
198 replicate scans and energy calibration (Ni foil with inflection point set to 8334.5 eV), and the  
199 Artemis program was used to generate phase and amplitude paths for Ni K-edge EXAFS

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

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

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

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<sub>short</sub> :CN<sub>long</sub>) with a  
229 maximum total second-shell CN of 5 (Arai, 2008). Thus, CN<sub>short</sub> :CN<sub>long</sub> 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 Software) 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<sub>3</sub>), and partial pressure of CO<sub>2</sub> 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 [  $2 \text{ =SOH} + \text{Ni}^{2+}$   
245  $\Leftrightarrow 2(\text{SOH})\text{Ni} + 2\text{H}^+$ ,  $\log K = -2.45$  ] 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

249 expanded version of the MINTEQA2 database. Between pH 5.0 and 7.0, the dominant Ni  
250 species in aqueous solution, under the initial experimental conditions considered here, is the  
251  $\text{Ni}^{2+}$  (hexaquo) (> 88 %). In addition to  $\text{Ni}^{2+}$  (hexaquo),  $\text{NiNO}_3^+$  is present and accounts for >  
252 11% of the Ni in solution. For the experiments with a pH value greater than 7.0, the aqueous  
253 Ni species include minor contributions from  $\text{NiHCO}_3^+$  and  $\text{NiCO}_3^0$ . Slow addition of Ni  
254 during the experiments over a 15-minutes period reduced the risk of precipitation of Ni above  
255 pH 7.8. For the experiments at pH 7.7, Ni occurs as: (1) 83.7%  $\text{Ni}^{2+}$  (hexaquo); (2) 10.7 %  
256  $\text{NiNO}_3^+$ ; (3) 4.1 %  $\text{NiHCO}_3^+$ ; and (4) 1.5 %  $\text{NiCO}_3^0$  for initial Ni concentrations ranging from  
257 17 to 426  $\mu\text{mol/L}$ .

258

#### 259 *2.4. Concentration determinations and column chromatographic purification of Ni*

260

261 All manipulations were performed in a class 1000 clean room and exclusively used  
262 acid-cleaned plasticware and teflonware. Solid samples were digested in 6 mol/L HCl at room  
263 temperature for 72 hours. The total concentrations of Ni and Fe in the solids were determined  
264 by quadrupole ICP-MS (X-series2, Thermo Scientific) at the Pôle Spectrométrie Océan (PSO,  
265 Brest, France). Nickel concentrations in the filtrates were first estimated by mass balance  
266 using the initial concentrations in solutions used at the start of each experiment and the Ni  
267 concentrations in the solids determined by quadrupole ICP-MS at the end of the experiment.  
268 Nickel concentrations were then recalculated by isotope dilution after isotope measurements.

269 For the separation of Ni onto chromatographic columns, an aliquot of each filtrate was  
270 evaporated to dryness at 80°C prior to redissolution in 1 ml of 6 mol/L HCl. A full description  
271 of the purification method can be found in Gueguen et al. (2013). Briefly, our two-step  
272 separation procedure involved: (1) separation of Fe onto an anion exchange chromatographic  
273 resin (BioRad AG1-X8, 100-200 mesh); (2) separation of Ni from the remaining matrix using

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<sub>3</sub> 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 <sup>61</sup>Ni and <sup>62</sup>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 <sup>58</sup>Ni, <sup>60</sup>Ni,  
288 <sup>61</sup>Ni, <sup>62</sup>Ni, <sup>64</sup>Ni, and potential isobaric interferences from Zn (measured on <sup>66</sup>Zn) and Fe  
289 (measured on <sup>57</sup>Fe). Argon oxide interferences (e.g., <sup>40</sup>Ar<sup>18</sup>O<sup>+</sup> on <sup>58</sup>Ni<sup>+</sup> and <sup>40</sup>Ar<sup>17</sup>O on <sup>57</sup>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 :

$$293 \quad \delta^{60/58}\text{Ni} (\text{‰}) = \left( \frac{^{60/58}\text{Ni}_{\text{sample}}}{^{60/58}\text{Ni}_{\text{NIST986}}} - 1 \right) \times 1000 \quad (1)$$

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,  $\delta^{60/58}\text{Ni}=0.33\text{‰}$ ; and  
297 USGS Nod-A-1,  $\delta^{60/58}\text{Ni}=1.04\text{‰}$ ) and was found to be  $\sim 0.06 \text{‰}$  (2sd).

298

### 299 3. Results

300

#### 301 3.1. Nickel sorption by Fe oxyhydroxides

302

303 The loadings of Ni onto both 2-line ferrihydrite and goethite expressed in terms of the  
304 percent of Ni sorbed for pH-dependent and varying initial [Ni] experiments are displayed in  
305 Table 1. The sorption of Ni onto 2-line ferrihydrite for pH ranging from 5.0 to 8.0 (i.e., pH-  
306 dependent experiments, with initial Ni concentration of 170  $\mu\text{mol/L}$ ) resulted in Ni uptake  
307 between < 1% and 45% translating into 0.02 to 0.62  $\mu\text{mol Ni/m}^2$  mineral (Figure 1a). At pH  
308 7.7 (varying initial Ni concentrations experiments, 17 to 426  $\mu\text{mol/L Ni}$ ), final Ni loadings on  
309 2-line ferrihydrite ranged from 0.11 to 1.71  $\mu\text{mol Ni/m}^2$  mineral (Figure 1), which correspond  
310 to a percentage of sorbed Ni between 25% and 78%.

311 Nickel sorption to goethite at pH 5.0, 6.0, and 8.0 resulted in Ni uptake between < 1%  
312 and 4.3% of the initial 170  $\mu\text{mol/L}$  aqueous Ni (Figure 1), corresponding to Ni loadings  
313 ranging from 0.04 and 0.28  $\mu\text{mol Ni/m}^2$ . At pH 7.7, Ni uptake from solutions with initial  
314 concentrations of 17, 170, and 426  $\mu\text{mol/L Ni}$  yielded final Ni loadings onto the mineral  
315 between 0.63 to 1.33  $\mu\text{mol Ni/m}^2$ , corresponding to percentage of sorbed Ni between 8% and  
316 19%.

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

322

#### 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<sup>2</sup>/g, solid concentrations close to 1  
334 g/L, and a goethite site density of 1 site per nm<sup>2</sup>. Adopting higher literature values for the  
335 latter (e.g., 2.3 sites per nm<sup>2</sup> (Davis and Kent, 1990) or 6 sites per nm<sup>2</sup> (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

343           Nickel K-edge EXAFS spectra were collected for six Ni-sorbed 2-line ferrihydrite  
344 samples (Fh-pH-05, Fh-C-07, Fh-C-08, Fh-C-09, and Fh-C-10) and one Ni-sorbed goethite  
345 sample (Goe-C-06) as indicated in Table 1. The Ni K-edge EXAFS spectra collected for the  
346 2-line ferrihydrite samples at pH 7.7 and 8.0 are similar in phase and amplitude despite  
347 different Ni-loadings and pH values (displayed in k-space with best fits; Figure 3). All Ni K-  
348 edge EXAFS spectra were fit with ~ 6 Ni-O atom pairs in the first-shell at a distance of 2.05 ±

349 0.01 Å (Table 3). For the Ni-Fe second-shell atom pairs, two sub-shells were required to  
350 describe the data: ~ 1.5 Ni-Fe (type 1) at  $3.10 \pm 0.02$  Å and ~ 0.6 Ni-Fe (type 2) at  $3.56\text{-}3.60$   
351  $\pm 0.06$  Å. Errors in the second shell coordination numbers were estimated using the fractional  
352 parameter error as an indicator. As these error values were low we estimated CN error to be  
353 ~25% of the value.

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

364

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

366

367 The Ni isotope composition of the initial Ni stock solution was determined at  $\delta^{60/58}\text{Ni}$   
368  $= -0.33 \pm 0.05$  ‰ (2sd, n=4, Table 1). The Ni isotope compositions of mineral-associated Ni  
369 (i.e, sorbed onto 2-line ferrihydrite and goethite) and solution are reported in Table 1.

370 The difference in Ni isotopic composition between the mineral sorbed-Ni and Ni  
371 remaining in solution, which we define as the fractionation factor, is expressed as  $\Delta^{60/58}\text{Ni}_{\text{min-}}$   
372  $\text{aq}$  (equation 2) according to:

373



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

375

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

383

384 
$$\delta^{60/58}\text{Ni}_{\text{bulk}} = (\% \text{Ni}_{\text{sorbed}}/100 \times \delta^{60/58}\text{Ni}_{\text{mineral}}) + ((1 - \% \text{Ni}_{\text{sorbed}}/100) \times \delta^{60/58}\text{Ni}_{\text{aqueous}}) \quad (3)$$

385

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

392 The pH-dependent adsorption experiments on 2-line ferrihydrite yielded surface  
393 loadings from 0.02 to 0.62  $\mu\text{mol Ni/m}^2$  mineral with  $\Delta^{60/58}\text{Ni}_{\text{min-aq}}$  values ranging from -0.37  
394 to -0.03 ‰ (Figure 6). At low loadings of Ni onto 2-line ferrihydrite, i.e., 0.02 – 0.04  $\mu\text{mol}$   
395  $\text{Ni/m}^2$  mineral which correspond to 1 and 3% percent of to the total added Ni sorbed in the pH  
396 5.0 and 6.0 experiments, Ni isotopes were not fractionated ( $\Delta^{60/58}\text{Ni}_{\text{min-aq}} = -0.03\text{‰}$ ) or weakly  
397 fractionated ( $\Delta^{60/58}\text{Ni}_{\text{min-aq}} = -0.12 \text{‰}$ ) respectively. Although Figure 6 seems to indicate that  
398 decreasing  $\Delta^{60/58}\text{Ni}_{\text{min-aq}}$  values are correlated with increasing pH for 2-line ferrihydrite, we

399 think these data are an artifact since low pH values (5.0 and 6.0) also correspond to very low  
400 Ni loadings (see discussion). For this reason, we decided to not include these data when  
401 discussing average Ni isotope fractionation factors. In contrast, at pH 7.7, the percent Ni  
402 sorbed was generally higher and Ni loadings of 0.32 – 1.71  $\mu\text{mol Ni/m}^2$  mineral were  
403 achieved, which represent between 23 and 78% Ni-sorbed on 2-line ferrihydrite. This gave a  
404 range of  $\Delta^{60/58}\text{Ni}_{\text{min-aq}}$  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  $\mu\text{mol Ni/m}^2$   
407 mineral), and Ni isotope fractionation was characterized by  $\Delta^{60/58}\text{Ni}_{\text{min-aq}}$  values between -0.96  
408 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  $\mu\text{mol Ni/m}^2$  mineral yielded  $\Delta^{60/58}\text{Ni}_{\text{min-aq}}$  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  $\Delta^{60/58}\text{Ni}_{\text{min-aq}} = -0.70$  ‰ and  $-0.88$  ‰ for pH 5.0 and 6.0, respectively. The largest  $\Delta^{60/58}\text{Ni}_{\text{min-}}$   
413  $\text{aq}$  value of  $-1.03$  ‰ was measured at pH 7.7 for goethite with the highest Ni loading.

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

421

#### 422 4. Discussion

423

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

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

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

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

474 second major coordination shell is composed of Fe atoms. The interatomic distances between  
475 Ni and Fe, as measured by Ni K-edge EXAFS spectroscopy, define the local coordination  
476 environment of the Ni surface species and Ni sorbed on ferrihydrite and goethite have been  
477 studied in detail (Waychunas et al., 2002; Arai, 2008; Juillot et al., 2008; Dublet et al., 2012;  
478 Cismasu et al., 2013). It was demonstrated that Ni sorbed on ferrihydrite occurs in octahedral  
479 coordination between Ni-O<sub>6</sub> and Fe-O<sub>6</sub> polyhedra with interatomic distances in the range of  
480 3.05-3.08 Å for edge-sharing type 1 surface complexes, 3.19-3.12 Å for edge-sharing type 2,  
481 and 4.03-4.07 Å for corner-sharing (Arai, 2008). Type 1 edge sharing is between Ni and Fe  
482 octahedra in the chains and type 2 surface complexes is between Ni and Fe octahedra in the  
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  
485 a chain of Fe-O<sub>6</sub> octahedra (i.e., type 1), edge-sharing between chains of Fe-O<sub>6</sub> octahedra (i.e.,  
486 type 2), and corner-sharing Fe-O<sub>6</sub> octahedra between double chains (Manceau and Drits,  
487 1993).

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

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 ( $3.10 \pm 0.02 \text{ \AA}$ ) 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 ( $3.57 \pm 0.06 \text{ \AA}$ ). 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  $3.07 \pm 0.03 \text{ \AA}$  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

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

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

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

541 For time-dependent experiments, we determine a range of  $\Delta^{60/58}\text{Ni}_{\text{min-aq}}$  values for the  
542 2-line ferrihydrite between  $-0.32 \pm 0.04$  and  $-0.38 \pm 0.06\text{‰}$ , and for goethite between  $-0.65$   
543  $\pm 0.07$  and  $-0.77 \pm 0.07\text{‰}$ . Therefore,  $\Delta^{60/58}\text{Ni}_{\text{min-aq}}$  values do not vary within uncertainties over  
544 the course of the experiments. This is in agreement with previous results of Wasylenki et al.  
545 (2015) showing no variations in  $\Delta^{60/58}\text{Ni}_{\text{min-aq}}$  values for 2-line ferrihydrite for experiment  
546 duration between a few hours to 30 days. There is also no appreciable difference in the  
547 magnitude of Ni isotope fractionation factor depending on the initial Ni concentration and  
548 sorption %, i.e.,  $\Delta^{60/58}\text{Ni}_{\text{min-aq}} = -0.35 \pm 0.01 \text{‰}$  (2sd, n=4) for an initial Ni concentration of

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

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



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  $\mu\text{mol Ni/m}^2$  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  $\Delta^{60/58}\text{Ni}_{\text{min-aq}}$  values (i.e., decrease) at low Ni-loading.

582

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

584

585 Our experiments showed that Ni sorbed to goethite is twice more fractionated towards  
586 lighter  $\Delta^{60/58}\text{Ni}_{\text{min-aq}}$  values ( $\sim -0.77 \text{ ‰}$ ) than Ni sorbed to 2-line ferrihydrite ( $\sim -0.35 \text{ ‰}$ ).

587 Nickel species in solution that are likely to be adsorbed onto minerals are the  $\text{Ni}^{2+}$   
588 (hexaquo) species (Peacock and Sherman, 2007a). The surface complexation model reported  
589 in Figure 2 predicts that under the experimental conditions used in our study Ni should sorb to  
590 goethite to a greater extent than we observed in our experiments. At pH values less than  $\sim 8.0$ ,  
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  
593 charged surface. The net negative surface charge of 2-line ferrihydrite tends to attract  
594 dissolved cations to its surface while the net positive surface charge of goethite tends to repel  
595 dissolved cations and ferrihydrite has a higher surface area than goethite. This is in agreement  
596 with the strong uptake of Ni from solution by 2-line ferrihydrite observed in our experiments  
597 and predicted by our surface complexation model (Figure 2).

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

614 Mechanism (1) : Protonation of aqueous or sorbed Ni. As a divalent cation, Ni has a  
615 relatively low ionic potential, e.g., in contrast to  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$ . Hence,  $\text{Ni}(\text{H}_2\text{O})_6^{2+}$  does not  
616 readily undergo hydrolysis and Ni tends to form relatively weak aqueous complexes with  
617 ligands when compared to trivalent cations. In addition, because we expect the presence of a  
618 single aqueous Ni species,  $\text{Ni}(\text{H}_2\text{O})_6^{2+}$ , in our experiments there should be no isotopic  
619 fractionation occurring in solution.

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

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

631 Mechanism (3): Bond distances between the metal and oxygen atoms and the  
632 presence of other atoms in the mineral structure. The minerals studied here were synthesized  
633 in the laboratory and are free of impurities. In addition, as discussed above, the Ni-O first-  
634 shell interatomic distances are indistinguishable among our 2-line ferrihydrite and goethite  
635 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% Ni<sup>2+</sup> (hexaquo),  
638 Ni(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup>, 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  
641 results indicate that the local coordination environment for Ni at the mineral surface is similar  
642 for all Ni loadings and pH values for 2-line ferrihydrite. To determine whether we can extend  
643 this finding to goethite, we compared two samples for which Ni K-edge EXAFS data were  
644 collected: (1) Goe-C-06 (1.33 μmol Ni/m<sup>2</sup>) and Fh-C-10 (1.71 μmol Ni/m<sup>2</sup>). These two  
645 samples have similar Ni loadings when the amount of adsorbed Ni is normalized by specific  
646 surface area (Table 1) and the Ni K-edge EXAFS-derived fit parameters for the Ni-O shell are  
647 identical within errors. In other words, the Ni species have the same coordination number and

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

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  
659 the Ni-Fe second-shell coordination environment when comparing two Ni-sorbed mineral  
660 samples having similar Ni loading when expressed in terms of surface area rather than total  
661 mass. Nickel sorbed to goethite has fewer Fe atoms in the second-shell than Ni sorbed to 2-  
662 line ferrihydrite. The goethite structure is known to generate three different surface functional  
663 groups based on the number of Fe atoms bonded to a surface oxygen (Essington, 2003) : type  
664 (1)  $\equiv\text{Fe}_3\text{-O}^{1/2-}$ , type (2)  $\equiv\text{Fe}_2\text{-O}^{1-}$ , and type (3)  $\equiv\text{Fe-O}^{3/2-}$ . In our experiments, sorption of  
665  $\text{Ni}(\text{H}_2\text{O})_6^{2+}$  by site type (3) is most consistent with the results. In addition, fewer Fe atoms in  
666 the second coordination shell is consistent with weaker surface complexes and the observed  
667 enrichment of light Ni isotopes in the Ni-sorbed to goethite sample leading to larger isotopic  
668 fractionation (i.e., larger fractionation factor  $\Delta\delta^{60/58}\text{Ni}_{\text{min-aq}}$ ) than for 2-line ferrihydrite.

669

670 *4.4. Implications for Ni isotope biogeochemical cycling in modern and ancient surface*  
671 *environments*

672

673 *4.4.1. Nickel isotope systematics during continental weathering*

674

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

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.,

698 2004), but ferrihydrite can be metastable in some environments (Navrotsky et al., 2008; Toner  
699 et al., 2012). The presence of large amounts of Ni incorporated in Fe-oxyhydroxides has been  
700 shown to slow the transformation of poorly crystalline Fe-oxyhydroxides to more crystalline  
701 phases (Cornell et al., 1992; Cornell and Schwertmann, 2003). During dissolution of Fe(III)-  
702 oxyhydroxides, Ni is released more slowly than Fe, which leads to enrichment in Ni in the  
703 residual solid phase (Cornell et al., 1992). The presence of organic ligands in seawater may  
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  
706 the two mineral phases as observed in this study, the overall Ni isotope composition of Fe-  
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  
709 be a major mechanism for explaining the enrichment in heavy Ni isotopes in river water  
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.,  
712 Amazon river) may contain some anthropogenic Ni as a by-product of fossil fuel burning,  
713 which may alter both the natural concentration of Ni in rivers and its isotopic composition.  
714 For instance, Gueguen et al. (2013) report a  $\delta^{60/58}\text{Ni}$  value of 0.5 ‰ in coal, which is heavier  
715 than the Bulk Silicate Earth isotopic composition. Such anthropogenic input could also  
716 explain the apparent Ni isotopic imbalance in the ocean (Cameron and Vance, 2014), thereby  
717 implying that Ni delivery to the ocean occurs under non steady-state conditions.

718

#### 719 *4.4.2. Application to Precambrian seawater chemistry and ancient Ni biogeochemical cycling*

720

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

723 decrease in the Ni delivery to the ocean at the onset of the Great Oxidation Event, at ca. 2.5  
724 Ga. Under the overall anoxic conditions and high Ni bioavailability of the Archean oceans,  
725 microorganisms such as methanogens may have been important primary producers. Given  
726 that methanogens fractionate light Ni isotopes by up to  $\sim -1.5$  ‰ (Cameron et al., 2009), such  
727 a shift in Ni utilization in the oceans should have left characteristic imprints in the Ni isotopic  
728 composition of Precambrian seawater. Because Fe-oxyhydroxides were probably an important  
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  
731 the Ni isotopic composition of Precambrian seawater from the Precambrian sediment record  
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  
734 chemical composition of seawater with biological evolution and diversification (Bekker et al.,  
735 2010). However, Fe-oxides such as hematite and magnetite are the predominant carrier of Ni  
736 in these deposits, although accessory minerals such as silicates (e.g., stilpnomelane) and  
737 carbonates may be also important. Because the nature and origin of the Fe-oxyhydroxide  
738 precursor in BIF remain poorly known, interpretations based on the Ni isotope composition in  
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.

741         Our results show that Ni isotope fractionation during abiotic reactions involving  
742 adsorption on Fe-oxides are of the same order of magnitude as for biotic reactions (i.e.,  
743 Cameron et al., 2009) and vary between different mineral surfaces i.e., from  $\sim -0.35$  ‰ (2-line  
744 ferrihydrite) to  $\sim -0.77$  ‰ (goethite). Hence, the use of Ni isotopes as biosignatures should be  
745 approached with caution, as Ni isotope fractionation produced by abiotic processes may mask  
746 any isotope signals related to biotic processes. This issue is critical for BIF studies because  
747 the large extent of Fe precipitation in seawater, leading to the accumulation of freshly formed

748 Fe-oxyhydroxides at the seafloor as likely BIF precursors, may also shift the isotopic  
749 composition Ni remaining in seawater.

750 In a previous study, Wasylenki et al. (2015) suggested that Ni isotopes in BIF should  
751 be offset by  $\sim -0.35$  ‰ relatively to seawater. We further propose that such an offset is likely  
752 a minimum value, considering that fractionation up to  $\sim -0.77$  ‰ is observed during sorption  
753 to goethite, regardless of potential kinetic isotope effects. Clearly, further study investigating  
754 the preservation of Ni isotope signatures during Fe-oxyhydroxide recrystallization to hematite  
755 and magnetite is warranted in order to directly apply Ni isotope systematics to the BIF record.  
756 Although Wasylenki et al. (2015) showed that there was apparently no isotope fractionation  
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  
759 durations as well as heating of the system should be explored to better evaluate the effect of  
760 ferrihydrite aging on Ni isotopes. The effect of silica (Eickhoff et al., 2014) and the possibility  
761 that it could affect the Ni isotope fractionation factor during BIF formation, has also to be  
762 considered when investigating the BIF record.

763

## 764 **5. Summary**

765

766 Consistent with previous studies (Wasylenki et al., 2015), we found that Ni isotopes  
767 are readily fractionated towards light Ni isotopes during adsorption to Fe-oxyhydroxide  
768 minerals. Building on that work, we have demonstrated that Ni sorbed to 2-line ferrihydrite is  
769 less fractionated than Ni sorbed to goethite with average  $\Delta^{60/58}\text{Ni}_{\text{min-aq}}$  values of  $-0.35 \pm 0.08$   
770 ‰ and  $-0.77 \pm 0.23$  ‰, respectively. No difference in  $\Delta^{60/58}\text{Ni}_{\text{min-aq}}$  values was observed either  
771 as a function of Ni loading or as a function of pH in both 2-line ferrihydrite and goethite. For  
772 both 2-line ferrihydrite and goethite, Ni K-edge EXAFS results indicate that there are no



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

785

786         The magnitude of isotope fractionation suggests that Ni adsorption to Fe-  
787 oxyhydroxides is a significant process controlling Ni isotope abundances in the natural  
788 environment. Our study also shows that such Ni isotope fractionation factors during Ni  
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  
792 Ni isotope (bio)signatures in ancient sedimentary rocks. This study underpins the need to  
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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798

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816

817 **Figure captions:**

818

819 **Figure 1:** Nickel loading to minerals ( $\mu\text{mol}/\text{m}^2$  mineral) as a function of (a) pH (data from  
820 pH-dependent experiments) and (b) initial aqueous concentration of Ni ( $\mu\text{mol}/\text{L}$ ) (data from  
821 varying initial Ni concentration experiments).

822

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

830

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

834

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

838

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

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

851

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

858

859 **Figure 7:** Ni isotope fractionation factors ( $\Delta^{60/58}\text{Ni}_{\text{min-aq}} = \delta^{60/58}\text{Ni}_{\text{mineral}} - \delta^{60/58}\text{Ni}_{\text{aqueous}}$ ) versus  
860 %-adsorption for (a) 2-line ferrihydrite and (b) goethite for each type of experiment. Pink dots  
861 are for pH-dependent experiments, brown dots for the variable initial Ni concentration  
862 experiments and blue dots are for the time-dependent experiments. The unfilled red datapoints  
863 in plot (a) (2-line ferrihydrite) correspond to very low Ni-sorbed samples (see main text for  
864 explanation).

865

866 **Table captions:**

867

868 **Table 1:** Sample information, summary of experimental conditions, Ni loading to the mineral  
869 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).

872

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

876

877 **Table 3:** Summary of Ni K-edge EXAFS fit parameters.

878

879

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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.

Mineral	Sample name	Type of experiment	pH	[Ni] <sub>aq</sub> <sup>initial</sup> (μmol/L)	Final loading to mineral (μmol Ni/g) <sup>f</sup>	Final loading to mineral (μmol Ni/m <sup>2</sup> ) <sup>f</sup>	% of Ni sorption <sup>d</sup>	δ <sup>60/58</sup> Ni <sub>mineral</sub>	2se <sup>e</sup>	δ <sup>60/58</sup> Ni <sub>aqueous</sub>	2se	Δ <sup>60/58</sup> Ni <sub>min-aq</sub> <sup>f</sup>	2se <sup>g</sup>	Mass balance (‰)
2-line Ferrihydrite <sup>a</sup>	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 <sup>b</sup>	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	-	-	-
<b>Average Ni standard solution<sup>h</sup></b>	-	-	-	-	-	-	-	-	-	<b>-0.33</b>	<b>0.05 (2sd)</b>	-	-	-
Nod-A-1 <sup>i</sup>	-	-	-	-	-	-	-	-	-	1.06	0.02	-	-	-
Nod-A-1 <sup>i</sup>	-	-	-	-	-	-	-	-	-	1.01	0.03	-	-	-
Nod-A-1 <sup>i</sup>	-	-	-	-	-	-	-	-	-	1.05	0.04	-	-	-
Nod-P-1 <sup>i</sup>	-	-	-	-	-	-	-	-	-	0.30	0.03	-	-	-
Nod-P-1 <sup>i</sup>	-	-	-	-	-	-	-	-	-	0.35	0.04	-	-	-
Nod-P-1 <sup>i</sup>	-	-	-	-	-	-	-	-	-	0.34	0.03	-	-	-
Nod-P-1 <sup>i</sup>	-	-	-	-	-	-	-	-	-	0.32	0.03	-	-	-

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

<sup>a</sup> 2-line ferrihydrite (0.014 mol Fe/g dry mineral)

<sup>b</sup> Goethite (0.015 mol Fe/g dry mineral)

<sup>c</sup> Final loading corresponds to the amount of Ni per gram or m<sup>2</sup> of mineral in the reactor. The amount of mineral added per reactor measured was ~ 0.15 g.

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

<sup>e</sup> 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).

<sup>f</sup> The difference in isotopic composition between the mineral and the supernatant solution is expressed as Δ<sup>60/58</sup>Ni<sub>min-aq</sub> = δ<sup>60/58</sup>Ni<sub>mineral</sub> - δ<sup>60/58</sup>Ni<sub>aqueous</sub>. This value corresponds to the fractionation factor during Ni adsorption on the mineral surface. A two-standard error was determined for this value by error propagation.

<sup>g</sup> '2se' corresponds to error propagation of the Δ<sup>60/58</sup>Ni<sub>min-aq</sub> values (2se = √((2se<sub>mineral</sub>)<sup>2</sup> + (2se<sub>aqueous</sub>)<sup>2</sup>)).

<sup>h</sup> 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.

<sup>i</sup> Nod-A-1 and Nod-P-1 are duplicates of USGS geostandards measured for monitoring the reproducibility of the data.

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.

Mineral*	Sample name	Duration of experiment (hours)	pH	[Ni] <sub>aq</sub> <sup>initial</sup> (μmol/L)	Final loading to mineral (μmol Ni/g)	Final loading to mineral (μmol Ni/m <sup>2</sup> )	% of Ni sorption	δ <sup>60/58</sup> Ni <sub>mineral</sub> 2se	δ <sup>60/58</sup> Ni <sub>aqueous</sub> 2se	Δ <sup>60/58</sup> Ni <sub>min-aq</sub> 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

\*See Table 1 for footnotes.

Table 3: Summary of Ni EXAFS fit parameters.

Sample Name	Path	CN	R (Å)	$\sigma^2$ (Å <sup>2</sup> )	$\Delta E_0$ (eV)	$\chi$	Red $\chi^2$	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 ± 0.0760	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				

CN: coordination number

R: interatomic distance

$\sigma^2$ : Debye-Waller factor

$\Delta E_0$ : energy shift

Red  $\chi^2$ : reduced chi squared statistic

$S_0^2$ : 0.96

K-range: 3-1

R-range: 1-4

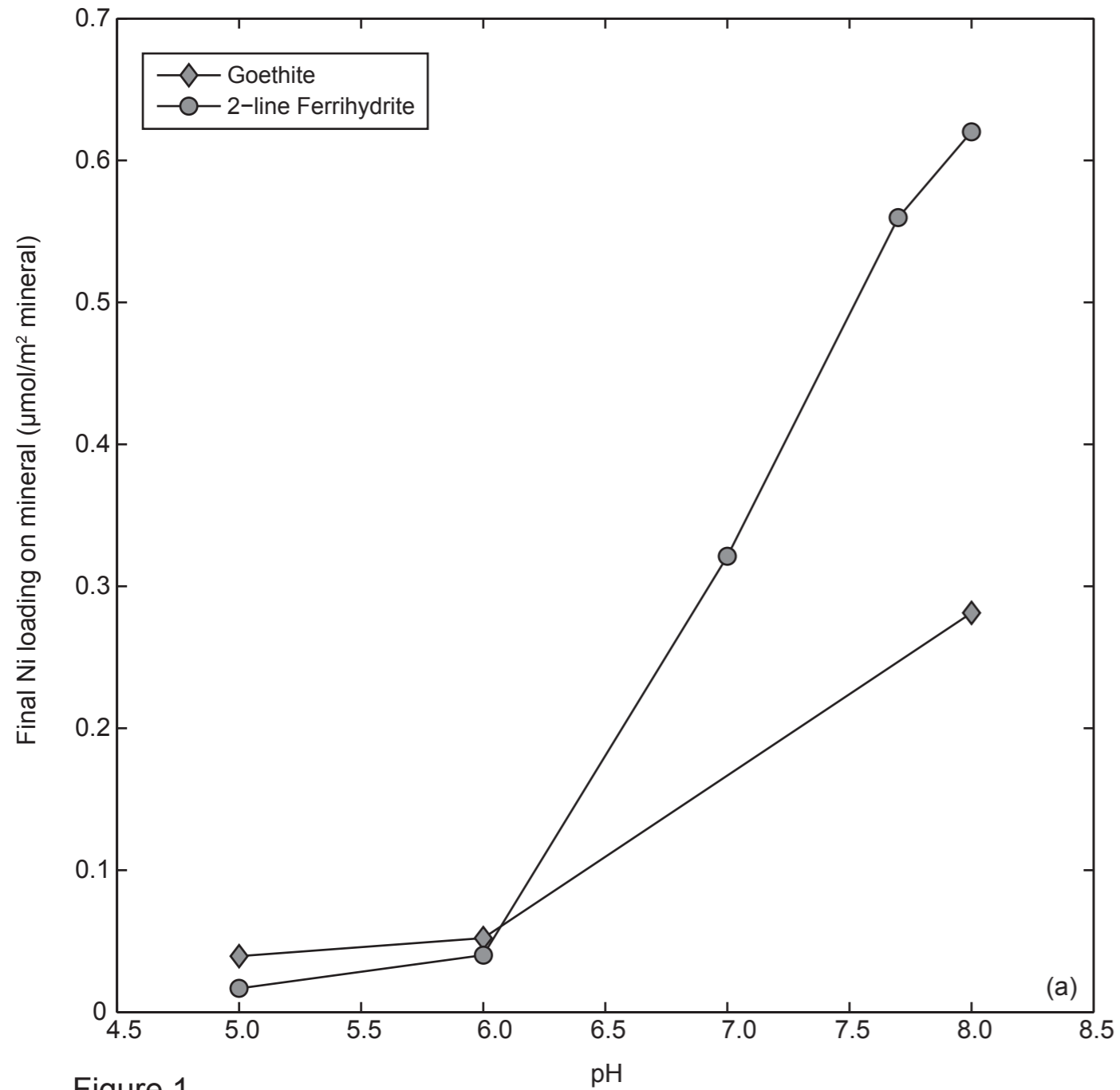
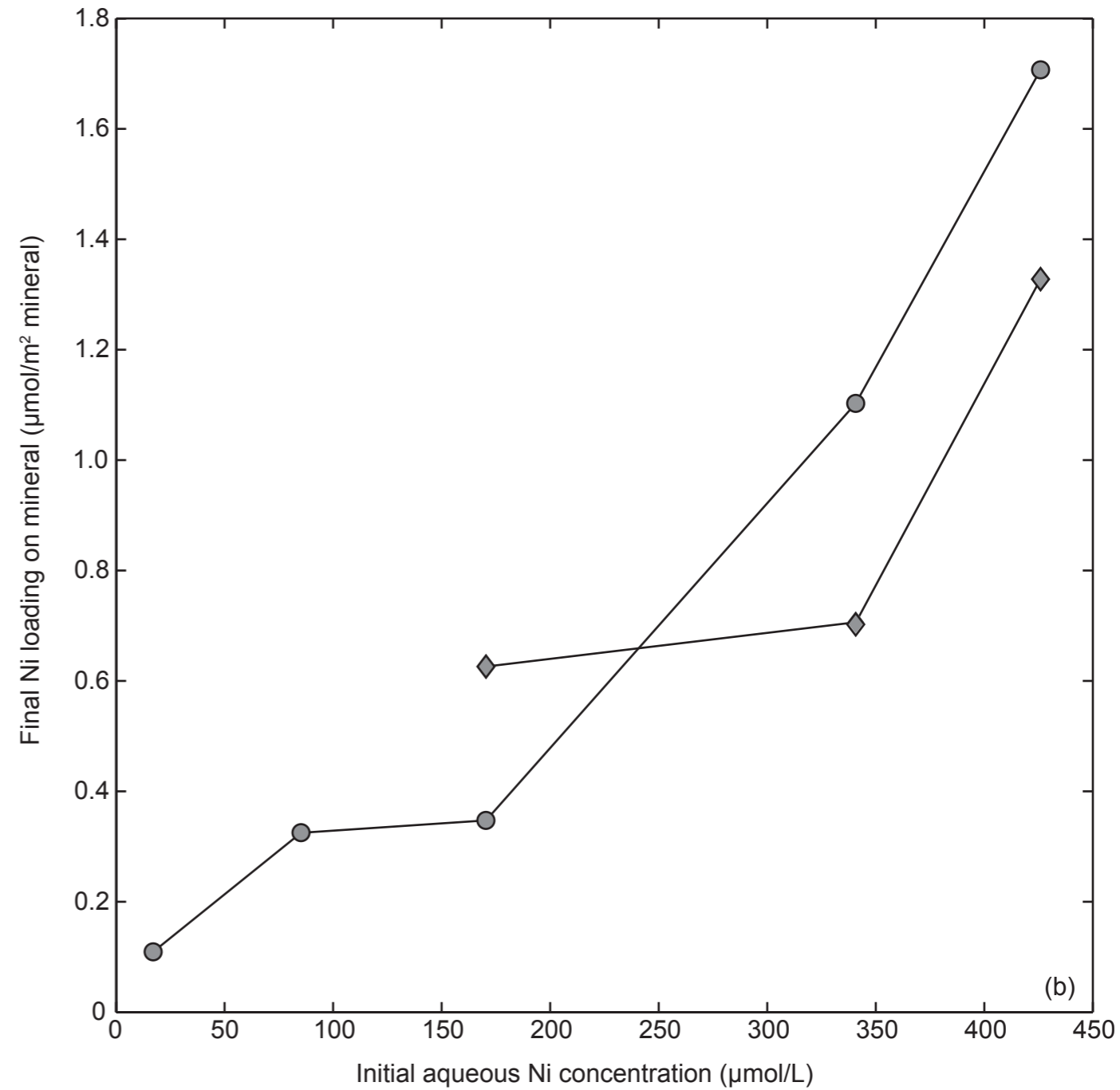


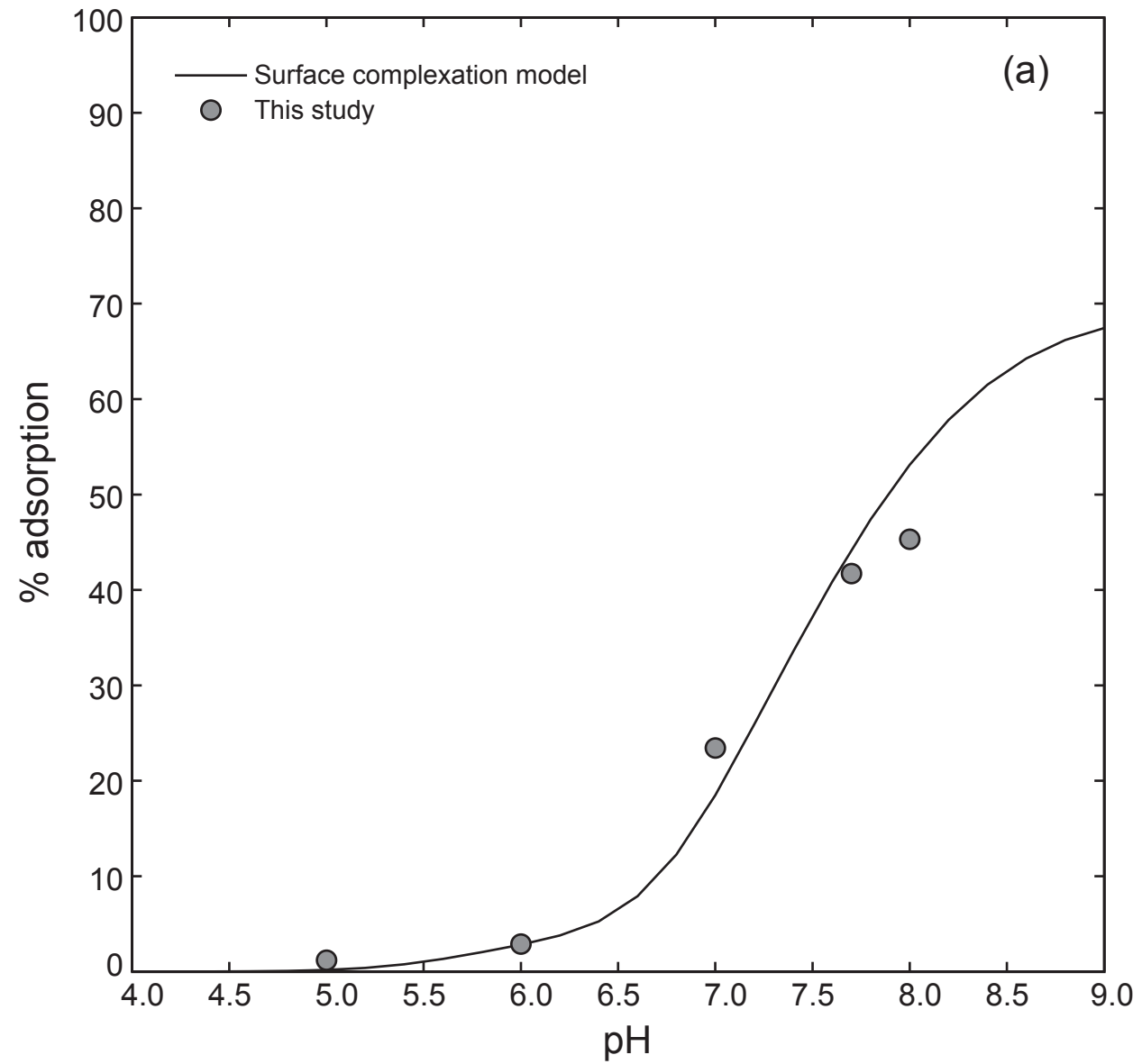
Figure 1



(b)



2-line ferrihydrite



Goethite

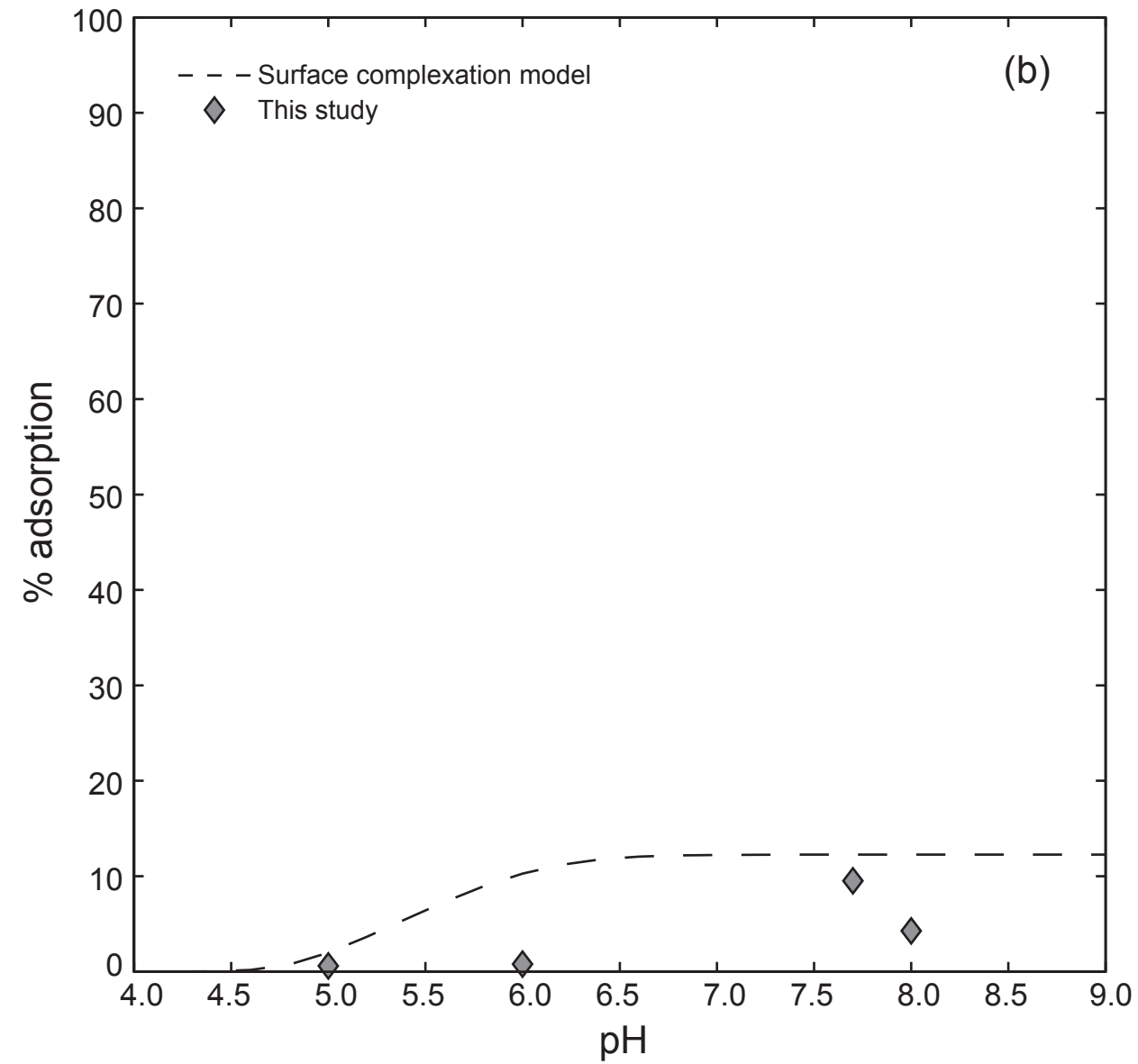


Figure 2

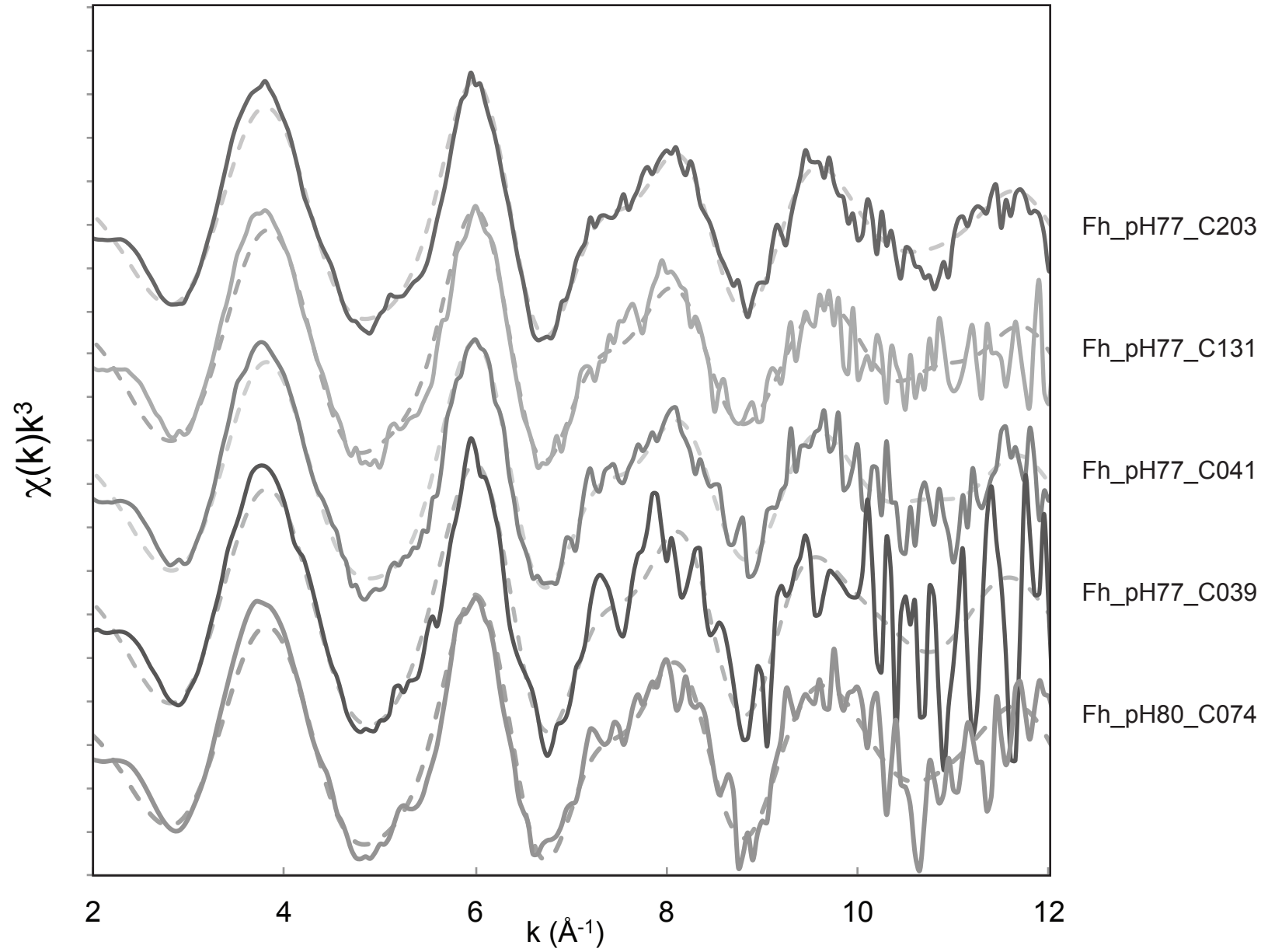


Figure 3

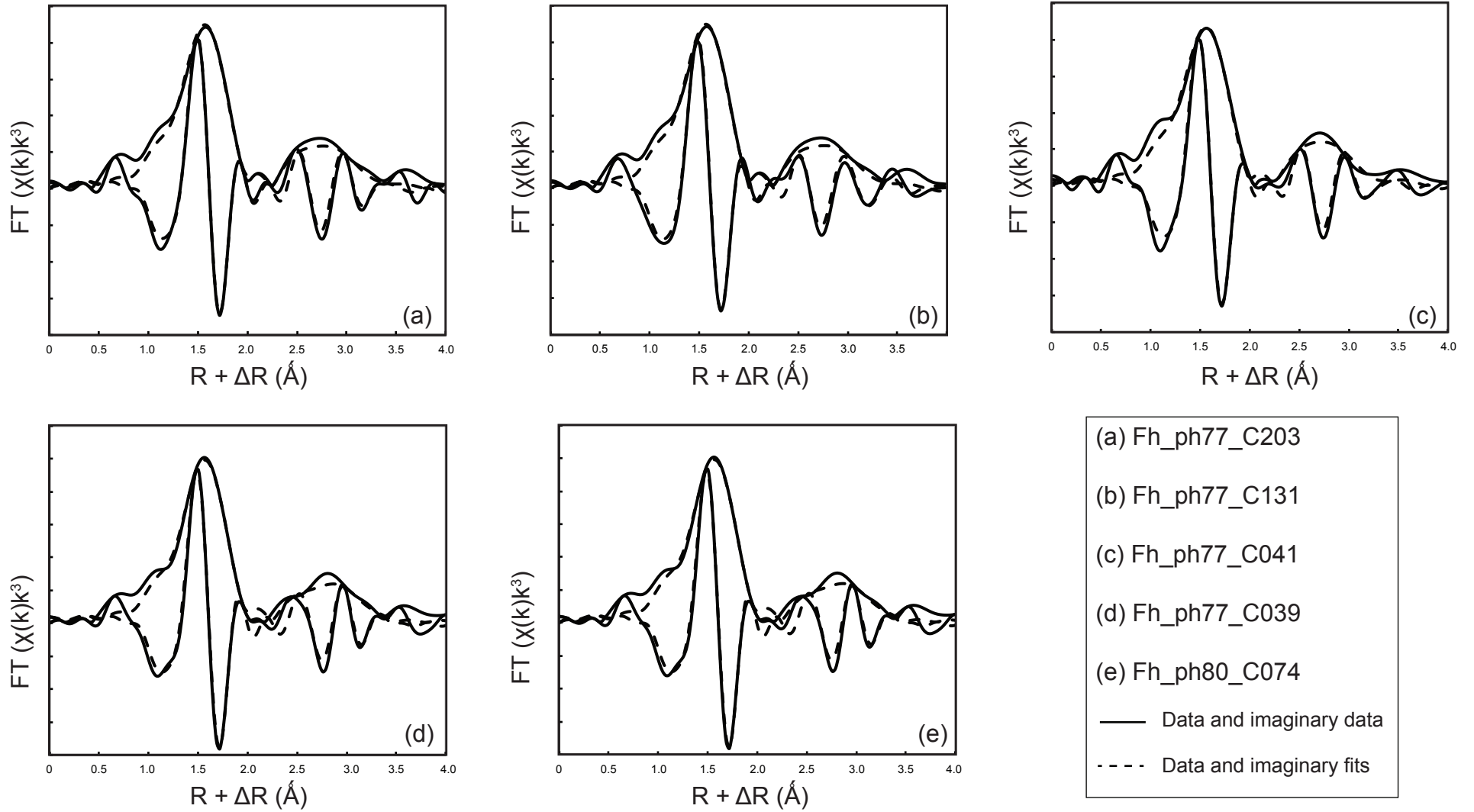


Figure 4

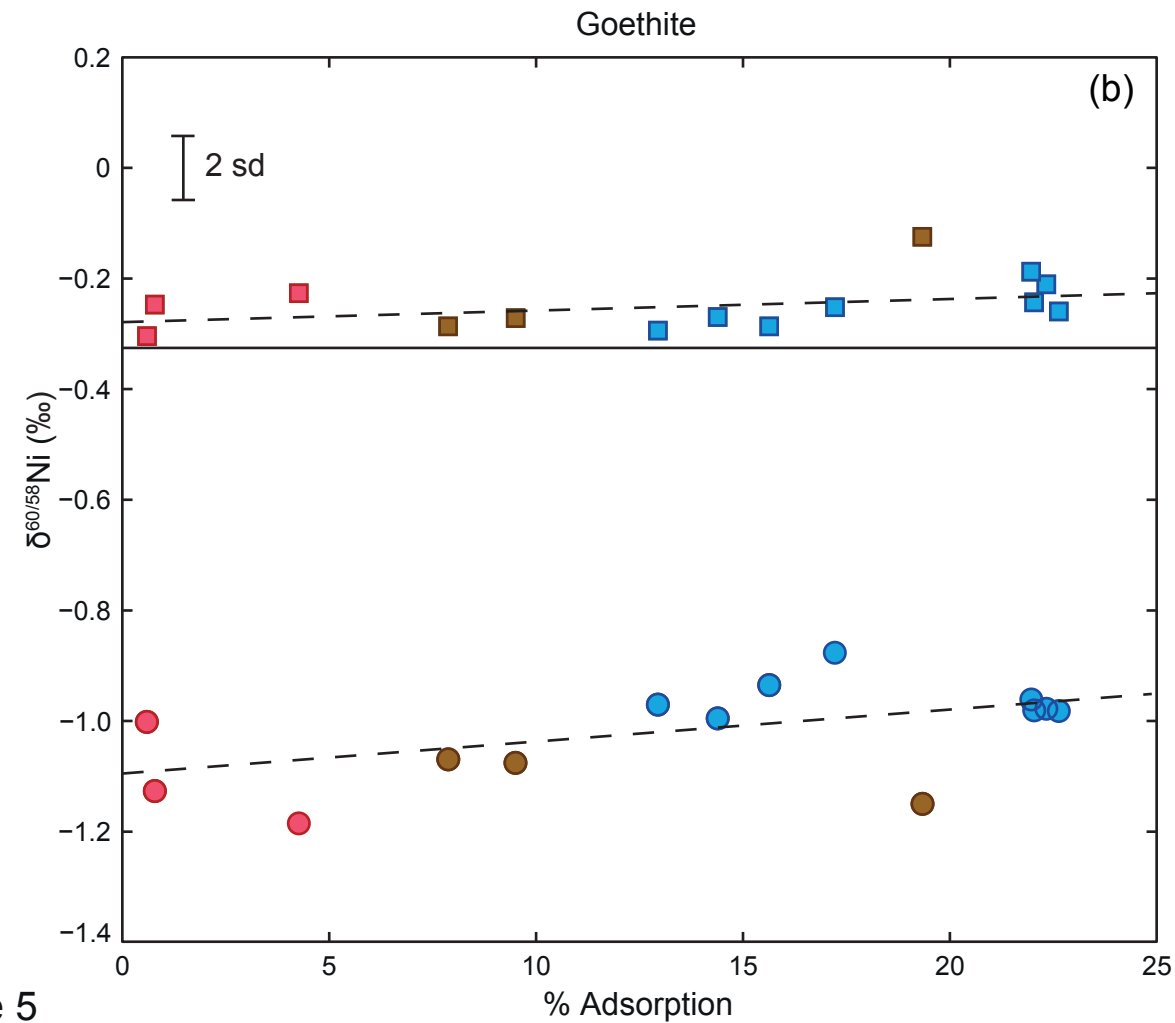
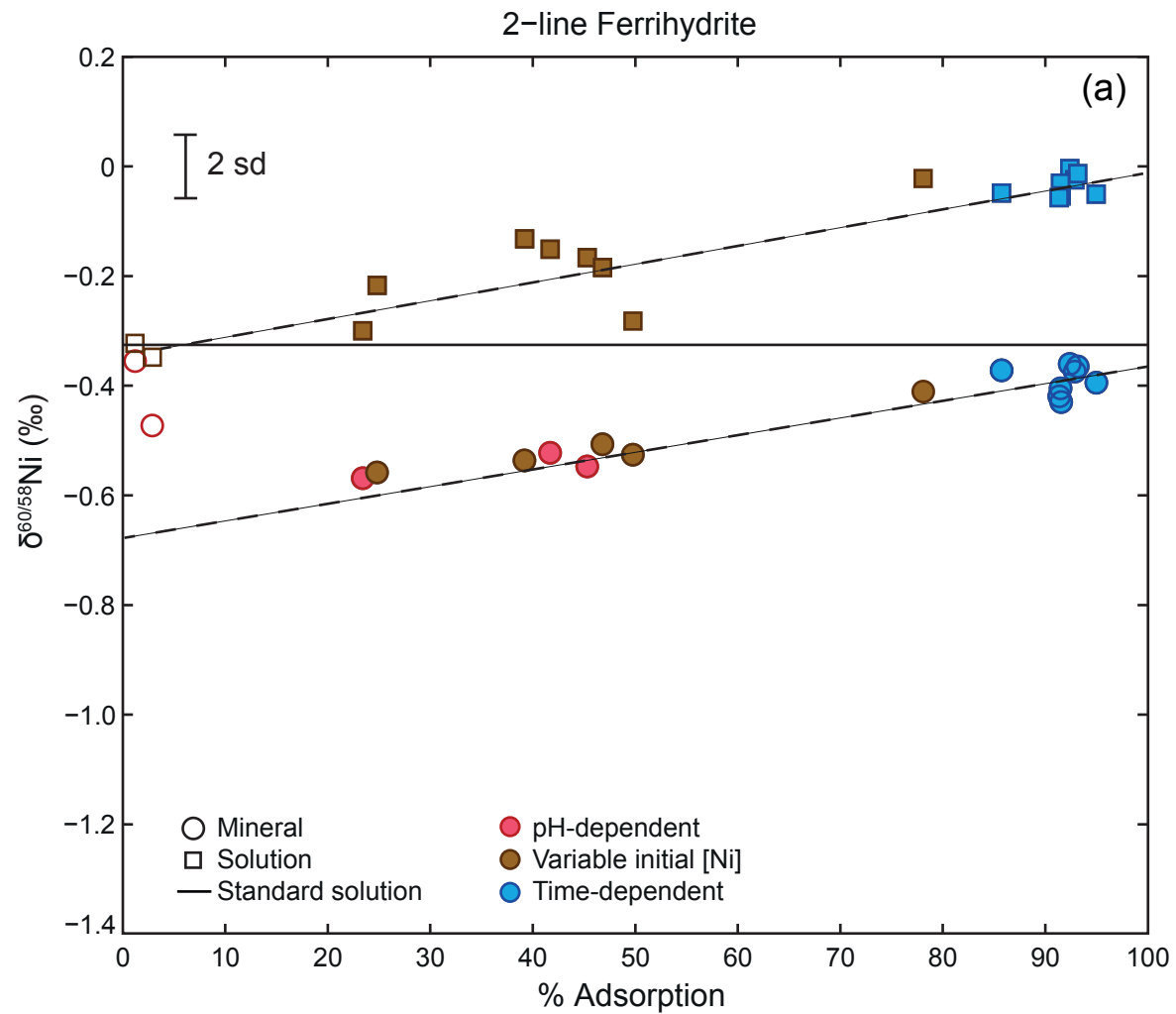


Figure 5

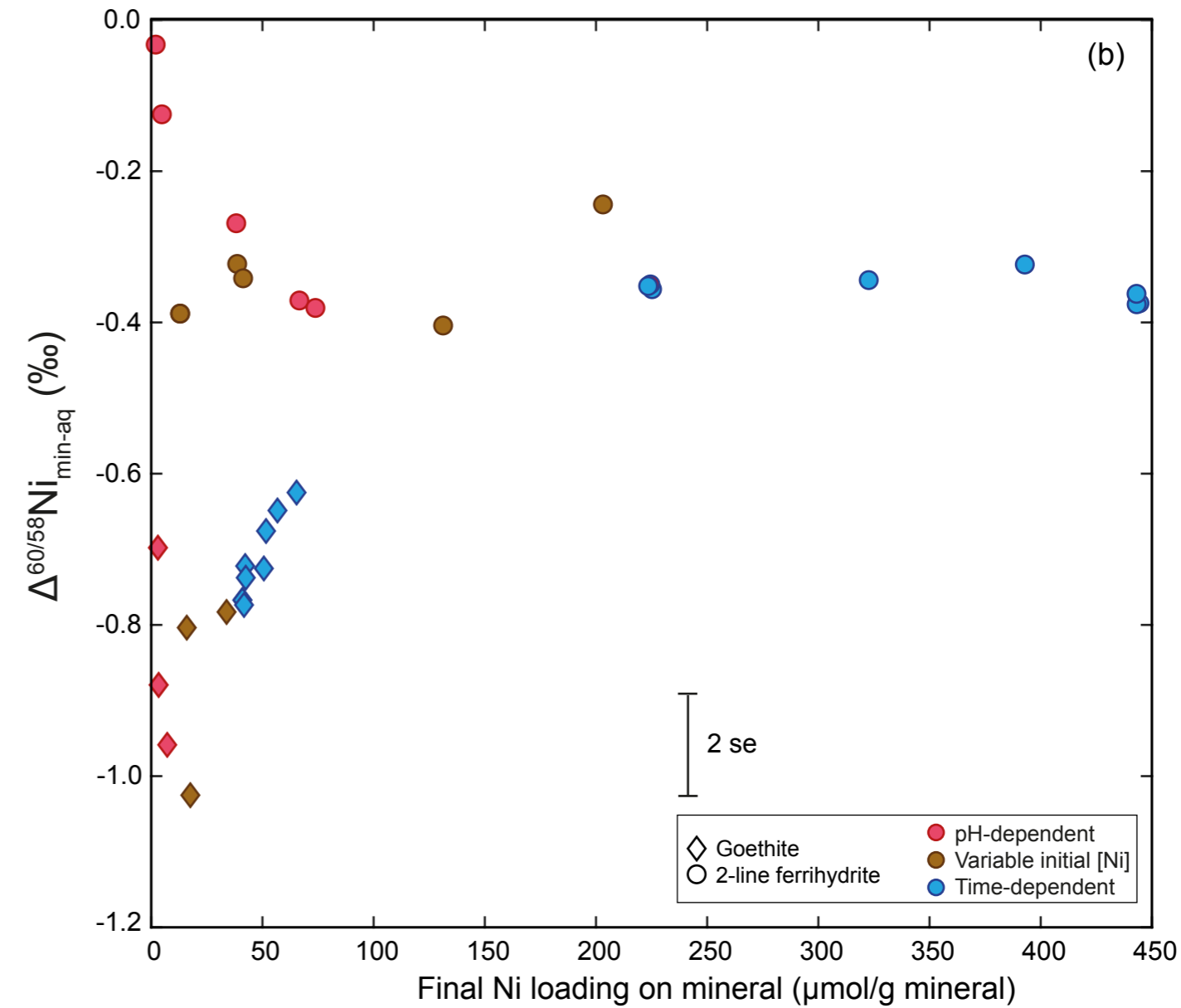
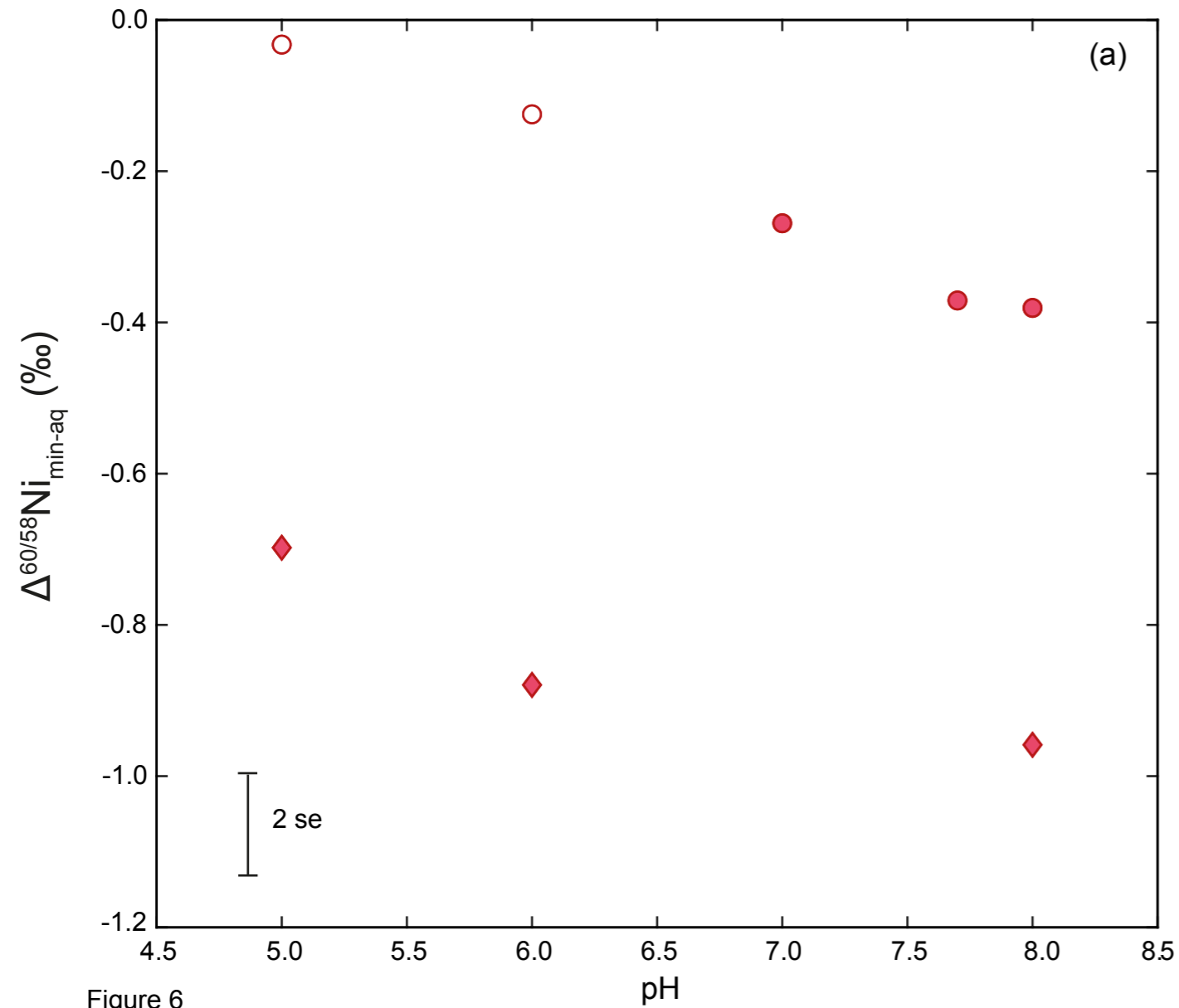


Figure 6

### 2-line ferrihydrite

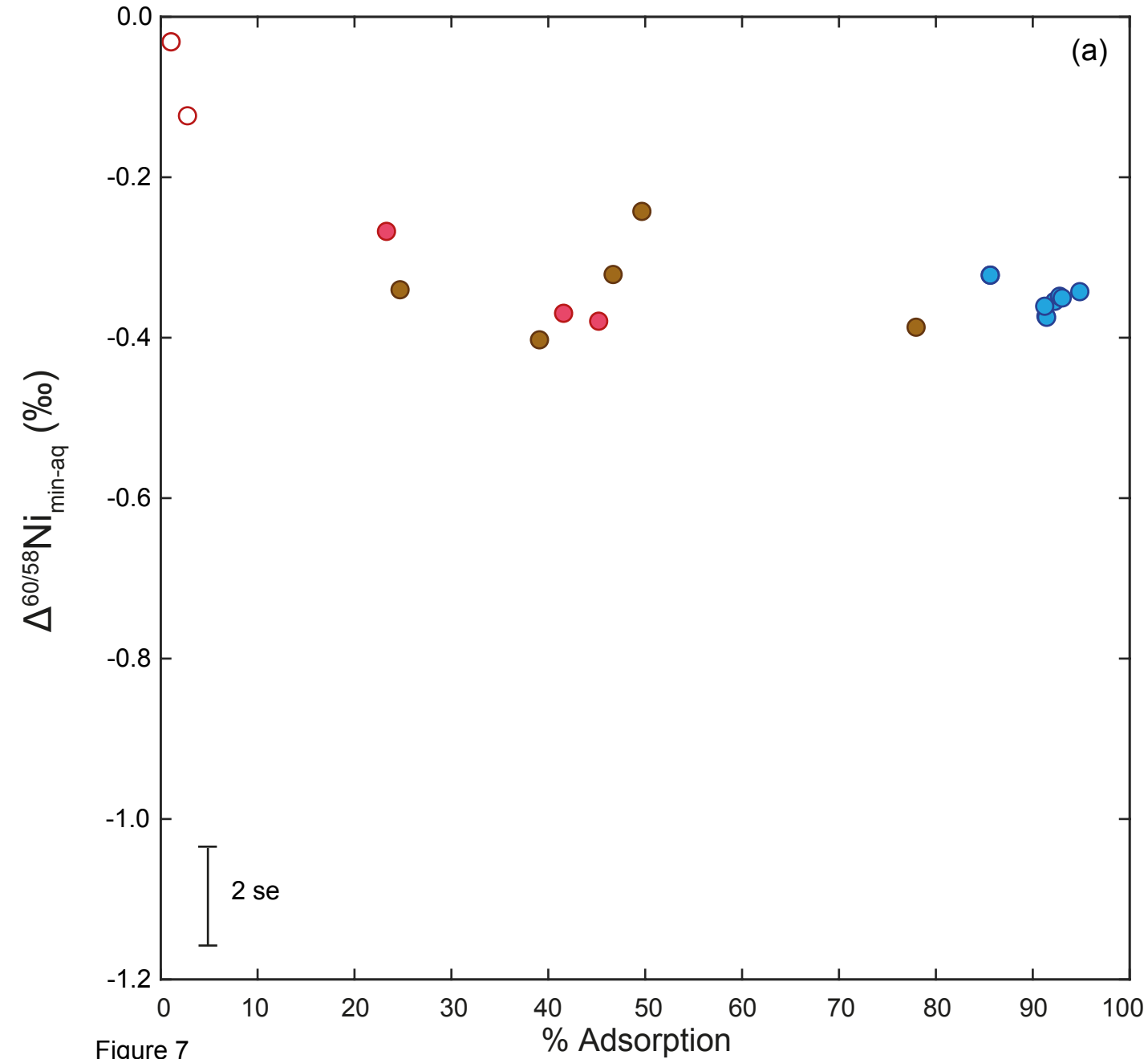
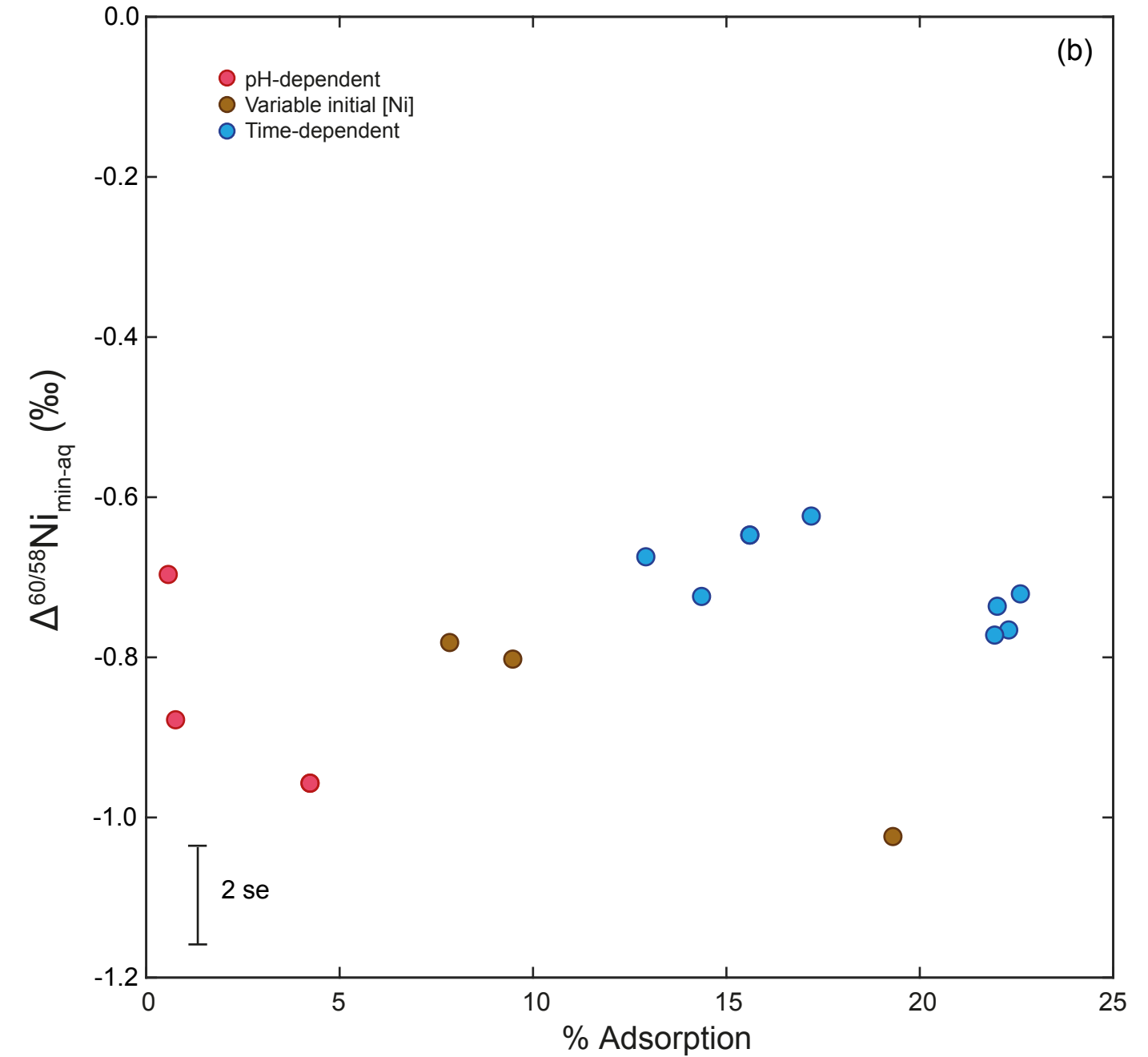


Figure 7

### Goethite



## **Electronic Annex**

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

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*Submitted to Chemical Geology*

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## Supplementary Figures :

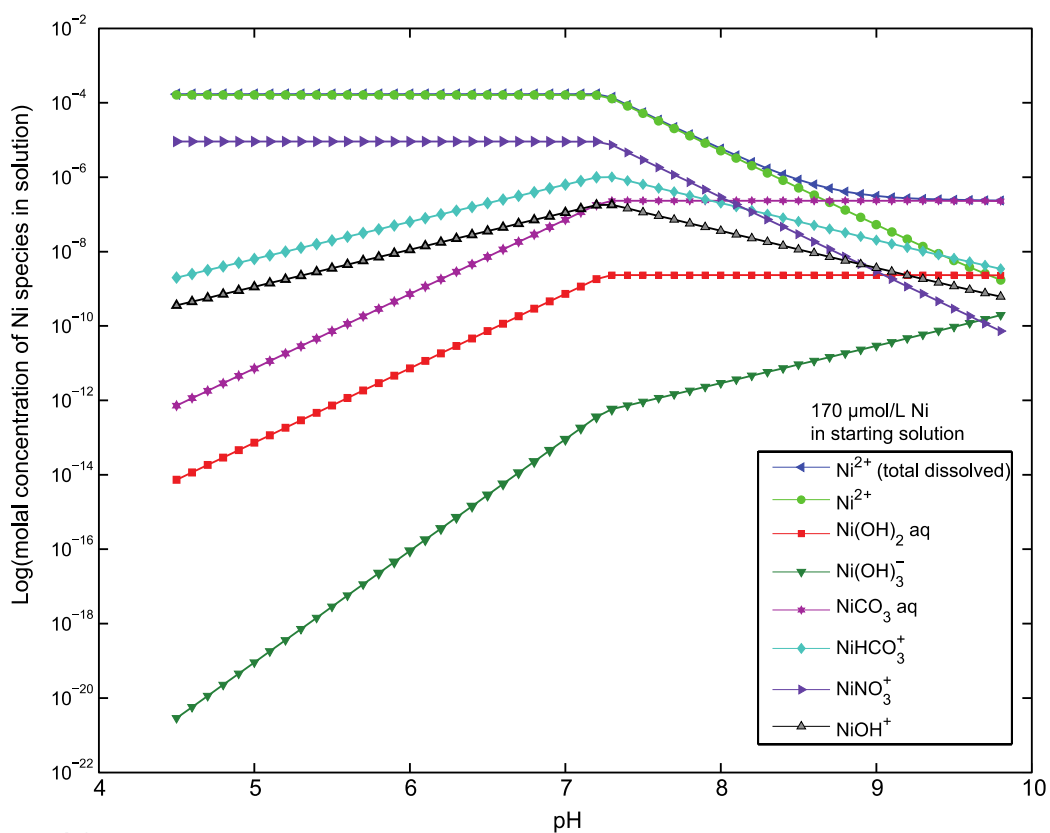
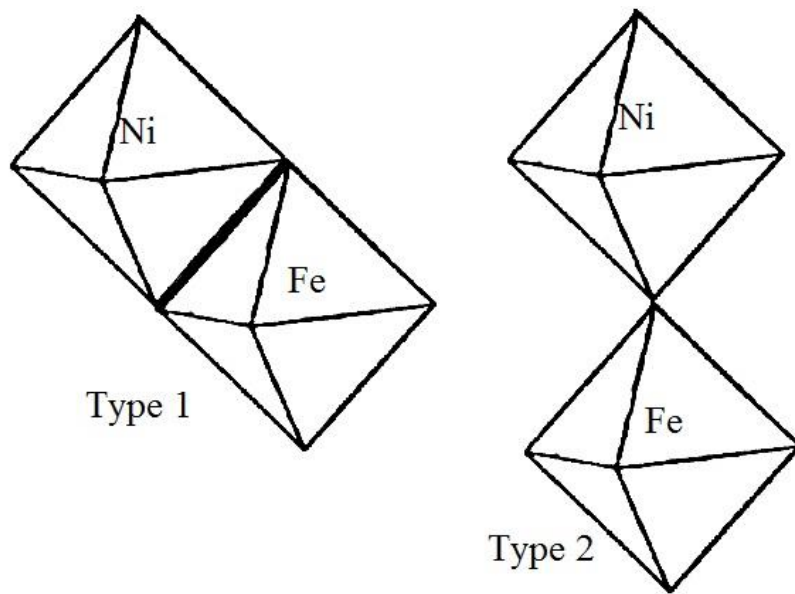


Figure A1

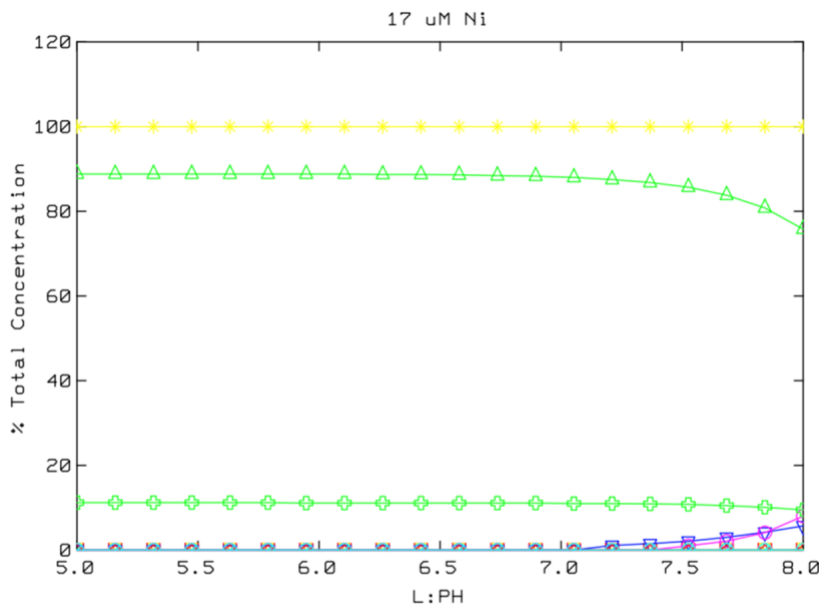
**Figure A1:** Nickel speciation modeling (logarithm of molal concentrations of different Ni species) versus pH of solution for 170 µmol/L of Ni in starting solution. The curves represent the different Ni species present in the system, i.e.,  $\text{Ni}^{2+}$ ,  $\text{Ni}(\text{OH})_{2\text{aq}}$ ,  $\text{Ni}(\text{OH})_3^-$ ,  $\text{NiCO}_{3\text{aq}}$ ,  $\text{NiHCO}_3^+$ ,  $\text{NiNO}_3^+$ ,  $\text{NiOH}^+$ .



**Figure A2:** Cartoon showing Ni bonding environment according to a “Type 1” configuration or a “Type 2” configuration.

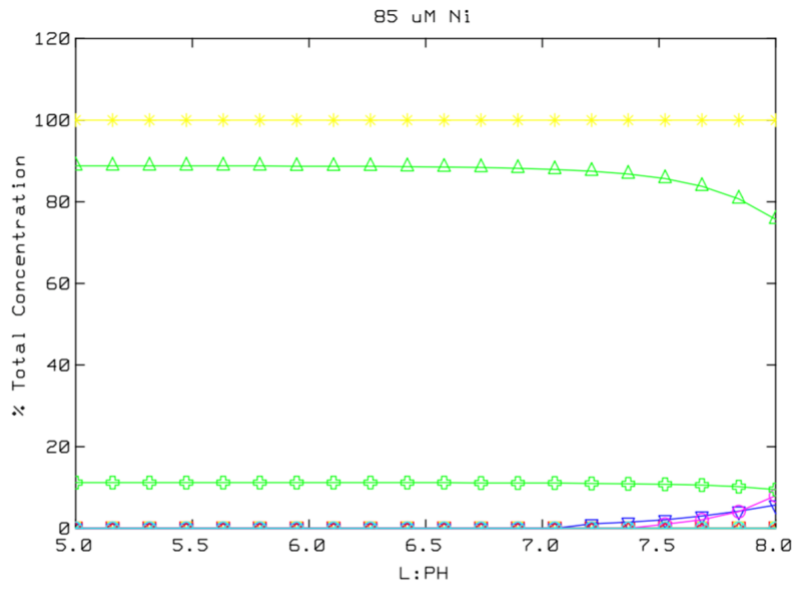


**Figure A3:** Nickel speciation versus pH of the solution for different initial Ni (aq), (a) 17  $\mu\text{mol Ni/L}$ , (b) 85  $\mu\text{mol Ni/L}$ , (c) 170  $\mu\text{mol Ni/L}$ , (d) 341  $\mu\text{mol Ni/L}$ , and (e) 426  $\mu\text{mol Ni/L}$ .



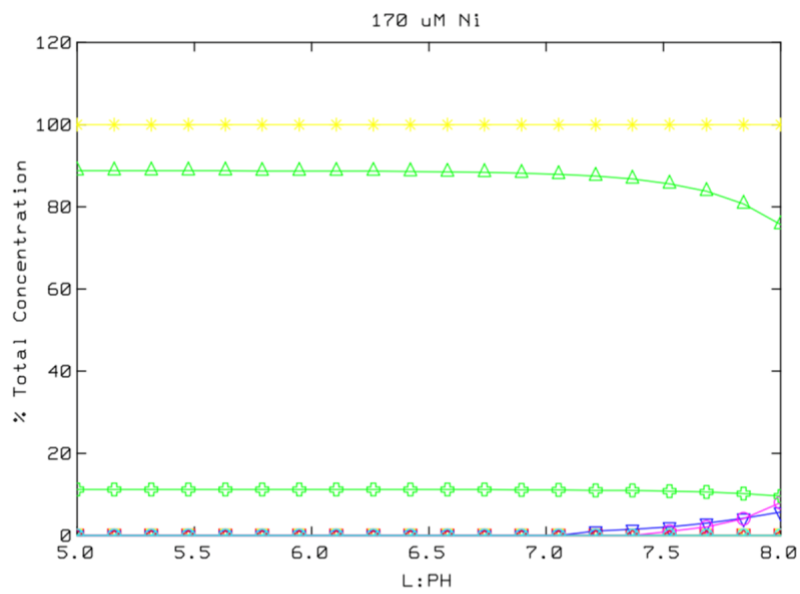
(a)

1: Ni(2+)  $\Delta$  2: NiOH+  $\square$  2: Ni(OH)2  $\diamond$  2: Ni(OH)3-  $\times$  2: NiHCO3+  $\nabla$   
 2: NiCO3 (aq)  $\circ$  2: NiNO3+  $\oplus$  5: BUNSENITE  $\star$  5: Ni(OH)2  $\circ$  7: TOTAL Ni  $\ast$



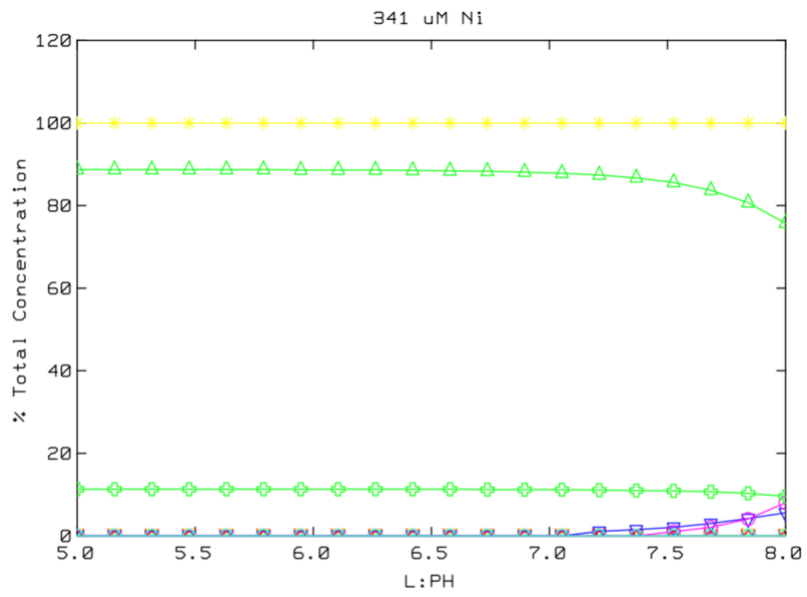
(b)

1: Ni(2+)  $\Delta$  2: NiOH+  $\square$  2: Ni(OH)2  $\diamond$  2: Ni(OH)3-  $\times$  2: NiHCO3+  $\nabla$   
 2: NiCO3 (aq)  $\circ$  2: NiNO3+  $\oplus$  5: BUNSENITE  $\star$  5: Ni(OH)2  $\circ$  7: TOTAL Ni(  $*$



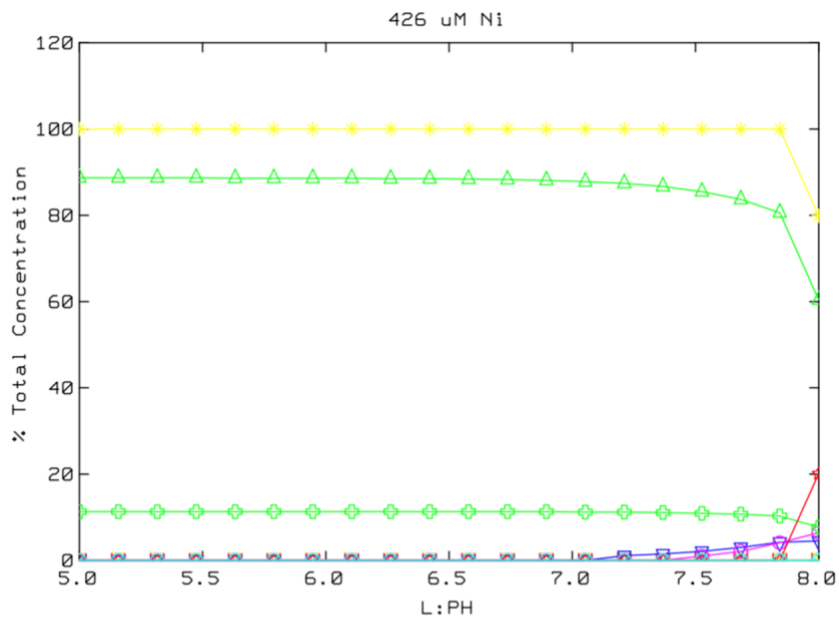
(c)

1: Ni(2+)  $\Delta$  2: NiOH+  $\square$  2: Ni(OH)2  $\diamond$  2: Ni(OH)3-  $\times$  2: NiHCO3+  $\nabla$   
 2: NiCO3 (aq)  $\circ$  2: NiNO3+  $\oplus$  5: BUNSENITE  $\star$  5: Ni(OH)2  $\circ$  7: TOTAL Ni(  $*$



(d)

1: Ni(2+)  $\Delta$  2: NiOH+  $\square$  2: Ni(OH)2  $\circ$  2: Ni(OH)3-  $\boxtimes$  2: NiHCO3+  $\nabla$   
 2: NiCO3 (aq)  $\circ$  2: NiNO3+  $\oplus$  5: BUNSENITE  $\star$  5: Ni(OH)2  $\circ$  7: TOTAL Ni  $\ast$



(e)

1: Ni(2+)  $\Delta$  2: NiOH+  $\square$  2: Ni(OH)2  $\circ$  2: Ni(OH)3-  $\boxtimes$  2: NiHCO3+  $\nabla$   
 2: NiCO3 (aq)  $\circ$  2: NiNO3+  $\oplus$  5: BUNSENITE  $\star$  5: Ni(OH)2  $\circ$  7: TOTAL Ni  $\ast$

## Supplementary Tables :

**Table S1:** Zeta potential measurement parameters.

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

**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 <sup>1</sup>	R (Å) <sup>2</sup>	$\sigma^2$ (Å <sup>2</sup> ) <sup>3</sup>	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	-	

<sup>1,2,3</sup> 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.
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