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1 **EXPERIMENTAL DETERMINATION OF Ni ISOTOPE**
2 **FRACTIONATION DURING Ni ADSORPTION FROM AN AQUEOUS**
3 **FLUID ONTO CALCITE SURFACES**

4
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10 London, UK.

11
12
13 **Abstract**

14 The fractionation of Ni isotopes during Ni adsorption from aqueous fluids onto calcite
15 surfaces was measured at 25 °C and as a function of pH from 7.7 to 8.9. Experiments showed
16 that the percent Ni adsorbed and the degree of Ni isotope fractionation attained constant values in
17 less than 30 hours after the calcite was exposed to the Ni bearing, calcite saturated aqueous
18 solution. The percentage of Ni adsorbed from the fluid onto the calcite surfaces increased from 9
19 to 67% as the pH increased over this range. Calcite preferentially adsorbs light Ni isotopes during
20 adsorption, resulting in a fractionation between adsorbed and aqueous, $\Delta^{60}\text{Ni}_{\text{calcite-fluid}}$, of -
21 0.52±0.16‰. This value is pH independent, within uncertainty, over the experimental pH range.
22 The preferential adsorption of light Ni isotopes into calcite likely results from the change in
23 coordination environment between adsorbed and aqueous nickel; the Ni-O length in the Ni-CO₃
24 bond formed at the calcite surface is greater than that in the Ni²⁺ aquo ion.

25
26 **1. INTRODUCTION**
27

28 The interpretation of the Ni isotope compositions in the marine record is facilitated by a
29 detailed understanding of the mechanisms and extent of Ni isotope fractionation during natural
30 fluid-mineral processes. Towards this goal, equilibrium isotopic fractionation between Ni
31 adsorbed onto calcite surfaces and its coexisting aqueous fluids was measured as a function of pH

32 at 25 °C. The purpose of this paper is to report the results of this experimental study and to use
33 these results to better understand the isotopic fractionation of Ni during its interaction with
34 mineral surfaces.

35 The quantification of isotopic fractionation among fluids and major minerals help constrain the
36 size and importance of element sources and sinks on a global scale. For example, the global
37 marine Ni budget is controlled by the input of dissolved Ni from river water, dissolution in the
38 oceans of riverine and atmospheric transported particulate material, Ni scavenging by sinking
39 marine mineral particles, and geothermal activity (Ciscato et al., 2018; Jeandel and Oelkers,
40 2015; Sclater et al., 1976). Based on isotopic compositions of these sources and sinks, several
41 studies concluded that another source of heavy Ni or another sink of light Ni is needed to account
42 for the Ni isotope composition of the global oceans (Cameron and Vance, 2014; Gall et al., 2013;
43 Gueguen et al., 2013; Porter et al., 2014). A number of processes have been suggested as the
44 possible light Ni sink, including the adsorption of Ni onto Fe and/or Mn oxide surfaces (Peacock
45 and Sherman, 2007). The role of such surfaces is underscored by the release of Ni from Mn
46 oxides as the age and transform in marine sediments (Atkins et al., 2014, 2016). Experimental
47 work by Wasylenki et al. (2015) shows that Ni sorption onto ferrihydrite surfaces favors the
48 incorporation of light Ni, leaving an isotopically a heavier aqueous Ni behind. Gall et al. (2013),
49 based on the analysis of the Ni isotope compositions of modern marine precipitated ferrihydrite,
50 concluded that the drawdown of light Ni by its sorption to ferrihydrite was, however, of
51 insufficient magnitude to balance the marine Ni cycle. An alternative sink to potentially resolve
52 this imbalance is the uptake of Ni by sulfides associated with anoxic or suboxic marine sediments
53 enriched in organic matter (Eiler et al., 2014; Gueguen et al., 2013). The present study is the first
54 of two manuscripts that evaluates the role of nickel-calcite interaction during natural processes.
55 This manuscript reports on the experimental measurement of Ni isotope fractionation as it
56 adsorbs ion calcite surfaces. A follow-up study will report experimental measurement of Ni
57 isotope fractionation during its co-precipitation with calcite. Taken together, these studies will
58 help illuminate the potential role of nickel-calcite interaction on the global marine Ni isotope
59 budget.

60 Nickel isotope fractionation has received attention due to its potential use as a tracer of
61 biochemical processes (Cameron et al., 2009). Nickel exhibits a nutrient-like behavior, with its
62 dissolved concentration ranging from 2 nmol/kg at the ocean surface to 12 nmol/kg at greater

63 depths (Sohrin and Bruland, 2011). Interest in Ni isotope fractionation as a tracer of organic
64 processes stems in part from results of ab-initio calculations performed by Fujii et al. (2011), who
65 reported that aqueous Ni-organic complexes exhibit a unique Ni isotope fractionation behavior.
66 Indeed, laboratory experiments documented significant Ni isotope fractionation during its
67 incorporation into methanogens (Cameron et al., 2009) and uptake by plants (Estrade et al.,
68 2015).

69 Nickel adsorption onto calcite surfaces is also of interest due to its unique adsorption
70 behavior. Ni adsorbs on calcite by rearranging the solid surface through the formation of Ni-
71 carbonate surface complexes (Hoffmann and Stipp, 2001; Stipp et al., 1994). These surface
72 complexes are partly hydrated and readily exchangeable due to the high hydration energy of Ni
73 (Zachara et al., 1991). Nevertheless, hydrated Ni complexes on calcite surfaces are more stable
74 than those of other divalent metal complexes (Hoffmann and Stipp, 2001). The degree to which
75 these unique Ni adsorption properties affect its isotopic fractionation will be evaluated with the
76 aid of this experimental study.

77

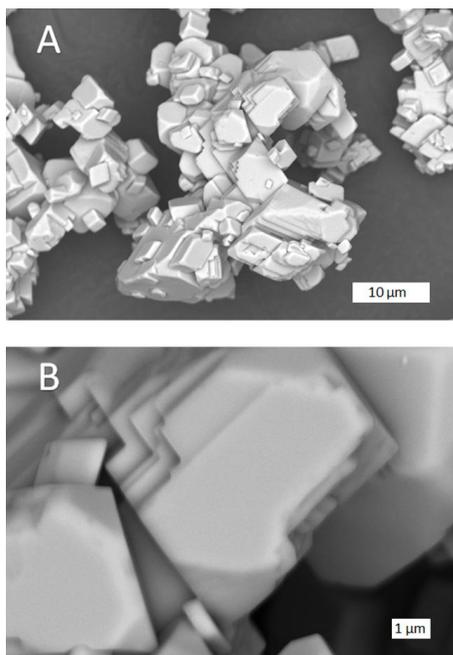
78 **2. MATERIALS AND METHODS**

79 **2.1 Experimental design**

80 Experiments were performed to determine the equilibrium Ni stable isotope fractionation
81 between aqueous Ni and Ni adsorbed on the calcite surface. Three series of experiments were
82 conducted. First, Ni was adsorbed onto calcite surfaces at constant pH and aqueous Ni
83 concentration as a function of time to evaluate the kinetics of this reaction. Second, Ni was
84 adsorbed onto calcite surfaces at constant pH and various aqueous Ni concentrations. Third, Ni
85 was adsorbed onto calcite surfaces at constant aqueous Ni concentrations and various pH. In all
86 cases, the concentration of Ni in the aqueous solution was kept below the solubility of gaspeite
87 (NiCO_3 , c.f. Lakshtanov and Stipp, 2007) to avoid its precipitation during the experiments. Each
88 experimental series consisted of a set of individual batch experiment, so that the fluid and solid
89 could be collected and analyzed at each experimental condition.

90 Synthetic high purity Merck MESURE® calcite was used for all experiments. Prior to its
91 use in the experiments, this calcite was first washed in distilled acetone, then pretreated according
92 to the method described by Reddy and Nancollas (1971). The purity of the resulting calcite

93 powder was assessed by X-ray diffraction using an INEL CPS-120 diffractometer with Co K α -
94 radiation having a detection limit of ~5%. The acquired diffraction patterns were compared to the
95 characteristic profile for calcite taken from the RRUFF database (Lafuente et al., 2016). This
96 comparison confirmed the solid to be pure calcite. The surface area of the resulting calcite was
97 0.31 ± 0.03 m²/g as determined by triple-point krypton adsorption according to the BET method
98 (Brunauer et al., 1938), using a Quantachrome Autosorb-1MP instrument. Scanning Electron
99 Microscope (SEM) images of this initial calcite were obtained using a JEOL JSM 6700F
100 spectrometer at the Raimond Castaing Center for micro-characterization in Toulouse, France.
101 Resulting images are displayed in Fig. 1. They show the rhombohedral morphology of the calcite
102 crystals, as well as intergrowth and agglomeration. These SEM images were also used to
103 determine the average length of the calcite crystal to be about 6 μ m.



104
105 Figure 1. SEM images of the synthetic calcite used in the present study. The scale bar in image A
106 is 10 μ m long, whereas the scale bar in image B is 1 μ m long.

107 The initial aqueous fluids used in the experiments were pre-equilibrated with the same
108 calcite used in the experiments. These pre-equilibrated fluids were prepared by adding
109 approximately 2 g of calcite to an aqueous solution having a total ionic strength of 0.01 mol/kg.
110 The initial fluids were prepared by adding reagent grade NaCl, HCl and/or NaOH to 18.2 M Ω
111 water obtained from a Millipore system. The pH of the aqueous solutions was then adjusted to a
112 value from 7.6 to 8.8 for the pH dependent experiments, or to 8.3 for the time dependent and

113 adsorption isotherm experiments by adding either HCl or NaOH. This fluid remained in contact
114 with the calcite for up to 3 weeks until the measured pH was constant. The pre-equilibrated fluids
115 were separated from the calcite by filtration using a Merck Millipore 0.22 μm teflon syringe filter
116 prior to its use. The aqueous Ni stock solutions added to these fluids for subsequent adsorption
117 experiments were created by dissolving Sigma-Aldrich, 99.99 %, trace metal basis $\text{Ni}(\text{NO}_3)_2$ to
118 18.2 M Ω water to obtain a total Ni concentration of 6 ppm Ni.

119 All adsorption experiments were performed in 50 mL screw top polycarbonate centrifuge
120 tubes. The polycarbonate tube reactors were cleaned before their use with 1 M double distilled
121 HCl for 24 hrs, then rinsed several times with 18.2 M Ω H_2O , and air dried. Before starting the Ni
122 sorption experiments, several tests were conducted to ensure that no nickel was adsorbed on the
123 walls of the polycarbonate tubes from aqueous solutions at the pHs investigated in this study.
124 These tests consisted of adding aqueous solutions containing 100ppb Ni to the reactors at various
125 pH. No measurable loss of Ni from the starting solution was observed after a period of 1 day
126 during which the reactor tubes were continuously shaken. It was thus assumed that all Ni lost
127 from solution during the experiments was due to its adsorption onto calcite surfaces.

128 Each experiment was initiated by placing a known quantity of calcite powder and 30 mL
129 of a Ni-free aqueous solution pre-equilibrated with calcite into the tube reactor. Each reactor was
130 closed and mixed on a rotator for 24 hours. After this time a selected quantity of the aqueous Ni
131 stock solution was added to the initial calcite-aqueous fluid mixture, prior to reclosing the tube.
132 This mixture was then returned to the rotator. Several additional experiments were run in the
133 absence of added Ni to verify no nickel was released to solution from the calcite present in the
134 reactor. After a given time period (72 hours for the pH dependent experiments, from 0.5 to 168
135 hrs for the time dependent series, and 24 hrs for the Ni adsorption isotherm), a reactor tube was
136 removed from the rotator and the reactor tube with its content was centrifuged for 15 minutes at
137 4500 rpm on an Eppendorf 5804 centrifuge. The reactor tube was then opened and the solids were
138 separated from the fluid phase using a 0.2 micron Teflon Merck Millipore filter. A minimum of
139 28.5 mL of fluid was recovered from each reactor. The collected fluids were separated into three
140 subsamples: one of the subsamples was used to measure pH immediately after sampling, while
141 the other two samples were acidified, one with ultrapure HNO_3 and the other with ultrapure HCl
142 for Ni elemental and isotopic analyses, respectively.

143

144 **2.2 Chemical analyses**

145 Nickel concentrations of the initial stock solutions and collected fluid samples of each
146 experiment were determined using an Atomic Absorption Spectrometer Perkin Elmer AAnalyst
147 600 together with a graphite furnace. Concentrations were obtained from measured absorbance
148 using a calibration curve generated from standards having concentrations ranging from 10-
149 100 ppb. New standards were prepared and new calibration curves were made each day the
150 analyses were performed. A 0.05M NH₄Cl matrix modifier was used during the measurements.
151 The uncertainties on these analyses, based upon duplicated measurements are estimated to be
152 $\pm 2\%$ whereas the detection limit was 1.5ppb.

153 The pH of fluid samples was measured immediately after sampling using a standard Mettler
154 Toledo glass pH electrode. This electrode was calibrated before every measurement using
155 Thermo Fisher pH=4.006, 6.865 and 9.183 buffer solutions at 25°C. The uncertainties on these
156 pH measurements are estimated to be ± 0.03 pH units.

157

158 **2.3 Ni isotope analysis**

159 **2.3.1 Isotopic notation**

160 Isotopic compositions in this paper are presented in delta notation, $\delta^{60}\text{Ni}$, corresponding to
161 the ratio of ^{60}Ni relative to ^{58}Ni normalized to the Sigma Aldrich ICP standard. This standard was
162 used rather than the certified SRM986 standard as what is essential to this study of fractionation
163 during adsorption is the change in $\delta^{60}\text{Ni}$ during experiments rather than its absolute value. The
164 difference in the Ni isotope composition the solid and the fluid phase ($\Delta^{60}\text{Ni}_{\text{solid-fluid}}$) is
165 defined by

$$166 \quad \Delta^{60}\text{Ni}_{\text{solid-fluid}} = \delta^{60}\text{Ni}_{\text{solid}} - \delta^{60}\text{Ni}_{\text{fluid}} \quad (1)$$

167 All isotopic measurements reported in this study were performed on the aqueous solutions after
168 filtration. These values used to determine the isotopic composition of the solids because 1) the
169 much higher sensitivity of solutions to the minor changes in isotopic composition compared to
170 the bulk solid, 2) the possibility that some Ni was present in the original calcite grains, 3) the

171 potential for some Ni to desorb from calcite surfaces after sampling, and 4) the possibility that
172 some Ni from the fluid phase would precipitate onto the calcite surfaces as they were dried.
173 Indeed several analyses of the solids recovered from the experiments showed their Ni isotope
174 compositions to be highly scattered and inconsistent. Because the reacting solution was
175 undersaturated with respect to NiCO₃ (gaspeite) and Ni adsorption on the reactor walls was
176 insignificant, it can be assumed that the loss of Ni from the aqueous solution was solely caused
177 by Ni sorption on calcite. The average isotopic composition of adsorbed Ni onto calcite during a
178 closed system adsorption experiment can thus be calculated from the initial and final Ni chemical
179 and isotopic compositions of the fluid and mass balance considerations taking account of (Criss,
180 1999)

$$181 \quad \delta^{60}\text{Ni}_{total}m_{\text{Ni},total} = \delta^{60}\text{Ni}_{solid}m_{\text{Ni},solid} + \delta^{60}\text{Ni}_{fluid}m_{\text{Ni},fluid} \quad (2)$$

182 where $m_{\text{Ni},solid}$ and $m_{\text{Ni},fluid}$ refer to the mass of Ni adsorbed onto the calcite surface and present in
183 the aqueous fluid phase, respectively. Note that $\delta^{60}\text{Ni}_{total}$ and $m_{\text{Ni},total}$ are constant during a
184 closed system reactor experiment. A similar approach to calculate the isotopic composition of
185 adsorbed elements was used for Mo (Barling and Anbar, 2004), B (Lemarchand et al.,
186 2005, Lemarchand et al., 2007), Cu and Zn (Balistreri et al., 2008), Si (Delstanche et al.,
187 2009, Oelze et al., 2014), and Ge (Pokrovsky et al., 2014). Equations (1) and (2) are used below
188 to calculate the isotopic composition of Ni adsorbed to calcite surfaces from corresponding fluid
189 isotope compositions.

190

191 **2.3.2 Sample purification**

192 Prior to the measurement of Ni isotope ratios by mass spectrometry, Ni was separated
193 using an approach based on Quitté and Oberli (2006). This separation procedure was performed
194 under a laminar flow hood using trace metal grade NH₄OH and H₂O₂, and doubly distilled HNO₃
195 and HCl. The overall purification of the samples consisted of five separation steps:

196 1) Step one began by evaporating the sample to dryness in Savillex Teflon containers. The
197 resulting residue was dissolved in 2 mL of 9 M aqueous HCl. An ion exchange column
198 was prepared by adding 1.8 mL of pre-cleaned, Bio-Rad 100–200 mesh AG1-X8 anion
199 resin to a 10-mL polypropylene column. The resin was cleaned with alternating 6M HCl

200 and 18.2 MΩ H₂O and then conditioned by passing 10 mL of 9M HCl through the
201 column. The 2 mL sample was then passed through the column to remove Fe from the
202 sample. Nickel eluted immediately. A further 4 mL of 9M HCl was added to the column
203 to ensure the complete recovery of Ni.

204 2) Step two aimed to remove Zn from the sample. It began by evaporating the Ni collected
205 from the first step to dryness and re-dissolving it into 2 mL of 2 M HCl. This sample was
206 passed through the same ion exchange column as in the first step described above but
207 conditioned this time by passing 10 mL of a 2M HCl through the column. The sample was
208 loaded on the column in 2mL 2M HCl, once again Ni eluted immediately, and a further 4
209 mL of 2M HCl was passed through the column to ensure the complete recovery of Ni.

210 3) Step three separated the major matrix elements from the sample. It began by evaporating
211 the Ni elution sample collected from step 2 to dryness then redissolving it into 5 mL of 1
212 M HCl and 1 mL of 1M ammonium citrate solution. The ammonium citrate solution was
213 prepared by mixing a citric acid solution and a trace grade NH₄OH solution. Once the pH
214 of the redissolved Ni bearing solution was adjusted to 8-9 using NH₄OH, the sample was
215 loaded onto a column filled with 2 mL of Triskem Nickel specific resin (based on
216 dimethylglyoxime, DMG). Prior to its use, this resin was cleaned with water and
217 ammonium citrate and conditioned with 5 mL of 0.2M of ammonium citrate whose pH
218 was adjusted to 8-9 using NH₄OH. After the sample was loaded onto the resin, it was
219 washed with 20 mL of 0.2 M ammonium citrate (adjusted to pH=8-9) to remove matrix
220 elements. Nickel was then recovered from the column by passing 12 mL of 3M HNO₃.
221 Three drops of perchloric acid were added to the recovered Ni fraction to destroy the
222 DMG-Ni complex and the sample was evaporated to dryness. The sample was then taken
223 up in 1mL of concentrated HNO₃ and 1mL of ultrapure H₂O₂ and heated for a few hours
224 to remove potential organics and ensure a complete release of Ni from the DMG-Ni
225 complex. The sample was then evaporated again. If necessary, this oxidation procedure
226 was repeated twice. The complete removal of this complex was verified by the white color
227 of the residual solids following the oxidation procedure.

228 4) Step four is a purification step. The cleaned residue was dissolved into 0.2mL of 18.2 MΩ
229 H₂O and passed through a column containing 0.12 mL of Bio-Rad AG50W-X8 resin

230 (200–400 mesh), previously cleaned twice with H₂O and 6M HCl, then conditioned with
 231 water. The matrix elements were removed with 2.5 mL of 0.2M HCl and then Ni was
 232 recovered in 0.5 mL of 3M HCl.

233 5) The final step removed any remaining Fe from the sample (including Fe released by the
 234 resin) following closely the protocol of step 1 or 2, replacing the 9M or 2M HCl by 6M
 235 HCl. A summary of these steps is provided in Table 1.

236 *Table 1 Summary of the purification procedure used to prepare fluid samples for Ni isotope*
 237 *analysis by mass spectrometry.*

	Reagent	volume (mL)
Col. 1		
Resin	AG1-X8	2
Conditioning	2M HCl	10
Load	2M HCl *	2
Ni elution	2M HCl	4
Col. 2		
Resin	AG1-X8	2
Conditioning	9M HCl	10
Load	9M HCl *	2
Ni elution	9M HCl	4
Col. 3		
Resin	Nickel specific	2
Conditioning	0.2M (NH ₄) ₃ C ₆ H ₈ O ₇	12
Load	1M (NH ₄) ₃ C ₆ H ₈ O ₇ + 1M HCl	1+5
clean matrix	0.2M (NH ₄) ₃ C ₆ H ₈ O ₇	20
Ni elution	3M HNO ₃	12
Col. 4		
Resin	AG50W-X8	0.15
Conditioning	H ₂ O	0.7
Load	H ₂ O	0.2
clean matrix	0.2M HCl	2.5
Ni elution	3M HCl	0.5
Col. 5		
Resin	AG1-X8	2
Conditioning	6M HCl	10
Load	2M HCl *	2
Ni elution	2M HCl	4

* Ni starts eluting during this step

238

239

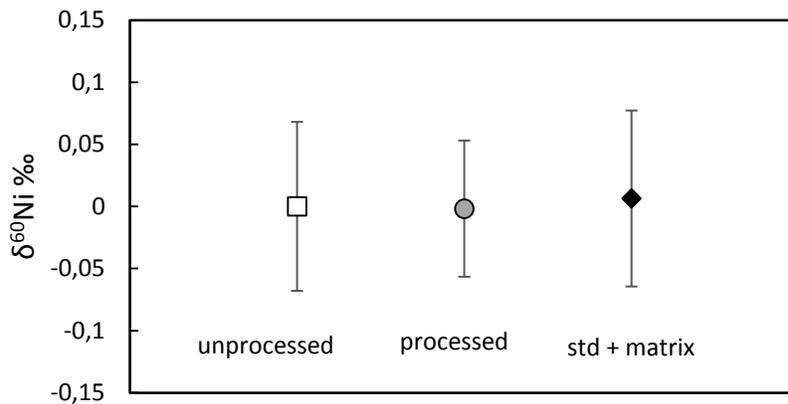
240 **2.3.3 Mass spectrometry**

241 The Ni bearing fluid sample recovered from step 5 of the purification procedure was dried.
242 This residue was dissolved into 0.1M HCl prior to isotopic analysis. Nickel isotope
243 measurements were performed at the Observatoire de Midi Pyrenees analytical platform in
244 Toulouse France, using a Thermo-Finnigan Neptune multi-collector inductively coupled plasma
245 mass spectrometer (MC-ICPMS) equipped with an Apex desolvating system connected to a
246 glass nebulizer, and fitted with a standard sample cone and a X skimmer cone. Samples were
247 measured in medium resolution mode to avoid interferences such as with ArO^+ . Instrumental
248 mass bias was corrected using sample-standard bracketing techniques and Cu doping; this
249 approach has been regularly validated in our laboratory using the PCC-1 standard yielding an
250 average value of $0.08 \pm 0.04\text{‰.amu}^{-1}$, in excellent agreement with literature data (Gall et al. 2012;
251 Gueguen et al. 2013; Chernonozhkin et al. 2016). The concentration of the measured samples,
252 always adjusted to match those of the standard within 10%, varied between 50 and 200 ppb, and
253 the Cu concentration was half that of Ni. Samples were measured in 2 cycles. During the first
254 cycle, stable Ni isotope masses were measured (58, 60, 61, 62 and 64) along with masses 57 and
255 66, which are used to correct for possible isobaric interference from ^{58}Fe and ^{64}Zn , respectively.
256 During the second cycle, Cu isotopes were measured together with Ni isotopes and used to
257 correct for instrumental mass bias. In detail, the Cu-doped standard was measured during every
258 other run, each sample interspersed between two standards. The instrumental mass bias was
259 calculated using the exponential law for the Cu isotope ratio in the sample (hence matrix
260 matched) and then applied to the Ni ratios; the Cu-corrected Ni ratios were then normalized to
261 the Cu-corrected average ratio of the two bracketing standards. Typically, a 200ppb Ni solution
262 yielded a total ion beam of 30V. To check for Ni fractionation during the column separation, two
263 tests were performed: (1) first, the Sigma Aldrich standard solution was processed through the
264 whole chemical separation procedure with every set of experimental samples and measured; (2)
265 second, a carbonate sample similar to those used in the experiments, initially devoid of Ni but
266 doped with our Sigma Aldrich Ni standard solution, was processed. Both tests yield a Ni isotope
267 composition indistinguishable from the matrix-free unprocessed standards. Hence, no isotopic
268 fractionation is observed for the processed standards relative to the corresponding unprocessed
269 standards, confirming that the chemical procedure is well suited to quantify the natural mass

270 dependent isotopic fractionation characteristic of our experimental samples (Figure 2). The 2SD
271 (standard deviations) of $\delta^{60}\text{Ni}$ was calculated based on multiple (typically 3) measurements of
272 each Ni sample and ranged from 0.01 to 0.19‰.

273 A double spike approach was not used for Ni isotope analyses in this study to avoid machine
274 contamination; the MC-ICPMS used in this study is also routinely used for the measurement of
275 Ni in cosmochemistry samples, which are particularly sensitive to small uncertainties in ^{61}Ni ,
276 ^{62}Ni and ^{64}Ni . The Cu doping method adopted in this study has been shown to have a
277 reproducibility comparable to that attained using a double spike approach (Quitté and Oberli,
278 2006).

279



280
281 Figure 2. Ni isotope compositions of processed and unprocessed standards used to validate the Ni
282 separation protocol. The open square represents the isotopic composition of the unprocessed
283 standard, the filled circle shows the composition of the processed standard, and the filled
284 diamond shows the composition of a standard diluted to the approximate concentration of the
285 experiments reported in this study (listed as std + matrix).

286

287 2.4 Geochemical Calculations

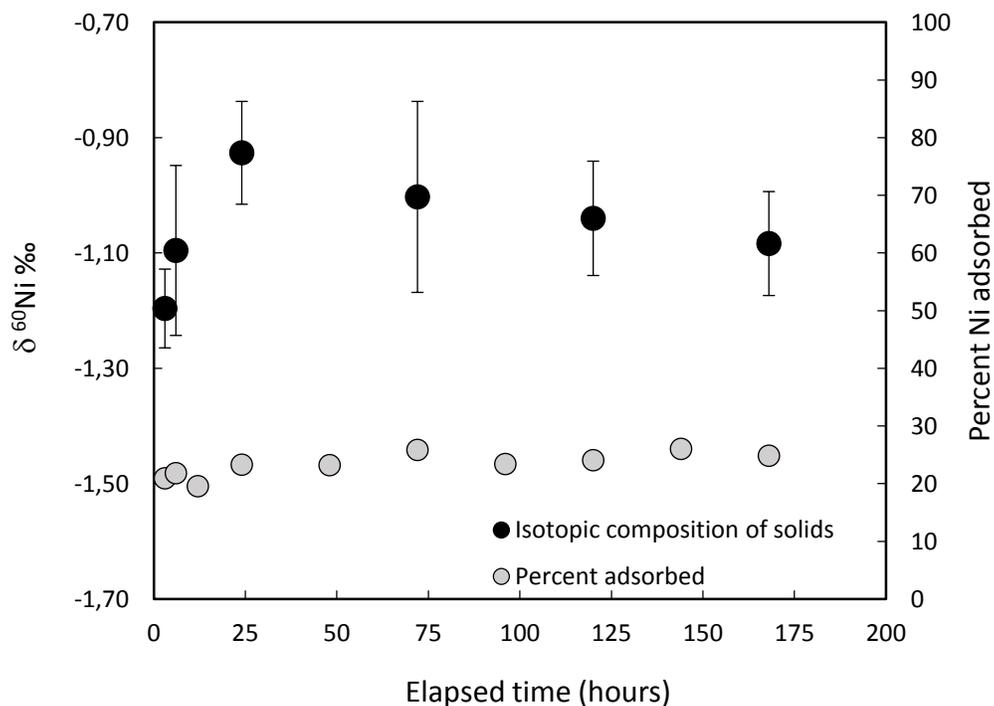
288 All thermodynamic calculations, including aqueous fluid speciation calculations and
289 mineral solubility calculations, were performed using PHREEQC (Parkhurst and Appelo, 2015)
290 together with its minteq.v4 database.

291

292 3. RESULTS

293 A total of 28 individual batch experiments were performed in the three series. The
 294 conditions and measured fluid compositions of these experiments are reported in Tables 2 and 3.
 295 The first experimental series, series K, was designed to assess if Ni adsorption onto calcite
 296 surfaces and its associated fractionation are time dependent. The results of this series are shown
 297 in Figure 3 for reaction times from 3 to 168 hrs. It can be seen that the extent of Ni adsorption
 298 increases slightly during the first 24 hrs but remains constant afterwards. In contrast, isotopic
 299 steady-state is attained only after ~30 hrs, although the isotopic composition of adsorbed Ni
 300 becomes very slightly lighter with time after this, which may reflect some incorporation of Ni
 301 into the calcite lattice.

302



303

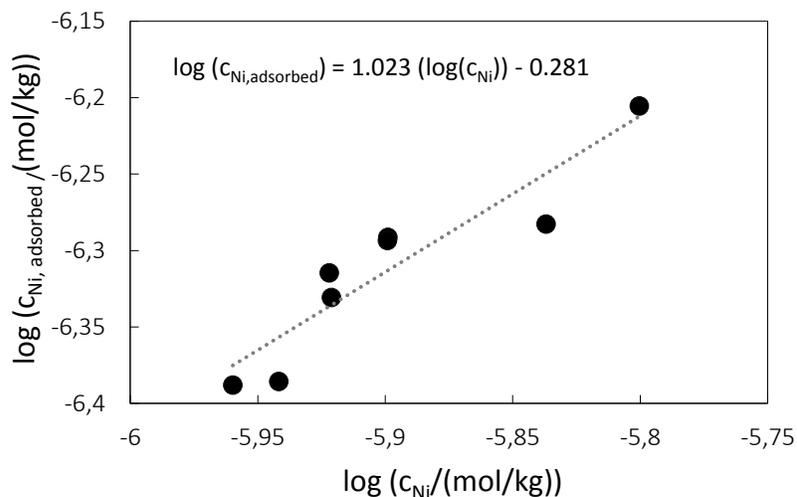
304 Figure 3. Percent of Ni adsorbed onto calcite surfaces and the Ni isotope composition of this
 305 adsorbed Ni as a function of elapsed time at 25 °C and pH 8.3. The percent Ni adsorbed is shown
 306 as grey circles and their values are given in the right hand scale, whereas the corresponding Ni
 307 isotope composition of the solids is shown as black circles, these values are given by the left axis.
 308 The isotope composition of the solids was obtained from the measured aqueous Ni isotope
 309 composition using mass balance considerations. The uncertainties on the measured adsorption
 310 percent are approximated by the symbol size. The 2D standard deviations of the Ni isotope
 311 compositions shown in this figure are provided in Table 3.

312

313 A second experimental series, series I, was designed to assess the partition coefficient of Ni
314 onto calcite surfaces. This series was run at a pH of 8.3 and the aqueous Ni concentrations varied
315 from 60 to 120 ppb. The Ni concentrations in this experimental series were limited on one hand
316 by the analytical detection limits for Ni and on the other hand by the requirement to keep this
317 fluid undersaturated with respect to gaspeite (NiCO_3). A linear correlation between the
318 concentration of aqueous Ni and adsorbed Ni was observed (see Fig. 4) consistent with
319 adsorption being the predominant mechanism for Ni loss from solution. The apparent partition
320 coefficient of Ni at pH=8.3 (K_d) was calculated to be

321
$$K_d = (m_{\text{Ni-ads}}/m_{\text{solid}})/(m_{\text{Ni-aq}}/m_{\text{solution}}) = 0.011.$$

322 where m_i refers to the mass of the subscripted species or phase. Note that Ni isotope
323 compositions were not determined for the samples collected from this experimental series.



324
325 Figure 4 Variation of the Ni concentration adsorbed onto calcite surfaces as a function of the
326 aqueous Ni concentration at 25 °C. The line shown through the data points corresponds to a least
327 squares fit of the data; the equation of this line is provided on the figure. The uncertainties in
328 these measurements are within the size of the symbols.

329

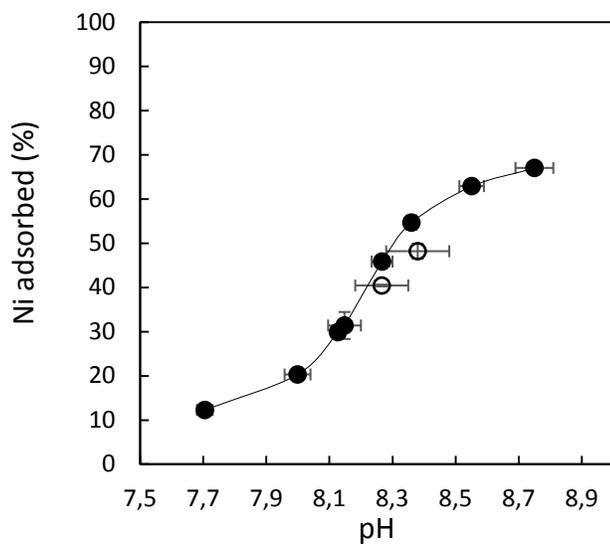
330

331 **Table 2: Measured aqueous and adsorbed Ni concentrations of samples collected from**
 332 **experimental series I, designed to determine partition functions at 25°C and pH 8.3.**

Experiment	Aqueous Ni conc. <i>Mol/kg</i>	Adsorbed Ni conc. <i>Mol/kg</i>
I01	1.10×10^{-6}	4.09×10^{-7}
I02	1.14×10^{-6}	4.11×10^{-7}
I03	1.26×10^{-6}	5.11×10^{-7}
I04	1.46×10^{-6}	5.21×10^{-7}
I05	1.58×10^{-6}	6.23×10^{-7}
I06	1.26×10^{-6}	5.09×10^{-7}
I07	1.20×10^{-6}	4.84×10^{-7}
I08	1.20×10^{-6}	4.67×10^{-7}

333
 334
 335 A third experimental series, series P, determined the amount of Ni adsorbed onto calcite
 336 surfaces as a function of pH from 7.6 to 8.8. The results, shown in Fig. 5, illustrate the increase in
 337 the percent of Ni adsorbed from 8.7 to 67 % as the pH increased over this range. The Ni isotope
 338 composition of the fluids and solids recovered from this experimental series, as well as those of
 339 experimental series P run for the same elapsed time, are plotted as a function of the fraction of Ni
 340 adsorbed on calcite in Fig 6a. Note that whereas the Ni isotope compositions of the fluids in this
 341 figure were directly determined from measurements, those of the solids were determined from the
 342 measured fluid compositions and mass balance constraints (see Eq. 2). The associated uncertainty
 343 was determined by error propagation, taking into account the uncertainty on the isotopic
 344 composition of the fluid and on the Ni concentrations of the fluid and solid phase. It can be seen
 345 that all experiments exhibit a preferential sorption lighter Ni lighter on the calcite surface, leaving
 346 the aqueous Ni isotopically heavier than the initial Ni stock solution which had a $\delta^{60}\text{Ni} = -$
 347 $0.63 \pm 0.05\%$. The offset between the aqueous fluid and adsorbed Ni compositions is independent
 348 of the percentage of Ni adsorbed within uncertainty, which suggests that Ni isotope fractionation
 349 during adsorption on calcite surface occurs at equilibrium. The extent of Ni isotope fractionation
 350 between the calcite surface and the aqueous fluid is plotted as a function of pH in Figure 6b. It
 351 can be seen that the difference in the Ni isotope composition between the solid and solution,
 352 $\Delta^{60}\text{Ni}_{\text{calcite-fluid}} = -0.52 \pm 0.16\%$, does not vary significantly as the pH increases from 7.7 to 8.6. A
 353 slight increase in $\Delta^{60}\text{Ni}_{\text{calcite-fluid}}$ (by about 0.04‰) at the lowest Ni surface coverage is suggested

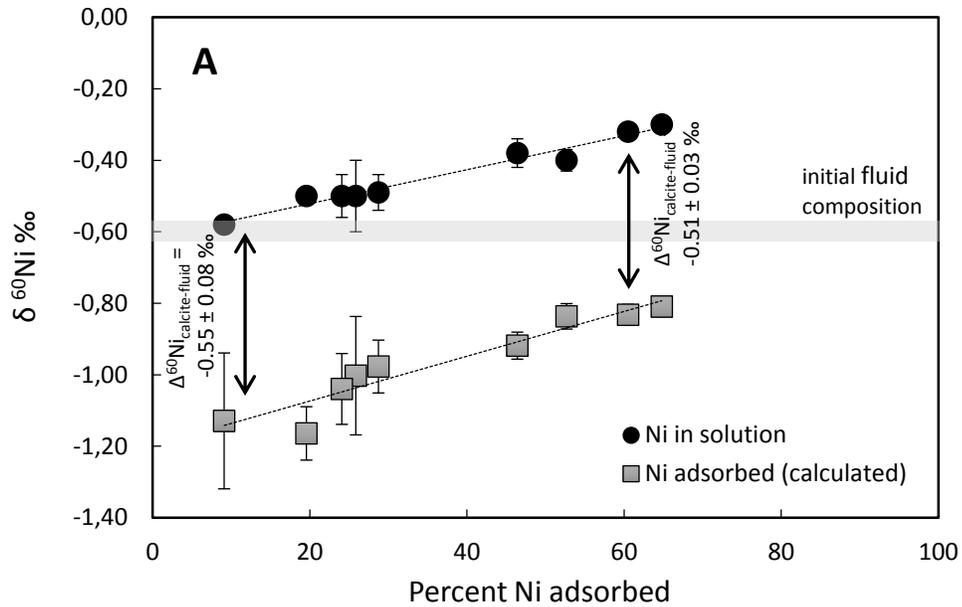
354 by the data. However, one should note the large uncertainty affecting the data for the lowest
355 extents of Ni sorption (see Fig. 6b).



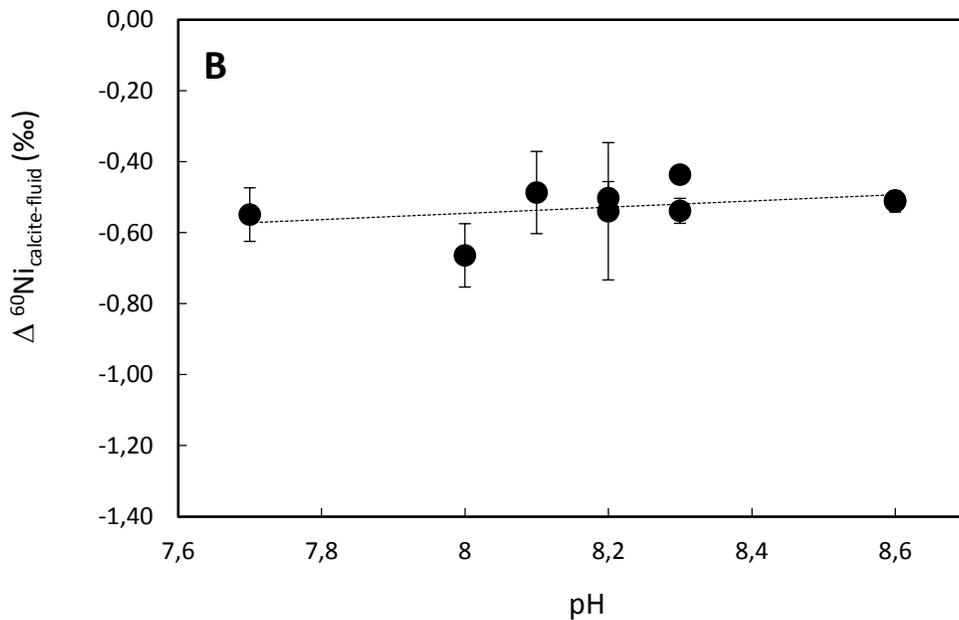
356

357 Figure 5. The percent Ni adsorbed from the aqueous solution onto calcite surfaces as a function of
358 pH at 25 °C. The filled symbols correspond to experiments where the isotopic compositions of Ni
359 were determined, whereas these were not determined for experiments shown as open symbols.

360



361



362

363 Figure 6 a) Ni isotope composition of the adsorbed and aqueous Ni as a function of
 364 Ni adsorbed and b) $\Delta^{60}\text{Ni}_{\text{calcite-fluid}}$ as a function of pH. In figure 6a, the black circles represent the
 365 Ni isotope compositions of the aqueous solutions, which were directly measured. The grey
 366 squares represent the isotopic compositions of the Ni adsorbed onto calcite surfaces, which were
 367 obtained from mass balance calculations – see text. The gray band shows the initial isotopic
 368 composition of the solution, which was $-0.63 \pm 0.05\text{‰}$. The dashed lines in these figures represent
 369 a least squares fit to the data points.

370 4. DISCUSSION

371 4.1 Comparison of Ni adsorption behavior with previous studies.

372 The nickel sorption isotherm, plotted on a log-log scale in Fig. 4, exhibits a linear trend
373 with a slope close to 1 similar to what has been reported in past studies (Belova et al., 2014;
374 Lakshtanov and Stipp, 2007; Zachara et al., 1991). This behavior indicates that Ni partitioning
375 between solid and liquid phases does not depend on the Ni concentration. The apparent partition
376 coefficient deduced from the data shown in Fig, 4, $K_{Ni} = 0.011$ at pH = 8.3 is in good agreement
377 with the value extracted from Zachara et al. (1991) at the same pH ($K_{Ni} = 0.012$). The maximum
378 Ni adsorption in the experiments presented above is attained after only a few hours, which is
379 consistent with previous work on the absorption onto calcite of Ni (Zachara et al., 1991) and
380 other divalent cations (McBride, 1980; Zachara et al., 1988). Our experiments show no variation
381 in the amount of Ni adsorbed on the calcite surface as time progresses; a similar behavior was
382 observed for Ni adsorption on ferrihydrites and goethite (Wasylenki et al. 2015) and Zn on calcite
383 (Dong and Wasylenki, 2016).

384 Nickel adsorption onto calcite surfaces increases with pH to at least pH ~ 9 which is in
385 agreement with the previous studies (Belova et al., 2014; Tahervand and Jalali, 2017; Zachara et
386 al., 1991). This behavior can be attributed to the buildup of a negative charge on calcite surface.
387 According to calcite surface complexation models (Pokrovsky et al., 2000, 1999; Van Cappellen
388 et al., 1993), Ni adsorption onto calcite can be described according to (Pokrovsky et al., 2002):



390 where >CO_3^- and $\text{>CO}_3\text{Ni}^+$ stand for a deprotonated carbonate site and the Ni surface complex
391 formed on this carbonate site, respectively. The increase of >CO_3^- concentration with increasing
392 pH to ~ 9 accounts for the observed corresponding increase of Ni sorption.

393 4.2 Interpretation of Ni isotope fractionation during its adsorption onto calcite surfaces.

394 A number of past studies have measured Ni isotope fractionation as it adsorbs onto
395 mineral surfaces. Wasylenki et al. (2015) determined the $\Delta^{60}\text{Ni}_{\text{ferrihydrite-fluid}}$ during 25 °C
396 adsorption experiments to be $-0.35 \pm 0.10\%$. Similarly Gueguen et al. (2018) reported an
397 identical $\Delta^{60}\text{Ni}_{\text{ferrihydrite-fluid}} = -0.35 \pm 0.08\%$. The adsorption of Ni from aqueous solution onto

398 goethite was reported to yield the greatest fractionation during Ni adsorption observed to date
399 with $\Delta^{60}\text{Ni}_{\text{goethite-fluid}} = -0.77 \pm 0.23\text{‰}$ (Gueguen et al., 2018). Spivak-Birndorf et al. (2018)
400 reported that nickel isotope fractionation from aqueous solution onto montmorillonite resulted in
401 a $\Delta^{60}\text{Ni}_{\text{montmorillonite-fluid}} = -0.11 \pm 0.09\text{‰}$. These values are similar with those generated during the
402 adsorption of Ni onto calcite in the present study, $\Delta^{60}\text{Ni}_{\text{calcite-fluid}} = -0.52 \pm 0.16\text{‰}$ (2SD).

403 This study shows that calcite preferably adsorbs light Ni isotopes. In contrast, calcite
404 preferentially adsorbs heavy Zn, with $\Delta^{66}\text{Zn}_{\text{adsorbed-solution}}$ averaging $0.41 \pm 0.18\text{‰}$ and $0.73 \pm 0.08\text{‰}$
405 in 0.1 and 0.7 M aqueous NaCl solutions, respectively (Dong and Wasylenki, 2016). The
406 preferential uptake of heavy Zn was interpreted to stem from a change in coordination between
407 the six-fold aqueous $\text{Zn}(\text{H}_2\text{O})_6^{2+}$ complex and Zn adsorbed on the calcite surface, which has a
408 four-fold coordination (Dong and Wasylenki, 2016). The tetrahedral coordination of Zn on the
409 calcite surface was confirmed through EXAFS analysis (Elzinga and Reeder, 2002). Similarly
410 changes in the coordination geometry of metal cations has shown has been shown to provoke
411 substantial isotopic fractionation for the adsorption of Zn on the surfaces of quartz or amorphous
412 SiO_2 (Nelson et al., 2017) and the adsorption of Ga isotopes on calcite and goethite surfaces
413 (Yuan et al., 2018). This behavior of Zn fractionation during its adsorption to calcite contrasts
414 with that of Ni, which likely does not change coordination number as it adsorbs to calcite
415 surfaces from aqueous solution. In cases where coordination number does not change upon
416 adsorption, small distortions of bond angles and lengths can also drive isotopic fractionation
417 (Brennecka et al., 2011; Gueguen et al., 2018; Juillot et al., 2008; Wasylenki et al., 2015, 2014).

418 Several experimental and theoretical studies have been carried out to determine the Ni-O
419 bond length in aqueous $\text{Ni}(\text{H}_2\text{O})_6^{2+}$. Experimentally measured bond lengths range between 2.05-
420 2.07 Å, as measured by XRD (Caminiti et al., 1977; Magini et al., 1982) and 2.07 Å, as measured
421 by EXAFS (Sandstrom, 1979). These values are in good agreement with DFT (Density
422 Functional Theory) calculations for the $\text{Ni}(\text{H}_2\text{O})_{18}^{2+}$ cluster (2.073 Å, Fujii et al., 2011). They are
423 slightly shorter than Ni-O bond length in gaspeite (NiCO_3) as determined by XRD (2.076 Å,
424 Pertlik, 1986). These observations suggest that the adsorption of Ni from aqueous solution to
425 calcite surfaces will result in a slight increase of the Ni-O bond length and induce an enrichment
426 in light isotope of the adsorbed Ni surface complex.

427 Previous studies reported that the isotopic fractionation of metals between a fluid and a
428 mineral phase also depends on the aqueous speciation of the metal (Balan et al., 2018; Fujii et al.,
429 2011, 2014; Mavromatis et al., 2018; Schott et al., 2016). As our experiments were performed at
430 pH ranging from 7.7 to 8.6, Ni aqueous speciation may have been impacted by the formation of
431 NiHCO_3^+ and NiCO_3° at the expense of aqueous Ni^{2+} with increasing pH. Based on the
432 thermodynamic constants for the aqueous Ni species included in the minteq.v4 database, Ni^{2+}
433 (referred to as $\text{Ni}(\text{H}_2\text{O})_6^{2+}$ above) accounts for 92% of total dissolved Ni at pH 7.7 but for only
434 48% at pH 8.6. Aqueous Ni^{2+} is replaced by NiHCO_3^+ and NiCO_3° as pH increases over this
435 range in our solutions. Whereas the concentrations of NiHCO_3^+ and NiCO_3° are negligible at pH
436 7.7, at pH 8.6 they represent 8 and 41% of dissolved nickel, respectively. Based on DFT
437 calculations of reduced partition function ratios among Ni aqueous species reported by Fujii et al.
438 (2014), the equilibrium fractionation factor at 25°C between aqueous Ni^{2+} and NiCO_3° ($\Delta^{60}\text{Ni}_{\text{Ni}^{2+}-\text{NiCO}_3^\circ}$)
439 is equal to -0.402‰ and that between Ni^{2+} and NiHCO_3^+ ($\Delta^{60}\text{Ni}_{\text{Ni}^{2+}-\text{NiHCO}_3^+}$) is -0.345‰.
440 As such the nickel carbonate and bicarbonate complexes present in solution at pH 8.6 should
441 make $\text{Ni}^{2+}_{(\text{aq})}$ and adsorbed Ni ~0.2‰ lighter than at pH 7.7. The data of the present study do not,
442 however, show enrichment of adsorbed Ni in light isotopes when the aqueous solution pH
443 increases from 7.7 to 8.6; although there is some scatter apparent in Figure 6b, the data trend
444 appears to show a slight increase in the uptake of heavier Ni with increasing pH. However, it
445 should be noted that there is significant uncertainty in the calculated aqueous speciation of Ni as
446 a function of pH in carbonate bearing solutions. For example, according to the stability constants
447 values of aqueous NiCO_3° and NiHCO_3^+ published by Baeyens et al. (2003), at pH 8.6 Ni^{2+}
448 would account for 69% of the total dissolved Ni, and NiCO_3° and NiHCO_3^+ for only 25 and 2%,
449 respectively. The subsequent enrichment of $\text{Ni}^{2+}_{(\text{aq})}$ and adsorbed Ni in light isotope would be of
450 ~0.1‰, which is within the uncertainty our isotopic measurements – see Fig 6b.

451 **4.3 Implications for natural systems.**

452 A number of previous works have concluded that our current understanding of the Ni
453 isotope balance in the oceans requires the identification of either another source of isotopically
454 heavy Ni or another sink of isotopically light Ni. Various processes have been suggested as the
455 possible light Ni sink including adsorption of Ni onto ferrihydrites or Mn-hydroxides and the
456 incorporation of Ni into sedimentary sulfides (Gueguen et al., 2013; Vance et al., 2016;

457 Wasylenki et al., 2015). The present study considered the possibility that Ni adsorption onto
458 calcite surfaces may also contribute to resolving this imbalance in the global marine Ni budget.
459 This study shows that light Ni is preferentially adsorbed onto calcite as $\Delta^{60}\text{Ni}_{\text{calcite-solution}} = -$
460 $0.52 \pm 0.16\%$. Although the mass of Ni removed from the ocean by adsorption onto calcite may
461 be too small to resolve the currently perceived Ni isotope imbalance, considering the large mass
462 of calcite formed annually, it may be a contributor to resolving this imbalance. The mass of Ni
463 removed by its co-precipitation with calcite may however, be far more significant. A detailed
464 calculation of such effects requires Ni fractionation factors during its co-precipitation, which will
465 be explored in a future study.

466

467 5. CONCLUSIONS

468 Experiments in the present study were performed to determine the degree of Ni isotope
469 fractionation imparted by the adsorption of Ni from an aqueous solution onto calcite surfaces.
470 The major results include:

- 471 1) No variation of the isotopic composition of Ni adsorbed onto calcite was observed with time.
- 472 2) Calcite surfaces preferentially adsorb isotopically light Ni with an average $\Delta^{60}\text{Ni}_{\text{calcite-fluid}} = -$
473 $0.52 \pm 0.16\%$. This value is independent of the amount of adsorbed nickel, within uncertainty,
474 indicating an equilibrium isotopic exchange process.
- 475 3) Ni does not change coordination number as it adsorbs to calcite surfaces from aqueous
476 solution, however, the Ni-O interatomic distance is slightly longer for Ni adsorbed to calcite as
477 it is for $\text{Ni}(\text{H}_2\text{O})_6^{2+}$. This change in coordination geometry is likely the mechanism driving the
478 fractionation of Ni isotopes during their incorporation on calcite.

479

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