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1 **Magnesium and carbon isotope fractionation during hydrated Mg-carbonate mineral**
2 **phase transformations**

3
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17 **Abstract**

18 The fractionation of carbon and magnesium isotopes is a potentially useful tracer of
19 natural weathering in ultramafic catchments and engineered CO₂ storage. To evaluate the use
20 of carbon and magnesium isotopes as tracers of ultramafic weathering and CO₂ storage, we
21 assessed the carbon and magnesium isotope fractionation between hydrous Mg-carbonate
22 minerals and fluid during a mineral phase transformation from nesquehonite [MgCO₃·3H₂O]
23 to dypingite [Mg₅(CO₃)₄(OH)₂·~5-8H₂O], two common products of ultramafic rock
24 weathering. Batch reactor experiments containing nesquehonite were conducted at 5°C, 25°C,
25 and 35°C and the evolution of mineralogical composition, fluid composition, and isotopic
26 composition were tracked over time. At 5°C, the solid remained nesquehonite throughout the
27 experiments, and isotopic equilibrium did not appear to be achieved between the solid and the
28 fluid phase for either carbon or magnesium. At 25°C, and 35°C a transformation from
29 nesquehonite to dypingite occurred by dissolution and re-precipitation, which resulted in
30 extensive exchange of Mg and C between solid and fluid. The phase transformation caused
31 the initial C and Mg isotopic composition of the solid phase to be overwritten. The extensive
32 isotopic exchange during the phase transformation suggests C and Mg isotopes likely
33 obtained approximate isotopic equilibrium between dypingite and fluid. For dypingite, the
34 $\Delta^{13}\text{C}_{\text{dyp-DIC}}$ was $4.74 \pm 0.12\text{‰}$ (VPDB) and $4.47 \pm 0.17\text{‰}$ (VPDB) at 25 and 35°C, respectively.
35 The $\Delta_{\text{meas}}^{26}\text{Mg}_{\text{dyp-fluid}}$ between solid and the bulk fluid was -0.76‰ , and $-0.98 \pm 0.08\text{‰}$ for
36 the 25 and 35°C experiments, respectively. There was no clear impact of temperature on Mg
37 or C isotope fractionation. The calculated $\Delta_{\text{calc}}^{26}\text{Mg}_{\text{dyp-Mg}^{2+}}$ between dypingite and the Mg²⁺
38 aquo species rather than bulk aqueous Mg values were positive. This indicates that if
39 dypingite is formed by the incorporation of the free Mg²⁺ ion in the solid, the solid is
40 preferentially enriched in the isotope of higher mass (²⁶Mg). This is opposite to anhydrous
41 Mg-bearing carbonate minerals, which tend to be depleted in ²⁶Mg relative to the forming

42 fluid. These data will help improve interpretation of carbon and magnesium isotope
43 compositions measured in natural and engineered ultramafic weathering environments, and
44 may help to trace the fate of anthropogenic CO₂ during engineered CO₂ storage efforts.
45

46 **1. Introduction**

47

48 The carbon, oxygen, and metal isotope compositions of naturally-forming carbonate
49 minerals are considered to be indicators of environmental conditions at the time of their
50 formation, and the Mg isotopic compositions of minerals and fluids in particular provide
51 valuable insight into modern weathering and element cycling processes (O’Neil and Barnes,
52 1971; Deines et al., 1974; Baumgartner and Valley, 2001; Deines, 2004; Tipper et al., 2010;
53 Wimpenny et al., 2010; Mavromatis et al., 2012; Pogge von Strandmann et al., 2012; Tipper
54 et al., 2012; Mavromatis et al., 2013; Shirokova et al., 2013; Beinlich et al., 2014; Li et al.,
55 2014; Mavromatis et al., 2014a; 2014b; Geske et al., 2015; Ryu et al., 2016; Hu et al., 2017;
56 Mavromatis et al., 2017a; 2017b; Beinlich et al., 2018; Oskierski et al., 2019). The isotopic
57 composition of minerals and fluids in engineered carbon storage environments are also
58 beginning to show promise as tracers of carbon storage and indicators of its efficiency (Power
59 et al., 2007, 2014; Wilson et al., 2009, 2010, 2011, 2014; Beinlich and Austrheim, 2012;
60 Harrison et al., 2013, 2016; Oskierski et al., 2013; McCutcheon et al., 2014; Oskierski et al.,
61 2016; Gras et al., 2017; Oelkers et al., 2019a; Pogge von Strandmann et al., 2019; Power et
62 al., 2019). The robust interpretation of isotopic compositions in both natural and engineered
63 environments requires knowledge of the mechanisms of isotopic fractionation, the magnitude
64 of fractionation between fluids and solids, the impact of temperature on fractionation, and the
65 stability of the isotopic compositions of the solid over time. Mineral growth rate, temperature,
66 fluid composition, mineral structure, cation-oxygen bond strengths, and precipitation pathway
67 exert strong controls on isotopic fractionation between solids and the fluid from which they
68 form (Criss, 1999; Mavromatis et al., 2012, 2015, 2017a, b; Schott et al., 2016; Stamm et al.,
69 2019).

70 Hydrated Mg-carbonate minerals like nesquehonite $[\text{MgCO}_3 \cdot 3\text{H}_2\text{O}]$ and dypingite
71 $[\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot \sim 5\text{-}8\text{H}_2\text{O}]$ are commonly formed during weathering of ultramafic rock in
72 natural and engineered systems, and have been identified as potential sinks to offset
73 anthropogenic CO_2 emissions (Wilson et al., 2006, 2009, 2011, 2014; Boschi et al., 2009;
74 Zhao et al., 2010; Pronost et al., 2011; Schaef et al., 2011, 2013; Assima et al., 2012; Bea et
75 al., 2012; Beinlich and Austrheim, 2012; Felmy et al., 2012; Hövelmann et al., 2012; Loring
76 et al., 2012; Montes-Hernandez et al., 2012; Harrison et al., 2013, 2015, 2016, 2017, 2019;
77 Power et al., 2013a; 2013b, 2014, 2019; Assima et al., 2014; Kristova et al., 2014; Chaka et
78 al., 2016; García del Real et al., 2016; Highfield et al., 2016; McCutcheon et al., 2016; Gras
79 et al., 2017; McCutcheon et al., 2017). A variety of hydrous magnesium carbonate minerals
80 exist and at Earth's surface conditions, their stability generally increases from more to less
81 hydrated phases (Langmuir, 1965; Canterford et al., 1984). Magnesite, the anhydrous Mg-
82 carbonate phase, is the most stable Mg-carbonate mineral, but does not readily form at Earth's
83 surface conditions (Hänchen et al., 2008; Saldi et al., 2009, 2012; Power et al., 2017; 2019).
84 The isotopic composition of hydrous Mg-carbonate minerals that form at or near Earth's
85 surface could be an important tracer of natural weathering processes and engineered CO_2
86 storage (Wilson et al., 2010; Power et al., 2014; 2019 Harrison et al., 2016; Gras et al., 2017;
87 Oskierski et al., 2016; 2019). Such potential applications have motivated a number of studies
88 on Mg or C isotopic fractionation between hydrous Mg-carbonate minerals and their forming
89 fluids (Wilson et al., 2010; Mavromatis et al., 2012; Shirokova et al., 2013; Oelkers et al.,
90 2018), but few have studied both Mg and C isotope behaviour together for the same mineral
91 or the impact of temperature on fractionation. The formation process of hydrous Mg-
92 carbonate minerals is complex, and may involve a combination of direct precipitation and
93 transformation of less-stable precursors (Hopkinson et al., 2008; Sutradhar et al., 2011;
94 Hopkinson et al., 2012; Ballirano et al., 2013; Kristova et al., 2014; Harrison et al., 2019;

95 Power et al., 2019; Ming and Franklin, 1985). This complicates the interpretation of isotopic
96 compositions; the impact of the mineral phase transformations on isotopic fractionation has
97 yet to be fully explored but may result in overwriting of isotopic compositions. To address
98 these complications, we build on past studies of Mg isotope fractionation by measuring the
99 temporal evolution of both C and Mg isotope compositions of co-existing reactive fluids and
100 the hydrous Mg-carbonate minerals nesquehonite and dypingite during the transformation of
101 nesquehonite to dypingite. Nesquehonite is less stable and is regarded as more hydrated than
102 dypingite, owing to a higher H₂O : Mg molar ratio (3 : 1 compared to ~1 to 1.6 : 1) despite
103 fewer moles of water per mole of nesquehonite.

104 The objectives of the present study are to 1) determine the magnitude of Mg and C
105 isotopic fractionation between nesquehonite and fluid and dypingite and fluid, 2) assess the
106 impact of temperature on Mg and C isotope fractionation between reactive fluid and these two
107 carbonate minerals, 3) evaluate the impact of mineral phase transformations on isotopic
108 compositions of hydrous Mg-carbonates, 4) provide insight into the potential utility of C and
109 Mg isotope fractionation as a proxy for Mg-carbonate precipitation when solid samples are
110 not available, and 5) provide further insight into the mechanisms of Mg isotope fractionation
111 between carbonate minerals and fluids.

112

113 **2. Methods**

114 *2.1 Experimental methods and analytical techniques*

115 The experimental protocol followed in this study is described in detail in Harrison et
116 al. (2019), in which the solubility products of nesquehonite and dypingite were determined. In
117 the present study, the samples of the Harrison et al. (2019) study have been further analyzed
118 to determine the stable carbon and magnesium isotopic composition of the carbonate minerals
119 and the fluid to which they were exposed. Briefly, experiments in our previous study

120 (Harrison et al., 2019) were conducted at 5, 25 and 35°C, with those at 25 and 35°C being
121 duplicated. The duplicates ran subsequently to the original and for a longer duration, to
122 observe the complete conversion of nesquehonite to dypingite. The shorter duration
123 experiments are referred to as “short-term” experiments, which ran for between 367-432 h,
124 and the longer duration as “long-term” experiments which ran for between 1368-2043 h. Each
125 experimental series consisted of a suite of nine to eleven sealed, closed-system batch reactors
126 at each fixed temperature. Initially 0.60 g of synthetic nesquehonite with ~73 g of an aqueous
127 solution containing 0.10 mol/L NaCl and 0.06 mol/L NaHCO₃ were introduced in each
128 reactor. The reactors (60 mL Nalgene bottles) were filled to have as little headspace as
129 possible in order to limit exchange of C with the atmosphere (some bubbles of air could not
130 be completely removed). The synthesis method for the initial nesquehonite is reported by
131 Harrison et al. (2019). At selected times an individual reactor was sampled in its entirety to
132 track the chemical and isotopic composition of the reactive aqueous solution, as well as
133 changes in the mineralogical and isotopic composition of the solids. The solution was
134 removed via a syringe, and filtered through a 0.22 µm polyethersulfone (PES) syringe filter.
135 Four aliquots were immediately acidified to 2% HNO₃ for subsequent analysis of Mg
136 concentrations and Mg isotopic compositions. A single aliquot was used for immediate pH
137 measurements and subsequent alkalinity measurements. For subsequent δ¹³C_{DIC} analysis,
138 fluids were stored in 2 mL air-tight vials with no headspace. All fluids were refrigerated prior
139 to subsequent analysis. Fluid pH was measured immediately after sampling using a Metrohm
140 913 pH-meter and a Metrohm combined electrode (6.0234.1000) that was calibrated using
141 NIST traceable buffer solutions at each experimental temperature, with an uncertainty of
142 approximately ±0.03 pH units.

143 The solids were separated from any remaining aqueous solution via vacuum filtration,
144 and were rinsed with distilled, de-ionized water to prevent NaCl precipitation. Solids were

145 dried at room temperature for ~48 h and stored in a desiccator prior to analysis. Dypingite was
146 formed *in situ* within the reactors at 25 °C and 35 °C through transformation of nesquehonite,
147 with long-term experiments designed to allow the complete transformation from nesquehonite
148 to dypingite. The phase transformation was tracked by changes in aqueous solution
149 composition and mineralogical data collected using X-ray diffraction (XRD). The
150 mineralogical data are reported in Harrison et al. (2019).

151 The alkalinity of all fluid samples was determined by HCl titration using an automated
152 Schott Titroline Alpha Plus titrator. Long term reproducibility of alkalinity analyses was
153 determined from repeated analysis of a standard; it was better than $\pm 0.36 \times 10^{-3}$ mol/L (3σ).
154 Dissolved inorganic carbon (DIC) concentrations were calculated using the geochemical
155 modelling program PHREEQC V.3 (Parkhurst and Appelo, 2013) with a modified LLNL
156 database (modifications to the database are described in Harrison et al. (2019)). The
157 uncertainty introduced by the calculation of DIC is not known, but was assumed to equal that
158 of the alkalinity measurement. Aqueous Mg concentrations were measured by atomic
159 absorption spectroscopy (AAS) using a Perkin Elmer AAnalyst 400. The quantification and
160 detection limits of Mg concentrations were 9.6×10^{-8} mol/L and 2.9×10^{-8} mol/L,
161 respectively, and reproducibility was better than 2% based on triplicate analysis of each
162 sample. Reported Mg concentrations represent averages of triplicate measurements of each
163 sample during one measurement session. The temporal evolution of the chemical composition
164 of the fluids is reported in Harrison et al. (2019) and reproduced here (Tables 1 and 2;
165 Electronic Annex 2 Table A2).

166

167 *2.2 Carbon isotope analyses*

168 Carbon isotope analyses of the solid carbonates were performed in continuous-flow
169 mode following the methodology of Breitenbach and Bernasconi (2011). Analyses were

170 conducted with a GasBench II coupled to a ThermoFinnigan MAT 253 mass spectrometer at
171 the Ruhr-University Bochum. The sampled solid carbonates are hydrophilic, therefore
172 exposure to the laboratory environment was minimized during sample preparation (i.e.,
173 weighing, transfer into vials) and analyses were performed within hours of sample
174 preparation. Between 90 and 120 μg of sample powder was weighed into borosilicate glass
175 vials. Samples were acid-digested at 70°C and analyzed together with international standards
176 NBS19, IAEA603, and CO-8. Results are reported as $\delta^{13}\text{C}_{\text{solid}}$ with respect to the Vienna
177 PeeDee belemnite (VPDB) standard. The external standard deviation for carbon isotope ratios
178 is $<0.08\text{‰}$ (n = approximately 32).

179 $\delta^{13}\text{C}$ is defined by equation 1:

$$180 \quad \delta^{13}\text{C} = \left(\frac{\left(\frac{^{13}\text{C}}{^{12}\text{C}} \right)_{\text{sample}}}{\left(\frac{^{13}\text{C}}{^{12}\text{C}} \right)_{\text{standard}}} - 1 \right) \times 1000 \quad (1)$$

181 The carbon isotopic composition of dissolved inorganic carbon ($\delta^{13}\text{C}_{\text{DIC}}$) was
182 measured at the Ruhr-University Bochum with a Thermo Fisher Scientific MAT253 equipped
183 with a GasBench and a GC Pal autosampler by CTC analytics. Samples were introduced into
184 vials that were previously flushed with He. The fluid was reacted with 65% phosphoric acid at
185 room temperature to release the CO_2 . Analysis of an internal Na_2CO_3 standard resulted in a
186 long-term 1σ reproducibility of $\pm 0.10\text{‰}$ for $\delta^{13}\text{C}_{\text{DIC}}$ in the time period of 2016-2017 ($n=54$).

187

188 *2.3. Magnesium isotope analyses*

189 The magnesium isotopic composition of selected aqueous Mg samples from each
190 experimental series and corresponding solids was determined following the procedure of
191 Mavromatis et al. (2012). Solid samples were digested in concentrated HNO_3 . Digested solids
192 and acidified liquid samples were evaporated to dryness and re-dissolved in 1N HNO_3 .
193 Samples were loaded onto 10 mL Bio-Rad poly-prep columns containing AG-50W-X12

194 cation exchange resin and eluted with 1 N HNO₃ to separate Mg from Na. About 15 µg of Mg
195 from each sample was loaded into each column and the yields after chromatographic
196 separation were better than 99% of the total Mg loaded in the columns. Magnesium isotopic
197 compositions were measured using a Thermo-Finnigan “Neptune” Multi Collector Inductively
198 Coupled Plasma Mass Spectrometer (MC-ICP-MS) at Géosciences Environnement Toulouse
199 (GET) laboratory (France). All samples were prepared in 0.35 N HNO₃ and introduced into
200 the Ar plasma with a large Stable Introduction System spray chamber (double Scott Cyclonic
201 spray chamber). Instrumental mass fractionation effects were corrected using sample-standard
202 bracketing, and all data are presented as δ^xMg with respect to DSM3 reference material
203 ($\delta^x\text{Mg} = ((^x\text{Mg}/^{24}\text{Mg})_{\text{sample}} / (^x\text{Mg}/^{24}\text{Mg})_{\text{DSM3}} - 1) \times 1000$) where x refers to the Mg mass of
204 interest. All sample analyses were run in triplicate over multiple measuring sessions with the
205 mean value presented in Table 2. The reproducibility of the δ²⁶Mg analyses was determined
206 using replicate analyses of the DSM3, CAM-1 and OUMg monoelemental Mg reference
207 standards and was typically better than 0.08‰. The reproducibility of the measurements is in
208 agreement with previously published values from the same laboratory (Mavromatis et al.,
209 2012, 2013, 2014a, 2014b; Pearce et al., 2012; Beinlich et al., 2014, 2018), as well as from
210 other laboratories (Bolou-Bi et al., 2009; Wombacher et al., 2009; Geske et al., 2015;
211 Riechelmann et al., 2016, 2018; Mavromatis et al., 2017a; 2017c). The reproducibility of
212 chromatographic separation was assessed by repeated analyses of selected samples and the
213 JDo-1 (dolomite) and IAPSO seawater as shown in Table 2, and was better than 0.08‰.

214

215 *2.4 Calculation of aqueous speciation and isotopic composition of carbon and magnesium* 216 *aqueous species*

217 In this study, aqueous speciation and mineral saturation states were calculated as in
218 Harrison et al. (2019), using PHREEQC V3 (Parkhurst and Appelo, 2013) and a modified

219 LLNL database updated to include aqueous Mg-carbonate complexes. The solubility products
 220 of nesquehonite and dypingite reported in Harrison et al. (2019) were used to calculate
 221 saturation states in the experiments. The isotopic composition of aqueous C species were
 222 calculated using fractionation factors reported in Zhang et al. (1995) (Table 1). In these
 223 calculations estimations of $\delta^{13}\text{C}_{\text{CO}_3^{2-}}$ is based on the sum of aqueous CO_3^{2-} and MgCO_3°
 224 species and for $\delta^{13}\text{C}_{\text{HCO}_3^-}$ on the sum of aqueous HCO_3^- and MgHCO_3^+ species, in an
 225 approach similar to that used to estimate B isotope fractionation between its two aqueous
 226 species (e.g. Noireaux et al., 2015). This approach is used because C isotope fractionation
 227 factors for MgCO_3° and MgHCO_3^+ aqueous species are unknown.

228 The isotope composition of the Mg aqueous species present in the reactive solutions
 229 was derived from the speciation calculations and the $^{26/24}\text{Mg}$ reduced partition function ratios
 230 (β) for $\text{Mg}^{2+}_{(\text{aq})}$ and aqueous inorganic Mg complexes reported by Schott et al. (2016). As
 231 such the isotopic composition of aqueous species relative to the bulk isotopic composition of
 232 the reactive solution has been calculated similar to Mavromatis et al. (2019) using the
 233 equation

$$234 \quad \delta^{26}\text{Mg}_i = \frac{\delta^{26}\text{Mg}_{\text{total}} - \sum_{j \neq i} (1000 \ln \beta_j - 1000 \ln \beta_i) \times f_j}{f_i} \quad (2)$$

235 where $\delta^{26}\text{Mg}_i$ is the isotopic composition of the i th species, f_i and f_j are the abundance
 236 fractions of the i th species and the sum of the abundance fractions of all the other species,
 237 respectively. The aqueous species considered in these calculations included: MgCO_3° ,
 238 MgOH^+ , Mg^{2+} , MgCl^+ , and MgHCO_3^+ . Estimation of $\ln \beta$ functions for 5 and 35°C were made
 239 by exponential fitting of the reduced partition functions in the range of 0 to 300°C based on
 240 the values of Schott et al. (2016). To compare, additional estimates of the $\ln \beta$ functions at
 241 25°C were conducted using the reduced partition functions calculated by Gao et al. (2018). In
 242 their study the authors propose a fractionation between $\text{MgHCO}_3^+(\text{aq})$ and $\text{Mg}^{2+}(\text{aq})$ of ~
 243 2.4%, which is 40% lower than that proposed by Schott et al. (2016). To estimate the isotopic

244 composition of Mg^{2+} in our experiments using the value of Gao et al. (2018), a similar 40%
245 reduction in theoretical estimates of MgCO_3° and MgCl^+ was applied (Table 2 and Electronic
246 Annex 2).

247

248 **3. Results**

249 *3.1 Mineral transformation*

250 As presented previously in Harrison et al. (2019) and shown in Fig. 1 and Table 1,
251 nesquehonite dissolved to reach equilibrium, before transforming to dypingite at 25°C and
252 35°C. Note that within this study we refer to dypingite as a single mineral phase although
253 precipitated solids may contain 5 or 8 water molecules per unit formula as reported by
254 Harrison et al. (2019). At 5°C, nesquehonite did not transform into a different phase during
255 the 1420 h experimental series. In contrast, at 25°C, minor amounts of dypingite were first
256 detected by XRD at 359 h in the long-term experimental series, and dypingite formed between
257 367 h and 1086 h during the short-term experimental series (see Harrison et al., 2019). This
258 change in mineral phase was also associated with a decrease in Mg concentration in the
259 reactive fluid (Table 2). At 35°C, the transformation from nesquehonite to dypingite was
260 more rapid than at 25°C. Dypingite was first detected at trace levels in the sample taken at 75
261 h from the short-term 35°C experimental series and in the sample taken after 123 h from the
262 long-term 35°C experimental series.

263

264 *3.2 Evolution of carbon isotopic composition*

265 There were two major sources of carbon at the onset of each experiment: the carbon in
266 the initial nesquehonite, and that in the dissolved inorganic carbon (DIC) from the NaHCO_3 in
267 the initial experimental solution. A small amount of carbon was also present in the small
268 volume of headspace present in each reactor, however given the low concentration of CO_2 in

269 laboratory air (~400 ppm), this is estimated to represent likely <0.01% of total C in the
270 reactors. The initial distribution of the mass of carbon between the two main sources of C,
271 nesquehonite and DIC, is nearly equal, with ~4.38 millimoles of carbon in DIC (~73 g of a 60
272 mM NaHCO₃ solution per reactor), and 4.34 millimoles of carbon in the initial nesquehonite
273 (0.60 g of nesquehonite per reactor). The initial isotopic composition of the two carbon
274 sources is very different (Table 1). Due to the large mass of nesquehonite required for the
275 experiments, it was synthesized in two batches, leading to a minor difference in initial C
276 isotopic composition of the solids between the short- and long-term experimental series. The
277 $\delta^{13}\text{C}_{\text{nsq}}$ value of the initial nesquehonite was -18.12‰ (VPDB), and -16.87‰ (VPDB) in the
278 short- and long-term experimental series, respectively. A fresh NaHCO₃ buffer solution was
279 generated for each of the five sets of experiments in this study, therefore the initial isotopic
280 composition of the DIC differs for each experimental run ($-4.26\text{‰} \leq \delta^{13}\text{C}_{\text{DIC}} \leq -4.01\text{‰}$, see
281 Table 1).

282 At all experimental temperatures, the $\delta^{13}\text{C}_{\text{DIC}}$ values exhibited an initial decrease by
283 the first sampling point (<12 h). In all experimental series, the $\delta^{13}\text{C}_{\text{DIC}}$ values decreased to
284 approximately $-7.5 \pm 0.3\text{‰}$ as long as the mineral phase of the solid in the reactor was
285 nesquehonite alone (Fig. 2). During the transformation of nesquehonite to dypingite in the 25
286 and 35°C experimental series, the $\delta^{13}\text{C}_{\text{DIC}}$ values continued to decrease (Fig. 2B and 2C). A
287 relatively constant value that averaged at $-11.87 \pm 0.24\text{‰}$ and $-11.92 \pm 0.11\text{‰}$ was achieved in
288 the long-term 25 and 35°C experiments after 1157 and 600 h, respectively (Fig. 2B and 2C).
289 This decrease in $\delta^{13}\text{C}_{\text{DIC}}$ values was accompanied by an increase in $\delta^{13}\text{C}_{\text{solid}}$ values (Fig. 2B
290 and 2C). At the first measured sampling point between (i.e., between 4 and 122 h depending
291 on the experiment, the solid had moderately higher $\delta^{13}\text{C}_{\text{solid}}$ values relative to the seed
292 material (by 0.44 to 1.38‰) except in the short-term 35°C experiment (Table 1). During
293 transformation of nesquehonite to dypingite, the solid phase $\delta^{13}\text{C}_{\text{solid}}$ values continued to

294 increase, stabilizing at an average of $-7.28 \pm 0.16\%$ (VPDB) ($n = 2$) and $-7.45 \pm 0.12\%$ (VPDB)
 295 ($n = 3$) in the long-term 25 and 35°C experimental series, respectively (Table 1; Fig. 2). The
 296 concurrent temporal variation of the $\delta^{13}\text{C}_{\text{DIC}}$ and $\delta^{13}\text{C}_{\text{solid}}$ values is better seen as the apparent
 297 fractionation factor between the solid and the reactive fluid which in this study is expressed
 298 as:

$$299 \quad \Delta^{13}\text{C}_{\text{solid-DIC}} = \delta^{13}\text{C}_{\text{solid}} - \delta^{13}\text{C}_{\text{DIC}} \quad (3)$$

300 The $\Delta^{13}\text{C}_{\text{solid-DIC}}$ is negative at all temperatures when nesquehonite is the only mineral phase
 301 present, but it changes to positive values as the transformation to dypingite progresses (Fig.
 302 3). When nesquehonite alone was present and the $\delta^{13}\text{C}_{\text{DIC}}$ and $\delta^{13}\text{C}_{\text{solid}}$ values were stable, the
 303 $\Delta^{13}\text{C}_{\text{nsq-DIC}}$ had an average value of $-10.15 \pm 0.37\%$ (VPDB) ($n = 4$), $-10.16 \pm 0.88\%$ (VPDB) (n
 304 $= 7$), and $-10.59 \pm 0.79\%$ (VPDB) ($n = 4$), at 5, 25, and 35°C, respectively including both the
 305 short- and long-term experimental series. The sample taken at 123 h in the long-term 35°C
 306 experiment was excluded from calculation of $\Delta^{13}\text{C}_{\text{solid-DIC}}$ for nesquehonite because trace
 307 dypingite was documented with XRD (Fig. 3; Table 1). The $\Delta^{13}\text{C}_{\text{dyp-DIC}}$ values were
 308 calculated when dypingite was the only phase detected with XRD; the value was an average
 309 of $4.74 \pm 0.12\%$ (VPDB) ($n = 2$) and $4.47 \pm 0.17\%$ (VPDB) ($n = 3$) in the long-term 25 and
 310 35°C experimental series, respectively. Thus no significant impact of temperature was
 311 observed for $\Delta^{13}\text{C}_{\text{solid-fluid}}$ values.

312 The change in pH during the mineral phase transformation resulted in a shift in
 313 aqueous C speciation, with a reduction in the amount of CO_3^{2-} (Fig. 1 and Electronic Annex
 314 1). However, the dominant species remained HCO_3^- throughout all experiments. The change
 315 in aqueous speciation implies that $\Delta^{13}\text{C}_{\text{solid-DIC}}$ will be impacted by pH. Therefore $\Delta^{13}\text{C}_{\text{solid-}}$
 316 CO_3^{2-} and $\Delta^{13}\text{C}_{\text{solid-HCO}_3^-}$ may allow better extrapolation of the reported $\Delta^{13}\text{C}_{\text{solid-fluid}}$ to other pH
 317 conditions. To facilitate calculation of $\Delta^{13}\text{C}_{\text{solid-CO}_3^{2-}}$ and $\Delta^{13}\text{C}_{\text{solid-HCO}_3^-}$, we have included the
 318 calculated values of $\delta^{13}\text{C}_{\text{CO}_3^{2-}}$ and $\delta^{13}\text{C}_{\text{HCO}_3^-}$ in Table 1. These numbers are uncertain as DIC

319 is also present as MgHCO_3^+ and MgCO_3^\ominus , and the impact of these complexes on $\delta^{13}\text{C}_{\text{CO}_3^{2-}}$ and
320 $\delta^{13}\text{C}_{\text{HCO}_3^-}$ is unknown. Therefore, here we mainly discuss $\Delta^{13}\text{C}_{\text{solid-DIC}}$ as the bulk $\delta^{13}\text{C}_{\text{DIC}}$ was
321 measured.

322

323 *3.3 Evolution of magnesium isotopic composition*

324 The Mg isotope composition of the synthetic nesquehonite used in the experimental
325 runs exhibits distinct values between that used in the short-term experimental series ($\delta^{26}\text{Mg} =$
326 $-1.38\text{‰} \pm 0.08\text{‰}$), and the long-term experimental series ($\delta^{26}\text{Mg} = -1.02\text{‰} \pm 0.08\text{‰}$; Table 2)
327 due to it being synthesized in two separate batches. The isotopic composition of the solids did
328 not change relative to the initial nesquehonite seed material in all experiments as long as the
329 mineral phase remained nesquehonite (Fig. 4). At 5°C , nesquehonite did not transform to
330 dypingite during the experimental series, and little change in isotopic composition of the solid
331 was observed (Fig. 4A). During the mineral phase transformation from nesquehonite to
332 dypingite, a decrease in $\delta^{26}\text{Mg}_{\text{solid}}$ values was observed (Figs. 4B and 4C). After this
333 transformation, the $\delta^{26}\text{Mg}_{\text{solid}}$ values were 0.08‰ to 0.20‰ lower than the initial solid in
334 the 25°C experiment and 0.20‰ lower than the initial solid in the 35°C experiment.

335 The only source of Mg in the reactors was that introduced in the initial nesquehonite.
336 Thus, the isotopic composition of the reactive fluids at early time in the experiments (i.e., <11
337 h) irrespective of reaction temperature exhibited isotopic compositions similar to that of the
338 seed nesquehonite. At 5°C , the isotopic composition of the fluid after 12 h of reaction time
339 was -1.36‰ , equal to that of the seed material within error (Table 2 and Fig. 4A). However,
340 by 24 h the fluid phase had higher $\delta^{26}\text{Mg}$ values relative to the solid by $\sim 0.18\text{‰}$ and remained
341 relatively constant until the end of the 5°C experimental series (Table 2), though the Mg
342 concentration stabilized after approximately 120 h (Fig. 6A; Harrison et al., 2019). Similarly,
343 after 24 h and 11 h of reaction time in the short-term experimental series conducted at 25 and

344 35°C respectively, the fluid phase had higher $\delta^{26}\text{Mg}$ values relative to the solid when
 345 nesquehonite was still the only detectable phase. After 359 h in the long-term 25°C
 346 experimental series, when dypingite was detectable with XRD, the fluid had higher $\delta^{26}\text{Mg}$
 347 values by $0.98\text{‰}\pm 0.05\text{‰}$ relative to the corresponding solid (Fig. 4B). The $\delta^{26}\text{Mg}_{fluid}$ values
 348 remained stable for the rest of the 1607 h experimental series, albeit with a slight decreasing
 349 trend (Fig. 4B). After 311 h in the long-term 35°C experimental series, when dypingite was
 350 the dominant phase, the fluid had higher $\delta^{26}\text{Mg}$ values by $0.98\text{‰}\pm 0.06\text{‰}$ relative to the
 351 corresponding solid, and remained relatively stable for the rest the experimental series. The
 352 stabilization of the Mg isotopic composition in the fluid phase in the 25 and 35°C
 353 experimental series corresponded to times for which significant amounts of dypingite was
 354 detected, although nesquehonite was still present in the solid phase at the time of Mg isotope
 355 stabilization in the fluid phase (Table 2). That is, the Mg isotope composition of the fluid
 356 stabilized before the mineral transformation was complete.

357 Magnesium isotope fractionation between the Mg-bearing solids and the reactive fluid,

358 $\Delta_{meas}^{26}\text{Mg}_{solid-fluid} \approx 1000\ln(a_{meas}^{26}\text{Mg}_{solid-fluid})$, has been estimated as:

$$359 \quad \Delta_{meas}^{26}\text{Mg}_{solid-fluid} = \delta^{26}\text{Mg}_{solid} - \delta^{26}\text{Mg}_{fluid} \quad (4)$$

360 The results of these calculations are reported in Table 2 and illustrated in Fig. 5. In
 361 experiments conducted at 5°C, where the only mineral phase was nesquehonite, the
 362 $\Delta_{meas}^{26}\text{Mg}_{nsq-fluid}$ value when the aqueous Mg concentration stabilized after 120 h was -
 363 $0.13\pm 0.03\text{‰}$ ($n = 3$) (Table 2). In the 25 and 35°C experiments, the $\Delta_{meas}^{26}\text{Mg}_{nsq-fluid}$ values
 364 were $-0.17\pm 0.05\text{‰}$ ($n=5$), and $-0.07\pm 0.10\text{‰}$ ($n=4$), respectively, when the mineral phase was
 365 nesquehonite alone and the Mg concentrations had stabilized in the fluid (after 24 h and 3 h
 366 in the 25 and 35 C experiments, respectively; Harrison et al., 2019; Figure 6A; Table 2).
 367 During the transformation of nesquehonite to dypingite, the $\Delta_{meas}^{26}\text{Mg}_{solid-fluid}$ values
 368 became progressively lower. In both the long-term 25 and 35°C experimental series, the

369 $\Delta_{meas}^{26}Mg_{solid-fluid}$ values became relatively constant after 359 and 311 h, respectively
 370 (Figure 5). The $\Delta_{meas}^{26}Mg_{dyp-fluid}$ were calculated for samples for which dypingite was the
 371 only phase detected with XRD, although $\Delta_{meas}^{26}Mg_{solid-fluid}$ values stabilized when
 372 nesquehonite was still present in the samples. The $\Delta_{meas}^{26}Mg_{dyp-fluid}$ were -0.76 ‰ (n = 1)
 373 and $-0.98 \pm 0.08\text{‰}$ (n = 2), respectively (Table 2).

374 Owing to the high concentration of dissolved inorganic carbon in the experiments (i.e.,
 375 ~60 to 81 mM; see Electronic annex Fig A1), ~50% of the aqueous Mg is present as
 376 $MgHCO_3^+_{(aq)}$ and $MgCO_3^0_{(aq)}$ in the reactive fluids prior to the phase transformation, and just
 377 under 50% of the aqueous Mg is present as these complexes after the phase transformation
 378 (Fig. 6). The formation of Mg-bearing aqueous carbonate complexes is predicted to be
 379 accompanied by an enrichment in ^{26}Mg of $MgHCO_3^+_{(aq)}$ and $MgCO_3^0_{(aq)}$ relative to $Mg^{2+}_{(aq)}$
 380 (Schott et al., 2016; Gao et al., 2018). This implies that in a highly alkaline fluid, like that
 381 used in our experiments, the $\delta^{26}Mg$ value of $Mg^{2+}_{(aq)}$ is lower compared to the bulk $\delta^{26}Mg$
 382 value of the fluid (i.e., the total aqueous Mg). The isotopic composition of $Mg^{2+}_{(aq)}$ in the
 383 experimental fluids was calculated using the $^{26/24}Mg$ reduced partition function ratios (β) of
 384 inorganic aqueous Mg species (Schott et al., 2016; Gao et al., 2018). These calculations
 385 indicated that the $\delta^{26}Mg$ value of $Mg^{2+}_{(aq)}$ is lower relative to bulk fluid $\delta^{26}Mg$ values at all
 386 experimental temperatures (Table 2). In contrast to the negative Mg isotope fractionation
 387 between solid and total $Mg_{(aq)}$, the fractionation between nesquehonite and $Mg^{2+}_{(aq)}$ and
 388 dypingite and $Mg^{2+}_{(aq)}$ was positive for all experiments (Fig. 5). The fractionation between
 389 solid and $Mg^{2+}_{(aq)}$ was calculated as:

$$390 \quad \Delta_{calc}^{26}Mg_{solid-Mg^{2+}(aq)} = \delta^{26}Mg_{solid} - \delta^{26}Mg_{Mg^{2+}(aq)} \quad (5)$$

391 The values were $0.84 \leq \Delta_{calc}^{26}Mg_{solid-Mg^{2+}(aq)} \leq 2.87$ for all experimental runs (Table 2).

392 The aqueous speciation and calculated isotopic composition of Mg^{2+} in all experiments is
 393 provided in Electronic Annex 2.

394

395 **4. Discussion**

396 *4.1 Carbon isotope fractionation between hydrous Mg carbonates and reactive fluid*

397 Nesquehonite dissolved to reach chemical equilibrium within ~120 h, 24 h, and 3 h in
398 the 5, 25, and 35°C experiments, respectively (Fig. 1). The presence of DIC in the initial
399 experimental fluids means that the $\delta^{13}\text{C}_{\text{DIC}}$ values should reflect mixing between initial
400 dissolved carbon, and that provided to solution when nesquehonite dissolves. As the
401 nesquehonite has $\delta^{13}\text{C}_{\text{solid}}$ values that are lower than the initial $\delta^{13}\text{C}_{\text{DIC}}$ values, isotopically
402 conservative dissolution would result in a change in $\delta^{13}\text{C}_{\text{DIC}}$ to lower values. This expected
403 reduction in $\delta^{13}\text{C}_{\text{DIC}}$ values is nominally consistent with observations during the approach of
404 nesquehonite to chemical equilibrium (Table 1). However, it has been observed that isotopic
405 fractionation can occur during net dissolution and at chemical equilibrium (e.g., Subhas et al.,
406 2017; Oelkers et al., 2019b; Gorski and Fantle, 2017; Pearce et al., 2012). To assess whether
407 the observed change in $\delta^{13}\text{C}_{\text{DIC}}$ values is consistent with conservative input of C isotopes from
408 nesquehonite dissolution alone, or if fractionation of the isotopes also occurs, we applied a
409 mixing model (Eq. 6):

$$410 \quad \delta^{13}\text{C}_{\text{DIC},t} \times \text{DIC}_t = (\delta^{13}\text{C}_{\text{DIC},i} \times \text{DIC}_i) + (\delta^{13}\text{C}_{\text{nsq},i} \times \text{DIC}_{\text{nsq}}) \quad (6)$$

411 where t and i denote reaction time and initial values, respectively and DIC_{nsq} is the
412 contribution to the DIC concentration from nesquehonite dissolution. The mixing model
413 assumes an isotopically homogeneous initial solid. Solving Equation 6 for $\delta^{13}\text{C}_{\text{DIC},t}$ indicates
414 that the measured $\delta^{13}\text{C}_{\text{DIC}}$ values are generally lower than calculated values, but within error,
415 for all temperatures (Table 1). A lower measured $\delta^{13}\text{C}_{\text{DIC}}$ value compared to that predicted
416 from the simple mixing model implies that isotopic fractionation may be occurring during net
417 nesquehontie dissolution, but given the high degree of uncertainty, this cannot be stated
418 definitively based on measured $\delta^{13}\text{C}_{\text{DIC}}$ values.

419 However, a minor increase in $\delta^{13}\text{C}$ values in the solid phase compared to the initial
420 nesquehonite was observed within the first ~24 h of each experimental series, except the
421 short-term 35°C experimental series, which exhibited a minor decrease in $\delta^{13}\text{C}$ value (Table
422 1). Assuming the solid is isotopically homogeneous, its bulk isotopic composition should not
423 change due to dissolution. The increase in $\delta^{13}\text{C}_{\text{solid}}$ values would correspond to a decrease in
424 $\delta^{13}\text{C}_{\text{DIC}}$ values, given an exchange of carbon isotopes between the fluid and the solid. This is
425 consistent with a lower measured $\delta^{13}\text{C}_{\text{DIC}}$ value than predicted by dissolution alone. Similarly,
426 an offset in Mg isotopic composition between solid and fluid was observed during net
427 dissolution of nesquehonite, in excess of measurement error (Fig. 5; Table 2). Together, these
428 observations indicate another process in addition to nesquehonite dissolution may have
429 occurred and resulted in C isotope fractionation. Isotopic exchange during net dissolution and
430 at chemical equilibrium have been observed for other minerals. The exchange of isotopes
431 between fluid and solid can result due to exchange of surface species, trace precipitation
432 occurring during bulk dissolution, or stable mineral recrystallization (e.g., Chanda et al.,
433 2019; Gorski and Fantle, 2017; Mavromatis et al., 2016; 2017b; Subhas et al., 2017).
434 However, the lack of knowledge of fractionation factors, and large uncertainty in calculated
435 values means the extent to which isotopic exchange occurred during the approach of
436 nesquehonite to chemical equilibrium cannot be precisely estimated in our experimental runs.

437 When nesquehonite was at chemical equilibrium in all experiments, $\Delta^{13}\text{C}_{\text{nsq-DIC}}$ was
438 negative and remained relatively constant until the phase transformation to dypingite began
439 (Table 1; Fig. 3). This is unlike most observations for carbonate minerals, which are typically
440 enriched in ^{13}C (i.e., higher $\delta^{13}\text{C}$) compared to the DIC of the aqueous solution from which
441 they have formed when at thermodynamic isotopic equilibrium (e.g., Deines, 2004; Rubinson
442 and Clayton, 1969; Zachmann and Johannes, 1989; Romanek et al., 1992; Wilson et al.,
443 2010). Nesquehonite chemical equilibrium was approached by dissolution, and there was not

444 evidence of extensive exchange of C isotopes between fluid and solid during dissolution or at
445 equilibrium. For example, in the 5°C experiment, nesquehonite reached chemical equilibrium
446 within ~120 h (Fig. 1A, Harrison et al., 2019), but the $\Delta^{13}\text{C}_{\text{nsq-DIC}}$ values remained nearly
447 constant after 24 h until the end of the 1420 h experiment. Although a minor amount of C
448 isotopic exchange was suspected to occur between fluid and solid, as described above, the
449 extent of exchange was uncertain and thus likely quite limited. It is therefore concluded that
450 isotopic equilibrium was not likely achieved between the bulk nesquehonite and fluid at any
451 temperature, despite achievement of chemical equilibrium.

452 In contrast to the C isotopic composition of nesquehonite, which likely reflects only
453 partial isotopic exchange between fluid and solid, the isotopic composition of fluid and solid
454 were significantly altered during the transformation to dypingite (Fig. 2). The $\Delta^{13}\text{C}_{\text{solid-DIC}}$
455 values increased during the phase transformation and stabilized when dypingite was the only
456 phase detectable. The large change in fluid and solid isotopic composition during the phase
457 transformation indicates the formation of dypingite likely occurs via the dissolution of
458 nesquehonite and re-precipitation from aqueous solution, facilitating substantial transfer of C
459 (see section 4.3). A dissolution-reprecipitation process implies it is more likely that dypingite
460 achieved C-isotopic equilibrium with the fluid compared to nesquehonite and fluid. Similarly,
461 the small variation of the $\Delta^{13}\text{C}_{\text{dyp-DIC}}$ value estimated for the samples collected after 1607 h at
462 25°C (n=2) and after 600 h at 35°C (n=3) when dypingite was at chemical equilibrium
463 suggests isotopic equilibrium was approached (Fig. 3). Additionally, these values have been
464 estimated from solids and corresponding fluids that equilibrated in individual batch reactors.
465 That means that several fluid-solid systems approached the same value. The positive $\Delta^{13}\text{C}_{\text{dyp-DIC}}$
466 and $\Delta^{13}\text{C}_{\text{dyp-HCO}_3^-}$ are consistent with previous abiotic studies indicating preferential
467 uptake of ^{13}C in carbonate minerals (Romanek et al., 1992; Jimenez-Lopez et al., 2006).
468 Moreover, the $\Delta^{13}\text{C}_{\text{dyp-DIC}}$ value estimated in this study at 25°C of $4.74 \pm 0.12\%$ is in fairly

469 good agreement with those reported by Mavromatis et al. (2015) (2.1 to 4.0‰) and Wilson et
470 al. (2010) (3.8±1.4‰). The large range in $^{13}\text{C}_{\text{dyp-DIC}}$ in Mavromatis et al. (2015) study is
471 attributed to precipitation occurring across a range of saturation states with respect to
472 dypingite, compared to the close-to-equilibrium conditions in the present experiments.

473

474 4.2 Magnesium isotope fractionation between hydrous Mg carbonates and reactive fluid

475 The average $\Delta_{\text{meas}}^{26}\text{Mg}_{\text{nsq-fluid}}$ values of the experiments where nesquehonite was the
476 sole phase in the reactor and the Mg concentrations in the fluid stabilized were -0.13±0.03‰
477 (n=3), -0.17±0.05‰ (n=5), and -0.07±0.10‰ (n=4), for the 5, 25, and 35°C experiments,
478 respectively (Fig. 4 and Table 2). The measured $\Delta_{\text{meas}}^{26}\text{Mg}_{\text{solid-fluid}}$ between nesquehonite
479 and reactive fluid are somewhat smaller in magnitude compared to that reported previously.
480 To our knowledge, Mg isotopic fractionation between nesquehonite and fluid is only reported
481 by Mavromatis et al. (2012). They conducted precipitation experiments of hydrous Mg
482 carbonate in the presence of *Gloeocapsa* sp. cyanobacteria at 25°C and measured a
483 $\Delta_{\text{meas}}^{26}\text{Mg}_{\text{nsq-fluid}}$ value of -0.63‰ for nesquehonite, though this value is based on a single
484 sample. In addition, the reactive fluid from which nesquehonite precipitated in the study of
485 Mavromatis et al. (2012) was supersaturated with respect to amorphous magnesium carbonate
486 (AMC; Purgstaller et al., 2019). Differences in $\Delta_{\text{meas}}^{26}\text{Mg}_{\text{nsq-fluid}}$ values between this
487 previous study and the present study may also reflect a lack of attainment of isotopic
488 equilibrium in the present study, as postulated for C isotopes in these experiments.

489 The dissolution and replacement of nesquehonite by dypingite facilitated extensive
490 exchange of Mg between the fluid and solid, as also observed for C isotopes. After the
491 mineralogical transformation the average values of $\Delta_{\text{meas}}^{26}\text{Mg}_{\text{dyp-fluid}}$ for dypingite were -
492 0.76‰ (n=1) and -0.98±0.08‰ (n=2) for the 25 and 35°C experiments, respectively. These
493 values are in relatively good agreement with the values reported in the Mavromatis et al.

494 (2012) study for the dypingite-fluid system within uncertainty (i.e., $-1.35 \pm 0.27\%$). Similarly,
495 the Mg isotope fractionation between natural hydromagnesite and the forming fluid in Lake
496 Salda (Turkey) exhibits a similar $\Delta_{meas}^{26}Mg_{solid-fluid}$ as observed in this study for dypingite
497 of about $-1.0 \pm 0.1\%$ (Shirokova et al., 2013). Dypingite and hydromagnesite have similar
498 crystal structures, but differ in the degree of hydration and crystallinity. Close fractionation
499 factors for these two minerals is plausible. The higher degree of hydration of Mg in dypingite
500 compared to hydromagnesite suggests that Mg isotope fractionation may respond differently
501 to growth rate effects between the two minerals, even if equilibrium fractionation factors were
502 similar (c.f., Pearce et al., 2012; Mavromatis et al., 2013). Thus, as was observed for C, the
503 Mg isotopes are more likely to have obtained equilibrium between dypingite and fluid than
504 nesquehonite and fluid. Notably, however, the time of stabilization of C and Mg isotopic
505 compositions differed. The carbon isotopic composition in both fluid and solid stabilized
506 more rapidly than Mg isotopes when nesquehonite was present. A measurable effect on the C
507 isotope compositions was observed earlier than for Mg when the phase transformation began
508 at 25 and 35°C, yet the Mg isotope compositions stabilized earlier than C isotope
509 compositions as the phase transformation completed (Tables 1 and 2). This difference in time
510 of stabilization of isotope compositions might reflect differences in relative fluid and solid
511 reservoir sizes (i.e., moles of C are approximately equal in solid and fluid whereas there is
512 more Mg in the solid than fluid), differences in the rate of exchange of C compared to Mg, or
513 different distances from equilibrium. For example, a greater amount of C might be required to
514 exchange before isotopic equilibrium is achieved. We could not distinguish these effects using
515 our data, however, it is important to note that Mg and C isotopes may not achieve equilibrium
516 over the same timescale owing to a variety of factors.

517 An interesting feature of the experimental results is that the $\Delta_{calc}^{26}Mg_{solid-Mg^{2+}(aq)}$
518 calculated using Eq. 5, exhibits positive values, while the $\Delta_{meas}^{26}Mg_{solid-fluid}$ is negative for

519 all the experiments (Fig. 5). The positive value for solid-Mg²⁺ fractionation indicates that the
520 solid is enriched in the heavier ²⁶Mg isotope relative to aqueous Mg²⁺, despite the solid being
521 depleted in ²⁶Mg compared to the bulk aqueous Mg. Unlike our observations for the hydrated
522 Mg-carbonates, the formation of the anhydrous phases magnesite and dolomite are
523 accompanied by depletion of the solid phase in ²⁶Mg relative to aqueous Mg²⁺ (Pearce et al.,
524 2012; Li et al., 2015; Schott et al., 2016). Solid phase depletion in ²⁶Mg relative to bulk fluid
525 Mg has also been observed during the incorporation of Mg in calcite and aragonite as a trace
526 element or impurity (Li et al., 2012; Saulnier et al., 2012; Mavromatis et al., 2013, 2017a,
527 2017c; Wang et al., 2013). This ²⁶Mg depletion in the solid phase has been attributed to the
528 shorter average Mg-O bond length of the hexa-coordinated aqueous Mg²⁺ compared to the
529 Mg-O bond length in the solid phase. The fluid phase Mg-O bond length of hydrated aqueous
530 Mg²⁺ is ~2.08/2.11 Å (Pavlov et al., 1998; Schott et al., 2016) whereas in anhydrous carbonate
531 minerals this bond length is consistently longer; 2.101 Å in magnesite (Schauble, 2011),
532 2.115 Å in dolomite (Antao et al., 2004) and between 2.11 and 2.16 Å in Mg-calcite (Finch
533 and Allison, 2007; Pinilla et al., 2015). Owing to the large variation of the Mg-O bond length
534 in hydrous Mg-carbonates, a direct correlation between this parameter and Mg isotope
535 fractionation is not straightforward. For example, nesquehonite is comprised of disordered
536 corner-sharing MgO₆ octahedra where Mg is directly coordinated to two water molecules and
537 the Mg-O bond distance in the unit cell ranges between 2.01 and 2.14 Å (Giester et al., 2000).
538 Therefore, it is difficult to assess whether a positive or negative fractionation between Mg²⁺
539 and solid should be expected. Nevertheless, the positive $\Delta_{calc}^{26}Mg_{dyp-Mg^{2+}(aq)}$ values for
540 dypingite in our study are in excellent agreement with those reported previously for
541 hydromagnesite by Oelkers et al. (2018). These authors studied the evolution of Mg isotope
542 fractionation between hydromagnesite and reactive fluid in experiments that lasted up to 574

543 d in carbonate-buffered solutions and presented bulk $\delta^{26}\text{Mg}$ values of the fluid and solid
544 phase.

545 Here, we calculate the magnesium isotope fractionation between hydromagnesite and
546 aqueous Mg^{2+} for selected samples from the Oelkers et al. (2018) study, under the assumption
547 that hydrated magnesium carbonates form by incorporation of Mg^{2+} . It should be noted,
548 however, that the formation mechanism of these carbonates is not known, and may not be
549 limited to Mg^{2+} incorporation only. Using the reduced partition functions presented by Schott
550 et al. (2016) in combination with Eq. 5 for the samples Hmgs-1.17, Hmgs-2.13, Hmgs-3.4 and
551 Hmgs-4.7 in the Oelkers et al. (2018) study, values of $\Delta_{\text{calc}}^{26}\text{Mg}_{\text{solid}-\text{Mg}^{2+}(\text{aq})}$ of 2.08, 2.57,
552 2.88 and 2.65‰ are determined, respectively (Electronic Annex 2 Table A1). The selected
553 samples represent the longest incubation time for which bulk fluid $\delta^{26}\text{Mg}$ values were
554 available and likely denote closest to isotopic equilibrium conditions. The positive
555 $\Delta_{\text{calc}}^{26}\text{Mg}_{\text{solid}-\text{Mg}^{2+}(\text{aq})}$ calculated for hydromagnesite in the Oelkers et al. (2018) study are
556 consistent with our observations for dypingite, though larger (see Table 2). It can be
557 concluded therefore, that hydrated Mg-carbonate minerals should be enriched in the Mg
558 isotope of higher mass (^{26}Mg) relative to aqueous Mg^{2+} . Observations of depletion of
559 hydrated Mg-carbonate minerals in ^{26}Mg therefore suggest aqueous speciation effects, or
560 growth by incorporation of complexed Mg. In our study, aqueous speciation and mineral
561 composition of the solid changed over time. Thus, it was not possible to conclude whether Mg
562 isotope fractionation was mainly controlled by crystallographic (i.e., bond length) or fluid
563 speciation factors. Nevertheless, it was clear that isotopic compositions obtained during
564 growth of a metastable phase are overwritten during replacement by a secondary, more stable
565 phase.

566 Finally, it is important to note that the aqueous species-specific $\Delta_{\text{calc}}^{26}\text{Mg}_{\text{solid}-\text{Mg}^{2+}(\text{aq})}$
567 values calculated using Eq. 5 are strongly dependent on the accuracy of the first-principle

568 calculations of β -values for the Mg isotope fractionation among aqueous species and may
569 therefore be somewhat uncertain. For example, in this study the isotopic composition of Mg^{2+}
570 has been calculated based on the β -values reported in Schott et al. (2016) and those of Gao et
571 al. (2018). The Schott et al. (2016) calculations considered only the first hydration shell of the
572 Mg aquo ion and small clusters of water molecules. The importance of the shell configuration
573 can be seen in the absolute values of the $\ln\beta$ functions; for a cluster of 6 water molecules the
574 $\ln\beta$ functions takes a value of 24.78 ‰, whereas for 18 water molecules it takes a value of
575 23.96 ‰ at 25°C (Schott et al., 2016). Similarly, the fractionation factors between the
576 aqueous species Mg^{2+} and $MgHCO_3^+$ have an offset of 40% in values reported by Schott et al.
577 (2016) compared to Gao et al. (2018) at 25°C (see Fig 5B). This variation may stem from the
578 absolute value of partition reduction functions (β) that generally should be more accurate with
579 the use of larger cluster models. In addition, it is not known whether the 40% offset between
580 the Schott et al. (2016) study and the Gao et al. (2018) study is valid for all aqueous species.
581 Moreover, there are no available data on the theoretical values of the reduced partition
582 function ratios for Mg in hydrated Mg carbonates thus considerable uncertainty is implied for
583 the actual values of $\Delta_{calc}^{26}Mg_{solid-Mg^{2+}(aq)}$ in these solids.

584

585 *4.3 Implications for the formation mechanisms and the application of isotopic composition of* 586 *hydrous Mg carbonates*

587 The mechanisms of hydrous Mg-carbonate mineral formation are not well-known and
588 often involve transformation from less-hydrated precursors (Davies and Bubela, 1973;
589 Hopkinson et al., 2008, 2012; Ballirano et al., 2013; Kristova et al., 2014; Harrison et al.,
590 2015, 2016, 2019; Power et al., 2019). As observed in this study, the phase transformation
591 between hydrated Mg-carbonate minerals is accompanied by a change in isotopic
592 composition. The large change in the C and Mg isotopic composition of the solid and fluid

593 phase (Figs. 2 and 4) during the mineral phase transformation reveals that there is extensive
594 exchange of atoms during this process. This isotopic exchange indicates that the mineral
595 phase transformation mainly occurs via a dissolution-reprecipitation mechanism. The
596 complete alteration of crystal morphology as observed by Harrison et al. (2019) is consistent
597 with bulk dissolution-reprecipitation of entire crystals, in contrast to observations of micro-
598 scale replacement in anhydrous biogenic carbonates (Pederson et al., 2019; Casella et al.,
599 2017). The overwriting of isotopic compositions during the phase transformation implies that
600 the use of the isotopic composition of hydrous magnesium carbonates as a tracer of initial
601 formation conditions or original source of CO₂ must be approached with some caution. The
602 measured solid composition may reflect the fluid composition at the time of a phase
603 transformation, rather than that of the fluid during the time of initial mineral precipitation.
604 However, our experimental results indicate only a partial alteration of isotopic compositions
605 at chemical equilibrium between nesquehonite and fluid on our experimental timescales, in
606 contrast to observations of significant Ca isotopic exchange between calcite and fluid under
607 chemical equilibrium (Oelkers et al., 2019b). This likely results from the very low rate of
608 exchange of water molecules in the hydration sphere of aqueous Mg compared to aqueous Ca
609 (Pokrovsky and Schott, 2002). The experimental observations suggest that extensive
610 exchange of isotopes between fluid and Mg-carbonate solids requires mineral transformation,
611 or perhaps longer timescales than used in our experiments.

612 Stable carbon isotopic compositions of Mg-carbonate minerals have been used to
613 assess the processes by which carbon is stored and cycled during weathering at Earth's
614 surface conditions in Mg-rich rock (Power et al., 2007, 2014, 2019; Wilson et al., 2009, 2010,
615 2011, 2014; Beinlich and Austrheim, 2012; Harrison et al., 2013; Oskierski et al., 2013; 2016;
616 2019; Shirokova et al., 2013; McCutcheon et al., 2014, 2019; Mervine et al., 2014; Falk et al.,
617 2016; Harrison et al., 2016; Gras et al., 2017). The Mg isotopic composition of fluids and

618 solids could also help distinguish between Mg-carbonate and Mg-clay formation in both
619 subsurface and near-surface CO₂-capturing environments (Oelkers et al., 2019a; Oskierski et
620 al., 2019). Knowledge of the direction and magnitude of isotope fractionation, and degree of
621 alteration of Mg and C isotopic compositions post-deposition, will facilitate more robust
622 interpretation of measured Mg and C isotopic compositions during both engineered and
623 natural carbon-storing processes. These isotopic compositions can be used to help assess the
624 type of Mg-bearing precipitate that formed if solid samples cannot be directly accessed for
625 analysis (e.g., subsurface CO₂ storage). For example, Mg-clay precipitation can reduce the
626 CO₂ storage capacity of storage reservoirs by removing the amount of Mg available to
627 precipitate with CO₂ (Rigopoulos et al., 2018; Oelkers et al., 2019a). Thus, robust
628 identification of clay precipitation versus Mg-carbonate precipitation using a combination of
629 C and Mg isotopes could prove a valuable tool to trace the efficacy of CO₂ removal
630 technologies. The use of these isotopes to assess carbon-storing processes cannot be
631 accomplished without knowledge of the fractionation factors for the different carbonate
632 minerals that can form. Thus, the $\Delta_{meas}^{26}Mg_{solid-fluid}$ and $\Delta^{13}C_{solid-DIC}$ determined in our
633 study can be used to help determine whether Mg-carbonate minerals are forming during
634 engineered CO₂ storage, particularly in Earth's near-surface environments when hydrous Mg-
635 carbonate mineral formation is favoured. Despite the overwriting of previous isotopic
636 compositions during mineral transformation, the observed isotopic fractionation between the
637 hydrated magnesium carbonates and fluid may still be useful indicators of ongoing mineral
638 weathering and carbon mineralization reactions.

639 Our results also highlight the importance of considering the speciation of the fluid
640 when interpreting isotopic compositions measured in the solid. As a growing body of research
641 demonstrates (Schott et al., 2016; Stamm et al., 2019), the speciation of a cation in solution
642 can strongly impact the apparent direction and extent of fractionation. In our experiments, a

643 negative Mg isotope fractionation between solid and bulk fluid is measured. However, a
644 positive $\Delta_{calc}^{26}Mg_{solid-Mg^{2+}(aq)}$ between solid and the Mg^{2+} aquo species is calculated. This is
645 attributed to the extensive complexation of aqueous Mg by dissolved carbonate species. The
646 difference between measured mineral - bulk fluid isotopic fractionation and the corresponding
647 calculated mineral - Mg^{2+} aquo species fractionation may be lessened or increased depending
648 on the fluid composition, thus Mg isotope compositions may also be useful indicators of fluid
649 pH and dissolved inorganic carbon concentration given further study under controlled fluid
650 composition.

651

652 **5. Conclusion**

653 In this study we examined the fractionation of C and Mg isotopes during the
654 transformation of nesquehonite to dypingite at 5, 25, and 35°C. These minerals are common
655 weathering products in ultramafic environments and are of interest for their capacity to store
656 CO₂ securely. Experiments revealed that nesquehonite did not transform to dypingite at 5°C,
657 and isotopic equilibrium between nesquehonite and solution may not have been achieved for
658 C or Mg. At 25°C and 35°C nesquehonite dissolved to reach equilibrium and subsequently
659 transformed to dypingite. The phase transformation occurred by dissolution-reprecipitation
660 and caused the initial isotopic composition of both the solid and fluid to be overwritten.
661 Extensive isotopic exchange of both Mg and C during the phase transformation indicated that
662 isotopic equilibrium between solid and fluid may have been obtained for dypingite. The
663 $\Delta^{13}C_{dyp-DIC}$ was $4.74 \pm 0.12\%$ (VPDB) and $4.47 \pm 0.17\%$ (VPDB) at 25 and 35°C, respectively.
664 The $\Delta^{26}Mg_{dyp-fluid}$ between solid and the bulk fluid was -0.76% , and $-0.98 \pm 0.08\%$ for the
665 25 and 35°C experiments, respectively. In contrast to the isotope fractionation measured
666 between solids and bulk aqueous Mg, the calculated isotope fractionation between dypingite
667 and the Mg^{2+} aquo species was positive. This indicates that aqueous speciation may impact

668 the fractionation between Mg-carbonates and fluids. There were no significant impacts of
669 temperature on either C or Mg isotope fractionation between fluid and solid. These data will
670 help improve interpretation of carbon and magnesium isotope compositions measured in
671 natural and engineered ultramafic weathering environments, and may help to trace the fate of
672 anthropogenic CO₂ during engineered CO₂ storage efforts by identification of the type of Mg-
673 bearing precipitate.

674

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676

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686

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1051 **Figure Captions**

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1053 **Figure 1.** Temporal evolution of pH and saturation indices of dypingite and nesquehonite at
1054 5°C (a), 25°C (b), and 35°C (c).

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1056 **Figure 2.** Temporal evolution of stable carbon isotope composition of solids and reactive
1057 fluids at 5°C (a), 25°C (b), and 35°C (c). The measurement error is smaller than the symbols
1058 unless otherwise shown. The grey dashed line indicates the approximate timing of onset of the
1059 phase transformation from nesquehonite to dypingite.

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1061 **Figure 3.** Temporal evolution of the carbon isotope fractionation between solid and reactive
1062 fluid at 5°C (a), 25°C (b), and 35°C (c).. The error is smaller than the symbols unless
1063 otherwise shown. The grey dashed line indicates the approximate timing of onset of the phase
1064 transformation from nesquehonite to dypingite.

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1066 **Figure 4.** Temporal evolution of the Mg isotope composition of solids and reactive fluids at
1067 5°C (a), 25°C (b), and 35°C (c). The error is smaller than the symbols unless otherwise
1068 shown. The grey dashed line indicates the approximate timing of onset of the phase
1069 transformation from nesquehonite to dypingite.

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1071 **Figure 5.** Temporal evolution of Mg isotope fractionation between solid and bulk reactive
1072 fluid and between solid and $\text{Mg}^{2+}_{(\text{aq})}$ at 5°C (a), 25°C (b), and 35°C (c). The measurement

1073 error is smaller than the symbols unless otherwise shown. The grey dashed line indicates the
1074 approximate timing of onset of the phase transformation from nesquehonite to dypingite.

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1076 **Figure 6.** Temporal evolution of Mg concentration and aqueous speciation at 5°C (a), 25°C
1077 (b), and 35°C (c). The long term experimental series are plotted for the 25 and 35°C
1078 experiments only.

1079 **Table 1. Carbon isotope composition of solids and fluids over time.**

Experiment	Time	$\delta^{13}\text{C}_{\text{solid}}$ (‰)	$\delta^{13}\text{C}_{\text{DIC}}$ (‰)	$\delta^{13}\text{C}_{\text{CO}_3}$ (‰)	$\delta^{13}\text{C}_{\text{HCO}_3}$ (‰)	$\Delta^{13}\text{C}_{\text{solid-DIC}}$ (‰) ^a	Mineralogical composition ^c	pH	DIC (mol/L; $\times 10^{-2}$)	DIC from nsq dissolution (mol/L; $\times 10^{-2}$)	Mixing model estimated $\delta^{13}\text{C}_{\text{DIC}}$ (‰)	Uncertainty on mixing model $\delta^{13}\text{C}_{\text{DIC}}$ (‰)
5	0 ^b	-18.12	-4.02	-7.08	-3.83	-14.10		8.25	6.00			
	12	-17.67	-7.34	-9.93	-6.68	-10.33 ($\Delta^{13}\text{C}_{\text{nsq-DIC}}$)	Nsq	9.41	7.49	1.49	-6.82	1.27
	24	-17.52	-7.24	-9.86	-6.61	-10.28 ($\Delta^{13}\text{C}_{\text{nsq-DIC}}$)	Nsq	9.39	7.75	1.75	-7.20	1.23
	1085	-17.46	-7.86	-10.46	-7.21	-9.60 ($\Delta^{13}\text{C}_{\text{nsq-DIC}}$)	Nsq	9.39	8.14	2.13	-7.72	1.18
	1420	-18.06	-7.68	-10.03	-6.78	-10.38 ($\Delta^{13}\text{C}_{\text{nsq-DIC}}$)	Nsq	9.59	7.62	1.62	-7.02	1.25
25_short	0 ^b	-18.12	-4.01	-5.89	-3.88	-14.10		8.15	5.97			
	4	-17.68	-7.08	-8.66	-6.65	-10.59 ($\Delta^{13}\text{C}_{\text{nsq-DIC}}$)	Nsq	9.20	7.52	1.55	-6.92	1.27
	12	-18.22	-7.2	-8.78	-6.77	-11.02 ($\Delta^{13}\text{C}_{\text{nsq-DIC}}$)	Nsq	9.20	7.31	1.34	-6.59	1.30
	24	-17.79	-7.28	-8.86	-6.85	-10.51 ($\Delta^{13}\text{C}_{\text{nsq-DIC}}$)	Nsq	9.19	7.50	1.53	-6.89	1.27
	49	-17.05	-7.39	-8.97	-6.96	-9.66 ($\Delta^{13}\text{C}_{\text{nsq-DIC}}$)	Nsq	9.19	7.52	1.55	-6.92	1.27
	120	-18.16	-7.40	-8.97	-6.96	-10.77 ($\Delta^{13}\text{C}_{\text{nsq-DIC}}$)	Nsq	9.20	7.54	1.57	-6.95	1.26
	367	-17.98	-7.84	-9.42	-7.41	-10.13 ($\Delta^{13}\text{C}_{\text{nsq-DIC}}$)	Nsq	9.19	7.59	1.62	-7.02	1.26
25_long	0 ^b	-16.87	-4.26	-6.15	-4.14	-12.61		8.23	5.92			
	122	-15.49	-7.07	-8.63	-6.62	-8.40 ($\Delta^{13}\text{C}_{\text{nsq-DIC}}$)	Nsq	9.23	7.23	1.31	-6.54	1.23
	359	-9.42	-10.53	-12.26	-10.25	1.11	Nsq+Dyp	8.94	7.77	n.a.	n.a.	n.a.
	1157	-7.53	-11.59	-13.37	-11.36	4.06	Dyp+Nsq	8.82	7.80	n.a.	n.a.	n.a.
	1607	-7.16	-11.97	-13.75	-11.74	4.82 ($\Delta^{13}\text{C}_{\text{dyp-DIC}}$)	Dyp	8.81	7.93	n.a.	n.a.	n.a.
	2043	-7.39	-12.04	-13.79	-11.78	4.65 ($\Delta^{13}\text{C}_{\text{dyp-DIC}}$)	Dyp	8.90	7.68	n.a.	n.a.	n.a.
35_short	0 ^b	-18.12	-4.23	-5.51	-4.12	-14.10		8.11	5.96			
	5	-18.36	-7.25	-8.34	-6.95	-11.11 ($\Delta^{13}\text{C}_{\text{nsq-DIC}}$)	Nsq	9.12	7.24	1.27	-6.68	1.32
	7	-18.07	-7.23	-8.31	-6.92	-10.84 ($\Delta^{13}\text{C}_{\text{nsq-DIC}}$)	Nsq	9.14	7.21	1.24	-6.63	1.32
	11	-18.24	-7.25	-8.34	-6.95	-10.99 ($\Delta^{13}\text{C}_{\text{nsq-DIC}}$)	Nsq	9.11	7.27	1.30	-6.72	1.31
	122	-17.16	-8.04	-9.13	-7.74	-9.12	Nsq+Dyp	9.12	7.33	n.a.	n.a.	n.a.
	243	-11.94	-9.96	-11.09	-9.70	-1.98	Nsq+Dyp	9.02	7.46	n.a.	n.a.	n.a.
	432	-9.78	-10.99	-12.19	-10.80	1.21	Dyp+Nsq	8.84	7.61	n.a.	n.a.	n.a.
	1368	-7.48	-12.06	-13.29	-11.90	4.58 ($\Delta^{13}\text{C}_{\text{dyp-DIC}}$)	Dyp	8.72	7.51	n.a.	n.a.	n.a.
35_long	0 ^b	-16.87	-4.12	-5.39	-4.00	-12.61		8.08	5.96			
	26	-16.09	-6.67	-7.74	-6.35	-9.42 ($\Delta^{13}\text{C}_{\text{nsq-DIC}}$)	Nsq	9.17	7.06	1.10	-6.11	1.26
	123	-15.46	-7.5	-8.60	-7.21	-7.96	Nsq (trace dyp)	9.09	7.26	n.a.	n.a.	n.a.
	244	-12.9	-10.63	-11.80	-10.41	-2.28	Nsq+Dyp	8.90	7.66	n.a.	n.a.	n.a.
	311	-10.01	-11.46	-12.66	-11.27	1.46	Dyp+Nsq	8.80	7.37	n.a.	n.a.	n.a.
	600	-7.32	-11.87	-13.11	-11.72	4.55 ($\Delta^{13}\text{C}_{\text{dyp-DIC}}$)	Dyp	8.64	7.77	n.a.	n.a.	n.a.
	932	-7.56	-11.85	-13.10	-11.71	4.28 ($\Delta^{13}\text{C}_{\text{dyp-DIC}}$)	Dyp	8.65	7.65	n.a.	n.a.	n.a.
	1368	-7.48	-12.06	-13.29	-11.90	4.58 ($\Delta^{13}\text{C}_{\text{dyp-DIC}}$)	Dyp	8.72	7.51	n.a.	n.a.	n.a.

1080 ^aValues used to calculate $\Delta^{13}\text{C}_{\text{solid-fluid}}$ between nesquehonite and fluid and dypingite and fluid are indicated by the labels $\Delta^{13}\text{C}_{\text{nsq-fluid}}$ and $\Delta^{13}\text{C}_{\text{dyp-fluid}}$, respectively.

1081 ^bDenotes the $\delta^{13}\text{C}$ values of seed nesquehonite and NaHCO_3 buffer solution used in each experiment.

1082 °Mineralogical composition determined by XRD as reported in Harrison et al. (2019). Nsq = nesquehonite; Dyp = dypingite. When more than one phase present, the dominant phase is reported
1083 first.

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1088 **Table 2. Magnesium isotope composition of fluids and solids over time.**

Experiment	Time (h)	Fluid				Solid				$\Delta^{26}\text{Mg}_{\text{solid-fluid}}^{\text{a}}$	Calculated $\delta^{26}\text{Mg}^{2+}$ (aq) ^b	$\Delta^{26}\text{Mg}_{\text{solid-Mg}^{2+}}$	Mineralogical composition ^c	Mg (mol/L; $\times 10^{-2}$)
		$\delta^{25}\text{Mg}$	2σ	$\delta^{26}\text{Mg}$	2σ	$\delta^{25}\text{Mg}$	2σ	$\delta^{26}\text{Mg}$	2σ					
5	0					-0.71	0.05	-1.38	0.08				Nsq	
	12	-0.72	0.03	-1.36	0.01	-0.69	0.02	-1.33	0.02	0.03	-4.00	2.67	Nsq	1.290
	24	-0.64	0.04	-1.20	0.02	-0.72	0.01	-1.39	0.03	-0.19	-3.85	2.45	Nsq	1.269
	367	-0.64	0.01	-1.21	0.06	-0.91	0.03	-1.36	0.00	$-0.15 (\Delta^{26}\text{Mg}_{\text{nsq-fluid}})$	-4.21	2.45	Nsq	1.505
	1085	-0.65	0.03	-1.24	0.02	-0.69	0.04	-1.34	0.03	$-0.10 (\Delta^{26}\text{Mg}_{\text{nsq-fluid}})$	-3.92	2.57	Nsq	1.498
	1420	-0.66	0.05	-1.25	0.02	-0.71	0.02	-1.38	0.06	$-0.13 (\Delta^{26}\text{Mg}_{\text{nsq-fluid}})$	-4.25	2.87	Nsq	1.502
25_short	0					-0.71	0.05	-1.38	0.08				Nsq	
	6	-0.64	0.02	-1.22	0.04	-0.71	0.01	-1.33	0.01	-0.11	-3.90	2.57	Nsq	1.094
	24	-0.67	0.06	-1.29	0.08	-0.73	0.05	-1.41	0.07	$-0.12 (\Delta^{26}\text{Mg}_{\text{nsq-fluid}})$	-3.93	2.52	Nsq	1.197
	49	-0.59	0.01	-1.13	0.03	-0.68	0.04	-1.32	0.08	$-0.19 (\Delta^{26}\text{Mg}_{\text{nsq-fluid}})$	-3.79	2.47	Nsq	1.183
	120	-0.66	0.02	-1.23	0.05	-0.74	0.09	-1.44	0.08	$-0.21 (\Delta^{26}\text{Mg}_{\text{nsq-fluid}})$	-3.89	2.44	Nsq	1.192
	367	-0.62	0.03	-1.19	0.04	-0.73	0.05	-1.42	0.09	$-0.23 (\Delta^{26}\text{Mg}_{\text{nsq-fluid}})$	-3.87	2.46	Nsq	1.216
	1086	-0.57	0.05	-1.09	0.08	-0.78	0.05	-1.50	0.05	-0.41	-3.74	2.24	Nsq+Dyp	1.113
25_long	0					-0.54	0.02	-1.02	0.08				Nsq	
	122	-0.50	0.04	-0.95	0.00	-0.55	0.02	-1.06	0.01	$-0.11 (\Delta^{26}\text{Mg}_{\text{nsq-fluid}})$	-3.63	2.57	Nsq	1.098
	359	-0.13	0.03	-0.24	0.05	-0.61	0.00	-1.22	0.01	-0.98	-2.47	1.25	Nsq+Dyp	1.119
	1157	-0.15	0.04	-0.29	0.05	-0.61	0.04	-1.21	0.01	-0.92	-2.31	1.10	Dyp+Nsq	1.065
	1607	-0.16	0.01	-0.34	0.05	-0.58	0.03	-1.10	0.05	$-0.76 (\Delta^{26}\text{Mg}_{\text{dyp-fluid}})$	-2.36	1.26	Dyp	1.051
35_short	0					-0.71	0.05	-1.38	0.08				Nsq	
	5	-0.64	0.02	-1.27	0.06	-0.69	0.05	-1.33	0.07	$-0.06 (\Delta^{26}\text{Mg}_{\text{nsq-fluid}})$	-3.93	2.60	Nsq	1.063
	7	-0.65	0.02	-1.27	0.07	-0.71	0.04	-1.35	0.01	$-0.08 (\Delta^{26}\text{Mg}_{\text{nsq-fluid}})$	-3.95	2.60	Nsq	1.047
	11	-0.64	0.02	-1.22	0.06	-0.73	0.03	-1.42	0.08	$-0.20 (\Delta^{26}\text{Mg}_{\text{nsq-fluid}})$	-3.87	2.45	Nsq	1.050
	122	-0.47	0.04	-0.92	0.08	-0.73	0.04	-1.38	0.05	-0.46	-3.58	2.20	Nsq+Dyp	1.054
	243	-0.33	0.02	-0.67	0.03	-0.78	0.04	-1.51	0.05	-0.84	-3.16	1.65	Nsq+Dyp	1.048g
432	-0.20	0.02	-0.38	0.06	-0.75	0.01	-1.43	0.07	-1.05	-2.60	1.18	Dyp+Nsq	0.900	
35_long	0					-0.54	0.02	-1.02	0.08				Nsq	
	26	-0.53	0.01	-0.99	0.08	-0.50	0.02	-0.94	0.01	$0.05 (\Delta^{26}\text{Mg}_{\text{nsq-fluid}})$	-3.71	2.76	Nsq	1.044
	123	-0.36	0.03	-0.70	0.05	-0.58	0.05	-1.10	0.06	-0.40	-3.31	2.21	Nsq (trace Dyp)	1.057
	244	-0.20	0.05	-0.43	0.05	-0.67	0.01	-1.26	0.05	-0.83	-2.73	1.47	Nsq+Dyp	1.138
	311	-0.11	0.04	-0.18	0.08	-0.61	0.04	-1.18	0.08	-1.00	-2.28	1.11	Dyp+Nsq	1.048
	600	-0.10	0.02	-0.18	0.03	-0.62	0.04	-1.21	0.01	$-1.03 (\Delta^{26}\text{Mg}_{\text{dyp-fluid}})$	-2.06	0.84	Dyp	0.930
	932	-0.16	0.02	-0.29	0.02	-0.64	0.02	-1.21	0.01	$-0.92 (\Delta^{26}\text{Mg}_{\text{dyp-fluid}})$	-2.20	0.99	Dyp	0.885
Standards														
	DSM3	0.00	0.03	0.00	0.04									
	CAM-1	-1.35	0.05	-2.64	0.06									
	OUMg	-1.45	0.06	-2.80	0.08									
	IAPSO	-0.42	0.05	-0.83	0.07									
JDo-1	-1.23	0.04	-2.41	0.08										

1089 ^aValues used to calculate $\Delta^{26}\text{Mg}_{\text{solid-fluid}}$ between nesquehonite and fluid and dypingite and fluid are indicated by the labels $\Delta^{26}\text{Mg}_{\text{nsq-fluid}}$ and $\Delta^{26}\text{Mg}_{\text{dyp-fluid}}$, respectively.

1090 ^bCalculated using Schott et al. (2016) reduced partition functions.

1091 ^cMineralogical composition determined by XRD as reported in Harrison et al. (2019). Nsq = nesquehonite; Dyp = dypingite. When more than one phase present, the dominant phase is reported

1092 first.

1093 **Electronic Annex 1.**

1094 Includes a figure showing dissolved inorganic carbon concentration and HCO_3^- and CO_3^{2-}
1095 concentration over time.

1096 **Electronic Annex 2.**

1097 Includes Table A1. Speciation of aqueous Mg and calculated isotopic composition of $\text{Mg}^{2+}_{(\text{aq})}$,

1098 $\Delta_{\text{calc}}^{26}\text{Mg}_{\text{solid}-\text{Mg}^{2+}}$, and $\Delta_{\text{meas}}^{26}\text{Mg}_{\text{solid}-\text{bulk fluid}}$ and Table A2. Fluid composition of all

1099 experimental timepoints.











