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1 Mechanisms controlling the Mg isotope composition of  
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4  
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17

18 **Abstract**

19 The alkaline playas near Atlin, British Columbia, Canada are likely one of the few surface  
20 environments on Earth where contemporaneous formation of hydromagnesite and magnesite  
21 occurs at temperatures that do not exceed 15 °C. This environment offers a unique  
22 opportunity to examine the impact of different formation mechanisms on Mg isotope  
23 compositions of Mg-carbonate minerals at low temperature. In this study, we report the Mg  
24 isotope composition of ultramafic bedrock, Mg-carbonate sediments, and both surface and  
25 ground waters in this geological setting. The composition of hydromagnesite suggests a  
26 Rayleigh-type distillation effect on the fluid Mg isotope ratios in unsaturated sediment above  
27 the water table. Through this mechanism of formation, hydromagnesite is progressively  
28 depleted in <sup>24</sup>Mg obtaining δ<sup>26</sup>Mg values as high as +1.14‰ near the sediment surface. In  
29 contrast, magnesite formation is characterized by enrichment of the solid phase in <sup>24</sup>Mg. The  
30 apparent Mg isotope fractionation factor during magnesite formation at ~ 10°C ranges  
31 between ~ 0.7±0.1‰ and 1.8±0.1‰. The distinct Mg isotope composition of hydromagnesite  
32 in comparison to magnesite supports magnesite formation occurring by precipitation from the  
33 fluid, or dissolution-reprecipitation, rather than solid-phase transformation from a hydrous  
34 Mg-carbonate precursor. Overall, the results provide insights on low temperature Mg-  
35 carbonate mineral formation that has implications for long-term storage of CO<sub>2</sub>.

36

## 37 **1. Introduction**

38           Engineered carbon storage in the form of carbonate minerals has been proposed as a  
39 climate change mitigation strategy (Lackner et al., 1995; Wilson et al., 2014; Harrison et al.,  
40 2013; Kelemen et al., 2011; Matter and Kelemen 2009; Matter et al., 2016; Power et al.,  
41 2013). In this respect, the formation of Mg-bearing carbonates is of great interest because Mg  
42 is an abundant element in Earth's crust and a major constituent of seawater. Indeed,  
43 ultramafic settings have a high potential for CO<sub>2</sub> uptake via the carbonation of Mg-silicate  
44 minerals. Despite the high concentration of Mg in aquatic environments and in silicate rocks,  
45 the formation of the thermodynamically most stable Mg-carbonate mineral, magnesite  
46 (MgCO<sub>3</sub>), is unlikely to occur at temperatures below 60 °C within timescales that would  
47 allow for its use as a CO<sub>2</sub> storage medium (Hänchen et al. 2008; Saldi et al., 2009; 2012  
48 Power et al., 2017). This limitation is due to the very slow exchange of water molecules  
49 between the hydration sphere of the aqueous Mg ion and bulk water, which kinetically  
50 inhibits magnesite formation (Bénézech et al., 2011; 2013). In low temperature environments  
51 the formation of hydrous Mg-carbonates such as lansfordite (MgCO<sub>3</sub>·5H<sub>2</sub>O), nesquehonite  
52 (MgCO<sub>3</sub>·3H<sub>2</sub>O) and hydromagnesite (Mg<sub>5</sub>(CO<sub>3</sub>)<sub>4</sub>(OH)<sub>2</sub>·4H<sub>2</sub>O) may occur and is often driven  
53 by evaporation (Hopkinson et al., 2008; 2012; Beinlich and Austrheim 2012; Harrison et al.,  
54 2013; 2015; 2016; 2017; Power et al., 2014; 2017; Wilson et al., 2009; 2014; Assima et al.,  
55 2014; Oskierski et al. 2016; McCutcheon et al., 2016; 2017; Turvey et al., 2018).

56           Owing to the measurable fractionation of Mg isotopes among natural waters, rocks,  
57 and plants (e.g., Young and Galy, 2004), this isotopic tool has been proven to be a powerful  
58 tracer of low-temperature biogeochemical processes such as plant growth, weathering and  
59 soil formation (e.g., Black et al., 2008; Pogge von Strandmann et al., 2008; Bolou-Bi et al.,  
60 2010; Illina et al., 2013; Opfergelt et al., 2014; Oelkers et al., 2015; Mavromatis et al., 2016;  
61 Kimmig et al., 2018). The large isotope fractionation between solid and fluid has also been

62 used to trace Mg isotope composition of oceanic water in the geological past (Pogge von  
63 Strandmann et al., 2014) as well as to constrain mineral formation temperature (Pearce et al.,  
64 2012). The Mg isotope composition of Mg-bearing carbonate minerals has been shown to be  
65 distinctly enriched in the lighter  $^{24}\text{Mg}$  isotope compared to silicate phases (e.g. Teng et al.,  
66 2017), which has helped to decipher the Mg cycle (Tipper et al., 2006). Recently, the  
67 potential application of Mg isotopes to trace engineered  $\text{CO}_2$  storage has been explored  
68 (Oelkers et al., 2019; Harrison et al., 2021).

69         The interpretation of the fractionation of Mg upon incorporation into carbonate  
70 minerals, however, is not always straightforward and may depend on mineral growth rate and  
71 formation pathway (Mavromatis et al., 2017b). For example, the incorporation of Mg in  
72 calcite is strongly affected by mineral growth rate effects (Mavromatis et al., 2013), whereas  
73 this growth-induced signature is rapidly erased in the case of Mg-calcite formation via an  
74 amorphous precursor (Mavromatis et al., 2017b). Although growth kinetic effects have been  
75 shown to affect the isotopic composition of Mg-bearing carbonates, which has direct  
76 implications for the interpretation of geological archives, growth rate effects have yet to be  
77 observed during the formation of hydrous Mg-carbonates. Indeed, the Mg isotope  
78 composition of nesquehonite and dypingite precipitated in laboratory experiments has been  
79 shown to be independent of growth kinetic effects and to be better described as a continuous  
80 exchange closed system process occurring at equilibrium conditions (Mavromatis et al.,  
81 2012). The same has been argued for the formation of hydromagnesite stromatolites in Lake  
82 Salda in Turkey (Shirokova et al., 2013). However, the experimental studies comprise  
83 examples of hydrous Mg-carbonate formation in conditions with low solid to fluid ratios. In  
84 contrast, geological settings such as the hydromagnesite-magnesite playas near Atlin, British  
85 Columbia, Canada are dominated by the solid phase. Differences in solid to fluid ratios  
86 impact the extent to which exchange between fluid and solid affect the isotopic composition

87 of solids, therefore studies in the field where solid:fluid ratios are high, provide additional  
88 insights into Mg isotope behavior between fluids and solids.

89 As described by Power et al. (2019) based on field observations and mineralogical  
90 data, the precipitation of hydromagnesite in Atlin is interpreted to be limited by the transport  
91 of Mg-rich waters through evaporation above the water table. In contrast, waters throughout  
92 the sediment profiles (saturated and unsaturated zones) are supersaturated with respect to  
93 magnesite and its precipitation is interpreted to be reaction-controlled (i.e., controlled by  
94 precipitation kinetics; Power et al., 2019). Therefore, this site offers the opportunity to  
95 contrast the impact of different formation processes on Mg isotope compositions of low  
96 temperature Mg-carbonate minerals. In this study, we examine the Mg isotope composition  
97 of the Mg-carbonate sediments in three depth profiles recovered from this unique and well-  
98 characterized environment. These profiles exhibit differences in abundance of magnesite and  
99 water table depth, resulting in different vertical Mg isotope composition of the solid phase.  
100 Our findings provide insight into Mg isotope fractionation behavior in Mg-carbonate  
101 minerals and the use of Mg-isotopes to trace the fate of carbon in CO<sub>2</sub> storage scenarios.

102

## 103 **2 Geologic setting and playa genesis**

104 Hydromagnesite–magnesite playas lie adjacent to the town of Atlin, British Columbia,  
105 Canada (Fig. 1a; 59°34' N, 133°42' W). A playa depositional model (Power et al., 2014) and  
106 investigation of magnesium carbonate formation (Power et al., 2019) are summarized here as  
107 background information for this study. The reader is referred to these previous studies for the  
108 data from which the playa genesis model was derived. The ultramafic bedrock in the Atlin  
109 region consists of a tectonically emplaced upper mantle section of oceanic lithosphere that is  
110 mainly composed of variably serpentinized harzburgite and minor dunite together with  
111 localized zones of hydrothermal quartz-magnesite alteration (listvenite) (Ash and Arksey,

112 1990a; Hansen et al., 2005). The weathering of this bedrock produces alkaline  $\text{Mg-HCO}_3^-$   
113 groundwater that discharges topographic lows where the playas lie (Power et al., 2014; Power  
114 et al., 2009). There are two groups of playas (total area  $\approx 0.2 \text{ km}^2$ ); a northern group and a  
115 southern group with the latter having water bodies and grassland areas in addition to Mg-  
116 carbonate mounds (Fig. 1).

117 The playas consist of three sedimentary units: Mg-carbonate sediments at the surface  
118 underlain by Ca-Mg-carbonate sediments, and then glaciolacustrine mud (Power et al., 2014).  
119 Glaciolacustrine mud was first deposited in glacial lakes and mainly contains silicate  
120 minerals (e.g., quartz, feldspars, micas). Over time, carbonate deposition overtook  
121 siliciclastic deposition as surface runoff declined and alkaline  $\text{Mg-HCO}_3^-$  groundwater  
122 became the dominant water source (Fig. 2a). Modern groundwater near the playas is  
123 supersaturated with respect to anhydrous Ca- and Mg-carbonate minerals including aragonite  
124 ( $\text{CaCO}_3$ ) and magnesite ( $\text{MgCO}_3$ ). Subaqueous carbonate deposition fills ponds with mainly  
125 aragonite, and through diagenesis a Ca-Mg-carbonate unit comprised of aragonite, ankerite  
126 ( $\text{Ca(Fe,Mg,Mn)(CO}_3)_2$ ), and disordered dolomite ( $\text{CaMg(CO}_3)_2$ ) formed overlying the  
127 glaciolacustrine deposit. A transition from subaqueous to subaerial sediment deposition is  
128 indicated by buried vegetation near the top of this Ca-Mg-carbonate unit (Fig. 2b).  
129 Radiocarbon dating of this vegetation indicates that the overlying Mg-carbonate unit began  
130 forming at most 8000 cal yr BP (Power et al., 2014). Hydrated Mg-carbonate precipitation is  
131 driven by the evaporation of  $\text{Mg-HCO}_3^-$  waters that are drawn to the surface by capillary  
132 action. This process manifests itself as mounds of sediments (10s cm high) that are  
133 dominated by hydromagnesite (Fig. 2c-2d). The average deposition rate for the Mg-carbonate  
134 unit is  $\sim 0.4 \text{ mm/yr}$  and its overlying weight results in subsidence, thus the boundary between  
135 this unit and the underlying Ca-Mg-carbonate unit now lies well below the water table.

136 The depositional model constrains magnesite formation to the Holocene and Earth's  
137 surface temperature. Sediment temperature in the present-day playas ranges from 3 °C at  
138 depth (10s cm below water table) to 14 °C at the surface in the summer. For comparison,  
139 clumped isotope geothermometry of magnesite collected from the surface of profile 4 gave a  
140 formation temperature in the range of 1–11 °C (Falk and Kelemen, 2015).

141

### 142 **3. Sampling and analytical techniques**

#### 143 **3.1 Sample collection**

144 Hand specimens of harzburgite, partially serpentinized harzburgite, serpentinite, and  
145 listvenite (quartz-carbonate altered serpentinite) were collected from the Atlin area (Fig. 1;  
146 Table 1). Sediments composed of hydromagnesite and magnesite were collected from three  
147 depth profiles in the southeastern (profiles 4 and 6) and northern playas (profile N. playa)  
148 (Figs. 1 and 3; see Power et al., 2014 for details on sampling). Depth sampling was carried  
149 out using an auger with sediments being collected in plastic bags and later dried at room  
150 temperature. Waters in the Atlin area included pond water atop Monarch Mountain, spring  
151 water collected at its base (~3.5 km to the southeast of the playas), groundwaters from private  
152 wells near Monarch Mountain and near the southern playas, surface waters from the northern  
153 and southeastern playas, and from the water table within the hydromagnesite-magnesite  
154 sediments (Fig. 1; Table 1). The wells were flushed a minimum of three times to obtain  
155 representative groundwater. All water samples were filtered (0.22 µm) into TraceClean™ 40  
156 mL amber borosilicate vials with a fluoropolymer resin/silicone septum and no headspace.  
157 Samples were stored at 4 °C before analysis. Presence of carbonate solids was not observed  
158 in these samples, which is consistent with the inability of magnesite to form at low and  
159 ambient temperatures. Selected samples from profile 4 were imaged using scanning electron  
160 microscopy as described by Power et al. (2019).



161

### 162 **3.2 Isotope analyses**

163 The magnesium isotope composition of solid and fluid samples was determined  
164 following the method described in Mavromatis et al. (2014b). Hydromagnesite was removed  
165 from one sample, 11AT1-J, to determine the composition of magnesite alone.

166 Hydromagnesite was removed by reacting the bulk sediment with diluted acetic acid (10 vol.  
167 %) for ~30 min. After this treatment the mineralogic composition of the solid was  
168 characterized using X-ray diffraction analysis to assess whether hydromagnesite was  
169 removed. All solids were then digested in concentrated HNO<sub>3</sub> and/or HF. Digested solids and  
170 acidified liquid samples were evaporated to dryness and re-dissolved in 1N HNO<sub>3</sub>. About 15  
171 µg of Mg was used for column chemistry in 10 mL Bio-Rad Poly-prep columns containing  
172 AG-50W-X12 cation exchange resin for Mg separation from matrix elements. The yields  
173 after chromatographic separation were better than 99% of the total Mg loaded in the columns.  
174 Magnesium isotopic compositions were measured using a Thermo-Finnigan “Neptune” Multi  
175 Collector Inductively Coupled Plasma Mass Spectrometer (MC-ICP-MS) at Géosciences  
176 Environnement Toulouse (GET) laboratory (France). All samples were prepared in 0.35 N  
177 HNO<sub>3</sub> and introduced into the Ar plasma with a large Stable Introduction System spray  
178 chamber (double Scott Cyclonic spray chamber). Instrumental mass fractionation effects  
179 were corrected using sample-standard bracketing, and all data are presented as δ<sup>x</sup>Mg with  
180 respect to DSM3 reference material ( $\delta^x\text{Mg} = ((^x\text{Mg}/^{24}\text{Mg})_{\text{sample}} / (^x\text{Mg}/^{24}\text{Mg})_{\text{DSM3}} - 1) \times 1000$ )  
181 where x refers to the Mg mass of interest. All sample analyses were run in triplicate with the  
182 mean value presented in Table 1. The reproducibility of the δ<sup>26</sup>Mg analyses was determined  
183 using replicate analyses of the DSM3, CAM-1 and OUMg monoelemental Mg reference  
184 standards and was typically better than 0.08‰. The reproducibility of the measurements is in  
185 agreement with previously published values from the same laboratory (Pearce et al., 2012;

186 Mavromatis et al., 2013; 2014a; Beinlich et al., 2014; 2018;), as well as from other  
187 laboratories (Bolou-Bi et al., 2009; Wombacher et al., 2009; Geske et al., 2015; Riechelmann  
188 et al., 2016; 2018; Mavromatis et al., 2017a; 2017c; Shalev et al., 2018). The reproducibility  
189 of chromatographic separation was assessed by repeated analyses of selected samples and the  
190 JDo-1 (dolomite) and IAPSO seawater as shown in Table 1, and was better than 0.08 ‰.

191

## 192 **4. Results**

### 193 *4.1 Isotopic composition of country rock, waters, and carbonate sediments*

194 The Mg isotope composition of the five rock samples (AT03-42, AT04-3, 04AT4,  
195 01AT5-2, AT03-20-PC2) representing various lithologies in the region exhibit a narrow  
196 range in  $\delta^{26}\text{Mg}$  with an average of  $-0.36\pm 0.07\text{‰}$  (Fig. 4 and Table 1). These samples consist  
197 of ultramafic rocks including harzburgite, serpentinite, and listvenite, and have Mg isotope  
198 compositions similar to that of the bulk Earth (i.e.,  $\delta^{26}\text{Mg} = -0.25\pm 0.07\text{‰}$ ; Teng, 2017). In  
199 contrast, the Mg isotope composition of the three water samples (16AT-water1; 16AT-  
200 water3; 16AT-water6) that were in contact with these country rocks are enriched in  $^{24}\text{Mg}$   
201 compared to the composition of the rocks and exhibit  $\delta^{26}\text{Mg}$  values that range from -1.20 to -  
202 0.97‰ (Table 1).

203 Magnesite and hydromagnesite are the two major Mg-carbonate phases in the playa  
204 sediments and their abundance varies significantly between the two depth profiles of the  
205 south playa (Fig. 3). The upper 280 cm of sediments in profile 6 contain less than 10 wt.%  
206 magnesite (Fig. 3; Table1), whereas in profile 4 the abundance of this mineral phases is as  
207 high as 96 wt.%. The samples where magnesite is the predominant phase are significantly  
208 enriched in  $^{24}\text{Mg}$  compared to all the other materials analyzed in this study exhibiting  $\delta^{26}\text{Mg}$   
209 compositions in a range between -2.11 and -2.95‰ (Fig. 4). For instance, sample 11AT1-J  
210 (96 wt.% mgs) has an isotopic composition of -2.63‰ and after hydromagnesite removal by

211 acid washing, its isotopic composition decreases to -2.95‰ (Table 1). Note here that mass-  
212 balance to determine the Mg isotope composition of the initial hydromagnesite in sample  
213 11AT1-J yields a  $\delta^{26}\text{Mg}$  composition  $>5.0\text{‰}$  which is unlikely to be realistic. There are  
214 several potential explanations for this such as mineralogical and isotopic inhomogeneity in  
215 the solids or presence of X-ray amorphous material in the initial sample that is unaccounted  
216 for by the mass balance calculation. In most of the carbonate sediments the anhydrous Mg-  
217 carbonate mineral is magnesite; however, in samples 11AT1-L and 12AT1-8E the abundance  
218 of magnesite is as low as 15-17 wt.% and other anhydrous Mg-bearing carbonates such as  
219 disordered dolomite  $[\text{CaMg}(\text{CO}_3)_2]$  and ankerite have been identified. Their relative  
220 abundances are listed in Table 1. Hydromagnesite-dominated sediments have higher  $\delta^{26}\text{Mg}$   
221 values compared to those dominated by magnesite and mixed anhydrous carbonates. The Mg  
222 isotope compositions of hydromagnesite-dominated samples span a wide range with  $\delta^{26}\text{Mg}$   
223 values from -0.92 to 1.14‰. Interestingly, the Mg isotope composition of hydromagnesite  
224 and, to a lesser extent magnesite, in all the sediment profiles, exhibits significant variation of  
225  $\delta^{26}\text{Mg}$  values with depth with the most  $^{24}\text{Mg}$  depleted samples near the surface (e.g., Fig. 5).  
226 Finally, the five water samples collected from the playa sediment water tables (n=2), the  
227 wetlands adjacent to the playas (n=2), and a well next the southern playa (n=1) exhibit a wide  
228 range of  $\delta^{26}\text{Mg}$  values between -0.36 and 0.60‰ (Table 1).

229

## 230 **5. Discussion**

### 231 **5.1 Formation of hydromagnesite**

232 Previous results indicate that the formation of hydromagnesite in the Atlin playas  
233 proceeds through transformation of more hydrated phases as well as by direct precipitation in  
234 the unsaturated zone of the Mg-carbonate unit. Details on the genesis model of  
235 hydromagnesite/magnesite playas in Atlin can be found in Power et al. (2009; 2014). Waters

236 at the water table are saturated with respect to hydromagnesite and lansfordite, the latter  
237 cementing sediments to form a hardpan. Evaporation draws water from the water table  
238 upwards, and evapo-concentration causes precipitation of mainly hydromagnesite throughout  
239 the unsaturated zone. This upward water movement is evidenced by stable isotope data that  
240 shows enrichment in  $^{13}\text{C}$  and  $^{18}\text{O}$  of the bulk sediments (mgs + hmg) towards the surface (see  
241 Fig.10 in Power et al., 2014). These enrichments are consistent with evaporation of water and  
242 degassing of  $\text{CO}_2$ -rich fluids. Selective analysis of only the hydromagnesite also showed  
243 enrichment in  $^{13}\text{C}$  and  $^{18}\text{O}$  towards the surface (see Fig. 8 in Power et al., 2019). At the scale  
244 of the playas, hydromagnesite formation is limited by these physical processes (capillary rise  
245 and evaporation) and is thus effectively transport-controlled (Power et al., 2019).

246 The formation of hydromagnesite due to the vertical transport of water from the water  
247 table upwards results in depletion of  $^{24}\text{Mg}$  of the sediments which obtain  $\delta^{26}\text{Mg}$  values as  
248 high as 1.14‰ (profile 6; near-surface sample 05AT1-8A; Fig. 5; Table 1). Note here that  
249 this sample contains ~7 wt. % magnesite, which suggests that the  $\delta^{26}\text{Mg}$  value of pure  
250 hydromagnesite may be even higher. This isotopic composition of the hydromagnesite-  
251 dominated sediments is the highest  $\delta^{26}\text{Mg}$  value recorded in the literature for carbonate  
252 minerals, to the best of our knowledge. In contrast to the highly depleted  $^{24}\text{Mg}$  composition  
253 of the sediments in Atlin, experimental studies have demonstrated that both hydrous and  
254 anhydrous Mg-bearing carbonate minerals tend to preferentially take up the lighter,  $^{24}\text{Mg}$   
255 isotope (e.g. Saulnier et al., 2012; Mavromatis et al., 2017a). For example, the study of  
256 hydromagnesite stromatolites in Lake Salda (SW Turkey) by Shirokova et al. (2011; 2013)  
257 revealed that Mg isotope fractionation between solids and bulk fluid is equal to  $-1.0 \pm 0.2\%$ .  
258 This fractionation factor is in excellent agreement with that reported by Oelkers et al. (2018)  
259 who conducted dissolution/precipitation experiments of hydromagnesite under laboratory  
260 conditions. If the same fractionation factor were applicable to the Atlin hydromagnesite, the

261  $^{24}\text{Mg}$ -depleted hydromagnesite-dominated sediment sample near the surface of profile 6  
262 (sample 05AT1-8A; Fig. 5) must be the result of mineral precipitation from a fluid with a  
263  $\delta^{26}\text{Mg}$  of +2.2‰. Such Mg isotope fluid compositions would be unusual, considering that the  
264 majority of water bodies at the Earth's surface exhibit  $\delta^{26}\text{Mg}$  values below 0.5‰ (Teng et al.,  
265 2017) and the most enriched solids measured record  $\delta^{26}\text{Mg}$  values of  $\sim 1.8\%$  (Liu et al.,  
266 2014). Note here that the bedrock samples in this area (i.e. harzburgite, serpentinite,  
267 listvenite) generate an average  $\delta^{26}\text{Mg}$  value of  $-0.36\pm 0.07\%$  or  $\sim 1.5\%$  lower than that of  
268 hydromagnesite. Moreover, all of the water samples analyzed from Atlin have  $\delta^{26}\text{Mg}$  values  
269 of  $< 0.6\%$  (see Table 1), although fluids from the unsaturated zone could not be sampled due  
270 to low water contents of the sediments. Together, these data suggest that the high  $\delta^{26}\text{Mg}$   
271 values of hydromagnesite in the near-surface sediments are unlikely to reflect equilibrium  
272 fractionation during mineral formation from an infinite aqueous Mg reservoir, as it requires  
273 an unfeasibly high  $\delta^{26}\text{Mg}$  composition of the fluid.

274       Likely these elevated  $\delta^{26}\text{Mg}$  values are the result of the precipitation of Mg-bearing  
275 carbonate minerals during the upward migration of Mg-rich water from the water table,  
276 generating a Rayleigh-type distillation effect. This is consistent with the previously  
277 postulated formation pathway for hydromagnesite in the Atlin playas, which stated that  
278 hydromagnesite precipitation is effectively transport-limited and depends on the  
279 replenishment of Mg-rich waters from depth (Power et al., 2014; 2019). The formation of  
280 hydromagnesite is driven by  $\text{CO}_2$  degassing and evaporation, and may also occur by  
281 transformation of more hydrated phases such as lansfordite. This formation model for  
282 hydromagnesite in the playas, derived from field observations, mineralogical data, and other  
283 isotopic results (Power et al., 2014; 2019), suggests that the unusually high  $\delta^{26}\text{Mg}$  values of  
284 the Mg-carbonate sediments likely reflects a combination of phase transformation and  
285 transport effects in a water-limited system. The upward migration of the Mg-bearing fluid

286 due to capillary rise could result in vertical variations in its isotopic composition related to  
287 mass transfer of Mg to the solid phase. Moreover, it has been observed in experiments that  
288 both Mg and C atoms in hydrated carbonate minerals undergo exchange with the fluid during  
289 mineral phase transformations. This exchange results in the isotopic composition being reset  
290 within a time frame of days to weeks (Harrison et al., 2021). This would make the Mg  
291 isotope compositions of the carbonate sediments sensitive to the contemporary fluid  
292 composition, even if they precipitated from an older fluid of different Mg isotope  
293 composition. The hydromagnesite-magnesite playas grow by precipitation throughout the  
294 sediment profile; therefore, the youngest sediments are not necessarily at the surface. Thus,  
295 the Mg-isotopic composition of the sediments that transformed post-deposition may reflect  
296 the composition of the fluid at depth different than their original precipitation. For instance, if  
297 lansfordite originally precipitated at the water table but later transformed to hydromagnesite  
298 above the water table, its composition would reflect exchange with the fluid above the water  
299 table. Unlike the experiments conducted by Harrison et al. (2021) however, where excess  
300 fluid was available for exchange, the Atlin sediments are dominated by solids, with a  
301 relatively small volume of fluid. Thus, the Mg budget and isotope composition at Atlin is  
302 effectively mineral buffered, limiting the extent to which isotopic exchange would “reset”  
303 isotopic compositions compared to fluid-rich experiments. The limited exchange is also  
304 supported by the co-variation of  $\delta^{26}\text{Mg}$  and  $\delta^{13}\text{C}$  values of the sediments ( $R^2= 0.72$ ;  $p<0.05$ ;  
305 Fig. 6). Indeed, the increasing  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values of surface sediments are indicative of  
306 degassing and evaporation suggesting reducing fluid contents in the pore space closer to the  
307 surface. At the same time, an increasing enrichment of  $^{26}\text{Mg}$  of the sediments is consistent  
308 with limited exchange of Mg between solid and fluid. Interestingly, higher  $\delta^{26}\text{Mg}$  and  $\delta^{13}\text{C}$   
309 values are observed in the near surface sediments of profile 6 compared to profile 4 (Figs. 5  
310 and 6), which we interpret to reflect the greater distance from the water table to the surface,

311 i.e., greater thickness of the unsaturated zone, in profile 6 compared to profile 4. This  
312 observation further supports the role of upward fluid migration on Mg, C, and O isotope  
313 composition of the forming solids.

314 If the precipitation of hydromagnesite-dominated sediments is envisioned as occurring  
315 along a 1-dimensional vertical flow path that is progressively depleted in  $^{24}\text{Mg}$  as Mg-  
316 carbonate minerals precipitate, then the isotopic composition of the Mg-carbonate minerals  
317 along the flow path may be explained as a distillation process. A 1-dimensional vertical flow  
318 path is assumed due to primarily vertical fluid transport in the unsaturated zone. As the  
319 precipitation of hydromagnesite is expected to be transport-controlled (Power et al., 2019), a  
320 Rayleigh-type distillation process may in part explain the observed trend in Mg isotope  
321 composition. Here we focus our discussion primarily on the South playa profiles, 4 and 6,  
322 due to a higher sample density, but the North playa samples exhibit similar trends.

323 The direct application of a Rayleigh-type equation in the hydromagnesite-dominated  
324 sediments of profiles 4 and 6 (Fig. 3) for the estimation of the amount of Mg removed from  
325 the fluid due to mineral formation is not straightforward. The Rayleigh equation is based on  
326 the assumption that the isotope fractionation factor is constant along the whole migration  
327 pathway of the fluid from the water table up to the surface, which in reality may not be true,  
328 as the abundances of magnesite and hydromagnesite vary above the water table between the  
329 two profiles (see Fig. 3). Note here that the same limitations exist for the N.playa profile,  
330 where the near surface sediment samples (n=2) are composed of ~80 wt. % hydromagnesite  
331 (Table 1). In addition, the precipitation of Mg-carbonate in the playa sediments only affects  
332 the isotope ratio but does not significantly lower the total concentration of dissolved Mg  
333 which is driven by evaporation, thereby allowing Mg-carbonates to maintain  
334 (super)saturation. It is also worth noting that the Rayleigh calculation refers to isotopic  
335 composition of the bulk fluid, although changes in chemical speciation due to precipitation

336 most likely affect the isotopic composition of the  $\text{Mg}^{2+}_{(\text{aq})}$  ion (Schott et al., 2016; Gao et al.,  
337 2018). An additional challenge in applying a Rayleigh model is that the initial Mg isotope  
338 composition of the forming fluid cannot be precisely constrained. Due to a lack of sufficient  
339 fluid volume to analyze in the near-surface sediments, the corresponding increase in  $\delta^{26}\text{Mg}$   
340 values in the fluid could not be measured. Notably, the  $\delta^{26}\text{Mg}$  values of the fluid at the water  
341 table in the profiles are the highest of all measured fluids, consistent with enrichment in  $^{26}\text{Mg}$   
342 due to carbonate precipitation. Furthermore, all water samples collected in Atlin playas are  
343 enriched in  $^{26}\text{Mg}$  compared to weathering water/runoff samples (Table 1).

344         Although the exact extent of Mg removal from the pore fluid cannot be estimated, the  
345 similarities in the mineralogical and isotopic composition of the bulk sediments below and  
346 directly above the water table and their further enrichment in  $^{26}\text{Mg}$  towards the surface  
347 suggest a unidirectional transport process occurring during sediment formation. For example,  
348 in profile 4, the  $\delta^{26}\text{Mg}$  composition of samples 05AT1-6I (below water table) and 05AT1-6D  
349 (directly above water table) is very similar at -1.09‰ and -0.92‰, respectively, whereas that  
350 of the near surface sample 05AT1-6A is significantly higher (-0.62‰). Similarly, in profile 6  
351 samples 05AT1-8P (below water table) and 05AT1-8G (directly above water table) have  
352 similar compositions (i.e. -0.41 and -0.21‰, respectively) compared to the near surface  
353 sample in this profile which has a  $\delta^{26}\text{Mg}$  value of 1.14‰. Although the greatest change in  
354  $\delta^{26}\text{Mg}$  values of hydromagnesite sediments occurs between samples near the water table and  
355 those at or near the surface, the minor enrichment in  $^{26}\text{Mg}$  between samples just below and  
356 just above the water table indicate a Rayleigh process may begin to occur below the water  
357 table. However, the majority of samples analyzed below the water table were comprised  
358 mainly of anhydrous carbonates (Table 1), so the prevalence of Rayleigh processes in the  
359 saturated zone cannot be determined.



360           The large difference in the isotopic composition of the sediments between the two  
361 south playa profiles can be assigned to two parameters. In profile 4, the water table occurs at  
362 ~90 cm below the surface, whereas in profile 6 it occurs at ~120 cm (Fig. 3). This longer  
363 pathway along which the Mg-bearing fluid has to move above the water table coincides with  
364 an increase of its Mg isotope ratio, consistent with a greater extent of hydromagnesite  
365 formation along the longer flow path. In addition to the difference in the water table depth  
366 between the two profiles, the presence of higher abundances of magnesite (see Fig. 3) in the  
367 sediments of profile 4 may affect the isotopic composition of the bulk sediments. Based on  
368 our observations of the magnesite-rich sediments, and the observations of Oskierski et al.  
369 (2019), magnesite preferentially uptakes the lighter  $^{24}\text{Mg}$  isotope compared to  
370 hydromagnesite formed at the same temperature.

371           Overall, the vertical distribution of Mg isotope composition of hydromagnesite  
372 sediments is broadly consistent with a Rayleigh distillation process along the flow path (Fig.  
373 5). This process points towards a precipitation reaction without significant post-depositional  
374 exchange of isotopes between fluid and solid. It also implies that in cases where Mg isotopes  
375 are used for mass-balance calculations and/or to distinguish precipitation of carbonates *versus*  
376 silicates, the potential for Rayleigh fractionation may complicate interpretations in Mg  
377 supply-limited environments.

378

## 379 **5.2 Formation of magnesite**

380           The Atlin playas are one of the most well-characterized sites for magnesite formation at  
381 Earth's surface conditions (Power et al., 2007; 2009; 2014; 2019). Textural and stable carbon  
382 and oxygen isotope data demonstrate that magnesite precipitates from pore waters as opposed  
383 to forming through transformation of hydromagnesite (Power et al., 2019). Magnesite grains  
384 exhibit crystal growth features including submicrometer cone-like terraced morphologies

385 above the water table and smooth crystal faces below the water table (Fig. 2e-f). This implies  
386 there may be variable crystal growth mechanisms and precipitation rates with depth. Fluids in  
387 both the saturated and unsaturated zones are highly supersaturated with respect to magnesite,  
388 implying its formation is reaction-controlled. Magnesite formation is likely nucleation-  
389 limited with long induction times and slow precipitation rates, whereas hydromagnesite can  
390 form more readily at low-temperature. Thus, these minerals are spatially, but not entirely  
391 temporally associated with one another, and the predominant fluids that have formed these  
392 two minerals may differ.

393 The rates of magnesite formation (nucleation + crystal growth) were estimated to lay in  
394 the range of  $10^{-13}$  to  $10^{-12}$  mol/m<sup>2</sup>/s with magnesite abundance increasing exponentially over  
395 time (Power et al., 2019). Playa surface sediments exhibit variable magnesite abundances  
396 ranging from <1 to ~40 wt.% (see Figure 5 in Power et al., 2014). This variability is likely a  
397 result of the heterogeneity of the playas, with Mg carbonate mounds being adjacent to  
398 grassland areas that are adjacent to ponds in a relatively small area (Fig. 1b). With this  
399 heterogeneity in mind and the expectation that magnesite abundance increases exponentially  
400 with time (Power et al., 2019), the greater abundance of magnesite in profile 4 compared to  
401 profile 6, may be due to these sediments being modestly older, or potentially due to  
402 differences in vertical fluid flow.

403 The  $\delta^{26}\text{Mg}$  composition of magnesite-bearing sediments in Atlin is significantly lower  
404 than those dominated by hydromagnesite (Fig. 4). Hence, if hydromagnesite is the precursor  
405 phase of magnesite in this environment, the transformation can only occur via a  
406 dissolution/re-precipitation process, as this would change the Mg isotope composition  
407 (Harrison et al., 2021). A solid-state transformation from hydromagnesite to magnesite can  
408 therefore be excluded. This observation clearly suggests that magnesite formation in low  
409 temperature environments like the Atlin playas is not taking place by solid-state

410 transformation of a hydromagnesite precursor but by direct precipitation from the fluid phase.  
411 This argument is further supported by textural observations as well as stable carbon and  
412 oxygen isotope compositions of the two phases previously reported by Power et al. (2019).  
413 For example, textures such as spiral crystal growth seen in magnesite from above the water  
414 table most likely result from direct precipitation and growth rather than transformation from  
415 hydromagnesite (Fig. 2f). Furthermore, stable carbon and oxygen isotope analyses of  
416 magnesite and hydromagnesite showed that these minerals have distinct isotopic  
417 compositions with the former likely being precipitated from waters with similar isotopic  
418 compositions to that of groundwater, and the latter forming from waters with compositions  
419 similar to that of surface waters (see Figure 9 in Power et al., 2019). This isotopic evidence  
420 supports hydromagnesite formation being driven by evaporation in the unsaturated zone  
421 towards the surface and magnesite forming initially at depth from pore waters with a more  
422 groundwater-like composition. Magnesium isotopes cannot be used in the same way as C and  
423 O isotopes to distinguish surface water vs groundwater, as the source of Mg is the same in  
424 both (i.e., groundwater).

425         The Mg isotope composition of magnesite-bearing sediments in Atlin provides a  
426 unique opportunity to directly constrain the Mg isotope fractionation factor between  
427 magnesite and forming fluid at ~10 °C. However, it should be noted here that an estimation  
428 of the Mg isotope fractionation factor between magnesite and fluid is not straightforward.  
429 The isotopic composition of the fluid (i.e., pore fluid) is uncertain and likely variable, and a  
430 number of other parameters may influence the Mg isotope fractionation including speciation  
431 of Mg in solution and formation of other Mg-bearing carbonate phases such as  
432 hydromagnesite, disordered dolomite, and ankerite. The abundance of magnesite in the  
433 sediment profiles is significantly higher below the water table, including a few samples that  
434 contain almost exclusively magnesite that can be seen in Fig. 3 and in Table 1. Starting with

435 the working hypothesis that the isotopic composition of the forming fluid of magnesite below  
436 the water table was constant over the last 8000 years and similar to that of the weathering  
437 fluid (i.e.  $\sim -1.1 \pm 0.1\text{‰}$ ) and taking into account that the magnesite growth rate is significantly  
438 slow as to not be affected by growth kinetics, a first estimation of the equilibrium Mg isotope  
439 fractionation factor between magnesite and fluid can be made. Note here that according to  
440 Power et al. (2019) the  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values of magnesite precipitated from groundwater  
441 denote formation under isotope equilibrium conditions. Sample 11AT1-J after the removal of  
442 hydromagnesite was used for calculation of the  $\Delta^{26}\text{Mg}_{\text{mgs-fluid}}$  as it was the only sample  
443 without other mineral phases. However, all magnesite-rich samples had similar  $\delta^{26}\text{Mg}$  values  
444 (Fig. 4, Table 1), including those in both the South and North playa despite being several  
445 hundred metres apart. Based on the isotopic composition of magnesite sample 11AT1-J after  
446 the removal of hydromagnesite (i.e.,  $-2.95\text{‰}$ , Table 1) the  $\Delta^{26}\text{Mg}_{\text{mgs-fluid}}$  value is equal to -  
447  $1.85 \pm 0.1\text{‰}$ . It should be noted that this is an apparent fractionation factor, with uncertainty  
448 arising from the use of an estimated fluid composition and potential isotopic heterogeneity of  
449 the solid.

450         Nevertheless, the estimated fractionation factor of  $-1.85 \pm 0.1\text{‰}$  is within a similar  
451 range to the value proposed by Pearce et al. (2012) who estimate a fractionation factor of  $\sim$ -  
452  $2.3\text{‰}$  at  $25\text{ °C}$  (Fig. 7) based on extrapolation of hydrothermal experiments at  $150$  and  $200$   
453  $\text{°C}$ . In addition, this value lays within the range of published theoretical calculations that span  
454 from  $-0.7\text{‰}$  (Pinilla et al., 2015) to  $-4.7\text{‰}$  (Schauble, 2011) at  $10\text{ °C}$  (Fig. 7). Note that these  
455 fractionation factors were derived from theoretical calculations that consider the isotopic  
456 composition of free  $\text{Mg}^{2+}_{(\text{aq})}$  ion in their calculations, whereas the values plotted for Atlin  
457 playa samples represent fractionation between bulk  $\text{Mg}_{(\text{aq})}$  and magnesite. Considering that  
458 magnesite growth proceeds via the standard ion-by-ion addition of  $\text{Mg}^{2+}$  on the growing  
459 mineral surface (Burton et al., 1951), the isotopic composition of the  $\text{Mg}^{2+}_{(\text{aq})}$  ions is likely to

460 be affected by the formation of Mg-carbonate aquo complexes such as  $\text{MgHCO}_3^+$  and  
461  $\text{MgCO}_3^0$  depending on their abundance in the fluid phase. The formation of these complexes  
462 is accompanied by a reduction from 6 water molecules in the inner hydration sphere of  
463  $\text{Mg}^{2+}_{(\text{aq})}$  ion to 5 or 4 in the carbonate-bearing complexes  $\text{MgCO}_3^0$  and  $\text{MgHCO}_3^+$  (Schott et  
464 al., 2016; Stefánsson et al., 2017). Speciation calculations of the pore fluid from profile 6  
465 using the data provided by Power et al. (2019) together with the reduced partitioning function  
466  $\beta$  by Schott et al. (2016) suggest that about 73.2% of Mg in the fluid is present as  $\text{Mg}^{2+}_{(\text{aq})}$  and  
467 the rest is complexed as  $\text{MgHCO}_3^+$  (19.5%) and  $\text{MgCO}_3^0$  (7.2%). The presence of these two  
468 carbonate-bearing aquo-complexes would reduce the  $\delta^{26}\text{Mg}$  composition of the  $\text{Mg}^{2+}_{(\text{aq})}$  in  
469 the fluid by 1.2‰. Thus, the effective isotope composition of  $\text{Mg}^{2+}_{(\text{aq})}$  would be  $-2.3 \pm 0.1$ ‰,  
470 suggesting that the Mg isotope fractionation between magnesite and aqueous Mg is small and  
471 about  $-0.7 \pm 0.1$ ‰ in excellent agreement with the value proposed by Pinilla et al. (2015).

472 Overall, the major limitation for the estimation of the Mg isotope fractionation  
473 between magnesite and fluid in Atlin is the formation of other Mg-bearing carbonate phases  
474 such as hydromagnesite and uncertainty regarding the isotopic composition of the fluid. The  
475 differences in the fractionation factors between the two mineral phases and the forming fluid,  
476 and the differences in the rates of formation and transformation of these phases makes a  
477 direct estimate of the magnesite fractionation factor challenging. Nevertheless, the  
478 magnesite-rich samples are consistently enriched in the isotope of lower mass,  $^{24}\text{Mg}$ , relative  
479 to hydromagnesite samples at  $\sim 10$  °C (Fig. 4). This is consistent with observations at higher  
480 temperature in laboratory experiments (Pearce et al., 2012; Perez-Fernandez et al., 2017).

481

### 482 **5.3 Implications for CO<sub>2</sub> storage in hydrous Mg-carbonates**

483 Given the unusual fluid source composition that would need to exist to generate the  
484 abnormally high  $\delta^{26}\text{Mg}$  values observed at the playa surface through equilibrium Mg isotope

485 fractionation, it is likely that the observed trends in Mg isotope composition above the water  
486 table are due to a distillation process along an upward, evaporation-driven flow path. The Mg  
487 isotope compositions therefore provide insight into the mechanism of playa formation. The  
488 depositional model proposed by Power et al. (2014) based on mineralogical evidence, field  
489 observations, and C and O isotopic data suggested that the precipitation of hydromagnesite  
490 occurred in the unsaturated zone and proceeded by a combination of transformation of more  
491 hydrated phases and precipitation from evaporation-influenced pore fluids. Further insight  
492 provided in Power et al. (2019) suggested that hydromagnesite precipitation was transport-  
493 controlled, in the sense that it (or a more hydrated phase) precipitates quickly upon reaching  
494 saturation as Mg-rich waters are transported from the water table and evaporate. This is  
495 consistent with the observed trend in Mg isotopes, which may reflect continuous enrichment  
496 of the fluid in  $^{26}\text{Mg}$  along the evaporation-driven flow path, as  $^{24}\text{Mg}$  is removed by carbonate  
497 precipitation.

498         Magnesium isotope compositions of solids and fluids have recently been applied as  
499 tracers of engineered  $\text{CO}_2$  storage and can be used to distinguish precipitation of Mg-  
500 carbonates, that store  $\text{CO}_2$ , and Mg-silicates, that do not store  $\text{CO}_2$  (Oelkers et al., 2019). This  
501 relies on the fact that secondary Mg-silicates tend to favour  $^{26}\text{Mg}$  relative to the fluid,  
502 whereas anhydrous Mg-carbonates tend to favour  $^{24}\text{Mg}$  relative to the fluid as has been  
503 observed previously in both high and low temperature systems (Beinlich et al., 2014;  
504 Oskierski et al., 2019). Our observations at Atlin suggest that consideration of a distillation  
505 process, when applicable, may help refine such interpretations. For example, Mg-carbonate  
506 precipitation in ultramafic mine tailings is often driven by evaporation and may be subject to  
507 a similar distillation process (Wilson et al., 2009).

508         The anhydrous Mg-carbonate mineral magnesite is the ideal carbon sink in terms of  
509 thermodynamic stability compared to hydrous carbonates (Power et al., 2013). However, its

510 formation in low temperature environments is unlikely to occur on short timescales (Hänchen  
511 et al., 2008; Saldi et al., 2012), thus making the hydrated Mg-carbonates the targets for CO<sub>2</sub>  
512 storage at near Earth's surface temperatures. Although hydromagnesite, dypingite and  
513 nesquehonite are common products of ultramafic rock weathering (Assima et al., 2014; Bea  
514 et al., 2012; Boschi et al., 2009; Chaka et al., 2016; Felmy et al., 2012; Garcia del Real et al.,  
515 2016; Gras et al., 2017; Highfield et al., 2016; Hövelmann et al., 2012; Kristova et al., 2014;  
516 Loring et al., 2012; Montes-Hernandez et al., 2012; Pronost et al., 2011; Schaef et al., 2011;  
517 2013; Zhao et al., 2010), previous studies on their formation that used Mg isotope systematics  
518 suggested a continuous exchange of Mg isotopes between the solid and the fluid phase at  
519 ~25°C (e.g., Mavromatis et al., 2012; Shirokova et al., 2013). Similar observations were  
520 made based on the  $\delta^{13}\text{C}$  value of the solid and the dissolved inorganic carbon composition of  
521 the forming fluid (Mavromatis et al., 2015) and likely reflect the high reactivity of these  
522 phases. However, Harrison et al. (2021) observed a lack of fluid-solid isotopic exchange  
523 between nesquehonite and fluid at 5 °C suggesting that lower temperatures may reduce the  
524 rate of isotope exchange. The apparent lack of post-depositional isotope exchange in the  
525 Atlin playas, as evidenced by the relative consistency with a distillation process which  
526 implies long-term stability of isotopic compositions of the formed minerals. Harrison et al.  
527 (2021) observed that the Mg isotope composition of hydrated carbonate minerals is  
528 substantially reset during transformation to less hydrated phases. However, the relatively  
529 small reservoir of dissolved Mg in the playa sediments relative to the amount of Mg in the  
530 solid likely limited the extent of this isotopic resetting even during lansfordite transformation  
531 to hydromagnesite. As, even if the fluid changed isotopic composition, the much larger  
532 reservoir of Mg in the solid would limit the extent to which bulk solid composition would  
533 change, unless a long-term, relatively high-volume flux of fluid with substantially different  
534 isotopic composition were present. This could in part explain the preservation of the strongly

535  $^{24}\text{Mg}$ -depleted sediments near the playa surface despite the tendency of these minerals to  
536 exchange with the fluid. The preservation of these isotopic signatures also suggest that once  
537 incorporated into the mineral, the Mg and C are likely stored for at least the 8,000-year time  
538 scale of the playa's existence. These findings are evidence of the long-term stability of  $\text{CO}_2$   
539 storage by hydrous Mg-carbonate at low temperature in both hydrous Mg-carbonates and  
540 anhydrous magnesite.

541

542

## 543 **6. Conclusions**

544         The Mg isotope composition of the hydromagnesite and magnesite sediments of the  
545 alkaline playas near Atlin, British Columbia, Canada, provide significant information  
546 regarding the formation conditions of these phases in low temperature environments.  
547 Hydromagnesite formation above the water table occurs via transport and evaporation of Mg-  
548 rich water, which imparts a  $^{24}\text{Mg}$  depleted isotope composition that is uncommon for Mg-  
549 bearing carbonate minerals. This depletion of  $^{24}\text{Mg}$  in hydromagnesite is interpreted to reflect  
550 a distillation process occurring during the migration of Mg-rich fluids towards the surface.  
551 This process has to be taken into consideration when interpreting Mg isotope composition of  
552 carbonate minerals formed where Mg transport may be the limiting factor. Several instances  
553 of Mg-carbonate mineral formation in near-surface environments are driven by evaporation  
554 (e.g., mine wastes; Wilson et al., 2009), therefore the impact of distillation on Mg isotope  
555 signatures may be important to the interpretation of Mg-isotope signatures in numerous  
556 natural and engineered environments where hydrous Mg-carbonates precipitate.

557         The Mg isotope compositions of co-existing hydromagnesite and magnesite are  
558 distinct, suggesting that the formation of magnesite does not occur via solid-state  
559 transformation of pre-existing hydromagnesite, but rather proceeds via direct precipitation



560 from the fluid phase or dissolution-reprecipitation. The first estimates for the Mg isotope  
561 fractionation during magnesite formation between 3 and 14 °C (average ~10 °C) are reported.  
562 The estimated fractionation factor of  $-1.8\pm 0.1\text{‰}$  is within the range of published theoretical  
563 calculations; however, if aqueous Mg speciation and associated isotope fractionation among  
564 aqueous species is considered, this value becomes  $-0.7\pm 0.1\text{‰}$  suggesting speciation may be  
565 of major significance during Mg-carbonate mineral formation in environments with high  
566 alkalinity.

567

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574

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893

894 Table 1: Magnesium isotope composition, mineralogy, location and depth of solid and liquid samples and reference materials analyzed in this  
 895 study.

Sample ID	Sample type	Depth (cm)	Mineralogy (wt %)			$\delta^{25}\text{Mg}$ (‰)	2 $\sigma$	$\delta^{26}\text{Mg}$ (‰)	2 $\sigma$	Notes
			HMg	Mgs	Other carbonates*					
<i>Solids – Country rocks</i>										
AT03-42	Rock	Surface				-0.21	0.04	-0.41	0.03	Partially serpentinized
01AT5-2	Rock	Surface				-0.23	0.03	-0.42	0.05	Listvenite
AT03-20-PC2	Rock	Surface				-0.15	0.04	-0.32	0.09	Partially serpentinized harzburgite
04AT4	Rock	Surface				-0.15	0.03	-0.30	0.03	Harzburgite
AT04-3	Rock	Surface				-0.13	0.04	-0.25	0.03	Serpentinite
<i>Solids- S. Playa Profile 4</i>										
05AT1-6A	Sediment	0-20	59.1	40.9		-0.31	0.01	-0.61	0.01	
05AT1-6D	Sediment	56-70	62.4	37.6		-0.46	0.03	-0.92	0.03	
05AT1-6I	Sediment	110-125	59.6	37.5	Nsq (2.9)	-0.57	0.01	-1.09	0.04	
05AT1-6K	Sediment	150-180	14.3	85.7		-1.28	0.02	-2.48	0.05	
11AT1-J	Sediment	180-189	4.1	95.9		-1.36	0.01	-2.63	0.03	
11AT1-Jmgs	Sediment	180-189		100		-1.52	0.03	-2.95	0.04	HMg removed; acid leaching
11AT1-1K	Sediment	237-248	4.5	33	Ara (25.8), Dol (35.4)	-1.17	0.03	-2.20	0.02	
11AT1-L	Sediment	272-279	2.2	17.1	Ara (43.6), Dol (26.6)	-1.20	0.00	-2.31	0.02	
<i>Solids- S. Playa Profile 6</i>										
05AT1-8A	Sediment	0-17	92.6	7.3		0.60	0.03	1.14	0.05	
05AT1-8C	Sediment	30-44	93	7		0.15	0.03	0.30	0.06	
05AT1-8E	Sediment	61-76	97.2	2.8		-0.10	0.01	-0.18	0.03	
05AT1-8G	Sediment	84-97	100			-0.11	0.04	-0.21	0.06	
05AT1-8P	Sediment	180-195	90.8	9.2		-0.22	0.01	-0.41	0.06	
05AT1-7R	Sediment	190-210	2.1	59.1	Dol (23.3), Ara (1.5), Amor, (13.9)	-1.31	0.02	-2.53	0.05	
05AT1-8X	Sediment	292-297	3.2	4.4	Ara (47.1), Cal (2.0), Dol (0.9),	-0.67	0.05	-1.30	0.05	

					Ank (6.1), Hun (5.7), Amor. (30.5)					
12AT1-8E	Sediment	362-368		15	Ara (54.8), Ank (10.7), Dol (7.3), Hun (2.5), Cal (0.3)	-1.14	0.03	-2.22	0.00	
<i>Solids- N.playa Profile</i>										
12AT-NA	Sediment	0-5	81	19		0.31	0.01	0.61	0.01	
12AT-NB	Sediment	30-46	76	24		0.12	0.02	0.23	0.02	
12AT-NC	Sediment	56-75	6	94		-1.08	0.03	-2.11	0.04	
12AT-ND	Sediment	89-99	2-4	96-98		-1.29	0.02	-2.47	0.08	
<i>Fluids</i>										
16AT-water1	Water					-0.51	0.04	-0.97	0.06	Pond on Monarch Mountain
16AT-water2	Water	30				0.31	0.01	0.60	0.01	Southeastern playa water table
16AT-water3	Water					-0.63	0.04	-1.20	0.03	122 m deep well water near Monarch Mountain
16AT-water4	Water					-0.17	0.04	-0.36	0.05	North playa wetland
16AT-water5	Water					0.12	0.05	0.25	0.06	Southeastern playa main wetland
16AT-water6	Water					-0.55	0.03	-1.07	0.03	Spring at base of Monarch Mountain
12AT-Norm	Water					0.14	0.02	0.28	0.03	35m deep well water near southeastern playa
12AT-Nplaya	Water	50				0.07	0.02	0.14	0.03	North playa water table
<i>Reference materials</i>										
DSM3						0.00	0.03	0.00	0.04	Monoelemental reference material
CAM-1						-1.34	0.03	-2.65	0.07	Monoelemental reference material
OUMg						-1.46	0.07	-2.82	0.06	Monoelemental reference material
IAPSO						-0.43	0.03	-0.83	0.08	Certified seawater
JDo-1						-1.26	0.07	-2.43	0.08	Certified dolomite reference material

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\* number in parenthesis denotes wt % of phase abundance according to XRD analyses.