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Mechanisms controlling the Mg isotope composition of
hydromagnesite-magnesite playas near Atlin, British
Columbia, Canada

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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 ^{24}Mg obtaining $\delta^{26}\text{Mg}$ values as high as +1.14‰ near the sediment surface. In
29 contrast, magnesite formation is characterized by enrichment of the solid phase in ^{24}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 CO₂.

36

1. Introduction

Engineered carbon storage in the form of carbonate minerals has been proposed as a climate change mitigation strategy (Lackner et al., 1995; Wilson et al., 2014; Harrison et al., 2013; Kelemen et al., 2011; Matter and Kelemen 2009; Matter et al., 2016; Power et al., 2013). In this respect, the formation of Mg-bearing carbonates is of great interest because Mg is an abundant element in Earth's crust and a major constituent of seawater. Indeed, ultramafic settings have a high potential for CO₂ uptake via the carbonation of Mg-silicate minerals. Despite the high concentration of Mg in aquatic environments and in silicate rocks, the formation of the thermodynamically most stable Mg-carbonate mineral, magnesite (MgCO₃), is unlikely to occur at temperatures below 60 °C within timescales that would allow for its use as a CO₂ storage medium (Hänchen et al. 2008; Saldi et al., 2009; 2012 Power et al., 2017). This limitation is due to the very slow exchange of water molecules between the hydration sphere of the aqueous Mg ion and bulk water, which kinetically inhibits magnesite formation (Bénézech et al., 2011; 2013). In low temperature environments the formation of hydrous Mg-carbonates such as lansfordite (MgCO₃·5H₂O), nesquehonite (MgCO₃·3H₂O) and hydromagnesite (Mg₅(CO₃)₄(OH)₂·4H₂O) may occur and is often driven by evaporation (Hopkinson et al., 2008; 2012; Beinlich and Austrheim 2012; Harrison et al., 2013; 2015; 2016; 2017; Power et al., 2014; 2017; Wilson et al., 2009; 2014; Assima et al., 2014; Oskierski et al. 2016; McCutcheon et al., 2016; 2017; Turvey et al., 2018).

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

used to trace Mg isotope composition of oceanic water in the geological past (Pogge von Strandmann et al., 2014) as well as to constrain mineral formation temperature (Pearce et al., 2012). The Mg isotope composition of Mg-bearing carbonate minerals has been shown to be distinctly enriched in the lighter ^{24}Mg isotope compared to silicate phases (e.g. Teng et al., 2017), which has helped to decipher the Mg cycle (Tipper et al., 2006). Recently, the potential application of Mg isotopes to trace engineered CO_2 storage has been explored (Oelkers et al., 2019; Harrison et al., 2021).

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

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

As described by Power et al. (2019) based on field observations and mineralogical data, the precipitation of hydromagnesite in Atlin is interpreted to be limited by the transport of Mg-rich waters through evaporation above the water table. In contrast, waters throughout the sediment profiles (saturated and unsaturated zones) are supersaturated with respect to magnesite and its precipitation is interpreted to be reaction-controlled (i.e., controlled by precipitation kinetics; Power et al., 2019). Therefore, this site offers the opportunity to contrast the impact of different formation processes on Mg isotope compositions of low temperature Mg-carbonate minerals. In this study, we examine the Mg isotope composition of the Mg-carbonate sediments in three depth profiles recovered from this unique and well-characterized environment. These profiles exhibit differences in abundance of magnesite and water table depth, resulting in different vertical Mg isotope composition of the solid phase. Our findings provide insight into Mg isotope fractionation behavior in Mg-carbonate minerals and the use of Mg-isotopes to trace the fate of carbon in CO₂ storage scenarios.

2 Geologic setting and playa genesis

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

1990a; Hansen et al., 2005). The weathering of this bedrock produces alkaline Mg-HCO_3^- groundwater that discharges topographic lows where the playas lie (Power et al., 2014; Power et al., 2009). There are two groups of playas (total area $\approx 0.2 \text{ km}^2$); a northern group and a southern group with the latter having water bodies and grassland areas in addition to Mg-carbonate mounds (Fig. 1).

The playas consist of three sedimentary units: Mg-carbonate sediments at the surface underlain by Ca-Mg-carbonate sediments, and then glaciolacustrine mud (Power et al., 2014). Glaciolacustrine mud was first deposited in glacial lakes and mainly contains silicate minerals (e.g., quartz, feldspars, micas). Over time, carbonate deposition overtook siliciclastic deposition as surface runoff declined and alkaline Mg-HCO_3^- groundwater became the dominant water source (Fig. 2a). Modern groundwater near the playas is supersaturated with respect to anhydrous Ca- and Mg-carbonate minerals including aragonite (CaCO_3) and magnesite (MgCO_3). Subaqueous carbonate deposition fills ponds with mainly aragonite, and through diagenesis a Ca-Mg-carbonate unit comprised of aragonite, ankerite ($\text{Ca(Fe,Mg,Mn)(CO}_3)_2$), and disordered dolomite ($\text{CaMg(CO}_3)_2$) formed overlying the glaciolacustrine deposit. A transition from subaqueous to subaerial sediment deposition is indicated by buried vegetation near the top of this Ca-Mg-carbonate unit (Fig. 2b). Radiocarbon dating of this vegetation indicates that the overlying Mg-carbonate unit began forming at most 8000 cal yr BP (Power et al., 2014). Hydrated Mg-carbonate precipitation is driven by the evaporation of Mg-HCO_3^- waters that are drawn to the surface by capillary action. This process manifests itself as mounds of sediments (10s cm high) that are dominated by hydromagnesite (Fig. 2c-2d). The average deposition rate for the Mg-carbonate unit is $\sim 0.4 \text{ mm/yr}$ and its overlying weight results in subsidence, thus the boundary between this unit and the underlying Ca-Mg-carbonate unit now lies well below the water table.

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

3. Sampling and analytical techniques

3.1 Sample collection

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

3.2 Isotope analyses

The magnesium isotope composition of solid and fluid samples was determined following the method described in Mavromatis et al. (2014b). Hydromagnesite was removed from one sample, 11AT1-J, to determine the composition of magnesite alone. Hydromagnesite was removed by reacting the bulk sediment with diluted acetic acid (10 vol. %) for ~30 min. After this treatment the mineralogic composition of the solid was characterized using X-ray diffraction analysis to assess whether hydromagnesite was removed. All solids were then digested in concentrated HNO₃ and/or HF. Digested solids and acidified liquid samples were evaporated to dryness and re-dissolved in 1N HNO₃. About 15 µg of Mg was used for column chemistry in 10 mL Bio-Rad Poly-prep columns containing AG-50W-X12 cation exchange resin for Mg separation from matrix elements. The yields after chromatographic separation were better than 99% of the total Mg loaded in the columns. Magnesium isotopic compositions were measured using a Thermo-Finnigan “Neptune” Multi Collector Inductively Coupled Plasma Mass Spectrometer (MC-ICP-MS) at Géosciences Environnement Toulouse (GET) laboratory (France). All samples were prepared in 0.35 N HNO₃ and introduced into the Ar plasma with a large Stable Introduction System spray chamber (double Scott Cyclonic spray chamber). Instrumental mass fractionation effects were corrected using sample-standard bracketing, and all data are presented as δ^xMg with respect to DSM3 reference material ($\delta^x\text{Mg} = ((^x\text{Mg}/^{24}\text{Mg})_{\text{sample}} / (^x\text{Mg}/^{24}\text{Mg})_{\text{DSM3}} - 1) \times 1000$) where x refers to the Mg mass of interest. All sample analyses were run in triplicate with the mean value presented in Table 1. The reproducibility of the δ²⁶Mg analyses was determined using replicate analyses of the DSM3, CAM-1 and OUMg monoelemental Mg reference standards and was typically better than 0.08‰. The reproducibility of the measurements is in agreement with previously published values from the same laboratory (Pearce et al., 2012;

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

4. Results

4.1 Isotopic composition of country rock, waters, and carbonate sediments

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

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

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

5. Discussion

5.1 Formation of hydromagnesite

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

at the water table are saturated with respect to hydromagnesite and lansfordite, the latter cementing sediments to form a hardpan. Evaporation draws water from the water table upwards, and evapo-concentration causes precipitation of mainly hydromagnesite throughout the unsaturated zone. This upward water movement is evidenced by stable isotope data that shows enrichment in ^{13}C and ^{18}O of the bulk sediments (mgs + hmg) towards the surface (see Fig.10 in Power et al., 2014). These enrichments are consistent with evaporation of water and degassing of CO_2 -rich fluids. Selective analysis of only the hydromagnesite also showed enrichment in ^{13}C and ^{18}O towards the surface (see Fig. 8 in Power et al., 2019). At the scale of the playas, hydromagnesite formation is limited by these physical processes (capillary rise and evaporation) and is thus effectively transport-controlled (Power et al., 2019).

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

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

Likely these elevated $\delta^{26}\text{Mg}$ values are the result of the precipitation of Mg-bearing carbonate minerals during the upward migration of Mg-rich water from the water table, generating a Rayleigh-type distillation effect. This is consistent with the previously postulated formation pathway for hydromagnesite in the Atlin playas, which stated that hydromagnesite precipitation is effectively transport-limited and depends on the replenishment of Mg-rich waters from depth (Power et al., 2014; 2019). The formation of hydromagnesite is driven by CO₂ degassing and evaporation, and may also occur by transformation of more hydrated phases such as lansfordite. This formation model for hydromagnesite in the playas, derived from field observations, mineralogical data, and other isotopic results (Power et al., 2014; 2019), suggests that the unusually high $\delta^{26}\text{Mg}$ values of the Mg-carbonate sediments likely reflects a combination of phase transformation and 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}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,

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

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

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

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

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

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

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

5.2 Formation of magnesite

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

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

The rates of magnesite formation (nucleation + crystal growth) were estimated to lay in the range of 10^{-13} to 10^{-12} mol/m²/s with magnesite abundance increasing exponentially over time (Power et al., 2019). Playa surface sediments exhibit variable magnesite abundances ranging from <1 to ~40 wt.% (see Figure 5 in Power et al., 2014). This variability is likely a result of the heterogeneity of the playas, with Mg carbonate mounds being adjacent to grassland areas that are adjacent to ponds in a relatively small area (Fig. 1b). With this heterogeneity in mind and the expectation that magnesite abundance increases exponentially with time (Power et al., 2019), the greater abundance of magnesite in profile 4 compared to profile 6, may be due to these sediments being modestly older, or potentially due to differences in vertical fluid flow.

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

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

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

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

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

be affected by the formation of Mg-carbonate aquo complexes such as MgHCO_3^+ and MgCO_3^0 depending on their abundance in the fluid phase. The formation of these complexes is accompanied by a reduction from 6 water molecules in the inner hydration sphere of $\text{Mg}^{2+}_{(\text{aq})}$ ion to 5 or 4 in the carbonate-bearing complexes MgCO_3^0 and MgHCO_3^+ (Schott et al., 2016; Stefánsson et al., 2017). Speciation calculations of the pore fluid from profile 6 using the data provided by Power et al. (2019) together with the reduced partitioning function β by Schott et al. (2016) suggest that about 73.2% of Mg in the fluid is present as $\text{Mg}^{2+}_{(\text{aq})}$ and the rest is complexed as MgHCO_3^+ (19.5%) and MgCO_3^0 (7.2%). The presence of these two carbonate-bearing aquo-complexes would reduce the $\delta^{26}\text{Mg}$ composition of the $\text{Mg}^{2+}_{(\text{aq})}$ in the fluid by 1.2‰. Thus, the effective isotope composition of $\text{Mg}^{2+}_{(\text{aq})}$ would be -2.3 ± 0.1 ‰, suggesting that the Mg isotope fractionation between magnesite and aqueous Mg is small and about -0.7 ± 0.1 ‰ in excellent agreement with the value proposed by Pinilla et al. (2015).

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

5.3 Implications for CO_2 storage in hydrous Mg-carbonates

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

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

Magnesium isotope compositions of solids and fluids have recently been applied as tracers of engineered CO_2 storage and can be used to distinguish precipitation of Mg-carbonates, that store CO_2 , and Mg-silicates, that do not store CO_2 (Oelkers et al., 2019). This relies on the fact that secondary Mg-silicates tend to favour ^{26}Mg relative to the fluid, whereas anhydrous Mg-carbonates tend to favour ^{24}Mg relative to the fluid as has been observed previously in both high and low temperature systems (Beinlich et al., 2014; Oskierski et al., 2019). Our observations at Atlin suggest that consideration of a distillation process, when applicable, may help refine such interpretations. For example, Mg-carbonate precipitation in ultramafic mine tailings is often driven by evaporation and may be subject to a similar distillation process (Wilson et al., 2009).

The anhydrous Mg-carbonate mineral magnesite is the ideal carbon sink in terms of 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 CO₂
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

²⁴Mg-depleted sediments near the playa surface despite the tendency of these minerals to exchange with the fluid. The preservation of these isotopic signatures also suggest that once incorporated into the mineral, the Mg and C are likely stored for at least the 8,000-year time scale of the playa's existence. These findings are evidence of the long-term stability of CO₂ storage by hydrous Mg-carbonate at low temperature in both hydrous Mg-carbonates and anhydrous magnesite.

6. Conclusions

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

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

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

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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 σ	$\delta^{26}\text{Mg}$ (‰)	2 σ	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.