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

Anna L. Harrison^{a*}, Pascale Bénézech^b, Jacques Schott^b, Eric H. Oelkers^{b,c}, and Vasileios
Mavromatis^b

^aDepartment of Geological Sciences and Geological Engineering and School of
Environmental Studies, Queen's University, K7L 3N6 Kingston, Canada

^bGéosciences Environnement Toulouse, GET – CNRS – IRD – OMP – Université de
Toulouse, 14, Avenue Edouard Belin, 31400 Toulouse, France

^cDepartment of Earth Sciences, University College London, Gower Street, WC1E 6BT
London, United Kingdom

*Corresponding author: anna.harrison@queensu.ca

Abstract

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

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

1. Introduction

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

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

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

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

2. Methods

2.1 Experimental methods and analytical techniques

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

(Harrison et al., 2019) were conducted at 5, 25 and 35°C, with those at 25 and 35°C being duplicated. The duplicates ran subsequently to the original and for a longer duration, to observe the complete conversion of nesquehonite to dypingite. The shorter duration experiments are referred to as “short-term” experiments, which ran for between 367-432 h, and the longer duration as “long-term” experiments which ran for between 1368-2043 h. Each experimental series consisted of a suite of nine to eleven sealed, closed-system batch reactors at each fixed temperature. Initially 0.60 g of synthetic nesquehonite with ~73 g of an aqueous solution containing 0.10 mol/L NaCl and 0.06 mol/L NaHCO₃ were introduced in each reactor. The reactors (60 mL Nalgene bottles) were filled to have as little headspace as possible in order to limit exchange of C with the atmosphere (some bubbles of air could not be completely removed). The synthesis method for the initial nesquehonite is reported by Harrison et al. (2019). At selected times an individual reactor was sampled in its entirety to track the chemical and isotopic composition of the reactive aqueous solution, as well as changes in the mineralogical and isotopic composition of the solids. The solution was removed via a syringe, and filtered through a 0.22 µm polyethersulfone (PES) syringe filter. Four aliquots were immediately acidified to 2% HNO₃ for subsequent analysis of Mg concentrations and Mg isotopic compositions. A single aliquot was used for immediate pH measurements and subsequent alkalinity measurements. For subsequent $\delta^{13}\text{C}_{\text{DIC}}$ analysis, fluids were stored in 2 mL air-tight vials with no headspace. All fluids were refrigerated prior to subsequent analysis. Fluid pH was measured immediately after sampling using a Metrohm 913 pH-meter and a Metrohm combined electrode (6.0234.1000) that was calibrated using NIST traceable buffer solutions at each experimental temperature, with an uncertainty of approximately ± 0.03 pH units.

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

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

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

2.2 Carbon isotope analyses

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

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

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

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

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

2.3. Magnesium isotope analyses

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

cation exchange resin and eluted with 1 N HNO₃ to separate Mg from Na. About 15 µg of Mg from each sample was loaded into each column and 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 over multiple measuring sessions with the mean value presented in Table 2. 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 (Mavromatis et al., 2012, 2013, 2014a, 2014b; Pearce et al., 2012; 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). 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 2, and was better than 0.08‰.

2.4 Calculation of aqueous speciation and isotopic composition of carbon and magnesium aqueous species

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

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

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

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

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

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

3. Results

3.1 Mineral transformation

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

3.2 Evolution of carbon isotopic composition

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

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

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

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

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

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

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

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

3.3 Evolution of magnesium isotopic composition

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

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

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

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

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

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

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

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

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

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

The values were $0.84 \leq \Delta_{calc}^{26}Mg_{solid-Mg^{2+}(aq)} \leq 2.87$ for all experimental runs (Table 2). The aqueous speciation and calculated isotopic composition of Mg^{2+} in all experiments is provided in Electronic Annex 2.

4. Discussion

4.1 Carbon isotope fractionation between hydrous Mg carbonates and reactive fluid

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

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

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

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

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

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

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

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

4.2 Magnesium isotope fractionation between hydrous Mg carbonates and reactive fluid

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

5. Conclusion

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

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

Acknowledgments

We are grateful to Jérôme Chmieleff for his support with MC-ICP-MS analyses. We thank Sebastian Breitenbach and Sylvia Riechelmann for conducting carbon isotopic analyses. We would like to acknowledge the Associate Editor, Matthew Fantle, Adrian Immenhauser, Chris Romanek and two anonymous reviewers for their helpful suggestions that improved this paper. This study benefited from the financial support of the ISIFoR Carnot institute (Institute for the Sustainable Engineering of Fossil Resources) under the project SERPCARB AAP-2016, by the French national programme LEFE/INSU and by a Marie Skłodowska-Curie Individual Fellowship awarded to ALH under grant agreement number 701478 (DryMIN) under the European Union's Horizon 2020 program.

References

- Antao S. M., Mulder W. H., Hassan I., Crichton W. A. and Parise J. B. (2004) Cation disorder in dolomite, $\text{CaMg}(\text{CO}_3)_2$, and its influence on the aragonite+magnesite $\leftrightarrow$ dolomite reaction boundary. *Am. Mineral.* **80**, 1142–1147.
- Assima G. P., Larachi F., Beaudoin G. and Molson J. (2012) CO_2 sequestration in chrysotile mining residues-implication of watering and passivation under environmental conditions. *Ind. Eng. Chem. Res.* **51**, 8726–8734.
- Assima G. P., Larachi F., Molson J. and Beaudoin G. (2014) Impact of temperature and oxygen availability on the dynamics of ambient CO_2 mineral sequestration by nickel mining residues. *Chem. Eng. J.* **240**, 394–403.
- Ballirano P., De Vito C., Mignardi S. and Ferrini V. (2013) Phase transitions in the $\text{MgCO}_3\text{-H}_2\text{O}$ system and the thermal decomposition of dypingite, $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 5\text{H}_2\text{O}$: Implications for geosequestration of carbon dioxide. *Chem. Geol.* **340**, 59–67.
- Baumgartner L. P. and Valley J. W. (2001) Stable isotope transport and contact metamorphic fluid flow. *Rev. Mineral. Geochemistry* **43**, 415–467.
- Bea S. A., Wilson S. A., Mayer K. U., Dipple G. M., Power I. M. and Gamazo P. (2012) Reactive Transport Modeling of Natural Carbon Sequestration in Ultramafic Mine Tailings. *Vadose Zo. J.* **11**.
- Beinlich A. and Austrheim H. (2012) In situ sequestration of atmospheric CO_2 at low temperature and surface cracking of serpentinized peridotite in mine shafts. *Chem. Geol.* **332–333**, 32–44.
- Beinlich A., Austrheim H., Mavromatis V., Grguric B., Putnis C. V. and Putnis A. (2018) Peridotite weathering is the missing ingredient of Earth's continental crust composition. *Nat. Commun.* **9**.
- Beinlich A., Mavromatis V., Austrheim H. and Oelkers E. H. (2014) Inter-mineral Mg isotope

712 fractionation during hydrothermal ultramafic rock alteration - Implications for the global
 713 Mg-cycle. *Earth Planet. Sci. Lett.* **392**, 166–176.

714 Bolou-Bi E. B., Vigier N., Brenot A. and Poszwa A. (2009) Magnesium isotope compositions
 715 of natural reference materials. *Geostand. Geoanalytical Res.* **33**, 95–109.

716 Boschi C., Dini A., Dallai L., Ruggieri G. and Gianelli G. (2009) Enhanced CO₂-mineral
 717 sequestration by cyclic hydraulic fracturing and Si-rich fluid infiltration into
 718 serpentinites at Malenrata (Tuscany, Italy). *Chem. Geol.* **265**, 209–226.

719 Breitenbach S. F. M. and Bernasconi S. M. (2011) Carbon and oxygen isotope analysis of
 720 small carbonate samples (20 to 100 µg) with a GasBench II preparation device. *Rapid*
 721 *Commun. Mass Spectrom.* **25**, 1910–1914.

722 Canterford J. H., Tsambourakis G. and Lambert B. (1984) Some observations on the
 723 properties of dypingite, Mg₅(CO₃)₄(OH)₂ • 5H₂O, and related minerals. *Mineral. Mag.*
 724 **48**, 437–442.

725 Casella, L.A., Griesshaber, E., Yin, X.F., Ziegler, A., Mavromatis, V., Muller, D., Ritter,
 726 A.C., Hippler, D., Harper, E.M., Dietzel, M., Immenhauser, A., Schone, B.R., Angiolini,
 727 L. and Schmahl, W.W. (2017) Experimental diagenesis: insights into aragonite to calcite
 728 transformation of *Arctica islandica* shells by hydrothermal treatment. *Biogeosciences* 14,
 729 1461-1492.

730 Chaka A. M., Felmy A. R. and Qafoku O. (2016) Ab initio thermodynamics of magnesium
 731 carbonates and hydrates in water-saturated supercritical CO₂ and CO₂-rich regions.
 732 *Chem. Geol.* **434**, 1–11.

733 Chanda P., Gorski C.A., Oakes R.L., and Fantle M.S. (2019) Low temperature stable mineral
 734 recrystallization of foraminiferal tests: Implications for the fidelity of geochemical
 735 proxies. *Earth Planet. Sci. Lett.* **509**, 428–440.

736 Criss R. E. (1999) *Principles of Stable Isotope Distributio.*, Oxford University Press, Oxford.

737 Davies P. J. and Bubela B. (1973) The transformation of nesquehonite into hydromagnesite.
738 *Chem. Geol.* **12**, 289–300.

739 Deines P. (2004) Carbon isotope effects in carbonate systems. *Geochim. Cosmochim. Acta* **68**,
740 2659–2679.

741 Deines P., Langmuir D. and Harmon R. S. (1974) Stable carbon isotope ratios and the
742 existence of a gas phase in the evolution of carbonate ground waters. *Geochim.*
743 *Cosmochim. Acta* **38**, 1147–1164.

744 Falk E. S., Guo W., Paukert A. N., Matter J. M., Mervine E. M. and Kelemen P. B. (2016)
745 Controls on the stable isotope compositions of travertine from hyperalkaline springs in
746 Oman: Insights from clumped isotope measurements. *Geochim. Cosmochim. Acta* **192**,
747 1–28.

748 Felmy A. R., Qafoku O., Arey B. W., Hu J. Z., Hu M., Todd Schaef H., Ilton E. S., Hess N. J.,
749 Pearce C. I., Feng J. and Rosso K. M. (2012) Reaction of water-saturated supercritical
750 CO₂ with forsterite: Evidence for magnesite formation at low temperatures. *Geochim.*
751 *Cosmochim. Acta* **91**, 271–282.

752 Finch A. A. and Allison N. (2007) Coordination of Sr and Mg in calcite and aragonite.
753 *Mineral. Mag.* **71**, 539–552.

754 Gao C., Cao X., Liu Q., Yang Y., Zhang S., He Y., Tang M. and Liu Y. (2018) Theoretical
755 calculations of equilibrium Mg isotope fractionations between minerals and aqueous
756 solutions. *Chem. Geol.* **488**, 62–75.

757 García del Real P., Maher K., Kluge T., Bird D. K., Brown G. E. and John C. M. (2016)
758 Clumped-isotope thermometry of magnesium carbonates in ultramafic rocks. *Geochim.*
759 *Cosmochim. Acta* **193**, 222–250.

760 Geske A., Goldstein R. H., Mavromatis V., Richter D. K., Buhl D., Kluge T., John C. M. and
761 Immenhauser A. (2015) The magnesium isotope ($\delta^{26}\text{Mg}$) signature of dolomites.

762 *Geochim. Cosmochim. Acta* **149**, 131–151.

763 Giester G., Lengauer C. L. and Rieck B. (2000) The crystal structure of nesquehonite,
 764 $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$, from Lavrion, Greece. *Mineral. Petrol.* **70**, 153–163.

765 Gras A., Beaudoin G., Molson J., Plante B., Bussière B., Lemieux J. M. and Dupont P. P.
 766 (2017) Isotopic evidence of passive mineral carbonation in mine wastes from the
 767 Dumont Nickel Project (Abitibi, Quebec). *Int. J. Greenhouse Gas Control* **60**, 10–23.

768 Gorski C.A., Fantle M. S. (2017) Stable mineral recrystallization in low temperature aqueous
 769 systems: A critical review. *Geochim. Cosmochim. Acta.* **198**, 439–465.

770 Hänchen M., Prigiobbe V., Baciocchi R. and Mazzotti M. (2008) Precipitation in the Mg-
 771 carbonate system-effects of temperature and CO_2 pressure. *Chem. Eng. Sci.* **63**, 1012–
 772 1028.

773 Harrison A. L., Dipple G. M., Power I. M. and Mayer K. U. (2015) Influence of surface
 774 passivation and water content on mineral reactions in unsaturated porous media:
 775 Implications for brucite carbonation and CO_2 sequestration. *Geochim. Cosmochim. Acta*
 776 **148**, 477–495.

777 Harrison A. L., Dipple G. M., Power I. M. and Mayer K. U. (2016) The impact of evolving
 778 mineral-water-gas interfacial areas on mineral-fluid reaction rates in unsaturated porous
 779 media. *Chem. Geol.* **421**, 65–80.

780 Harrison A. L., Dipple G. M., Song W., Power I. M., Mayer K. U., Beinlich A. and Sinton D.
 781 (2017) Changes in mineral reactivity driven by pore fluid mobility in partially wetted
 782 porous media. *Chem. Geol.* **463**, 1–11.

783 Harrison A. L., Mavromatis V., Oelkers E. H. and Bénézech P. (2019) Solubility of the
 784 hydrated Mg-carbonates nesquehonite and dypingite from 5 to 35°C: Implications for
 785 CO_2 storage and the relative stability of Mg-carbonates. *Chem. Geol.* **504**, 123–135.

786 Harrison A. L., Power I. M. and Dipple G. M. (2013) Accelerated carbonation of brucite in

mine tailings for carbon sequestration. *Environ. Sci. Technol.* **47**, 126–134.

Highfield J., Chen J., Haghighatlari M., Åbacka J. and Zevenhoven R. (2016) Low-temperature gas-solid carbonation of magnesia and magnesium hydroxide promoted by non-immersive contact with water. *RSC Adv.* **6**, 89655–89664.

Hopkinson L., Kristova P., Rutt K. and Cressey G. (2012) Phase transitions in the system MgO-CO₂-H₂O during CO₂ degassing of Mg-bearing solutions. *Geochim. Cosmochim. Acta* **76**, 1–13.

Hopkinson L., Rutt K. and Cressey G. (2008) The Transformation of Nesquehonite to Hydromagnesite in the System CaO-MgO-H₂O-CO₂ : An Experimental Spectroscopic Study. *J. Geol.* **116**, 387–400.

Hövelmann J., Putnis C. V., Ruiz-Agudo E. and Austrheim H. (2012) Direct nanoscale observations of CO₂ sequestration during brucite [Mg(OH)₂] dissolution. *Environ. Sci. Technol.* **46**, 5253–5260.

Hu Z., Hu W., Wang X., Lu Y., Wang L., Liao Z. and Li W. (2017) Resetting of Mg isotopes between calcite and dolomite during burial metamorphism: Outlook of Mg isotopes as geothermometer and seawater proxy. *Geochim. Cosmochim. Acta* **208**, 24–40.

Jimenez-Lopez C., Romanek C. S. and Caballero E. (2006) Carbon isotope fractionation in synthetic magnesian calcite. *Geochim. Cosmochim. Acta* **70**, 1163–1171.

Kristova P., Hopkinson L. J., Rutt K. J., Hunter H. M. A. and Cressey G. (2014) Carbonate mineral paragenesis and reaction kinetics in the system MgO-CaO-CO₂-H₂O in presence of chloride or nitrate ions at near surface ambient temperatures. *Appl. Geochemistry* **50**, 16–24.

Langmuir D. (1965) Stability of carbonates in the system MgO-CO₂-H₂O. *J. Geol.* **73**, 730–754.

Li W., Beard B. L., Li C. and Johnson C. M. (2014) Magnesium isotope fractionation between

812 brucite [Mg(OH)₂] and Mg aqueous species: Implications for silicate weathering and
813 biogeochemical processes. *Earth Planet. Sci. Lett.* **394**, 82–93.

814 Li W., Beard B. L., Li C., Xu H. and Johnson C. M. (2015) Experimental calibration of Mg
815 isotope fractionation between dolomite and aqueous solution and its geological
816 implications. *Geochim. Cosmochim. Acta* **157**, 164–181.

817 Li W., Chakraborty S., Beard B. L., Romanek C. S. and Johnson C. M. (2012) Magnesium
818 isotope fractionation during precipitation of inorganic calcite under laboratory
819 conditions. *Earth Planet. Sci. Lett.* **333–334**, 304–316.

820 Loring J. S., Thompson C. J., Zhang C., Wang Z., Schaef H. T. and Rosso K. M. (2012) In
821 situ infrared spectroscopic study of brucite carbonation in dry to water-saturated
822 supercritical carbon dioxide. *J. Phys. Chem. A* **116**, 4768–77.

823 Mavromatis V., Bundeleva I. A., Shirokova L. S., Millo C., Pokrovsky O. S., Bénézech P.,
824 Ader M. and Oelkers E. H. (2015) The continuous re-equilibration of carbon isotope
825 compositions of hydrous Mg carbonates in the presence of cyanobacteria. *Chem. Geol.*
826 **404**, 41–51.

827 Mavromatis V., Gautier Q., Bosc O. and Schott J. (2013) Kinetics of Mg partition and Mg
828 stable isotope fractionation during its incorporation in calcite. *Geochim. Cosmochim.*
829 *Acta* **114**, 188–203.

830 Mavromatis V., González A. G., Dietzel M. and Schott J. (2019) Zinc isotope fractionation
831 during the inorganic precipitation of calcite – towards a new pH proxy. *Geochim.*
832 *Cosmochim. Acta* **244**, 99–112.

833 Mavromatis V., Harrison A. L., Eisenhauer A. and Dietzel M. (2017b) Strontium isotope
834 fractionation during strontianite (SrCO₃) dissolution, precipitation and at equilibrium.
835 *Geochim. Cosmochim. Acta* **218**, 201–214.

836 Mavromatis V., Immenhauser A., Buhl D., Purgstaller B., Baldermann A. and Dietzel M.

837 (2017c) Effect of organic ligands on Mg partitioning and Mg isotope fractionation during
 838 low-temperature precipitation of calcite in the absence of growth rate effects. *Geochim.*
 839 *Cosmochim. Acta* **207**, 139–153.

840 Mavromatis V., Meister P. and Oelkers E. H. (2014b) Using stable Mg isotopes to distinguish
 841 dolomite formation mechanisms: A case study from the Peru Margin. *Chem. Geol.* **385**,
 842 84–91.

843 Mavromatis V., Pearce C. R., Shirokova L. S., Bundeleva I. A., Pokrovsky O. S., Benezeth P.
 844 and Oelkers E. H. (2012) Magnesium isotope fractionation during hydrous magnesium
 845 carbonate precipitation with and without cyanobacteria. *Geochim. Cosmochim. Acta* **76**,
 846 161–174.

847 Mavromatis V., Prokushkin A. S., Pokrovsky O. S., Viers J. and Korets M. A. (2014a)
 848 Magnesium isotopes in permafrost-dominated Central Siberian larch forest watersheds.
 849 *Geochim. Cosmochim. Acta* **147**, 76–89.

850 Mavromatis V., Purgstaller B., Dietzel M., Buhl D., Immenhauser A. and Schott J. (2017a)
 851 Impact of amorphous precursor phases on magnesium isotope signatures of Mg-calcite.
 852 *Earth Planet. Sci. Lett.* **464**, 227–236.

853 Mavromatis V., van Zuilen K., Purgstaller B., Baldermann A., Nägler T. F. and Dietzel M.
 854 (2016) Barium isotope fractionation during witherite (BaCO_3) dissolution, precipitation
 855 and at equilibrium. *Geochim. Cosmochim. Acta* **190**, 72–84.

856 McCutcheon J., Power I. M., Harrison A. L., Dipple G. M. and Southam G. (2014) A
 857 greenhouse-scale photosynthetic microbial bioreactor for carbon sequestration in
 858 magnesium carbonate minerals. *Environ. Sci. Technol.* **48**, 9142–9151.

859 McCutcheon J., Power I. M., Shuster J., Harrison A. L., Dipple G. M. and Southam G. (2019)
 860 Carbon sequestration in biogenic magnesite and other magnesium carbonate minerals.
 861 *Environ. Sci. Technol.*

862 McCutcheon J., Turvey C., Wilson S., Hamilton J. and Southam G. (2017) Experimental
863 deployment of microbial mineral carbonation at an asbestos mine: Potential applications
864 to carbon storage and tailings stabilization. *Minerals* **7**, 191.

865 McCutcheon J., Wilson S. A. and Southam G. (2016) Microbially accelerated carbonate
866 mineral precipitation as a strategy for in situ carbon sequestration and rehabilitation of
867 asbestos mine sites. *Environ. Sci. Technol.* **50**, 1419–1427.

868 Mervine E. M., Humphris S. E., Sims K. W. W., Kelemen P. B. and Jenkins W. J. (2014)
869 Carbonation rates of peridotite in the Samail Ophiolite, Sultanate of Oman, constrained
870 through ^{14}C dating and stable isotopes. *Geochim. Cosmochim. Acta* **126**, 371–397.

871 Ming, D.W., and W.T. Franklin. 1985. Synthesis and characterization of lansfordite and
872 nesquehonite. *Soil Sci. Soc. Am. J.* **49**, 1303–1308.

873 Montes-Hernandez G., Renard F., Chiriac R., Findling N. and Toche F. (2012) Rapid
874 precipitation of magnesite microcrystals from $\text{Mg}(\text{OH})_2\text{-H}_2\text{O-CO}_2$ slurry enhanced by
875 NaOH and a heat-aging step (from similar to 20 to 90 °C). *Cryst. Growth Des.* **12**, 5233–
876 5240.

877 Noireaux, J., Mavromatis, V., Gaillardet, J., Schott, J., Montouillout, V., Louvat, P., Rollion-
878 Bard, C. and Neuville, D.R. (2015) Crystallographic control on the boron isotope paleo-
879 pH proxy. *Earth Planet. Sci. Lett.* **430**, 398–407.

880 O’Neil J. R. and Barnes I. (1971) ^{13}C and ^{18}O compositions in some fresh-water carbonates
881 associated with ultramafic rocks and serpentinites: Western United States. *Geochim.*
882 *Cosmochim. Acta* **35**, 687–697.

883 Oelkers E. H., Berninger U. N., Pérez-Fernández A., Chmieleff J. and Mavromatis V. (2018)
884 The temporal evolution of magnesium isotope fractionation during hydromagnesite
885 dissolution, precipitation, and at equilibrium. *Geochim. Cosmochim. Acta* **226**, 36–49.

886 Oelkers E. H., Butcher R., Pogge von Strandmann P. A. E., Schuessler J. A., von

887 Blanckenburg F., Snæbjörnsdóttir S., Mesfin K., Aradóttir E. S., Gunnarsson I.,
 888 Sigfússon B., Gunnlaugsson E., Matter J. M., Stute M. and Gislason S. R. (2019a) Using
 889 stable Mg isotope signatures to assess the fate of magnesium during the in situ
 890 mineralisation of CO₂ and H₂S at the CarbFix site in SW-Iceland. *Geochim. Cosmochim.*
 891 *Acta* **245**, 542–555.

892 Oelkers E. H., Pogge von Strandmann P. A. E. and Mavromatis V. (2019b) The rapid
 893 resetting of the Ca isotopic signatures of calcite at ambient temperature during its
 894 congruent dissolution, precipitation, and at equilibrium. *Chem. Geol.* **512**, 1–10.

895 Oskierski H. C., Beinlich A., Mavromatis V. and Dlugogorski B. Z. (2019) Mg isotope
 896 fractionation during continental weathering and low temperature carbonation of
 897 ultramafic rocks. *Geochim. Cosmochim. Acta* **262**, 60–77.

898 Oskierski Hans C., Dlugogorski B. Z. and Jacobsen G. (2013) Sequestration of atmospheric
 899 CO₂ in chrysotile mine tailings of the Woodsreef Asbestos Mine, Australia: Quantitative
 900 mineralogy, isotopic fingerprinting and carbonation rates. *Chem. Geol.* **358**, 156–169.

901 Oskierski H. C., Dlugogorski B. Z., Oliver T. K. and Jacobsen G. (2016) Chemical and
 902 isotopic signatures of waters associated with the carbonation of ultramafic mine tailings,
 903 Woodsreef Asbestos Mine, Australia. *Chem. Geol.* **436**, 11–23.

904 Parkhurst D. L. and Appelo C. A. J. (2013) Description of Input and Examples for PHREEQC
 905 Version 3 — A Computer Program for Speciation, Batch-Reaction, One-Dimensional
 906 Transport , and Inverse Geochemical Calculations. *U.S. Geol. Surv. Tech. Methods, B.* **6**,
 907 chapter A43, 6-43A.

908 Pavlov M., Siegbahn P. E. M. and Sandström M. (1998) Hydration of beryllium, magnesium,
 909 calcium, and zinc ions using density functional theory. *J. Phys. Chem. A* **102**, 219–228.

910 Pearce C. R., Saldi G. D., Schott J. and Oelkers E. H. (2012) Isotopic fractionation during
 911 congruent dissolution, precipitation and at equilibrium: Evidence from Mg isotopes.

912 *Geochim. Cosmochim. Acta* **92**, 170–183.

913 Pederson, C., Mavromatis, V., Dietzel, M., Rollion-Bard, C., Nehrke, G., Jons, N., Jochum,
 914 K.P. and Immenhauser, A. (2019) Diagenesis of mollusc aragonite and the role of fluid
 915 reservoirs. *Earth Planet. Sci. Lett.* 514, 130–142.

916 Pinilla C., Blanchard M., Balan E., Natarajan S. K., Vuilleumier R. and Mauri F. (2015)
 917 Equilibrium magnesium isotope fractionation between aqueous Mg^{2+} and carbonate
 918 minerals: Insights from path integral molecular dynamics. *Geochim. Cosmochim. Acta*
 919 **163**, 126–139.

920 Pogge von Strandmann P. A. E., Burton K. W., Snæbjörnsdóttir S. O., Sigfússon B., Aradóttir
 921 E. S., Gunnarsson I., Alfredsson H. A., Mesfin K. G., Oelkers E. H. and Gislason S. R.
 922 (2019) Rapid CO_2 mineralisation into calcite at the CarbFix storage site quantified using
 923 calcium isotopes. *Nat. Commun.* **10**, 1983.

924 Pogge von Strandmann P. A. E., Opfergelt S., Lai Y. J., Sigfússon B., Gislason S. R. and
 925 Burton K. W. (2012) Lithium, magnesium and silicon isotope behaviour accompanying
 926 weathering in a basaltic soil and pore water profile in Iceland. *Earth Planet. Sci. Lett.*
 927 **339–340**, 11–23.

928 Pokrovsky O. S. and Schott J. (2002) Surface chemistry and dissolution kinetics of divalent
 929 metal carbonates. *Environ. Sci. Technol.* **36**, 426–432.

930 Power I. M., Harrison A. L., Dipple G. M. and Southam G. (2013b) Carbon sequestration via
 931 carbonic anhydrase facilitated magnesium carbonate precipitation. *Int. J. Greenhouse*
 932 *Gas Control* **16**, 145–155.

933 Power I. M., Harrison A. L., Dipple G. M., Wilson S. A., Barker S.L.L. and Fallon S. J.
 934 (2019) Magnesite formation in playa environments near Atlin, British Columbia,
 935 Canada. *Geochim. Cosmochim. Acta* **255**, 1–24.

936 Power I. M., Harrison A. L., Dipple G. M., Wilson S. A., Kelemen P. B., Hitch M. and

937 Southam G. (2013a) Carbon Mineralization: From Natural Analogues to Engineered
 938 Systems. *Rev. Mineral. Geochemistry* **77**, 305–360.

939 Power I. M., Kenward P. A., Dipple G. M. and Raudsepp M. (2017) Room Temperature
 940 Magnesite Precipitation. *Cryst. Growth Des.* **17**, 5652–5659.

941 Power I. M., Wilson S. A., Harrison A. L., Dipple G. M., Mccutcheon J., Southam G. and
 942 Kenward P. A. (2014) A depositional model for hydromagnesite-magnesite playas near
 943 Atlin, British Columbia, Canada. *Sedimentology* **61**, 1701–1733.

944 Power I. M., Wilson S. A., Thom J. M., Dipple G. M. and Southam G. (2007) Biologically
 945 induced mineralization of dypingite by cyanobacteria from an alkaline wetland near
 946 Atlin, British Columbia, Canada. *Geochem. Trans.* **8**, 1–16.

947 Pronost J., Beaudoin G., Tremblay J., Larachi F., Duchesne J., Hébert R. and Constantin M.
 948 (2011) Carbon sequestration kinetic and storage capacity of ultramafic mining waste.
 949 *Environ. Sci. Technol.* **45**, 9413–9420.

950 Purgstaller, B., K. E. Goetschl, V. Mavromatis, and M. Dietzel (2019) Solubility
 951 investigations in the amorphous calcium magnesium carbonate system. *CrystEngComm*
 952 **21**, 155–164.

953 Riechelmann S., Mavromatis V., Buhl D., Dietzel M., Eisenhauer A. and Immenhauser A.
 954 (2016) Impact of diagenetic alteration on brachiopod shell magnesium isotope ($\delta^{26}\text{Mg}$)
 955 signatures: Experimental versus field data. *Chem. Geol.* **440**, 191–206.

956 Riechelmann S., Mavromatis V., Buhl D., Dietzel M., Hoffmann R., Jöns N., Kell-Duivestien
 957 I. and Immenhauser A. (2018) Echinoid skeletal carbonate as archive of past seawater
 958 magnesium isotope signatures – Potential and limitations. *Geochim. Cosmochim. Acta*
 959 **235**, 333–359.

960 Rigopoulos I., Harrison A. L., Delimitis A., Ioannou I., Efstathiou A. M., Kyratsi T. and
 961 Oelkers E. H. (2018) Carbon sequestration via enhanced weathering of peridotites and

962 basalts in seawater. *Appl. Geochemistry* **91**, 197–207.

963 Romanek C. S., Grossman E. L. and Morse J. W. (1992) Carbon isotopic fractionation in
 964 synthetic aragonite and calcite: Effects of temperature and precipitation rate. *Geochim.*
 965 *Cosmochim. Acta* **56**, 419–430.

966 Rubinson M. and Clayton R. N. (1969) Carbon-13 fractionation between aragonite and
 967 calcite. *Geochim. Cosmochim. Acta* **33**, 997–1002.

968 Ryu J. S., Vigier N., Decarreau A., Lee S. W., Lee K. S., Song H. and Petit S. (2016)
 969 Experimental investigation of Mg isotope fractionation during mineral dissolution and
 970 clay formation. *Chem. Geol.* **445**, 135–145.

971 Saldi G. D., Jordan G., Schott J. and Oelkers E. H. (2009) Magnesite growth rates as a
 972 function of temperature and saturation state. *Geochim. Cosmochim. Acta* **73**, 5646–5657.

973 Saldi G. D., Schott J., Pokrovsky O. S., Gautier Q. and Oelkers E. H. (2012) An experimental
 974 study of magnesite precipitation rates at neutral to alkaline conditions and 100–200°C as
 975 a function of pH, aqueous solution composition and chemical affinity. *Geochim.*
 976 *Cosmochim. Acta* **83**, 93–109.

977 Saulnier S., Rollion-Bard C., Vigier N. and Chaussidon M. (2012) Mg isotope fractionation
 978 during calcite precipitation: An experimental study. *Geochim. Cosmochim. Acta* **91**, 75–
 979 91.

980 Schaef H. T., Mcgrail B. P., Loring J. L., Bowden M. E., Arey B. W. and Rosso K. M. (2013)
 981 Forsterite [Mg₂SiO₄] carbonation in wet supercritical CO₂: An in situ high-pressure X-
 982 ray diffraction study. *Environ. Sci. Technol.* **47**, 174–181.

983 Schaef H. T., Windisch C. F., McGrail B. P., Martin P. F. and Rosso K. M. (2011) Brucite
 984 [Mg(OH)₂] carbonation in wet supercritical CO₂: An in situ high pressure X-ray
 985 diffraction study. *Geochim. Cosmochim. Acta* **75**, 7458–7471.

986 Schauble E. A. (2011) First-principles estimates of equilibrium magnesium isotope

987 fractionation in silicate, oxide, carbonate and hexaaquamagnesium(2+) crystals.
 988 *Geochim. Cosmochim. Acta* **75**, 844–869.

989 Schott J., Mavromatis V., Fujii T., Pearce C. R. and Oelkers E. H. (2016) The control of
 990 carbonate mineral Mg isotope composition by aqueous speciation: Theoretical and
 991 experimental modeling. *Chem. Geol.* **445**, 120–134.

992 Shirokova L. S., Mavromatis V., Bundeleva I. A., Pokrovsky O. S., Bénézech P., Gérard E.,
 993 Pearce C. R. and Oelkers E. H. (2013) Using Mg Isotopes to trace cyanobacterially
 994 mediated magnesium carbonate Precipitation in alkaline lakes. *Aquat. Geochemistry* **19**,
 995 1–24.

996 Stamm F. M., Zambardi T., Chmieleff J., Schott J., von Blanckenburg F. and Oelkers E. H.
 997 (2019) The experimental determination of equilibrium Si isotope fractionation factors
 998 among H_4SiO_4^0 , H_3SiO_4^- and amorphous silica ($\text{SiO}_2 \cdot 0.32\text{H}_2\text{O}$) at 25 and 75°C using
 999 the three-isotope method. *Geochim. Cosmochim. Acta* **255**, 49–68.

1000 Subhas A.V., Adkins J.F., Rollins N.E., Naviaux J., Erez J., Berelson, W.M. (2017) Catalysis
 1001 and chemical mechanisms of calcite dissolution in seawater. *PNAS* **114**, 8175–8180.

1002 Sutradhar N., Sinhamahapatra A., Pahari S. K., Pal P., Bajaj H. C., Mukhopadhyay I. and
 1003 Panda A. B. (2011) Controlled synthesis of different morphologies of MgO and their use
 1004 as solid base catalysts. *J. Phys. Chem. C* **115**, 12308–12316.

1005 Tipper E. T., Gaillardet J., Louvat P., Capmas F. and White A. F. (2010) Mg isotope
 1006 constraints on soil pore-fluid chemistry: Evidence from Santa Cruz, California. *Geochim.*
 1007 *Cosmochim. Acta* **74**, 3883–3896.

1008 Tipper E. T., Lemarchand E., Hindshaw R. S., Reynolds B. C. and Bourdon B. (2012)
 1009 Seasonal sensitivity of weathering processes: Hints from magnesium isotopes in a glacial
 1010 stream. *Chem. Geol.* **312–313**, 80–92.

1011 Wang Z., Hu P., Gaetani G., Liu C., Saenger C., Cohen A. and Hart S. (2013) Experimental

1012 calibration of Mg isotope fractionation between aragonite and seawater. *Geochim.*
1013 *Cosmochim. Acta* **102**, 113–123.

1014 Wilson S. A., Barker S. L. L., Dipple G. M. and Atudorei V. (2010) Isotopic disequilibrium
1015 during uptake of atmospheric CO₂ into mine process waters: Implications for CO₂
1016 sequestration. *Environ. Sci. Technol.* **44**, 9522–9529.

1017 Wilson S. A., Dipple G. M., Power I. M., Barker S. L. L., Fallon S. J. and Southam G. (2011)
1018 Subarctic weathering of mineral wastes provides a sink for atmospheric CO₂. *Environ.*
1019 *Sci. Technol.* **45**, 7727–7736.

1020 Wilson S. A., Dipple G. M., Power I. M., Thom J. M., Anderson R. G., Raudsepp M., Gabites
1021 J. E. and Southam G. (2009) Carbon dioxide fixation within mine wastes of ultramafic-
1022 hosted ore deposits: Examples from the Clinton Creek and Cassiar Chrysotile deposits,
1023 Canada. *Econ. Geol.* **104**, 95–112.

1024 Wilson S. A., Harrison A. L., Dipple G. M., Power I. M., Barker S. L. L., Ulrich Mayer K.,
1025 Fallon S. J., Raudsepp M. and Southam G. (2014) Offsetting of CO₂ emissions by air
1026 capture in mine tailings at the Mount Keith Nickel Mine, Western Australia: Rates,
1027 controls and prospects for carbon neutral mining. *Int. J. Greenh. Gas Control* **25**, 121–
1028 140.

1029 Wilson S. A., Raudsepp M. and Dipple G. M. (2006) Verifying and quantifying carbon
1030 fixation in minerals from serpentine-rich mine tailings using the Rietveld method with
1031 X-ray powder diffraction data. *Am. Mineral.* **91**, 1331–1341.

1032 Wimpenny J., Gíslason S. R., James R. H., Gannoun A., Pogge Von Strandmann P. A. E. and
1033 Burton K. W. (2010) The behaviour of Li and Mg isotopes during primary phase
1034 dissolution and secondary mineral formation in basalt. *Geochim. Cosmochim. Acta* **74**,
1035 5259–5279.

1036 Wombacher F., Eisenhauer A., Heuser A. and Weyer S. (2009) Separation of Mg, Ca and Fe

1037 from geological reference materials for stable isotope ratio analyses by MC-ICP-MS and
 1038 double-spike TIMS. *J. Anal. At. Spectrom.* **24**, 627–636.
 1039 Zachmann D. and Johannes W. (1989) Cryptocrystalline magnesite. *Monogr. Ser. Miner.*
 1040 *Depos.* **28**, 15–28.
 1041 Zhang, J., Quay, P.D. and Wilbur, D.O. (1995) Carbon isotope fractionation during gas-water
 1042 exchange and dissolution of CO₂. *Geochim. Cosmochim. Acta* 59, 107-114.
 1043 Zhao L., Sang L. and Chen J. U. N. (2010) Aqueous carbonation of natural brucite: Relevance
 1044 to CO₂ sequestration. **44**, 406–411.
 1045
 1046
 1047
 1048
 1049
 1050

Figure Captions

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

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

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

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

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

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

1075

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

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

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

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

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

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

1084

1085

1086

1087

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

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

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

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

1091 ^cMineralogical composition determined by XRD as reported in Harrison et al. (2019). Nsq = nesquehonite; Dyp = dypingite. When more than one phase present, the dominant phase is reported
1092 first.

1093 **Electronic Annex 1.**

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

1096 **Electronic Annex 2.**

1097 Includes Table A1. Speciation of aqueous Mg and calculated isotopic composition of $\text{Mg}^{2+}_{(\text{aq})}$,
1098 $\Delta_{\text{calc}}^{26}\text{Mg}_{\text{solid}-\text{Mg}^{2+}}$, and $\Delta_{\text{meas}}^{26}\text{Mg}_{\text{solid}-\text{bulk fluid}}$ and Table A2. Fluid composition of all
1099 experimental timepoints.