Exchange and fractionation of Mg isotopes between epsomite and saturated MgSO$_4$ solution

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Received 26 July 2010; accepted in revised form 2 January 2011; available online 1 February 2011

Abstract

The equilibrium Mg isotope fractionation factor between epsomite and aqueous MgSO$_4$ solution has been measured using the three isotope method in recrystallization experiments conducted at 7, 20, and 40 °C. Complete or near-complete isotopic exchange was achieved within 14 days in all experiments. The Mg isotope exchange rate between epsomite and MgSO$_4$ solution is dependent on the temperature, epsomite seed crystal grain size, and experimental agitation method. The Mg isotope fractionation factors ($\Delta^{26}M_{\text{eps-sol}}$) at 7, 20, and 40 °C are 0.63 ± 0.07$, 0.58 ± 0.16$, and 0.56 ± 0.03$, respectively. These values are indistinguishable within error, indicating that the Mg isotope composition of epsomite is relatively insensitive to temperature. The magnitude of the isotope fractionation factor ($\Delta^{26}M_{\text{eps-sol}}$ = ca. 0.6$\%$ between 7 and 40 °C) indicates that significant Mg isotope variations can be produced in evaporite sequences, and Mg isotopes may therefore constrain the degree of closed-system behavior, paleo-humidity, and hydrological history of evaporative environments.

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1. INTRODUCTION

Magnesium sulfates are highly soluble minerals, and some forms of Mg sulfate (epsomite: MgSO$_4$·7H$_2$O, hexahydrite: MgSO$_4$·6H$_2$O and kieserite: MgSO$_4$·H$_2$O) are widespread and occur in Phanerozoic evaporate sequences (e.g., Hardie, 1990). Magnesium sulfate is also present on the surface of Mars, where, for example, up to 36 wt.% sulfate has been found in some outcrops on the Martian surface, of which Mg sulfate is the most abundant (Clark et al., 2005). On the Martian surface, sulfates are a major water reservoir and thus it is inferred that at least at one point in time aqueous alteration occurred on parts of the Martian surface (e.g., Wang et al., 2008).

High-precision measurements of stable Mg isotopes indicate that this isotope system holds great promise to fingerprint various geological and biogeochemical processes (e.g., Galy et al., 2002; Chang et al., 2004; Young and Galy, 2004; Pearson et al., 2006; Tipper et al., 2006; Pogge von Strandmann, 2008; Hippler et al., 2009; Shen et al., 2009; Bolou-Bi et al., 2010; Higgins and Schrag, 2010; Li et al., 2010). The majority of stable Mg isotope studies to date have focused on natural samples, and relatively few experimental determinations of stable Mg isotope fractionation factors have been made (e.g., Kisakurek et al., 2009; Immenhauser et al., 2010). There have been no studies of the isotopic fractionation of Mg between sulfates and saturated solutions.

In this study, a recrystallization approach was used to determine the equilibrium Mg isotope fractionation factor between solid and aqueous phases of MgSO$_4$ at 7, 20, and 40 °C. A $^{26}$Mg-enriched tracer was used to constrain the rate and extent of isotopic exchange between the two phases, following the “three-isotope exchange method” that has been applied to oxygen and iron isotope systems (e.g., Matsuhisa et al., 1978; Matthews et al., 1983a,b; Shahar et al., 2008; Beard et al., 2010). This study is the first to apply the “three-isotope exchange method” to the Mg isotope system at low temperature. Our results demonstrate...
that the isotopic exchange between epsomite and solution is rapid and that heavier Mg isotopes preferentially partition into epsomite relative to the solution under equilibrium conditions.

2. ANALYTICAL METHODS

Magnesium isotope measurements were made using a Micromass IsoProbe MC-ICP-MS, a single-focusing mass spectrometer that uses a collision cell to thermalize the ion beam. Helium was used as the collision gas for thermalization and H₂ was used as a reactive gas to minimize isobaric interferences at masses 25 and 26, which are thought to be ¹⁹H¹⁸O, ¹²C²H₂, and ¹²C¹⁴N, respectively. Because these samples are enriched in ²⁵Mg, complete washout between samples that have large differences in Mg isotope composition by up to ~20% in ²⁵Mg/²⁴Mg is critical, and thus we employ the methods developed by Beard et al. (2010) to minimize wash-out effects by using a wet plasma and reducing the cone voltage of the IsoProbe. Magnesium solutions were introduced into the Ar plasma using a self-generated plasma. Dilution of magnesium solutions was carried out with 0.3 ppm Mg using a soft aspirating 100 μL/min nebulizer tip and a cyclonic spray chamber cooled to 5 °C, and the cone voltage was set to 50–80 V. These conditions produce a total Mg ion intensity of 5×10⁻⁸ A using a 3 ppm Mg solution. Washout between samples used a 2% HNO₃ solution for 6 min. Overall, the “on-peak” blank acid produced a typical ion intensity of 1.2×10⁻¹⁴, -1.7×10⁻¹⁶, and -7.8×10⁻¹⁶ A at masses 25, 24, and 26, respectively that did not change during an analytical session.

Magnesium isotope ratios were determined using a sample-standard bracketing technique. Samples were typically diluted to 3 ppm ±5%. Matrix effects associated with Mg concentration were corrected by analysis of the standard solution diluted over a range of 1.5–4.5 ppm Mg, following methods discussed by Albarède and Beard (2004), which typically resulted in a correction of less than 0.02‰ in ²⁶Mg/²⁴Mg for the samples. Isotope ratios are subtracted for on-peak zeros using a 30 s on-peak acid blank measurement prior to forty 10-s on-peak integrations of the analyte solution. This measurement routine results in a typical internal (2 standard error) precision of better than ±0.04‰ in ²⁶Mg/²⁴Mg and ±0.02‰ for ²⁵Mg/²⁴Mg.

Prior to isotope analysis, saturated MgSO₄ solutions or epsomite samples were dissolved in 200 μL 0.2 M HCl and loaded onto an ion-exchange column that contained 0.3 mL of Biorad AG MP-50 cation exchange resin that had been pre-conditioned with 2 mL 0.2 M HCl. Sulfate was eluted using 3 mL 0.2 M HCl, and Mg²⁺ was quantitatively removed using 3 mL 6 M HCl. The MgCl₂ solution was heated at 120 °C with five drops of concentrated HNO₃ and three drops of 30% H₂O₂ to dryness three times to convert the Mg salt into the nitric form. Recovery of Mg was ~90% and yields were determined spectrophotometrically using the calmagite colorimetric method (Chauhan and Ray Sarkar, 1969). We note that the slightly less than 100% recovery may be caused by bubbling during H₂O₂ treatment, and therefore does not reflect loss on the columns.

We evaluated this ion-exchange method for bias in Mg isotope data by analysis of an in-house Mg standard solution that was passed through the ion-exchange column procedure, and the measured isotopic composition of these samples match the isotopic composition of this standard (Table 1). Moreover, we evaluated matrix effects by spiking the ultrapure Mg standard solution with H₂SO₄ to produce a solution with a ~1.5:1 M sulfate to Mg ratio, and this purified solution matches the Mg isotope composition of the unadulterated sample. Total Mg procedural blanks were determined using isotope dilution and a ²⁶Mg spike, and were 9.4 ± 3.7 ng (2 S.D., n = 2), which is negligible (<0.1% of the Mg in a sample). Accuracy and external precision of Mg isotope ratio measurements were evaluated by analysis of four ultrapure Mg standard solutions that defined a ~3‰ spread in ²⁶Mg/²⁴Mg (Table 1). The external long-term reproducibility (2 S.D) of this technique is better than 0.15‰ for ²⁶Mg/²⁴Mg and 0.1‰ for ²⁵Mg/²⁴Mg, as determined by replicate analyses of the four ultrapure Mg standard solutions. The accuracy of this method is shown by the reproducibility of the Mg isotope composition of two recognized Mg isotope standards, DSM3 and Cambridge (Galy et al., 2003; Table 1), as well as 10 analyses of in-house Mg standard that were processed through the entire analytical method that produced the same isotopic composition as the pure solution (Table 1).

Magnesium isotope compositions are reported using the standard per mil (‰) notation of δ²⁶Mg and δ²⁵Mg for the ²⁶Mg/²⁴Mg and ²⁵Mg/²⁴Mg isotope ratios, respectively, where

\[ \delta^{26}\text{Mg} = \left( \frac{^{26}\text{Mg}_{\text{sample}}}{^{26}\text{Mg}_{\text{DSM3}}} \right) - 1 \times 1000 \] (1)

\[ \delta^{25}\text{Mg} = \left( \frac{^{25}\text{Mg}_{\text{sample}}}{^{25}\text{Mg}_{\text{DSM3}}} \right) - 1 \times 1000 \] (2)

DSM3 is the international Mg isotope standard (Galy et al., 2003). Fractionation in Mg isotope compositions between two phases A and B is expressed as:

\[ \Delta^{26}\text{Mg}_{A-B} = \delta^{26}\text{Mg}_{A} - \delta^{26}\text{Mg}_{B} \approx 10^3 \ln \left( \frac{^{26}\text{Mg}_{A}}{^{26}\text{Mg}_{B}} \right) \] (3)

\[ \Delta^{25}\text{Mg}_{A-B} = \delta^{25}\text{Mg}_{A} - \delta^{25}\text{Mg}_{B} \approx 10^3 \ln \left( \frac{^{25}\text{Mg}_{A}}{^{25}\text{Mg}_{B}} \right) \] (4)

Note that the Δ²⁵Mg� defined here is different from the Δ²⁵Mg parameter, which has been used to discern the existence of radiogenic ²⁶Mg* due to decay of the short-lived ⁶⁰Fe in meteorites, or to evaluate subtle differences between equilibrium and kinetic mass-dependent fractionation laws (e.g., Young et al., 2002; Young and Galy, 2004).

3. EXPERIMENT DESIGN

We employed a “three-isotope” method (e.g., Matsuhisa et al., 1978; Matthews et al., 1983a,b; Shahar et al., 2008; Beard et al., 2010) to evaluate the Mg isotope exchange kinetics and approach to Mg isotope equilibrium between epsomite and saturated MgSO₄ solutions at 7, 20, and 40 °C. Magnesium isotope exchange was promoted by a recrystallization process, where fine-grained epsomite seed crystals were suspended in saturated MgSO₄ solutions and the epsomite crystals recrystallized into coarser grains. This recrystallization process is termed “Ostwald ripening”,
where the growth of larger crystals occurs through dissolution of smaller crystals (e.g., Stoffregen et al., 1994). It is important to note that the concentration of the MgSO₄ solution did not change with time in these experiments, indicating that there was no net mass transfer of Mg. This recrystallization experimental technique is an excellent method for promoting equilibrium isotope exchange because recrystallization experiments are less likely to incorporate kinetic effects relative to those that employ a simple synthesis approach, as the free-energy changes that drive recrystallization tend to be much smaller, on the order of those associated with isotopic exchange (Matthews et al., 1983a). Moreover, this recrystallization approach is the only effective way to attain isotope exchange at low temperatures (<100 °C), because isotope exchange via solid-state diffusion is only practical at high temperatures.

The three-isotope method involves isotope exchange between two components, where one component contains “normal” Mg and the other component is enriched in ²⁵Mg. On a δ²⁵Mg-δ²⁶Mg diagram, all terrestrial samples that have normal Mg isotope compositions plot on a line with a slope of about 0.52, which is defined as the primary or terrestrial fractionation line (for more details, see Young and Galy, 2004). The component that has natural Mg plots on the terrestrial fractionation line, but the component that is spiked with ²⁵Mg does not (Fig. 1). As the two components undergo isotopic exchange, their isotopic compositions evolve toward isotopic equilibrium. At isotopic equilibrium, the two components will lie along a secondary mass-fractionation line that is parallel to the terrestrial fractionation line, whose position on a δ²⁵Mg-δ²⁶Mg plot is dictated by the isotopic mass balance of the two components (Fig. 1). In our experiments we used an enriched ²⁵Mg isotope tracer, where a ²⁵Mg-enriched MgSO₄ solution was reacted with epsomite that had “normal” isotope composition, as well as the reverse, where the MgSO₄ solution with “normal” isotope composition was reacted that had ²⁵Mg-enriched epsomite. The enriched ²⁵Mg spike (²⁵Mg: 0.80%, ²⁶Mg: 98.88%, ²⁴Mg: 0.32%) was obtained from Oak Ridge National Lab. The spike and natural Mg were mixed with a ratio of about 1:500 for preparing the spiked starting material that had a δ²⁵Mg value of ca. 19‰. The amount of ²⁶Mg and ²⁴Mg from the spike is negligible compared to the bulk Mg and the ²⁶Mg/²⁴Mg ratio of the natural Mg is basically unchanged after spiking (<0.3‰ shift).

The recrystallization experiments were carried out at three different temperatures (7 °C: Experiments 7A, 7B; 20 °C: Experiments 20A, 20B; 40 °C: Experiments 40A, 40B, Fig. 2 and Table 2), using both the normal epsomite (A-series) and ²⁵Mg-enriched epsomite (B-series) for the starting crystals. All experimental reagents were thermally stabilized for 2 days before mixing. Experiments at 7 and 20 °C were carried out in a walk-in refrigerator and air-conditioned room, respectively. The temperature variation during the experiments at 7 and 20 °C was monitored with thermometers and estimated to be ±1 °C. Based on the solubility data for epsomite (Archer and Rard, 1998; Mullin, 2001), a 2 °C variation in temperature would cause the Mg concentration of the MgSO₄ solution to vary by 3.2‰ at 7 °C and 2.7‰ at 20 °C. These variations lie within the range of the direct measurement of Mg concentration of the MgSO₄ solution using isotope dilution (shown in the following section), indicating no significant net dissolution or precipitation, despite extensive recrystallization. Experiments at 40 °C were carried out in a water bath where temperature varied less than ±0.1 °C.

Each experiment used 10–20 centrifuge tubes of identically prepared mixtures of crystals and solution, where individual tubes were sacrificed and sampled for isotopic analysis for time-series sampling. Centrifuge tubes were sealed to minimize fluid loss during re-crystallization, and tests showed that the daily loss of H₂O was <0.05 mg at 7 °C, <0.2 mg at 20 °C, and <0.4 mg at 40 °C. Net
extrapolation of the time-series ($t$isotopic compositions at 100% exchange ($t$the system. If the isotopic exchange is slow and incomplete, the fractionation line is controlled by the isotopic mass balance of fractionation line. Note that the position of the secondary fractionation line, which is parallel to the terrestrial fractionation line due to the presence of a $^{25}$Mg spike. As isotopic exchange between the two phases proceeds, the isotopic compositions of the two evolve toward a value that reflects 100% isotopic exchange between the two phases proceeds, the isotopic

tF) can be obtained by extrapolation of the time-series ($t_0$, $t_1$, $t_2$, ...) isotope data to the secondary fractionation line. If isotopic exchange occurs under equilibrium conditions, the extrapolated value at 100% exchange will be equal to the equilibrium isotope fractionation factor.

precipitation of epsomite caused by leaking of water vapor are therefore, insignificant relative to the large weight of the starting MgSO_4 solution (>350 mg). Each centrifuge tube was loaded with 0.10–0.13 g of epsomite, and between 0.2 and 0.4 mL of saturated MgSO_4 solution; all weights and volumes were measured precisely to monitor mass balance. The variation in the molar ratio of Mg contained in epsomite and saturated MgSO_4 solution in different centrifuge tubes was <2%. Centrifuge tubes were constantly mixed on a roller or an orbital shaker, and Table 2 contains a summary of experimental conditions.

Centrifuge tubes were sampled in a time series in an exponential fashion (e.g., 1 day, 2 day, 4 day, 8 days ...), and most samples were duplicated at each time. Separation of the supernatant from the epsomite was initially carried out by centrifugation (5000 rpm for >5 min). Supernatant was then extracted and filtered using a 0.45 μm nylon syringe filter to ensure that the MgSO_4 solution was free of epsomite. Epsomite retained in the centrifuge tubes was washed twice with 0.7 mL 40% (vol/vol) ethanol solution, followed by shaking, centrifugation and removal of the ethanol; washing with 40% ethanol is essential for removing the interstitial MgSO_4 solution with negligible dissolution of epsomite crystals. For experiments at 7 and 20 °C, these procedures were carried out in a walk-in refrigerator and air-conditioned room, respectively, at the same temperatures of the experiments. For experiments at 40 °C, separation was carried out in an oven with temperature set at 40 °C. In all cases, the centrifuge, all the syringes, filters and the ethanol solution were equilibrated at the experiment temperature for >5 h prior to separation. The washed epsomite was split into two aliquots; one aliquot was used for XRD analysis, which confirmed that all reacted solids were epsomite, and the other aliquot was dissolved in 0.2 mL of 0.2 M HCl and processed through ion-exchange columns for Mg isotope analysis.

Commercially available epsomite is too coarse-grained (0.1–1 mm diameter) to permit recrystallization on reasonable experimental time-scales, and reduction in size via grinding is not practical because crushing produces a phase transition from epsomite (MgSO_4·7H_2O) to hexahydrite (MgSO_4·6H_2O), as well as a heterogeneous size distribution (Electronic Appendix 1). We therefore, developed two methods to synthesize fine-grained epsomite of relatively uniform grain size. One method produced finer-grained epsomite than the other. In general, epsomite was synthesized by preparing a saturated MgSO_4 solution at 20 ± 1 °C, followed by initiation of precipitation by addition of 100% ethanol to the solution while the material was being sonicated in an ultrasonicator. Ethanol has a high affinity for H_2O, which induces oversaturation and epsomite precipitation; ultrasonic agitation suspended the newly-formed epsomite crystals into the bulk ethanol solution, which produced a fine-grained and homogeneous epsomite suspension of small crystals. The different epsomite grain sizes were produced by using different rates of ethanol addition to the saturated MgSO_4 solution and the manner in which...
the ethanol plus MgSO₄ solution was mixed via shaking and ultrasonication. Fine-grained epsomite was synthesized by adding 0.6 mL of saturated MgSO₄ solution to 30 mL of ethanol over 6 min in an ultrasonic bath, following by 40 min of ultrasonic treatment. This finer-grained epsomite was made using Mg that had a “normal” Mg isotope composition and the average grain size was 2–5 μm (see below). The coarser-grained epsomite was made using a ²⁵Mg-enriched solution. This epsomite was synthesized by adding 30 mL of ethanol to 3 mL of the saturated ²⁵Mg-enriched MgSO₄ solution and shaking, followed by ultrasonication for 25 min. This technique produced epsomite that had an average grain size of 30–50 μm.

All synthesized epsomite was separated from the solution by transferring the mixture to 30 mL centrifuge tubes and centrifuging at 4500 rpm for 10 min. The solution was decanted, and the epsomite was dried by purging the headspace with N₂ gas flowing at 10 mL/min. In order to avoid phase transformation, the N₂ gas was initially bubbled through a saturated aqueous NaCl solution at 20°C, which buffers the gas to a humidity of 76%, which is within the stability field of epsomite (Electronic Appendix 2; Fig. 2). Gas purging was done until the weight of the centrifuge tube was constant to within ±5 mg, which took approximately 7 days.

The synthesized materials before and after N₂ purging were confirmed to be pure epsomite by XRD analysis. We were not able to determine the surface area of the epsomite by BET because epsomite looses water and transforms to other phases rapidly under vacuum. We therefore, determined the approximate size of epsomite via SEM and optical microscopy (Electronic Appendix 3; Fig. 3), which showed that the finer-grained, isotopically “normal” epsomite varied between 0.5 and 10 μm in size of the elongated dimension (average 2–5 μm). The coarser-grained, ²⁵Mg-enriched epsomite varied between 5 and 100 μm in size of the elongated dimension (average 30–50 μm). No fluid inclusions were observed in the epsomite crystals.

### 4. RESULTS

The grain size of the epsomite increased significantly during the experiments (Fig. 3). Growth of epsomite was continuous throughout the experiment period, although the most dramatic change in grain size occurred at the beginning of the experiments. For example, in Experiment 20A (normal epsomite + spiked solution at 20°C; Table 2), the grain size of epsomite increased from 2–5 μm to ca. 20 × 100 μm after 1 day, further grew up to 50 × 150 μm after 4 days, and after 65 days the average size of the epsomite grains were about 200 × 500 μm. The growth of epsomite in Experiment 20B is similar except that the grain size was relatively larger in the early stages of the recrystallization experiment (Fig. 3), which is likely due to the larger starting grain size. Recrystallization at 40°C produced the most rapid increase in crystal size. At this temperature, the epsomite grains after 15 days of recrystallization were larger than the epsomite grains after 60 days of recrystallization at 20°C (Table 2). Growth of epsomite at 7°C was the slowest. The morphology of the recrystallized epsomite at 7°C was also distinct, and had

<table>
<thead>
<tr>
<th>Experiment series ID</th>
<th>Temperature (°C)</th>
<th>Agitation method</th>
<th>Starting material</th>
<th>Initial average epsomite crystal size (μm)</th>
<th>Final average epsomite crystal size (μm)</th>
<th>Molar ratio of magnesium Mg₂₅/Mg₅₀⁺</th>
<th>Molar ratio of magnesium Mg₂₅/Mg₅₀⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>7A</td>
<td>7 ± 1</td>
<td>Roller</td>
<td>Isotopically normal epsomite + spiked MgSO₄ solution</td>
<td>2–5</td>
<td>150 × 700 μm @ 31 days</td>
<td>1.36 ± 0.04</td>
<td>1.56 ± 0.04</td>
</tr>
<tr>
<td>7B</td>
<td>7 ± 1</td>
<td>Roller</td>
<td>Spiked epsomite + isotopically normal MgSO₄ solution</td>
<td>30–50</td>
<td>100 × 500 μm @ 15 days</td>
<td>1.36 ± 0.04</td>
<td>1.56 ± 0.04</td>
</tr>
<tr>
<td>20A</td>
<td>20 ± 1</td>
<td>Roller</td>
<td>Isotopically normal epsomite + spiked MgSO₄ solution</td>
<td>2–5</td>
<td>300 × 800 μm @ 65 days</td>
<td>1.83 ± 0.04</td>
<td>1.85 ± 0.02</td>
</tr>
<tr>
<td>20B</td>
<td>20 ± 1</td>
<td>Roller</td>
<td>Spiked epsomite + isotopically normal MgSO₄ solution</td>
<td>30–50</td>
<td>300 × 800 μm @ 64 days</td>
<td>2.35 ± 0.04</td>
<td>2.35 ± 0.04</td>
</tr>
<tr>
<td>40A</td>
<td>40 ± 0.1</td>
<td>Orbital shaker</td>
<td>Isotopically normal epsomite + spiked MgSO₄ solution</td>
<td>2–5</td>
<td>300 × 1000 μm @ 16 days</td>
<td>2.35 ± 0.04</td>
<td>2.35 ± 0.04</td>
</tr>
<tr>
<td>40B</td>
<td>40 ± 0.1</td>
<td>Orbital shaker</td>
<td>Spiked epsomite + isotopically normal MgSO₄ solution</td>
<td>30–50</td>
<td>300 × 1000 μm @ 15 days</td>
<td>2.35 ± 0.04</td>
<td>2.35 ± 0.04</td>
</tr>
</tbody>
</table>
more elongated shapes than epsomite produced in the 20 and 40 °C experiments (Table 2).

The concentration of Mg in the solutions for all experiments remained constant within the uncertainty of the concentration estimates based on Mg ion intensity during isotopic analysis and by spectrophotometry. This uncertainty was likely ±10% to 20% when considering dilution errors associated with the highly concentrated MgSO₄ solutions. In order to more rigorously evaluate if there was net mass transfer during the re-crystallization experiments, a series of normal epsomite and normal saturated MgSO₄ solutions were prepared and allowed to recrystallize over the same time duration as the 25Mg-enriched experiments and the concentration of the MgSO₄ solution was measured using isotope dilution mass spectrometry. These high-precision concentration measurements show that there was no variability in the Mg concentration, confirming that there was no net mass transfer in the recrystallization experiments (Fig. 4).

The Mg isotope compositions of epsomite and MgSO₄ solution in the recrystallization experiments varied with time, and the general temporal trends of δ²⁶Mg and δ²⁵Mg values for epsomite and MgSO₄ solutions were very similar (Figs. 5–7; Electronic Appendix 4). Generally speaking, the starting epsomite and MgSO₄ solution had similar δ²⁶Mg values (ca. −0.4 to −0.5‰) and these diverged within 1–7 days, and remained constant at δ²⁶Mgₑps = −0.1 to −0.2‰ and δ²⁶Mgₑsol = −0.7 to −0.8‰ for the remainder of the

Fig. 3. Photomicrographs of representative epsomite grains at different time points for experiments run at 20 °C.
experiments. Correspondingly, the Mg isotope fractionation factors ($\Delta^{26}\text{Mgeps–sol}$) increased from $/C^{24}_0$ to $/C^{24}_0.6$ after 1–7 days and stabilized afterwards. By contrast, the starting epsomite and MgSO$_4$ solution had distinct $\delta^{25}\text{Mg}$ values and these values converged within 1–7 days and then remained constant during additional re-crystallization. For A-series experiments (7A, 20A, and 40A), the $^{25}\text{Mg}$-enriched starting MgSO$_4$ solutions had an initial $\delta^{25}\text{Mg}$ value of 18–19‰ and a Mg molar proportion of 61–70%, relative to that of the initial epsomite ($\delta^{25}\text{Mg} = -0.27 \pm 0.10\%_\text{oo}$, Mg molar proportion of 30–39%), and these values converged towards 11–12‰. For B-series experiments (7B, 20B, and 40B), the $^{25}\text{Mg}$-enriched starting epsomite had an initial $\delta^{25}\text{Mg}$ value of 18.74 ± 0.06‰, and a molar proportion of 30–39% relative to that of the starting MgSO$_4$ solution ($\delta^{25}\text{Mg} = -0.2$ to $-0.3\%_\text{oo}$, Mg molar proportion of 61–70%), and these values converged towards 5–6‰. Changes in $\delta^{25}\text{Mg}$ values were accompanied by changes in the apparent measured Mg isotope fractionation factors, where the initial $\Delta^{25}\text{Mgeps–sol}$ changed from $\sim -19\%_\text{oo}$ (for A-series experiments) or $\sim 19\%_\text{oo}$ (for B-series experiments) to $\sim 0.3\%_\text{oo}$ at the end of the experiments.

Despite the similarity in the general temporal trends of $\delta^{26}\text{Mg}$ and $\delta^{25}\text{Mg}$ values in the experiments, there are differences in the time over which $\delta^{26}\text{Mg}$ and $\delta^{25}\text{Mg}$ values of the epsomite and MgSO$_4$ solution converged to constant values. In general, for a given temperature, it took less time
for the $\delta^{26}\text{Mg}$ and $\delta^{25}\text{Mg}$ values to stabilize in experiment series A. For the same experiment series (either A or B), the experiments at 20°C reached a stable isotopic composition faster than those at 7°C. Quantitative discussion of the isotope exchange in these experiments is provided in the next section.

5. DISCUSSION

5.1. Kinetics of Mg isotope exchange

The kinetics of Mg isotope exchange between solution and epsomite were constrained using $^{25}\text{Mg}$-enriched tracers. Following approaches taken by previous studies (e.g., Johnson et al., 2002; Welch et al., 2003), the degree of isotope exchange toward isotopic equilibrium is defined by:

$$F = (\delta_t - \delta_i)/(\delta_e - \delta_i)$$

where $\delta_i$ is the isotopic composition at a given time $t$, and $\delta_t$ and $\delta_e$ are the initial and equilibrium isotopic compositions, respectively. In a two-component isotope exchange experiment, $F$ can be calculated from the isotopic compositions of either phase and the two $F$ values are expected to be the same. In this study, calculation of $F$ using $\delta^{25}\text{Mg}$ data from epsomite or MgSO$_4$ solution yields consistent results (Electronic Appendix 4). The $\delta_e$ value is determined from the isotopic mass-balance of the starting materials and further corrected for mass-dependent isotopic fractionation between epsomite and MgSO$_4$ solution by iteration (Matthews et al., 1983b). In our previous work (e.g., Johnson et al., 2002; Welch et al., 2003) we did not make this correction because the isotopic contrast between the two components was much greater ($\sim 460\permil$ per mass unit difference) as compared to this study, where the isotopic contrast was only $\sim 19\permil$ per mass unit difference.

Substituting $F$ into the general rate equation produces:

$$-d(1 - F)/dt = k_n(1 - F)^n$$

where $k_n$ is the rate constant and $n$ is the order of the reaction that is generally an integer from 0 to 3. Most isotope exchange reactions have been reported to follow a first-order ($n = 1$) or second-order ($n = 2$) rate law (e.g., Huang and Tsai, 1970; Graham, 1981; Criss et al., 1987; Johnson et al., 2002; Welch et al., 2003). The integrated forms of the first-order and second-order rate functions are:

$$\ln(1 - F) = -k_1t$$

for $n = 1$

$$F/(1 - F) = k_2t$$

for $n = 2$

Fig. 6. Plots of $\delta^{26}\text{Mg}$ and $\delta^{25}\text{Mg}$ values of epsomite and MgSO$_4$ solution, as well as $\Delta^{26}\text{Mg}_{\text{eps-sol}}$ and $\Delta^{25}\text{Mg}_{\text{eps-sol}}$ fractionations, as a function of time for experiments at 20°C. The solid lines show the values of $\delta^{25}\text{Mg}_{\text{eps}}$, $\delta^{25}\text{Mg}_{\text{sol}}$ and $\Delta^{25}\text{Mg}_{\text{eps-sol}}$ predicted using the second-order rate constant obtained by regression (for details, see Section 5.1).
The Mg isotope exchange data in this study are better fit by a second-order rate law than a first-order law (Fig. 8). An intercept at $t = 0$ of zero is required for both a 1st and 2nd order rate law, and for Experiment 7B, the $R^2$ of regressions with a zero intercept are 0.12–0.29 for first-order rate law and 0.77–0.99 for second-order rate law. The rate constants for the different recrystallization experiments were obtained by regression of the best-fitting second-order rate function, and the rate constants are tabulated in Table 3. In each experiment, the reaction constants calculated from $F$ values were used to construct the theoretical values of $\delta^{26}\text{Mg}_{\text{epsi}}, \delta^{25}\text{Mg}_{\text{solute}}$ and $\Delta^{26}\text{Mg}_{\text{epsi-sol}}$ with time. The calculated curves match the measured data points well (Figs. 5–7).

A detailed discussion of the implications of first- or second-order rate laws as applied to the current experiments is beyond the scope of this paper, and instead we use the derived rate constants to address the question of equilibrium or kinetic isotope fractionation upon isotopic exchange. Although the “three-isotope method” is an excellent approach for determining the extent of isotopic exchange, it does not strictly prove attainment of isotopic equilibrium. For example, if 100% exchange occurs via very rapid dissolution and re-precipitation, it is possible that the measured isotopic fractionation reflects a kinetic isotope effect imposed by limits of ion dehydration and advancing crystallization fronts, which produce isotopic gradients in solution. It is important to stress that 100% isotopic exchange is not the same as attainment of equilibrium, mass-dependent isotopic fractionation if exchange occurred under kinetically controlled conditions, and there is some confusion on these points in the literature. It is certainly possible, for example, that the increase in crystal size that occurs during Ostwald ripening could occur quickly enough so that Mg isotope equilibrium between the crystal surface and the fluid was not maintained. Such a condition could produce isotopic compositions that plot on the secondary fractionation line (Fig. 1), indicating 100% exchange, but $\Delta^{26}\text{Mg}_{A-B}$ and $\Delta^{25}\text{Mg}_{A-B}$ fractionation factors could reflect, at least in part, kinetic fractionations.

We assess the possibility that complete or near-complete Mg isotope exchange was associated with kinetic, mass-dependent fractionation through comparison of the second-order rate constants and the experiment conditions in terms of grain size of epsomite, temperature, and agitation methods. Under the same temperature and agitation methods, experiments that used finer-grained starting epsomite yielded higher rate constants than experiments that...
involved coarser-grained epsomite. For example, $k_{7a}$ is about 6–7 times greater than $k_{7b}$, and $k_{20a}$ is about 4–5 times greater than $k_{20b}$ (Table 3), and this correlates with the smaller initial epsomite crystals of Experiments 7A and 20A (Table 1). Comparison of the same starting epsomite crystal size and agitation method, isotopic exchange was faster at higher temperature (Table 3). Relations between rates of isotope exchange and crystal size and temperature are well documented in the literature (e.g., Matthews et al., 1983b; Zhang, 2008). Finally, the mechanism of agitation can have an influence on the rate constant. Agitation was used in all experiments to minimize generation of static boundary layers or pore volumes. The high temperature (40°C) experiments required an orbital shaker, whereas the lower temperature experiments were better suited to use of a horizontal roller. The rate constant for Experiment 40B is higher than the 20B and 7B experiments which would be predicted based on temperature changes. However, for 40A, the rate constant is low relative to that expected for the high temperature conditions (Table 3) and this may be due to compaction that may have preferentially occurred for finer-grained epsomite crystals coupled with the lower suspension efficiency of the orbital shaker compared to the roller. Once compaction occurs, the surface area available for isotope exchange would be significantly limited.

5.2. Mg isotope fractionation factor between epsomite and saturated MgSO$_4$ solution

The three-isotope method permits determination of the isotope fractionation factor in a two-component system that has undergone partial isotopic exchange through extrapolation to a fractionation factor at 100% exchange (e.g., Matsuhisa et al., 1978; Matthews et al., 1983a,b). Extrapolation is generally illustrated on a three-isotope plot, which in the case of Mg, would be a $^{26}\text{Mg}/^{24}\text{Mg}-^{25}\text{Mg}/^{24}\text{Mg}$ diagram, through projection of exchange trajectories from initial compositions to a secondary mass-fractionation line (Electronic Appendix 5); numerous examples of this approach exist for O and Fe isotopes (e.g., Matsuhisa et al., 1978; Matthews et al., 1983a,b; Shahar et al., 2008; Beard et al., 2010). Uncertainties, however, are introduced using a traditional three-isotope plot if different time points have changes in molar mass balance between the two components, as may occur, for example, in non-representative sampling of a single large reactor, or if different reactors are used for each time point and there is some variability in initial moles of reactants. In this study, we recast the three-isotope exchange rates in terms of fraction of exchange (F) for the two components, which eliminates variability due to small differences in the Mg molar ratio of epsomite and solution for each reactor. Extrapolation of the $^{26}\text{Mg}$ values of epsomite and MgSO$_4$ solutions to an F value of 100 percent isotope exchange permits a rigorous determination of the Mg isotope fractionation factor and associated uncertainties (Fig. 9 and Table 3).

<table>
<thead>
<tr>
<th>Experiment ID</th>
<th>Second-order rate law constant (day$^{-1}$)</th>
<th>Isotope fractionation factor</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>K</td>
<td>1 SE</td>
</tr>
<tr>
<td>7A</td>
<td>Solution: 7.18</td>
<td>2.07</td>
</tr>
<tr>
<td></td>
<td>Epsomite: 9.88</td>
<td>2.02</td>
</tr>
<tr>
<td>7B</td>
<td>Solution: 1.36</td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td>Epsomite: 1.26</td>
<td>0.04</td>
</tr>
<tr>
<td>20A</td>
<td>Solution: 11.68</td>
<td>1.67</td>
</tr>
<tr>
<td></td>
<td>Epsomite: 12.85</td>
<td>3.97</td>
</tr>
<tr>
<td>20B</td>
<td>Solution: 3.10</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td>Epsomite: 2.38</td>
<td>0.51</td>
</tr>
<tr>
<td>40A</td>
<td>Solution: 3.89</td>
<td>0.11</td>
</tr>
<tr>
<td></td>
<td>Epsomite: 2.97</td>
<td>0.68</td>
</tr>
<tr>
<td>40B</td>
<td>Solution: 4.37</td>
<td>0.20</td>
</tr>
<tr>
<td></td>
<td>Epsomite: 6.63</td>
<td>1.17</td>
</tr>
</tbody>
</table>
As shown in Table 3, for experiments at the same temperature, the $\Delta^{26}\text{Mg}_{\text{eps-sol}}$ values are indistinguishable within error, despite the many-fold difference in the exchange-rate constants. Kinetic effects on oxygen isotope fractionation during carbonate synthesis have been recognized to correlate with precipitation rates (e.g., de Villiers et al., 1995; Kim et al., 2006, 2009; Dietzel et al., 2009), and Ca isotope fractionation factors during calcite precipitation have been interpreted to be related to precipitation rates, reflecting kinetic isotope effects (Lemarchand et al., 2004). The independence of the $\Delta^{26}\text{Mg}_{\text{eps-sol}}$ fractionations relative to reaction rate implies attainment of isotopic equilibrium in these experiments. We note that it is not possible to infer kinetic versus equilibrium fractionation based on differences in mass-dependent $^{26}\text{Mg}/^{24}\text{Mg} - ^{25}\text{Mg}/^{24}\text{Mg}$ fractionation lines (e.g., Young et al., 2002; Young and Galy, 2004) because we used enriched isotope tracers.

The $\Delta^{26}\text{Mg}_{\text{eps-sol}}$ fractionations at different temperatures are essentially indistinguishable within error (Table 3). Combining the results from A and B-series experiments, the $\Delta^{26}\text{Mg}_{\text{eps-sol}}$ fractionation is $0.63 \pm 0.07\%_\text{o}$ at 7 °C, $0.58 \pm 0.16\%_\text{o}$ at 20 °C and $0.56 \pm 0.03\%_\text{o}$ at 40 °C. The relative insensitivity of the $\Delta^{26}\text{Mg}_{\text{eps-sol}}$ fractionation factor to temperature likely reflects the small magnitude of the fractionation factor at low temperatures. Equilibrium isotope fractionations generally decrease as temperature
increases, in proportion to 1/T² for most cases (Bigeleisen and Mayer, 1947; Urey, 1947; O’Neil, 1986; Schauble, 2004). The function of the best-fitting regression line for the data in a Δ²⁶Mg–1/T² diagram (Fig. 10), assuming zero fractionation at infinite temperature, is:

$$\Delta^{26}\text{Mg}_{\text{eps-sol}} = 0.0510(±0.0026) \times 10^6/1^2$$

(9)

This function should be valid for extrapolating to different temperatures, assuming a 1/T² relation is valid and that there are no reversals in the epsomite-solution fractionation factor. Note that in practice, T should be confined to the stability region of epsomite (between 1.8 and 48.3 °C under 1 bar pressure). Δ²⁶Mg_{eps-sol} fractions calculated using Eq. 9 are calculated to be 0.65‰ at 7 °C, 0.57‰ at 20 °C and 0.52‰ at 40 °C, and these lie within error of those measured in the experiments.

Recently, Schauble (2010) calculated the reduced partition function ratios (RPFR) for ²⁶Mg/²⁴Mg for aqueous Mg and a number of minerals including meridianite (MgSO₄·11H₂O) by ab initio quantum mechanical calculations, and predicted that the Δ²⁶Mg_{mer-sol} fractionation is +0.3‰ at 20 °C (Fig. 10). We suggest that there should be little difference in the RPFR for Mg in meridianite and epsomite because water molecules are weakly attached in both minerals. If the RPFR of ²⁶Mg/²⁴Mg for meridianite (MgSO₄·11H₂O) by Schauble (2010) is combined with the RPFR of ²⁶Mg/²⁴Mg for aqueous Mg calculated separately by Rustad et al. (2010), the predicted Δ²⁶Mg_{mer-sol} fractionation is +2.2‰ at 20 °C (Fig. 10). Although the discrepancy between the two predictions for meridianite-aqueous fractionation factors indicates discrepancies in predicted RPFRs for aqueous Mg that must be resolved, the positive direction of predicted Mg isotope fractionations in meridianite is consistent with epsomite determined in this study. Compared to heavier metal sulfates, Li et al. (2008) measured the Cu isotope fractionation factor between chalcocite (CuSO₄·5H₂O) and saturated CuSO₄ solution, which they determined to produce a Δ²⁶Cu_{chalc-sol} fractionation of 0.17‰. This, in addition the present study, suggests that heavier isotopes of metal ions preferentially partition into sulfates relative to aqueous species. The smaller Cu isotope fractionation relative to that of Mg generally follows that expected relative to mass (e.g., O’Neil, 1986; Schauble, 2004).

The current study indicates that Mg isotopes in sulfates fractionate in the opposite direction between Mg-bearing calcite and aqueous solution. A number of field and laboratory studies have shown that Mg in inorganically precipitated calcite is isotopically lighter than Mg in aqueous solution by 2–3‰ in δ²⁶Mg (e.g., Galy et al., 2002; Kisakurek et al., 2009; Immenhauser et al., 2010). The Mg isotope fractionation measured in this study provides some qualitative insight into the bonding of the metal cation in mineral-aqueous systems. In both carbonate-solution and epsomite-solution systems, Mg²⁺ in aqueous solutions are hydrated, where each Mg²⁺ is bonded to six H₂O molecules to form an octahedral aquo ion ([Mg(OH₂)₆]²⁺) (Richens, 1997). The [Mg(OH₂)₆][²⁺] octahedron is retained in the epsomite structure, and bonds SO₄²⁻ and a “spare” seventh H₂O molecule with hydrogen bonds to form a stable mineral (Fortes, 2005). In contrast, there is no H₂O molecule in the carbonate lattice, and Mg²⁺ must dehydrate before bonding with CO₂ to form carbonate. We speculate that the positive values for Δ²⁶Mg_{eps-sol} may reflect stronger hydrogen bonds on [Mg(OH₂)₆][²⁺] octahedra in epsomite than in MgSO₄ solution. The negative values for Δ²⁶Mg_{carb-sol} may reflect the difference in strength and configuration of bonds directly on Mg²⁺ ions between aqueous solution and carbonates (Rustad et al., 2010; Schauble, 2010), and/or kinetic isotope effects during dehydration of [Mg(OH₂)₆][²⁺] aquo ions in carbonate precipitation (Immenhauser et al., 2010).

### 5.3. Applications

The relatively small epsomite–solution Mg isotope fractionation factor, coupled with the modest influence of evaporite formation on the Mg budget in Earth’s ocean (Holland, 1984; Wolery and Sleep, 1988; Wilkinson and Algeo, 1989; Berner and Berner, 1996), indicates that the Earth’s oceanic Mg isotope composition is not likely to be influenced by evaporite formation. Instead, the results here suggest that Mg isotopes may be a sensitive indicator of the extent of evaporite precipitation in a confined system such as a salt lake or lagoon. To illustrate the use of Mg isotopes to trace evaporite evolution, a simple model is constructed, where it is assumed that (1) the Mg isotope composition of the starting reservoir and possible Mg influx
equals that of seawater ($\delta^{26}\text{Mg} = -0.8_{\text{iso}}$) Tipper et al., 2006, 2008; Hippler et al., 2009), and (2) epsomite is the dominant Mg-bearing evaporite and $\Delta^{26}\text{Mg}_{\text{eps-sol}}$ is 0.6‰. In a closed system, the Mg isotope composition of evaporite follows a Rayleigh fractionation behavior, and the $\delta^{26}\text{Mg}$ values of epsomite reaches as low as $-2_{\text{iso}}$ when 95% of the Mg is precipitated (Fig. 11). By contrast, when the system is partly open to an influx of replenished Mg, such as may occur in an inland salt lake or a lagoon, the decrease in $\delta^{26}\text{Mg}$ values of epsomite relative to the degree of evaporation is much less dramatic (Fig. 11). For example, in a system where the influx of Mg is 70% of the Mg loss by evaporation, the $\delta^{26}\text{Mg}$ value of epsomite is about $-1_{\text{iso}}$ when 95% of the Mg is precipitated. In a restricted basin setting, these models show that it is difficult to reconstruct the Mg isotope composition of seawater from evaporites. Because, however, the $\delta^{26}\text{Mg}$ values of epsomite decreases monotonically in all cases, the Mg isotope composition of evaporite can be used as an effective means for distinguishing drought-wet cycles of an evaporative ancient basin, where the lowest $\delta^{26}\text{Mg}$ values would represent the cessation of an evaporation event at the end of a drought, whereas an increase in $\delta^{26}\text{Mg}$ values in subsequent evaporites would record a wetter period and an influx of Mg-bearing fluids.

It should be noted that carbonate is an important component of the mineral assemblage of precipitates during evaporation of seawater and development of brines on Earth, because Mg also partitions into carbonates and significant Mg isotope fractionations have been reported between carbonates and solution (Galy et al., 2002; Chang et al., 2004; Pogge von Strandmann, 2008; Hippler et al., 2009). Precipitation of carbonates, therefore, may add to the complexity of the Mg isotope systematics in evaporites, but this can be evaluated based on the lithologies present in an evaporite sequence. In contrast, carbonates may have been less important in the evaporite sequences on Mars, because evidence so far suggests that the sulfur cycle, instead of a carbon cycle, dominated surficial processes on ancient Mars (McLennan et al., 2007; Wang et al., 2009). The significance of Mg sulfates on the Martian surface (e.g., Wang et al., 2008) suggests that the Mg isotope compositions of evaporites from Mars would provide important constraints on the evaporative history of early Mars.

6. CONCLUSIONS

Magnesium isotope fractionation between epsomite and aqueous $\text{MgSO}_4$ solution has been constrained by a set of three-isotope experiments, which demonstrate that complete or near-complete Mg isotope exchange was achieved within 14 days in all experiments. Isotopic exchange was driven by recrystallization of epsomite, during which the net Mg transfer was insignificant compared with the mass of Mg that underwent isotopic exchange. The Mg isotope exchange rate between epsomite and $\text{MgSO}_4$ solution is dependent on the temperature, grain size of initial epsomite, and agitation methods used in the experiments. As expected, isotopic exchange rates were greatest at high temperature, and when a smaller grain size was used for the initial epsomite. The measured epsomite-solution Mg isotope fractionation factors are inferred to reflect equilibrium conditions because they were independent of the rate of recrystallization. Equilibrium Mg isotope fractionation factors between epsomite and aqueous $\text{MgSO}_4$ solution at experiments at 7, 20, and 40 °C were indistinguishable within error, as the $\Delta^{26}\text{Mg}_{\text{eps-sol}}$ fractionations cluster around 0.6‰.

ACKNOWLEDGMENTS

Dr. Andrew Czaja helped in SEM analysis; Dr. Hiromi Konishi, and Mr. Fangfu Zhang provided assist in XRD analysis. We thank Dr. Max Coleman for helpful discussions. The paper benefited from constructive comments of E. Tipper, N. Vigier, and an anonymous reviewer, as well as editorial comments by AE M. Rehkämper. This study was supported by the NASA Astrobiology Institute.

APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.gca.2011.01.023.

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*Associate editor: Mark Rehkamper*