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- **Project Title** Interface Induced Carbonate Mineralization: A Fundamental Geochemical Process Relevant to Carbon Sequestration
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#### FINAL REPORT

### Background

Vast majority of literature work concludes that the strong  $Mg^{2^+}$  hydration is the ultimate blockage to low-T anhydrous Mg-CO<sub>3</sub> crystallization and the incorporation of  $Mg^{2^+}$  in carbonate (i.e. the dolomite problem). A direct manifestation of the strong Mg-H<sub>2</sub>O association can be found in the products of low-T Mg-CO<sub>3</sub> precipitation which yields exclusively hydrated phases (barringtonite MgCO<sub>3</sub>·2H<sub>2</sub>O, nesquehonite MgCO<sub>3</sub>·3H<sub>2</sub>O, lansfordite MgCO<sub>3</sub>·5H<sub>2</sub>O; hydromagnesite Mg<sub>5</sub>(CO<sub>3</sub>)<sub>4</sub>(OH)<sub>2</sub>·4H<sub>2</sub>O, dypingite Mg<sub>5</sub>(CO<sub>3</sub>)<sub>4</sub>(OH)<sub>2</sub>·5H<sub>2</sub>O, and artinite Mg<sub>2</sub>(CO<sub>3</sub>)(OH)<sub>2</sub>·3H<sub>2</sub>O) depending on experimental conditions<sup>1</sup>. However, a closer look at these minerals indicates that rarely any obvious and predictive trend can be deduced concerning their water content. For example, it is widely known that tri-hydrated nesquehonite is the most commonly formed at ambient condition and magnesite only occurs at T > 60 – 100 °C<sup>2,3,4</sup>. If higher T favors the dehydration as shown by the shift from tri-hydrate to anhydrate at increasing temperature, we would expected to see di-hydrate (barringtonite) or even mono-hydrate en route. Yet it was reported that higher T (> ~ 40 °C) only brings up various basic forms<sup>5,6,7,8</sup>. Furthermore, if octahedron is the dominant geometry of Mg<sup>2+</sup> hydration shell

(<sup>9</sup>, why is there no hex-hydrate Mg-CO<sub>3</sub> but only penta-hydrated lansfordite? More curiously, if the hydration shell of Mg is weakened or breached, or if crystallization can be performed under dry (i.e. non-aqueous) conditions at low temperature, will magnesite form? Whereas those observations come out simply from curiosity, it may hold the key for us to expand our understanding of the Mg-Ca-CO<sub>2</sub>-H<sub>2</sub>O system and ultimately may shed light on the dolomite problem.

Despite the large body of literature documenting the assumed inhibitory role of cation hydration, little work has been found to directly test the solvation effect. Thus, the current understanding on the part water plays in obstructing magnesite (and dolomite) formation leads to an intriguing and yet fundamental question: will anhydrous Mg carbonate salts precipitate readily if the cation solvation shells are non-aqueous? In the last funding period, we followed this trail of thought by testing the possibility of magnesium carbonate crystallization in water-methanol binary solvent and pure methanol. It was expected that the presence of methanol in the solvent would at least distort the hydration shell around  $Mg^{2+}$  due to the hydrogen bond formation. As such, we anticipated possibility of anhydrous magnesium carbonate phase (crystalline or amorphous) precipitation in the experiments, particularly at dry conditions. Experimental results however did not reveal the formation of any anhydrous MgCO<sub>3</sub> salts, suggesting methanol may not be able to affect the hydration shell significantly. On the other hand, the results showed the precipitation of amorphous Mg-CO<sub>3</sub> containing phase, implicating the difficulty of MgCO<sub>3</sub> crystallization when the availability of water is limited. To further elucidate the role of water, we conducted more experiments in this funding period using aprotic solvents to completely eliminate the presence of free protons in the solution so that the carbonate equilibria have no chance to shift toward carbonic acid to produce H<sub>2</sub>O. The overall goal is to test the role of cation hydration in MgCO<sub>3</sub> crystallization and to provide direct insight into the dolomite problem.

In this funding period, we explored the possibility of magnesite (MgCO<sub>3</sub>) and dolomite (CaMg(CO<sub>3</sub>)<sub>2</sub>) formation under ambient conditions in dry formamide (an organic solvent, O=CH-NH<sub>2</sub>). We chose formamide because it has a high dielectric constant ( $\varepsilon = 109.8$ ) and resembles water in many physical properties, such as density, dipole moment and surface tension. The strong polarity of formamide allows us to

prepare high-concentration solutions containing  $Mg^{2+}$  (and  $Ca^{2+}$ ) cations or  $CO_3$  anions. In addition, the hydrogen bonding between formamide molecules is also much weaker than that between water molecules due to the stronger steric effect<sup>10</sup>, which is indicative of a much weaker solvation effect on the solute ions.

## **Results and Discussion**

We started our experiments by first making stock solutions of 0.1M of MgCl<sub>2</sub> (stock 1), 0.1M of (Ca,Mg)Cl<sub>2</sub> (stock 2), and 0.1 M CsCO<sub>3</sub> (stock 3) in formamide. Stock 2 was made such that  $[Mg^{2+}]+[Ca^{2+}] = 0.1$  M while the Mg/Ca (molar) ratio varied from 1:5 to 5:1. We then carried out the synthesis by mixing or titrating stock 3 into stock 1 or stock 2 at room temperature in an open (to air) setting (see Methods). Consistent with the prediction of cation hydration hypothesis, precipitation occurred either immediately upon the mixing or gradually during the titration. However, X-ray diffraction (XRD) analyses of the isolated solid phases (Fig. 1) showed that the precipitates' crystallinity was highly dependent of the Mg mol % content in the solution. In the pure-Mg system (combination of stock 1&3) (Fig. 1a), exclusively amorphous material was formed. Infrared spectroscopy (IR) analyses of these amorphous phases (Fig. 2) confirmed that they were composed of disordered carbonate with characteristic peaks in the 870 cm<sup>-1</sup>, 1080 cm<sup>-1</sup>, and 1430 cm<sup>-1</sup> regions, and were anhydrous in nature (no water absorption near 3400 cm<sup>-1</sup>). In the high-Mg, mixed-cation experiments (the combination of stock 2&3), the lack of crystallinity remained as the precipitates from solutions with Mg/Ca = 5:1 and 2:1 showed no diffraction peaks in their XRD spectra (Fig. 1 b-c). We note that the amorphous nature of the precipitates from high-Mg systems was not altered by changing the mixing rate of the stock solutions, e.g., by titrating stock 3 into stock 1 or 2 over a period of ~4 h or mixing the two within 1 min. Continuous decline in the Mg content finally led to the development of crystalline phases when Mg mol % in the solutions was decreased below  $\sim$ 50%. For example, at Mg/Ca = 1:1, disordered dolomite of moderate crystallinity was observed; and at Mg/Ca = 1:2 and 1:5, magnesian calcite of good crystallinity was formed (Fig. 1d-e). Using a previously established method<sup>11</sup>, we determined the Mg contents in the crystalline phases to be  $\sim 37$ mol% (1:1), ~23-25 mol% (1:2), and 9-10 mol% (1:5), respectively. ICP-OES analyses upon dissolving the precipitates in 1% HNO<sub>3</sub> solution (Table 1) fully corroborated the

XRD results showing a Mg accounts of 71, 60, 40, 26, and ~15 mol % in the 5:1, 2:1, 1:1, 1:2, and 1:5 systems, respectively. It is worth noting that the amorphous phases were quite stable as no discernable XRD diffraction pattern was detected on the samples ~ 120 days after the synthesis.

The evolving crystallinity and composition in the precipitates were further revealed by scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HR-TEM) coupled with energy dispersive spectroscopy (EDS). SEM analyses (Fig. 3) indicated that the precipitates in high Mg/Ca (5:1, 2:1) and pure-Mg solutions were composed of nano-sized spheres with no specific crystal habit whereas those in low Mg/Ca conditions (1:5, 1:2) appeared as (sub)micron sized euhedral crystals, consistent with the XRD analyses. TEM images (Fig. xx to yy) suggested that the crystals formed in the 1:1 and 1:2 solutions becomes significantly elongated relative to those (almost perfectly euhedral) seen in the 1:5 samples, agreeing well with previously observed Mg<sup>2+</sup> effect on calcite morphology in AFM study<sup>12</sup>. Selected Area Diffraction (SAED) pattern showed the presence of both amorphous and crystalline phases in the 1:1 solutions (Fig. 4B, 2&3) and the exclusive amorphous nature of the precipitates in 5:1 (Fig. 4C2) and pure-Mg solution (Fig. 4D). EDS analyses estimated that the crystalline  $Ca-Mg-CO_3$  phase (rhombohedral to oval-shaped, Fig. 4A1) in the 1:2 solutions were composed of ~ 32 mol % of MgCO<sub>3</sub> (Fig. 4A2). Further increase to Mg/Ca ratio to 1:1 raised the MgCO<sub>3</sub> content to ~38 mol % in nano-crystals and ~47 mol % in amorphous phase (Fig. B, inset). The distribution of  $Mg^{2+}$  and  $Ca^{2+}$  in the dolomitic species formed in the 1:1 solutions (over-shaped crystals in Fig. 4B1) appeared to be completely random (Fig. 4B2).

Both EDS (Fig. 4) and ICP-OES (Table 1) detected the presence of small quantities of Cs in the precipitates, more in amorphous phases than in crystals. The higher level of Cs associated with lower crystallinity, along with the coupled appearance of Cs and Cl in amorphous phases (Fig. 4), seem to suggest that Cs may exist in lattice as well as in surface adsorption or as trapped residual solute.

These findings are of significance in multiple fronts. First of all, the lack of crystallinity in the precipitates harvested in magnesium-only and high Mg/Ca solutions suggest that long-range orders in the  $Mg_xCa_{(1-x)}CO_3$  solid cannot be readily achieved at

high magnesium % content (x > 0.38 in our experiments), exposing a previously unrecognized intrinsic difficulty for  $Mg^{2+}$  and  $CO_3^{2-}$  to attain the *R3c* (in magnesite) or R3 (in dolomite) arrangements at ambient conditions. It is noteworthy that such difficulty is unlikely caused by the reaction kinetics of  $Mg^{2+}$  and  $CO_3^{2-}$  because varied mixing rates (i.e., slow titration versus quick mixing) showed little effect on the precipitate's morphology and crystallinity. Secondly, in contrast to the widely reported crystallization of magnesium carbonate hydrates such as nesquehonite, MgCO<sub>3</sub>·3H<sub>2</sub>O, (monoclinic,  $P2_1/n$  from aqueous environments at ambient conditions, the observed formation of amorphous MgCO<sub>3</sub> anhydrates in the present study implies that water facilitates the nucleation process by direct incorporation into the lattice. Thirdly, comparing the partitioning behavior of Mg in this study (in formamide) with those in previous work (in water) (Fig. 4), we found that far higher molar % of Mg was incorporated into the crystalline solids (calcite) formed in non-aqueous environments. For example, the distribution coefficient for Mg,  $D_{Mg} = (Mg/Ca)_{solid}/(Mg/Ca)_{solution}$ , was estimated to be ~ 0.6 - 0.8 in this study, about one order of magnitude higher than that in water at similar conditions  $(0.02 - 0.09, \text{ depending on the specific experiments})^{13}$ . This observation is consistent with the hypothesized role of water in limiting Mg-rich carbonate formation and likely constitutes the first direct evidence that quantifies the hindrance of cation hydration on  $Mg^{2+}$  incorporation into calcite lattice. Lastly, our experimental approach provided a synthetic route to produce anhydrous amorphous magnesium carbonate at room temperature and atmospheric  $pCO_2$ , which may help to extend the current effort in understanding amorphous calcium carbonate (ACC)<sup>14</sup> to amorphous magnesium carbonate (AMC), both of which provide a low energy pathway for carbonate mineralization in biological (organic-rich) environments. To the best of our knowledge, no literature report is available to date documenting the formation of anhydrous AMC although the synthesis of hydrous forms,  $Ca_{1-x}Mg_xCO_3 \cdot nH_2O$  ( $0 \le x \le 1$ ), was achieved at elevated temperature<sup>15</sup>.

We ascribe the major difficulty in anhydrous MgCO<sub>3</sub> mineralization at ambient conditions to the reduced freedom of the CO<sub>3</sub> groups in magnesite that, consequently, incurs a high-energy (chiefly from entropy decrease) penalty for the crystallization process. Previous studies on the crystal structure of carbonate minerals revealed that, Mg and O form much more compact octahedra in magnesite than Ca and O do in calcite. As a result, the CO<sub>3</sub> groups in magnesite have far less freedom in motion than those in calcite, although the C-O interatomic distance is nearly uniform in the two minerals, due to the stronger interactions between the Mg-O octahedra<sup>16</sup>. For example, the CO<sub>3</sub> group within the calcite structure can undergo translational, librational (i.e. rotational), or screw motions depending on the energy level of the environment, whereas only translational motion is allowed for the CO<sub>3</sub> group in magnesite. The enhanced lattice restriction in magnesite is also confirmed by the outcome of structural refinement for calcite and magnesite formed under different temperature/pressure conditions<sup>17</sup>. Specifically, the C-O and O-O interatomic distances in the magnesite-CO<sub>3</sub> groups maintain a much higher stability when external conditions change, resulting in a lower overall distortion in the groups at higher temperature/pressure, presumably due to the stronger confinement by the highly compact and rigid Mg-O octahedra. Some researchers<sup>18</sup> even suggested that the CO<sub>3</sub>-structural change is mainly responsive to the expansion/compaction of the Mg-O octahedra at the elevated temperature/pressure.

Building on these lines of previous understanding, we deduce that the specific configuration of Mg and CO<sub>3</sub> in magnesite, where the CO<sub>3</sub> groups are precisely and securely interlocked between the Mg-O octahedra, may be rather difficult to reach at ambient conditions. Unless the Mg-O octahedra are efficiently compressed so that the CO<sub>3</sub> group can have more freedom in motion (Fig. 5), the energy barrier for forming an ordered Mg-CO<sub>3</sub> arrangement may be too high to be overcome at low temperature/pressure conditions due to the entropic loss associated with the atoms' strict spatial distribution. Therefore, we attribute the main force inhibiting Mg-CO<sub>3</sub> crystallization in water-free environments to the thermodynamic hindrance resulting from the entropy decrease associated with intensified restrictions on the CO<sub>3</sub> groups in magnesite.

Other than the high energy barrier for establishing long-range order in anhydrous MgCO<sub>3</sub> salt, the amorphism of the Mg<sub>x</sub>Ca<sub>(1-x)</sub>CO<sub>3</sub> phases (x > 0.37) in our high-Mg systems may also result from the internal lattice strains and stresses induced by the large size- and charge-density-mismatch between Mg<sup>2+</sup> and Ca<sup>2+</sup>. Both experimental and computational investigations in the literature provided evidence indicating that calcite

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crystals with low concentrations of Mg are stable in structure<sup>19</sup> (17, 67-69); these studies, however, predicted that high concentrations of Mg ( $\geq \sim 50$  atom %) may prevent crystal formation due to the increasing structural stiffness and distortion resulted from the random Mg-substitution of Ca. Recent studies<sup>20</sup> using computational methods reported that substituting Ca by Mg in calcite crystals can alter the cation-C and the cation-cation interatomic distances significantly and cause local tilt of the CO<sub>3</sub><sup>2-</sup> groups while maintaining the C-O (within the CO<sub>3</sub><sup>2-</sup>) and the cation-O bond lengths. Moreover, literature data indicated that pyramidal distortion of the CO<sub>3</sub> group needs to occur in magnesite to satisfy the *R*<u>3</u>*c* space-group symmetry<sup>21</sup>. Altogether, these structural distortions at high lattice-Mg content will stiffen the crystal structure by reducing the equilibrium volume and raising the bulk modulus. Our experimental observations that no crystalline phase with Mg mol% greater than ~37% can precipitate directly from high-Mg solutions is largely in line with these previous understanding.

## Conclusion

In summary, we have approached the long-standing geochemical question why anhydrous high-Mg carbonate minerals (i.e., magnesite and dolomite) cannot be formed at ambient conditions from a new perspective by exploring the formation of MgCO<sub>3</sub> and Mg<sub>x</sub>Ca<sub>(1-x)</sub>CO<sub>3</sub> in non-aqueous solutions. Data collected from our experiments in this funding period suggest that a fundamental barrier, other than cation hydration, exists that prevents Mg<sup>2+</sup> and CO<sub>3</sub><sup>2-</sup> ions from forming long-range ordered structures. We propose that this barrier mainly stems from the lattice limitation on the spatial configuration of CO<sub>3</sub> groups in magnesite crystals. On the other hand, the measured higher distribution coefficients of Mg between magnesian calcites formed in the absence and presence of water give us a first direct proof to support and quantify the cation hydration effect. These findings may expand our current understanding of the Mg(-Ca)-CO<sub>3</sub> system and provide important insight into dolomite/magnesite formation as well as the processes involved in biomineralization and mineral carbonation.

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### **Table & Figure Captions**

- Table 1. Chemical compositions of the precipitated solids by inductively couple plasmaoptical emission spectroscopy (ICP-OES).
- Figure 1. X-ray diffraction analyses of the precipitated solids in formamide solutions at 22°C, atmospheric conditions. The corresponding peak positions for calcite (green) and dolomite (red) are indicated.
- Figure 2: Infrared spectroscopy analysis of the amorphous solids formed in puremagnesium and high [Mg<sup>2+</sup>]/[Ca<sup>2+</sup>] solutions.
- Figure 3: SEM images of the precipitated solids in formamide solutions. (a)  $[Mg^{2^+}]/[Ca^{2^+}] = 1:5$ ; (b)  $[Mg^{2^+}]/[Ca^{2^+}] = 1:1$ ; (c)  $[Mg^{2^+}]/[Ca^{2^+}] = 5:1$ ; and (d) pure-magnesium. The indicated scale bars are 200 nm. Notice the lack of morphology in the precipitates in the 5:1 and pure-Mg solutions.
- Figure 4: TEM and EDS analyses of the precipitated solids. A1: round-cornered rhombohedral crystals formed in the 1:2 solution. A2: Close examination of an individual unit shows that they are polycrystalline and comprise nanoscale crystals. Inset displays an EDS spectrum for the nanocrystals at the bulk edge (with ~32 mol % of MgCO<sub>3</sub>). B1: Amorphous and oval-shaped crystalline phases formed in the 1:1 solution. EDS spectra of various spots (e.g., the upper right for the dash-circled area and the lower right for the solid-circled one) show that both types of solids are composed of Ca-Mg-CO<sub>3</sub>, of which the amorphous consists of 47 mol % of MgCO<sub>3</sub> content and the crystalline consists of 37 mol %. Trace amounts of Cs, Na, and Cl were also observed in the EDS spectra, likely due to the adsorption of residue solutes at the precipitates' surface. B2: Close examination of an oval-shaped unit reveals that they are polycrystalline and comprise nano-scale crystals, as those less elongated ones in the 1:2 (Mg/Ca) system. Inset is a selected-area electron diffraction (SAED) pattern for the [010] zone axis, displaying the characteristic diffraction arcs for Ca-rich dolomite and suggesting the existence of low-angled grain boundaries between the nanocrystals. The distribution of  $Ca^{2+}$  and  $Mg^{2+}$  cations in these polycrystals is highly random because no super-lattice reflections i.e., (003) were observed. B3: High-resolution images of the dolomite nanocrystals with a fast Fourier transform (FFT) pattern for the [010] zone axis. No super-lattice fringes or reflections were observed. C1: Microscopic images of the precipitates in the 5:1 (Mg/Ca) system, indicating that highly fine and amorphous phases were formed. Inset is an EDS spectrum for the solids which consist of 73 mol % of MgCO<sub>3</sub>, where Na, Cl, and Cs were also detected. C2: High-resolution images and a SAED pattern for the precipitates confirming their amorphous nature. D1: Microscopic images of the precipitates in the pure-Mg system. The EDS and SAED analyses indicate that these solids are amorphous and dominantly consist of MgCO<sub>3</sub>.

- Figure 5: Comparison of the Mg-distribution coefficients in the crystalline/amorphous Mg-Ca-CO<sub>3</sub> phases formed in formamide (this study) and in water (previous studies). The results for this study are based on ICP-OES (solid triangle) and XRD (void triangle) analyses, respectively. The results for previous studies are average values (with error bars) of those from Mucci and Morse, 1983, Mucci 1986, Hartley and Mucci, 1996, and Huang and Fairchild, 2001.
- Figure 6. (Left) Ambient-pressure structure of magnesite. The arrows indicate the direction in which the MgO<sub>6</sub> octahedra may rotate upon compression. (Right) High-pressure structure of magnesite. The MgO<sub>6</sub> octahedra have rotated about *c*-axis and are approaching alignment with one another, allowing for a lengthening of the C-O bond. This results in a lengthening of the C-O bond and a noticeable enlargement of the carbonate group relative to the MgO<sub>6</sub> octahedra. (from Santillan *et al.*, 2005).





Figure 2



Figure 3





Figure 5



Figure 6

# References

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