Enhancing Magnesite Formation at Low Temperature and High CO₂ Pressure: The Impact of Seed Crystals and Minor Components

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Abstract

The formation of magnesite was followed in aqueous solution containing initially added $\text{Mg}(\text{OH})_2$ equilibrated with supercritical carbon dioxide (90 atm pressure, 50°C) in the presence of introduced magnesite particles and minor components, $\text{Co}(\text{II})$. As expected, the introduction of magnesite particles accelerated the formation of magnesite from solution. However, the formation rate of magnesite was even greater when small concentrations of $\text{Co}(\text{II})$ were introduced, indicating that the increased rate of magnesite formation in the presence of $\text{Co}(\text{II})$ was not solely due to the addition of a growth promoting surface. Detailed analysis of the magnesite particles by scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersive spectroscopy (EDS), and atom probe tomography (APT) revealed that the originally added $\text{Co}(\text{II})$ was concentrated in the center but also present throughout the growing magnesite particles. Addition of the $\text{Co}(\text{II})$ in different chemical forms (i.e. as solid phase CoCO_3 or $\text{Co}(\text{OH})_2$) could alter the growth rate of magnesite depending upon the addition of bicarbonate to the starting solution. Geochemical modeling calculations indicate that this difference is related to the thermodynamic stability of these different phases in the initial solutions. More broadly, these results indicate that the presence of even small concentrations of foreign ions that form carbonate compounds with a similar structure as magnesite can be incorporated into the magnesite lattice, accelerating the formation of anhydrous carbonates in natural environments.

Introduction

Although the mechanisms of formation and dissolution of carbonate minerals have been studied for decades, recently such research has taken on an added importance since formation of these phases, most notably calcium and magnesium carbonates, is one of the primary means of permanently sequestering carbon dioxide in deep geologic formations (Gunter and Perkins, 1993; Rochelle et al., 1996; Gunter et al., 2000; Kaszuba et al., 2003; Pruess et al., 2003; Kaszuba et al., 2005; Oelkers and Schott, 2005; Suto et al., 2007; Xu et al., 2007; Oelkers et al., 2008; Kwak et al., 2010; Kwak et al., 2011; Felmy et al., 2012; Wang and Giammar, 2013; Sissmann et al., 2014). One of the most important minerals that can form under high partial pressures of CO₂ and in the presence of ultramafic rocks or other basic, magnesium containing rocks is magnesite (MgCO₃). Although the thermodynamically stable magnesium carbonate phase (Christ and Hostetler, 1970; Kittrick and Peryea, 1986; Hanchen et al., 2008; Benezeth et al., 2011), the precipitation of magnesite from aqueous solution at low temperature is inhibited presumably by the strong hydration energy of the Mg²⁺ ion (Langmuir, 1965; Christ and Hostetler, 1970; Sayles and Fyfe, 1973).

One means of circumventing the sluggish precipitation kinetics of magnesite is to introduce a templating surface or seed crystal that overcomes the possible barriers to nucleation and accelerates particle growth (Kittrick and Peryea, 1986; Saldi et al., 2009; Saldi et al., 2012; King et al., 2013). For example, Kittrick and Peryea (1986) performed solubility studies at low temperature (25°C) using natural magnesite particles. Their calculated solubility product (log K_{sp} = -7.59) was close to the most recent value of -7.80 determined by Benezeth et al. (2011). In addition, Wiklund et al. (Wiklund et al., 2001) clearly show the growth of magnesite on the surface of rhodochrosite (MnCO₃) at 90°C. In this case the surface precipitation of magnesite

prevented the rhodochrosite from being oxidized by peroxide. In addition to possible templating surface reactions, recent studies by Saldi (Saldi et al., 2013), Romanek (Romanek et al., 2009) and Sissmann (Sissmann et al. 2014 demonstrate that introducing small concentrations of foreign ions, e.g. Fe(II), into the magnesite structure accelerates magnesite formation.

In geochemical systems magnesite formation from aqueous solutions at low temperature (35 and 50°C) is a slow process even at high partial pressures of CO₂. Therefore, it is interesting that Kralik et al. (Kralik et al., 1989) determined that all microcrystalline magnesites in ultramafic rocks are formed at surface or near surface temperatures. Studies by Melezhik et al. (Melezhik et al., 2001) also showed that magnesite often formed at low temperature in hypersaline environments and contained small amounts of divalent metal ions (e.g. Ca(II), Fe(II) or Mn(II)).

Here we report the formation of magnesite from aqueous solution under conditions of low temperature (50°C) and high partial pressure of CO₂ (90 atm) in the presence of either magnesite particles or Co(II) ions produced by the dissolution of CoCO₃ or Co(OH)₂. The results are compared to previous studies in the absence of magnesite or presence of minor components. The distribution of low concentrations of Co(II) in the precipitated magnesite was determined by a combination of Scanning Electron Microscopy/Energy-Dispersive X-Ray Spectroscopy (SEM/EDS), Transmission Electron Microscopy (TEM/EDS) and Atom Probe Tomography (APT). Low concentrations of Co(II), which forms a carbonate compound with a structure similar to magnesite, were incorporated into the magnesite lattice and greatly accelerated the nucleation and growth of magnesite. The importance of surface templating versus solid solution formation is distinguished.

Experimental Methods

Mg(OH)₂ was purchased from Sigma Aldrich. CoCO₃ and Co(OH)₂ were purchased from AlfaAesar. SEM/EDS analysis of the Mg(OH)₂ showed the presence of Ca as a minor component. The purity of CoCO₃ and Co(OH)₂ were 99.5% and 99.9% respectively. MgCO₃ was prepared by reacting a suspension of 0.58g Mg(OH)₂ and 10mL deionized water in supercritical carbon dioxide, scCO₂, (50°C and, 90atm) for 28days. XRD analysis of the powder after reaction showed that the final product was composed only of magnesite.

The reactivity studies were conducted in stainless steel vessels (Model 4790, Parr Instrument Company) with a net volume of approximately 33 cm³. All the experiments were conducted at 50°C and 90atm of CO₂ pressure for 14 days. Brucite (0.1164g) was added to stainless steel vials along with 2mL of deionized water. Small amounts of MgCO₃, CoCO₃, or Co(OH)₂ were initially mixed with deionized water or 0.1M NaHCO₃ and sonicated for 10 minutes to create a well-mixed suspension. A small volume of this suspension was diluted to 2mL and transferred into stainless steel vials containing Mg(OH)₂. Control experiments without seed crystals were also performed. The concentration of the seed/minor components was 0.85% by mass. Stainless steel vials were placed inside each reactor vessel and the vessel was pressurized with CO₂ according to the procedure described in Felmy (Felmy et al., 2012) and Qafoku (Qafoku et al., 2012).

After 14 days of reaction time, reaction vessels were quickly depressurized and the suspensions were passed through a gentle vacuum filtration unit to rapidly separate liquid from solid phases. Solid reaction products were dried at 50°C for 24 hours prior to further analysis.

Bulk powder X-ray diffraction analyses of powdered samples mounted on zero background quartz slides were carried out on a Philips X'Pert MPD system. SEM analysis was

performed using the FEI Quanta 3DFEG Dual Beam microscope operated at 5 kV for imaging and 20 kV for EDS. Imaging of the SEM prepared samples was performed both by dispersing the particles onto carbon tape and then coating the samples with ~5nm of carbon to help with charge effects, and by mounting the particles in epoxy and polishing the samples using a series of diamond compounds. Compositional analysis was performed with an Oxford 80mm² SDD electron dispersive spectrometry (EDS) detector. For quantitative (EDS) analysis, calculated K factors provided by INCA software were used. Both secondary electron images (SE) and backscatter images were recorded (BSE). Samples for TEM were prepared using an FEI Helios 600 Nanolab Dual Beam instrument. Samples were lifted out for analysis using standard FIB-TEM lamella procedures. All samples were given a low keV polishing cleanup to minimize the amorphous damage from the gallium beam.

TEM analysis was performed using the FEI Titan 80-300 operated at 300 kV. The microscope is equipped with CEOS aberration corrector for the probe-forming lens, which enables sub-angstrom image resolution in Scanning Transmission Electron Microscopy (STEM) mode. In this work, the STEM imaging was performed with High Angle Annular Dark Field (HAADF) detector. Compositional analysis was performed with EDAX Si(Li) electron dispersive spectrometry (EDS) detector. When performing EDS mapping analysis, the electron dose rate on the sample was minimized by sub-pixel scanning, and artificially defocusing the probe to reduce electron density until no significant damaged was observed on the sample. For quantitative (EDS) analysis, k factors provided by FEI TIA software were used.

Needle-shaped specimens for APT analysis were prepared using a dual beam focused ion beam/scanning electron microscope (FEI Helios 600 Nanolab) lift out technique modified based on the method detailed by Thompson et al. (Thompson et al., 2007). Powders consisting of

particles ranging in size between 1 μm – 1.6 μm were first dispersed onto (100) Si substrate and coated with ~5 nm of carbon to minimize charge effects. Each APT specimen was prepared from a single particle (~ 1.3 μm). In order to reduce excessive Ga^+ implantation during FIB specimen preparation, a Pt capping layer was deposited over the top of the particle consisting of approximately 200 nm of electron-beam deposited Pt. The tungsten needle of a nanomanipulator was then attached to the edge of an individual particle and lifted away from the surface. A triangular wedge-like shape was then made by milling on two adjacent sides of the particle. The triangle wedge particle was then attached to commercially-available (Cameca Instruments) Si micropost array substrates. Using an annular milling pattern, each specimen was milled into a needle-shaped morphology having an end radius of curvature of approximately 60 nm followed by a low-kV (2 kV) Ga^+ exposure to remove most of the damaged layer. APT experiments were conducted with a CAMECA LEAP 4000X HR equipped with an ultraviolet ($\lambda=355$ nm) laser and a high-resolution reflectron lens. The APT specimens were held at 40 K during analysis in ultrahigh vacuum ($<1 \times 10^{-8}$ Pa). Laser pulse energies of about 20 pJ pulse⁻¹ with the pulse frequency of 160 kHz was used. The detection rate remained at 0.3% for the analysis.

Results and Discussion

The XRD analysis of the precipitates formed after one and fourteen days of reaction after seeding with magnesite particles are shown in Figure 1. After one day of reaction there is no clear evidence for the presence of the small amounts of introduced magnesite (0.8%). The majority of the solid is still $\text{Mg}(\text{OH})_2$. There is also evidence for the formation of small amounts of hydromagnesite (note the small peaks at $18^\circ 2\theta$ and $33^\circ 2\theta$, Figure 1a). After 14 days of reaction the XRD analysis indicates that magnesite has begun to grow (see Figure 1b), but that

brucite is still present along with the expected magnesium carbonate precipitates hydromagnesite and nesquehonite (Cheng and Li, 2010; Back et al., 2011; Case et al., 2011; Hopkinson et al., 2012; Wang and Li, 2012). For comparison, XRD analysis of samples without added magnesite, Figure 1c, show a very similar pattern to those with added magnesite, Figure 1b, except for the absence of peaks characteristic of magnesite.

The XRD results are in agreement with SEM analysis of the precipitates which shows the presence of particles with a rhombedral morphology characteristic of magnesite only for the 14 day samples with added magnesite, Figure 2.

Therefore, as expected, the initial presence of seed particles accelerates the formation of magnesite from solution, presumably by providing a surface for the growth of additional structural magnesite. Unfortunately, it is difficult to gain any further insight into the magnesite formation process by adding additional seed magnesite crystals since it is impossible to distinguish newly grown magnesite from pre-existing magnesite surfaces. In order to distinguish newly formed magnesite surface growth we elected to add Co(II) as a Mg(II) analog since the lattice match between CoCO_3 and MgCO_3 is quite close (see Table 1) and Co(II) is not subject to oxidation like other divalent metal ions that can substitute into magnesite in geochemical systems (e.g. Fe(II), or Mn(II) (Melezhik et al., 2001).

XRD analysis of samples after 14 days of reaction with added CoCO_3 (0.8 wt %), Figure 3, show that the material is nearly pure magnesite and that essentially all of the original brucite had dissolved. These results indicate that the addition of CoCO_3 as a precursor phase increased the nucleation rate or growth rate of magnesite. The reaction product has the same rhombedral geometry as magnesite, see Figure 4. Clearly, the rate of magnesite formation in the samples with added CoCO_3 was much greater than the rate of formation when magnesite particles were

added as a seed. This possibly indicates that the increased rate with added CoCO_3 was not solely as a result of providing a surface template to enhance growth.

To further examine if magnesite formation in presence of minor components was due to a surface template mechanism, we added Co in a different form (Co(OH)_2) that would not serve as a surface template. XRD analysis of the precipitates after 14 days of reaction, Figure 5a, show greatly reduced magnesite formation. However, if a small amount of NaHCO_3 (0.1M) was added to the solutions along with the Co(OH)_2 then the rate of magnesite formation was again greatly accelerated (see the XRD analysis of the precipitates in Figure 5b). In contrast, if the same concentration of NaHCO_3 (0.1M) was added in the absence of any Co containing compound then the formation of magnesite was minimal. The particle size of the precipitates with added Co(OH)_2 was about 1 μm , Figure 6, which is large enough for detailed examination of the Co distribution within the magnesite particles by SEM/EDS. The results, Figure 7a, showed that as expected the Co was concentrated in the center of the particles, but that significantly Co was also found throughout the particle. The presence of Co throughout the particle was surprising since we believed that if Co served strictly as a surface template it should be exclusively in the center of the particles where it would impact the initial nucleation of the solid. A salient question is whether the core is pure CoCO_3 or not; this is difficult to assess with SEM/EDS as the signal is averaged over the entire depth of the particle. As described below, APT was used, in part, to resolve this issue.

In order to measure the atomic-scale radial compositional variation of Co, we conducted a detailed examination of the magnesite particles by APT. The tomographic nature of the APT analysis not only yields the distribution of the Co within each magnesite particles but also a qualitative assessment within any arbitrary volume within the reconstruction. Figure 8(a) shows

the distribution of all detected Co atoms from a 10 nm slice throughout the tip. The background-subtracted 1-dimensional composition profile of Co and Ga is shown in Figure 8(b). Note that the unintentional implantation of low-kV Ga^+ from the FIB sample preparation is observed with no contribution to the observed Co distribution beyond 10 nm from the analyzed surface. The distribution shows a relatively low Co concentration of $\sim 0.4\%$ total atoms nearer the particle surface (i.e. apex of the reconstruction at $z = 0$) that increases to $\sim 1.2\%$ towards the center. The results are in good agreement with the SEM/EDS analysis above and consistent with the small amount of Co that was initially added during the initiation of growth. However, the distribution of Co within the particle also indicates that CoCO_3 did not serve as a simple templating surface. In addition, the continuous monotonic increase of Co concentration from the surface towards the center is evidence for Co concentration variation in aqueous solution during the magnesite particle growth.

Whereas enhancement of magnesite formation by addition of magnesite seed particles is not unexpected, the facilitation of magnesite formation by Co-solids (CoCO_3 and Co(OH)_2) warrants further discussion.

In a mixture of hydroxide phases, where Co(OH)_2 is less soluble than Mg(OH)_2 , and before any CO_2 from the added supercritical CO_2 reaches the surface, the dissolution of these phases will maintain a high pH ($\sim 9 - 10$). At this condition only minor amounts of Mg or Co will dissolve¹. To quantify this reaction we used the OLI software package (OLI Inc. 2012) which contains thermodynamic data for all of the relevant Mg(II) and Co(II) hydrolysis reactions, as well as the thermodynamic data for the aqueous complexation reactions with carbonate and the formation of the solid phases, including CoCO_3 , magnesite, hydromagnesite, and nesquehonite.

¹ Mg(OH)_2 and Co(OH)_2 can also form an even more stable solid solution phase (Giovannelli et al. 2012) which would only act to further stabilize the added Co(OH)_2 .

The results show, that as expected, at a temperature of 50°C, the calculated pH is 9.6 and only low concentrations of Mg ($\sim 10^{-4}\text{M}$) and Co($\sim 10^{-6}\text{M}$) are predicted. Such conditions should approximate the solution composition near the surface before any $\text{CO}_2(\text{g})$ begins to react with the precipitates. As the $\text{CO}_2(\text{g})$ begins to react with this high pH environment the $\text{CO}_2(\text{aq})$ is transformed to bicarbonate or carbonate ions and this results in a lowering of the pH and precipitation of carbonate containing phases. Interestingly, the OLI software package predicts this added CO_2 will react with the large mass of $\text{Mg}(\text{OH})_2$ producing hydromagnesite with the more insoluble and stable $\text{Co}(\text{OH})_2$ remaining as a solid phase.

In the case of Co initially added as CoCO_3 to $\text{Mg}(\text{OH})_2$, and before any CO_2 reaches the surface, the carbonate phase is predicted to dissolve. This initial dissolution of unstable CoCO_3 , we hypothesize, provides a mechanism for $\text{Co}(\text{II})$ to enter the aqueous phase where it can be incorporated into magnesite. As mentioned above, this dissolution mechanism appears not to exist if Co was initially added as stable $\text{Co}(\text{OH})_2$, since the hydroxide phase is not predicted to dissolve until all of the $\text{Mg}(\text{OH})_2$ has first dissolved. When NaHCO_3 was added to the suspension containing $\text{Co}(\text{OH})_2$ then $\text{Co}(\text{OH})_2$ dissolved, thus providing a source of $\text{Co}(\text{II})$ to the aqueous phase which can then be incorporated into magnesite. This mechanism explains why the addition of bicarbonate to suspensions containing $\text{Co}(\text{OH})_2$ enhanced the growth of magnesite whereas, suspension without bicarbonate did not show enhanced formation of magnesite.

Summary and Conclusions

In this study, the rate of formation of magnesite can be enhanced by the addition of magnesite seed particles that presumably could serve as templating surfaces for further growth and by addition of small concentrations of divalent metal ions (i.e., $\text{Co}(\text{II})$) than can substitute

into the growing magnesite particles. Incorporation of minor/trace Co(II) can be essential for promoting the nucleation and growth of magnesite over the relatively short time frames of these experiments. However, this mechanism relies on the ready availability of Co(II) which precludes the presence of stable, sparingly soluble Co(II) solid phases.

Our results also show that the rate of formation of magnesite is different when $\text{CoCO}_3(\text{s})$ or $\text{Co}(\text{OH})_2(\text{s})$ is added to the initial suspensions; despite the fact that CoCO_3 or $\text{Co}(\text{OH})_2$ were only a small fraction of $\text{Mg}(\text{OH})_2$ and did not impact the final solution composition. Nonetheless, the different forms of added Co are very important in the initial stages of reaction. In this regard, it is important to note that for Co to be incorporated into the growing magnesite particle Co must first dissolve from the added solid phase. Likewise, we speculate that similar constraints apply to the incorporation of other minor/trace metals that might facilitate the nucleation and growth of magnesite in natural systems.

Finally, even though the formation kinetics of magnesite can be slow, these results support the inclusion of magnesite as an equilibrium phase in reactive transport simulations of carbon dioxide sequestration in subsurface formations, given the presence of divalent ions (Fe(II), Mn(II), Ca(II)) in natural systems.

Acknowledgement

This work was supported by the Geosciences Research Program in the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences & Biosciences. A portion of this research was performed using EMSL, a national scientific user facility sponsored by the U.S. Department of Energy's Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory. Pacific Northwest National Laboratory (PNNL) is a multi-program national laboratory operated for DOE by Battelle.

Figure 1. XRD patterns for samples after 1 day(a) and 14 days (b) of reaction compared to previous research at 14 days of reaction for samples that did not include added magnesite (c).

Figure 2. SEM image of samples reacted for 14 days in the presence of added magnesite (0.8% by mass).

Figure 3. XRD patterns of reacted samples after 14 days addition of CoCO_3 (0.8% by mass)

Figure 4. SEM image of samples reacted for 14 days with added trace $\text{CoCO}_3(\text{s})$ (0.8% by mass).

Figure 5. XRD images of reacted solutions at 14 days in the presence of initially added $\text{Co}(\text{OH})_2$. (a) absence of initially added NaHCO_3 , b) in the presence of initially added 0.1M NaHCO_3 .

Figure 6. SEM image of magnesite particles grown in solutions with initially added $\text{Co}(\text{OH})_2$ and in 0.1M NaHCO_3 .

Fig.7. (a) STEM HAADF image from a cross section of the magnesite particle reacted for 14 days with $\text{Co}(\text{OH})_2$ particle. (b) EDS map showing the relative distribution of Co in the particle. Core region of the particle is enriched in Co. (c) Extracted EDS spectra from the core and outer regions of the magnesite particle.

Figure 8. APT images of Co distribution in magnesite particles reacted for 14 days in the presence Co(OH)_2 particles, (a) the distribution of Co viewed from a 10 nm thick slice taken from the $56 \times 10 \times 110 \text{ nm}^3$ reconstructed volume. The apex of the reconstruction is closer to the surface of the analyzed particle and the bottom of the reconstruction is closer to the center of the analyzed particle, (b) the 1D distribution of Co concentration (at %) along the z axis. The blue and red lines represent the concentration of Co and Ga, respectively. A maximum error of 0.02% was determined for data points.

Table 1. Percentage difference relative to magnesite for the a and c lattice parameters of different divalent metal carbonates. Also shown is the percentage difference based on the surface area (SA) of the (104) surface. Information on MgCO_3 , CoCO_3 and MnCO_3 from Zhang and Reeder (Zhang and Reeder, 1999), FeCO_3 from Zhang et al. (Zhang et al., 1998), and CaCO_3 from Markgraf and Reeder (Markgraf and Reeder, 1985).

Phase	a(Å)	$\Delta(\%)$	c(Å)	$\Delta(\%)$	(104) SA (Å ²)	$\Delta(\%)$
MgCO_3	4.636	0.0	15.017	0.0	34.0	0.0
CoCO_3	4.660	0.5	14.979	-0.3	34.2	0.7
FeCO_3	4.691	1.2	15.368	2.3	35.0	2.9
MnCO_3	4.776	3.0	15.690	4.5	36.3	6.8
CaCO_3	4.988	7.6	17.061	13.6	40.4	18.8

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