Relative Contributions of Mg Hydration and Molecular Structural Restraints to the Barrier of Dolomite Crystallization: A Comparison of Aqueous and Non-Aqueous Crystallization in (BaMg)CO$_3$ and (CaMg)CO$_3$ Systems

Shi Zhou, Yuebo Wang and Henry Teng *

School of Earth System Science, Tianjin University, Tianjin 300072, China; tjuzhoushi@gmail.com (S.Z.); wangyuebo@tju.edu.cn (Y.W.)
* Correspondence: huihenry.teng@tju.edu.cn or hteng@gwu.edu

Abstract: Carbonate mineralization is reasonably well-understood in the Ca–CO$_2$–H$_2$O system but continuously poses difficulties to grasp when Mg is present. One of the outstanding questions is the lack of success in dolomite MgCa(CO$_3$)$_2$ crystallization at atmospheric conditions. The conventional view holds that hydration retards the reactivity of Mg$^{2+}$ and is supported by solvation shell chemistry. This theory however is at odds with the easy formation of norsethite MgBa(CO$_3$)$_2$, a structural analogue of dolomite, leading to the premise that crystal or molecular structural constrains may also be at play. The present study represents our attempts to evaluate the separate contributions of the two barriers. Crystallization in the Mg–Ba–CO$_2$ system was examined in a non-aqueous environment and in H$_2$O to isolate the effect of hydration by determining the minimal relative abundance of Mg required for norsethite formation. The results, showing an increase from 1:5 to 6:4 in the solution Mg/Ba ratio, represented a ~88% reduction in Mg$^{2+}$ reactivity, presumably due to the hydration effect. Further analyses in the context of transition state theory indicated that the decreased Mg$^{2+}$ reactivity in aqueous solutions was equivalent to an approximately 5 kJ/mol energy penalty for the formation of the activated complex. Assuming the inability of dolomite to crystallizes in aqueous solutions originates from the ~40 kJ/mol higher (relative to norsethite) Gibbs energy of formation for the activated complex, a hydration effect was estimated to account for ~12% of the energy barrier. The analyses present here may be simplistic but nevertheless consistent with the available thermodynamic data that show the activated complex of dolomite crystallization reaction is entropically favored in comparison with that of norsethite formation but is significantly less stable due to the weak chemical bonding state.

Keywords: norsethite; dolomite; transition state theory; activated complex; crystallization barrier; hydration

1. Introduction

Interests in carbonates trace back to 1870s, with the first recognition that CaCO$_3$ may form different polymorphs [1]. Since then, our knowledge base in this field has expanded immensely in virtually all fronts of related areas, first in crystallography [2,3] and mineralogy [4,5], followed by crystallization/dissolution as well as mineral–water interfacial reactions [6–11]. Modern-time motivation to study carbonates lies chiefly in the need to understand biomineralization [12] and the unique chemistry of mineral crystallization and dissolution where the thermodynamic equilibria between CO$_2$ (g), HCO$_3^-$ and CO$_3^{2-}$ (aq), and alkali earth metals control long-term climate [13,14]. To date, significance advances have revealed various physiochemical aspects of carbonate behavior and reactivity, both in geological and biological settings.

Looking at carbonate minerals in the Earth’s crust as a whole, however, one cannot help but notice the puzzling question of dolomite mineralization [15]. Despite belonging
to the same crystal system (trigonal/rhombohedral) as calcite CaCO$_3$ (the most well-studied member of carbonate minerals) and composing ~50% of the world carbonate formations [16], dolomite MgCa(CO$_3$)$_2$ has not been shown to crystallize in inorganic systems at ambient conditions. Dolomite is constructed in a highly ordered structure where not only do the cations and anions separate themselves into individual layers along the c-axis but the two cations, Ca$^{2+}$ and Mg$^{2+}$, also alternate instead of forming mixed layers. Additionally, rather than taking a uniform orientation, the planar CO$_3^{2-}$ units are situated perpendicularly to the c direction and rotate 60° around the axis in each successive layer. Dolomite (R3) differs from calcite (R3c) only in the absence of the c-glide plane because of the alternation of cation layers along the c-axis. Intuitively, the resemblance and similarity between the element Ca and Mg (alkaline earth metals in adjacent periods) may indicate that the formation of dolomite can be simply executed by Mg partially replacing Ca in calcite. The experimental tests thus far however have shown that this conjecture is nowhere close to reality.

The difficulty to incorporate Mg into the calcite structure at ambient conditions is overwhelmingly attributed to the stronger (relative to Ca$^{2+}$) hydration of Mg$^{2+}$ ions [17–20]. The rationale for this reasoning is the heightened charge density of the Mg$^{2+}$ ion originating from the cation’s smaller size (ionic radius 0.72 Å) relative to Ca$^{2+}$ [21]. Assuming a spherical geometry, the charges per surface area on magnesium cations are thus nearly twice of that on calcium cations. A high surface charge density can lead to a substantial charge transfer from ions to solvent, resulting in reduced reactivity of the ions. For magnesium, the net charge on the central Mg$^{2+}$ of Mg[H$_2$O]$_{6}^{2+}$ was calculated to be only 1.18 [15]. In addition, the hydration energy for Mg$^{2+}$ is estimated at about ~30% greater than that for Ca$^{2+}$ [22–28], indicating indeed a lower reactivity of Mg$^{2+}$ in an aqueous environment.

Oddly, the cation hydration retardation theory does not seem to offer valid predictions when applied to siderite (FeCO$_3$, R3c). Using the same arguments for the lack of magnesite MgCO$_3$ formation at atmospheric conditions, the model is set to predict that the ferrous carbonate phase is at least equally difficult to crystallize in ambient aqueous solutions given that Fe$^{2+}$ has a similar size (0.61–0.78 Å depending on the spin state) and a slightly higher (~7%) hydration energy in comparison with Mg$^{2+}$. However, it is well-known [29] that siderite mineralizes frequently at surface conditions, such as in the scale layers on steel pipes in industrial settings related to oil and gas production and transportation. More critically, direct tests of magnesite crystallization in the absence of water (i.e., non-aqueous Mg$^{2+}$ solvation) have not supported the Mg hydration theory. Crucially insightful data with regard to the non-aqueous synthesis of MgCO$_3$ was first provided by a century-old study where Neuberg and Rewald [30] examined the interactions of CO$_2$ gas with CaO and MgO in methanolic suspensions. In the case of CaO, a gel-like compound was obtained and subsequently identified as calcite. For the MgO experiment, no solid product was observed in the end. A more recent study [31] at settings slightly different (higher T and P at 50–70 °C and 3 bar pCO$_2$) from those used by Neuberg and Rewald obtained an anhydrous magnesium carbonate precipitate but only found to be nano-aggregates of amorphous MgCO$_3$. In light of the hydration retardation theory’s implication that magnesite (and dolomite) should crystallize if the hydration shell around Mg$^{2+}$ is breached or weakened, these results seem to strongly contradict the assumed hydration effect as all of the syntheses were performed in the absence of water.

An even more intriguing case inconsistent with the Mg hydration retardation theory is the binary carbonate mineral norsethite MgBa(CO$_3$)$_2$ [32,33]. Other than the size difference between the cation pairs of Mg vs. Ba (~0.8 Å) and Mg vs. Ca (~0.3 Å), norsethite is very similar to dolomite structure-wise, with the main distinction being that the orientations of the carbonate groups are more flexible instead of strictly fixed to a 60° rotation in adjacent layers [33]. Owing to this difference, norsethite may not be considered a true isotypic analogue of dolomite in a strict sense but, nonetheless, has a similar stacking order in the c direction with regard to cation–anion and cation–cation relationships. What is paradoxical is that, while dolomite has not been crystallized at atmospheric conditions thus
far, norsethite can precipitate readily in a room temperature aqueous environment [34–36]. Although the results from a number of recent studies [37–42] indicated that the reaction pathway may involve dissolution–recrystallization of certain precursors, the routineness of norsethite formation clearly demonstrates that Mg$^{2+}$ can dehydrate efficiently to enter the lattice of anhydrous carbonate crystals at ambient conditions. More importantly, the relative cation size (Mg to Ba vs. Mg to Ca) and the anion orientation are all structural factors, and the mere fact that a change in such parameters can result in the crystallization of ordered binary magnesium carbonate MgBa(CO$_3$)$_2$ argue strongly for a more important role of atomic arrangement along the reaction coordinate of dolomite formation, aside from Mg hydration. We suspect the aspect of structural restraints may lie chiefly in the transition state of the crystallization reactions because the Gibbs energy of formation for dolomite ($-2148.90$ kJ/mol) [43] and norsethite ($-2167 \pm 2$ kJ/mol) [40] is not significantly different. The goal of this study is to test this hypothesis and to assess the relative weight of Mg hydration and the structural limitation. We carry out crystallization experiments in H$_2$O solutions and a non-aqueous solvent to determine the minimal relative abundance of Mg needed to form norsethite and use the difference in the determined minima to estimate the magnitude of the hydration effect. We then apply the transition state theory (TST) to further evaluate the contribution of Mg hydration to the reduction in the activated complex. Finally, we compare the Mg hydration effect and the activation free energy of dolomite crystallization to gauge the approximate scale of the structural restraints in the overall reaction process.

2. Methods

2.1. Crystallization Experiments

Aqueous stock solutions were prepared from BaCl$_2$, MgCl$_2$, and NaHCO$_3$ using distilled deionized water. Chloride solutions containing 1, 10, 40, and 50 mM/L of metal ions were prepared first for Mg and Ba separately, followed by mixing varied proportions of the MgCl$_2$ and BaCl$_2$ solutions to achieve the desired levels of the Mg-to-Ba ratio (Mg/Ba, from 4:6 to 9:1). The concentration of sodium bicarbonate solution varied from 5 to 250 mM. In a typical synthesis experiment, 20 mL of NaHCO$_3$ solution were slowly titrated into 20 mL of a mixed cation chloride solution, sealed, and left still for ten days. Speciation, ionic activities, and supersaturation states of each experimental solution were calculated via the computer code PHREEQC. The solubility product for witherite and norsethite were assumed to be $K_{sp,wt} = 10^{-8.56}$ (PHREEQC database) and $K_{sp,nr} = 10^{-17.73}$ [40].

Non-aqueous experiments were carried out in formamide (O=CH–NH$_2$, FMD) that has a weaker (relative to H$_2$O) autoionization ( autoprotolysis constant $10^{-16}$ vs. $10^{-14}$) but a stronger polarity (dielectric constant 109 vs. 78) [44] and can dissolve inorganic salt easily to make experimental solutions. Stock solutions of 0.2M MgCl$_2$, 0.2M BaCl$_2$, and 0.2 Cs$_2$CO$_3$ were prepared by dissolving the corresponding salt compounds that were pre-dried in an oven at 60 °C. The experimental solutions with varied Mg/Ba content (5:1, 2:1, 1:1, 1:2, and 1:5) were then made by mixing that of MgCl$_2$ and BaCl$_2$ in desired proportion, followed by slow titration into the Cs$_2$CO$_3$ stock. The final solution was kept closed and still for 24 h.

All experiments were conducted at room temperature ($25 \pm 1$ °C). At the end of crystallization experiments, individual solutions were centrifuged (10,000 rpm, 10 min) and the solid was collected; washed extensively in ethanol to remove the residual Na$^+$, Cs$^+$, and Cl$^-$; and oven-dried at below 30 °C. Chemicals and solvent used in the synthesis experiments were of analytical grade and purchased from Shanghai Aladdin Bio-Chem Technology Co.

2.2. Precipitate Identification

The crystallinity and mineral composition of the precipitates were characterized by powder X-ray diffraction (XRD) using a Riguka MiniFlex 600 instrument (Cu K$_{α1}$ radiation). The diffractograms were collected from 3–70° with a scanning rate of 2°/min. Prior to
of 15

instrumental analysis, the precipitates were dispersed in alcohol and pipetted on a zero-
background monocristalline silicon sample holder and placed into the diffractometer once
dried. The diffractograms were analyzed using the package of MDI Jade 6. Other than
XRD characterization, the precipitates were not checked for impurity contents of Na, Cs,
and Cl through chemical analyses.

3. Results

A total of 82 synthesis experiments (Table 1) were carried out in aqueous solutions
with various combinations of supersaturation, cation-to-anion ratio ([Mg + Ba]/CO$_3$),
and relative concentrations of Mg to Ba (Mg/Ba). All experiments were performed in
supersaturated solutions with reference to norsethite (0.3 < log$\Omega_N$ < 5.46, where $\Omega_N$
is the ratio of ionic activity product to the solubility product of norsethite), with all but six of
them undersaturated with respect to witherite (−0.63 < log$\Omega_W$ < 2.33). Altogether, crystal
formation was observed in 74 of the experimental runs (Table 1), of which 26 exhibited
XRD signals of norsethite crystallization. The experiments that did not show crystallization
either had low supersaturation with respect to norsethite (log$\Omega_N$ < 1) and undersaturation
to witherite or had a high level of Mg presence (Mg:Ba > 7:3) but low supersaturation
relative to witherite (log$\Omega_W$ < 0.4).

Exclusive formation of norsethite required a strong presence of Mg (Mg/Ba > 7/3);
decreasing Mg usually led to co-precipitation of norsethite and witherite first, followed by
sole occurrence of witherite (Figure 1). The minimal requirement of Mg/Ba for norsethite
to be a component of the crystallization product was 6/4, and this value appeared to be
positively correlated with $\Omega_N$ and the cation-to-anion ratio in the experimental solutions.
For example, at log$\Omega_N$ ≈ 2 to 2.5 and cation/anion ≈ 0.28, norsethite crystallized along
with witherite in solutions with Mg:Ba = 6:4; when log$\Omega_N$ increased to approximately 5–5.5
and cation/anion ≈ 21–22, norsethite was only detected at the conditions of Mg:Ba = 8:2.
On the other hand, the exclusion of norsethite from crystallization (i.e., witherite was the
sole product) could occur at any level of Mg/Ba and any supersaturation (with respect to
both norsethite and witherite) as long as the cation-to-anion ratio was sufficiently large
(usually > 80 ~ 100). For example, at log$\Omega_N$ ≈ 2.2 to 2.7 and cation/anion ≈ 130–140,
witherite was the only phase found in solution at log$\Omega_W$ ≈ 0.3–1.0, same as the experiments
where log$\Omega_N$ ≈ 4.0–4.5, cation/anion ≈ 161–177, and log$\Omega_W$ ≈ 1.2–1.8.

A much simpler outcome was observed in formamide containing varied amounts
of Mg$^{2+}$ and Ba$^{2+}$ at a fixed concentration of ([Mg] + [Ba]). Unlike the results in aqueous
environment where norsethite formation required Mg dominated solution chemistry and in
fact was never observed once Mg/Ba < 6/4, norsthite was shown to be a major component
of the precipitate at Mg:Ba = 1:2 along with witherite and the single solid phase at
Mg/Ba = 1 (Figure 2). Similar to the observations in H$_2$O, a reduction in the relative
abundance of Mg suppressed norsethite crystallization and ultimately led to a dominant
occurrence of witherite at Mg/Ba = 1/5 (Figure 2, traces of norsethite still visible). Different
from aqueous experiments, however, a strong Mg presence with Mg/Ba = 2 and 5 in
FMD did not promote norsethite crystallization but instead led to the formation of an
amorphous phase in both cases (Figures 2 and 3). The amorphous precipitate appeared as
nano-aggregate (Figure 3 upper) of particulate constituents with approximately uniform
sizes of <10 nm (Figure 3 upper). In contrast, the crystalline phases (Figure 3 middle
and lower) exhibited a conglomerate form with individual crystals of 20–100 nm in size
(Figure 3 middle and lower).
Table 1. Solution chemistry and mineral composition of aqueous synthesis experiments (SI<sub>nrs</sub> and SI<sub>wit</sub>: saturation Index with respect to norsethite (N) and witherite (W); Mg/Ba: activity ratio aMg<sup>2+</sup>/aBa<sup>2+</sup>; np: no precipitation).

| (Mg,Ba)Cl<sub>2</sub> [M] | NaHCO<sub>3</sub> [M] | Mg/Ba | SI<sub>nrs</sub> | SI<sub>wit</sub> | aMg<sup>2+</sup> [mM] | aBa<sup>2+</sup> [mM] | aCO<sub>3</sub><sup>2−</sup> [mM] | Mineral Phase |
|--------------------------|---------------------|-------|----------------|---------------|----------------|----------------|----------------|----------------|
| 0.005                    | 9:1                 | 2.03  | 0.24           | 0.103         | 0.012          | 0.405         | N              |
|                          | 8:2                 | 2.28  | 0.54           | 0.092         | 0.023          | 0.406         | N              |
|                          | 7:3                 | 2.4   | 0.71           | 0.080         | 0.035          | 0.406         | N              |
|                          | 6:4                 | 2.45  | 0.84           | 0.069         | 0.047          | 0.406         | W + N          |
|                          | 5:5                 | 2.47  | 0.94           | 0.058         | 0.059          | 0.406         | W              |
|                          | 0.05                | 9:1   | 1.88           | 0.16          | 0.158          | 0.018         | 0.225          | N              |
|                          | 8:2                 | 2.13  | 0.47           | 0.140         | 0.036          | 0.225         | N              |
|                          | 7:3                 | 2.25  | 0.64           | 0.123         | 0.054          | 0.225         | N + W          |
|                          | 6:4                 | 2.31  | 0.77           | 0.105         | 0.072          | 0.226         | W              |
|                          | 5:5                 | 2.33  | 0.87           | 0.088         | 0.089          | 0.226         | W              |
|                          | 0.01                | 9:1   | 0.8            | −0.38         | 0.305          | 0.034         | 0.034          | N              |
|                          | 8:2                 | 1.05  | −0.08          | 0.271         | 0.068          | 0.034         | N              |
|                          | 7:3                 | 1.17  | 0.1            | 0.237         | 0.102          | 0.034         | W              |
|                          | 6:4                 | 1.24  | 0.23           | 0.203         | 0.136          | 0.034         | W              |
|                          | 5:5                 | 1.26  | 0.33           | 0.169         | 0.170          | 0.034         | W              |
|                          | 0.005               | 9:1   | 0.3            | −0.63         | 0.334          | 0.037         | 0.017          | np             |
|                          | 8:2                 | 0.55  | −0.33          | 0.387         | 0.074          | 0.017         | np             |
|                          | 7:3                 | 0.68  | −0.15          | 0.260         | 0.115          | 0.018         | np             |
|                          | 6:4                 | 0.74  | −0.02          | 0.223         | 0.148          | 0.018         | np             |
|                          | 5:5                 | 0.76  | 0.08           | 0.185         | 0.186          | 0.018         | np             |
|                          | 0.25                | 9:1   | 3.93           | 1.18          | 1.035          | 0.116         | 0.363          | N              |
|                          | 8:2                 | 4.18  | 1.49           | 0.919         | 0.232          | 0.365         | N              |
|                          | 7:3                 | 4.30  | 1.67           | 0.804         | 0.348          | 0.366         | N              |
|                          | 6:4                 | 4.36  | 1.79           | 0.689         | 0.463          | 0.368         | N + W          |
|                          | 5:5                 | 4.39  | 1.89           | 0.574         | 0.579          | 0.369         | W              |
|                          | 4:6                 | 4.37  | 1.97           | 0.459         | 0.694          | 0.371         | W              |
|                          | 0.1                 | 9:1   | 3.66           | 1.05          | 1.554          | 0.173         | 0.179          | N              |
|                          | 8:2                 | 3.92  | 1.35           | 1.380         | 0.345          | 0.180         | N + W          |
|                          | 7:3                 | 4.04  | 1.53           | 1.207         | 0.517          | 0.182         | W + N          |
|                          | 6:4                 | 4.11  | 1.66           | 1.033         | 0.671          | 0.183         | W              |
|                          | 5:5                 | 4.13  | 1.76           | 0.861         | 0.862          | 0.185         | W              |
|                          | 4:6                 | 4.12  | 1.84           | 0.688         | 1.032          | 0.186         | W              |
|                          | 0.01                | 9:1   | 3.31           | 0.87          | 1.954          | 0.215         | 0.096          | N + W          |
|                          | 8:2                 | 3.57  | 1.18           | 1.736         | 0.431          | 0.097         | W              |
|                          | 7:3                 | 3.70  | 1.36           | 1.513         | 0.655          | 0.098         | W              |
|                          | 6:4                 | 3.77  | 1.49           | 1.300         | 0.860          | 0.099         | W              |
|                          | 5:5                 | 3.80  | 1.59           | 1.082         | 1.074          | 0.101         | W              |
|                          | 4:6                 | 2.79  | 1.68           | 0.865         | 1.288          | 0.102         | W              |
|                          | 0.005               | 9:1   | 1.61           | 0.02          | 2.694          | 0.293         | 0.010          | np             |
|                          | 8:2                 | 1.87  | 0.33           | 2.395         | 0.585          | 0.010         | np             |
|                          | 7:3                 | 2.00  | 0.51           | 2.095         | 0.877          | 0.010         | np             |
|                          | 6:4                 | 2.08  | 0.64           | 1.795         | 1.170          | 0.010         | W              |
|                          | 5:5                 | 2.11  | 0.75           | 1.496         | 1.462          | 0.011         | W              |
|                          | 4:6                 | 2.11  | 0.83           | 1.197         | 1.754          | 0.011         | W              |
Table 1. Cont.

| (Mg,Ba)Cl2 [M] | NaHCO3 [M] | Mg/Ba | SI\textsubscript{ins} | SI\textsubscript{wlt} | aMg\textsuperscript{2+} [mM] | aBa\textsuperscript{2+} [mM] | aCO\textsubscript{3}\textsuperscript{2−} [mM] | Mineral Phase |
|----------------|------------|-------|-----------------|----------------|----------------|----------------|----------------|---------------|
| 0.25           |            |       |                 |                 |                |                |                |               |
| 0.04           | 9:1        | 4.87  | 1.65            | 4.125           | 0.448          | 0.275          | N              |               |
|                | 8:2        | 5.13  | 1.96            | 3.662           | 0.895          | 0.279          | N + W          |               |
|                | 7:3        | 5.26  | 2.14            | 3.200           | 1.341          | 0.282          | W              |               |
| 0.1            | 9:1        | 4.41  | 1.41            | 5.824           | 0.617          | 0.115          | N              |               |
|                | 8:2        | 4.67  | 1.72            | 5.171           | 1.233          | 0.117          | W + N          |               |
|                | 7:3        | 4.8   | 1.90            | 4.518           | 1.847          | 0.119          | W              |               |
| 0.05           | 9:1        | 3.93  | 1.13            | 6.843           | 0.715          | 0.057          | W              |               |
|                | 8:2        | 4.20  | 1.48            | 6.077           | 1.430          | 0.058          | W              |               |
|                | 7:3        | 4.33  | 1.67            | 5.312           | 2.143          | 0.059          | W              |               |
| 0.01           | 9:1        | 2.63  | 0.52            | 7.993           | 0.824          | 0.011          | W              |               |
|                | 8:2        | 2.90  | 0.83            | 7.104           | 1.648          | 0.013          | W              |               |
|                | 7:3        | 3.04  | 1.02            | 6.215           | 2.471          | 0.016          | W              |               |
| 0.005          | 9:1        | 2.03  | 0.22            | 8.166           | 0.840          | 0.005          | W              |               |
|                | 8:2        | 2.31  | 0.53            | 7.259           | 1.680          | 0.006          | W              |               |
|                | 7:3        | 2.45  | 0.72            | 6.351           | 2.520          | 0.006          | W              |               |
| 0.25           |            |       |                 |                 |                |                |                |               |
| 0.5            | 9:1        | 5.00  | 1.71            | 5.145           | 0.554          | 0.256          | N              |               |
|                | 8:2        | 5.26  | 2.02            | 4.566           | 1.105          | 0.260          | N + W          |               |
|                | 7:3        | 5.39  | 2.2             | 3.989           | 1.656          | 0.263          | W              |               |
|                | 6:4        | 5.46  | 2.33            | 3.414           | 2.205          | 0.267          | W              |               |
| 0.1            | 9:1        | 4.49  | 1.45            | 7.142           | 0.747          | 0.104          | W + N          |               |
|                | 8:2        | 4.76  | 1.76            | 6.340           | 1.493          | 0.107          | W              |               |
|                | 7:3        | 4.89  | 1.95            | 5.540           | 2.236          | 0.109          | W              |               |
|                | 6:4        | 4.97  | 2.08            | 4.742           | 2.978          | 0.111          | W              |               |
| 0.05           | 9:1        | 4.00  | 1.2             | 8.277           | 0.854          | 0.051          | W              |               |
|                | 8:2        | 4.27  | 1.51            | 7.351           | 1.706          | 0.053          | W              |               |
|                | 7:3        | 4.41  | 1.7             | 6.427           | 2.558          | 0.054          | W              |               |
|                | 6:4        | 4.48  | 1.83            | 5.504           | 3.408          | 0.055          | W              |               |

Figure 1. A sample XRD spectra of the precipitates in aqueous experiments in solutions containing 0.25 M NaHCO\textsubscript{3} and 0.01 M (Mg,Ba)Cl\textsubscript{2} (ns: norsethite; wt: witherite; bottom spectrum: Mg/Ba = 7/3; bottom spectrum: Mg/Ba = 6/4 (top); middle spectrum: Mg/Ba = 5/5).
Figure 2. XRD spectra of the precipitates in the FMD experiments (ns: norsethite, wt: witherite). All visible peaks below $2\theta$ of 55° were able to be assigned to norsethite and witherite, suggesting that those two minerals may be the only phases that occurred in the experiments. Notice the lack of crystallinity at conditions of 2Mg:1Ba and 5Mg:1Ba as well as the presence of norsethite (10.1) and (00.3) peaks at 1Mg:5Ba.

Figure 3. SEM photomicrographs of the precipitates in FMD experiments (upper: Mg/Ba = 5:1, amorphous aggregates; middle: Mg/Ba = 1:1, rhombohedral norsethite; lower: Mg/Ba = 1:5, lenticular witherite).
4. Discussion

4.1. Hydration Hindrance

Two observations stand out distinctively from the aqueous experiments. (1) Incongruent crystallization ([Mg/Ca]solid/[Mg/Ca]solution ≠ 1) occurred for exclusive norsethite formation as the solutions were required to have more Mg than Ba with an observed minimal value of Mg/Ba ≈ 7/3, and (2) norsethite was never detected in solutions with Mg/Ba < 6/4, whereas witherite could crystallize in Mg²⁺ dominated (as strong as Mg:Ba = 9:1) conditions (provided that the cation-to-anion ratio is high). The requirement of Mg-enriched solution to precipitate norsethite was observed previously by Lippmann [4] and Hood et al. [36] with a relative abundance of Mg/Ba ≈ 1.6 while maintaining CO₃²⁻ at a fixed concentration (0.5 M). A plausible conclusion we can draw from these findings is that the stronger hydration of magnesium (than of Ba²⁺) may have limited Mg²⁺ from being in the free (dehydrated) state, so much so that 50% more Mg²⁺ was needed to match the quantity of free Ba²⁺ ions in the solutions. At the opposite end, although witherite appeared to form more easily in the Mg–Ba–CO₃–H₂O system given that the log Ω_w is smaller throughout the experiments by a factor of 2–10 in comparison with log Ω_n, norsethite nevertheless crystallizes readily and can often be the exclusive precipitate at specific conditions (Mg/Ba > ~7/3, cation/anion < ~60). Aqueous crystallization of norsethite at ambient conditions is known all along [4,35,38,45,46] but is not known to require additional energy input other than supersaturation, and thus, it is inconsistent with the view that Mg²⁺–H₂O interactions act as a barrier to preventing magnesium ions from entering the rhombohedral carbonate lattice.

Contrasting with the Mg-rich requirement for norsethite precipitation in aqueous environment, norsethite can crystallize in Mg-depleted FMD solutions with Mg/Ba = 1/2–1/5. These observations on the one hand appear to be largely in line with the expectations of the Mg hydration theory, considering that the binding energy of Mg²⁺ with FMD (~125 kcal/mol [47]) is significantly smaller than with H₂O (~260 kcal/mol [22,48]), and the hydrogen bonds between formamide molecules (8–13 kJ/mol for NH···O and NH···N) are meaningfully weaker than that between water molecules (21 kJ/mol for OH···O) [49]. Simply put, it is reasonable to assume that, while the stronger (relative to Ba²⁺) hydration of Mg²⁺ dictates that magnesium ions stay largely in a hydrated form in aqueous solutions, the FMD solvation shell around Mg²⁺ is not as rigid and tight as the hydration shell, allowing for the presence of sufficient amount of free magnesium ion to participate in the crystallization reactions. On the other hand, the same rationale would lead one to expect the crystallization of anhydrous magnesium carbonate in FMD when this assumption is extended to Mg dominated conditions. However, experimental results, showing the lack of crystallinity in precipitates formed at conditions of Mg/Ba > 1 (Figure 2), defied this logic reasoning. Furthermore, in comparison with the amorphous calcium carbonate (ACC) formed in the presence of Mg ions, the Mg–Ba–CO₃ amorphous precipitate (Figure 3 upper) had a rather evenly distributed particle size instead of a mixture of distinctly sized populations [50], suggesting the occurrence of a monotonous short range order (the recurrence of Ba–O and Mg–O coordination) rather than the commonly observed Ca–ACC (mainly Ca–O order) and Mg–ACC (both Ca–O and Mg–O order) in the Mg–Ca–CO₃ system.

4.2. Structural Restraints

The lack of long-range orders in carbonate precipitates formed in Mg-rich FMD solutions was first observed in the Ca–Mg–CO₃ system [51], where different from the Ba–Mg–CO₃ system of concern in this study, congruent crystallization of MgCa(CO₃)₂ (dolomite) did not occur; high Mg (37% mole ratio) calcite instead formed at Mg/Ca = 1. Given the absence of H₂O in the experiments, the authors deduced that hydration may be an external force that is partially responsible for hindering dolomite and magnesite formation at ambient conditions, and crystal structural restraints, particularly reduced freedom of the CO₃ groups and the increased lattice strains resulting from the size difference between
Mg$^{2+}$ and Ca$^{2+}$ ions, may be the inherent factor preventing magnesium from entering the trigonal carbonate structure at ambient conditions. A later study [52] presented additional evidence embracing the premise that Mg for Ca substitution in calcite is limited to < 40%. In the context of lacking dolomite formation in the Ca–Mg–CO$_2$–FMD system, the unhindered crystallization of norsethite at Mg/Ba = 1 observed in the present study appears to be consistent with the view of structural restraints. This is because, unlike dolomite (R3), the CO$_3$ groups in the norsethite (low temperature polymorph, R3c) are not as rigidly constrained. The refined norsethite structure by Effenberger et al. [33] indicates that the carbonate groups stacked along the c direction do not strictly alternate their orientations in adjacent layers but instead rotate clockwise and anti-clockwise successively within a plane and in the c-axis (compare Figure 9a,c in Effenberger et al., 2014 [33]). In doing so, the unit cell doubles its size in the c-direction and the resultant structure allows for the large cation Ba$^{2+}$ to increase its coordination number while maintaining the octahedral coordination of the smaller ion Mg$^{2+}$ without creating much stress. In contrast, the dolomite structure does not have the luxury to relax because the R3 symmetry dictates that the planar CO$_3$ rotates 60° in alternate layers. Thus, it appears that the lack of flexibility in the a-b plane is a key parameter limiting dolomite crystallization at ambient conditions. In their study of PbMg(CO$_3$)$_2$ and norsethite crystallization, Pimentel and Pina [39] observed a reduction in the formation rate associated with the cation size decrease from Ba to Pb and proposed that the shape and relative size of the constituent coordination polyhedra may play a fundamental role (may be more relevant than magnesium hydration) in controlling the stability of dolomite-like structures such as those involving Mg$^{2+}$, Ca$^{2+}$, Ba$^{2+}$, Pb$^{2+}$, and Sr$^{2+}$. Together, the findings to date suggest that structural flexibility in terms of adapting to the variable coordination of the non-Mg cations is critical for long range order development in all rhombohedral binary carbonate systems.

Considerations in structural restraints also lead us to speculate that magnesium carbonate formation may be an initial step in the reaction pathways of dolomite and norsethite crystallization. Two lines of thought are factored in this proposition. First, anhydrous carbonate can crystallize into two crystal systems: trigonal or orthorhombic. A general understanding [53–55] is that minerals with cations smaller than Ca$^{2+}$ (ionic radius \( r = 100 \text{ pm} \)) adopt the trigonal structure (metal ions coordinated by six oxygens), whereas those larger than Ca$^{2+}$ usually take on the orthorhombic form (metal ions coordinated by nine oxygens). Calcium, being the pivot, can be either trigonal (calcite) or orthorhombic (aragonite). As such, it is expected that magnesite MgCO$_3$ and witherite Ba(CO$_3$)$_2$ are exclusively trigonal and orthorhombic, respectively, given the cation size of Mg$^{2+}$ (\( r = 72 \text{ pm} \)) and Ba$^{2+}$ (\( r = 152 \text{ pm} \)). When binary systems are concerned, while it is conceivable that dolomite and proto-dolomite adopt a trigonal structure (because of the structural flexibility of calcium carbonate), the rationale for norsethite’s structural preference is not so distinctly discernable due to the trigonal and orthorhombic combination of the end members. The fact that norsethite ends up in the trigonal system indicates that the rhombohedral structure in principle is the thermodynamically more stable one for a Mg–Ba binary carbonate crystal. Moreover, the occurrence of norsethite and witherite co-crystallization signals that, while Ba can be incorporated in both trigonal and orthorhombic structures, magnesium on the other hand can only enter crystals with trigonal symmetry. Thus, on the basis that magnesium and barium do not form solid solution (Ba,Mg)CO$_3$, we deduce that the initial step of norsethite crystallization is more likely the formation of magnesite units, which allow for a later or subsequent incorporation of Ba for the nucleation to continue. Conversely, if witherite is the first unit to form, the inability of Mg to enter the orthorhombic structure leads to a discontinuation of the crystallization process without the formation of norsethite in the end. Second, a common behavior of the Ca–Mg–CO$_2$ and Ba–Mg–CO$_2$ system in non-aqueous environment is the lack of crystalline precipitates in Mg-dominated solutions. This is surprising because ~33% to ~17% of solvated cations in those scenarios (Mg/Ba and Mg/Ca = 2 and 5, this study and Xu et al., 2013 [51]) are barium and calcium and should result in witherite and calcite crystallization, as they did.
in aqueous environments. A plausible interpretation is that $\text{Mg}^{2+}$, which may be less stable in an un-hydrated form due to the high charge density relative to $\text{Ba}$ and $\text{Ca}$ ions, has the advantage to bind with $\text{CO}_3^{2-}$ first. When Mg is the minority ion in the solution and binds preferentially with carbonate ions, $\text{Ba}^{2+}$ and $\text{Ca}^{2+}$ can interact with the remaining $\text{CO}_3^{2-}$ to form witherite and calcite or can be incorporated in the prior-formed $\text{Mg}-\text{CO}_3$ unit to crystallize in norsethite and high-Mg calcite. In Mg-dominating solutions, however, rapid interactions of Mg with $\text{CO}_3$ ions lead to amorphous magnesium carbonate precipitation (on the assumption that the $\text{Mg}-\text{CO}_3$ units cannot stack to form 3D crystalline structures due to the entropy penalty in the $\text{CO}_3$ groups) [51] and a quick consumption of $\text{CO}_3^{2+}$, leaving $\text{Ba}^{2+}$ and $\text{Ca}^{2+}$ behind to stay in the solution without their host minerals witherite and calcite or to occur as minor components in the amorphous phases.

It is worth noting that a number of previous studies actually found [4,38,40,45,56] $\text{BaCO}_3$, instead of $\text{MgCO}_3$, being a precursor of norsethite at atmospheric conditions. Considering the recent finding that norsethite formation proceeds through a crystallization (chiefly of $\text{Na}_3\text{Mg}(\text{CO}_3)_2\text{Cl}$, with minor witherite and norsethite)–dissolution–recrystallization (of norethite) pathway [38], we suspect the incorporation of $\text{Ba}$ into the trigonal carbonate structure (or the transformation of $\text{BaCO}_3$ from orthorhombic to rhombohedral class) is a kinetically unfavored process. This may be especially true at low T, where the formation of ordered $\text{MgCO}_3$ is challenging and the orthorhombic template for $\text{BaCO}_3$ to epitaxially grow on is lacking. As such, witherite is expected to form first but dissolves subsequently to release $\text{Ba}^{2+}$ once $\text{MgCO}_3$ units are in place to crystallize $\text{MgBa(CO}_3)_2$. At higher T when magnesite can readily form and the orthorhombic to rhombohedral transformation for $\text{BaCO}_3$ is less hindered, one should expect $\text{MgCO}_3$ to be a precursor of norsethite. This view is in fact consistent with the experimental observation that magnesite is the only precursor during norsethite crystallization at temperatures above 100 °C [57].

4.3. Relative Effect of Mg Hydration and Structural Restraints

The above discussion seems to converge on a conclusion that both Mg hydration and lattice structure are in play in limiting dolomite formation at ambient conditions. We now try to evaluate the relative importance of the two barriers. At a microscopic level, crystallization is characterized by the process of particle attachment and detachment. One effective approach to quantify this process is through the application of the transition state theory. Since dolomite (and magnesite in the same sense) is the thermodynamically stable phase at ambient conditions [18,58–61], the difficulty to crystallize such minerals is safely ascribed to the reaction kinetics. In the TST approach, the kinetic limitations can be assessed specifically by examining the concentration of the activated complex at constant temperature. To a first-degree approximation, we assume the nucleation of norsethite proceeds through the following reaction (Equation (1)):

$$\text{Mg}^{2+} + \text{Ba}^{2+} + 2\text{CO}_3^{2-} \rightleftharpoons (\text{MgCO}_3\cdot\text{BaCO}_3)^\dagger \rightarrow \text{MgBa(CO}_3)_2$$ (1)

where $(\text{BaCO}_3\cdot\text{MgCO}_3)^\dagger$ refers to the activated complex and $\text{Mg}^{2+}$, $\text{Ba}^{2+}$, and $\text{CO}_3^{2-}$ are the effective concentrations of the reactant ions. As the TST model is thermodynamics based, the following relations exist in the Ba–Mg–$\text{CO}_3$ system (Equation (2)):

$$K_N^\dagger = \frac{[(\text{MgCO}_3\cdot\text{BaCO}_3)^\dagger][\text{Mg}^{2+}][\text{Ba}^{2+}][\text{CO}_3^{2-}]}{2} = \exp(-\Delta G_N^\dagger/RT)$$ (2)

where $K_N^\dagger$ and $\Delta G_N^\dagger$ are the equilibrium formation constants and the activation free energy (Gibbs energy of formation of the activated complex) for norsethite crystallization. It then follows that the concentration of the activated complex satisfies the following expression (Equation (3)):

$$[(\text{MgCO}_3\cdot\text{BaCO}_3)^\dagger] = [\text{Mg}^{2+}][\text{Ba}^{2+}][\text{CO}_3^{2-}]^2\exp(-\Delta G_N^\dagger/RT)$$ (3)
Note that the maximal concentration for the activated complex implicated by Equation (3) can only be achieved at the conditions of $[\text{Mg}^{2+}] / [\text{Ba}^{2+}] = 1$. This is because the charge neutrality requirement for chemical reactions stipulates the total cation concentration ($[\text{Mg}^{2+}] + [\text{Ba}^{2+}]$) in the system to be a fixed value, and consequently, the ionic activity product of the cations reaches the maximum at equal relative abundance for each individual cation. As the minimal relative abundance of Mg for norsethite crystallization is $\text{Mg}/\text{Ba} = 1/5$, the increased value of $\text{Mg}/\text{Ba} = 6/4$ in water suggests that hydration may have reduced the availability of free Mg ions (or the reactivity of Mg$^{2+}$) by ≈80%.

Applying the TST theory to the Ca–Mg–CO$_2$ system, we may have the following relations (Equations (4)–(6)):

$$\text{Mg}^{2+} + \text{Ca}^{2+} + 2\text{CO}_3^{2−} \rightleftharpoons (\text{MgCO}_3\text{CaCO}_3)^\ddagger \rightarrow \text{MgCa(}\text{CO}_3\text{)}_2$$ (4)

$$K^D_T = [(\text{MgCO}_3\text{CaCO}_3)^\ddagger] / [\text{Mg}^{2+}\text{Ca}^{2+}][\text{CO}_3^{2−}]^2 = \exp(–\Delta G^D_T / RT)$$ (5)

$$[(\text{MgCO}_3\text{CaCO}_3)^\ddagger] = [\text{Mg}^{2+}][\text{Ca}^{2+}][\text{CO}_3^{2−}]^2[\exp(–\Delta G^D_T / RT)]$$ (6)

The similarity of these equations to Equations (1)–(3) suggests that the weakened solvation effect on Mg in FMD should also lead to the formation of dolomite (at least proto-dolomite) in the non-aqueous solution with Mg/Ca = 1 if the magnitude of $\exp(–\Delta G^D_T / RT)$ is comparable with that for norsethite crystallization. Published $\Delta G^\ddagger$ values for the two binary phases do not support this prediction as $\Delta G^D_T$ is greater than $\Delta G^D_N$ by more than 50%. Since the solvation effect of FMD on Mg should be the same in both systems, the higher $\Delta G^D_T$ in conjunction with the lack of any carbonate phases with Mg:Ca ≈ 1 in the Mg–Ca–CO$_2$ non-aqueous solutions indicates that, besides Mg hydration, additional hindrance inherent to the Gibbs free energy of the activated complex exists in restricting the formation of dolomite and proto-dolomite at ambient conditions.

The free energy term $\exp(–\Delta G^\ddagger / RT)$ can be further break down to $\exp(–\Delta H^\ddagger / RT)\exp((\Delta S^\ddagger / T))$ based upon the fundamental relation of $G = H – TS$. Here, the enthalpic component is a reflection of bond strength, and the entropy term is the spatial configuration of the activated complex. The published data (Table 2) [40, 62–66] reveal that $(\text{MgCO}_3\text{CaCO}_3)^\ddagger$ is in fact an entropically more favored species than $(\text{MgCO}_3\text{BaCO}_3)^\ddagger$, stating that the high $\Delta G^D_T$ is derived primarily from the enthalpic contribution, i.e., weaker bonding in the activated complex. The Ca–O bond is only ~17% weaker than the Ba–O bond (dissociation energy 464 kJ/mole and 563 kJ/mole, respectively), indicating the $\Delta H^\ddagger$ for $(\text{MgCO}_3\text{CaCO}_3)^\ddagger$ and $(\text{MgCO}_3\text{BaCO}_3)^\ddagger$ should only differ slightly as long as the spatial arrangement of atoms (i.e., bond angle and distance) in the two species are similar. The fact that $\Delta H^D_T$ (132 kJ/mole) is more than ~80% higher than $\Delta H^D_N$ (77.52 kJ/mole) suggests the existence of a significant structural difference between the two activation states, consistent with the entropic factor of the two species ($\Delta S^D_N = −18.1 \text{ J/K/mole}$ and $\Delta S^D_T = 29.7 \text{ J/K/mole}$). A potential explanation is that $(\text{MgCO}_3\text{BaCO}_3)^\ddagger$ may have a more ordered structure due to the inability of Mg$^{2+}$ and Ba$^{2+}$ to form a single mixed layer, so that the oxygens in the CO$_3$ groups can bind to Mg in the +c direction and Ba in the −c direction without distorting the bond lengths on either side. On the contrary, $(\text{CaCO}_3\text{MgCO}_3)^\ddagger$ may be more disordered because Ca and Mg can replace each other in any binding geometry, resulting in oxygen–metal bonds in any orientation of the CO$_3$ groups having both Ca and Mg attached. Consequently, the bonds cannot adopt the optimal length and angle due to the size difference of Ca and Mg ions (bond length Mg–O 2.082 Å, Ca–O 2.382 Å in dolomite). After all, activated complexes differ from but resemble the products one way or the other. It is therefore reasonable to speculate that the ordered structure of norsethite and the common occurrence of disordered (Ca,Mg)CO$_3$ phases may be a reflection of the corresponding activated complex one way or the other.
Table 2. Thermodynamic properties of the activated complexes for different carbonate minerals [24,40,62,63,66].

| Mineral   | T(K) | ΔH° (kJmol⁻¹) | ΔS° (JK⁻¹mol⁻¹) | ΔG° (kJmol⁻¹) |
|-----------|------|--------------|----------------|--------------|
| calcite   | 298  | 44.2         | −120.3         | 81.3         |
| norsethite| 298  | 77.5         | −18.1          | 82.9         |
| dolomite  | 298  | 132.0        | 29.7           | 125.4        |

Finally, the estimated ~88% reduction in [Mg²⁺] due to hydration leads to a reaction quotient ~eight times smaller than the equilibrium formation constant (K‡N) for the activated complex (Equation (2)), equivalent to a ~5 kJ/mol energy deficiency to reach the required ΔG‡N. The magnitude of fluctuation in the reported ΔG‡N (~79–84 kJ/mol, Table 3) in solutions with various levels of the Mg:Ba ratio seems to agree with such a small effect of Mg hydration. While this energy penalty can be compensated by raising the relative abundance of Mg in solutions for norsethite formation, the same cannot be said for dolomite. Assuming that dolomite crystallizes in aqueous solutions if the ΔG‡ of the reaction (~125 kJ/mol) is lowered to a value close to that for norsethite (~80 kJ/mol, which incidentally is nearly identical to that for calcite, Table 2), on the basis that the ~45 kJ/mol difference between ΔG‡D and ΔG‡N (Table 2) results from a combination of Mg hydration and structural constraints, our data suggest that the former accounts for ~12% while the latter accounts for ~88% of the dolomite mineralization barrier.

Table 3. Thermodynamic properties of the activated complexes for norsethite formation in solutions with different values of the Mg-to-Ba ratio [40].

| Mg/Ba (Approximate Number) | T(K) | ΔH° (kJmol⁻¹) | ΔS° (JK⁻¹mol⁻¹) | ΔG° (kJmol⁻¹) |
|---------------------------|------|--------------|----------------|--------------|
| 10                        | 298  | 95.8         | 39.0           | 84.1         |
| 20                        | 298  | 77.6         | −9.0           | 80.3         |
| 40                        | 298  | 70.1         | −29.6          | 78.9         |

5. Summary

The Mg–Ba–CO₂ system was investigated through crystallization experiments at various conditions in water and a non-aqueous environment to determine the minimal Mg/Ba values at which norsethite can crystallize, and the measured difference was used to estimate the hydration effect on Mg²⁺ reactivity in the crystallization reactions. The experimental data suggest that hydration may have suppressed the reactivity of Mg²⁺ by close to 88% relative to that in FMD. Application of the TST model to the norsethite system revealed that the hydration effect on Mg has resulted in a reaction quotient that is approximately eight-fold smaller than the equilibrium formation constant for the activated complex, equivalent to ~5 kJ/mol energy penalty. In comparison to dolomite, the TST parameters indicate that the activated complex for norsethite crystallization appears to be entropically unfavored but has a significantly stronger bonding strength, leading to the activation free energy ~50% lower than for dolomite crystallization. The ~5 kJ/mol energy penalty originating from Mg²⁺ hydration is approximately equivalent to ~12% of the difference between ΔG‡D and ΔG‡N, suggesting the hindrance for ambient condition dolomite mineralization may be derived primarily from the weaker bonding state in the transition state.

It is important to note that the simple approach adopted in this study may not be completely appropriate and can lead to erroneous conclusions. An important assumption made here is that the reaction pathway, the activated complex in specific, is similar for dolomite and norsethite crystallization reactions. Although less likely, it is still possible that the transition states of the reactions in Equations (1) and (4) differ to a certain degree. In addition, the assumption that ΔG‡D needs to be lowered to a level close to ΔG‡N in order for dolomite to crystallize may also be overly simplistic. For example, laboratory synthesis of dolomite is often possible at conditions near or above 100 °C [67]. At this temperature, ΔG‡D is in fact approximately 5 kJ/mol lower than that at 298 K (Table 2).
and can be fully accounted for by the Mg hydration effect. Despite the uncertainties, the results from the approach appear to be able to rationalize the fact that crystallization of the ordered binary carbonate MgBa(CO$_3$)$_2$ can proceed at the relative Mg abundance of Mg:Ba = 6:4 in ambient aqueous solutions, while at the similar conditions, not even disordered (MgBa)CO$_3$ with Mg content greater than 10% [68–74] can readily form.

**Author Contributions:** H.T. conceptualized this study and drafted the manuscript. S.Z. and Y.W. carried out the crystallization experiments and material characterization and helped to finalize the manuscript. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was funded by the National Natural Science Foundation of China, grant No. NNSFC-41972041.

**Data Availability Statement:** The data presented in this study are available in the article.

**Acknowledgments:** We thank two anonymous reviewers and the academic editor Carlos Pina for their constructive suggestions and comments that have greatly improved this manuscript.

**Conflicts of Interest:** The authors declare no conflict of interest.

**References**

1. Sorby, H.C. XII.—On the cause of the production of different secondary forms of crystals. *Mineral. Mag. J. Mineral. Soc.* **1879**, *3*, 111–113. [CrossRef]
2. Bragg, W. The analysis of crystals by the X-ray spectrometer. *Proc. R. Soc. Lond.* **1914**, *89*, 468–489.
3. Wyckoff, R.W.G. The crystal structures of some carbonates of the calcite group. *Am. J. Sci.* **1920**, *4*, 317–360. [CrossRef]
4. Lippmann, F. Crystal chemistry of sedimentary carbonate minerals. In *Sedimentary Carbonate Minerals*; Springer: Berlin/Heidelberg, Germany, 1973; pp. 5–96.
5. Reeder, R.J.; Barber, D.J. *Carbonates: Mineralogy and chemistry*; Mineralogical Society of America: Washington, DC, USA, 1983; Volume 11.
6. Plummer, L.; Wigley, T.; Parkhurst, D. The kinetics of calcite dissolution in CO$_2$-water systems at 5°C to 60°C and 0.0 to 1.0 atm CO$_2$. *Am. J. Sci.* **1978**, *278*, 179–216. [CrossRef]
7. Busenberg, E.; Plummer, L.; Mumpton, F. A comparative study of the dissolution and crystal growth kinetics of calcite and aragonite. *Stud. Diagenesis USGS Bull.* **1986**, *1578*, 139–168.
8. Teng, H.H.; Dove, P.M.; Orme, C.A.; De Yoreo, J. Thermodynamics of calcite growth: Baseline for understanding biomineral formation. *Science* **1998**, *282*, 724–727. [CrossRef] [PubMed]
9. Morse, J.W.; Arvidson, R.S.; Lüttge, A. Calcium carbonate formation and dissolution. *Chem. Rev.* **2007**, *107*, 342–381. [CrossRef]
10. Urosevic, M.; Rodriguez-Navarro, C.; Putnis, C.V.; Cardell, C.; Putnis, A.; Ruiz-Agudo, E. In situ nanoscale observations of the dissolution of [1014] dolomite cleavage surfaces. *Geochim. Cosmochim. Acta* **2012**, *80*, 1–13. [CrossRef]
11. Chang, B.; Li, C.; Liu, D.; Foster, I.; Tripati, A.; Lloyd, M.K.; Maradiaga, I.; Luo, G.; An, Z.; She, Z. Massive formation of early diagenetic dolomite in the Ediacaran ocean: Constraints on the “dolomite problem”. *Proc. Natl. Acad. Sci. USA* **2020**, *117*, 14005–14014. [CrossRef] [PubMed]
12. Cusack, M.; Freer, A. Biomineralization: Elemental and organic influence in carbonate systems. *Chem. Rev.* **2008**, *108*, 4433–4454. [CrossRef] [PubMed]
13. Raymo, M.E.; Ruddiman, W.F. Tectonic forcing of late Cenozoic climate. *Nature* **1992**, *359*, 117–122. [CrossRef]
14. Royer, D.L.; Berner, R.A.; Park, J. Climate sensitivity constrained by CO$_2$ concentrations over the past 420 million years. *Nature* **2007**, *446*, 530–532. [CrossRef] [PubMed]
15. Bock, C.W.; Kaufman, A.; Glusker, J.P. Coordination of water to magnesium cations. *Inorg. Chem.* **2012**, *51*, 724–727. [CrossRef] [PubMed]
16. Zengler, D.; Dunham, J.; Ethington, R.L. *Concepts and Models of Dolomitization*; SEPM Society for Sedimentary Geology: Tulsa, OK, USA, 1980.
17. Christ, C.; Hostetler, P. Studies in the system MgO-SiO$_2$-CO$_2$-H$_2$O (II); the activity-product constant of magnesite. *Am. J. Sci.* **1970**, *268*, 439–453. [CrossRef]
18. Sayles, F.; Fyfe, W. The crystalization of magnesite from aqueous solution. *Geochim. Cosmochim. Acta* **1973**, *37*, 87–99. [CrossRef]
19. Deelman, J. Low-temperature synthesis of eitelite, Na$_2$CO$_3$·MgCO$_3$. *Neues Jahrhbuch für Mineralogie. Monatshefte* **1984**, *10*, 468–480.
20. Deelman, J. Breaking Ostwald’s rule. *Chem. Erde-Geochem.* **2001**, *61*, 224–235.
21. Shannon, R.D. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallogr. Sect. A: Cryst. Phys. Diffr. Theor. Gen. Crystallogr.* **1976**, *32*, 751–767. [CrossRef]
22. Pavlov, M.; Siegbahn, P.E.; Sandström, M. Hydration of beryllium, magnesium, calcium, and zinc ions using density functional theory. *J. Phys. Chem. A* **1998**, *102*, 219–228. [CrossRef]
23. Markham, G.D.; Glusker, J.P.; Bock, C.W. The arrangement of first- and second-sphere water molecules in divalent magnesium complexes: Results from molecular orbital and density functional theory and from structural crystallography. *J. Phys. Chem. B* 2002, 106, 5118–5134. [CrossRef]

24. Andersson, M.P.; Stipp, S.L. Predicting hydration energies for multivalent ions. *J. Comput. Chem. 2014*, 35, 2070–2075. [CrossRef] [PubMed]

25. Ikeda, T.; Boero, M.; Terakura, K. Hydration properties of magnesium and calcium ions from constrained first principles molecular dynamics. *J. Chem. Phys.*, 2007, 127, 074503. [CrossRef] [PubMed]

26. Katz, A.K.; Glusker, J.P.; Beebe, S.A.; Bock, C.W. Calcium ion coordination: A comparison with that of beryllium, magnesium, and zinc. *J. Am. Chem. Soc.* 1996, 118, 5752–5763. [CrossRef]

27. Bruni, F.; Imberti, S.; Mancinelli, R.; Ricci, M. Aqueous solutions of divalent chlorides: Ions hydration shell and water structure. *J. Chem. Phys.* 2012, 136, 064520. [CrossRef]

28. Di Tommaso, D.; de Leeuw, N.H. First principles simulations of the structural and dynamical properties of hydrated metal ions Mg$^{2+}$ and solvated metal carbonates (Me=Ca, Mg, and Sr). *Cryst. Growth Des.* 2010, 10, 4292–4302. [CrossRef]

29. Ingham, B.; Ko, M.; Laycock, N.; Kirby, N.M.; Williams, D.E. First stages of siderite crystallisation during CO$_2$ corrosion of steel evaluated using in situ synchrotron small- and wide-angle X-ray scattering. *Faraday Discuss.* 2015, 180, 171–190. [CrossRef]

30. Neuberg, C.; Rewald, B. Ueber kolloide und gelatinöse Verbindungen der Erdalkalien. *Z. Für Chem. Und Ind. Der Kolloide 1908*, 2, 354–357. [CrossRef]

31. Forsgren, J.; Frykstrand, S.; Grandfield, K.; Mihryan, A.; Strømme, M. A template-free, ultra-adsorbing, high surface area carbonate nanostructure. *PloS ONE* 2013, 8, e68486. [CrossRef]

32. Ende, M.; Effenberger, H.; Miletich, R. Evolution of the α-BaMg(CO$_3$)$_2$ low-temperature superstructure and the tricritical nature of its α–β phase transition. *Acta Crystallogr. Sect. B Struct. Sci. Cryst. Eng. Mater.* 2017, 73, 827–835. [CrossRef]

33. Lippmann, F. Die Kristallstruktur des Norsethit, BaMg(CO$_3$)$_2$. *Naturwissenschaften* 1967, 54, 514. [CrossRef]

34. Lippmann, F. Syntheses of BaMg(CO$_3$)$_2$ (Norsethite) at 20°C and the Formation of Dolomite in Sediments. In *Recent Developments in Carbonate Sedimentology in Central Europe*; Springer: Berlin/Heidelberg, Germany, 1968; pp. 33–37.

35. Hood, W.C.; Steidl, P.F.; Tschopp, D.G. Precipitation of norsethite at room temperature. *Am. Mineral. J. Earth Planet. Mater.* 1974, 59, 471–474.

36. Bötcher, M.E. Stable isotope fractionation during experimental formation of norsethite (BaMg(CO$_3$)$_2$): A mineral analogue of dolomite. *Aquat. Geochem.* 2000, 6, 201–212. [CrossRef]

37. Pimentel, C.; Pina, C.M. The formation of the dolomite-analogue norsethite: Reaction pathway and cation ordering. *Geochem. Cosmochim. Acta* 2014, 142, 217–223. [CrossRef]

38. Pimentel, C.; Pina, C.M. Reaction pathways towards the formation of dolomite-analogues at ambient conditions. *Geochem. Cosmochim. Acta* 2016, 178, 259–267. [CrossRef]

39. Lindner, M.; Saldi, G.D.; Carrocci, S.; Bénézeth, P.; Schott, J.; Jordan, G. On the growth of anhydrous Mg-bearing carbonates–Implications from norsethite growth kinetics. *Geochem. Cosmochim. Acta* 2018, 238, 424–437. [CrossRef]

40. Liu, C.; Li, W. Transformation of amorphous precursor to crystalline carbonate: Insights from Mg isotopes in the dolomite-analogue mineral norsethite [BaMg(CO$_3$)$_2$]. *Geochem. Cosmochim. Acta* 2020, 272, 1–20. [CrossRef]

41. Zhang, Y.-F.; Yao, Q.-Z.; Qian, F.-J.; Li, H.; Zhou, G.-T.; Fu, S.-Q. Formation pathway of norsethite dominated by solution chemistry under ambient conditions. *Am. Mineral. J. Earth Planet. Mater.* 2021, 106, 1306–1318. [CrossRef]

42. Rock, P.A.; Mandell, G.K.; Casey, W.H.; Walling, E.M. Gibbs energy of formation of dolomite from electrochemical cell measurements and theoretical calculations. *Am. J. Sci.* 2003, 301, 103–111. [CrossRef]

43. Bada, J.L.; Chalmers, J.H.; Cleaves, H.J. Is formamide a geochemically plausible prebiotic solvent? *Phys. Chem. Chem. Phys.* 2016, 18, 20085. [CrossRef] [PubMed]

44. Morrow, D.; Ricketts, B. Chemical controls on the precipitation of mineral analogues of dolomite: The sulfate enigma. *Geology* 1986, 14, 408–410. [CrossRef]

45. Longo, J.M.; Voight, K.C. Synthesis of mixed-metal carbonates by grinding. *Solid State Ion.* 1989, 32, 409–412. [CrossRef]

46. Mercero, J.M.; Fowler, J.E.; Ugalde, J.M. Aluminum (III) interactions with the acid derivative amino acid chains. *J. Phys. Chem. A* 2000, 104, 7053–7060. [CrossRef]

47. Peschke, M.; Blades, A.T.; Kebarle, P. Hydration energies and entropies for Mg$^{2+}$, Ca$^{2+}$, Sr$^{2+}$, and Ba$^{2+}$ from gas-phase ion-water molecule equilibria determinations. *J. Phys. Chem. A* 1998, 102, 9978–9985. [CrossRef]

48. Grushka, E.; Grinberg, N. *Advances in Chromatography*; CRC Press: Boca Raton, FL, USA, 2006; Volume 45.

49. Mergelsberg, S.T.; Yoreo, J.; Miller, Q.; Michel, F.M.; Dove, P.M. Metastable solubility and local structure of amorphous calcium carbonate (ACC). *Geochem. Cosmochim. Acta* 2020, 289. [CrossRef]

50. Xu, J.; Yan, C.; Zhang, F.F.; Konishi, H.; Xu, H.F.; Teng, H.H. Testing the cation–hydration effect on the crystallization of Ca-Mg-CO$_3$ systems. *Proc. Natl. Acad. Sci. USA* 2013, 110, 17750–17755. [CrossRef] [PubMed]

51. Hong, M.; Xu, J.; Teng, H.H. Evolution of calcite growth morphology in the presence of magnesium: Implications for the dolomite problem. *Geochem. Cosmochim. Acta* 2016, 172, 55–64. [CrossRef]
53. Speer, J.A. Crystal chemistry and phase relations of orthorhombic carbonates. Rev. Mineral. Geochem. 1983, 11, 145–190.
54. Reeder, R.J. Crystal chemistry of the rhombohedral carbonates. Rev. Mineral. Geochem. 1983, 11, 1–47.
55. Speer, J.A. Crystal chemistry and phase relations of orthorhombic carbonates. In Carbonates; De Gruyter: Berlin, Germany, 2018; pp. 145–190.
56. Lindner, M.; Jordan, G. On the growth of witherite and its replacement by the Mg-bearing double carbonate norsethite: Implications for the dolomite problem. Am. Mineral. 2018, 103, 252–259. [CrossRef]
57. Lindner, M.; Saldi, G.D.; Jordan, G.; Schott, J. On the effect of aqueous barium on magnesite growth—A new route for the precipitation of the ordered anhydrous Mg-bearing double carbonate norsethite. Chem. Geol. 2017, 460, 93–105. [CrossRef]
58. Graf, D.L.; Goldsmith, J.R. Some hydrothermal syntheses of dolomite and protodolomite. J. Geol. 1956, 64, 173–186. [CrossRef]
59. Tribble, J.S.; Arvidson, R.S.; Lane III, M.; Mackenzie, F.T. Crystal chemistry, and thermodynamic and kinetic properties of calcite, dolomite, apatite, and biogenic silica: Applications to petrologic problems. Sediment. Geol. 1995, 95, 11–37. [CrossRef]
60. Land, L.S. The Isotopic and Trace Element Geochemistry of Dolomite: The State of the Art; SEPM Society for Sedimentary Geology: Tulsa, OK, USA, 1980.
61. Rosenberg, P.; Holland, H. Calcite-dolomite-magnesite stability relations in solutions at elevated temperatures. Science 1964, 145, 700–701. [CrossRef] [PubMed]
62. Nancollas, G.H.; Reddy, M.M. The crystallization of calcium carbonate. II. Calcite growth mechanism. J. Colloid Interface Sci. 1971, 37, 824–830. [CrossRef]
63. Wiechers, H.; Sturrock, P.; Marais, G. Calcium carbonate crystallization kinetics. Water Res. 1975, 9, 835–845. [CrossRef]
64. Kazmierczak, T.; Tomson, M.; Nancollas, G. Crystal growth of calcium carbonate. A controlled composition kinetic study. J. Phys. Chem. 1982, 86, 103–107. [CrossRef]
65. Arvidson, R.S.; Mackenzie, F.T. The dolomite problem; control of precipitation kinetics by temperature and saturation state. Am. J. Sci. 1999, 299, 257–288. [CrossRef]
66. Arvidson, R.S.; Mackenzie, F.T. Tentative kinetic model for dolomite precipitation rate and its application to dolomite distribution. Aquat. Geochem. 1997, 2, 273–298. [CrossRef]
67. Gregg, J.M.; Bish, D.L.; Kaczmarek, S.E.; Machel, H.G. Mineralogy, nucleation and growth of dolomite in the laboratory and sedimentary environment: A review. Sedimentology 2015, 62, 1749–1769. [CrossRef]
68. Mucci, A.; Morse, J.W. The incorporation of Mg$^{2+}$ and Sr$^{2+}$ into calcite overgrowths: Influences of growth rate and solution composition. Geochim. Cosmochim. Acta 1983, 47, 217–233. [CrossRef]
69. Mucci, A. Growth kinetics and composition of magnesian calcite overgrowths precipitated from seawater: Quantitative influence of orthophosphate ions. Geochim. Cosmochim. Acta 1986, 50, 2255–2265. [CrossRef]
70. Hartley, G.; Mucci, A. The influence of P$_{CO_2}$ on the partitioning of magnesium in calcite overgrowths precipitated from artificial seawater at 25°C and 1 atm total pressure. Geochim. Cosmochim. Acta 1996, 60, 315–324. [CrossRef]
71. Huang, Y.; Fairchild, I.J. Partitioning of Sr$^{2+}$ and Mg$^{2+}$ into calcite under karst-analogue experimental conditions. Geochim. Cosmochim. Acta 2001, 65, 47–62. [CrossRef]
72. Katz, A. The interaction of magnesium with calcite during crystal growth at 25–90°C and one atmosphere. Geochim. Cosmochim. Acta 1973, 37, 1563–1586. [CrossRef]
73. Berner, R. The role of magnesium in the crystal growth of calcite and aragonite from sea water. Geochim. Cosmochim. Acta 1975, 39, 489–504. [CrossRef]
74. Oomori, T.; Kaneshima, H.; Maezato, Y.; Kitano, Y. Distribution coefficient of Mg$^{2+}$ ions between calcite and solution at 10–50°C. Mar. Chem. 1987, 20, 327–336. [CrossRef]