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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)CO₃ and (CaMg)CO₃ Systems

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Abstract: Carbonate mineralization is reasonably well-understood in the Ca–CO₂–H₂O system but continuously poses difficulties to grasp when Mg is present. One of the outstanding questions is the lack of success in dolomite MgCa(CO₃)₂ crystallization at atmospheric conditions. The conventional view holds that hydration retards the reactivity of Mg²⁺ and is supported by solvation shell chemistry. This theory however is at odds with the easy formation of norsethite MgBa(CO₃)₂, a structural analogue of dolomite, leading to the premise that crystal or molecular structural constraints 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–CO₂ system was examined in a non-aqueous environment and in H₂O 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 Mg²⁺ reactivity, presumably due to the hydration effect. Further analyses in the context of transition state theory indicated that the decreased Mg²⁺ 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 crystallize 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 CaCO₃ 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 CO₂ (g), HCO₃[−] and CO₃^{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 $\text{MgCa}(\text{CO}_3)_2$ 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 ($R\bar{3}$) differs from calcite ($R\bar{3}c$) 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 $\text{Mg}[\text{H}_2\text{O}]_6^{2+}$ 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 , $R\bar{3}c$). 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 $p\text{CO}_2$) 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 $\text{MgBa}(\text{CO}_3)_2$ [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 $\text{MgBa}(\text{CO}_3)_2$ 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 ($-2167 \pm 2 \text{ kJ/mol}$) [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_2O 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 $K_{\text{sp,wt}} = 10^{-8.56}$ (PHREEQC database) and $K_{\text{sp,nr}} = 10^{-17.73}$ [40].

Non-aqueous experiments were carried out in formamide ($\text{O}=\text{CH}-\text{NH}_2$, FMD) that has a weaker (relative to H_2O) 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_2CO_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_2CO_3 stock. The final solution was kept closed and still for 24 h.

All experiments were conducted at room temperature ($25 \pm 1^\circ\text{C}$). 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 ($\text{Cu K}\alpha_1$ radiation). The diffractograms were collected from $3\text{--}70^\circ$ with a scanning rate of $2^\circ/\text{min}$. Prior to

instrumental analysis, the precipitates were dispersed in alcohol and pipetted on a zero-background monocrystalline 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 ($[\text{Mg} + \text{Ba}]/\text{CO}_3$), 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 Ω_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 Ω_N and the cation-to-anion ratio in the experimental solutions. For example, at $\log\Omega_N \approx 2$ 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 $> 80 \sim 100$). For example, at $\log\Omega_N \approx 2.2$ to 2.7 and cation/anion ≈ 130 –140, witherite was the only phase found in solution at $\log\Omega_W \approx 0.3$ –1.0, same as the experiments where $\log\Omega_N \approx 4.0$ –4.5, cation/anion ≈ 161 –177, and $\log\Omega_W \approx 1.2$ –1.8.

A much simpler outcome was observed in formamide containing varied amounts of Mg^{2+} and Ba^{2+} at a fixed concentration of $([\text{Mg}] + [\text{Ba}])$. Unlike the results in aqueous environment where norsethite formation required Mg dominated solution chemistry and in fact was never observed once Mg/Ba $< 6/4$, norsethite 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_2O , 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_{nrs} and SI_{wit} : saturation Index with respect to norsethite (N) and witherite (W); Mg/Ba: activity ratio aMg^{2+}/aBa^{2+} ; np: no precipitation).

(Mg,Ba)Cl ₂ [M]	NaHCO ₃ [M]	Mg/Ba	SI_{nrs}	SI_{wit}	aMg^{2+} [mM]	aBa^{2+} [mM]	aCO_3^{2-} [mM]	Mineral Phase
0.001	0.25	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
	0.1	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
	0.05	9:1	1.66	0.05	0.205	0.023	0.135	N
		8:2	1.92	0.36	0.183	0.046	0.135	N
		7:3	2.04	0.53	0.160	0.070	0.135	W
		6:4	2.09	0.66	0.137	0.093	0.135	W
		5:5	2.11	0.76	0.114	0.016	0.136	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
0.01	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
	0.05	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
	0.01	9:1	2.18	0.3	2.575	0.280	0.019	W
		8:2	2.44	0.61	2.288	0.560	0.020	W
		7:3	2.57	0.79	2.001	0.840	0.20	W
		6:4	2.65	0.93	1.715	1.120	0.21	W
		5:5	2.68	1.03	1.429	1.400	0.021	W
		4:6	2.66	1.12	1.143	1.680	0.022	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)Cl ₂ [M]	NaHCO ₃ [M]	Mg/Ba	SI _{nrs}	SI _{wit}	aMg ²⁺ [mM]	aBa ²⁺ [mM]	aCO ₃ ^{2−} [mM]	Mineral Phase
0.04	0.25	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	1.17	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
0.05	0.25	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 NaHCO₃ and 0.01M (Mg,Ba)Cl₂ (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 2θ 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 ($[\text{Mg}/\text{Ca}]_{\text{solid}}/[\text{Mg}/\text{Ca}]_{\text{solution}} \neq 1$) occurred for exclusive norsethite formation as the solutions were required to have more Mg than Ba with an observed minimal value of $\text{Mg}/\text{Ba} \approx 7/3$, and (2) norsethite was never detected in solutions with $\text{Mg}/\text{Ba} < 6/4$, whereas witherite could crystallize in Mg^{2+} dominated (as strong as $\text{Mg}:\text{Ba} = 9:1$) 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 $\text{Mg}/\text{Ba} \approx 1.6$ while maintaining CO_3^{2-} 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 Ba^{2+}) may have limited Mg^{2+} from being in the free (dehydrated) state, so much so that 50% more Mg^{2+} was needed to match the quantity of free Ba^{2+} ions in the solutions. At the opposite end, although witherite appeared to form more easily in the $\text{Mg}-\text{Ba}-\text{CO}_2-\text{H}_2\text{O}$ system given that the $\log \Omega_W$ is smaller throughout the experiments by a factor of 2–10 in comparison with $\log \Omega_N$, norsethite nevertheless crystallizes readily and can often be the exclusive precipitate at specific conditions ($\text{Mg}/\text{Ba} > \sim 7/3$, cation/anion $< \sim 60$). 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 $\text{Mg}^{2+}-\text{H}_2\text{O}$ 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 $\text{Mg}/\text{Ba} = 1/2-1/5$. 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 Mg^{2+} with FMD (~ 125 kcal/mol [47]) is significantly smaller than with H_2O (~ 260 kcal/mol [22,48]), and the hydrogen bonds between formamide molecules ($8-13$ kJ/mol for $\text{NH}\cdots\text{O}$ and $\text{NH}\cdots\text{N}$) are meaningfully weaker than that between water molecules (21 kJ/mol for $\text{OH}\cdots\text{O}$) [49]. Simply put, it is reasonable to assume that, while the stronger (relative to Ba^{2+}) hydration of Mg^{2+} dictates that magnesium ions stay largely in a hydrated form in aqueous solutions, the FMD solvation shell around Mg^{2+} 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 $\text{Mg}/\text{Ba} > 1$ (Figure 2), defied this logic reasoning. Furthermore, in comparison with the amorphous calcium carbonate (ACC) formed in the presence of Mg ions, the $\text{Mg}-\text{Ba}-\text{CO}_3$ 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 $\text{Mg}-\text{Ca}-\text{CO}_3$ 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 $\text{Ca}-\text{Mg}-\text{CO}_2$ system [51], where different from the $\text{Ba}-\text{Mg}-\text{CO}_2$ system of concern in this study, congruent crystallization of $\text{MgCa}(\text{CO}_3)_2$ (dolomite) did not occur; high Mg (37% mole ratio) calcite instead formed at $\text{Mg}/\text{Ca} = 1$. Given the absence of H_2O 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 CO_3 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 ($R\bar{3}$), the CO_3 groups in the norsethite (low temperature polymorph, $R\bar{3}c$) 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 $R\bar{3}$ 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 $\text{PbMg}(\text{CO}_3)_2$ 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 $r = 100$ 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 $\text{Ba}(\text{CO}_3)_2$ are exclusively trigonal and orthorhombic, respectively, given the cation size of Mg^{2+} ($r = 72$ pm) and Ba^{2+} ($r = 152$ 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-precipitation 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 $(\text{Ba,Mg})\text{CO}_3$, 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 Mg^{2+} , which may be less stable in an un-hydrated form due to the high charge density relative to Ba and Ca ions, has the advantage to bind with CO_3^{2-} first. When Mg is the minority ion in the solution and binds preferentially with carbonate ions, Ba^{2+} and Ca^{2+} can interact with the remaining CO_3^{2-} to form witherite and calcite or can be incorporated in the prior-formed Mg- CO_3 unit to crystallize in norsethite and high-Mg calcite. In Mg-dominating solutions, however, rapid interactions of Mg with CO_3 ions lead to amorphous magnesium carbonate precipitation (on the assumption that the Mg- CO_3 units cannot stack to form 3D crystalline structures due to the entropy penalty in the CO_3 groups) [51] and a quick consumption of CO_3^{2+} , leaving Ba^{2+} and 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] BaCO_3 , instead of 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 Ba into the trigonal carbonate structure (or the transformation of 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 MgCO_3 is challenging and the orthorhombic template for BaCO_3 to epitaxially grow on is lacking. As such, witherite is expected to form first but dissolves subsequently to release Ba^{2+} once MgCO_3 units are in place to crystallize $\text{MgBa}(\text{CO}_3)_2$. At higher T when magnesite can readily form and the orthorhombic to rhombohedral transformation for BaCO_3 is less hindered, one should expect 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)):

where $(\text{BaCO}_3 \cdot \text{MgCO}_3)^\ddagger$ refers to the activated complex and Mg^{2+} , Ba^{2+} , and 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– CO_2 system (Equation (2)):

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

where $K_N^\ddagger$ and $\Delta G_N^\ddagger$ 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)):

$$[(\text{MgCO}_3 \cdot \text{BaCO}_3)^\ddagger] = [\text{Mg}^{2+}][\text{Ba}^{2+}][\text{CO}_3^{2-}]^2 \exp(-\Delta G_N^\ddagger / RT) \quad (3)$$

Note that the maximal concentration for the activated complex implicated by Equation (3) can only be achieved at the conditions of $[Mg^{2+}]/[Ba^{2+}] = 1$. This is because the charge neutrality requirement for chemical reactions stipulates the total cation concentration ($[Mg^{2+}] + [Ba^{2+}]$) 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 cations. As the minimal relative abundance of Mg for norsethite to form in FMD is $Mg/Ba = 1/5$, the increased value of $Mg/Ba = 6/4$ in water suggests that hydration may have reduced the availability of free Mg ions (or the reactivity of Mg^{2+}) by ~88%.

Applying the TST theory to the Ca–Mg–CO₂ system, we may have the following relations (Equations (4)–(6)):

$$K_D^\ddagger = [(MgCO_3 \cdot CaCO_3)^\ddagger] / [Mg^{2+}][Ca^{2+}][CO_3^{2-}]^2 = \exp(-\Delta G_D^\ddagger / RT) \quad (5)$$

$$[(MgCO_3 \cdot CaCO_3)^\ddagger] = [Mg^{2+}][Ca^{2+}][CO_3^{2-}]^2 \exp(-\Delta G_D^\ddagger / RT) \quad (6)$$

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 $[\exp(-\Delta G_D^\ddagger / RT)]$ is comparable with that for norsethite crystallization. Published $\Delta G^\ddagger$ values for the two binary phases do not support this prediction as $\Delta G_D^\ddagger$ is greater than $\Delta G_N^\ddagger$ by more than 50%. Since the solvation effect of FMD on Mg should be the same in both systems, the higher $\Delta G_D^\ddagger$ in conjunction with the lack of any carbonate phases with $Mg:Ca \approx 1$ in the Mg–Ca–CO₂ 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 $(MgCO_3 \cdot CaCO_3)^\ddagger$ is in fact an entropically more favored species than $(MgCO_3 \cdot BaCO_3)^\ddagger$ is, stating that the high $\Delta G_D^\ddagger$ 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/mol and 563 kJ/mol, respectively), indicating the $\Delta H^\ddagger$ for $(MgCO_3 \cdot CaCO_3)^\ddagger$ and $(MgCO_3 \cdot BaCO_3)^\ddagger$ 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 $\Delta H_D^\ddagger$ (132 kJ/mol) is more than ~80% higher than $\Delta H_N^\ddagger$ (77.52 kJ/mol) suggests the existence of a significant structural difference between the two activation states, consistent with the entropic factor of the two species ($\Delta S_N^\ddagger = -18.1$ J/K/mol and $\Delta S_D^\ddagger = 29.7$ J/K/mol). A potential explanation is that $(MgCO_3 \cdot BaCO_3)^\ddagger$ 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 CO₃ 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, $(CaCO_3 \cdot MgCO_3)^\ddagger$ 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 CO₃ 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)CO₃ 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)	$\Delta H^\ddagger$ (kJmol ^{−1})	$\Delta S^\ddagger$ (JK ^{−1} mol ^{−1})	$\Delta G^\ddagger$ (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 ($K_N^\ddagger$) for the activated complex (Equation (2)), equivalent to a ~5 kJ/mol energy deficiency to reach the required $\Delta G_N^\ddagger$. The magnitude of fluctuation in the reported $\Delta G_N^\ddagger$ (~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 $\Delta G^\ddagger$ of the reaction (~125 kJ/mol) is lowered to a value close to that for norsethite (~80 kJ/mol, which incidentally is nearly identically to that for calcite, Table 2), on the basis that the ~45 kJ/mol difference between $\Delta G_D^\ddagger$ and $\Delta G_N^\ddagger$ (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)	$\Delta H^\ddagger$ (kJmol ^{−1})	$\Delta S^\ddagger$ (JK ^{−1} mol ^{−1})	$\Delta G^\ddagger$ (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 $\Delta G_D^\ddagger$ and $\Delta G_N^\ddagger$, 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 $\Delta G_D^\ddagger$ needs to be lowered to a level close to $\Delta G_N^\ddagger$ 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, $\Delta G_D^\ddagger$ 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 $\text{MgBa}(\text{CO}_3)_2$ can proceed at the relative Mg abundance of $\text{Mg}:\text{Ba} = 6:4$ in ambient aqueous solutions, while at the similar conditions, not even disordered $(\text{MgBa})\text{CO}_3$ with Mg content greater than 10% [68–74] can readily form.

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