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 $CaCO_3 \cdot \frac{1}{2}H_2O$ 

Pbcr



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 $Mg_xCa_{(1-x)}CO_3\cdot\frac{1}{2}H_2O$ 

P2₁/c

# Magnesium Impurities Decide the Structure of Calcium Carbonate Hemihydrate

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### 1. INTRODUCTION

experimental conditions.

Calcium carbonate is an abundant material found predominantly in sedimentary deposits and as a product of biomineralization, being the main constituent of skeletons and shells of marine organisms. As a major carbon reservoir, it plays a crucial role in the global carbon cycle and is of prime importance for palaeoenvironmental and palaeoclimate reconstructions<sup>1,2</sup> and the monitoring of ocean acidification.<sup>3</sup>

the unit cell, which assumes the monoclinic arrangement  $(P2_1/c)$ 

originally proposed. This is consistent with the magnesium-rich

At Earth surface temperatures and pressures, the most stable forms of calcium carbonate are the three anhydrous crystalline phases, i.e., calcite, aragonite, and vaterite, in order of decreasing thermodynamic stability. While less stable at ambient conditions and much rarer in geological settings than their water-free counterparts, the hydrated phases are often found as intermediates during calcium carbonate crystallization.<sup>4-6</sup> Hydrated calcium carbonate has the general formula  $CaCO_3 \cdot xH_2 O_1$ , with a water content x so far limited to either 1 (monohydrocalcite) or 6 (ikaite), and are known to form in both biogenic and abiogenic conditions.<sup>7–10</sup> Over the past decade, several studies presented evidence that carbonate minerals nucleate and grow via a different and more complex mechanism than conventionally envisaged within the classical nucleation theory.  $^{11-15}$  In particular, the anhydrous polymorphs are often found to be the final products of a series of extensive structural reorganization and dehydration events involving the formation of amorphous calcium carbonate (ACC) particles and of hydrated calcium carbonate intermediates.<sup>16–18</sup>

Recently, an experimental study reported the discovery of a new hydromorph of calcium carbonate, characterized by x = 0.5, calcium carbonate hemihydrate<sup>19</sup> CaCO<sub>3</sub> $\cdot \frac{1}{2}$ H<sub>2</sub>O. This phase was found to form from amorphous calcium carbonate in a magnesium-rich aqueous solution, suggesting a dehy-

dration-inhibiting effect of the Mg<sup>2+</sup> ions.<sup>19</sup> Magnesium ions are known to play a significant role in many of the formation and transformation stages of carbonate minerals, both in laboratory experiments<sup>20,21</sup> and in natural environments to the extent that it is often used as a palaeoenvironmental proxy.<sup>22-25</sup> The stabilizing effect of magnesium ions on amorphous calcium carbonate and the other crystalline hydrates has been reported before.  $^{20,26-29}$  Indeed, Mg<sup>2+</sup> ions are known to inhibit calcite crystallization<sup>30–32</sup> by significantly slowing down its growth rate.<sup>33</sup> This favors the formation of less stable phases such as aragonite<sup>34,35</sup> and monohydrocalcite.<sup>36–38</sup> In the case of monohydrocalcite, a mechanism was proposed whereby a Mg-bearing ACC is first formed from Mgrich solutions, then crystallizes and matures to a Mg-bearing monohydrocalcite and only in the last stage is magnesium released from the mineral to form minor hydromagnesite.<sup>3</sup> Considering the close water content between MHC and hemihydrate, a possible incorporation of Mg in the hemihydrate structure should also be considered and its consequences on the structure and properties of this new hydromorph need to be determined. However, given the nanometric size and the metastable transient nature of this phase, determining the location and distribution of Mg ions either within the crystal structure or on the particle's surface remains experimentally challenging.

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Tabl	e 1. Fractional	Coordina	tes of the Expe	rimental and	d Calculate	d Structure	of Calcium	Carbonate	Hemihydrate	Resulting
from	Force Field-Ba	ased (FF)	and PBE0-DC	(DFT) Geo	ometry Opt	imization <sup>a</sup>				

		experiment				FF			PBE0-DC DFT	
	x/a	y/b	z/c		x/a	y/b	z/c	x/a	y/b	z/c
Ca1	0.1327	0.3560	0.4973	Ca	0.13266	0.35598	0.49726	0.13847	0.36419	0.49984
Ca2	0.3640	0.6453	0.4993							
C1	0.604	0.846	0.254	С	0.60455	0.84156	0.26427	0.60942	0.84191	0.26595
01	0.621	0.932	0.119	0	0.60709	0.92447	0.10238	0.61060	0.92210	0.10372
O2	0.467	0.798	0.306	0	0.48525	0.79095	0.32029	0.49093	0.79307	0.32231
O3	0.722	0.845	0.343	0	0.72293	0.80858	0.35779	0.72969	0.81430	0.35768
C2	0.112	0.669	0.224							
O4	0.115	0.588	0.400							
O5	0.982	0.722	0.188							
06	0.235	0.701	0.146							
Ow	0.722	0.986	0.680	Ow	0.74358	0.99567	0.69636	0.75001	0.99998	0.69045
Н	-	-	-	Н	0.71876	0.92252	0.58609	0.73101	0.92947	0.58863
Н	-	-	-							

"The position of the hydrogen atoms was not determined experimentally. Note that a nonconventional setting of the crystallographic axes was chosen to facilitate comparison with the experiment.

Here, computer simulations can provide a more detailed description of the calcium carbonate hemihydrate structure at the atomic level and improve our understanding of its formation mechanisms and thermodynamic stability. Indeed, Density Functional Theory (DFT) was successfully used to describe the structures and hydrogen bonding properties of the structural water of the two previously known hydrates, monohydrocalcite and ikaite.<sup>39</sup> Although many DFT schemes fail at predicting the thermodynamics of water incorporation into calcium carbonate minerals, appropriately fitted dispersion-corrected hybrid functionals, such as PBE0-DC,<sup>40</sup> can provide a reliable description of the anhydrous and low water content phases. Furthermore, theoretical approaches provide an efficient way to assess the effect of cationic substitutions at the atomistic level in minerals, as shown by the previous computational studies of Mg incorporation in both anhydrous<sup>41</sup> and hydrated<sup>42</sup> calcium carbonates.

This paper investigates the structure and properties of calcium carbonate hemihydrate using both first-principles and classical theoretical methods. After determining the position of the hydrogen atoms, the effect of magnesium impurities on the hemihydrate structure is analyzed, and a prediction of its stability relative to the other anhydrous and pure end-member carbonate phases is provided.

### 2. COMPUTATIONAL METHODS

This study makes use of both Density Functional Theory (DFT) and force field (FF) methods.

The CRYSTAL17 package<sup>43</sup> was used for the DFT calculations along with the PBE0-DC functional containing 25% of exact Hartree– Fock (HF) exchange and an empirical long-range correction for oxygen–oxygen interactions,<sup>40</sup> with the  $C_6^{OO}$  dispersion coefficient fitted against the calcite vs aragonite enthalpy difference. This scheme provides accurate structural parameters for both monohydrocalcite and ikaite, including those related to their hydrogen bond pattern,<sup>39</sup> while improving the description of their thermodynamic features with respect to that obtained with other DFT and DFT-D schemes. Allelectron Gaussian-type basis sets successfully used in numerous studies on calcium carbonate phases<sup>39,44–46</sup> were adopted for Ca, O, C, and H atoms. Details on specific parameters, geometry optimization, and vibrational frequency calculation were the same as in Demichelis et al.<sup>40</sup> Regarding classical lattice dynamics, a force field specifically developed for magnesium and calcium carbonate phases<sup>47</sup> was used within the program GULP.<sup>48</sup> Geometry optimization was performed via constant pressure relaxation of the atomic positions starting from the experimental configuration<sup>19</sup> and using a shrinking factor of 8 in all directions to sample the phonons within the Brillouin zone with a Monkhorst–Pack mesh. Carbonate anions were treated as molecular fragments with a fixed connectivity, and intramolecular Coulombic interactions were removed. The cutoff for the pairwise interactions was set at 9 Å using a taper function to smooth the truncation over the last 3 Å.

The X-ray diffraction (XRD) patterns corresponding to the geometry-optimized structures were simulated using an in-house code with 0.05°  $2\theta$  full width at half-maximum (fwhm) and a 0.01°  $2\theta$ spacing. A  $\lambda$  = 0.49596 Å wavelength that corresponds to the value reported for the I22 beamline at the European Synchrotron Facility (ESRF, Grenoble, France) was chosen for an easier comparison with the original paper. A comparison between experimental structures and geometries optimized with DFT for reference carbonate minerals is given in Figure S3. The number and position of reflections in the simulated XRD patterns of the experimental structures are well reproduced in those based on the theoretical structures. A small shift of about  $2\theta \approx +0.05^{\circ}$  is observed in the case of monohydrocalcite and the Mg-bearing carbonate phases. It results from the underestimation of the cell volume of  $\sim 1.5-2\%$  after geometry optimization compared to the experimental structure. In comparison, the cell volume of calcite only decreased by 0.07%.

## 3. RESULTS AND DISCUSSION

**3.1. Structure of CaCO\_3 \cdot \frac{1}{2}H\_2O.** The structure of calcium carbonate hemihydrate was optimized starting from the experimental geometry. As the position of the hydrogen atoms is undetermined in the original paper,<sup>19</sup> different orientations for the water molecules have been considered and geometry optimization was performed via force field (FF) methods. All the structures optimize to one specific orientation whose coordinates are reported in Table 1. This optimized structure assumes a higher symmetry than that experimentally proposed and the cell becomes orthorhombic. The space group was identified to be *Pbcn*, which is consistent with the presence of a c-glide plane along [010] observed from ADT (automated electron diffraction tomography) in the original paper. For a more straightforward comparison with the experimental structure, geometry optimization was also performed with

atoms arranged in the nonstandard space group *Pnca*, and lead to the same final structure. Note that a nonstandard setting of the crystallographic axes will be used throughout this manuscript in order to facilitate comparison with the experiment.

In the optimized structure, water molecules are tilted from the (100) plane by a  $\pm 16^{\circ}$  angle (DFT) or a  $\pm 20^{\circ}$  angle (FF) alternatively along the [010] direction (Figure 1). The



Figure 1. Optimized structure of calcium carbonate hemihydrate viewed along [100] (top) and [001] (bottom) with oxygen atoms in red, calcium in blue, carbon in green, and hydrogen atoms in white.

hydrogen atoms point alternatively inward and outward along the [100] direction. This is at variance with the proposed orientation of water molecules represented in Figure 4 of the original paper in which they appear to be tilted from the (001) plane by about 30°.

Geometry optimization and phonon calculation were also conducted at the DFT level of theory and lead to the same optimized structure, with variations in fractional coordinates of less than 1% compared to the force field values (Table 1). The absence of imaginary modes in the vibrational frequencies calculated from phonon calculations confirmed that the optimized structure was a minimum energy configuration. The experimental and calculated cell parameters, bulk and shear modulus of calcite, monohydrocalcite, and calcium carbonate hemihydrate are reported in Table 2. For these three phases, the relative differences between experimental and calculated cell parameters are less than 4% and 1.6% in the case of force field and PBE0-DC calculations, respectively. The very good agreement between computed and measured quantities confirms, as already observed in previous work,<sup>47</sup> that the methodology is accurate and highly predictive for all calcium carbonate phases.

**3.2. Structural Analysis of Mg\_x Ca\_{1-x}CO\_3 \cdot \frac{1}{2}H\_2O.** Given that a high concentration of magnesium was present in the growth environment of the hemihydrate phase in the work of Zou et al.,<sup>19</sup> with a Mg/Ca molar ratio of ~5/1, cationic substitutions of Mg for Ca were also considered. Indeed, the introduction of magnesium in calcium sites causes the  $\beta$  angle to distort and the cell to assume a monoclinic symmetry (Figure 2). Trends in cell parameters for 3.125%, 6.25%, 50%, and 100% magnesium contents are reported in Table 3. As a full analysis of this solid solution is computationally demanding and out of the scope of this paper, a limited number of configurations have been considered, with the sole aim of providing evidence for magnesium being responsible for the experimental structure being monoclinic.

Full and 50% magnesium for calcium substitutions were carried out directly on the calcium carbonate hemihydrate unit cell, whereas a  $2 \times 2 \times 2$  supercell with 32 independent cationic sites was built for all other Mg/Ca ratios. Regarding the 50% magnesium substitution, the two nonequivalent

Table 2. Experimental and Calculated Cell Parameters of Calcite, Monohydrocalcite, and Calcium Carbonate Hemihydrate, with Calculated Reuss and Voigt Bulk (K) and Shear (G) Moduli<sup>*a*</sup>

		calcite		n	nonohydrocalci	te		hemihydrate	
	Exp. <sup>49,50</sup>	FF	PBE0-DC	Exp. <sup>9</sup>	FF	PBE0-DC	Exp. <sup>19</sup>	FF	PBE0-DC
space group	R3c	R3c	R3c	P31	$P3_1$	P31	$P2_{1}/c$	Pbcn	Pbcn
a (Å)	4.9877	4.940	4.993	10.5547	10.246	10.471	9.331	9.384	9.322
b (Å)	4.9877	4.940	4.993	10.5547	10.246	10.471	10.436	10.505	10.477
c (Å)	17.0558	17.101	17.016	7.564	7.470	7.532	6.162	5.898	6.061
$\alpha$ (deg)	90	90	90	90	90	90	90.00	90.00	90.00
$\beta$ (deg)	90	90	90	90	90	90	90.52	90.00	90.00
γ (deg)	120	120	120	120	120	120	90.00	90.00	90.00
V (Å <sup>3</sup> )	367.45	361.3	367.3	729.79	679.1	715.2	600.02	581.4	592.0
$K_{\rm v}({ m GPa})$	76.1	95.8	88.7	-	56.6	55.5	-	66.6	61.8
K <sub>r</sub> (Gpa)	-	85.0	80.3	-	56.6	55.4	-	54.9	57.3
$G_{\rm v}({ m Gpa})$	32.8	42.8	40.1	-	35.1	33.5	-	36.2	33.0
$G_{\rm r}({ m Gpa})$	-	33.8	31.0	-	34.7	33.0	-	27.8	26.8

"Note that a nonconventional setting of the crystallographic axes was used to report the calculated cell parameters of hemihydrate. In the standard setting, the latter would become a = 10.477 Å, b = 6.061 Å, and c = 9.322 Å for the DFT optimized structure.

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**Figure 2.** Evolution of the  $\beta$  angle as a function of the fraction of Mg substituted cationic sites for structures optimized using DFT (red circles), and at the force field level of theory with (blue triangles) and without (blue squares) imposing the cell to be monoclinic.

cationic sites have both been considered and lead to the same cell distortion, from orthorhombic to monoclinic, with  $\beta$  = 91.818° in the case of a force field-based optimization. This transformation from orthorhombic to monoclinic is more pronounced for the structure optimized using DFT, leading to a  $\beta$  angle of 94.293°. Force field-based geometry optimization of calcium carbonate hemihydrate containing 3.125% and 6.25% Mg produced nearly the same cell deformations regardless of the substitution site as shown by the calculated standard deviations for the cell parameters averaged over all possible configurations (Table S1). Therefore, only one configuration for each Mg substitution rate was chosen and optimized using DFT. To simulate both Mg/Ca ratios, symmetry constraints have to be removed, and the optimized structures are no longer orthorhombic but triclinic with all angles different from 90°. However, two distinct trends are observed, with  $\alpha$  and  $\gamma$  remaining closer to 90° and  $\beta$  differing more significantly, indicating a monoclinic-like behavior, consistent with the monoclinic cell observed in the case of a 50% Mg substitution. Indeed, force field-based geometry optimization of the 3.125% Mg-substituted carbonate hemihydrate structure with angles fixed at  $90^{\circ}$  lead to an increase of less than 0.2 kJ/mol in lattice energy (i.e., 0.0001%) with respect to the unconstrained relaxation.

The hypothetical Mg substituted phase, MgCO<sub>3</sub>  $\cdot \frac{1}{2}$ H<sub>2</sub>O, has been modeled in both a *Pnca* and *P*2<sub>1</sub>/*c* arrangement, and optimized to the same orthorhombic structure, thus exhibiting the same behavior as the pure calcium phase.

The evolution of the  $\beta$  angle as a function of the magnesium content is shown in Figure 2. Only the pure phases of calcium and magnesium carbonate hemihydrate exhibit a value of exactly 90°.  $\beta$  first increases as the Mg content increases, with a maximum deviation from 90° observed for the x = 50%composition, then decreases to reach 90° again for x = 100%. From the structural data shown in Table 3 and Figure 2, we can thus conclude that the Mg/Ca ratio is one of the main factors determining the value of  $\beta$ .

An attempt was made to estimate the effect of Mg substitution on the stability of calcium carbonate hemihydrate by considering the following reactions:

	x = 0	x = 0.	.03125	x = 0	0.0625	x = 0.25	ж =	- 0.5	x = 0.75	x = 0	19375	x = 0.	96875	×	= 1
	FF	FF	DFT	FF	DFT	FF	FF	DFT	FF	FF	DFT	FF	DFT	FF	DFT
Space group	Pbcn	$\overline{PI}$	$P\overline{1}$	ΡĪ	ΡĪ	PĪ	$P2_1/c$	$P2_1/c$	Pī	ΡĪ	Pī	Pī	ΡĪ	Pbcn	Pbcn
a (Å)	9.384	9.379	9.322	9.381	9.286	9.327	9.144	8.968	600.6	8.986	8.886	8.937	8.837	8.859	8.875
b (Å)	10.505	10.472	10.464	10.472	10.371	10.239	9.945	9.394	9.642	9.375	8.965	9.352	9.095	9.307	8.960
c (Å)	5.898	5.894	6.038	5.896	6.088	5.894	5.756	6.425	5.767	5.704	6.001	5.683	5.967	5.720	5.988
$\alpha$ (deg)	90.00	89.880	89.933	89.554	90.183	89.545	000.06	90.000	89.868	90.037	90.006	90.074	900.06	90.000	90.000
$\beta$ (deg)	90.00	90.079	90.090	90.123	90.381	91.260	91.818	94.293	90.644	90.160	90.493	90.137	90.335	90.000	90.000
$\gamma$ (deg)	90.00	89.997	89.945	89.938	90.304	90.075	90.00	90.000	89.775	89.755	90.024	89.808	90.168	90.000	90.000
<sup>a</sup> Considering t	he ability of t	he force field	d to reprodu	tce the trend	in $\beta$ angle s	een with DF	T calculatio	ons, the $x = 0$	0.25 and 0.75	5 fractions w	rere only calı	culated using	the classica	ll force field	in ordeı

Table 3. Cell Parameters of the x = 0, x = 0.03125, x = 0.0625, x = 0.25, x = 0.5, x = 0.9375, x = 0.96875, and x = 1 Mg<sub>x</sub>Ca<sub>1-x</sub>CO<sub>3</sub>· $\frac{1}{2}$ H<sub>2</sub>O Optimized Structures,

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Table 4. Thermodynamic Functions Associated with the Process of Forming Mg-Substituted Calcium Carbonate Hemihydrate from Monohydrocalcite and Pure Calcium or Magnesium Carbonate<sup>4</sup>

	Δ	H	Δ	S	Δ	G
reaction	DFT	FF	DFT	FF	DFT	FF
$CaCO_3 + CaCO_3 \cdot H_2O \rightarrow 2CaCO_3 \cdot 0.5H_2O$	+15.9	+23.0	+1.65	+8.83	+15.4	+20.4
$MgCO_3 + CaCO_3 \cdot H_2O \rightarrow 2Mg_{0.5}Ca_{0.5}CO_3 \cdot 0.5H_2O$	+71.8	+50.1	+20.9	+21.2	+65.5	+43.8
$CaCO_{3} + Mg_{0.9375}Ca_{0.0625}CO_{3} \cdot H_{2} O \rightarrow 2Mg_{0.03125}Ca_{0.96875}CO_{3} \cdot 0.5H_{2}O$		+23.8		+9.97		+20.8
$CaCO_3 + Mg_{0.25}Ca_{0.75}CO_3 \cdot H_2O \rightarrow 2Mg_{0.125}Ca_{0.875}CO_3 \cdot 0.5H_2O$		+30.8		+19.3		+25.1
$MgCO_{3} + Mg_{0.75}Ca_{0.25}CO_{3} \cdot H_{2}O \rightarrow 2Mg_{0.875}Ca_{0.125}CO_{3} \cdot 0.5H_{2}O$		+37.1		+20.3		+31.1
<sup>*</sup> Values are reported per reaction, with the entropy in J/(K.mol) and	all others of	quantities in	kJ/mol.			

Table 5. Thermodynamics Functions Associated to the Aragonite  $\rightarrow$  Calcite and CaCO<sub>3</sub> + nH<sub>2</sub>O  $\rightarrow$  CaCO<sub>3</sub>·nH<sub>2</sub>O Processes at 298.15 K

	$\Delta H (kJ/m$	ol)	$\Delta S$ (J/K.	mol)	$\Delta G (kJ/r)$	nol)
	Exp	DFT	Exp	DFT	Exp	DFT
Aragonite	$+0.44 \pm 0.05^{51}$	+0.4 <sup>40</sup>	$+4.3 \pm 0.2^{51}$	+4.0 <sup>40</sup>	$-0.8 \pm 0.2^{51}$	$-0.8^{40}$
Monohydrocalcite	$-4.53^{52}$	$-4.9^{40}$	$-31.96^{52}$	$-32.5^{40}$	+4.99 <sup>52</sup>	+4.8 <sup>40</sup>
Ikaite	$-49.14^{52}$	$-32.4^{40}$	$-201.01^{52}$	$-146.4^{40}$	$+10.76^{52}$	+11.2 <sup>40</sup>
Hemihydrate	n.a.	+5.5	n.a.	-15.5	n.a	+10.1
$CaCO_3 \cdot \frac{3}{4}H_2O P2_1$	n.a.	+10.9	n.a	-6.1	n.a.	+16.7
$CaCO_3 \cdot \frac{3}{4}H_2O$ Pc	n.a.	+16.5	n.a.	-5.2	n.a.	+22.0

$$CaCO_3 \cdot H_2O + CaCO_3 \rightarrow 2CaCO_3 \cdot 0.5H_2O$$
(1)

$$MgCO_{3} + CaCO_{3} \cdot H_{2}O \rightarrow 2Mg_{0.5}Ca_{0.5}CO_{3} \cdot 0.5H_{2}O$$
(2)

These reactions all involve direct comparison between dense systems with covalent bonds and strong ionic interactions, i.e., the anhydrous phases CaCO<sub>3</sub> and MgCO<sub>3</sub>, and hydrated compounds in which a wider range of interaction types may be relevant. Estimating relative stabilities with DFT is therefore subject to caution. Previous studies show that DFT can successfully predict the energetics of low water content phases, but are less accurate with ikaite, the high-water content phases.<sup>40</sup> The maximum water content in these reactions is that of monohydrocalcite (1 water molecule per formula unit) and its energetics is accurate with the DFT method adopted in this paper.<sup>40</sup> Both reactions are endothermic and endergonic with  $\Delta H = +15.9 \text{ kJ/mol}$  and  $\Delta G = +15.4 \text{ kJ/mol}$  for eq 1,  $\Delta H$ = +71.8 kJ/mol and  $\Delta G$  = +65.5 kJ/mol for eq 2 (Table 4). The sign and trends observed in the thermodynamic functions calculated with DFT are well reproduced by the force field although with a systematic overestimation of  $\Delta H$  and  $\Delta G$  of about 6 kJ/mol in eq 1 and a systematic underestimation of about 21 kJ/mol in eq 2. Equation 2 is about four times more endothermic than eq 1, which indicates that the 50% Mgsubstituted carbonate hemihydrate phase is not more stable relative to monohydrocalcite and magnesite/calcite than the pure Ca phase.

A full study of the stabilities of all possible Mg-substituted hemihydrate phases using DFT would be computationally expensive and beyond the scope of the paper. However, trends can easily be obtained with the force-field-based approach. Similar calculations have therefore been performed at the classical level of theory to investigate the reaction that forms 12.5% and 87.5% Mg-calcium carbonate hemihydrate. They lead to enthalpy differences of +30.8 and +37.1 kJ/mol, respectively, which fall between the  $\Delta H$  values obtained for eq 1 and eq 2. This would suggest that a greater instability is achieved with the more distorted phase, i.e., 50% Mgsubstituted carbonate hemihydrate, with a trend for instability following that of the  $\beta$  angle. Finally, the reaction that forms 3.125% Mg-calcium carbonate hemihydrate leads to  $\Delta G$  and  $\Delta H$  values sensibly close to that of eq 1, and only higher by +0.4 and +0.8 kJ/mol, respectively. While these differences are within the accuracy of the method, they show that small amounts of Mg incorporated into the hemihydrate structure are not expected to significantly lower its stability.

The energetics associated with the hydration process of calcite to form calcium carbonate hemihydrate were also explored (Table 5). The methodology used to compute the thermodynamics of liquid water rests on an ice-phase approach which was described in detail in Demichelis et al.<sup>40</sup> and resulted in a good agreement with experimental data for monohydrocalcite. The hydration reaction leading to the formation of calcium carbonate is endothermic and less favorable than for the other hydrates, which could explain the difficulty of observing this phase experimentally and why it has only just recently been discovered.

**3.3. Structural Analysis of Mg\_xCa\_{1-x}CO\_3 \cdot \frac{3}{4}H\_2O.** Little structural information is available for the second calcium carbonate hydromorph that has recently been observed,  $CaCO_3 \cdot \frac{3}{4}H_2O$ .<sup>19</sup> Its structure is given as being monoclinic (*P*2<sub>1</sub>) in the original paper, and only the cell parameters are reported. As this is beyond the scope of this paper, a brief analysis is here presented with the aim of providing a starting point for future works.

Considering that  $CaCO_3 \cdot \frac{3}{4}H_2O$  forms in the same environment with the hemihydrate phase, and that the hemihydrate phase has sites that could potentially accommodate additional water molecules, we use the experimental structure of hemihydrate ( $P2_1/c$ ) as a reference structure, and we added two water molecules to the four already present in its primitive cell.

There are two main ways of distributing the two additional water molecules within the hemihydrate structure without pubs.acs.org/crystal

	Table 6. Experimental and Calculated	(Force Field	) Cell Parameters of CaCO <sub>3</sub>	$\cdot \frac{3}{2}H_2O$ for Different Configurations
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						FF	-optimized	configuration	ons				
	Exp <sup>19</sup>	M3-1	M3-2	M4-1	M4-2	M4-3	M4-4	O3-1	O3-2	O4-1	O4-2	O4-3	O4-4
Space group	$P2_1$	P1	P1	P1	P1	P1	P1	$P2_1$	$P2_1$	P <sub>c</sub>	$P_{c}$	$P_{c}$	P1
a (Å)	9.51	9.449	9.448	9.379	9.423	9.423	9.553	9.416	9.416	9.379	9.423	9.423	9.553
b (Å)	6.16	10.410	10.440	10.513	10.538	10.538	10.389	10.405	10.405	10.513	10.538	10.538	10.389
c (Å)	11.26	6.125	6.096	5.988	5.924	5.924	6.089	6.155	6.155	5.988	5.924	5.294	6.089
$\alpha$ (deg)	90	84.653	84.731	89.999	90.000	90.000	85.093	84.610	84.610	90.000	90.000	90.000	94.907
$\beta$ (deg)	112.3	89.811	89.610	90.002	90.000	90.000	89.648	90.000	90.000	90.000	90.000	90.000	89.649
γ (deg)	90	90.316	90.191	89.576	88.205	88.205	89.205	90.000	90.000	90.424	91.795	91.795	90.795
V (Å <sup>3</sup> )	610.55	599.84	598.65	590.35	587.97	587.96	602.03	600.34	600.34	590.34	587.96	587.96	602.03
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<sup>a</sup>The first letter (M or O) corresponds to the initial  $P2_1/c$  or *Pbcn* arrangement for calcium carbonate hemihydrate; the second symbol corresponds to the number of water molecules located at y = 0.5.

significant rearrangement: either by adding one molecule at y = 0 and the other at y = 0.5 in an "I-centered" fashion, or by having the two additional molecules located at y = 0.5. From there, different orientations for the additional two molecules, i.e., parallel, antiparallel, or perpendicular with respect to the other water molecules, were tested and reported in Figure S1. Although they do not constitute an exhaustive list of possibilities, these initial configurations all optimized to a P1 triclinic crystal structure with complete loss of all symmetry elements.

Given that geometry optimization of calcium carbonate hemihydrate with DFT resulted in a structure with higher symmetry than the experimentally suggested  $P2_1/c$  arrangement, we also attempted to add the two additional water molecules starting from the optimized *Pbcn* hemihydrate structure. These configurations and the FF-optimized geometries are shown in Figure S2. All but one of the initial configurations optimized to a monoclinic structure with a  $P2_1$ geometry for the configurations with an "I-centered" addition of the two extra water molecules, whereas those with addition of both water molecules at y = 0.5 optimized to a  $P_c$  geometry (Table 6).

These two monoclinic geometries were then optimized with DFT, leading to the structures shown in Figure 3 and cell



Figure 3. Optimized structures (DFT) of two possible configurations for  $CaCO_3 \cdot 0.75H_2O$  viewed along [100] (left), [010] (middle), and [001] (right). Colors as in Figure 1.

parameters reported in Table 7. In both cases, the symmetry elements and space group obtained from force field

Table 7. Experimental and Calculated (DFT) Cell Parameters of  $CaCO_3 \cdot \frac{3}{4}H_2O$ 

	experimental <sup>19</sup>	DFT	DFT
Space group	$P2_1$	$P2_1$	$P_{c}$
a (Å)	9.51	6.208	10.579
b (Å)	6.16	9.447	6.040
c (Å)	11.26	10.545	9.521
$\alpha$ (deg)	90	90.000	90.000
$\beta$ (deg)	112.3	94.568	92.845
γ (deg)	90	90.000	90.000
V (Å <sup>3</sup> )	610.55	616.42	607.61

optimization were conserved. With  $\beta = 94.568^{\circ}$  and  $\beta = 92.845^{\circ}$  for the  $P2_1$  and  $P_c$  structures, respectively, the  $\beta$  values remained significantly lower than the 112.3° angle reported in the experimental study.

These preliminary results suggest that, similarly to magnesium ions, water incorporation into the hemihydrate structure could result in symmetry lowering from an orthorhombic to a monoclinic system. Vibrational frequencies were calculated for the two structures, and the absence of imaginary modes confirmed they both corresponded to minimum energy configurations. Compared to hemihydrate, the hydration reactions to form either the  $P2_1$  or  $P_c$  $CaCO_3 \cdot \frac{3}{4}H_2O$  phases from calcite and water at 298.15 K are more endothermic, with  $\Delta H = +10.9$  and +16.5 kJ/mol, respectively, and more endergonic, with  $\Delta G = +16.7$  and +22.0kJ/mol, respectively (Table 5). A less stable hydromorph than hemihydrate would be expected considering that very minor quantities, a few percent, of that phase were suggested to have formed in the experimental study. The P21 structure also appears to be more stable than the  $P_c$  arrangement, which would be consistent with the space group obtained experimentally.

Further work and a proper crystal structure determination approach remains to be carried out to establish if either of these structures, particularly the  $P2_1$  geometry, correspond to the global minimum, so as to ultimately confirm the existence of a CaCO<sub>3</sub> $\cdot \frac{3}{4}$ H<sub>2</sub>O phase.

**3.4. Simulated X-ray Diffraction Patterns.** The number of reflections in the simulated XRD patterns of the DFT-optimized structures of calcite, dolomite, and magnesite and



**Figure 4.** Simulated XRD patterns of the experimentally and theoretically determined structures of calcium carbonate hemihydrate referred to as  $P2_1/c$  and *Pbcn*, respectively (a), and of the 3.125%, 6.25%, 50%, and 100% magnesium-substituted hemihydrate (b). (c) Selected section of the XRD patterns showing (011) and (020) reflections in pure Ca- and Mg-substituted hemihydrate. The position of the reflections is indicated by a vertical line. Patterns are shifted vertically for comparison.

monohydrocalcite and their relative intensities reproduce that of the experimental structures well (Figure S3). A small shift in the position of the diffraction peak of about  $0.05^{\circ}$  toward higher  $2\theta$  values is observed in the theoretical patterns of monohydrocalcite and the Mg-bearing phases.

Regarding calcium carbonate hemihydrate, the optimized structure presents a higher symmetry than the experimental structure reported in the original paper. The Pbcn space group is characterized by the same diffraction conditions on (h0l), (0k0), and (00l) lines as the  $P2_1/c$  space group, as well as additional ones on the (0kl), (hk0), and (h00) reflections. Simulated XRD patterns corresponding to the experimentally and computationally determined structures of calcium carbonate hemihydrate are shown in Figure 4a. The XRD pattern of theoretical hemihydrate exhibits fewer reflections as expected for the higher symmetry space group Pbcn. Compared to the  $P2_1/c$  structure, the (120), (021), (130), (300), and (002) reflections are absent from the diffractogram in the 4- $11^{\circ} 2\theta$  range. The most intense diffraction peak reported experimentally is a double peak corresponding to the (011)and (020) reflections. While these two reflections are also

present in the simulated XRD pattern of the *Pbcn* structure, they occur at closer  $2\theta$  values, with  $\Delta 2\theta = 0.01^{\circ}$ , and are not resolved when simulating the XRD pattern with a  $0.05^{\circ}$  fwhm, thus leading to the single peak in Figure 4a.

In contrast, the simulated XRD patterns for hemihydrate containing 3.125% and 6.25% Mg are more similar to that of the hemihydrate structure in a  $P2_1/c$  arrangement proposed the original paper (Figure 4b), which is consistent with the symmetry lowering induced by magnesium substitution. Indeed, with the  $\lambda = 0.49596$  Å X-ray wavelength used in the experiment, small amounts of Mg substitution lead to a  $2\theta$ spacing between the (011) and (020) reflections of the same order as for the experimental structure, about +0.1°, and appear as a double peak when simulating the pattern with a  $0.05^{\circ}$  fwhm. The small shift of about +0.05° toward higher  $2\theta$ values relative to the pattern of the experimental structure is comparable to the one observed for dolomite and magnesite relative to calcite, and is likely due to an underestimation of the cell volume by the DFT calculations (Figure 4c). Some of the reflections observed experimentally that were absent in the XRD pattern of the *Pbcn* structure, e.g., (300) and (002), are

# Table 8. Experimental and Calculated Raman and Infrared Peak Positions in cm<sup>-1</sup> for Calcium Carbonate Hemihydrate, Mg-Substituted Hemihydrate, Monohydrocalcite, and Ikaite<sup>a</sup>

		CaC	0.5H2	0	Mg <sub>0.5</sub> Ca <sub>0.5</sub> C	CO <sub>3</sub> ·0.5H <sub>2</sub> O		monohy	drocalcite			ik	aite	
	Rai	nan		IR	Raman	IR	Ra	man	]	IR	Ra	man	]	IR
Assignment	Exp <sup>19</sup>	Calc.	Exp <sup>19</sup>	Calc.	Calc	Calc	Exp <sup>54</sup>	Calc.	Exp <sup>54</sup>	Calc.	Exp <sup>54</sup>	Calc.	Exp <sup>54</sup>	Calc.
$\nu_4 \text{ CO}_3$ in-	700	708	692	(731)	(699–710)	(684–705)	699	(678)	698	(722)	722	(724)	720	(762)
plane bending	731	741	723	794	(735–757)	(869-881)	723	723	762	(785)			743	(789)
$\nu_2~{\rm CO}_3$ out-of-	862	879	860	875	971	970-984	876	(848)	872	(898)	873	(948)	876	(897)
plane bending			866	886				(906)						
$\nu_1 \operatorname{CO}_3$	1102	1130	1096	1130	1127	1127	1069	1099	1063	1099	1072	1108	1085	1098
symmetric stretching					1157									
$\nu_3 CO_3$	1423	1461	1392	1428	1428	1429	-	1454	1401	1454	1483	1465	1411	1461
asymmetric	1483	1551	1423	1448-1456	1522	1460		1476	1492	1525			1425	1463
stretching	1579	1638	1490	1537	1633	1486-1493		1525		1553				
			1524	1550		1519								
HOH bending	1661	1729	1659	1729	1663	1636-1682	-	1703	1700	1704	-	1661	1616	1656
								1719		1719		1703	1644	1666
												1727	1673	1697
OH stretching	3285	3530	3290	3529	3171	3177	3224	3353	3236	3353	3182	3342	3216	3336
	3382		3379	3532	3740	3739-3744	3326	3431	3327	3431	3240	3410	3361	3412
							3425	3470	3400	3447	3423	3462	3404	3442
								3538		3472		3549	3468	3459
										3481		3588	3502	3500
										3538			3543	3521
														3566

"Note that peak attribution is more complex in the low frequency region of the infrared and Raman spectra due to the large amount of calculated lattice modes and would require a mode-by-mode analysis that is beyond the scope of this paper. Tentative attributions based on simple comparison with the experiment are noted in parentheses.

also found in the XRD pattern of the 3.125% and 6.25% Mg phases, although some remain missing such as (021) and (130). The latter two lines are present in the XRD pattern of 50% Mg hemihydrate, but some of the peak positions are significantly shifted toward higher  $2\theta$  angles compared to the pure Ca and low Mg phases. For instance, the (011) and (020) reflections occur at 5.4° and 6.1°  $2\theta$ , respectively, and lead to two distinct peaks. Not all possible magnesium substitutions were explored, which could explain why none of the simulated XRD patterns of Mg-bearing hemihydrate shown here fully overlap with the experimental one. However, the qualitative agreement found in XRD as well as the deviation of the  $\beta$  angle from  $90^\circ$  seem to suggest that small amounts of Mg were incorporated in the experimental structure. As per the 50% Mg phase, the spacings between peaks are modified in the XRD pattern of the pure Mg end-member, with the (011) and (020)reflections at 5.7° and 6.3°  $2\theta$ , respectively, also resulting in two distinct peaks. However, the diffractogram presents fewer lines, which is consistent with this phase's higher symmetry.

**3.5. Vibrational Properties of Calcium Carbonate Hemihydrate.** The calculated IR and Raman modes of Caand Mg-substituted carbonate hemihydrate are reported in Table 8 along with those of ikaite and monohydrocalcite.

The calculated IR spectrum of calcium carbonate hemihydrate displays the characteristic bands ascribed to the internal vibrations of the carbonate groups and structural water (Figure 5). Intense bands observed between 1420 and 1550 cm<sup>-1</sup> are related to the  $\nu_3$  CO<sub>3</sub> asymmetric stretching mode of structural carbonate groups, while the  $\nu_1$  CO<sub>3</sub> symmetric stretching mode corresponds to the weak band at 1130 cm<sup>-1</sup>. The low-frequency region displays the  $\nu_4$  and  $\nu_2$  CO<sub>3</sub> bending bands at 731–794 cm<sup>-1</sup> and 875–886 cm<sup>-1</sup>, respectively. The bending and stretching modes of the structural water are calculated at 1729 cm<sup>-1</sup> and 3529–3532 cm<sup>-1</sup>, respectively. The main experimental feature of the infrared spectrum of hemihydrate reported by Zou et al.<sup>19</sup> is the splitting of the  $\nu_3$  CO<sub>3</sub> asymmetric stretching mode into 4 peaks, contrary to ACC and monohydrocalcite, for which the mode is split into two peaks only. This characteristic is reproduced by our DFT calculations, although one of the peaks in the hemihydrate spectrum presents a shoulder at 1456 cm<sup>-1</sup>. Similarly, the calculated harmonic frequencies for the  $\nu_3$  CO<sub>3</sub> mode of monohydrocalcite include a third and less intense peak at 1553 cm<sup>-1</sup>, which was also reported in previous DFT calculations of the vibrational properties of monohydrocalcite.<sup>53</sup>

Overall, a good agreement is observed between calculated and experimental frequencies of calcium carbonate hemihydrate (Figure S4a) with the exception of the OH stretching bands that are overestimated by about  $\sim 200 \text{ cm}^{-1}$ , as expected when neglecting anharmonicity. In contrast, a poorer agreement with the experimental frequencies is observed in the case of the 50% Mg-substituted phase. This is particularly apparent when looking at the OH stretching bands as well as the  $\nu_2$  and  $\nu_4$  CO<sub>3</sub> bending modes in the low-frequency region of the spectrum. Compared to the pure calcium phase, the two OH stretching bands are split further apart, while the  $\nu_3$  CO<sub>3</sub> peaks are brought closer together. In an attempt to check for possible isotopic effects, the IR spectra were recalculated by changing the atomic mass of 12.5% and 50% Ca to that of Mg, starting from the pure Ca Pbcn structure, which did not modify the spectra (Figure S5). Conversely, the atomic mass substitution of all Mg atoms for Ca, starting from the  $P2_1/c$  structure of the 50% Mg-substituted hemihydrate, lead to no differences in the



Figure 5. Selected regions of the IR spectra of ikaite, monohydrocalcite, pure calcium and 50% Mg substituted carbonate hemihydrate showing the structural  $CO_3$  bands in the 400–1200 cm<sup>-1</sup> (a) and 1300–1800 cm<sup>-1</sup> (b) ranges and OH stretching bands (c). The latter is shifted by ~200 cm<sup>-1</sup> with respect to experimental values due to the calculations being harmonic. Spectra are shifted vertically for comparison. The position of the experimental IR bands of calcium carbonate hemihydrate are reported as vertical dashed lines.

IR spectra. This indicates that the positions of these bands are characteristic of the crystal structure.

As for Raman frequencies, the calculated Raman shifts of calcium carbonate hemihydrate agree well with the experimental ones (Figure S4b). The position of the intense  $\nu_1$  CO<sub>3</sub> band is characteristic of the hydromorph (Figure 6).



**Figure 6.** Raman  $\nu_1$  CO<sub>3</sub> mode of monohydrocalcite, ikaite, calcium, and 50% Mg substituted carbonate hemihydrate. Spectra are shifted vertically for comparison.

Compared to the peaks of monohydrocalcite at 1099 cm<sup>-1</sup> and ikaite at 1108 cm<sup>-1</sup>, the  $\nu_1$  CO<sub>3</sub> band in the Raman spectrum of hemihydrate is shifted toward higher frequencies, at 1130 cm<sup>-1</sup>. The calculated resonances are consistent with the order observed experimentally and overestimate their experimental counterparts by about 30 cm<sup>-1</sup>. In contrast, in the 50% Mg-substituted compound, the  $\nu_1$  CO<sub>3</sub> band is split into two peaks at 1127 and 1157 cm<sup>-1</sup>, respectively. The fact that only a single peak was observed experimentally is consistent with the results from the structural and XRD data suggesting that only small amounts of magnesium could have been incorporated in the hemihydrate structure.

#### 4. CONCLUSION

Theoretical investigation of the recently discovered hemihydrate of calcium carbonate,  $CaCO_3 \cdot \frac{1}{2}H_2O$ , revealed a higher symmetry than reported in the original article, with a *Pbcn* space group instead of  $P2_1/c$ . Partial substitution of calcium with magnesium lowers the symmetry to the experimental monoclinic space group, with a maximum distortion of the  $\beta$ angle for a  $Ca_{0.5}Mg_{0.5}CO_3 \cdot \frac{1}{2}H_2O$  composition.

Based on the theoretical results, we suggest that the calcium carbonate hemihydrate compound was not pure and contained Mg impurities in its structure. As the experimental conditions involved a high Mg to Ca ratio, this is consistent with the observation that initially high supersaturation conditions can lead to rapid precipitation and less distinction between Mg and Ca ions thus resulting in higher Mg contents in the crystal structure.<sup>20,37</sup>

Similarly to magnesium, the inclusion of additional water molecules into the hemihydrate structure can lead to structural changes and rearrangement into a monoclinic system. The eventuality of another new hydromorph,  $CaCO_3 \cdot \frac{3}{4}H_2O$ , was also considered, as suggested by Zou et al.<sup>19</sup> Preliminary results suggest that a  $P2_1$  structure could be stable, which is consistent with the experimental findings. However, further data, both experimental and computational, is required to confirm its existence and determine precisely its structure.

#### ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.cgd.0c01282.

Table S1: Cell parameters averaged over all combinations as a function of the Mg substitution content; Figures S1 and S2: Initial configurations and FFoptimized structures for  $CaCO_3 \cdot 0.75H_2O$ ; Figure S3: Simulated XRD patterns of magnesite, dolomite, calcite, and monohydrocalcite; Figure S4: Experimental and calculated harmonic infrared and Raman frequencies; Figure S5: IR spectra of calcium carbonate hemihydrate after isotopic substitution of 12.5% and 50% calcium with the atomic mass of magnesium and of 50% Mg substituted hemihydrate after isotopic substitution of all Mg atoms to Ca atomic mass (PDF)

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#### Notes

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# REFERENCES

(1) Beck, J. W.; Edwards, R. L.; Ito, E.; Taylor, F. W.; Recy, F.; Rougerie, J.; Joannot, P.; Henin, C. Sea-Surface Temperature from Coral Skeletal Strontium/Calcium Ratios. *Science* **1992**, *257*, 644– 647.

(2) Eiler, J. M. Paleoclimate Reconstruction using Carbonate Clumped Isotope Thermometry. *Quat. Sci. Rev.* 2011, 30, 3575–3588.

(3) Millero, F. J. The Marine Inorganic Carbon Cycle. *Chem. Rev.* 2007, 107, 308-341.

(4) Tang, C. C.; Thompson, S. P.; Parker, J. E.; Lennie, A. R.; Azough, F.; Kato, K. The Ikaite-to-Vaterite Transformation: New Evidence from Diffraction and Imaging. *J. Appl. Crystallogr.* **2009**, *42*, 225–233.

(5) Zhang, Z.; Xie, Y.; Xu, X.; Pan, H.; Tang, R. Transformation of Amorphous Calcium Carbonate into Aragonite. *J. Cryst. Growth* **2012**, 343, 62–67.

(6) Besselink, R.; Rodriguez-Blanco, J. D.; Stawski, T. M.; Benning, L. G.; Tobler, D. J. How Short-lived Ikaite Affects Calcite Crystallization. *Cryst. Growth Des.* **2017**, *17* (12), 6224–6230.

(7) Skinner, H. C. W.; Osbaldiston, G. W.; Wilner, A. N. Monohydrocalcite in a Guinea Pig Bladder Stone, a novel occurrence. *Am. Mineral.* **1977**, *62*, 273–277.

(8) Lowenstam, H. A. Minerals Formed by Organisms. Science 1981, 211, 1126–1131.

(9) Swainson, I. P. The Structure of Monohydrocalcite and the Phase Composition of the Beachrock Deposits of Lake Butler and Lake Fellmongery, South Australia. *Am. Mineral.* **2008**, *93*, 1014–1018.

(10) Dieckmann, G. S.; Nehrke, G.; Papadimitriou, S.; Göttlicher, J.; Steininger, R.; Kennedy, H.; Wolf-Gladrow, D.; Thomas, D. N. Calcium Carbonate as Ikaite Crystals in Antarctic Sea Ice. *Geophys. Res. Lett.* **2008**, *35*, 35.

(11) Gebauer, D.; Völkel, A.; Cölfen, H. Stable Prenucleation Calcium Carbonate Clusters. *Science* **2008**, 322, 1819–1822.

(12) Demichelis, R.; Raiteri, P.; Gale, J. D.; Quigley, D.; Gebauer, D. Stable Prenucleation Mineral Clusters are Liquid-like Ionic Polymers. *Nat. Commun.* **2011**, *2*, 590.

(13) Pouget, E. M.; Bomans, P. H. H.; Goos, J. A. C. M.; Frederik, P. M. G.; de Sommerdijk, N. A. J. M. The Initial Stages of Templatecontrolled CaCO3 Formation Revealed by Cryo-TEM. *Science* **2009**, 323, 1455–1458.

(14) Wallace, A. F.; Fernandez-Martinez, A.; Raiteri, P.; Gale, J. D.; Banfield, J. F.; Waychunas, G. A.; De Yoreo, J. J. Microscopic Evidence for Liquid-liquid Separation in Supersaturated CaCO3 Solutions. *Science* **2013**, *341*, 885–889.

(15) Sebastiani, F.; Wolf, S. L. P.; Born, B.; Luong, T. Q.; Cölfen, H.; Gebauer, D.; Havenith, M. Water Dynamics from THz Spectroscopy Seveal the Locus of a Liquid-liquid Binodal Limit in Aqueous CaCO3 Solutions. *Angew. Chem., Int. Ed.* **2017**, *56*, 490–495.

(16) Neumann, M.; Epple, M. Monohydrocalcite and Its Relationship to Hydrated Amorphous Calcium Carbonate in Biominerals. *Eur. J. Inorg. Chem.* **2007**, 2007, 1953–1957.

(17) Gebauer, D.; Gunawidjaja, P. N.; Ko, J. Y. P.; Bacsik, Z.; Aziz, B.; Liu, L. J.; Hu, Y. F.; Bergstrom, L.; Tai, C. W.; Sham, T.-K.; Eden, M.; Hedin, N. Proto-Calcite and Proto-Vaterite in Amorphous Calcium Carbonates. *Angew. Chem., Int. Ed.* **2010**, *49*, 8889–8891.

(18) Gebauer, D.; Raiteri, P.; Gale, J. D.; Coelfen, H. On Classical and Non-classical Views on Nucleation. *Am. J. Sci.* 2018, 318, 969–988.

(19) Zou, Z.; Wouter, J. E. M.; Matveeva, G.; Jensen, A. C. S.; Bertinetti, L.; Hood, M. A.; Sun, C.; Gilbert, P. U. P. A.; Polishchuk, I.; Pokroy, B.; Mahamid, J.; Politi, Y.; Weiner, S.; Werner, P.; Bette, S.; Dinnebier, R.; Kolb, U.; Zolotoyabko, E.; Fratzl, P. A Hydrated Crystalline Calcium Carbonate Phase: Calcium Carbonate Hemihydrate. *Science* **2019**, *363* (6425), 396–400.

(20) Loste, E.; Wilson, R. M.; Seshadri, R.; Meldrum, F. C. The Role of Magnesium in Stabilising Amorphous Calcium Carbonate and Controlling Calcite Morphologies. *J. Cryst. Growth* **2003**, *254*, 206–218.

(21) Radha, A. V.; Navrotsky, A. Thermodynamics of Carbonates. *Rev. Mineral. Geochem.* 2013, 77, 73–121.

(22) Rosenthal, Y.; Boyle, E. A.; Slowey, N. Temperature Control on the Incorporation of Magnesium, Strontium, Fluorine, and Cadmium into Benthic Foraminiferal Shells from Little Bahama Bank: Prospects for Thermocline Paleoceanography. *Geochim. Cosmochim. Acta* **1997**, *61*, 3633–3643. (23) Riechelmann, S.; Buhl, D.; Schroder-Ritzrau, A.; Riechelmann, D. F. C.; Richter, D. K.; Vonhof, H. B.; Wassenburg, J. A.; Geske, A.; Spotl, C.; Immenhauser, A. The Magnesium Isotope Record of Cave Carbonate Archives. *Clim. Past* **2012**, *8*, 1849–1867.

(24) Riechelmann, S.; Schroder-Ritzrau, A.; Wassenburg, J. A.; Schreuer, J.; Richter, D. K.; Riechelmann, D. F. C.; Terente, M.; Constantin, S.; Mangini, A.; Immenhauser, A. Physicochemical Characteristics of Drip Waters: Influence on Mineralogy and Crystal Morphology of Recent Cave Carbonate Precipitates. *Geochim. Cosmochim. Acta* 2014, 145, 13–29.

(25) Saenger, C.; Wang, Z. Magnesium Isotope Fractionation in Biogenic and Abiogenic Carbonates: Implications for Paleoenvironmental Proxies. *Quat. Sci. Rev.* **2014**, *90*, 1–21.

(26) Raz, S.; Hamilton, P. C.; Wilt, F. H.; Weiner, S.; Addadi, L. The Transient Phase of Amorphous Calcium Carbonate in Sea Urchin Larval Spicules: The Involvement of Proteins and Magnesium Ions in its Formation and Stabilization. *Adv. Funct. Mater.* **2003**, *13*, 480–486.

(27) Politi, Y.; Batchelor, D. R.; Zaslansky, P.; Chmelka, B. F.; Weaver, J. C.; Sagi, I.; Weiner, S.; Addadi, L. Role of Magnesium Ion in the Stabilization of Biogenic Amorphous Calcium Carbonate: a Structure-Function Investigation. *Chem. Mater.* **2010**, *22*, 161–166.

(28) Rodriguez-Blanco, J. D.; Shaw, S.; Bots, P.; Roncal-Herrero, T.; Benning, L. G. The Role of pH and Mg on the Stability and Crystallization of Amorphous Calcium Carbonate. *J. Alloys Compd.* **2012**, 536, S477–S479.

(29) Konrad, F.; Purgstaller, B.; Gallien, F.; Mavromatis, V.; Gane, P.; Dietzel, M. Influence of Aqueous Mg Concentration on the Transformation of Amorphous Calcium Carbonate. *J. Cryst. Growth* **2018**, 498, 381–390.

(30) Mucci, A.; Morse, J. W. The Solubility of Calcite in Seawater Solutions of Various Magnesium Concentration,  $I_t$ =0.697m at 25 = C and one Atmosphere Total Pressure. *Geochim. Cosmochim. Acta* **1984**, 48, 815–822.

(31) Davis, K. J. The Role of  $Mg^{2+}$  as an Impurity in Calcite Growth. *Science* **2000**, 290, 1134–1137.

(32) Chen, T.; Neville, A.; Yuan, M. Assessing the effect of  $Mg^{2+}$  on CaCO<sub>3</sub> Scale Formation-Bulk Precipitation and Surface Deposition. *J. Cryst. Growth* **2005**, 275, 1341–1347.

(33) Zhang, Y.; Dawe, R. A. Influence of Mg2+ on the Kinetics of Calcite Precipitation and Calcite Crystal Morphology. *Chem. Geol.* **2000**, *163*, 129–138.

(34) Niedermayr, A.; Kohler, S. J.; Dietzel, M. Impacts of Aqueous Carbonate Accumulation Rate, Magnesium and Polyaspartic Acid on Calcium Carbonate Formation  $(6-40^{\circ} \text{ C})$ . *Chem. Geol.* **2013**, 340, 105–120.

(35) Munemoto, T.; Fukushi, F. Transformation Kinetics of Monohydrocalcite to Aragonite in Aqueous Solutions. J. Mineral. Petrol. Sci. 2008, 103, 345–349.

(36) Fukushi, K.; Munemoto, T.; Sakai, M.; Yagi, S. Monohydrocalcite: a Promising Remediation Material for Hazardous Anions. *Sci. Technol. Adv. Mater.* **2011**, *12*, 064702.

(37) Rodriguez-Blanco, J. D.; Shaw, S.; Bots, P.; Roncal-Herrero, T.; Benning, L. G. The Role of Mg in the Crystallization of Monohydrocalcite. *Geochim. Cosmochim. Acta* **2014**, *127*, 204–220.

(38) Blue, C. R.; Giuffre, A.; Mergelsberg, S.; Han, N.; De Yoreo, J. J.; Dove, P. M. Chemical and Physical Controls on the Transformation of Amorphous Calcium Carbonate into Crystalline CaCO<sub>3</sub> Polymorphs. *Geochim. Cosmochim. Acta* **2017**, *196*, 179–196.

(39) Demichelis, R.; Raiteri, P.; Gale, J. D. Structure of Hydrated Calcium Carbonates: A First-Principles Study. *J. Cryst. Growth* **2014**, 401, 33–37.

(40) Demichelis, R.; Raiteri, P.; Gale, J. D.; Dovesi, R. Examining the Accuracy of Density Functional Theory for Predicting the Thermodynamics of Water Incorporation into Minerals: the Hydrates of Calcium Carbonate. *J. Phys. Chem. C* **2013**, *117*, 17814–17823.

(41) Stashans, A.; Chamba, G. A New Insight on the Role of Mg in Calcite. *Int. J. Quantum Chem.* **2011**, *111*, 2436–2443.

(42) Chaka, A. M. Quantifying the Impact of Magnesium on the Stability and Water Binding Energy of Hydrated Calcium Carbonates by Ab Initio Thermodynamics. *J. Phys. Chem. A* **2019**, *123*, 2908–2923.

(43) Dovesi, R.; Pascale, F.; Civalleri, B.; Doll, N. M.; Harrison, I.; Bush, P.; D'Arco, Y.; Noel, M.; Rerat, P.; Carbonniere, M.; Causà, S.; Salustro, V.; Lacivita, B.; Kirtman, A. M.; Ferrari, F. S.; Gentile, J.; Baima, M.; Ferrero, R. The CRYSTAL Code, 1976–2020 and Beyond, a Long Story. J. Chem. Phys. **2020**, 152, 204111.

(44) Valenzano, L.; Noël, Y.; Orlando, R.; Zicovich-Wilson, C. M.; Ferrero, M.; Dovesi, R. Ab Initio Vibrational Spectra and Dielectric Properties of Carbonates: Magnesite, Calcite and Dolomite. *Theor. Chem. Acc.* **2007**, *117*, 991–1000.

(45) Carteret, C.; De La Pierre, M.; Dussot, M.; Pascale, F.; Erba, A.; Dovesi, R. The Vibrational Spectrum of CaCO3 Aragonite: a Combined Experimental and Quantum-Mechanical Investigation. *J. Chem. Phys.* **2013**, *138*, 014201.

(46) Demichelis, R.; Raiteri, P.; Gale, J. D.; Dovesi, R. The Multiple Structures of Vaterite. *Cryst. Growth Des.* **2013**, *13*, 2247–2251.

(47) Raiteri, P.; Demichelis, R.; Gale, J. D. Thermodynamically Consistent Force Field for Molecular Dynamics Simulations of Alkaline-Earth Carbonates and Their Aqueous Speciation. *J. Phys. Chem. C* 2015, *119*, 24447–24458.

(48) Gale, J. D. GULP: Capabilities and Prospects. Z. Kristallogr. -Cryst. Mater. 2005, 220, 552–554.

(49) Antao, S. M.; Hassan, I.; Mulder, W. H.; Lee, P. L.; Toby, B. H. In Situ Study of the R-3c R-3m Orientational Disorder in Calcite. *Phys. Chem. Miner.* **2009**, *36*, 159–169.

(50) Chen, C.-C.; Lin, C.-C.; Liu, L.-G.; Sinogeikin, S. V.; Bass, J. D. Elasticity of Single-Crystal Calcite and Rhodochrosite by Brillouin Spectroscopy. *Am. Mineral.* **2001**, *86*, 1525–1529.

(51) Wolf, G.; Lerchner, J.; Schmidt, H.; Gamsjager, H.; Konigsberger, E.; Schmidt, P. Thermodynamics of CaCO3 Phase Transitions. J. Therm. Anal. **1996**, 46, 353–359.

(52) Konigsberger, E.; Konigsberger, L. C.; Gamsjager, H. Low Temperature Thermodynamic Model for the System  $Na_2CO_3$ -MgCO<sub>3</sub>-CaCO<sub>3</sub>-H<sub>2</sub>O. *Geochim. Cosmochim. Acta* **1999**, 63, 3105–3199.

(53) Costa, S. N.; Freire, V. N.; Caetano, E. W. S.; Maia, F. F.; Barboza, C. A.; Fulco, U. L.; Albulquerque, E. L. DFT Calculations with van der Waals Interactions of Hydrated Calcium Carbonate Crystals CaCO3·( $H_2O$ ,  $6H_2O$ ): Structural, Electronic, Optical, and Vibrational Properties. J. Phys. Chem. A **2016**, 120, 5752–5765.

(54) Coleyshaw, E. E.; Crump, G.; Griffith, W. P. Vibrational Spectra of the Hydrated Carbonate Minerals Ikaite, Monohydrocalcite, Lansfordite and Nesquehonite. *Spectrochim. Acta, Part A* 2003, *59*, 2231–2239.