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Structure of hydrated calcium carbonates: a first-principles study.[☆]

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Abstract

The structures of both ikaite ($\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$) and monohydrocalcite ($\text{CaCO}_3 \cdot \text{H}_2\text{O}$) were computed at the PBE0 level of theory, using all electron Gaussian type basis sets. Correction for the long-range dispersion contribution was included for the oxygen-oxygen interactions by using an additive pairwise term with the atomic coefficients fitted against the calcite vs aragonite enthalpy difference. The potential chirality of monohydrocalcite is discussed, as well as the helical motifs created by the three-fold rototranslational axes parallel to the [001] direction. These elements represent a significant link between monohydrocalcite and vaterite, both appearing as intermediate species during CaCO_3 crystallization from amorphous calcium carbonate. The hydrogen bond pattern, never fully discussed for monohydrocalcite, is here described and compared to the available experimental data. Both phases are characterized by the presence of hydrogen bonds of moderate to high strength. Water molecules in monohydrocalcite interact quite strongly with 2 CO_3^{2-} units through such hydrogen bonds, whereas their interaction with each other is minor. On the contrary, water molecules in ikaite create a complex network of hydrogen bonds, where each water molecule is strongly hydrogen bonded to one CO_3^{2-} anion and to one or two other water molecules.

Keywords: B1. ikaite, B1. monohydrocalcite, A1. DFT, A1. chirality, A1. structure, A1. hydrogen bond

1. Introduction

Ikaite ($\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$) and monohydrocalcite ($\text{CaCO}_3 \cdot \text{H}_2\text{O}$) are two hydrated crystalline phases of calcium carbonate. Despite their rare occurrence under geological conditions, due to the water-free phases (calcite, aragonite and vaterite) being more stable at ambient conditions, they often form as intermediates during calcium carbonate crystallization, both under biogenic and abiogenic conditions.[1, 2]

In the past few years the idea that carbonate minerals can grow and nucleate through a different sequence of association processes to that conventionally envisaged when considering the classical nucleation pathway has been validated and confirmed by several studies.[3, 4, 5] However, a full understanding of the pathway to nucleation and ultimately polymorph selection is still a matter of debate. In this context, a detailed characterization of the phases that may or may not appear during these processes represents valuable information in understanding the full complexity of the aqueous calcium carbonate system.

Hydrated carbonates are often found to crystallize from amorphous calcium carbonate (ACC) particles and then undergo dehydration, with commensurate structural reorganization, that leads to the final anhydrous phases.[6, 7, 8, 9] Moreover, due to their similar composition (one water molecule per

CaCO_3 unit), monohydrocalcite is also used as a reference material to investigate biogenic ACC.[9, 10, 11, 12]

Despite the fact that several investigations of the structure of hydrated calcium carbonates are present in the literature,[1, 2, 13] an accurate description of their features at the atomic level is still missing. Determining the structural details of ikaite and monohydrocalcite is essential to understanding the reasons for their formation from ACC, their high solubility, their low stability, and their specific stoichiometry.

Computer models can play a significant role in achieving this task, not only because they allow for an accurate investigation of the inter-atomic interactions that contribute to stabilizing or destabilizing a particular structure, but also for their ability to describe reaction intermediates and hypothetical conditions that are not accessible to experimental techniques.

In this paper, the structures of ikaite and monohydrocalcite are investigated by applying first principles methods based on Density Functional Theory (DFT). The computational details are summarized in Section 2. Section 3 describes and compares the structures of monohydrocalcite and ikaite at the atomic level, including their hydrogen bonding pattern, with the aim of providing an accurate reference for the pure crystalline phases.

2. Computational Methods

The present calculations were performed at the DFT level of theory as implemented in the CRYSTAL09 package.[14] All electron Gaussian-type basis sets were adopted, as optimized for calcite[15] and successfully used to investigate a number of properties of several calcium carbonate phases[16, 17, 18, 19].

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Extensive work aimed at assessing the accuracy of several exchange-correlation functionals in predicting the structure, stability and vibrational properties of minerals, including calcium carbonates, has been recently undertaken.[20, 21, 22, 19] In general, hybrid Hartree-Fock (HF)/DFT functionals provide accurate results for minerals containing H atoms in their structure. The inclusion of an empirical long-range correction for dispersive interactions, as suggested by Grimme[23], is expected to improve the results for systems characterized by hydrogen bonds and/or non-negligible van der Waals interactions, providing that the appropriate atomic dispersion coefficients are derived or fitted for the materials under consideration.[24, 25] For these reasons, the PBE0-DC functional was used.[19] It consists of adding the empirical long range correction (D) for oxygen-oxygen interactions, with the atomic coefficients fitted against the calcite vs aragonite enthalpy difference (C stands for carbonates) to the PBE0 [26] hybrid functional. Details regarding the fitting of parameters and on the effects of including dispersion on the structure and formation energy of hydrated carbonates are discussed in Ref. [19].

The parameters controlling the Coulomb and HF exchange series accuracy were set to 10^{-8} (T_1 to T_4) and 10^{-18} (T_5), while the threshold for selecting bielectronic terms that can be approximated by bipolar expansion was set to 10^{-18} . The reciprocal space was sampled using a Monkhorst-Pack mesh with a shrinking factor of 8, corresponding to 90 (monohydrocalcite) and 150 (ikaite) independent \mathbf{k} vectors in the irreducible Brillouin zone. The DFT exchange-correlation contribution was evaluated by numerical integration over the unit cell volume, using a pruned grid with 75 radial and 974 angular points. The accuracy of the adopted grid can be assessed through the error on the numerically integrated density, which is on the order of $10^{-4}|e|$ out of a total of 220 and 540 $|e|$ in ikaite and monohydrocalcite, respectively.

Structure optimizations were performed by use of analytical energy gradients with respect to atomic coordinates and unit-cell parameters within a quasi-Newtonian scheme, combined with the Broyden-Fletcher-Goldfarb-Shanno scheme for Hessian updating. Convergence was checked using the energy, root-mean-square and absolute value of the largest component of both the residual gradients and the nuclear displacements. The energy threshold between two subsequent optimization steps was set to 10^{-7} a.u.; the thresholds on the root-mean-square of the gradient components and of the nuclear displacements to $3.0 \cdot 10^{-4}$ and $1.2 \cdot 10^{-3}$ a.u., respectively; the thresholds on the maximum components of the gradients and displacements were set to $4.5 \cdot 10^{-4}$ and $1.8 \cdot 10^{-3}$ a.u., respectively.

Harmonic vibrational frequencies of OH stretching modes and their anharmonicity were estimated by solving numerically the one-dimensional Schrödinger equation, starting from the total energies evaluated in a series of displacements of H atoms along the O-H bond direction (scanning from $d_{OH}+0.3$ Å to $d_{OH}-0.2$ Å).[27] The Self-Consistent Field convergence with respect to the energy was set to 10^{-8} a.u. for geometry optimization and to 10^{-10} a.u. for O-H frequency calculation. Further details on the approach and computational parameters here adopted can be found in Ref. [14] and references therein.

3. Structure and hydrogen-bond pattern

Monohydrocalcite ($\text{CaCO}_3 \cdot \text{H}_2\text{O}$, $P3_1$ space group) has a hexagonal unit cell (Figure 1) containing 9 formula units, three of which are symmetry independent and represent the asymmetric unit. In the following, the 12 oxygen atoms in the asymmetric unit will be labeled $O_W(1,2,3)$ and $O_C(4-12)$, where W and C indicate that the oxygen is part of a water molecule and of a carbonate anion, respectively. Calcium atoms in monohydrocalcite are 8-fold coordinated by six O_C , belonging to four CO_3^{2-} groups, and two O_W (see Figure 2a). Each O_C is first nearest neighbor to two Ca atoms, whereas only two O_C per CO_3^{2-} anion are involved in hydrogen bonding. Each water molecule is H-bonded through the two H atoms to two different CO_3^{2-} groups, and interacts very weakly with the other water molecules (the minimum distance between the oxygen atoms of two water molecules is ~ 4 Å). O_W in contrast is not involved as an acceptor in any hydrogen bonding.

The presence of a rototranslational symmetry axis make the structure of monohydrocalcite particularly intriguing. In particular, as shown in Figure 1, there are three three-fold rotational axes parallel to the c lattice vector in the unit cell, which have a translational component of $1/3$. They are responsible for creating the triangular motifs projected on the plane perpendicular to the [001] direction, each of which consist of a "helical" chain of carbonate and water molecules, with a period of c , and coordinating Ca^{2+} ions inside.

As also suggested by its space group, monohydrocalcite is then intrinsically chiral ($P3_1|P3_2$). This new way of looking at the monohydrocalcite structure - as a chiral crystal made of parallel helices - might be an important element that links this intermediate to the other species appearing during calcium carbonate nucleation and crystal growth. Indeed, the first event during the growth of calcium carbonate has recently been shown to involve the formation of pre-nucleation clusters that can assume polymeric hydrated structures.[28] The hypothesis of vaterite being chiral has also recently been proposed,[18] due to this system assuming multiple structures, some of which possess a chiral space group. The structural link between vaterite and monohydrocalcite is particularly significant, as both these phases appear as intermediate species in successive nucleation steps that start with formation of ACC and lead to the production of either calcite or aragonite crystals. In particular, the space group of monohydrocalcite is a subgroup of those of hexagonal vaterite, where three-fold rototranslational axes, parallel to the [001] direction with a screw vector of $1/3$ and period of c , create trigonal (pseudo-hexagonal) motifs.

Ikaite ($\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$, $C2/c$ space group) has a monoclinic, centered unit cell containing 4 formula units. The corresponding primitive cell contains 2 formula units, and the asymmetric unit contains 13 atoms: 1 Ca, 1 C, 3 O_W , 2 O_C and 6 H. The structure of ikaite is very unusual because it contains CaCO_3^0 ion pairs separated from each other by water molecules.[2] In ikaite, Ca^{2+} ions are also 8-fold coordinated by two O_C atoms belonging to the same carbonate ion and six O_W (Figure 2b).

Figure 3 shows the details of this complex structure. Here C, Ca and one out of three O_C atoms lie on planes parallel to that

defined by a and b lattice parameters. The single ion-pairs are connected to the others by means of a highly organized network of strong hydrogen bonds that involve both water molecules and carbonate anions. For each carbonate anion, two O_C are involved in the coordination of one single Ca atom and are the acceptor of two hydrogen bonds, whereas the third one, not involved in Ca coordination, is the acceptor of four hydrogen bonds. All water molecules are hydrogen bond donors through both their H atoms, whereas only two out of three O_W are hydrogen bond acceptors. Each O_W coordinates one Ca atom. A scheme showing the hydrogen bond network around the isolated CaCO_3^0 ion pair is given in Figure 4.

Structural parameters are reported in Tables 1 and 2. The agreement with experiments for ikaite, which is also the most complex structure, is outstanding. This confirms the robustness of the methods and parameters adopted in this work. Differences between calculated and experimental bond distances in monohydrocalcite are probably due to impurities present in the natural samples used in the structure determination.[1]

Table 2 reports all the parameters related to the hydrogen bonding structural features. Both systems are characterized by quite strong hydrogen bonds, with distances ranging from 1.763 to 1.918 Å in monohydrocalcite, and from 1.720 to 1.844 Å in ikaite, with $\text{H}\hat{\text{O}}\text{H}$ angles close to the ideal value of 180° .

The strength of the hydrogen bonds can be estimated through the value of the anharmonicity constants ($\omega_e\chi_e$) associated with the OH stretching modes. This constant links the vibrational frequency obtained under the harmonic assumption (ω_e) with its corresponding anharmonic value ($\omega_{01} = \omega_e - 2\omega_e\chi_e$), and has been estimated by displacing H atoms along the O-H bond direction, while keeping all the other geometrical parameters frozen, and then fitting the energies corresponding to each displacement to extract ω_{01} and the first overtone ω_{02} , with $\omega_e\chi_e = \frac{2\omega_{01} - \omega_{02}}{2}$. This approach has the limitation that, if H gets too close to its neighbors repulsion will start to increase, due to other phonon modes being frozen, leading to an unphysical increase of $\omega_e\chi_e$. In this respect, minerals such as brucite, portlandite, katoite and chabazite, where H is not involved in any hydrogen bond and has its second nearest neighbor more than 2 Å further away, are ideal cases and $\omega_e\chi_e$ for OH stretching modes falls between 75 and 90 cm^{-1} . At the other extreme, diaspore is characterized by very strong hydrogen bonds, with $\text{H}\cdots\text{O}$ distances of 1.69 Å, and the resulting $\omega_e\chi_e = 206 \text{ cm}^{-1}$ is a clear overestimation of the real constant, which would be about half this value (see Table 9 in Ref.[29]).

The deviation of the calculated $\omega_e\chi_e$ with respect to the ideal case where H is the terminus of a chain and is not involved in any hydrogen bond[27, 30] can then be used to estimate the strength of the interaction of H with its neighbors and then of the hydrogen bond. In the present case, $\omega_e\chi_e$ ranges from 125.9 to 163.3 cm^{-1} in monohydrocalcite and from 128.9 to 170.0 cm^{-1} in ikaite, indicating that in both systems hydrogen bonds range from medium to high strength.

In order to estimate the level of interaction between water molecules in the structures, the full harmonic vibrational spectrum has been computed by diagonalizing the dynamical matrix. This was obtained by numerical central finite differenti-

ation of the analytical forces with respect to atomic Cartesian coordinates, using a displacement of 0.003 Å. The totally symmetric modes associated with the six irreducible OH groups are reported in Table 3, and compared to those reported in Table 2, obtained by considering each OH group as an independent oscillator. They are also compared to the values obtained by substituting all H atoms in the unit cell with deuterium, except for the one involved in the hydrogen bond. Both these differences give a measure of how much the various oscillators interact with each other and, as a consequence, also of how much water molecules interact. It turns out that in monohydrocalcite these intermolecular interactions are relatively small ($\Delta\omega_e \approx 20$ and $-16.1 \leq \Delta D_{17} \leq 9.9 \text{ cm}^{-1}$), whereas, as expected, water-water interactions make an important contribution towards stabilizing the structure of ikaite, the maximum (average in parenthesis) absolute $\Delta\omega_e$ and ΔD_{23} being as much as 115.7 (51.5) and 131.7 (41.8) cm^{-1} , respectively.

There is at the moment no accurate and complete set of vibrational measurements available for monohydrocalcite and ikaite. To the authors' knowledge, the best determination is the one provided by Coleyshaw et al.,[31] where the nature of the modes is only partly discussed, the symmetry of the peaks is not fully assigned and the intensities are not reported. This, combined with the fact that natural and synthetic samples give different spectroscopic signals in the OH stretching region, makes any comparison with the present data very difficult. For this reason, the full vibrational spectra of monohydrocalcite and ikaite and their comparison to experimental data will be presented and discussed elsewhere.

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Table 1: Calculated structural parameters of monohydrocalcite and ikaite, along with comparison to experimental data:^a lattice parameters (Å and degrees), primitive cell volume (Å³), density (ρ , g cm⁻³), Ca-O bond distances (Å). In ikaite, $\alpha = \gamma = 90^\circ$; in monohydrocalcite $\alpha = 90^\circ$ and $\gamma = 120^\circ$. Details of the hydrogen bonds are given in Table 2.

	Monohydrocalcite		Ikaite	
	calc.	exp.	calc.	exp.
a	10.4713	10.5547	8.6787	8.7316
b	10.4713	10.5547	8.2453	8.2830
c	7.5319	7.5644	10.8300	10.9629
β	90	90	108.90	110.361
Vol	715.21	729.79	733.18	743.34
ρ	2.46	2.42	1.88	1.83
$Ca - O_C(max)^b$	2.510	2.624	2.439	2.442
$Ca - O_C(min)$	2.396	2.323	2.439	2.442
$Ca - O_C(av.)$	2.448	2.455	2.439	2.442
$Ca - O_W(max)$	2.492	2.535	2.541	2.545
$Ca - O_W(min)$	2.468	2.444	2.390	2.387
$Ca - O_W(av.)$	2.480	2.501	2.483	2.473

^a Data for monohydrocalcite are from Ref. [1] (neutron diffraction on natural samples); data for ikaite are from Ref. [2] (neutron diffraction on synthetic deuterated samples, 4 K).

^b max , min and $av.$ stand for maximum, minimum and average.

Table 2: Structural details of hydrogen bonds (HB) in monohydrocalcite and ikaite (only the irreducible H atoms, six for each structure, are considered). Bond distances (d , Å), hydrogen bond angle (α , degrees), harmonic stretching frequency (ω_e , cm⁻¹) and anharmonicity constants ($\omega_e\chi_e$, cm⁻¹) are reported. Experimental data from neutron diffraction[1, 2] are shown in italics (deuterated samples at 4 K for ikaite).

bond	d_{OH}	ω_e	$\omega_e\chi_e$	HB	d_{HB}	α_{HB}
Monohydrocalcite						
O _W (1)-H1	0.984	3452.1	147.8	H1...O _C (4)	1.835	176.1
	<i>0.967</i>	-	-		<i>2.086</i>	<i>167.7</i>
O _W (1)-H2	0.982	3496.5	139.4	H2...O _C (5)	1.849	171.9
	<i>0.959</i>	-	-		<i>2.020</i>	<i>161.3</i>
O _W (2)-H3	0.983	3471.5	144.5	H3...O _C (6)	1.849	177.4
	<i>0.953</i>	-	-		<i>1.965</i>	<i>177.6</i>
O _W (2)-H4	0.982	3484.7	140.8	H4...O _C (7)	1.832	172.1
	<i>0.964</i>	-	-		<i>1.955</i>	<i>153.5</i>
O _W (3)-H5	0.988	3375.7	163.3	H5...O _C (8)	1.763	177.5
	<i>0.958</i>	-	-		<i>1.739</i>	<i>166.7</i>
O _W (3)-H6	0.979	3548.6	125.9	H6...O _C (9)	1.918	171.2
	<i>0.963</i>	-	-		<i>1.883</i>	<i>170.9</i>
Ikaite						
O _W (1)-H1	0.982	3472.3	145.1	H1...O _C (4)	1.765	173.2
	<i>0.979</i>	-	-		<i>1.775</i>	<i>172.2</i>
O _W (1)-H2	0.977	3558.1	128.9	H2...O _W (2)	1.844	172.2
	<i>0.965</i>	-	-		<i>1.961</i>	<i>167.6</i>
O _W (2)-H3	0.980	3506.8	137.6	H3...O _C (5)	1.831	164.8
	<i>0.983</i>	-	-		<i>1.927</i>	<i>160.4</i>
O _W (2)-H4	0.984	3432.7	138.8	H4...O _W (3)	1.755	168.3
	<i>0.981</i>	-	-		<i>1.822</i>	<i>166.6</i>
O _W (3)-H5	0.986	3403.0	170.0	H5...O _C (4)	1.720	179.3
	<i>0.993</i>	-	-		<i>1.762</i>	<i>178.7</i>
O _W (3)-H6	0.980	3517.2	142.7	H6...O _C (5)	1.742	162.9
	<i>0.970</i>	-	-		<i>1.762</i>	<i>161.7</i>

Table 3: Harmonic vibrational frequencies associated with the totally symmetric stretching modes of the six symmetry independent OH units ($\omega_e(A)$ and $\omega_e(A_g)$, cm⁻¹). The comparison with the same frequencies as calculated in Table 2 ($\Delta\omega_e$) and as obtained by substituting all but one of the H atoms by D in the unit cell (all but H1 for O_W(1)-H1, all but H2 for O_W(1)-H2 and so on, ΔD_{17} and ΔD_{23}) is shown.

	Monohydrocalcite			Ikaite		
	$\omega_e(A)$	$\Delta\omega_e$	ΔD_{17}	$\omega_e(A_g)$	$\Delta\omega_e$	ΔD_{23}
O _W (1)-H1	3432.2	+19.9	+1.2	3588.0	-115.7	-131.7
O _W (1)-H2	3466.6	+29.9	+9.9	3548.8	+9.3	+4.6
O _W (2)-H3	3450.1	+21.4	+2.1	3461.5	+45.3	+33.7
O _W (2)-H4	3482.4	+2.3	-16.1	3410.1	+22.6	+11.7
O _W (3)-H5	3353.9	+21.8	+0.5	3341.9	+61.1	+33.1
O _W (3)-H6	3538.3	+10.3	-1.5	3461.9	+55.3	+35.8

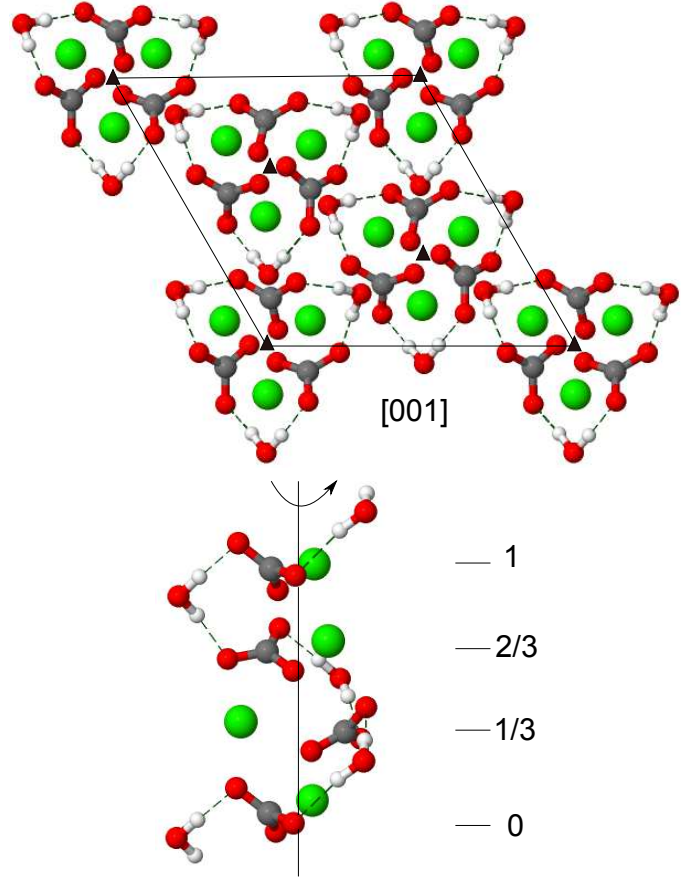


Figure 1: Monohydrocalcite: view of the unit cell along the [001] direction (upper panel) and view of the effect of the three-fold rototranslational axis along [001] in creating the triangular "helical" motifs (on e of which is illustrated in the lower panel). The rototranslational axis (black triangles and vertical line in the upper and lower panels, respectively) and the translations of 1/3, 2/3 and 1 are emphasized. Oxygen atoms are colored in red, hydrogen in white, carbon in grey and calcium in green; green dotted lines represent hydrogen bonds.

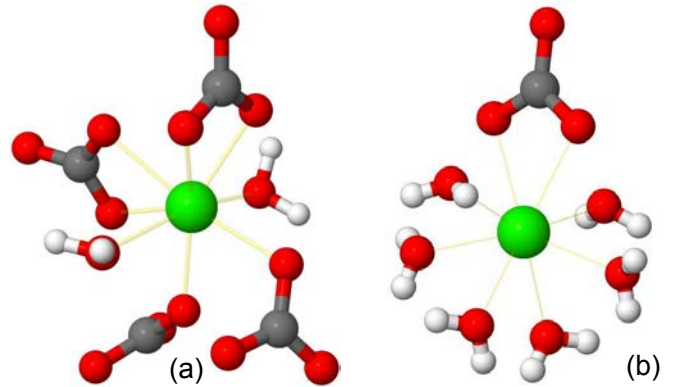


Figure 2: Coordination of calcium in monohydrocalcite (a) and ikaite (b). Colors as in Figure 1.

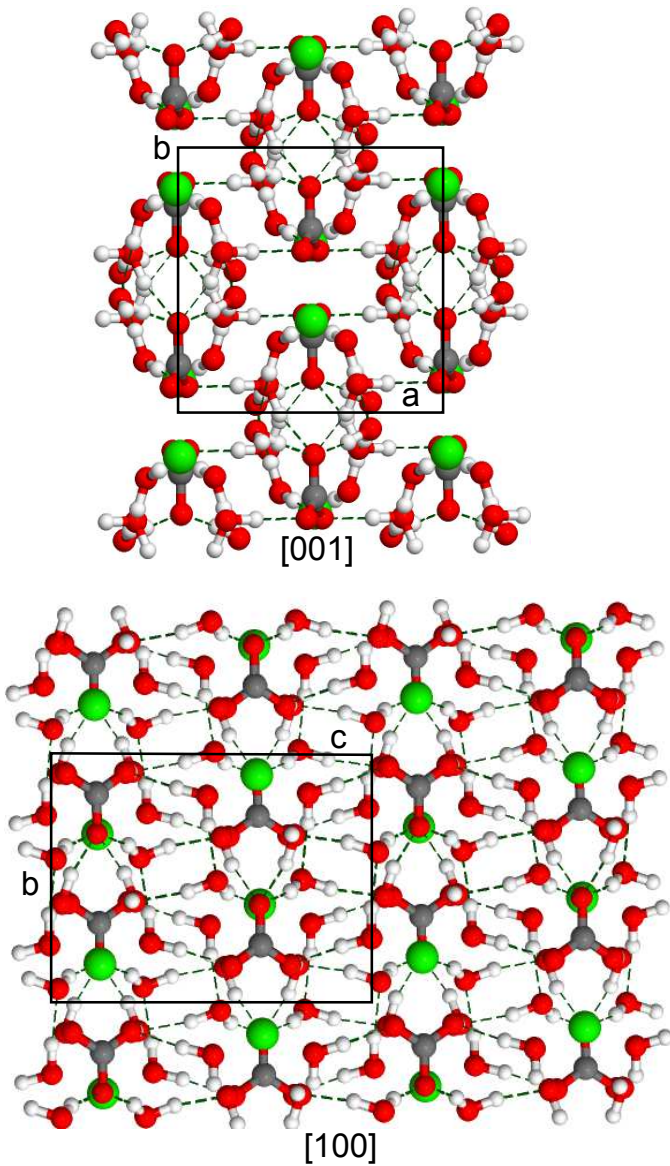


Figure 3: Ikaite: view of the conventional cell along the [001] and [100] directions. Colors as in Figure 1.

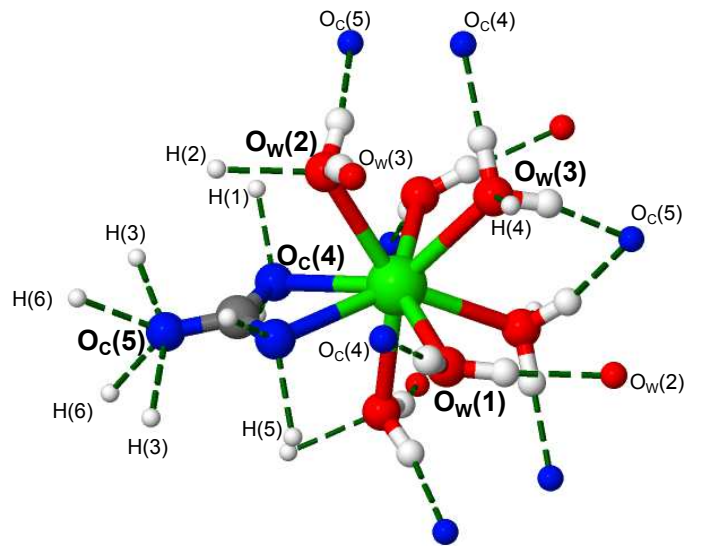


Figure 4: Hydrogen bond network around the CaCO_3^0 ion pair in ikaite. Oxygen atoms belonging to the carbonate anions (O_C) are in blue, the other colors are as in Figure 1. The five symmetry independent O atoms, four of which coordinate calcium, are labeled in bold; hydrogen bond donors and acceptors towards $\text{O}_W(1-3)$ and $\text{O}_C(4,5)$ are represented with a reduced van der Waals radius and labeled with a smaller font. Details on bond distances and angles in Table 2.