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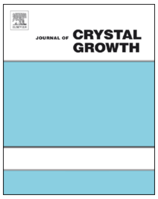

Structure of hydrated calcium carbonates: A first-principles study ☆

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The structures of both ikaite ($CaCO_3 \cdot 6H_2O$) and monohydrocalcite ($CaCO_3 \cdot H_2O$) 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.

1. Introduction

Ikaite ($CaCO_3 \cdot 6H_2O$) and monohydrocalcite ($CaCO_3 \cdot H_2O$) 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 [3–5]. 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 [6–9]. 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 [9–12].

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 for 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 interatomic 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

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successfully used to investigate a number of properties of several calcium carbonate phases [16–19].

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 [20–22,19]. 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–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 **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 the 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 3.0×10^{-4} and 1.2×10^{-3} a.u., respectively; the thresholds on the maximum components of the gradients and displacements were set to 4.5×10^{-4} and 1.8×10^{-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 ($CaCO_3 \cdot H_2O$, $P3_1$ space group) has an hexagonal unit cell (Fig. 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 Fig. 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.

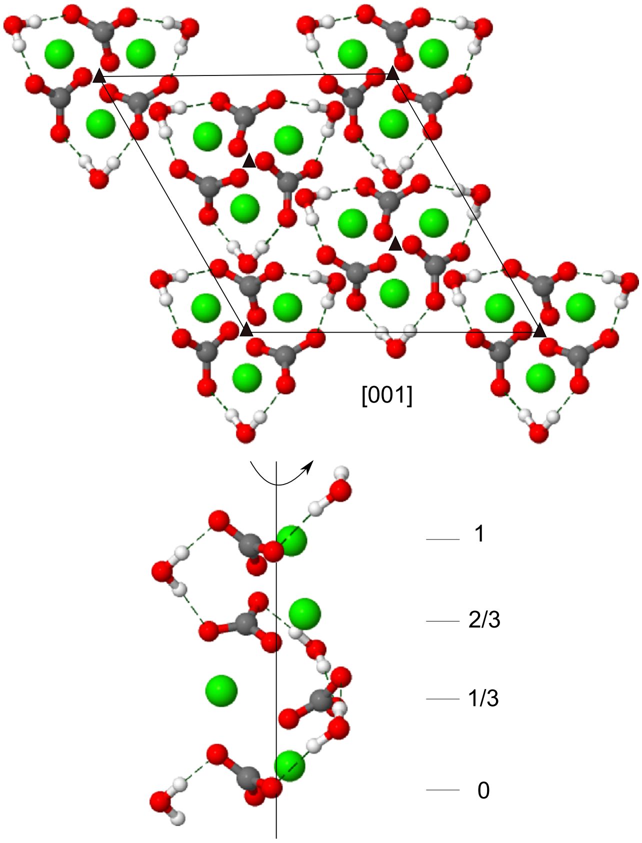

Fig. 1. Monohydrocalcite: view of the unit cell along the [001] direction (upper panel) and view of the effect of the three-fold rototranslational axis along [001] in creating the triangular “helical” motifs (one of which is illustrated in the lower panel). The rototranslational axis (black triangles 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 gray and calcium in green; green dotted lines represent hydrogen bonds. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this paper.)

The presence of a rototranslational symmetry axis make the structure of monohydrocalcite particularly intriguing. In particular, as shown in Fig. 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 consists 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 up 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