



# Distortions of the calcite and aragonite atomic structures from interstitial water



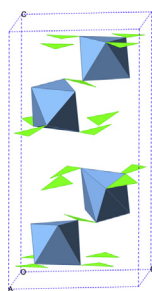
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## HIGHLIGHTS

- Low concentrations of water in the calcite or aragonite structures lead to tilting of the carbonate planes.
- This is consistent with IR observations from amorphous calcium carbonate.
- It does not explain amorphous diffraction patterns.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Amorphous calcium carbonate (ACC), as observed by diffraction or infra-red spectroscopy, is especially significant as a precursor in biomineralization. The atomic structure and mechanisms for transformation to the crystalline phases are still unknown. It is conceivable that insertion of water molecules could give rise to distortions that result in the observed diffraction patterns and infrared spectra. We use the VASP density functional theory code to relax model supercells with 24 formula units of  $\text{CaCO}_3$  where we have inserted up to 5 water molecules, corresponding to 3.75 wt%. The main effect is tilting of the carbonate planes, which can be as high as  $50^\circ$ . This leads to a range of Ca–O distances that are consistent with the observed changes in the IR spectra in ACC. The spread in cation–cation distances is not enough to destroy coherent diffraction from regions 70 nm across, and so does not explain amorphous diffraction profiles.

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## 1. Introduction

Calcium carbonate in its various polymorphs is ubiquitous in the animal kingdom and as calcite is the most abundant biomineral. It is mainly found in protective shells of marine animals such as molluscs and brachiopods [1]. The other well-known polymorph, aragonite, is a key constituent of the nacre of mother of pearl and coral. Biominerals, in living organisms, are known to form elaborate

structures even though diffraction shows them to be single crystals. Investigation of the growing spine in the larva of the sea urchin showed that the spicule was initially deposited as an amorphous phase that then transformed into calcite [2]. It is now known that many biominerals, including carbonate apatite in bone, are first deposited as amorphous precursor phases [3]. Amorphous calcium carbonate (ACC) can also be synthesized artificially by a number of different methods, though it might not be the same as biogenic ACC [4]. Some forms of amorphous calcium carbonate (ACC) transform quickly to the crystalline phase, others can be stable for long periods [5]. The magnesium content is also variable, the grinding tooth of the sea urchin can have up to 40% (atomic) Mg [6–8].

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While some amorphous carbonates have high water content, equivalent to monohydrocalcite, others are believed to be anhydrous [9].

The structure of ACC and the mechanisms by which it transforms to calcite or aragonite are still largely unknown. The physical evidence for the amorphous phase is an absence of optical birefringence, lack of crystalline reflections in electron or X-ray diffraction, a high ratio of the  $\nu_2$  to  $\nu_4$  peak in infra-red spectroscopy [2] and differences in the Ca L white lines in X-ray photoelectron spectroscopy. Two different forms of ACC have been identified in the X-ray photoemission microscopy of the sea urchin larva spicule [10]. From an analysis of calculations of the fine structure Rez and Blackwell [11] showed that these could arise from different ordering of the calcium coordination polyhedra.

There are various stages in the process of generating the calcite and aragonite crystal structures from amorphous precursors. Gebauer et al. [12], on the basis of Ca ion measurements and thermodynamic arguments, suggested that pre nucleation clusters formed on a macromolecular template, which then became amorphous nanoparticles. These subsequently assembled to form crystalline domains. Pouget et al. [13], using cryo electron microscopy, also provided support for the role of pre-nucleation clusters. Using Ca–O distances measured from EXAFS and NMR chemical shifts Gebauer et al. [14] showed that ACC comes in two forms, one showing a greater similarity to calcite while the other more closely resembled vaterite. They named these phases proto-calcite and proto-vaterite and suggested that they were an example of poly amorphism, which is the subject of a recent review by Cartwright [15]. There is also evidence of proto aragonite from recent high pressure X-ray and Raman studies of the transformation of ACC [16].

Radha et al. [17] and Forbes et al. [18] showed that the transformation starts with a metastable form of hydrated ACC that then becomes more stable, before losing its water and becoming anhydrous ACC, that then transforms to a crystalline phase. Molecular dynamics calculations showed the critical role of water in the growth of ACC [19]. Michel et al. [20] demonstrated from X-ray diffraction that synthetic ACC lacked structural coherence and long-range order beyond 1.5 nm. In more recent work a Reverse Monte Carlo fitting procedure was used to develop a structural model for hydrated synthetic ACC that consisted of a porous Ca framework with channels containing water and carbonate molecules [21]. Molecular dynamics simulations by Singer et al. [22] showed that there was significant structural reorganization of this framework resulting in shrinkage of the channels. However observations using synchrotron X-diffraction to follow structural changes during dehydration did not show any changes in the Ca rich framework until the final stages [23]. This is consistent with the TGA/DSC measurements of Ihli et al. [24] that indicated that it was the loss of the final 15% of water that triggered crystallization.

Given that Mg has been found in ACC it is possible that random Mg substitution for Ca could lead to structural distortions that result in diffraction patterns that are similar to those from amorphous materials. Radha has suggested that Mg concentrations below 20 atomic % give rise to more energetically stable amorphous phases [25]. Although it is believed that some forms of ACC are anhydrous, it is not possible to detect water at very low concentrations, less than about 3 wt% [9]. It is therefore conceivable that all ACC has some water as a minor constituent and this interstitial water could also lead to distortions giving rise to amorphous diffraction patterns.

Computational modeling [26] has played an important part in generating plausible structures for the amorphous phase and investigating the role of water in the transformation process. Most of these studies have been based on molecular dynamics

calculations using force fields [19]. One outcome of these investigations is the suggestion that prenucleation clusters could be polymers of calcium and carbonate ions [27]. Given the critical role of water, its effect on stabilizing the crystalline hydrated phases of calcium carbonate has been studied by Demichelis et al. [28] using DFT calculations. She found that although the structures were accurately reproduced, the DFT calculations could not give correct energies of hydration.

We are not so much concerned with energies of hydration, but with the distortions that might arise when water is incorporated into calcium carbonate structures, and whether these distortions can explain various experimental observations of ACC. In particular we are interested in possible structural arrangements in the final stages of the transformation to a crystalline polymorph. To model possible distortions even with minimal water content, up to 5 interstitial water molecules were inserted in calcite or aragonite supercells with 24  $\text{CaCO}_3$  formula units. These were relaxed to achieve a minimum energy configuration. The main effect was tilting of the carbonate planes, up to about  $50^\circ$ . The carbonate groups remained largely intact and undistorted. Tilt of carbonate planes is sufficient to explain loss of optical birefringence and suppression of the  $\nu_4$  peak in IR absorption. The cations were also subject to small displacements from their positions in the undistorted structure, but these were insufficient to explain diffraction profiles characteristic of an amorphous material.

## 2. Methods

In any simulation there is always a compromise between using a large model with many atoms that might better represent the natural system and the computational cost that might limit the number of configurations that can be explored. Since the minimum energy configurations were determined from 1st principles electronic structure calculations using the VASP plane wave pseudopotential density functional theory (DFT) code [29] the models were limited to 120 atoms. A  $2 \times 2 \times 1$  supercell for calcite was constructed from the original hexagonal cell. The cell contained 24 formula units as shown in Fig. 1a. For aragonite the supercell was  $2 \times 1 \times 3$  the original orthorhombic cell and again contained 120 atoms or 24 formula units as shown in Fig. 2a. The labels for the water interstitial positions are shown in Fig. 1b for calcite and Fig. 2b for aragonite. Different configurations with between 3 and 5 water molecules, corresponding to 2.25–3.75 wt % respectively are shown as Table 1.

The minimum energy configurations with the corresponding total energy for all these starting structures were determined using the parallel version of VASP on the ASU Saguaro computing cluster. The ultrasoft local density approximation (LDA) pseudopotentials were used with a  $3 \times 3 \times 1$  grid of k points. As a check both Projected Augmented Wave Generalized Gradient approximation (PAW GGA) and PBE pseudopotentials were used for the same starting configuration in selected cases. Both cell size and shape and atom positions were allowed to relax and the energy was converged to 0.0001 eV, with forces less than 0.05 eV/Å.

To evaluate distortions in the carbonate planes vector products for each of the 3 pairs of Carbon–Oxygen bonds were calculated as shown in Fig. 3, in addition to the Carbon oxygen bond distances. The distribution of carbon–oxygen distances and the displacement of the carbon atom from the plane defined by the 3 oxygen atoms was also calculated. The tilt of the carbonate planes was determined by comparing the vector product of Carbon Oxygen pairs with the c axis vector of the original unit cell. Distributions of cation nearest neighbor distances were also extracted from the atom positions files.

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