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Carbonate orientational order and superlattice structure in vaterite

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Abstract:

Vaterite is considered to play an important role as a precursor phase in the formation of calcium carbonate phases, including those related to biomineralization. An accurate description of vaterite’s structure associated with the order of carbonate groups is essential to understanding the formation, stabilization, and functionality of vaterite in organisms. Molecular dynamics simulations, synchrotron X-ray diffraction, and transmission electron microscopy have been combined in order to investigate the structure of vaterite. The electrostatic interactions between Ca and neighboring CO$_3$ groups promote local and long-range ordering of CO$_3$ groups, which may result in a superstructure of vaterite. Molecular dynamics simulations show that the superstructure (P6$_5$22) with ordered carbonate ions has a relatively lower energy than the disordered structure. The kinetics of the disorder-to-order transition suggests that the transition is rapid and that the superstructure is expected to form. X-ray diffraction data confirm the presence of the P6$_5$22 superstructure. The measured diffraction peaks are consistent with the calculated diffraction peaks, especially those weak peaks predicted as a result of the superstructure. Transmission electron microscopy also reveals minor satellite electron diffraction peaks with the more intense peaks of the primary pattern, suggesting a superlattice structure resulted from ordering in both crystallographic $ab$ plan and $c$ direction, which is consistent with the proposed superstructure.

**KEY WORDS:** B1. calcium carbonate; B1. vaterite; A1. order and disorder; A1. X-ray diffraction; A1. Transmission electron microscopy
1. Introduction

Vaterite is the least thermodynamically stable phase among the three anhydrous, crystalline calcium carbonates: calcite, aragonite, and vaterite. However, vaterite forms without difficulty and can be stabilized by organic molecules at surfaces. By simply mixing calcium and carbonate salt solutions, vaterite crystallizes within minutes [1]. This is driven by the thermodynamics of nucleation, which is a balance of the free energy of the surface of small vaterite crystals vs. their bulk thermochemical properties. In nature, vaterite occurs in a variety of biological environments, including pearls [2-4], the human heart [5], otoliths [6], and sea squirts [7]. Vaterite formed in these environments is mostly stabilized by template-induced surface interactions with biomolecules or organic molecules. This process is based on a large number of experimental observations [5, 8-14]. However, questions remain as to: Why do organisms choose to create vaterite over the other relatively more stable phases? How is vaterite nucleated and stabilized? What is the function of vaterite in these organisms? Before these questions can be addressed, the structure of vaterite needs to be fully understood. The basic structure of vaterite was proposed over 50 years ago [15, 16], but the stacking sequences and the resulting superstructure have not been resolved. There have been some determinations, such as supercell size, mentioned in earlier single crystal x-ray diffraction studies [15, 16]. However, details of the superstructure have not been fully described. This is mainly due to the lack of large, high-quality, single crystals, as well as the absence of appropriate structure models for the superstructure of vaterite. The absence of knowledge about the vaterite structure has hindered the understanding of crystallization and biomineralization of vaterite in natural systems.
The widely used vaterite structure model is a disordered carbonate structure [16]. However, growing evidence from recent studies suggests that this model is not adequate for describing the structure for a number of vaterites from experiments [7, 17-21]. In the basic structure, carbonate planes are randomly orientated in three orientations parallel to [001], and there is only one crystallographic site for the carbon atom of CO$_3$ group. Raman and infrared spectroscopic methods have been used to study the vibrational modes of CO$_3$ ions in vaterite, and these studies focused on the space group and site symmetry [22-25]. They show that there are two [23] or three [18] distinct vibration frequencies of symmetric stretching mode of the CO$_3$ ion, indicating two or three [18] different C sites, respectively. In the latter experiments, synthetic, biological, and geological samples have been used [18]. In addition, a recent NMR study shows that there are two resonance frequencies related to the carbon [26], again, indicating two different C sites in the structure. Although there is a discrepancy in terms of the number of different crystallographic sites, these experiments confirm the inadequacy of the original structure model [16]. Basic questions regarding the superstructure remain unanswered, such as: How many carbon crystallographic sites are there in the vaterite structure? What are the unit cell size, space group, and crystallographic positions of the atoms? However, it is difficult to establish a new structure model based on spectroscopic methods alone. Even for single crystal X-ray diffraction methods, an appropriate structure model is necessary as a starting point. Recently, a new superstructure model was proposed mainly based on molecular dynamics simulations and first-principles calculations [17]. Although this new superstructure answers some of questions related to the structure and thermodynamics properties, the details of the structure have not been confirmed by experimental observations. Most recent interest in the vaterite structure has resulted in a number of new structure models based on a microtwinning hypothesis [19], DFT
calculations [20], automated diffraction tomography and electron diffraction of nanometer sized vaterite [21], molecular dynamics simulations [27], and HRTEM data of a biogenic vaterite sample [7].

In this paper, the superstructure and the order-disorder transformation of the CO$_3$ groups are discussed in terms of the local interactions between CO$_3$ groups and Ca. Molecular dynamics simulation results and the proposed superstructure based on these theoretical calculations and experimental data from literature are discussed in the light of new experimental evidences based on X-ray diffraction and high-resolution transmission electron microscopy.

2. Methods

2.1 Molecular modeling

Molecular dynamics simulations have been performed to understand the basic structure, superlattice structure, and order-disorder transition. In these simulations, the three-dimensional periodic boundary conditions were employed using the program GROMACS [28, 29]. For van der Waals interactions, Lennard-Jones 12-6 potentials are used and the interaction cutoff distance is 10 Å. For bonding interactions, harmonic C-O stretching and O-C-O bending interactions were used within the carbonate ion. The positions of all atoms in the simulation cell and the unit cell parameters were not constrained and therefore free to move. All simulations were carried out using an NPT ensemble (i.e., constant pressure and temperature). The potentials and parameter settings for the MD simulations are reported in previous publications [17, 27]. Simulated annealing MD simulations were also carried out to simulate the temperature effect on the order-disorder transition in vaterite. The simulated annealing method allows simulating dynamic
changes of order-disorder and phase transition in a single simulation. More details of the potential parameters and MD simulations were presented in previous publications [17, 27].

2.2 Experiments: crystal synthesis and characterization

Crystal synthesis

Crystal aggregates of vaterite, in the form of hexagonal plates, approximately 0.1-0.3 mm across, were grown by connecting two conical glass flasks containing 0.1 M solutions of CaCl$_2$ and NH$_4$HCO$_3$ with a distilled water bridge made of a PVC tube into which the ions can diffuse. The arrangement was permitted to stand undisturbed in a constant room temperature for 35 days. At the end of experiment, the inner walls of the bridge were partially coated with crystalline precipitates of calcite and vaterite crystals. Figure 1a shows SEM images of the vaterite crystal aggregates along with calcite single crystals on the wall of the tube. The vaterite crystals form flower-like shaped aggregates, and each of the petals is a single vaterite crystal (Figure 1b) [30]. The calcite was formed nearby as rhombohedron calcite single crystals. The individual vaterite crystals are only a few micrometers thick and 50-100 micrometers wide. These vaterite crystals are stable at ambient condition over two years. Calcite crystals are much larger. Aragonite crystals were not observed. The calcium carbonate phases were identified by the morphologies of different phases and confirmed by X-ray diffraction and Raman spectroscopic methods.

X-ray diffraction measurement

Due to the small sample size and small amount of the samples, all x-ray diffraction experiments were performed using synchrotron x-ray techniques. The powder x-ray diffraction patterns of vaterite were measured at GSECARS (beam 13-ID-D) at APS using a monochromatic
x-ray beam (wavelength 0.3344Å). The diffraction images were recorded with a CCD detector and then integrated into two dimensional patterns with software Fit2D. The sample-detector distance and other facility parameters were refined with CeO$_2$ as an external standard. The observed powder XRD pattern was fit using a Rietveld refinement-like method based on the proposed structure models. In order to check the superlattice, very small single crystals (thickness ~1 µm) were selected and checked using a sub-micro x-ray beam 2-ID-D at APS (beam size 0.2 µm).

**Transmission electron microscopy**

Fine particles of vaterite were placed on a holey-carbon film supported by copper grids. The crystallographic parameters of vaterite were determined by transmission electron microscopy (TEM) using a JEOL JEM-2010F operated at 200 keV. The electron beam intensity was reduced in order to avoid electron beam damage. Bright- and dark-field imaging was used to detect local domain structures. Selected-area electron diffraction (SAED) and high-resolution TEM (HRTEM) images were obtained. Calculated electron diffraction patterns using Java Electron Microscope Simulation (JEMS) software package [31] were compared to the experimental results. The fast Fourier transform (FFT) patterns associated with HRTEM images were calculated using Gatan Digital Micrograph software. The FFT-filtered images were obtained to illustrate the superlattice structure. The chemical composition (CaCO$_3$) was confirmed by the energy dispersive spectroscopy (EDS).

3. **Results and Discussions**

3.1 **Local electrostatic interaction and tendency of orientational ordering of CO$_3$ groups**
Vaterite has the same chemical composition as calcite and aragonite but with a different crystal structure in terms of symmetry, orientations of the CO$_3$ groups, and coordination environment of the Ca$^{2+}$ ions. Currently, the crystal structure has not completely resolved, but some basic features emerge. The Ca$^{2+}$ ions are in a hexagonal sublattice, which suggests the crystal has a hexagonal or hexagonal-compatible symmetry. The CO$_3$ groups are parallel to the $c$-axis, suggested by its optical properties of uniaxial positive interference figures with $n_ω$=1.55 and $n_ε$=1.65 [16]. Early single crystal $x$-ray diffraction studies proposed a disordered basic structure model [15, 16]. However, diffuse streaks and satellite reflections in the diffractions suggest possible superstructures. Many questions regarding the superstructure remain unanswered, especially possible causes and details of the proposed superstructure [16]. A simple analysis outlined in the next paragraph suggests that the CO$_3^{2-}$ groups in the neighboring unit cells have a tendency to be orientationally ordered because of the electrostatic interactions between them, and this ordering could induce a superstructure if the ordering extends from short range among the neighbors in long range. In this analysis, electrostatic interactions between neighboring CO$_3^{2-}$ groups in the Ca$^{2+}$ lattice are considered.

Calcium carbonate vaterite consists of divalent Ca$^{2+}$ and CO$_3^{2-}$ species in the structure. The Ca$^{2+}$ ions form a hexagonal lattice and each of them occupies a vertex of trigonal prisms. The CO$_3^{2-}$ plane is parallel to the crystallographic [001] direction and each of the CO$_3^{2-}$ groups is located at the center of the trigonal prism. All of the O atoms of CO$_3^{2-}$ point to the middle of the prism edges, one to the lateral edge and the other two to the base edge. For a single CO$_3^{2-}$ ion in a Ca$^{2+}$ trigonal prism, there are three such favorable orientations with equal possibilities. If all the CO$_3^{2-}$ ions are randomly distributed over these three preferred orientations, a disordered crystal structure with one third occupancy for each orientation will result. This structure was
proposed by Kamhi in 1963, based on single crystal X-ray diffraction experiment data [16], and it is illustrated in Figure 2a. The three possible orientations are also depicted in both Figures 2b and 2c (dashed and solid symbols). However, the CO$_3^{2-}$ ions are expected not only to interact with its closest Ca$^{2+}$ atoms but also with CO$_3^{2-}$ groups located in the neighboring Ca$^{2+}$ prisms. This interaction is predominately electrostatic in nature because of highly ionic character of the Ca$^{2+}$ and CO$_3^{2-}$ species in the crystal. Thus, the random orientation is not electrostatically favorable because some of the possible mutual orientations between the two CO$_3^{2-}$ groups are not electrostatically stable. For instance, Figure 2b shows one of such possible CO$_3^{2-}$ orientations (solid symbols) if assuming random orientation. In this configuration, the two neighboring CO$_3^{2-}$ ions each with one of their O atoms point to the same lateral edge shared by the two prisms where the CO$_3^{2-}$ ions are centered. The repulsive interaction with the like charge between the two O atoms (negatively charged) of the CO$_3^{2-}$ ions makes such local configuration unstable. A relatively more stable configuration is shown in Figure 2c, where such repulsive interaction is avoided. Such local interactions between the neighboring CO$_3^{2-}$ ions are expected to also involve non-neighboring CO$_3^{2-}$ groups. If this local ordering is extended and becomes long range, an ordered structure will emerge. However, it is difficult to determine what ordered structure might be if it is only based on the schematic illustrations based on the local electrostatic consideration. Since the basic disordered structure was proposed over a half century ago in 1963 [16], a range of experiments have been accumulated including vibrational spectroscopy [18, 22-25], nuclear magnetic resonance [26, 32], pair distribution function analysis based on synchrotron based X-ray scattering [26], X-ray diffraction [19], automated diffraction tomography and electron diffraction of nanometer sized vaterite [21], and HRTEM data of a biogenic vaterite sample [7]. Many of these experimental results [18, 26, 32] are inconsistent with the disordered structure
model [16]. However, these experimental efforts have not provided enough constraints to establish a new structure model to address both the details of the possible superstructure and causes of the superstructure.

### 3.2 Superlattice structure based molecular dynamics simulations and first-principles calculations

Based on first-principles calculations and molecular-dynamics simulations, a new structure model for vaterite was recently proposed [17]. These simulations suggest that the CO$_3$ orientational ordering can induce long-range structural order and superstructure. The new structure model has a space group of P6$_3$22 (#179) [17], and unit cell is 9 times larger (z=18) than the basic structure (Z=2). The $a$, $b$ axes are $\sqrt{3}$ times of these of the pseudo-cell, and are rotated 30° with respect to the pseudo-cell (the basic structure), and $c$ is 3 times longer than the pseudo-cell. With respect to the basic structure, this new structure is a result of ordering both in the crystallographic $a$ and $b$ plane and in the $c$ direction, and is only involved the orientation of carbonate ions in the crystal. This new structure model is consistent with the structure character that the CO$_3$ is parallel to the $c$-axis, and Ca ions are in a hexagonal sub-lattice [15, 16], and that there are two crystallographic sites for C as suggested by an NMR study [26]. The size and orientation of the unit cells of the superstructure and the basic structure are highlighted in Figure 3.

Energetically, the superstructure is more stable than the disorder structure including the consideration of the configuration entropic contribution related to the disordering in the disordered structure. The energy contribution from the loss in configuration entropy is relatively small [$k_B$·$T$·$\ln(3)$ ~2.7 kJ/mol] at room temperature if a complete disorder of the CO$_3$ ions over
three orientations in the disordered structure is assumed. The potential energy change from disordered to ordered vaterite is about -11 kJ/mol per CaCO$_3$. In order to address the kinetics of the disorder-order transition, additional molecular modeling was performed based on temperature annealed molecular dynamics simulations and standard NPT ensemble molecular dynamics simulations at various temperatures [27]. The results show that the calculated activation energy for the transition is 94 ± 10 kJ/mol with a pre-exponential factor of ~1.6×10$^{13}$ s$^{-1}$. A good linear fit of the logarithmic transition rate to inverse temperature (the Arrhenius plot) indicates that the transition is controlled by a single activation process that is thermally activated. And this transition is related to the rotational motion of CO$_3$ ions in vaterite. By extrapolating these kinetic parameters to room temperature, the disorder to order transition occurs within half an hour, suggesting a fast transition process.

A recent experiment shows that by rapid mixing calcium and carbonate salts solutions, amorphous calcium carbonates will form immediately, then within minutes, vaterite will form [1]. However, from these experiments, it does not become clear how the vaterite is transformed from the amorphous phase. Recent experiments show the transition from the amorphous phase is complex [8, 33], and vaterite crystals most likely inherit the disordered nature of the amorphous phase and the initially formed vaterite may be disordered. This leads to the present experimental study to use X-ray diffraction and high resolution transmission electron microscopic method to understand the disorder structure and superstructure in vaterite.

3.3 X-ray diffraction peaks related to superlattice structure

Rietveld-like refinement was performed on the observed powder diffraction data using a number of previously and recently proposed structure models in the literature. In order to make a
consistent comparison, same procedure was used in the fits of the observed and calculated XRD patterns. The fitting results are illustrated in Fig. 4. The calculated XRD pattern based on the disordered P63/mmc hexagonal model (Fig. 4a) [16] cover all the strong observed diffraction peaks. The model structure was first proposed by Kamhi in 1963 [16] and is considered as the basic structure model for vaterite. However, there are some broad diffraction peaks in the observed pattern with 2θ angle at 7.6° and 10°, which cannot be generated from the model. In order to interpret these additional weak diffractions, Meyer has proposed an ordered orthorhombic structure model before [34]. The model has Pbnm symmetry and can cover most of the observed diffraction peaks including most of the weak ones (Fig. 4b) except at 2θ angle ~7.6°. This model yields a good fitting value with $R_B=13.3\%$ and $R_{wp}=17.9$. However, recent DFT calculations suggest the structure model is not likely because the calculated cell parameters based this structure model are ~10% off the experimental values and the structure is energetically unstable [17, 20], suggesting that pure data fitting may lead to incorrect answer. Later, Meyer pointed out that these weak diffractions were due to an incommensurate superlattice of the basic hexagonal unit cell [15]. Meyer suggested a possible hexagonal unit cell with lattice parameters of $\sqrt{3}$ and 2 times of the basic lattice parameters $a$ and $c$, respectively. This superlattice may cover all the weak diffraction peaks of vaterite, but the author did not give the details.

We also tried to refine the experimental XRD pattern with another ordered vaterite structure model proposed by Le Bail [19]. This model has very close lattice parameters with those proposed by Meyer [34], but with a different space group Ama2. Our refinement results indicated that this model cannot cover most of the weak diffraction peaks from the superlattice (Fig. 4d). In Le Bail’s paper [19], the authors assumed that the weak diffraction peak with 2θ angle at 7.6° is due to small amount residual of calcite in the vaterite sample. In fact, this peak has a little shift
from the strongest diffraction peak [104] of calcite, and our Raman measurement also did not find calcite residual in our vaterite samples.

Fig. 4e shows the fitting results with the three-layer superlattice P6₅₂₂ model proposed recently by Wang and Becker [17]. It is apparently that all the weak diffraction peaks can be covered by this model, and fitting with this model results the best R values (R_B=13.2%, and R_wp=16.7%). The a and b lattice parameters are equal to or \( \sqrt{3} \) times of the basic a, and the c parameter is 3c of the basic unit cell. Two other models recently proposed in the literature are the vaterite 2-layer monoclinic model with a C2/c (#15) space group based on electron diffraction data [21], and three-layer trigonal model with a P3₂₂₁ (#154) space group [20] based on first-principles calculations at the athermal limit using previously proposed P6₅₂₂ model as their starting configuration. Independently, the C2/c structure model was also derived from molecular dynamics simulations although the unit cell parameters differ slightly [27]. Following the same procedure, refinements were carried out on these two models. The results show that the R_B and R_wp values of both these two models (Figures 4c,f) are larger than the values based on the hexagonal P6₅₂₂ model. Not surprisingly, these two models also reproduce most of the weak diffraction peaks not produced by the basic P6₃/mmc disordered hexagonal model. This is because the P3₂₂₁ model is derived from the P6₅₂₂ model, and C2/c model is close related to the P6₅₂₂ model as discussed previously [21, 27]. In addition, the energy difference between P3₂₂₁ and P6₅₂₂ models was calculated to be small, around 1 kJ/mole or less, which is close to the limit of the accuracy of the methods employed [20]. It needs to be mentioned that the selection of unit cells for the above structure models is closely related to the basic unit cell. The site assignment of Ca in vaterite may be more or less similar in all the structure models, but the assignments of site and orientations of CO₃ groups in vaterite unit cell are different. Lippmann
proposed a vaterite structure [35], which is based on the high-temperature phase of YbBO₃ [36] and an early model for vaterite [37] where details of the structure were not given. Therefore, the Lippmann model was not selected for comparison in this study.

Based on X-ray powder diffraction pattern refinements discussed above, the three-layer hexagonal P6₅22 model is still in closer agreement with the XRD data presented here than other models proposed in the literature, which reproduces most of the weak diffractions from the superlattice, in addition to the main peaks. However, the model also generates an additional peak in lower 2θ angle, which is not found from the observed XRD patterns.

### 3.4 Super lattice structure of vaterite revealed by high resolution transmission electron microscopy

Figure 5 shows an electron diffraction pattern of vaterite with the electron beam perpendicular to the (001) plane. The electron diffraction pattern clearly shows six-fold rotational symmetry, consistent with the hexagonal crystal structure along [001]. Two sets of diffraction peaks co-exist in the pattern, and the intensity of the primary set is stronger than the satellite set. The calculated d-spacing is 4.1 Å for the primary pattern, and 7.1 Å for the weaker satellite pattern. The high resolution TEM image along [001] is shown in Figure 6a. The real space inter-plane distance between the reciprocal lattice fringes in Figure 6a is measured to be ~4.1 Å, which is consistent with the d-spacing calculated from the primary diffraction pattern in Figure 5. The major pattern in the high resolution image (Figure 6a) is consistent with the basic structure [16], which has a hexagonal symmetry and the unit cell a and b dimensions are 4.1 Å. However, because of the lower electron diffraction intensity of the minor diffraction in Figure 5, a superlattice structure does not show in the HRTEM image (Figure 6a).
The selected area electron diffraction in Figure 5 shows the existence of the minor satellite electron diffraction peaks besides the primary diffraction peaks, which indicates an ordered superstructure existed in the crystal. Figure 6b highlights the two sets of diffractions and there is a 30° rotation between the two sets of diffractions. By performing the reverse Fourier transform of each of the diffraction patterns separately, two HRTEM images are obtained (Figures 6c, 6d). The image in Figure 6c is generated from the primary diffraction pattern. The lattice pattern in Figure 6c is consistent with the original image (Figure 6a) without separating the two sets of the diffractions. The image in Figure 6d is generated form the minor diffraction pattern. The atomic lattice structure has a 30° rotation from the basic lattice and the d-spacing is 7.1 Å, \(\sqrt{3}\) times of the basic lattice, suggesting a superlattice structure. The basic lattice and the superlattice are highlighted in Figures 6e and 6f, and they resemble the lattice structures based on theoretical calculations as shown in Figure 3. The superlattice revealed by the HRTEM (Figures 6 c,d) is consistent with the P6\(_5\)22 structure model proposed from the theoretical calculations [17], suggesting the superstructure originated from CO\(_3\) orientational ordering in the \(ab\) plane.

In order to obtain the structural information along the normal to the \(ab\) plane, the electron diffraction pattern with electron beam tilted away from the [001] direction is needed. Figure 7a shows a SAED pattern of [421] zone. Again, two sets of diffraction peaks are clearly seen. TEM diffraction patterns were simulated based on the three models with superlattice structures, i.e., the three-layer P6\(_5\)22 hexagonal model [17], the 2-layer C2/c monoclinic model [21, 27] and three-layer P3\(_2\)21 trigonal model [20], and the disordered model, i.e., the P6\(_3\)/mmc basic structure model [16]. The results suggest that, although all of three superlattice models reproduce the two sets of diffraction peaks, the P6\(_5\)22 hexagonal model (Figure 7b) reproduces the diffraction pattern better than the other two superlattice models. The basic disordered model
(Figure 7c), on the other hand, differs significantly from Figure 7a. This result suggests that the hexagonal P6$_5$22 superlattice model is consistent with the experimental observation.

4. Concluding remarks

As evidenced by X-ray diffraction and TEM observations, synthetic vaterite has a superlattice structure that is more closely consistent with the P6$_5$22 superstructure model based on theoretical studies [17, 27]. It is interesting that, in terms of X-ray diffraction refinement, other recently proposed structures [20, 21] also reproduce the weak diffraction peaks originated from the ordering of CO$_3$ groups. As pointed out in a recent article, the vaterite structure has some complexity, that is it may contain multiple domains with different characteristics, which cannot be explained by any existing models [7]. Since more than one structure has been found, is it possible that vaterite crystallizes into several of them in different ratios and under different conditions and/or with different organic or inorganic impurities? Since these newly derived crystal structures [17, 19-21, 27] have long-range carbonate ordering that is more energetically favorable than the disordered counterparts, the question is how well any given sample will actually be ordered. However, it is difficult to establish a new structure model based on experimental data alone. In order to answer the above mentioned questions, both theory and experimental methods are essential for the resolution of the structure. The present results are expected to stimulate new experimental and theoretical investigations on vaterite. Understanding the structure and thermodynamics of vaterite may lead to answer some fundamental questions such as the nucleation, growth and stabilization of vaterite in biological systems and scale formation, and carbonate formations in geologic systems and the intriguing occurrence of vaterite in biological systems.
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FIGURE CAPTIONS

**Figure 1.** SEM images of vaterite crystal aggregates. (a) Low magnification; (b) High magnification.

**Figure 2** (a) Crystal structure of vaterite with disordered CO$_3^{2-}$ group [16]. Each CO$_3$ has a 1/3 occupancy. Ca$^{2+}$ ions form a hexagonal lattice. (b) and (c) Schematic view of Ca$^{2+}$ lattice (shown as 2+ charge inside a circle) and CO$_3^{2-}$ orientations. Thin dashed-lines highlight the pseudo unit cells. Three possible orientations of CO$_3$ ions are shown in dashed and solid symbols. The configuration in (b) where the two neighboring CO$_3$ ions are pointing to the same edge of the prisms is less stable than the one in (c) where the two neighboring CO$_3$ ions are pointing to different edges because of electrostatic repulsion between the oxygen atoms of CO$_3$ in the former configuration.

**Figure 3.** Structure of a snapshot from molecular dynamics simulation with the dashed lines highlighting the basic pseudocell and supercell. The structure is projected on (001) plane. The large balls are calcium atoms. The balls and sticks are carbonate groups.

**Figure 4.** The observed and calculated XRD patterns with different structure models (a) The basic hexagonal structure; (b) the orthorhombic model with space group of Pbnm; (c) the three-layer trigonal model with a space group of P3$_2$21; (d) the orthorhombic model with space group of Ama2; (e) the three-layer hexagonal model with space group of P6$_3$22; (f) the monoclinic model with space group of C2/c.
**Figure 5.** Transmission electron microscopy SAED of a single crystal diffraction pattern. Electron beam is along [001].

**Figure 6.** (a) An HRTEM image shows the three fold symmetry along [001]. (b) A fast Fourier transform corresponding to the image (a). Two sets of diffraction peaks present and were highlighted with small and larger circles respectively. (c) The HRTEM image generated from the primary diffraction peaks in Figure 4b. (d) The HRTEM image generated from the satellite diffraction peaks in Figure 4b. (e) The HRTEM image of the highlighted region in Figure 4c. (f) The HRTEM image of the highlighted region in Figure 4d. The basic lattice and superlattice are highlighted in Figure 4e, 4f.

**Figure 7.** An experimental SAED pattern along [421] zone (a) is compared to the simulated TEM diffraction patterns based on the superstructure (b) [17] and the basic structure (c) [16].
References


Figure 1 SEM image of synthetic vaterite
Figure 2. Crystal structure of vaterite

(a)
Figure 3. Structure of a snapshot from molecular dynamics simulation
Figure 4 X-ray diffraction patterns refined with different structure models
Figure 5 An electron diffraction pattern along vaterite [001] zone axis
Figure 6 TEM images
Figure 7. SAED pattern