

Growth evolution in calcium carbonate microparticles involving mixed vaterite-aragonite structures

Daniyal Younas¹, Elizaveta Sidler¹, Chayene G. Anchietta¹, Seniz Ucar^{2,3}, Per Erik Vullum⁴,
Ragnvald H. Mathiesen¹, Federico Zontone⁵, Raffaella Cabriolu¹, Yuriy Chushkin⁵,
Dag Werner Breiby¹, and Basab Chattopadhyay^{1,*}

¹Department of Physics, Norwegian University of Science and Technology (NTNU), Høgskoleringen 5, 7491 Trondheim, Norway

²Department of Chemical Engineering, Norwegian University of Science and Technology (NTNU), 7491 Trondheim, Norway

³Department of Metallurgical and Materials Engineering, Middle East Technical University, 06800 Ankara, Turkey

⁴Department of Materials and Nanotechnology, SINTEF Industry, 7465 Trondheim, Norway

⁵ESRF—The European Synchrotron, 71 Avenue des Martyrs, 38043 Grenoble Cedex 09, France



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Calcium carbonate (CaCO_3) is a widely occurring mineral that is crucial to many natural and synthetic processes. CaCO_3 crystallizes in three anhydrous polymorphs and often serves as a model system to study nucleation and growth phenomena. In this article, we employ coherent diffraction imaging coupled with wide-angle x-ray diffraction (CXDI-WAXD) to investigate the three-dimensional (3D) morphology and crystal structure of CaCO_3 microparticles crystallized under different reaction temperatures. We report particles containing both vaterite and aragonite, which we interpret as an intermediate growth stage between early vaterite and later aragonite formation. The results are based on the density variations observed in the 3D tomographic CXDI images, x-ray diffraction, and focussed ion beam-transmission electron microscopy study of the mixed vaterite-aragonite microparticles. A computational study based on Monte Carlo and molecular dynamics energy minimization was used to identify the small energetic variations between the different crystalline forms of CaCO_3 . The results presented in this article provide a better understanding of the morphology-structure correlation for CaCO_3 polymorphs, depicting a transitional stage where both vaterite and aragonite coexist.

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I. INTRODUCTION

Calcium carbonate (CaCO_3) is a widely occurring mineral in natural and synthetic environments, mainly forming through precipitation in aqueous systems. It crystallizes into three anhydrous polymorphs—calcite, aragonite, and vaterite, each with distinct structural and thermodynamic properties. While calcite is the most stable phase under ambient conditions, the metastable phases—vaterite and aragonite—play crucial roles in biomineralization, industrial applications, and environmental processes. In biomineralization, many marine organisms, including corals and molluscs, produce calcite, aragonite, and rarely vaterite as major components of their skeletal structures [1,2]. CaCO_3 plays a significant role in environmental processes; it acts as a sink for carbon dioxide in the oceans and contributes to the buffering capacity of marine ecosystems, thereby influencing global carbon cycles and climate regulation [3,4]. In industrial applications, the distinct physical properties of aragonite make it a valuable additive in the manufacturing of cements [5,6], paints [7], and other composite materials, where its fine-grained morphology can

improve product performance [8]. Vaterite, on the other hand, is a metastable form of CaCO_3 , which gradually transforms to calcite or aragonite over time or with increasing temperature. Vaterite can be formed in different morphologies based on the reaction conditions: A porous spherical structure can be formed via an intermediate amorphous CaCO_3 (ACC), or self-assembled hexagonal plates that nucleate directly from solution [9]. Vaterite is used for biomedical and pharmaceutical applications as it has a high dissolution rate and high specific surface area [10–12].

Understanding the factors governing the formation of CaCO_3 is essential for controlling the precipitation in both natural and engineered systems. Temperature is a key parameter influencing the phase selection of CaCO_3 . Aragonite typically forms at elevated temperatures and in marine environments [2,13], whereas vaterite appears in supersaturated solutions but rapidly transforms into more stable phases [14]. Temperature and supersaturation are important in controlling not just which CaCO_3 polymorph forms, but also when and how a given phase appears in the crystallization pathway. ACC is often considered a precursor phase due to its high solubility and lack of long-range order, which makes it reactive and useful in controlled crystallization processes [15,16]. Calcite, the thermodynamically stable polymorph, forms directly at low supersaturation or by the dissolution-reprecipitation of metastable intermediates like ACC or vaterite, especially at elevated supersaturation [17]. Even though both vaterite and ACC are less stable than aragonite and calcite, these phases are essential for understanding the full lifecycle of CaCO_3 in

*Contact author: basab.chattopadhyay@ntnu.no

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both biological pathways and synthetic material development [18].

The precise mechanisms driving the formation of CaCO_3 polymorphs continue to be debated [17,19]. Several scientific questions are unsolved such as whether the nuclei formation can be explained by classical nucleation, binodal, or spinodal decomposition, whether crystal growth follows the classical or nonclassical pathways, and if phase transformation proceeds by dissolution recrystallization or solid-state transformation. Addressing these knowledge gaps is essential for improving models of carbonate precipitation in fields such as biomineralization, geochemistry, and materials science.

Coherent x-ray diffraction imaging (CXDI) [20,21] combined with wide-angle x-ray diffraction (WAXD) [22–24] provides a powerful approach to studying CaCO_3 phase transitions at the nanoscale. CXDI enables three-dimensional nanoscopic imaging of crystallite morphology, while WAXD reveals the crystal phases present in a microparticle. In CXDI, a highly coherent plane wave with coherence volume exceeding the size of the sample interacts with an isolated object, resulting in a unique speckle pattern recorded in the far-field (Fraunhofer) diffraction regime. The intensity captured by the detector, $I(\mathbf{q})$, is mathematically connected to the electron density distribution of the sample $\rho(\mathbf{r})$ via the Fourier transform (FT): $I(\mathbf{q}) \propto |F(\mathbf{q})|^2$, where $F(\mathbf{q}) = |F(\mathbf{q})| \exp[-i\varphi(\mathbf{q})] = \text{FT}[\rho(\mathbf{r})]$ and $\mathbf{q}$ denotes the scattering vector. Since detectors only measure intensity, the phase information $\varphi(\mathbf{q})$ is lost, requiring numerical reconstruction through phase retrieval methods. Previously, we have used CXDI to observe porosity changes during the solid-state transformation of vaterite to calcite, which provided direct evidence of structural evolution in CaCO_3 microparticles [25]. CXDI has also shown that solid CaCO_3 microspheres undergo self-transformation into core-shell and hollow hierarchical structures, a process influenced by polymer additives like polystyrene sulfonate [26].

In this article, we investigate the temperature-driven precipitation of CaCO_3 , leading to the formation of vaterite and aragonite. By employing combined CXDI-WAXD, we address open questions regarding the structural evolution of these polymorphs and the thermodynamic conditions that govern their transformation. The results from CXDI-WAXD were complemented by Focused Ion Beam-Transmission Electron Microscopy (FIB-TEM) measurements, and Monte Carlo (MC) and molecular dynamics (MD) simulations. The results presented in this article provide a better understanding of the morphology-structure correlation for CaCO_3 polymorphs, which is also relevant for the understanding of the crystallization pathways with implications across food, environment, construction, and pharmaceuticals industries.

II. METHODS

A. Sample preparation

CaCO_3 was precipitated in a reaction chamber where precursor solutions of 0.5 L of 2 mM of Na_2CO_3 and 0.05 L of 10 mM of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ were mixed in the presence of 50 mM NaCl. The reaction was repeated for three different temperatures, viz. 25, 35, and 45 °C, with a reaction time of

either 300 or 1500 s. The reaction was stopped by pouring the solution into a vacuum filter, washing with ethanol, and finally drying the particles at 40 °C for 24 h. More details of the sample preparation are provided in Sec. 1 of the Supplemental Material [27]. The particle batches were named S1, S2, and S3 for the three sample preparation temperatures 25, 35, and 45 °C, respectively. The reaction time is given as a subscript, and when multiple samples from the sample batch are measured, a superscript is used; e.g., for two particles measured at 25 °C and reaction time of 300 s, the samples are referred to as $\text{S1}_{300}^{\text{a}}$ and $\text{S1}_{300}^{\text{b}}$.

X-ray powder diffraction data (XRD) of the bulk samples for all the different precipitation conditions were collected with a Bruker D8 DaVinci powder diffractometer using CuK_α radiation ($\lambda = 1.5418 \text{ \AA}$). The XRD patterns were recorded in the 2θ range of 20°–80° with a scanning rate of 1° min^{-1} (see Fig. S1 of the Supplemental Material [27]), which shows all the collected XRD data. The crystal structures used to index the powder diffraction patterns are listed in Table S1 of the Supplemental Material [27] based on reported crystal structures of vaterite [28], aragonite [29], and calcite [30]. Quantitative phase analyses of the diffraction data were performed by Rietveld refinement with the GSASII software [31], with the results summarized in Table S2 of the Supplemental Material [27]. There is uncertainty in the estimates of the minor phases in the XRD data due to considerable overlap between the diffraction peaks of vaterite, aragonite, and calcite (see the indexed peaks in Figs. S1 and S4 of the Supplemental Material [27]).

B. Coherent x-ray diffraction imaging and wide-angle x-ray diffraction

Coherent x-ray diffraction imaging in tandem with wide-angle x-ray diffraction measurements was performed at the beamline ID10-COH of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. A highly coherent and monochromatic beam with photon energy 7.24 keV was used to illuminate the sample with a collimated pencil beam from the high-energy low-emittance Extremely Brilliant Source (EBS) [32]. Silicon nitride (Si_3N_4) membranes ($3 \times 3 \text{ mm}^2$ and 100 nm thick) from Silson Ltd. (Warwickshire, UK) were used to mount the CaCO_3 microparticles. The samples were prepared by dipping the membranes into a diluted colloidal solution of the CaCO_3 particles in ethanol, ensuring that the particles were well dispersed on the membranes. The beam size was $10 \times 10 \mu\text{m}^2$, the scattering patterns were collected using an Eiger2-4M (Dectris) detector with a pixel size of $75 \mu\text{m} \times 75 \mu\text{m}$ and a sample-to-detector distance of 7.15 m, which gives a real space reconstruction voxel size of $16 \times 16 \times 16 \text{ nm}^3$. The oversampling condition is at the heart of CXDI, requiring that the coherent diffraction patterns are sampled at least twice finer than the Nyquist frequency [20]. For better reconstructions, we use a linear oversampling ratio of 3, which implies that the sample size s fulfils $s \leq \frac{D\lambda}{3p}$, where D is the sample-to-detector distance, λ is the x-ray photon wavelength, and p is the detector pixel size. With our experimental setup, the oversampling condition is met for samples smaller than $\sim 6 \mu\text{m}$ in diameter.

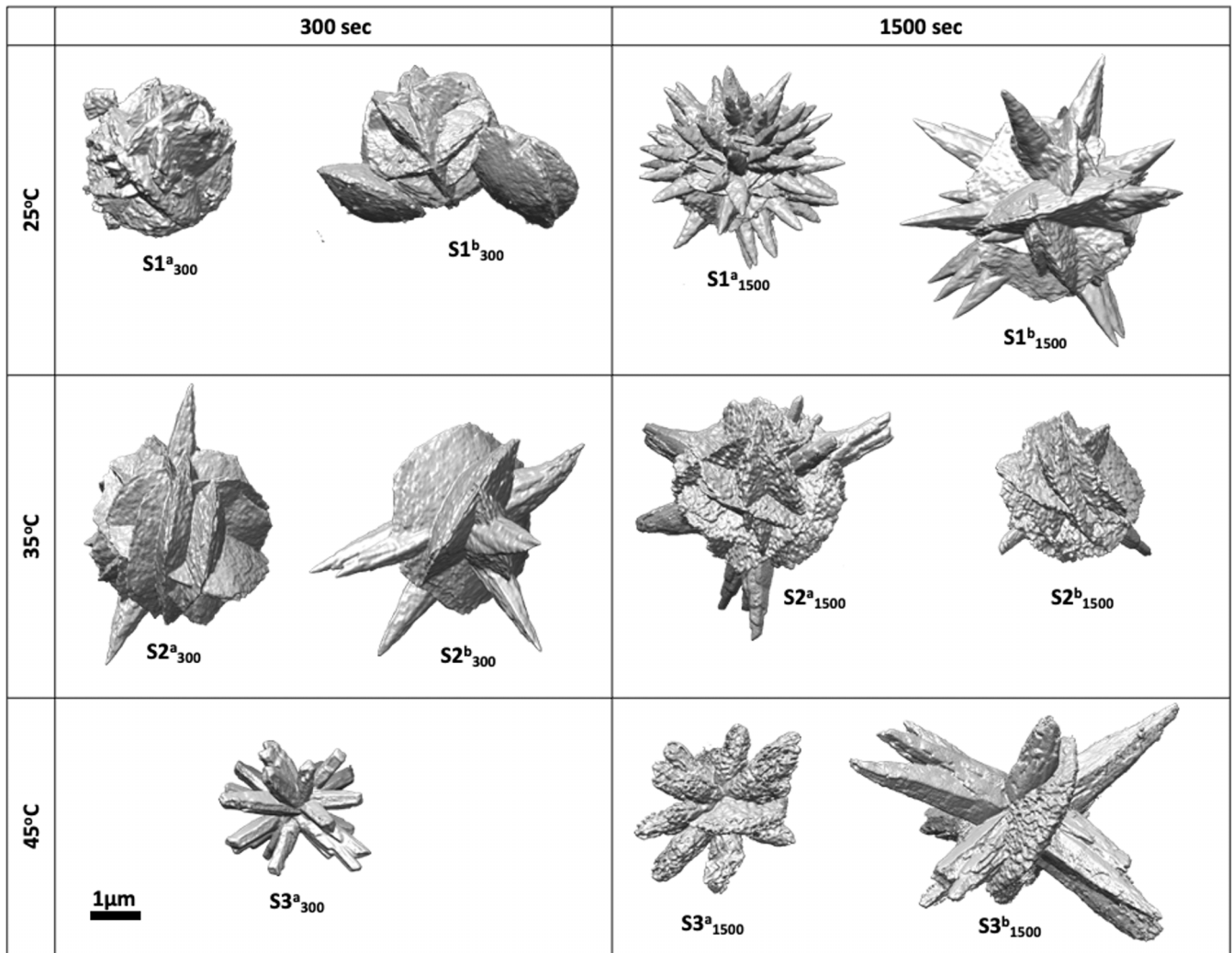


FIG. 1. 3D surface renderings of all the particles studied in the CXDI-WAXD experiments.

The measurements were taken by choosing one CaCO_3 particle at a time from those dispersed on the Si_3N_4 membrane, which was attached to the goniometer. The goniometer enabled the membrane to be rotated about a vertical axis through the particle with angle ω roughly from -80° to 80° with an angular step size of 0.2° . The experimental geometry is illustrated schematically in Fig. S3 of the Supplemental Material [27]. The exposure time for each particle was set between 2 and 3 s (based on the intensity of the scattering signal). One background measurement was recorded in a nearby region of the membrane outside of the particle for each projection.

The PyNX software package [33] developed at the ESRF was used to reconstruct the three-dimensional electron density $\rho(\mathbf{r})$ of CaCO_3 microparticles. The phase retrieval in PyNX was done using the established algorithms of hybrid input-output (HIO) and error reduction (ER) [34]. A dynamic support constraint based on the shrink-wrap algorithm [35] was applied to enforce zero electron density outside the support while confining the nonzero electron density within. The reconstruction

procedure was run for 1000 iterations for each dataset, and the 40 highest-quality reconstructions [36,37] were selected and averaged to reduce noise. The central region of the diffraction pattern containing the lowest spatial frequencies was not measured due to the presence of the beam stop; this can potentially lead to artefacts in the final density reconstruction. Postprocessing of the reconstructed volumes was conducted using custom in-house scripts based on total variation minimization [38]. Visualizations were made using Fiji [39] and UCSF-Chimera [40].

The WAXD patterns were acquired simultaneously with the CXDI measurements as outlined in our previous works [23,24] using a “Mythen 1K” 1D detector. The WAXD detector was offset from the direct beam trajectory to allow the small-angle scattered x-rays to propagate undisturbed to the Eiger-4M detector. For analyses of the WAXD data, the background was subtracted, and the channel number was converted to scattering vector q (with units of $\text{\AA}^{-1}$) using the known Bragg peak positions of a LaB_6 powder. The geometry of the setup gave a q range of $0.75\text{--}3.39 \text{\AA}^{-1}$ in the WAXD measurements. Figure 1 shows isosurface views of all the

reconstructed CaCO_3 microparticles with their names, including the reaction temperatures and times; corresponding WAXD data are shown in Fig. S4 of the Supplemental Material [27].

C. Focused ion beam-transmission electron microscopy

The transmission electron microscopy (TEM) lamella was prepared by focused ion beam (FIB) using a Helios G4 UX from Thermo Fisher Scientific on a sample from the same batch as S2_{300}^a . A protection layer of platinum was first deposited on top of the particle. The first part of the protection layer was made by e-beam-assisted deposition to avoid ion-beam damage to the top part of the CaCO_3 particle. The lamella was cut and transferred to a Cu liftout grid before final thinning. All coarse thinning was done with 30 kV acceleration voltage for the Ga^+ ions. Final thinning was first done at 5 kV and then at 2 kV on either side of the lamella to minimize surface damage. TEM was performed with a double spherical aberration corrected, cold field emission gun JEOL ARM 200FC, operated at 200 kV. Selected area electron diffraction (SAED) patterns were attained from circular regions with a diameter of 150 nm.

D. Molecular computations

A combined MC and MD simulation study was carried out to identify minimum energy sequences of CaCO_3 clusters exhibiting structural motifs of calcite, aragonite, and vaterite. In the simulations, the CaCO_3 clusters were modeled as isolated systems in vacuum, hence neglecting solvent interactions. In the first stage, MC was used to optimize the overall shape of the clusters as a function of their size, moving the simple (Ca^{2+}) and complex ions (CO_3^{2-}) on a lattice whose ionic sites correspond to the experimental crystalline structures of one of the three polymorphs of CaCO_3 . The crystal structures used are essentially the same as those employed to index the experimental diffraction data (Table S1 of the Supplemental Material [27]). The force field that has been used [41–43] describes CaCO_3 as a virtually ionic compound, whose anion consists of the covalently bonded planar CO_3^{2-} unit. MC was used to minimize the energy of the clusters and corresponding growth facets using a fast algorithm that explores a reduced phase space corresponding to the nodes of the crystal lattice, treating the CO_3^{2-} unit as rigid. This optimization step essentially replaces the Wulff construction [44,45] that is used to predict equilibrium shapes for large clusters, which in the context of our simulations corresponds to more than 10^4 CaCO_3 units. The results of this MC optimization are shown in Fig. S2 of the Supplemental Material [27], where the three distinct sequences of clusters preserve the calcite, vaterite, and aragonite bulk phases. The properties of the clusters belonging to the three sequences were characterized by computing the cohesive energy of the locally relaxed configurations, defined through the force field [41]. The MC-optimized structures were then used as input for a second stage, in which each cluster was relaxed via quenched MD minimization, where atomic velocities were reset to zero whenever an increase in potential energy was detected, driving the system toward a local energy minimum. Such a constraint ensures that the cluster

evolution remains near the local potential energy minimum associated with the calcite, aragonite, or vaterite structures generated in the first optimization stage. It has been verified that this protocol results in three distinct sequences of clusters of increasing size that, despite distortions, are still recognizable as belonging to the three homogeneous crystal phases. The formation free energy (F) was then estimated within the harmonic approximation, based on the vibrational spectrum computed with respect to the local minimum resulting from the quenched MD relaxation. Further details of the computational methodology are provided in Sec. 2 of the Supplemental Material [27].

III. RESULTS AND DISCUSSION

A. CXDI-WAXD

The combined CXDI-WAXD measurement protocol was used to investigate the morphological and structural information of the CaCO_3 precipitates. The precipitation of CaCO_3 was carried out under different conditions of time duration, temperature, and supersaturation. For the selected reaction temperatures, CaCO_3 microparticles were extracted after times of either 300 or 1500 s. 3D surface renderings of all the measured particles are shown in Fig. 1, demonstrating the systematically changing morphologies that arise due to the different reaction conditions.

We shall start the presentation of our results with samples S1_{300}^a , S2_{300}^a , and S3_{300}^a , which correspond to the particles retracted from solution after a reaction time of 300 s at 25, 35, and 45 °C respectively; cross-sectional views of the interior of the particles are shown in Fig. 2(a). The variations in (electron) density across the three CaCO_3 samples precipitated at different temperatures are evident in Fig. 2(a), highlighting the influence of temperature on the structure and organization of the CaCO_3 phases at a reaction time of 300 s. The density contrast provides an overview of the crystal shape with distinct differences between S1_{300}^a , S2_{300}^a , and S3_{300}^a [Fig. 2(a)]. Despite the relatively small difference in bulk densities between the CaCO_3 crystalline phases of vaterite (2.65 g/cm³) and aragonite (2.93 g/cm³), we can distinguish between these crystal phases in S2_{300}^a [marked with black arrows in Fig. 2(a)] by detecting subtle density gradients and structural heterogeneity within the particles. The current study is an early example of using CXDI phase contrast to resolve small density variations (see also Refs. [46,47]).

The WAXD data obtained alongside with CXDI measurements in Figs. 2(b) and 2(c) and Fig. S4 of the Supplemental Material [27] further support these findings. Figure 2(b) shows a polar plot of diffracted intensity as a function of ω and q , $I(\omega, q)$, while Fig. 2(c) shows the corresponding ω -integrated data $I(q)$. The WAXD data presented in Figs. 2(b) and 2(c) clearly indicate that a phase change took place from particles with vaterite structure formed at 25 °C, to aragonite particles at 45 °C. In S2_{300}^a (35 °C), where both vaterite and aragonite were present, the observed spatial density variations reflect the intermediate nature of the crystallization process. The WAXD data of S2_{300}^a do not provide conclusive evidence of the coexistence of vaterite and aragonite as the Bragg diffraction peaks of aragonite were presumably oriented such that they were not

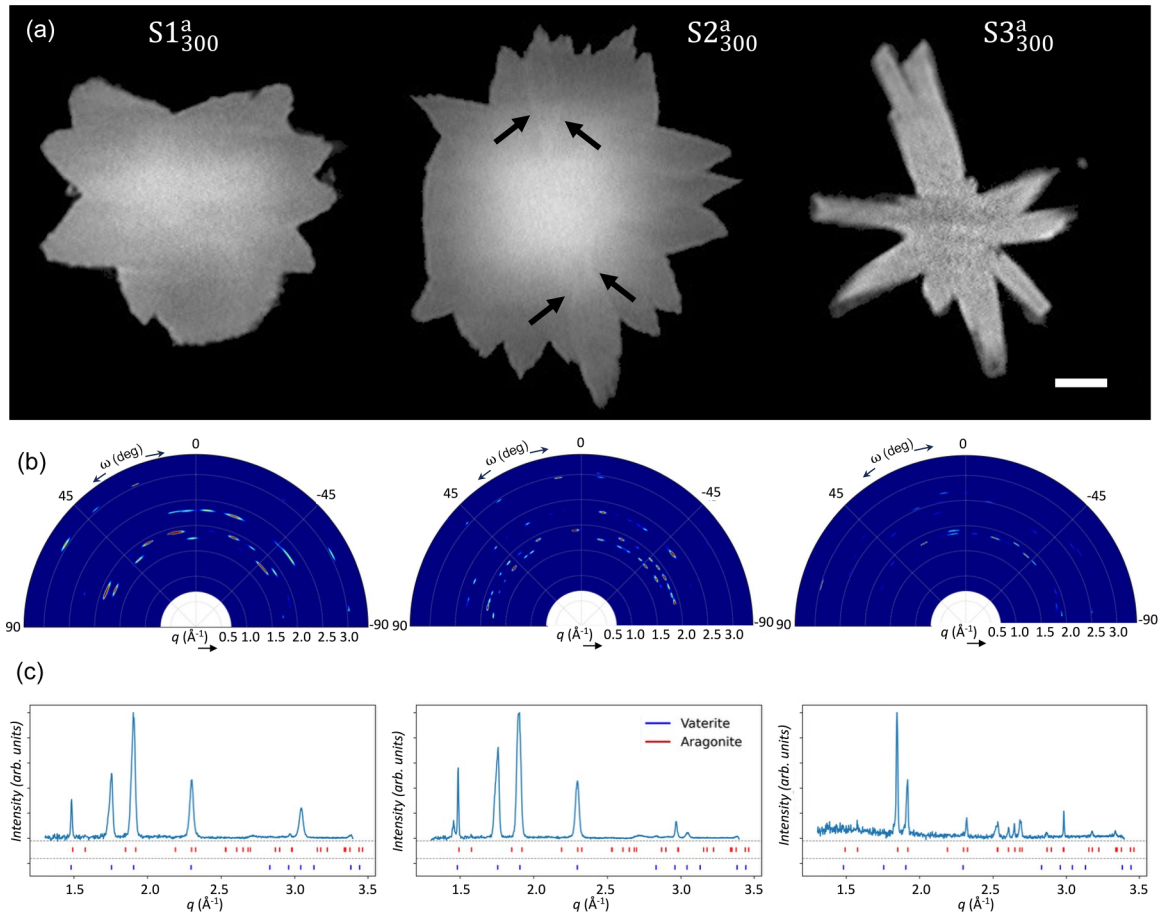


FIG. 2. CXDI-WAXD results for $S1_{300}^a$, $S2_{300}^a$, and $S3_{300}^a$ corresponding to precipitation temperatures of 25, 35, and 45 °C, respectively. (a) Cross sections of CXDI electron density reconstructions. The black arrows are discussed in the main text. (b) Polar plots representing Bragg diffraction as a function of ω (°) and q ($\text{\AA}^{-1}$), where ω depicts the sample rotation. (c) Azimuthally integrated diffraction plots with the Bragg peaks indexed to the crystal structures of vaterite and aragonite. Scale bar is 500 nm.

detected with our experimental configuration; note that the 1D WAXD detector collected data only in a narrow vertical section of reciprocal space and with a step size of 0.2° (cf. Sec. II B). However, both the XRD data obtained for a powder (Fig. S1 of the Supplemental Material [27]) and the WAXD data of the identically prepared particle $S2_{300}^b$ (Fig. S4 of the Supplemental Material [27]) confirm the presence of aragonite with the appearance of a unique aragonite III diffraction peak (at $q = 1.85 \text{\AA}^{-1}$).

In the temperature range of 25–50 °C and under the used precipitation conditions, all three anhydrous polymorphs CaCO_3 can be present [17,48]. The absence of aragonite in $S1_{300}^a$ (25 °C) suggests that at this temperature, vaterite is the dominant phase. The presence of calcite as a minor phase is evident from the bulk XRD data (cf. Fig. S1 of the Supplemental Material [27]). However, the microparticles studied with CXDI did not show any presence of calcite (Figs. 1 and S4 of the Supplemental Material [27]), which can be attributed to the very small amounts of calcite in the bulk powder or due to their small size (and correspondingly low scattering power), that they are ignored during preliminary particle selection during CXDI measurements.

At 45 °C, aragonite emerged as the dominant crystal phase with $S3_{300}^a$ being pure aragonite, which is evident from

Fig. 2 and Fig. S1 of the Supplemental Material [27]. Higher temperatures promoted increased ion mobility and different nucleation pathways, evidently affecting the formation of different CaCO_3 polymorphs. These findings are consistent with literature reports showing that the polymorphic distribution of CaCO_3 during solution precipitation is strongly temperature dependent, as vaterite typically dominates near room temperature, whereas aragonite becomes the kinetically preferred phase at temperatures above 40 °C [14]. In Fig. 2(b), the WAXD data are represented with polar plots where the scattered intensity is plotted as a function of ω (°) and q ($\text{\AA}^{-1}$), where ω denotes the sample rotation. The polar diffraction maps are useful tools for appreciating the presence of preferred orientation of the crystallites (texture) within the particle. As seen from Fig. 2(b), we observe an apparently nonsystematic polycrystalline distribution of diffraction intensity for the Bragg peaks (distinct q values), implying that there is no single preferred orientation of the crystallites within the studied microparticles. Such pseudorandom crystallite orientations can be attributed to heterogeneous nucleation and growth mechanisms, as observed in spherulitic growth of both vaterite and aragonite [49].

Figure 3 presents 3D isosurface views of three different samples, visualizing how the shape and surface

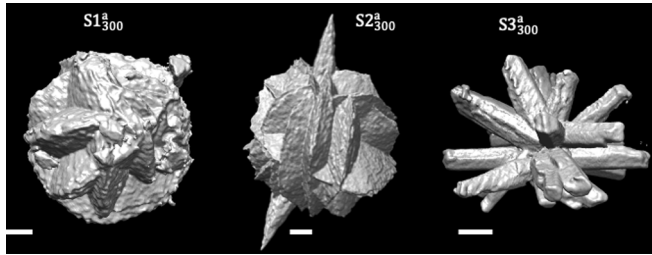


FIG. 3. 3D surface renderings of $S1^a_{300}$, $S2^a_{300}$, and $S3^a_{300}$. Scale bars are 500 nm.

features of precipitated particles evolve systematically with precipitation temperature. A morphological transition is observed (see Figs. 1 and 3), from the nested hexagonal platelets ($S1^a_{300}$, 25 °C), via a hybrid structure ($S2^a_{300}$, 35 °C), to interconnected rod-shaped crystals ($S3^a_{300}$, 45 °C). For $S3^a_{300}$, the presence of extended aragonite crystals is clearly visible. Sample $S2^a_{300}$ (35 °C) exhibits an intermediate transitional step, where both hexagonal discs and elongated spicules coexist. Such vaterite-aragonite coexistence was prominent at 1500 s (cf. Fig. 1), reinforcing the notion that such composite particles represent a transitional stage, where vaterite begins converting into the more stable aragonite phase.

For the temperatures (25, 35, and 45 °C) and concentration (concentration product of Ca^{2+} and CO_3^{2-} ions was 2.73×10^{-3} mol/L) used in our experiments, the solutions are supersaturated with respect to all the three anhydrous phases of CaCO_3 , and close to the kinetic stability zones of vaterite and aragonite (cf. Fig. S5 of the Supplemental Material [27] and Refs. [17,48]). It is important to note that the precipitation and growth reactions reported here were performed in a large reaction volume to ensure a more representative preparation method by removing interface effects. Additionally, it should be noted that by the nature of our approach, different particles were measured at different times and temperatures to capture the morphological evolution. The observed transformation from particles having the hexagonal platelet-like morphology of vaterite to particles having rod-shaped aragonite crystals with increasing temperature can be influenced by factors such as supersaturation levels, ionic interactions, and kinetic effects. Further, the exact onset time of nucleation may in principle be different for the different particles, meaning that the time evolution presented here may not fully capture the real growth evolution mechanism. The samples shown in Figs. 2 and 3— $S1^a_{300}$, $S2^a_{300}$, and $S3^a_{300}$ —give the most representative depiction of CaCO_3 morphology evolution under the given reaction conditions.

At 25 °C and 300 s, we observe nested hexagonal platelets within spherical vaterite particles in both $S1^a_{300}$ and $S1^b_{300}$ (cf. Fig. 1). To elucidate how these CaCO_3 particles grew, a 3D surface rendering of $S1^b_{300}$ is presented in Fig. 4 that provides insights into the early-stage growth, transformation, and structural organization of vaterite particles. The presence of several distinct fragments, including a single hexagonal platelet, two twinned hexagonal plates, and a spherical particle with several intercalated hexagonal platelets, suggests multiple growth stages. The angle between the two twinned hexagonal crystals, highlighted in purple in Fig. 4(b), is

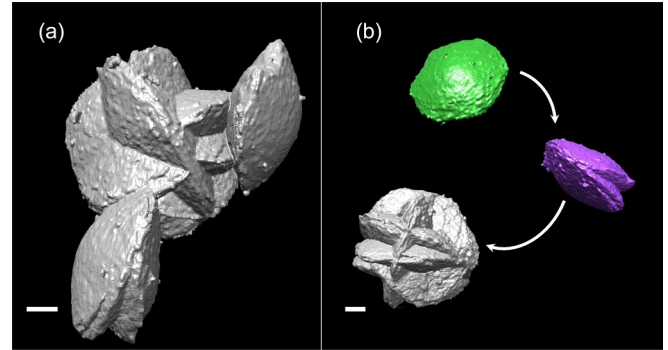


FIG. 4. 3D surface rendering of $S1^b_{300}$. (a) The entire particle $S1^b_{300}$ as imaged with CXDI. (b) Computationally exploded view of the different fragments for better visualization of their morphology with a single hexagonal platelet (green) and two twinned platelets (purple). Scale bars are 500 nm. The arrows suggest the temporal growth progression.

estimated to be $\sim 15(4)^\circ$, which can be attributed to the misorientations during growth (twinning) [50]. Vaterite exists in different polytypes, and pseudo-hexagonal domains can form in our experiments due to the reaction conditions that promote rapid nucleation and growth [51–55]. The surfaces of the hexagonal platelets serve as secondary nucleation sites and show additional growth features with intercalated hexagonal platelets [Figs. 4(a) and 4(b)]. These findings support a multi-step growth pathway of vaterite where defects, twinning, and templated growth all contribute to its final particle morphology. The ambiguity in determining the exact crystal structure of vaterite remains a much-researched topic with focus on exploring the structural complexity of vaterite [51–55], which is understood by the prevalence of stacking faults [51,53,55].

At 35 °C, we observed the presence of vaterite and aragonite in the same microparticle, as seen in Figs. 2 and 3. Such vaterite-aragonite composites were also observed with particles precipitated at 25 °C and with a long reaction time of 1500 s. Figure 5 depicts the electron density maps obtained from CXDI of several mixed vaterite-aragonite particles that we observed in our study. Although the presence of the two different crystal forms can be visually identified [as also seen in Fig. 2(a)], automatic segmentation into vaterite and aragonite was challenging due to overlapping density values which can be partly attributed to the missing scattered intensities near the direct beam (due to the presence of the beam stop), corresponding to the lowest spatial frequencies, which were not recorded in our CXDI experiments. The regions consisting of vaterite and aragonite are marked as V and A, respectively, and aragonite is highlighted in false color, which helps visualize the spatial distribution of each phase, providing clues about nucleation sites and growth patterns. The fact that aragonite appears in well-defined regions with sharp interfaces indicates a direct transformation driven by nucleation of the more stable phase, where aragonite grows at the expense of vaterite.

B. FIB-TEM analysis

To further elucidate the vaterite-aragonite phase coexistence, FIB-TEM analysis was conducted on a particle similar

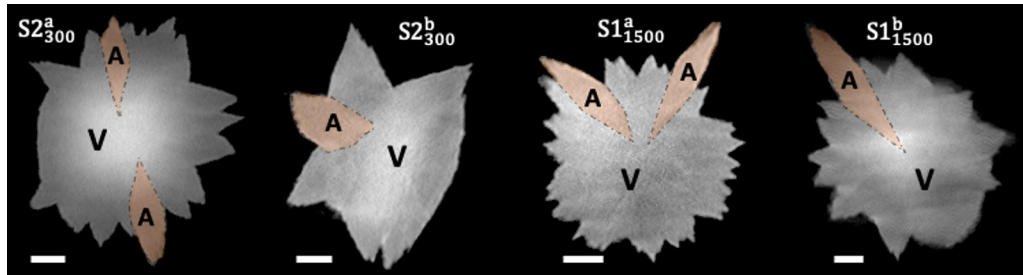


FIG. 5. Vaterite-aragonite composites. CXDI electron density maps of samples showing the presence of both vaterite and aragonite, which is highlighted in false color as A; vaterite is marked as V. Scale bars are 500 nm. The same figure without the false coloring is provided in Fig. S6 of the Supplemental Material [27].

to $S2^a_{300}$ as studied with CXDI in Figs. 1 and 3. It is important to mention that such mixed vaterite-aragonite particles were also observed for particles precipitated at 45 °C and with a reaction time of 1500 s. As we have noted earlier (Figs. 2 and 3, and Fig. S1 of the Supplemental Material [27]), the powder and the single-particle data for 45 °C and 300 s correspond to pure aragonite. The transition from pure aragonite in $S3^a_{300}$ to mixed vaterite-aragonite in $S3^a_{1500}$ (and $S3^b_{1500}$) is not favored thermodynamically. It should be noted that the particles at different times were obtained in separate precipitation experiments, and hence they are not representatives of the exact stages of the same reaction.

The FIB-TEM analysis, combined with electron diffraction patterns, was used to identify the CaCO_3 phases within a microparticle and complement the results obtained from CXDI. Figure 6(a) shows a secondary scanning electron microscopy (SEM) image of the vaterite-aragonite composite particle used in the FIB-TEM analyses. The external morphology of the chosen particle was similar to the vaterite-aragonite particles presented in Figs. 1 and 3. The black line in Fig. 6(a) indicates the region where the FIB sectioning was performed. As seen from the low-angle annular dark field scanning transmission electron microscopy (LAADF STEM) image in Fig. 6(b), cross section of the mixed vaterite-aragonite microparticle prepared with FIB showed no contrast between vaterite and aragonite. The SAED patterns shown in Figs. 6(c) and 6(d) were measured within the elongated spicule (orange circle) and hexagonal platelets (yellow circle), which are morphological features characteristic of vaterite and aragonite, respectively.

The SAED pattern from the elongated spicule in Fig. 6(c) (cf. orange circle) matched perfectly with that of the [100] zone axis of aragonite. The measured real-space distances of 7.97(8) Å along [010] and 5.74(6) Å along [001] align with the expected crystallographic parameters of orthorhombic aragonite [30] ($Pmcn$ space group, see Table S1 of the Supplemental Material [27]) confirming that the observed CaCO_3 region was aragonite, with high crystallinity and well-defined structural order. The second diffraction pattern [cf. Fig. 6(d)], from the hexagonal platelets (yellow circle), does not match any known diffraction peaks of aragonite. Based on simulations using the software “Recipro” [56], the SAED pattern in Fig. 6(d) matches with the vaterite crystal structure when the electron beam is close to the $[1\bar{1}1]$ zone axis [8,28,57,58]. This result gives strong support that both vaterite

and aragonite coexist in the same particle, as also inferred from the CXDI analysis.

C. Monte Carlo and molecular dynamics simulations

The crystal structures after the MC optimization and after the MD minimization are shown in Fig. S2 of the Supplemental Material [27], where we can observe that simulated clusters of calcite, aragonite, and vaterite have distinct morphologies. In Fig. S7 of the Supplemental Material [27], the cohesive energy per CaCO_3 unit is shown as a function of cluster size for the MC energy minimized structures. It is important to note that the results refer to simulations of CaCO_3 clusters

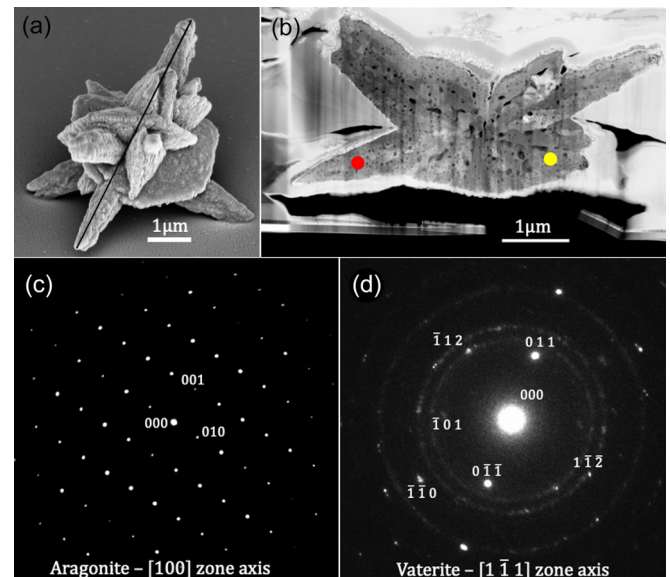


FIG. 6. FIB-TEM and SAED data. (a) SEM image of the vaterite-aragonite composite particle used for the FIB-TEM study. (b) LAADF STEM cross section image of vaterite-aragonite microparticle after FIB sectioning. The orange and yellow circles correspond to the regions where the SAED patterns were obtained. The two regions show the characteristic morphologies of aragonite and vaterite, with spicules and platelets, respectively. The SAED pattern for the region marked with an orange circle is shown in panel (c) and for the one marked with yellow circles in panel (d). The diffraction pattern in panel (c) can be indexed with the crystal structure of aragonite, and the one in panel (d) can be indexed to the structure of vaterite.

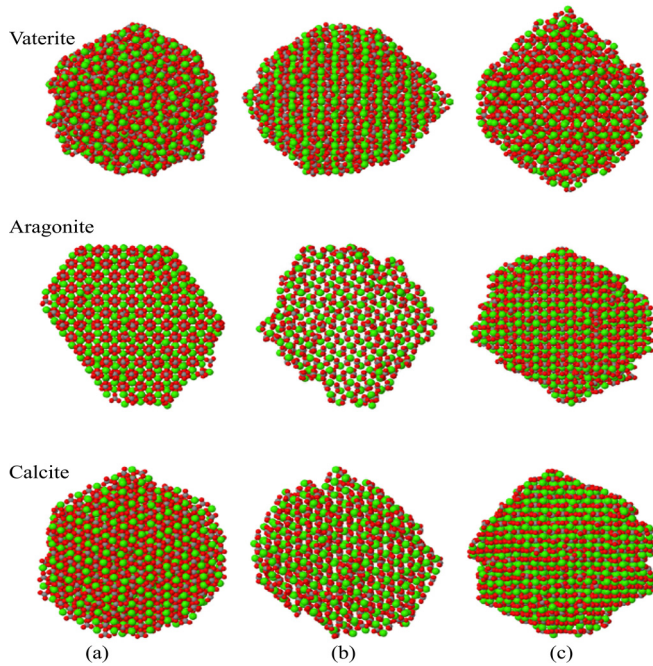


FIG. 7. MD simulations. Structures of vaterite (top row), aragonite (middle row), and calcite (bottom row) along three orthogonal directions in panels (a), (b), and (c) corresponding to the z , x , and y axis, respectively.

in empty space, without the presence of solvent molecules. The calculations suggest that for sufficiently small clusters ($N_{\text{ions}} < 50$), calcite, vaterite, and aragonite exhibit similar cohesive energy, making them indistinguishable, which is intuitively reasonable. However, as the cluster size increases, calcite and aragonite exhibit lower cohesive energy than vaterite (cf. Fig. S7 of the Supplemental Material [27]), thus within the uncertainty of the simulations supporting the experimental fact that vaterite is less stable than calcite and aragonite, and may convert into a more stable phase, while aragonite and calcite persist as competing polymorphs. Vaterite, being less stable, was observed in the experiments as a transient phase, suggesting that kinetic factors influence polymorph selection in the nucleation process. As seen in our experiments and others, vaterite forms initially at low temperature before transforming into aragonite or calcite [14,59,60].

Figure 7 presents the cluster structures after the MD relaxation, starting from the three sequences generated by the MC lattice optimization shown in Figs. S2(a)–S2(c) of the Supplemental Material [27]. The stable morphology of vaterite corresponds to the hexagonal structure with tapered corners that is observed experimentally in micrometer-sized particles [cf. Fig. 4(b)]. On the other hand, for aragonite and calcite, we observe sharper boundaries that can be compared to the extended rod-shaped morphology in aragonite microparticles as in Fig. 3 and the commonly observed rhombohedron morphology in calcite [61,62].

In Fig. S8 of the Supplemental Material [27], the Gibb's free energy of formation $F(T)$ from $T = 0$ to $T = 400$ K is shown for calcite, aragonite, and vaterite clusters, each consisting of 1000 molecules. Figure S8(a) of the Supplemental

Material [27], in particular, shows that aragonite and calcite are the competing stable polymorphs, and Fig. S8(b) of the Supplemental Material [27] shows that the difference in $F(T)$ between aragonite and vaterite decreases with increasing temperature. It is evident from Fig. S8(b) of the Supplemental Material [27] that for the precipitation temperatures used in our experiments, viz. 25, 35, and 45 °C, the difference in $F(T)$ exhibits similar values. This is consistent with the reported precipitation diagram of CaCO_3 [17] (cf. Fig. S5 of the Supplemental Material [27]), which suggests that the experimental conditions are near the phase boundary between vaterite and aragonite; hence, transitions between the two can occur due to both kinetic and thermodynamic factors. It should be noted that the calculations were all done in free space, which is not representative of the precipitation process that we observe in our experimental studies. More details on the formation free energy calculations are given in the Supplemental Material [27]. Future efforts will be dedicated to establishing a representative theoretical model that accounts for the interactions between the aqueous solvent and the Ca^{2+} and CO_3^{2-} ions.

IV. CONCLUSIONS

We report the first direct visualization of internal nanoscale density variations in CaCO_3 using CXDI, confirming the coexistence of vaterite and aragonite within individual particles. CXDI revealed localized aragonite nucleation sites within a vaterite matrix at 35 °C, which was supported by FIB-TEM analyses. MC-MD simulations allowed us to estimate that the difference in free energy of formation under our experimental conditions is low and that the transition between vaterite and aragonite is driven by both thermodynamic and kinetic factors. Hence, dissolution-precipitation process can probably be the dominating process since we observe mixed phases at higher reaction times and temperatures. Our findings reinforced the notion that CaCO_3 crystallization and growth is a complex multistep process influenced by the precursor phases, twinning, and secondary nucleation. The appearance of a mixed-phase particle containing both vaterite and aragonite was visualized, providing a 3D view of the transformation of vaterite to aragonite as a function of temperature. These insights can contribute to a deeper understanding of biomineralization mechanisms and the fundamental principles governing CaCO_3 phase stability. The study of CaCO_3 precipitation, particularly the nucleation and early growth stages, presents major challenges. The microscopic size of the nuclei, the fast evolution rate, and the stochastic nature of the phenomenon make these stages difficult to capture and analyse. This inherent variability requires advanced experimental techniques capable of resolving rapid, nanoscale changes in structure and composition. Hence, an obvious follow-up to this study would be to develop a bespoke sample environment and experimental protocol to perform a dynamic CXDI-WAXD experiment in order to resolve the nanoscale changes in structure and morphology during phase transformations in CaCO_3 as well as in other functional materials.

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DATA AVAILABILITY

The data that support the findings of this article are openly available [63].

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