Aragonite growth in water-alcohol mixtures: Classical or nonclassical crystallization?

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<th>Journal:</th>
<th>2011 MRS Fall Meeting</th>
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<td>Manuscript ID:</td>
<td>Draft</td>
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<td>Manuscript Type:</td>
<td>Symposium NN</td>
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<td>Date Submitted by the Author:</td>
<td>n/a</td>
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<td>Complete List of Authors:</td>
<td>Sand, Karina Rodriguez-Blanco, Juan Diego; University of Leeds, School of Earth and Environment Makovicky, Emil; University of Copenhagen, Geography and Geology Benning, Liane; University of Leeds, School of Earth and Environment Stipp, Susan; University of Copenhagen, Chemistry</td>
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<tr>
<td>Keywords:</td>
<td>crystal growth, ethanol, self-assembly</td>
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Aragonite growth in water-alcohol mixtures: Classical or nonclassical crystallization?

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ABSTRACT

Aragonite can grow from calcium carbonate solutions as the favored phase, at ambient conditions, in the presence of 1:1 volume % water:ethanol. Its form is branched needles, with pseudohexagonal symmetry. Morphological evidence demonstrates that all precipitated aragonite is twinned. The recently popularized hypothesis of nonclassical growth by nanocrystal self assembly cannot describe the aragonite crystal form. Rather, its formation is effectively described as spherulitic growth, i.e. by classical crystal growth theory.

INTRODUCTION

Calcium carbonate has three nonhydrous crystalline polymorphs: vaterite, aragonite and calcite. Aragonite, the orthorhombic form, is not the stable phase at ambient conditions unless the temperature is >40 °C or a calcite growth inhibitor is present [1,2]. In this study, aragonite was obtained at ambient conditions, by adding ethanol to the aqueous solution [3,4].

Aragonite is a common CaCO_3 biomineral, preferred by organisms because of its flexibility (e.g. as an inner shell layer in mollusks: nacre). It is well established that aragonite forms pseudohexagonal cyclic twins both in nature and in controlled experiments [5,6]. Aragonite twinning has three orientations for component individuals (1, 2 and 3), where the crystallographic a axis of each twin individual emerges perpendicular to the needle axis through the edge of the needle (Figure 1). The Individuals twin on the {110} symmetry planes by reflection on (110) with an angle between the a axes of 116.18°. The ideal hexagonal angle is 120° (Figure 1).

Nonclassical crystal growth has been much discussed in the recent literature. Both classical and nonclassical growth have been invoked to explain CaCO_3 polymorph formation [7-12]. Classical nucleation theory describes the formation of critical nuclei by bonding of single molecules or ion-by-ion, so the unit cell is replicated without structural change in the bulk or at the surface. Nonclassical growth is described as the oriented aggregation of primary nanoparticles or nuclei in the presence of additives (e.g. polymers), producing a coherent crystal. This nonclassical hypothesis has become popular for describing the formation of CaCO_3 polymorphs, when additives are present in growth solution. For the polymorphs, vaterite and aragonite, self assembly of CaCO_3 nuclei has been proposed [13-18], even though the same crystal form is obtained regardless of the presence or absence of additives. The aim of this study was to explore the aragonite growth mechanism qualitatively, by combining mineralogical, crystallographic and morphologic data from experiments in the presence of alcohols.
**EXPERIMENTAL DETAILS**

All chemicals were of analytical grade and we used ultrapure deionised (DI) water (Milli-Q; resistivity >18 MΩ cm⁻¹; Millipore Corporation). The ethanol was HPLC grade and all chemicals were used as purchased. The aragonite crystals were precipitated in 1:1 volume % water:ethanol solutions at room temperature (24 °C ±1 °C). Stock solutions were prepared to give a final concentration of 25 mM Na₂CO₃ and CaCl₂ in the reaction vessel, considering the ethanol as part of the liquid. For the synthesis, the Na₂CO₃ was mixed with the alcohol and shaken vigorously for five seconds before adding the CaCl₂ solution. The reaction vessel was placed on a shaking table running at 80 revolutions per minute (RPM). We used a reaction vessel of 1 L and withdrew 20 mL aliquots using a pipette after 1 hour, 5 hours, 1 day, 1 week, 1 month and 4 months of reaction. The precipitate was vacuum filtered using 0.4 µm cyclopore track etched membranes. The collected solids were rinsed with ethanol and kept dry until analysis by X-ray diffraction (XRD) and scanning electron microscopy (SEM). XRD data were obtained using a Bruker D8 Advance Diffractometer, with scan range from 5 to 75° 2θ and step size of 0.018° 2θ. The Kα₂/Kα₁ ratio was 0.5. SEM images were acquired using a Quanta 200F with a field emission gun (FEG). Samples were coated with 2-3 nm of Au or Pt/Pd and imaged at a working distance of 3-4 mm at 2 to 3 keV.
DISCUSSION

In all experiments, the first phase to form was amorphous calcium carbonate (ACC). All of the samples were dominated by aragonite (98-100 volume %). A few contained 0-2 volume % calcite but no vaterite was observed. SEM images (Figure 2) showed that aragonite typically precipitated as bundles of branching pseudohexagonal needles. These consisted of small segments, that after 1 hour of reaction were on the order of 10-200 nm long (Figure 2a). The segments increased in size with time and some grew larger at the expense of others, by Ostwald ripening (Figure 2a-e). The segments (Figure 2b-c, short white arrows) that make up the needles are separated by well expressed grooves perpendicular to the long axis of the needle and an irregular, subvertical winding seam parallel to the needle length (Figure 1b, boxes). The segments have a straight edge along the face expressed on the needle, which produces needle corners (Figure 2c-d, long white arrows). A central void, visible in broken needles (Figure 2d, insert) reveals a pseudohexagonal arrangement of the segments and confirms that the segments are composed of individual crystals.

Figure 2. SEM images of aragonite from samples taken after: (a-b) 1 hour, (c) 1 week, (d-e) 4 months of reaction. a) Aragonite needles branch and form bundles; b-e) most individual segments (short white arrows) are separated by horizontal and subvertical winding seams (in boxes) and grooves perpendicular to the needle length. The middle of the segments that marks the face of the needles is a straight edge that represents the corner of the needles (long white arrows); d) A broken needle (insert) reveals a central cavity and confirms the pseudohexagonal arrangement of the segments.
Comparing our aragonite needles with large natural and synthetic aragonite crystals \cite{5,19,6,20} lead us to conclude that the majority of aragonite needles were composite interpenetration twins, where each needle face corresponds to \{110\} faces, from two distinct, adjacent twin individuals (Figure 1). Interpenetration twins are initiated from a contact twin of two individuals (1 and 2 in Figure 1). The third twin individual (3) attaches to Individual 1 or 2 (2, as in the case of Figure 1) while overgrowth from Individual 1 (1') and 2 (2') to the opposite side has started. Each regularly twinned pair produces an angle of 63.82° between a twin individual and the overgrowth portion of the other individual. Angle calculations are made from the aragonite lattice data of Pilati et al. \cite{21}.

The twinning angle between Individual 1 and 2 is 116.18°, which leaves 63.82° for the angle between Individual 2 and the overgrown portion from Individual 1 (1'). This is similar for the twinning of Individual 2 to 3. That means that there is only 52.36° left to the individuals not related by twinning (i.e. Individuals 1 and 3). This systematic behavior leads to pseudohexagonal twin prisms with twin contacts at 63.82°, producing pairs of exactly parallel \{110\} faces. In contrast, the forced contact of the individuals not related by twinning results in two concave faces on the opposite sides of the twin (Figure 1). Adjacent individuals appear to have a contact plane on \{130\} but this plane is not a twinning plane. Calculations show that the $a$ axes of two crystals twinned on \{130\} produce an angle of 56.32°, instead of the observed 63.82°, illustrating that the contact plane in the interpenetration twin is not a plane with simple Miller indices.

These observations raise a question about the proposed mechanism of nanoaggregation for aragonite. If primary nanoparticles were to associate after nucleation, they would attach by twinning on and adhesion to the \{110\} face and use one of the four twinning orientations that this face offers. Such an arrangement would produce a chaotic, fine grained aggregate instead of a needle. Instead, the overwhelming majority of the aragonite aggregates produce needles with contacts on the \{130\} faces. The \{130\} face is not a twin face, nor a preferred crystal plane for aragonite, so the nanoparticles in this arrangement can only be explained by interpenetration twinning.

Aragonite needles have been produced in many other studies using various additives and experimental regimes. Branching aragonite needles are well known and are not unique to a specific additive or set of conditions. This means that a common growth mechanism must exist. In our experiments, the saturation index (SI) changes during the nucleation and crystallization processes. When the solutions were initially mixed, SI, hence the driving force of crystallization, was high, and as the ACC precipitated and aragonite grew, SI decreased. High initial supersaturation and decreasing SI have been shown to strongly influence the morphology of the precipitate \cite{22-24}; spherulitic growth is common at high SI \cite{24,25}.

Spherulitic growth has been described by Granasy et al. \cite{26} and in our understanding of spherulite formation, nuclei that form on the growing surface are simply grown over if they are not aligned with their fastest growing direction parallel to the needles. This results in needles that are all essentially parallel, except at the growth front, where misoriented nuclei can grow because they face a continuous supply of material from the solution. The development of Category 2 spherulites of acicular crystals, as described by Granasy et al. \cite{26}, is shown in Figure 3aii–iii and perfectly matches the form of the aragonite needles observed in our study (Figure 3b). Figure 3 shows that the $c$ directions (white arrows) of the aragonite needles diverge, whereas their $a$ directions converge into the ‘eye’ region (black arrows).
Figure 3. Spherulitic growth model of Category 2 spherulites modified from Granasy et al. [26]. The aragonite morphology from our study (b) matches stages a) ii to iii in the top of the figure. The black arrows point toward the “eye” region in the spherulites where growth along c (white arrow) survives.

CONCLUSIONS

Morphological investigations, combined with crystallographic evaluation of aragonite twinning, demonstrate that the aragonite crystals observed in our study are twin intergrowths. Twinning occurs on the common twin plane \{110\} and with intergrowth contact on \(~\{130\}\) faces. The \{130\} face is not a twin plane and the contacts observed along this plane cannot be explained by any current theories of nanoparticle aggregation by self assembly. There is good evidence to conclude that the polycrystalline aragonite needles were formed by spherulitic growth by classical, ion-by-ion attachment. This conclusion applies to all aragonite crystals with branching needle morphology.

ACKNOWLEDGMENTS

We sincerely thank Keld West and the NanoGeoScience group for help and discussion; Caroline Hem, Helene Almind and Pieter Boots for XRD analysis and TOPAS advice; and Berit Wenzell and Zoltan Balogh from CEN, DTU for SEM training. Funding was provided by the Nano-Chalk Venture, from the Danish National Advanced Technology Foundation (HTF) and Maersk Oil and Gas A/S. J.D.R.B acknowledge a fellowship from the Marie Curie EU-FP6 MINGRO Research and Training Network under contract MRTNCT-2006-035488. The NanoGeoScience Laboratory was initially established through a grant from the Danish Natural Sciences Research Council.
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