

## Habit Modification in Synthetic Crystals of Aragonite and Vaterite

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The addition of  $\text{Li}^+$  to supersaturated calcium hydrogen carbonate solutions results in the preferential expression of the (001) faces of aragonite whereas addition of poly  $\alpha,\beta$ -aspartate induces vaterite nucleation and the formation of helicoid morphologies.

Calcium carbonates (calcite, aragonite and vaterite) are important inorganic, geological and bioinorganic materials, and the control of crystal shape and texture is important to the industrial (pigments, brighteners and fillers) and biological (structural support, gravity sensors and deterrence) uses of these materials. Although many studies have shown that a wide range of inorganic and organic additives can influence the shape of calcite crystals grown in the laboratory from supersaturated solutions,<sup>1-6</sup> there are no corresponding examples, as far as we know, of modifications in the morphology of synthetic aragonite or vaterite. We now describe methods by which specific morphological changes can be induced in aragonite and vaterite crystals grown from supersaturated solutions.

Habit modification of aragonite crystals was based on previous observations which showed that  $\text{Li}^+$  ions can selectively stabilize the basal (001) faces of the thermodynamically stable polymorph, calcite.<sup>7</sup> This effect has been rationalized by atomistic simulation which indicated that incorporation of  $\text{Li}^+$  ions into surface  $\text{Ca}^{2+}$  lattice sites specifically lowers the surface energy of the polar (001) plane of calcite.<sup>8,9</sup> Moreover, because the spatial arrangement of  $\text{Ca}^{2+}$  ions is very similar in the (001) planes of both calcite and aragonite, an analogous effect might be expected for the metastable polymorph. Indeed, aragonite crystals grown in the presence, but not the absence, of  $\text{Li}^+$  were characterized by well-defined outgrowths consisting of six prismatic side faces truncated by a relatively large and flat pseudo-hexagonal end-face (Fig. 1).<sup>†</sup> The angular relations between these faces were consistent with the indexing of the end face as (001), with four {110} and two {010} side faces. Interestingly, the large (001) face is reminiscent of the tabular aragonite morphology observed in the nacreous shells of many molluscs.<sup>10</sup>

The presence of  $\text{Li}^+$  in the above experiments had no influence on the morphology of vaterite. This is consistent with a common mechanism of morphological modification based on the structural correspondence of the aragonite and calcite (001) faces and their dissimilarity to the vaterite structure. Both the calcite and aragonite (001) faces consist of a uncharged layer of  $\text{Ca}^{2+}$  ions with interatomic spacings of approximately 0.5 nm, but differ in that the  $\text{Ca}^{2+}$  net of aragonite is distorted from

hexagonal and there are two layers of carbonates and not one between each  $\text{Ca}^{2+}$  (001) plane. As the aragonite (001) plane is either all cationic or anionic, there is a net dipole along the [001] direction which could be neutralized by  $\text{Li}^+$  incorporation into empty surface lattice sites such that the (001) face is preferentially stabilized and expressed in the growth morphology.

Changes in the morphology of vaterite were achieved by growing crystals from supersaturated solutions containing a linear poly  $\alpha,\beta$ -aspartate of  $M_r$  7100.<sup>‡</sup> Previous studies have shown that macromolecules such as polyvinyl alcohol and fish antifreeze proteins are highly selective for vaterite nucleation,<sup>6</sup> whilst poly  $\alpha$ -aspartate is a potent inhibitor of calcite crystallization,<sup>12-14</sup> but there are no reports describing morphological modifications in vaterite crystallization. Addition of the linear

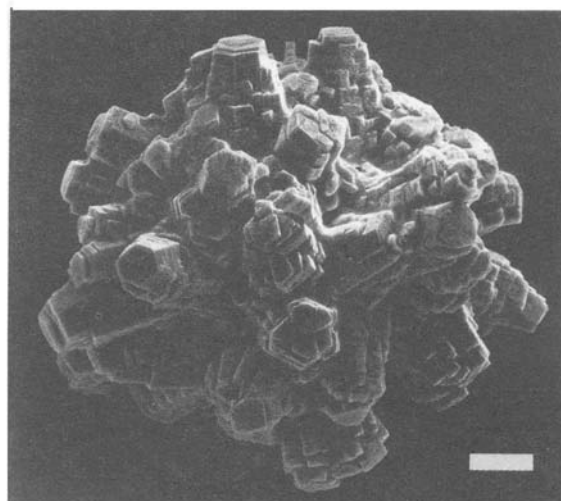


Fig. 1 Scanning electron micrograph showing the expression of (001) tabular faces in aragonite crystals grown in the presence of  $200 \text{ mmol dm}^{-3}$   $\text{Li}^+$ . Scale bar =  $10 \mu\text{m}$ .

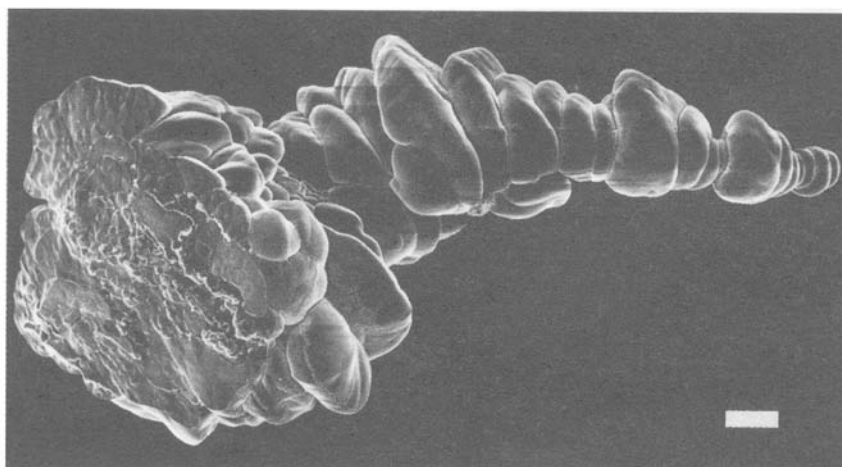
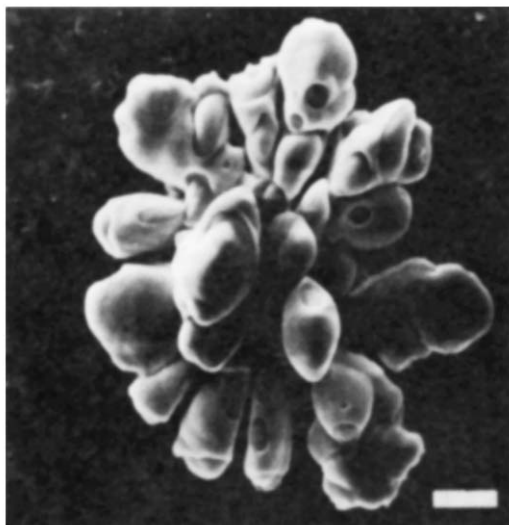


Fig. 2 Scanning electron micrograph showing the helicoid outgrowth of stacked vaterite disks from a disordered polycrystalline aggregate. The crystals were grown in the presence of  $10 \text{ mg dm}^{-3}$  of a linear poly  $\alpha,\beta$ -aspartate of  $M_r$  7100. Scale bar =  $10 \mu\text{m}$ .

poly  $\alpha,\beta$ -aspartate to the crystallization medium resulted in almost exclusive nucleation of vaterite whereas the control crystals were predominantly calcite with approximately 10–15 mass% of vaterite in the form of a characteristic intergrown floret morphology.<sup>15</sup> By comparison, rounded polycrystalline aggregates of vaterite (50–500  $\mu\text{m}$  in size) were observed after 40 h of growth in the presence of the peptide. These aggregates consisted of a random intergrowth of disk-shaped units and had unusual helicoid outgrowths (Fig. 2). The outgrowths were up to three times the size of the associated aggregate and appeared to consist of either a right- or left-handed stack of disk-shaped vaterite crystals aligned along their  $c$  axes.

The formation of helicoid architectures of vaterite is reminiscent of the unusual morphologies sometimes observed in experiments involving the crystallization of inorganic salts in partially solubilized silica gels<sup>16</sup> or in viscous media.<sup>17</sup> In turn, these observations are similar to those commonly reported in 'crystal gardens'. In general, diffusion-limited processes involving the formation and subsequent rupture of inorganic semi-permeable membranes associated with the surface of the developing crystals have been postulated to account for these observations.<sup>18</sup> In this regard, electron micrographs of the early stages of helicoid formation clearly showed the presence of a surface membrane on the vaterite crystals (Fig. 3). Thus, it is probable that the adsorption of poly  $\alpha,\beta$ -aspartic acid at high surface concentration on the crystal faces of vaterite results in an amorphous  $\text{CaCO}_3$ -peptide gel which inhibits further crystal growth. In addition, the electron micrographs show microscopic pores in the surface coating (Fig. 3) suggesting that localised fragmentation of this membrane, perhaps due to increasing osmotic pressure in the gel, could be responsible for episodic outgrowth along a direction dictated by supersaturation and diffusion gradients in the surrounding medium. Moreover, the presence of the helical twist suggests that a screw dislocation along the vaterite  $c$  axis couples with the diffusion gradients in



**Fig. 3** Scanning electron micrograph showing the early stages of growth of vaterite crystals in the presence of poly  $\alpha,\beta$ -aspartate. The crystals are coated in a surface membrane containing macropores. Scale bar = 10  $\mu\text{m}$ .

propagating the crystallization process. This is probably a generic process—for example, a recent preliminary study reports the formation of helical calcite morphologies in supersaturated solutions containing poly L-aspartic acid<sup>19</sup>—and is not highly dependent on any precise structural recognition at the gel–crystal interface.

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## Footnotes

† Calcium carbonate crystallization was carried out in the absence and presence of  $\text{Li}^+$  ( $[\text{Li}^+] = 200 \text{ mmol dm}^{-3}$ ;  $[\text{Ca}]:[\text{Li}]$  mol ratio = 1:20) according to a previous procedure.<sup>7</sup> X-Ray diffraction and scanning electron microscopy showed that, with and without  $\text{Li}^+$ , the product after 100 hours was a mixture of calcite, aragonite and vaterite, in a ratio of approximately 60:30:10, respectively. No changes in the lattice parameters were observed for each of the three polymorphs grown in the presence of  $\text{Li}^+$ . Aragonite crystals in the control experiments were in the form of multicrystalline aggregates of intergrown needle-shaped crystals elongated along the  $c$  axis.

‡ Crystals of calcium carbonate were grown from supersaturated calcium hydrogen carbonate solutions containing 1–10  $\text{mg dm}^{-3}$  of a linear poly  $\alpha,\beta$ -aspartate of  $M_r$  7100.<sup>11</sup> The experimental protocol was similar to that used in the aragonite experiments described above. Crystallization in the presence of the peptide was kinetically inhibited, although the final crystal yield after 100 h was similar to that in the control experiments. Lower levels of additive (0.05–0.5  $\text{mg dm}^{-3}$ ) also favoured the precipitation of vaterite but had no effect on the morphology or texture of the crystals.

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