Biomineral vaterite spicules do not grow from amorphous calcium carbonate, they grow ion by ion from solution

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Biominerals formed by animals provide skeletal support, and many other functions. They were previously shown to grow by aggregation of amorphous nanoparticles [1], but never to grow ion-by-ion from solution, which is a common growth mechanism for abiotic crystals. We analyze vaterite ($CaCO_3$) multi-crystalline spicules from the solitary tunicate *Herdmania momus*, with Polarization-dependent Imaging Contrast (PIC)-mapping [2], scanning and aberration-corrected transmission electron microscopies. Quantitative PIC-mapping data measured 0°-30° angle spreads between immediately adjacent crystals. There are no organic layers at the interface between crystals, hence a new, unknown growth mechanism must be invoked, with crystal nucleation constrained within 30°. Two observations are consistent with crystal growth from solution: vaterite microcrystals express crystal faces, and are smooth at the nanoscale after cryo-fracture [3].

The observation of 30° angle spreads, lack of interfacial organic layers, and smooth fracture figures broadens the range of known biomineralization mechanisms and may inspire novel synthetic crystal growth strategies. Spherulitic [4] growth from solution is one possible mechanism consistent with all these observations.

[1] De Yoreo *et al*. (2015) *Science* **349**. [2] Gilbert *et al*. (2011) *Proc. Natl. Acad. Sci.* **108**, 11350-11355. [3] Pokroy *et al*. (2015) *Chem. Mater.* **27**, 6516–6523. [4] Shtukenberg *et al*. (2011) *Chem. Rev.* **112**, 1805-1838.