

Transport of Amorphous Calcium Carbonate to Forming Nacre

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With a sophisticated brick-and-mortar or columnar ultrastructure providing enhanced toughness and beautiful iridescence, nacre, or mother-of-pearl, has long been a major subject in biomineralization research. Recently, DeVol et al. [1] confirmed that nacre is formed via amorphous calcium carbonate (ACC) precursors with direct evidence from X-ray PhotoEmission Electron spectroMicroscopy (X-PEEM) [2–5]. The ACC phases only persist in the towers of forming tablets in red abalone nacre, and fully crystallize in mature nacre. However, ACC is well known for its naturally short lifetime because it crystallizes once it comes into contact with water or with an already formed crystal. How the amorphous precursors stay amorphous during transport down to the base of forming nacre towers, and how they traverse previously-formed organic sheets, with extrapallial fluid or gel in between, remains a mystery. Our hypothesis is that the ACC precursor particles are transported by specialized cell processes that deposit ACC directly onto the surface of forming tablets, without much contact with the extrapallial fluid or the gel environment. In this study, we use Scanning Electron Microscopy (SEM), and X-PEEM to directly reveal the deposition pathway of ACC precursors from cells to form nacre in red abalone (*Haliotis rufescens*). If confirmed, this work will demonstrate how aragonite tablets are formed from ACC precursors, and is strikingly similar to the mechanism observed in sea urchin spicules: in both systems ACC transport occurs in intracellular vesicles [6] and deposition is directly and actively done by cells all the way to the mineral surface [7, 8], which grows particle by particle [9]. Nacre and spicules are dramatically different structurally, morphologically, chemically, and mechanically. If our hypothesized mechanism is confirmed in red abalone forming nacre, it may be possible to generalize the formation processes to other biominerals.

[1] R. T. DeVol *et al.*, *J. Am. Chem. Soc.* **137**, 13325–13333 (2015). [2] G. De Stasio *et al.*, *Phys. Rev. E.* **47**, 2117–2121 (1993). [3] G. De Stasio *et al.*, *Ultramicroscopy.* **98**, 57–62 (2003). [4] B. Gilbert *et al.*, *Ultramicroscopy.* **83**, 129–139 (2000). [5] P. U. P. A. Gilbert *et al.*, *Proc. Natl. Acad. Sci. U. S. A.* **108**, 11350–11355 (2011). [6] N. Vidavsky *et al.*, *Proc. Natl. Acad. Sci. U. S. A.* **111**, 39–44 (2014). [7] E. Beniash *et al.*, *Proc. R. Soc. B Biol. Sci.* **264**, 461–465 (1997). [8] E. Beniash *et al.*, *J. Struct. Biol.* **125**, 50–62 (1999). [9] J. J. De Yoreo *et al.*, *Science.* **349**, aaa6760 (2015).