Crystallization by particle attachment (CPA) in biominerals over 550 million years

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Diverse marine organisms form their biominerals using crystallization by particle attachment (CPA)(1) of the same two amorphous calcium carbonate (ACC) precursor phases, which then crystallize into either calcite or aragonite, respectively, in echinoderms (2-4) or mollusk shell nacre (5) and coral skeletons (6), as revealed by difficult, lengthy, synchrotron spectromicroscopy experiments (7).

Much simpler SEM experiments show that when the biominerals are formed via attachment of ACC nanoparticles, they also appear nanoparticulate after cryofracturing, with nanoparticle size in the 50-400 nm range. The latter is thus a proxy for the former. Vaterite crystals from tunicate spicules, which do not form via ACC (8), do not exhibit nanoparticulate cryofracture-figure. Having validated this proxy on well-known, modern biominerals, we used nanoparticulate texture as a proxy for crystallization by CPA in modern and fossil biominerals.

We find that CPA is convergent: it has evolved independently in diverse phyla, including the oldest know animal fossil, the Ediacaran *Cloudina* (550 Ma), Cambrian (500 Ma) shelly fossils, nacre from the Ordovician (450 Ma), the Cretaceous (100 Ma), the Miocene (13 Ma) and modern (0 Ma) mollusks.

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