Morphogenesis and chemical coupling in silica biomorphs

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Bizarre as it might seem, purely inorganic processes may produce self-assembled complex crystalline materials that –like those produced by living organisms- are not controlled by crystallographic symmetry. Such a kind of crystalline materials must be -by definition- polycrystalline, because the restricted point symmetry of the single crystal must be expanded in order to develop complexity. Complexity means in this context self-assembled shapes with either positive or negative Gaussian constant curvature. Silica biomorphs is a synthetic type of material that shares with life complexity, morphology, hierarchy and self-assembly yet they are remarkably simple in chemical terms (1,2). The synthesis requires only a source of carbonate ions (e.g. atmospheric CO2), strong alkaline aqueous solutions, silica and alkaline-earth cations (Ba and Sr, Ca). Under these alkaline conditions, the precipitation of alkaline-earth carbonates (witherite, strontianite or calcite/aragonite) coupled with silica yields aggregates made of millions of nanocrystals exhibiting self-assembled complex non-crystallographic morphologies. There have been significant advances in the understanding of these fascinating and challenging structures (see reference 1). A phenomenological explanation of the morphogenesis of these complex structures has been already achieved (3) while the chemistry triggering their formation is thought to be an autocatalytic process due to the coupling of silica and carbonate precipitation, because of their reverse solubility with respect to pH. This theory has not been yet experimentally validated because the difficulty to measure pH oscillations at the scale of hundred of microns. Another fascinating feature, still unexplained, is the role of crystal structure in controlling the morphology of silica biomorphs. It is known that shapes with continuous curvature are only made by aragonite-type structures (aragonite, witherite, strontianite), while rombohedrical type structures (calcite) only form complex fractal shapes. I will review in this talk the latest experimental achievements towards a better understanding of silica biomorphs, namely a) high-resolution pH monitoring in real time and space by fluorescence optical microscopy and b) experiments designed to relate shape with crystal structure. The findings will be discussed in the framework of the current theory of formation of silica biomorphs.

1. M. Kellermeier, H Cölfen, and J.M. García-Ruiz. *European Journal of Inorganic Chemistry* (2012) 5123–5144. Doi: 10.1002/ejic.20121029.

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