Confinement and Additives Lead to Control over Calcium Sulfate and Phosphate Polymorph

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It is widely known that nanoscale confinement and additives can control the polymorphs of organic crystals, there have been few systematic studies of the precipitation of inorganic crystals in constrained volumes. To investigate this further, the precipitation of calcium sulfate and calcium phosphate in confinement were studied, principally using TEM. Two half-crossed cylinders were used to create an annular wedge which provided a separation that varies continuously from zero to tens of microns. The focus is on the stability and transformation of mestable and amorphous phases.

For calcium sulfate, the crystal polymorph changed from calcium sulfate dihydrate to amorphous calcium sulfate via calcium sulfate hemihydrate with enhanced confinement. Interestingly, the growth of calcium sulfate is also inhibited by the presence of additives. The combined effects of confinement and additives are investigated. With the addition of inhibitors like poly(acrylic acid) or sodium triphosphate, the lifetimes of the amorphous phase and hemihydrate were extended with increased concentration of additives. It was therefore suggested that these results not only have immediate relevance to salt weathering and biomineralization processes, but are also important to the many crystallization and aggregation-driven processes occurring in small volumes.

The work also investigates the effect of confinement on the crystallization of calcium phosphate (CaP) crystals in the presence and absence of PAsp. Some thin plate-like octacalcium phosphate (OCP) crystals were formed, at the surface separation of 1 μm, in the absence of PAsp. Interestingly, with addition of PAsp, agglomerations of nanoparticles were nanospheres also observed, shown as OCP. Amorphous calcium phosphate was observed in both confinement and additive. Although the method and reaction system employed was rather simple so it cannot be considered as a direct mimic of calcium phosphate precipitation in collagen, we do believe the experiments can provide insight into the control mechanisms which may operate *in vivo*.