

Confinement of calcium carbonate – solution interfaces

ROSA M. ESPINOSA-MARZAL

University of Illinois at Urbana-Champaign –
Email: rosae@illinois.edu

Understanding the effect of nanoconfinement on the solution composition near the mineral surface is crucial in revealing the mechanisms of (bio)mineralization, because the confined thin film of aqueous electrolyte, which provides the path for ions and water to the buried mineral interface, can behave totally different from the unconfined solution. Two mineral-solution interfaces are discussed in this talk. First, I will provide a general conceptual picture of Derjaguin–Landau–Verwey–Overbeek (DLVO) and non-DLVO forces considering calcite's nonclassical Stern layer. I will show that the confined calcite interface is composed of water layers and calcium ions of different hydration states, which can be distinguished by the different size of the resolved layers and the applied work to squeeze the species out in force measurements. The proposed picture is in good agreement with our knowledge about the unconfined calcite interface, but our results indicate that nanoconfinement affects the population of calcium ions of different hydration states at the calcite–solution interface. It is also discussed how the supersaturation of the nanoconfined solution can be tuned by varying calcium concentration, as well as the implications for the mineral dissolution-recrystallization process under nanoconfinement.

The second example is focused on amorphous calcium carbonate (ACC) nanoparticles that have aggregated under the spatial confinement provided by nano-globules of a biomimetic polymer. The colloidal stability of ACC nanoparticles is determined by the interplay among the surface properties of ACC, the organic template, and the additives. Force measurements and x-ray/light scattering are combined to comprehensively understand how the ACC interfacial properties and interaction forces influence the colloidal stability of ACC nanoparticles in solution. It is shown that non-DLVO steric repulsive forces play a key role on the stability of the selected system.

Calcium carbonate mineralization occurring in confined spaces and nanopores is central to many natural processes occurring at or near the Earth's surface. Our work scrutinizes the greatly unexplored relation between surface science and mineralization in order to understand the physicochemical phenomena occurring at nanoconfined mineral interfaces.