

Effects of acidic organic molecules on the solvation of biologically relevant divalent cations

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Biomolecules rich in aspartic acid (Asp) are known to play a role in biomineral morphology and polymorph selection, and have been shown to greatly enhance the growth kinetics of calcite. These compounds may favor calcification by partially desolvating cations to lower the energy barrier to mineralization [1]. To test the idea that biomolecular species modulate ion hydration environments, we investigated the influence of acidic amino acids and dipeptides on the solvation of divalent cations using molecular dynamics (MD). For each simulation we monitored the hydration environment of a divalent cation (Mg, Ca, Sr) in the presence of an acidic amino acid or dipeptide (Asp, AspAsp, AspLeu). Calculated radial distribution functions were used to determine the structure of the primary hydration shell at various cation-organic separation distances. Free energy profiles for the complexation of cations in solution by carboxylate moieties were generated by umbrella sampling and the weighted histogram analysis method (WHAM). All simulations were carried out with the LAMMPS software employing the TIP3P model of water, CHARMM22 force field, and Åqvist ion-water potentials [2].

We show the hydration environments of Ca and Sr are perturbed as the ions approach the negatively charged amino acid carboxylate groups. Complexation of Ca and Sr by the carboxylate oxygen atoms results in a decreased total first shell coordination number relative to the ions in bulk water. The primary solvation shell of Mg is largely unchanged by organics until the physical replacement of a water molecule with a carboxylate oxygen, which appears to be highly unfavorable energetically. Proximity to organics has no effect upon ion-oxygen distances of waters in the first hydration sphere. The calculated energy barrier for Ca association with the biomolecules is very small (a few kT). For Sr, sterics appear to prevent the larger ion from taking the same path of approach as Ca, resulting in a larger energy cost. The findings suggest origins of biomolecule-specific influences on nucleation and growth of calcium carbonates and phosphates and the roles of matrix organic molecules in biomineral phase selection.

[1] Elhadj *et al.* (2006) *Proc. Natl. Acad. Sci. USA* **103** 19237.

[2] Åqvist (1990) *J. Phys. Chem.* **94** 8021.

Stability of dissolution flutes under turbulent flow

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Dissolution of mineral surfaces such as carbonate, gypsum or ice under turbulent flow can lead to periodic roughness on a centimeter scale, known as scallops. Flutes are ripple-like scallops, normal to flow. Such structures are important paleoflow indicators in caves. It has previously been known that dissolution flutes can become stable in time, except for stiff translation of the whole pattern both normal to and parallel with the surface [1]. This shape stability requires a certain compatibility between flute shape and the resulting dissolution profile. We will present simulation results from 2D hydrodynamics modelling using a k -epsilon turbulence model in a fixed geometry, coupled with gypsum dissolution and the mean-flow advection and eddy diffusion of calcium and sulphate. The numerical simulations reproduce the dissolution profile required for shape stability, except for poor resolution of flow separation at the flute crest. To obtain a reasonable dissolution profile, it was necessary to include the effect of turbulence on the thickness of the diffusion-limiting boundary layer. The study demonstrates the feasibility of modelling surface dissolution and precipitation under complex, turbulent flow. Such modelling may aid the interpretation of natural structures in terms of flow velocity and flow reversal.

[1] Blumberg & Curl (1974) *J. Fluid Mech.* **65** 735-751.