

Effect of Organic - Mediated Water Restructuring in Modifying Mineral Precipitation Rates

Nita Sahai, Donald Mkhonto, Yang Yang and Zhijun Zhu

Department of Geoscience, University of Wisconsin, Madison, WI 53706

We used Molecular Dynamics (MD) simulations and bioinformatics approach to study the mechanisms of organic-mediated nucleation and growth of hydroxyapatite (HAP) and calcite. A 10 amino-acid anion peptide did not promote templated nucleation of crystalline HAP within the 25 ns time-scale of the simulation, but rather, an amorphous Ca-PO_4 precursor. The peptide interacted with the HAP (001), (100) and (110) surfaces (Fig. 1 a- c) non-specifically (no templating), and the peptide could not penetrate the surface solvation layer. A small anionic ligand, succinate, was also unable to displace surface hydration waters from the calcite surface over the simulation period. When removed manually, succinate adsorbed preferentially in specific step directions, thus, controlling crystal growth by modifying step movement rates but, again, stereochemical templating was not the controlling factor. A balance of electrostatic and solvation energies were important in determining binding geometry and energy.

The results of our studies indicate that the computational approaches developed here may be extended to understand the formation of other sparingly soluble minerals such as barite that are formed in petroleum recovery pipes. Beyond petroleum chemistry and recovery, our study also provides a fundamental basis for understanding the mechanistic controls on the formation of unusual crystal morphologies of biominerals that may serve as biosignatures on Earth and, potentially, on other worlds, for designing biomimetic materials synthesis pathways and for technological processes such as scale inhibition.

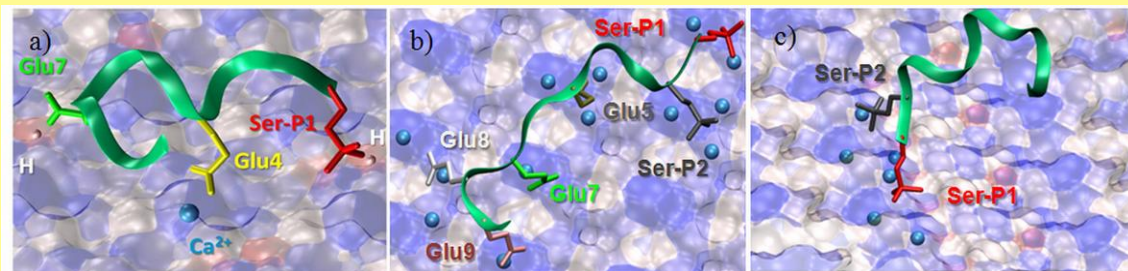


Figure 1. Lowest-energy peptide structures adsorbed on HAP crystal faces: (a) (001), (b) (100), and (c) (110). The peptide backbone is rendered in ribbons. The sidechains which form direct interactions with HAP surface ions (represented in CPK with hydrogen in white and Ca^{2+} in cyan) are rendered in licorice with their names labeled. The HAP surface is rendered in the surf mode. A water layer separates the peptide from the surface, and the anionic side-chains (glutamate and phosphorylated serine) do not match Ca^{2+} positions on the HAP surfaces, implying no stereochemical templating effect.

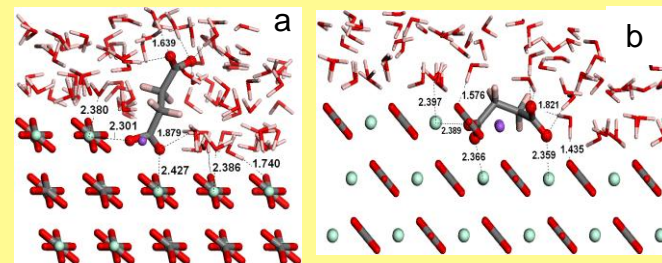


Figure 2. Structures of the solvated succinate molecule, where surface water has been removed manually to allow direct binding, on the (104) face at (a) vicinal obtuse step and (b) obtuse CO_3^- - terminated step. Ca = green, O = red, C = grey, H = pink, Na = purple.