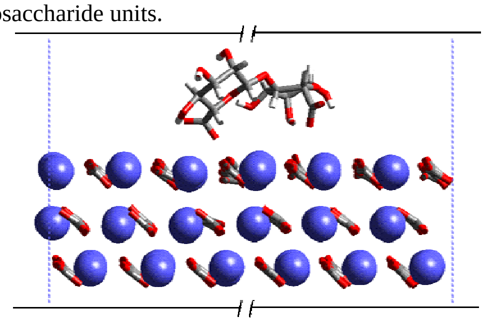
Alginic Acid Conformations and the Calcite-Water Interface

R.T. CYGAN[1] T.D. PERRY[2] AND R. MITCHELL[2]

[1] Geochemistry Department, Sandia National Laboratories; rtcygan@sandia.gov
[2] Division of Engineering and Applied Sciences, Harvard University; tperry@deas.harvard.edu; mitchell@deas.harvard.edu

Solution and surface complexes of polysaccharides are observed in many environments and are important for predictive environmental modeling and numerous industrial technology applications [1,2]. The complexities of the cation-organic interactions are well suited for predictive molecular modeling. Conformation and configuration of polysaccharides and their influence on cation binding and calcite dissolution can be critically evaluated. Alginic acid was chosen as a model polymer system and representative disaccharide and polysaccharide subunits were developed. Molecular dynamics simulation of the torsion angles of the ether linkage between various monomeric subunits identified local and global energy minima for selected disaccharides. The simulations indicate stable disaccharide configurations and a common global energy minimum for all disaccharide models at $\Phi = 274 \pm 7°$, $\Psi = 227 \pm 5°$, where Φ and Ψ are the torsion angles about the ether linkage. The ability of disaccharide subunits to bind calcium ions and to associate with the $(10\bar{1}4)$ surface of calcite was also investigated. Molecular models of disaccharide interactions with calcite, including explicit hydration, provide binding energy differences for conformations that are related to the proximity and residence densities of the electron-donating moieties with calcium ions on the calcite surface. These differences are controlled, in part, by the torsion of the ether linkage between monosaccharide units.



MD snapshot of an equilibrated disaccharide bound to the calcite surface through multiple carboxylate and hydroxyl moieties. Water molecules have been removed, and a subset of the simulation cell is shown, to assist in visualization.

References

[1] Perry, T.D., Cygan, R.T., and Mitchell, R. (2006) *GCA*, **70**, in press.
[2] Welch, S.A. and Vandevivere, P. (1994) *Geomicrobiology Journal*, **12,** 227-238.