

Developing models to predict silicate mineral dissolution

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The goal of this project is to develop a model that allows prediction of the rate of silicate mineral dissolution over a wide range of pH and temperature. Such a model would be useful for rate prediction when data is unavailable as well as to elucidate inconsistencies among published data for mineral dissolution kinetics. We describe an empirical model and an approach to seek theoretical constraints on this model.

Previous experiments have identified key factors which affect silicate dissolution rates and have been included in an empirical model. Casey and Westrich [1] showed that the rate of water exchange around an octahedral cation is correlated to the mineral dissolution rates in orthosilicates; a similar but weaker correlation has been observed in pyroxenes [2]. This does not necessarily suggest that water is exchanging at this cation in the the dissolution mechanism since this correlation: the correlation could be an indirect measure of metal-O bond strength within a mineral structure. It has also been suggested that minerals with a lower connectedness (the number of bridging oxygens per tetrahedron) dissolve more quickly than minerals with a higher degree of polymerization.

We compiled data from approximately 70 laboratory studies of silicate dissolution (see ChemXSeer (<http://chemxseer.ist.psu.edu/>), an online database focused on environmental kinetics data). Minerals considered include orthosilicate, pyroxene, amphibole, sorosilicate, and phyllosilicate groups. We observe a strong correlation between $\log r$ and pH, k_{solvs} , connectedness, and temperature.

We are furthermore using *ab initio* quantum mechanical modeling of hydrolysis of cations in silicate structures as a function of cation identity to establish a theoretically based underpinning to the empirical model. We are using this approach to calculate rate constants as a function of pH using the POLYRATE program [3].

[1] Casey & Westrich (1992) *Nature* **355**, 157-159.
[2] Banfield *et al.* (1995) *GCA* **59**, 19-31. [3] Nangia & Garrison (2008) *J. Phys. Chem. A*.

Carbonate precipitation potential by cyanobacterial activity in high Arctic cryptoendolithic habitats

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Cryptoendolithic habitats are host to a wide variety of microorganisms including cyanobacteria, algae, fungi and heterotrophic bacteria and are found in both hot and cold deserts. Low pH conditions are normally associated with these habitats due to the generation of acidity by fungi, but recent studies [1, 2] reveal elevated pH conditions associated with cyanobacterial-dominated microbial communities. These high pH conditions are result from the activation of a carbon concentrating mechanism in these microorganisms to generate OH⁻ ions that are expelled from the cell into the surrounding microenvironment. In addition to enhancing dissolution of the sandstone framework including etching of quartz grains and dissolution of silica-rich intergranular cements [1] elevated concentrations of Ca²⁺ ions in proximity to these communities [2] suggest that they can induce carbonate precipitation during photosynthesis [1].

Although described previously from aquatic environments [3], little is known about mechanisms for carbonate biomineralization in terrestrial habitats. The current study investigates the potential for carbonate precipitation by cyanobacteria isolated from high Arctic cryptoendolithic habitats around Eureka, Ellesmere Island, Nunavut (80°00'N, 85°55'W). Through examination of specific surface functional groups, potentiometric titration experiments and TEM observations, we propose that the same mechanism for carbonate biomineralization can occur here, whereby binding of metal cations onto cell surfaces – combined with excess production of OH⁻ during cyanobacterial photosynthesis – generate conditions suitable for mineral precipitation in this high pH setting to create unique terrestrial biosignatures in silicate rocks.

[1] Büdel *et al.* (2004) *Geobiology* **2**, 261-268. [2] Omelon *et al.* (2007) *Microb Ecol* **54**, 740-752. [3] Thompson *et al.* (1998) *Geology* **18**, 995-998.