

Evaluating fluid dynamic and geochemical perturbations in seafloor hydrothermal systems by subsurface biofilms using a novel flow-through experimental apparatus

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The experimental design is able to monitor deviations in temperature, fluid flow, and sulfur redox chemistry in real-time as a result of fluid mixing and biomineralization. Potentially, the overall effect of subsurface biofilms and biomineralization on fluid flow and mixing of endmember fluids through porous chimney deposits is large. A novel flow-through experimental design allows the evaluation of changes in fluid flow, hydraulic conductivity and permeability using infrared technology to monitor temperature change resulting from mixing of two end-member fluids simulating hydrothermal and ambient seawater sources. Preliminary results using the abiotic precipitation of amorphous Fe (III) oxyhydroxide as a proxy for subsurface biomass/microbial biomineralization show distinct disruption of fluid flow and mixing patterns on a centimeter scale. We are working with a model culture of *Thiomicrospira thermophila* strain EPR 85 (C. Vetriani, Rutgers Univ.), which has an optimal temperature range of 35-40°C, optimal pH of 6.0, and the ability to grow chemoautotrophically by oxidizing thiosulfate to sulfate or amorphous elemental sulfur [1]. Chemical shifts in the sulfur redox system can be monitored using electrochemical techniques developed by Luther *et al.* [2] both within the apparatus and in the outflow stream.

[1] Takai *et al.* (2004) *IJSEM* **54**, 2325-2333. [2] Luther *et al.* (2002) *ACS* **811**, 54-73.

Thermodynamic and phase behavior of alkali-bearing framework silicates

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A principal interest of this laboratory has been the thermodynamic mixing properties of solid-solution series and their correlation with phase equilibria. Although we have investigated mixing in feldspar, feldspathoid, zeolite, mica, glass, and apatite systems, much of our work has focused on framework silicates. What follows are some of our observations: On the effect of Al-Si order/disorder in alkali feldspars, ordered microcline/low-albite feldspars have greater enthalpies of mixing (H_{ex}) than disordered sanidine/analbite analogs, correlating well with the higher critical temperature (T_C) of the ordered-feldspar solvus. H_{ex} values for Rb-K feldspars are far less than those of Na-K feldspars, reflecting relative sizes of the substituting cations. The substitution of ternary An in K-Na feldspars decreases mixing energies, as it shortens the K-Na substitutional span across the series.

Nepheline-kalsilite crystalline solutions behave differently than feldspars, as the end members have different structures, nepheline with two different-sized alkali sites and kalsilite with one. Al:Si ratio has a large energetic effect on both end-member and mixing enthalpies, and as well on solvus T_C , which varies by 300 °C among three series having different Si contents. Calorimetric and phase equilibrium data, when taken together, suggest that excess entropy must play a significant role in nepheline-kalsilite thermodynamic behavior.

We also have studied thermal expansion in multiple framework silicate series, with particularly interesting results for feldspars. Relationships are shown well on a plot of thermal expansion coefficient (α) against room-temperature volume (V_{RT}). In $AlSi_3$ feldspars, expansion is controlled largely by size of the monovalent alkali-site occupant, where chemical expansion limits thermal expansion. In Al_2Si_2 feldspars, expansion is uniformly limited by partially-covalent bonds between divalent-site occupants and bridging Al-O-Si oxygens, regardless of cation size. Coupled substitution in plagioclase, Ba-K, and Ca-K feldspar series shows expansion behavior that rapidly transitions from one control (bonding) to the other (ion size). Generally, α varies linearly as a function of V_{RT} between the relevant end members of any series. Thus, the thermal expansion of a feldspar can be determined simply from knowledge of its chemical system and room-temperature volume. These relationships make it easy to calculate the volumes of mixing for any feldspar series as $f(T)$.