Effect of Al/B ratio on the dissolution of nepheline glass, $Na_3(Al, B)_{1-4}Si_4O_{16}$

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The release of alkalis from glass, via metal-H^+ counter diffusion, is widely recognized as an important mechanism in the initial stages of glass-water interactions. Our findings from experiments conducted with other boroaluminosilicate glass compositions suggest the alkali exchange (Na-IEX) mechanism may be more important than previously realized. To evaluate the factors that affect the Na-IEX mechanism, flow-through experiments were conducted as a function of pH at 40°C on four glass compositions along the nepheline-malinkoite join. The composition of each glass varied inversely in wt% of Al (5 to 20 wt%), and B (20 to 5 wt%) with Na (25 wt%) and Si (50 wt%) making up the remaining amount. The influence of glass structure on the glass corrosion rate was probed by magic-angle spinning nuclear magnetic resonance (MAS-NMR) spectroscopy in which the local coordination environments of ^{27}Al, ^{11}B, and ^{29}Si for each glass composition were determined.

MAS-NMR spectra suggest changes in three- and four-fold coordinated B as the B/Al ratio was manipulated. Preliminary evaluation of the B local coordination, suggest that as the wt% of B increased from 5 to 20 wt%, the relative concentration of tetrahedrally coordinated B also increased, although more data is needed. Unlike B which has two coordinations, Al and Si are only tetrahedrally coordinated.

Results from the flow-through experiments showed a typical matrix dissolution rate increase with an increase in pH for all glass compositions. In contrast to matrix disssolution, as pH decreases the mechanism of Na-IEX becomes more important. In other words, as matrix dissolution decreases and the concentration of H^+ increases the influence of Na-IEX on glass dissolution increases.

The results obtained in this study emphasize the importance of glass structure on the mechanism of alkali-ion exchange.

Dissolution rate dependence on reactive surface sites

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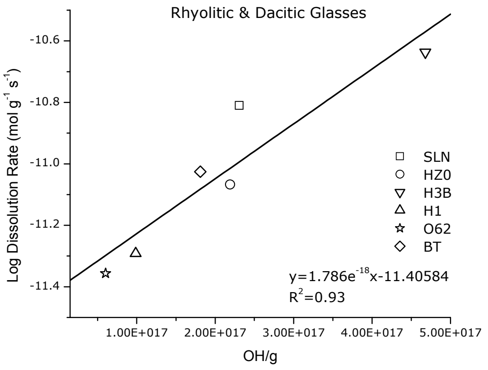
Dissolution rates are known to be dependent upon bulk mineral composition (*e.g.* cation species), but very little information is available regarding the molecular level surface composition and how it affects dissolution rates. A critical element for understanding the mechanisms and kinetics of adsorption and dissolution of natural minerals is their surface chemistry. To that end, we have used solid state nuclear magnetic resonance (NMR) to quantify the reactive site density on a suite of rhyolitic, dacitic, and basaltic glasses [1].



The above graph depicts surface hydroxyl groups per gram as measured by ^{19}F NMR correlated to dissolution rates normalized to mass, rather than BET or geometric surface area. Surface modification with a molecular probe containing fluorine generates a large NMR signal, allowing very low surface area materials to be examined (<1 m^2/g). Although our molecular probe method cannot currently distinguish between aluminols and silanols we are investigating new NMR methodologies capable of targeting and quantifying specific surface hydroxyl species.

Reference

[1] Domenik Wolff-Boenisch et al. (2004) *Geochimica et Cosmochimica Acta*, 68 (23), 4845-4858