Speciation of water in basaltic to rhyolitic glasses investigated through ^{1}H MAS NMR

*Michael R Ackerson[1], Bjorn Mysen[1], George Cody[1]

1. Geophysical Laboratory of the Carnegie Institution for Science

Water plays a significant role in the chemical and physical properties of silicate melts, the stability of mineral phases, and magmatic eruptive style. Understanding the mechanisms by which water is incorporated into melts [as molecular water (H_2O_{mol}) or hydroxyl (OH^-)] is critical to interpreting water's role in magmas[1] in subduction zones. We performed ^{1}H solid-state magic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy on a suite of glass compositions from basalt to rhyolite and water contents from 1-20 wt. pct. H_2O at lower crustal pressures (1.5 GPa) to assess the influence of glass chemistry on the incorporation mechanisms and structure of water in volcanic glasses and melts.
The ^{1}H MAS NMR spectra contain information on the speciation of water and the bonding environment of ^{1}H in quenched glasses at their glass transition temperature. The ratio of the area of the centerband to that of the centerband plus the spinning side bands in ^{1}H MAS NMR spectra has been demonstrated as a technique to estimate H_2O_{mol}/OH^- in glasses[2], because an increase in the amount structurally-bound H_2O_{mol} in quenched glasses increases the intensity of the sideband peaks. The NMR spectra from basalt, andesite and rhyolite glasses with the same water content (e.g., 5 wt. pct.) exhibit similar centerband/sideband area ratios suggesting a near-constant H_2O_{mol}/OH^- with a slight shift toward larger sidebands suggesting a minor increase in H_2O_{mol} with increasing NBO/T. FTIR observations of water speciation in quenched silicate glasses[3] suggest that at high water contents, a majority of water in a melt should be incorporated as H_2O_{mol}. However, the low sideband intensities of a water-saturated rhyolite glass indicate that most of the water in the glass is incorporated as OH^-. Furthermore, at high water contents (50 mol pct.), OH^- interacting with alkali and alkaline earth species (M-OH) could cause an increase in the polymerization of the melt compared to OH-groups formed by interaction with tetrahedral cations (Si-OH or Al-OH), which will significantly lower melt polymerization. While ^{1}H NMR cannot directly resolve which cations are bonded to OH^-, future experiments using ^{23}Na and ^{29}Si NMR of these glasses will allow us to determine the degree to which OH^- is interacting with alkalis, alkaline earths, silicon and aluminum, yielding information on water solubility mechanisms and coincident melt polymerization as a function of bulk composition and bulk water content of the glasses. Combined, these datasets will provide critical information on the influence of water on melt polymerization.
In addition to information on water speciation, the frequency of the centerband in ^{1}H NMR spectra is directly proportional to the average O-H-O distance in the glasses. Increasing NBO/T of glasses from rhyolite to basalt results in a marginal decrease in the centerband frequency from 4.2 ppm to 2.7 ppm suggesting a slight overall decrease in O-H bond length with increasing NBO/T. Combined with Raman, ^{29}Si and ^{23}Na NMR, this peak shift could shed light on the specific solution mechanisms governing OH^- incorporation in silicate melts.
The results of this study are consistent with ^{1}H NMR investigations of simple systems that suggest the activities of cationic species in the melt influence the solubility mechanisms of OH^-[4]. Given that water is a critical component in the generation and evolution of subduction zone magmatism, this study is an important step toward a better understanding of the behavior of water in melts.

[1]Mysen, "Water-Melt Interaction in Hydrous Magmatic Systems at High Temperature and Pressure"
[2]Eckert et al., "Water in Silicate Glasses: Quantification and Structural Studies by 1H Solid Echo and MAS NMR Methods."

[3]Ihinger et al., “The speciation of dissolved water in rhyolitic melt.”
[4]Xue, “Water Speciation in Hydrous Silicate and Aluminosilicate Glasses: Direct Evidence from Si-29-H-1 and Al-27-H-1 Double-Resonance NMR.”

Keywords: water, NMR, rhyolite, basalt