H_2O diffusion in rhyolite at 1-2 GPa

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Water diffusion in silicate melts is crucial for understanding various volcanic processes, including bubble formation and growth, magma degassing, and magma fragmentation. H_2O diffusivity in rhyolite were previously measured at 0.1-810 MPa (Zhang *et al*., 1991; Zhang and Behrens, 2000). To better constrain the pressure effect on H_2O diffusion, we conducted diffusion-couple experiments at 407-1629°C and 1-2 GPa in piston-cylinder apparatus. After experiments, samples are doubly polished to ~200 µm thickness, and H_2O concentration profile along the centerline is measured using FTIR microscope.

Compared to Zhang and Behrens (2000), H_2O diffusivity at 1-2 GPa increases less rapidly with water cotent. H_2O diffusivity in rhyolite melt decreases from one atmosphere to 2 GPa, and such negative pressure effect is more remarkable as the temperature decreases, which leads to a larger activation energy at higher pressure. If the model of Zhang and Behrens (2000) at <2 wt.% water content is extrapolated to 2 GPa, the prediction results in roughly the same activation energy, but the predicted diffusivity is systematically lower than our measurements by a factor of about 3, which suggests a smaller pressure effect and therefore a smaller activation volume. By combining previous data and our measurements and assuming total H_2O diffusivity is proportional to total H_2O concentration, a new H_2O diffusivity model at <2 wt.% water content has been constructed, which better constrains the pressure dependence. We are also developing a general H_2O diffusivity model applicable to higher water contents and 0.1-2000 MPa.

References

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The accuracy of $\delta^{11}B$ measurements of foraminifera

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The pH of seawater reflects the speciation of dissolved carbon and hence also, in part, the extent of the partitioning of carbon dioxide between the oceans and atmosphere. Reconstructions of past seawater pH therefore allow investigations of, for example, the concentration of CO_2 in the past and the mechanisms of glacial-interglacial CO_2 change.

A number of contributions have demonstrated that the boron isotopic composition of marine carbonates, such as foraminifera, record the pH of the seawater in which they grew. Sample size requirements have led to most workers measuring the small amounts of boron in foraminifera by negative-ion thermal ionisation mass spectrometry (NTIMS), which has very high ion yields. What is more, this technique uses the Ca (plus trace metals) of the dissolved marine carbonate as an activator, requiring no additional purification and/or concentration of boron, which greatly simplifies the approach. We show here, by a comparison between the $\delta^{11}B$ of samples and solutions measured by both total evaporation NTIMS and multicollector inductively coupled plasma mass spectrometry (MC-ICPMS), that this latter feature, although seemingly advantageous, results in a significant bias in the $\delta^{11}B$ measurement by NTIMS.

We conclude that organic carbon, probably hosted within the foraminiferal shell and hence inadequately oxidised during cleaning, has a detrimental and variable effect on the thermal ionisation of boron. This effect does not necessarily relate to the presence of CN^- molecules and results in the TE-NTIMS $\delta^{11}B$ measurements being shifted to heavier not lighter values as would be expected from CNO- interference at mass 42. This matrix effect may go some way to explaining the reported large $\delta^{11}B$ differences between laboratories for similar foraminiferal samples (up to 6 ‰ disagreement by NTIMS). With careful treatment, reliable $\delta^{11}B$ data can be generated by NTIMS. However, we hope that this realisation, along with a modified loading technique outlined here, makes $\delta^{11}B$ isotope measurements by negative thermal ionisation techniques more routine and accurate.