Japan Geoscience Union Meeting 2015
(May 24th - 28th at Makuhari, Chiba, Japan)

SCG14-12 Room:303 Time:May 25 17:00-17:15

Experimental study on the origin of the D/H fractionation between silicate melts and aqueous fluids at HT/HP conditions

LE LOSQ, Charles[1*] ; CODY, George D.[1] ; DALOU, Celia[2] ; MYSEN, Bjorn O.[1]

[1]GL, Carnegie Institution for Science, [2]University of Minnesota

Subduction zones are open paths for the exchange of volatile elements between the geosphere and the atmo-, hydro- and biospheres on Earth. Water is present in the subducting slab as hydrated minerals and is released at high pressure (P) and temperature (T) during the subduction. This results in a hydrated mantle wedge, and eventually promotes volcanism in the fore-arc and back-arc regions. The water cycle can be tracked by measuring the δD of various geochemical observables. In particular, δD measured in melt inclusions trapped in crystals in back-arc magmas may reflect the δD of the slab fluids. From those values, it may be possible to assess the amount of water released from the slab to the mantle wedge by using mass balance models. However, this relies on knowledge of how D and H fractionate between silicate melts and aqueous fluids at high P and T. Results from in situ experiments of silicate-H_2O systems in a Hydrothermal Diamond Anvil Cell (HDAC) show that 1000 ln ($\alpha_{melt-fluid}$ = $[D/H]_{melt}/[D/H]_{fluid}$) values can reach -100 ‰ at 1073 K and $\sim$1 GPa, conditions similar to those at the onset of fluid-saturated melting in subduction settings. Such values are high, particularly when compared to those observed in minerals: for instance, the 1000 ln ($\alpha_{phlogopite-fluid}$) is about 7 ‰ at 1073 K. Considering that, the origin of such fractionation appears surprising. One explanation may be that, in addition to the zero-point energy contribution that usually drive equilibrium isotopic fractionation, D/H intramolecular fractionation within silicate melts may promote D/H exchange between coexisting aqueous fluids and silicate melts. Such effect is suggested by recent results from ^{2}H and ^{1}H MAS NMR of $Na_2Si_4O_9$ quenched melts equilibrated with various amounts of $(D_xH_{(1-x)})_2O$ (x = D/[D+H]) at 1673 K and 1.5 GPa, which show differences in the partitioning of D and H in the structure of the melts at their glass transition temperature.

To address this problem, we studied how the O-H and O-D bond strengths change with temperature and pressure in aqueous fluids and silicate melts for a series of HDAC experiments performed with aluminosilicate melts coexisting with fluids with various H_2O-D_2O mixtures. We also examined the local environments of H and D with ^{2}H and ^{1}H Magic Angle Spinning Nuclear Magnetic Resonance (MAS NMR) spectroscopy in $M_2Si_4O_9$ glasses (M = Li, Na or K) with 1, 3 and 6 wt% of pure H_2O or pure D_2O, and with 3 wt% of a H_2O-D_2O mixture.

Comparison of the in situ Raman spectroscopic signals assigned to O-H and O-D stretching vibrations in fluids and melts at given P-T shows significant differences in the distribution of O-H and O-D bond distances and thus strengths between melts and fluids. These differences are correlated with the observed fractionation. They may be related to the fact that water can reside as molecules (H_2O_{mol}) or as OH groups bonded to the ionic structure of the melt, the two species presenting differences in O-H bond strength. Such effect might be enhanced by an intramolecular fractionation of D and H that occurs in the melt. Indeed, comparison of ^{2}H and ^{1}H MAS NMR spectra of the $M_2Si_4O_9$ glasses shows that D and H populate the same environments, but H is more concentrated in an environment with an oxygen-oxygen distance around 295 pm. Therefore, D and H do not have the same distribution within the structure of melts at their glass transition temperature. This may arise from a volume effect and/or from an isotopic effect on the equilibrium $H_2O_{mol} + OD \rightleftharpoons D_2O_{mol} + OH$. In any case, this effect, in turn, can explain the large fractionation factors observed in the HDAC experiments. They may also lead to large δD variations in subduction zone processes, which makes use of δD to trace water cycling more complex.

Keywords: hydrogen isotopes, silicate melt, silicate glass, NMR spectroscopy, Raman spectroscopy, HDAC in situ experiments