

## C-O-H volatiles, redox variation and hydrogen isotope fractionation in silicate-COH systems in subduction zones

MYSEN, Bjorn<sup>1\*</sup>

<sup>1</sup>Geophysical Laboratory, CIW

The structural behavior of volatiles in silicate-C-O-H melts and fluids aids in characterization of element partitioning and as well as isotope fractionation (e. g., D/H recycling) in subduction zones. In order to characterize this behavior, experiments were conducted in-situ to 900 °C and 1.6 GPa under reducing and oxidizing conditions. Vibrational spectroscopy (infrared and Raman) was employed for structural characterization and for determination of hydrogen isotope partitioning within and between haploandesitic melts and fluids in alkali aluminosilicate-COH systems.

Under oxidizing conditions, melt and fluid comprise CO<sub>2</sub>, CO<sub>3</sub>-groups, HCO<sub>3</sub>-groups, H<sub>2</sub>O, and silicate components. The abundance ratios, CO<sub>3</sub>/CO<sub>2</sub> and CO<sub>3</sub>/HCO<sub>3</sub>, decreases with increasing temperature and pressure with  $\Delta H$ -values for the exchange equilibria between -15 and -25 kJ/mol. The abundance ratio, CO<sub>3</sub>/silicate, also decreases with increasing temperature and pressure. Hydrogen isotope exchange within coexisting fluids and melts yields  $\Delta H$ -values near 14 and 34 kJ/mol, respectively, which results in  $\Delta H = -25$  kJ/mol for D/H exchange between coexisting fluid and melt. Lack of spectroscopic resolution precluded determination of D/H behavior in the bicarbonate (HCO<sub>3</sub>) species.

Under reducing conditions (near that to the iron-wustite oxygen fugacity buffer), melt and fluid comprise molecular CH<sub>4</sub>, CH<sub>3</sub>-groups, H<sub>2</sub>, OH-groups, and H<sub>2</sub>O. Hydrogen isotope exchange within fluids and melts yields  $\Delta H$  near -5 and -1 kJ/mol, respectively with a  $\Delta H$ -value for D/H exchange between coexisting fluid and melt of -4kJ/mol. The D/H exchange between CH<sub>4</sub> and CD<sub>4</sub> species results in  $\Delta H$  near 40 kJ/mol, whereas the  $\Delta H$ -value is near -4 kJ/mol under oxidizing conditions where  $\Delta H$ -values average near -6 kJ/mol for D/H exchange between hydrous melt and silicate-saturated aqueous fluid.

The redox-dependent D/H-behavior reflects species-dependent bond strengths. Therefore, D/H fractionation between C-O-H volatiles, released during subduction, and both residual subducting materials, and overlying mantle wedge likely will vary with depth. Somewhat analogous pressure-dependence can be seen in olivine/melt transition metal partition coefficients, which may vary by as much as 100% simply by transforming carbon-speciation from methane-rich to carbon dioxide-rich and, therefore-likely depend on depth in subduction zones. This variation depth dependence partly is because subduction zone redox conditions vary with depth and partly because the solubility of C-O-H volatiles in silicate melts and of silicate in coexisting fluid are pressure-dependent.

Keywords: melt structure, COH volatiles, spectroscopy, isotope fractionation, high-pressure experiments