

## In-situ determination of NOHD species in coexisting silicate melt and fluid

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In-situ measurements of solubility and speciation of N-O-H-D volatiles in coexisting fluid and melt were made at high pressure and temperature to estimate the effect of N-O-H-D volatiles on physical properties of magma. The experiment was performed using a Bassett-type hydrothermal diamond anvil cell with Raman spectroscopy as a structural probe. Silicate composition was (Na<sub>2</sub>O-4SiO<sub>2</sub>)<sub>90</sub>(Na<sub>2</sub>O-4NaAlO<sub>2</sub>)<sub>10</sub>. Water is a liquid mixture of H<sub>2</sub>O and D<sub>2</sub>O (H<sub>2</sub>O:D<sub>2</sub>O=50:50 in volume ratio). Nitrogen was supplied from Ag(14/15=0.7/0.3)N<sub>3</sub>. Pressure was measured with one-phonon Raman shift of carbon-13 diamond [1]. The in-situ measurements were conducted in the pressure and temperature range of 425-800 °C and 100-1300 MPa, respectively. Temperature was initially raised up to 800 °C and then decreased to the desired values. Experiments were conducted in two different redox conditions. Oxidizing conditions were obtained by using no buffer and reducing condition controlled with the Mo-MoO<sub>2</sub> buffer based on the reaction  $\text{Mo}+2\text{H}_2\text{O}=\text{MoO}_2+2\text{H}_2$ . In the reducing condition, fO<sub>2</sub> was near that of the iron-wustite buffer. In the experiments under oxidizing conditions, only molecular N<sub>2</sub> was observed in coexisting silicate melt and NOH fluid. The <sup>14</sup>N<sub>2</sub> and <sup>15</sup>N<sub>2</sub> can be clearly distinguished. However, the isotope partitioning between fluid and melt is uncertain because of the low nitrogen solubility in the melt. For experiments under reducing conditions, nitrogen in the fluid was reduced to NH<sub>3</sub> coexisting with H<sub>2</sub>O+H<sub>2</sub>(+D<sub>2</sub>O+D<sub>2</sub>). In coexisting melt, both molecular NH<sub>3</sub> and NH<sub>2</sub> groups were observed in the pressure and temperature range investigated. The ammine groups bonded directly to Si<sup>4+</sup> to Si-NH<sub>2</sub> bonding. In the spectra of fluid, there is evidence for both NH<sub>3</sub> and probably ND<sub>3</sub> in addition to H<sub>2</sub>O, D<sub>2</sub>O, H<sub>2</sub>, and D<sub>2</sub>. Partitioning of D and H between the coexisting phases was determined spectroscopically. SiNH<sub>2</sub> groups were also detected in melt and probably generated by the reaction, Si-O-Si+NH<sub>3</sub>=Si-NH<sub>2</sub>+H-O-Si. This reaction depolymerizes the network of SiO<sub>4</sub> tetrahedra and will affect, therefore melt properties that depend on silicate polymerization (melt viscosity, diffusion, mineral/melt partitioning).

From these data, it is clear that nitrogen in the Earth's interior cannot be modeled simply as a N<sub>2</sub> molecule, whether in melt or fluid. The reduced nitrogen species have a different solubility, different solution mechanisms and probably different nitrogen and hydrogen isotopic behaviors. These results do, therefore affect modeling of earth degassing based on assumed behavior of nitrogen.

[1] Mysen, B. O., Yamashita, S., (2010). *Geochimica et Cosmochimica Acta* 74, 4577-4588

Keywords: fluid, speciation, distribution, silicate melt, diamond anvil cell, in-situ