

SCG009-01

Room:301A

Time:May 23 14:15-14:45

Speciation of P in and partitioning between aqueous fluids and silicate melts to upper mantle temperatures and pressures

Bjorn Mysen^{1*}

¹Geophysical Lab, CIW

Evidence from high-grade metarphic terranes suggest that phosphorus solubility and solution mechanisms in silicate melts and aqueous fluids depend on composition resulting from a range of possible P-bearing structural complexes. The structure of phosphorus-bearing, H₂O-saturated silicate melts, silicate-saturated aqueous fluids, and silicate-rich single phase (supercritical) liquids has been characterized, therefore, via in-situ experiments from ambient temperatures and pressures to 800°C/1486 MPa. The solution mechanisms and partitioning of structural species between fluids and melts were determined with the aid of confocal microRaman and with FTIR spectroscopy backed up with published phosphorus-31 MAS NMR data [1]. The experiments were conducted in an Ir-gasketed hydrothermal diamond anvil cell. Temperature and pressure were recorded with thermocouples (1°C uncertainty) and pressure- and temperature-dependent Raman shift of ¹³C diamonds (40 MPa uncertainty). Starting materials were aluminum-free Na₂O·4SiO₂ (NS4) and with 10 mol % Al₂O₃ (NA10) substituting for SiO₂, both with 5 mol % P₂O₅. These compositions enabled characterization of phosphorus behavior with coexisting haploandesite melt and aluminosilicate-saturated aqueous fluids with variable Al-content.

Aluminosilicate species of Q₀, Q₁, Q₂, and Q₃ type exist in coexisting fluid and melt and in single phase liquid together with phosphate species, PO₄, P₂O₇, and Q_nP. In the Q_nP notation, the n-value denotes the number of oxygen in the structural species shared with P and Si. Al substitutes for Si predominantly in the Q_nP species. In melts, the abundance of the most depolymerized silicate species, Q₀, is positively correlated with temperature and pressure, whereas that of the most polymerized species, Q₃, decreases with temperature and pressure. In the silicate solute in aqueous fluids, the opposite relationship exists with Q₀ abundance decreasing and Q₃ (and Q₁ and Q₂) abundance increasing with increasing temperature and pressure. The silicate melts, therefore, become increasingly depolymerized and the silicate solute in aqueous fluids decreasingly depolymerized. The P₂O₇ and Q_nP are the dominant phosphate species in fluid, melt, and single phase liquid with orthophosphate, PO₄, playing a subordinate role. The fluid/melt partition coefficients for P₂O₇ and Q_nP species are in the 0.15-0.7 range with that of Q_nP being greater than that of P₂O₇. The PO₄ fluid/melt partition coefficients are <0.2. In all cases, the partition coefficients increase with increasing temperature and pressure. There is no clear influence of Al₂O₃. Hence, it appears that P-bearing complexes in fluids and melts are associated with Na⁺. Mobility of phosphorus during metamorphic processes likely is principally governed by availability of alkali metals (and perhaps alkaline earths), whereas Al/Si-ratio may be a less important composition parameter. The P-partitioning between fluids and melts likely are significantly pressure-dependent because fluid and melt speciation is sensitive to pressure.

[1] Cody, B. O., Mysen, B. O., Saghi-Szabo, G., and Tossell, J. A., 2001. *Geochim. Cosmochim. Acta* 65, 2395.

Keywords: melt structure, aqueous fluid, phosphorus species, species partitioning, spectroscopy