

P⁵⁺ and Ti⁴⁺ solution mechanisms of and partitioning between fluids and melts at crustal and upper mantle pressure and temperature

BJORN O. MYSEN

Geophysical Laboratory, Carnegie Instn. Washington, 5251
Broad Branch Rd., NW, USA (bmysen@ciw.edu)

Solution mechanisms of P- and Ti-bearing, H₂O-saturated silicate melts, silicate-saturated aqueous fluids, and silicate-rich single phase (supercritical) liquids have been characterized *in situ* to 900°C/2.2 GPa with vibrational spectroscopy as structural tool. Partitioning of P- and Ti species between fluid and melt was also determined. Starting materials were aluminum-free Na₂O•4SiO₂ (NS4) and with 10 mol % Al₂O₃ (NA10) substituting for SiO₂, with 10 mol % TiO₂ or 5 mol % P₂O₅. The structure of Ti-bearing aqueous fluids in equilibrium with rutile was also characterized.

Aluminosilicate species of Q⁰, Q¹, Q², and Q³ type exist in coexisting fluid and melt in both Ti- and P-bearing systems. 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, Q³ (and Q¹ and Q²) abundance increases with temperature and pressure. The phosphate species in melts and fluids are of PO₄, P₂O₇, and QⁿP type. In the Ti-bearing silicate systems, isolated TiO₄ tetrahedra in melts and fluids probably share oxygen with neighboring silicate tetrahedra. The Ti in aqueous fluids in TiO₂ (rutile)-H₂O comprises polyhedra with greater oxygen coordination numbers.

The fluid/melt partition coefficients for P₂O₇ and QⁿP species are in the 0.15-0.7 range. The PO₄ fluid/melt partition coefficients are <0.2. These partition coefficients increase with increasing temperature and pressure. There is no clear influence of Al₂O₃. The fluid/melt partition coefficient of Ti in the equivalent Ti-bearing systems increases from ~0.1 to ~0.5 in the 200°-500°C and 0.4-1 GPa temperature and pressure range with greater values in Al-bearing systems. The Ti concentration in aqueous fluids coexisting with rutile in the same pressure and temperature range is ≤10% of that in the silicate systems.

The P-bearing complexes in fluids and melts are associated with Na⁺ in the silicate systems, whereas Ti⁴⁺ in silicate systems may form more complex complexes that involve both Na⁺ and Al³⁺. Formation of such complexes can enhance Ti and P solubility in aqueous fluids can enhance their solubility by at least an order of magnitude compared with silicate-saturated systems.

***In situ*, high-pressure/-temperature experimental determination of structure-property relations in silicate melt-COHN systems**

BJORN O. MYSEN

Geophysical Laboratory, Carnegie Instn. Washington, 5251
Broad Branch Rd., NW, USA (bmysen@ciw.edu)

Volatiles in the COHN system, when dissolved in silicate melts, affect their transport and thermodynamic properties. Quantitative characterization of solution mechanisms, central to characterization of melt properties, has been carried out while melts and coexisting COHN fluids were at the desired pressure and temperature.

In aluminosilicate melt-H₂O, the ΔH of the water speciation equilibrium, H₂O^o(melt) + O (melt) \rightleftharpoons 2OH (melt), is ~30 kJ/mol with ΔH positively correlated with Al/(Al+Si) of the melt. This speciation equilibrium coupled with an appropriate silicate speciation equilibrium becomes, Qⁿ (M) + H₂O \rightleftharpoons Qⁿ⁻¹ (H), where (M) and (H) denotes metal cation and protons associated with nonbridging oxygen. The ΔH for the reaction is ~6±2 kJ/mol with a slight positive correlation with Al/(Al+Si).

In melt-COH and melt-NOH systems, f_{O₂} is an additional variable affecting solubility and solution mechanisms. From haplobasalt to haploandesite melt-COH, the carbon solubility at upper mantle pressures and temperatures decreases from ~2 wt% to ~1 wt% in equilibrium with CO₂ gas, whereas under reducing conditions, decrease is from about 0.3 to about 0.15 wt% in equilibrium with NH₄+H₂ gas. Oxidized carbon is dissolved dominantly as CO₃ groups, whereas reduced carbon in the COH system is dissolved as a mixture of CH₃ groups and CH₄ molecules. In compositionally analogous NOH-saturated melts, under oxidizing conditions, nitrogen solubility is insensitive to melt composition, whereas in reduced melts, the solubility decreases from ~1 wt% to ~0.3 wt% in equilibrium with NH₃ gas in the composition range from haploandesite to haplobasalt. The solubility increases rapidly with decreasing f_{O₂}. Oxidized N is dissolved as N₂ molecules, whereas reduced nitrogen is dissolved as NH₂ groups and NH₃.

By changing f_{O₂} from oxidized to reduced, resultant changes of C and N solution mechanisms in melt-COHN systems cause NBO/T changes, which affect transport properties. For example, melt viscosity under oxidizing and conditions is, $\eta=4.4+0.75[0.35-(X_{CO_2}/50)]^{-4.1}$, whereas under reducing conditions it is, $\eta=4.4+0.75[0.35+(X_{CH_4}/30.3)]^{-4.1}$. This illustrates how redox conditions alone can change melt properties relevant to magmatic processes in the Earth's interior.