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Silicate-C-O-H-N fluids and melts at upper mantle temperatures, pressures, and redox conditions

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The speciation of C-O-H-N volatiles and silicate components in fluids and solubility and solution mechanisms of C-O-H-N volatiles in aluminosilicate melts have been determined experimentally, mostly *in situ* with the sample at high temperature and pressure corresponding to those of the upper mantle, as a function of melt composition and redox conditions. In silicate-O-H systems, molecular H_2O and OH groups linked to the silicate network exist in silicate and aluminosilicate-saturated fluids and in water-saturated melts.

The delta H of the water speciation equilibrium, H_2O+O=2OH, is ˜30 kJ/mol. The delta H of hydrogen bonding is ˜10 and ˜20 kJ/mol for melt and fluid, respectively. Hydrogen bonding is not detected above about 500 deg C. Silicate speciation in fluid and in melt comprises similar Q-species with delta H of the solution reaction ˜400 kJ/mol. In silicate-C-O-H systems, under oxidizing conditions (such as that controlled by the magnetite-hematite, MH, buffer, for example) the CO_2 solubility in melts, where it exists as molecular CO_2 and CO_3 groups, is in the 1-4wt% range between ˜1 and 3 GPa and upper mantle temperatures. Its solution mechanism is CO_2+Q^n=CO_3 +Q^{n+1}. This equilibrium probably shifts to the right with temperature and left with pressure [1]. Alkalis and alkaline earths dissolve in C-O-H fluid as complexes with CO_3. Silicate is not detectable in CO_2 fluid. Methane, CH_4, is the dominant C-species in melts at $f_{H2}\geq$MW (magnetite-wustite), whereas in fluids, more reducing conditions [iron-wustite (IW) buffer] are necessary to form detectable CH_4. Methane solubility in melts is 10-30% of that of CO_2. At f_{H2}(IW) the dominant fluid species are CH_4+H_2+H_2O. In coexisting melt, CH_3 groups linked to the silicate melt structure via Si-CH_3 bonding coexist with molecular CH_4 with a solution mechanism, CH_4+Q^1=CH_3+Q^0. The C(melt)/C(fluid) partition coefficient is in the 0.01-0.1 range with a delta H-value near 50 kJ/mol. In silicate-NOH systems, under oxidizing conditions [f_{H2}(MH)] nitrogen exists principally as N_2. Under reducing conditions, f_{H2}(MW), the nitrogen oxidation state is lowered with $NH_2{}^+$ groups dominating in fluid and melt. At the more reducing f_{H2}(IW) condition, NH_3+$NH_2{}^+$ fluid coexisting with NH_3+$NH_2{}^-$+H_2+H_2O species in melt with the ammine groups bonded directly to Si^{4+} (Si-NH_2) and solution mechanism, NH_3+Q^1=NH_2+Q^0. The N(melt)/N(fluid) is $\leq$0.1 with a delta H near 50 kJ/mol. The nitrogen solubility under these conditions are 2-3 times greater than for oxidized nitrogen.

The f_{H2}-dependent speciation C-O-H-N volatile components result in f_{H2}-dependent thermodynamic and transport properties of fluids and melts in the interior of the Earth and terrestrial planets. Reduced and oxidized C-O-H-N species exist fluids and melts in the modern mantle, whereas reduced species dominated in the young Earth. In fluids, the solubility of nominally incompatible trace elements can increase by orders of magnitude upon its saturation with silicate components. Trace element and stable isotope partitioning between fluids and melt can change by >100% for the same reason. Dissolved C-O-H-N volatile components in melts can have similar effects. Silicate solute in C-O-H-N fluids also governs the fluid and melt equation of state. For example, dissolved silicate in fluid can increase its density by $\geq$20% compared with pure H_2O at 1 GPa.

[1] Guillot, B. and Sator, N. (2011). Geochim. Cosmochim. Acta, 75, 1829.