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Silicate solute in aqueous fluids governs trace element and stable isotope behavior in subduction zones

Mysen Bjorn[1]*
MYSEN, Bjorn[1]*

[1]Geophysical Laboratory, CIW, USA
[1]Geophysical Laboratory, CIW, USA

Physical and chemical properties of fluids equilibrated with subducting deep crust and overlying upper mantle are saturated in silicate components [1]. These components govern physical and chemical properties of the fluids. For example, the solution behavior of volatile components such as hydrogen, carbon, and nitrogen, which form bonding with silicate components in fluids, will differ from the behavior in pure H_2O fluids [2]. This can also affect isotope fractionation between fluids and condensed silicate materials.

In pure H_2O, hydrogen bonding plays a role to temperatures <600 ℃ at pressures in the 1 GPa-range with a $\triangle$H for hydrogen bond formation near 20 kJ/mol. At temperatures less than 600 ℃, physical properties of fluids, including density, compressibility, and viscosity, are non-linear functions of temperature, whereas at higher temperature and in the absence of hydrogen bonding, these properties tend to become linear functions of temperature. Solution of silicate components in aqueous fluids changes these relationship. The silica solubility in equilibrium with quartz/coesite reaches >5 mol/kg near 5 GPa and 900 ℃ with polymerized silicate species, SiO_4, Si_2O_7, and SiO_3 in the fluid. In equilibrium with enstatite and forsterite, the silicate solubility is ~50% less and only SiO_4 and Si_2O_7 species exist in the fluids. Those variables affect D/H isotope ratios. For example, the fluid/melt partition coefficients for hydrogen, KH, varies by ~40% as a function of variable silicate speciation in fluids in the 500 ℃-800 ℃/0.5-1 GPa temperature and pressure range. The hydrogen fluid/melt partition coefficient exceeds that of deuterium. Their temperature-dependence also differs so that for the exchange equilibrium of D and H between coexisting water-saturated melt and silicate-saturated aqueous fluid, the $\triangle$H is between -4 and -6 kJ/mol. This difference is because in the more silicate-rich fluids (higher proportion of polymerized silicate species), the abundance ratio, OD/OH, is higher in the more polymerized silicate species in the fluid. As a result, increasing pressure, which leads to increasingly polymerization of silicate, will cause the D/H ratio of the fluid will increase. This also means that D/H fractionation between aqueous fluid and condensed silicate increases with increasing pressure.

Interaction between dissolved silicate components and other elements can also affect their solubility and, therefore, their roles as geochemical tracers. For example, in the system rutile+H_2O, the Ti solubility in the few-GPa-range at ~1000 ℃ is on the order of 1-100 ppm as compared with thousands of ppm in silicate-saturated aqueous solution [3]. This difference between pure H_2O and silicate-saturated fluid is related to interaction with the silicate species dissolved in the fluid, $2M_6Si_2O_7 + 4H_2O + TiO_2 = 4(MH)_2SiO_4 + M_4TiO_4$, where M is a metal cation. Similar situation likely exist for other nominally insoluble, highly charged elements (e.g., Al^{3+}, Zr^{4+}, Hf^{4+}, P^{5+}).

When modeling isotope fractionation and partitioning of nominally insoluble elements between fluid and condensed phases (melts and minerals) in the deep crust and upper mantle of the Earth, the silicate solute concentration and structure in the fluid and the water concentration and structure of silicate melts both can have major effects on the fractionation factors. These factors depend on the element or isotope ratio in question. They also vary with pressure (and likely temperature) because the structure if dissolved silicate in aqueous fluids varies with pressure and temperature.

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