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Structures and transport properties of supercritical SiO_2-H_2O and $NaAlSi_3O_8$-H_2O fluids

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Abstract

Speciation and transport properties of supercritical fluids is critical for understanding their behavior in the Earth's interior. Here, we report a systematic first principles molecular dynamics simulation study of the structure, speciation, self-diffusivity (D), and viscosity (η) of SiO_2 melt, $NaAlSi_3O_8$ melt, SiO_2-H_2O and $NaAlSi_3O_8$-H_2O fluids at 2000–3500 K with 0–70 wt% H_2O. Our calculations show that as the water content increases, the proportion of Q^0 species (Q^n species, where n is the number of bridging oxygens in an individual Si/Al-O polyhedra) increases while Q^4 decreases. The proportions of Q^1, Q^2, and Q^3 species first increase and then decrease with increasing water content. The diffusivity sequence for the supercritical SiO_2-H_2O fluids is $D_H > D_O > D_{Si}$, and for the supercritical $NaAlSi_3O_8$-H_2O fluids, on the whole, is $D_{Na} \approx D_H > D_O > D_{Al} \approx D_{Si}$. The viscosities of the two systems decrease drastically at the beginning of the increase in water content, and then decrease slowly. We demonstrate that the exponential decrease in the viscosity of polymerized silicate melt with increasing water content is due to a sharp decrease in the proportion of Q^4 species and increase in Si-O-H. The typical structural feature of supercritical fluid is that it contains a large amount of easy-to-flow partially polymerized or depolymerized protonated silicate units, which leads to a low viscosity while being enriched in silicate. This feature provides supercritical fluids the potential to transport elements that are hard to migrate in aqueous fluids or hydrous silicate melts, such as high field strength elements.

Keywords: Supercritical fluid, SiO_2-H_2O, $NaAlSi_3O_8$-H_2O, first principles, speciation, transport properties