Structures and transport properties of supercritical SiO$_2$-H$_2$O and NaAlSi$_3$O$_8$-H$_2$O 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 ($\eta$) of SiO$_2$ melt, NaAlSi$_3$O$_8$ melt, SiO$_2$-H$_2$O and NaAlSi$_3$O$_8$-H$_2$O fluids at 2000–3500 K with 0–70 wt% H$_2$O. Our calculations show that as the water content increases, the proportion of $Q^4$ species ($Q^4$ 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$_2$O fluids is $D_{D_{\text{H}_2\text{O}}}$>$D_{D_{\text{SiO}_2}}$>$D_{D_{\text{Si}_0}}$, and for the supercritical NaAlSi$_3$O$_8$-H$_2$O fluids, on the whole, is $D_{D_{\text{NaAlSi}_3\text{O}_8}}$=$D_{D_{\text{SiO}_2}}$>$D_{D_{\text{Si}_0}}$>$D_{D_{\text{NaAlSi}_3\text{O}_8}}$. 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$_2$O, NaAlSi$_3$O$_8$-H$_2$O, first principles, speciation, transport properties

**Introduction**

Silicate melts and aqueous fluids inside the Earth play an important role in magmatism and mineralization processes. Previous studies have shown that with increasing temperature and pressure, the solubility of silicate in aqueous fluids increases, and the solubility of water in silicate melts also increases (Audéat and Keppler 2005; Dolejs and Manning 2010; Newton and Manning 2008). When hydrous silicate melts are completely miscible with aqueous fluids, the phase boundary between the two liquids no longer exists, and a single phase is formed (Shen and Keppler 1997; Wang et al. 2021), i.e., supercritical geofluid, or supercritical fluid (Hermann et al. 2013; Manning 2004, 2018; Ni et al. 2017; Shen and Keppler 1997). Hydrous silicate melts can transport a large number of elements (Xiong et al. 2009) but may not be able to migrate over long distances due to their high viscosity. Although aqueous fluids have high mobility due to their low viscosity, they are generally considered to be too dilute, resulting in a limited capacity to transport solutes (Spandler et al. 2007). Supercritical fluids not only have compositions and structures close to those of hydrous silicate melts but also have high diffusivity and low viscosity, similar to aqueous fluids. Therefore, supercritical fluids have a great ability to transport elements, and thus they are thought to be a high-quality agent for mass transfer (especially for incompatible elements) in subduction zones (Chen et al. 2018, 2021; Ni et al. 2017; Thomas et al. 2019).

Complete miscibility between some hydrous silicate melts and aqueous fluids has been observed experimentally, and the location of the second critical endpoint has been determined for some systems. For example, the second critical endpoint of the SiO$_2$-H$_2$O system was found to be ~1353 K and 0.93–0.97 GPa (Hunt and Manning 2012; Kennedy et al. 1962). Complete miscibility between hydrous silicate melt and aqueous fluid in the NaAlSi$_3$O$_8$-H$_2$O system has been observed too, and it was found that the critical temperature decreases with pressure, from 1262 K at 1.06 GPa to 896 K at 1.65 GPa (Shen and Keppler 1997). After that, the second critical endpoint in the NaAlSi$_3$O$_8$-H$_2$O system was found to occur at 973 K and 1.5 GPa (Stalder et al. 2000). Recently, Makhluf et al. (2020) experimentally determined that the second critical endpoint of the NaAlSi$_3$O$_8$-H$_2$O system is at 932 K and 1.63 GPa. In addition, the second critical endpoints in the KAlSi$_3$O$_8$-H$_2$O, SrAl$_2$Si$_2$O$_7$-H$_2$O, peridotite-H$_2$O, and basalt-H$_2$O systems were determined (Mibe et al. 2004, 2008, 2007, 2011). However, many basic properties are still lacking, such as microscopic structure, speciation, diffusivity, viscosity, etc. (Ni et al. 2017). To our knowledge, in terms of Si speciation, a very limited number of supercritical systems were studied (Mibe et al. 2008; Mysen 2010, 2013), and a systematic understanding is still lacking. For example, although most of Si was observed to be in the form of dimer in supercritical KAlSi$_3$O$_8$-H$_2$O fluid with...