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 behaviour 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$^0$ 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$_2$O fluids is $D_H > D_O > D_{Si}$, and for the supercritical NaAlSi$_3$O$_8$–H$_2$O 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 silicate units bonded to hydrogen, 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
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 (Audétat 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; Manning, 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., 2021; Chen et al., 2018; 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 $\sim$1353 K and 0.93 – 0.97 GPa (Hunt and Manning, 2012; Kennedy et al., 1962). Complete miscibility between hydrous silicate melt and aqueous fluid in the NaAlSi$_3$O$_8$–H$_2$O system has
been observed too, and it was found that the critical temperature decreasing 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 NaAlSi₃O₈–H₂O 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 NaAlSi₃O₈–H₂O system is at 932 K and 1.63 GPa. In addition, the second critical endpoints in the KAlSi₃O₈–H₂O, SrAl₂Si₂O₈–H₂O, peridotite–H₂O and basalt–H₂O systems were also determined (Mibe et al., 2008; Mibe et al., 2004; Mibe et al., 2007; Mibe et al., 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; Mysen et al., 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 KAlSi₃O₈–H₂O fluid with a water content of 60 wt% (Mibe et al., 2008), how the speciation changes with water content remains unclear. In addition, some studies focused on the systems that are close to but still below the pressure-temperature conditions of supercritical fluids (e.g., Steele-MacInnis and Schmidt, 2014; Zotov and Keppler, 2002). In terms of viscosity, interestingly, it was found that with the increase of water content, the viscosity of albite–H₂O system decreases exponentially within the first 20 wt% H₂O but after the supercritical albite–H₂O fluid is formed, the viscosity decays almost linearly to the viscosity of pure water (Audétat and Keppler, 2004). The mechanism for this behaviour still needs more understanding. At present, it is still challenging for experiments to accurately determine the microstructure of supercritical fluids (Mibe et al., 2008) and the viscosity at high pressure and temperature (Sun et al., 2018). The lack of quantitative studies makes it impossible to establish the relationship between the microscopic
properties and its macroscopic behaviors or to draw a picture of the evolution of supercritical fluids in geological processes.

Molecular modeling is an effective method to study the properties of silicate–H$_2$O systems over a broad range of temperatures and pressures. But previous theoretical studies mainly focused on (hydrous) silicate melts and aqueous fluids (e.g., de Koker et al., 2013; Dingwell et al., 1998; Dingwell et al., 1996; Dufils et al., 2020; Ghosh and Karki, 2011; Gillan et al., 2016; Karki et al., 2018; Karki and Stixrude, 2010; Manning, 2018; Romano et al., 2001; Sun et al., 2020; Yang et al., 2017). So far, only one work using first-principles method to study supercritical SiO$_2$–H$_2$O fluid with 23.1 wt% H$_2$O has been reported (Spiekermann et al., 2016). Therefore, microscopic structure, speciation and transport properties of supercritical silicate–H$_2$O system are urgently needed for understanding the geological roles of supercritical fluids in the Earth's interior.

Here, we use first principles molecular dynamics method to study the structure, speciation, self-diffusivity and viscosity of SiO$_2$–H$_2$O and NaAlSi$_3$O$_8$–H$_2$O systems at 2000 – 3500 K. The evolution of these properties with increasing water content have been obtained. The transfer mechanism of H in supercritical fluids is discussed. We uncover the mechanism of the decrease in the viscosity of polymerized silicate melt with increasing water content and further discuss the effect of supercritical fluids on element migration.

**COMPUTATIONAL METHODS**

First principles molecular dynamics (FPMD) simulations of SiO$_2$–H$_2$O and NaAlSi$_3$O$_8$–H$_2$O systems (H$_2$O concentration in the range of 0 wt% – 70 wt%) were performed in the DFT code VASP (Kresse and Furthmuller, 1996a; Kresse and Furthmuller, 1996b; Kresse and Hafner, 1993;
Kresse and Hafner, 1994). The Perdew-Burke-Ernzerhof (PBE) functional (Perdew et al., 1996) was used with Grimme–D3 (i.e., PBE–D3) dispersion correction (Grimme et al., 2010). Many density functional approximations (such as PBE) do not describe long-ranged electron correlation effects well. The DFT–D3 scheme is the most commonly used method, which reproduces the inter- and intramolecular dispersion interactions reasonably (Caldeweyher et al., 2019; Grimme et al., 2010; Grimme et al., 2011). Since the systems in our study contain water, the use of PBE–D3 method is a better choice (Li et al., 2022). A plane wave cut-off of 500 ~ 520 eV and gamma point Brillouin zone sampling were used. The convergence of k-point mesh and cutoff energy were tested and found to converge the total energy to within 1 meV/atom and 3 meV/atom, respectively. The electronic self-consistency convergence criterion for the total energy was set to $10^{-5}$ eV. Our simulations were performed in the $NVT$ ensemble with a time step of 0.5 (1.0) fs for hydrous (anhydrous) liquid. Our research focuses on the properties of supercritical fluids. For comparison, we also investigated the systems with low water content. The SiO$_2$–H$_2$O systems and NaAlSi$_3$O$_8$–H$_2$O systems contain 180–210 atoms (Table 1) and 172–316 atoms (Table 2), respectively, depending on the water content. Each SiO$_2$–H$_2$O system was first melted and equilibrated at 6000 K and then cooled to 3500 K, 3000 K and 2600 K. Each NaAlSi$_3$O$_8$–H$_2$O system was melted and cooled to 3000 K, 2500 K and 2000 K adopting the same strategy. The run durations for reaching thermal equilibrium varied from 10 ~ 20 ps. Following this, we finally performed 100-ps simulations except for the NaAlSi$_3$O$_8$–H$_2$O system with 60 wt% H$_2$O, which was ran for 50 ps.

For each model, we first calculated the pressure of the models under four different volumes to obtain the pressure–volume curves. Then, the volume corresponding to approximately 1 ~ 4 GPa was obtained for the simulation (Table 1 and Table 2). This puts the temperature-pressure
conditions simulated in this study above the critical curves of the SiO$_2$–H$_2$O and NaAlSi$_3$O$_8$–H$_2$O systems (Figure S1 in Supporting Information). The pressure correction for Pulay stress is included based on the method of de Koker et al. (2008). The absolute value of the Pulay correction was less than 0.2 GPa for all models. The pressure correction for PBE under binding was not applied due to lack of experimental data in the hydrous system.

The self-diffusion coefficient was calculated with the Einstein relation (Allen and Tildesley, 1989). The shear viscosity was derived from the stress autocorrelation function (ACF) over time according to the Green-Kubo relation (Allen and Tildesley, 1989). Three off-diagonal components of the stress tensor are used to calculate the shear viscosity. The pairwise radial distribution function (RDF) was used to analyze the structures. The cutoff radius used in the analysis of species is defined as the position of the first minimum in RDF. The cutoff radius is uniquely determined at each state point. The stress ACF and RDF in this study can be found in Figures S8, S9, S15 and S16 in Supporting Information.

RESULTS

Speciation and Structure

$Q^n$ Speciation. In silicate fluids, both pressure (Wang et al., 2014) and network modifiers can break the bridging oxygen (BO) bonds (Si/Al–O–Si/Al), resulting in a varying distribution of $Q^n$ species. A $Q^4$ species is a Si/Al–O polyhedra with 4 BOs, and a $Q^0$ species is a Si/Al–O polyhedra with 0 BO (i.e., it is not attached to any other polyhedra). In most cases, $Q^0$ notation is generally used in structures with 4 coordinated Si/Al. When the pressure increases, Si/Al can be 5-coordinate and 6-coordinate. In this case, n will be greater than 4, and $Q^5$ or even $Q^6$ will appear in the structure (Bajgain et al., 2019). In addition to pressure and network modifiers,
water can also break the Si/Al–O–Si/Al network by reacting with BO, thereby converting higher $Q^n$ species to lower $Q^n$ species. $Q^n$ species provides information about local network structure in silicate fluids. As shown in Figure 1, we calculated the $Q^n$ species for the SiO$_2$–H$_2$O systems at 2600 K, 3000 K and 3500 K, and for the NaAlSi$_3$O$_8$–H$_2$O systems at 2000 K, 2500 K and 3000 K. Our $Q^0 \sim Q^4$ species generally agree with those obtained in the first-principles study by Spiekermann et al. (2016) for SiO$_2$–H$_2$O system with 23.1 wt% H$_2$O at 3000 K (Figure 1b). In addition to $Q^0 \sim Q^4$ species, there was also a small amount of $Q^5$ species present in the systems. On the whole, the SiO$_2$–H$_2$O and NaAlSi$_3$O$_8$–H$_2$O systems show the similar distribution of $Q^n$ species. The proportion of $Q^0$ increases with increasing water content while $Q^4$ decreases. The proportions of $Q^2$ and $Q^3$ first increase and then decrease with increasing water content. Although we only observed that the proportion of $Q^1$ increases first and then decreases when the water content exceeds 60 wt% at 3000 K in the SiO$_2$–H$_2$O systems (Figure 1b), it can be inferred that $Q^1$ will also decrease at higher water content at 2600 K and 3500 K in the SiO$_2$–H$_2$O systems. This $Q^1$ behaviour can also be inferred to occur in the NaAlSi$_3$O$_8$–H$_2$O systems. The maximum values for the proportions of $Q^3$ and $Q^2$ in the two systems at 3000 K occur at the positions where the water content is 20 wt% and 40 wt%, respectively. For example, in the NaAlSi$_3$O$_8$–H$_2$O systems at 3000 K, $Q^3$ initially increases to 37.4% as H$_2$O increases to 20 wt% and then decreases to 6.9% as H$_2$O increases to 60 wt%. $Q^2$ increases to 34.4% as H$_2$O increases to 40 wt% and then decreases. These maximum values also have the same positions in the SiO$_2$–H$_2$O systems at 2600 K and 3500 K and in the NaAlSi$_3$O$_8$–H$_2$O systems at 2000 K. But these positions are slightly different in the NaAlSi$_3$O$_8$–H$_2$O systems at 2500 K, and the maximum values for $Q^3$ and $Q^2$ occur at the positions where the water content is 10 wt% and 30 wt%, respectively. This is actually due to the water content interval that we adopted. We speculate that
the true maximum values for $Q^3$ and $Q^2$ in the SiO$_2$–H$_2$O and the NaAlSi$_3$O$_8$–H$_2$O systems occur in the range of 10–20 wt% H$_2$O and 30–40 wt% H$_2$O, respectively. The maximum value for the proportion of $Q^1$ probably occurs in the range of 60–70 wt% H$_2$O. Experimental studies on quenched hydrous [Na$_2$Si$_4$O$_9$–Na$_2$(NaAl)$_4$O$_9$] system by Mysen (2007) also found that the $Q^3$-abundance passes through a maximum in the 7–10 wt % H$_2$O with Al/(Al+Si) = 0.25 (Figure 1f).

**Oxygen Speciation and Polymerization.** As the only anion in the SiO$_2$–H$_2$O systems and the NaAlSi$_3$O$_8$–H$_2$O systems, oxygen mainly exists in the form of bridging oxygen (BO, i.e. an oxygen atom is bonded to more than one network former), nonbridging oxygen (NBO, i.e. an oxygen atom is only bonded to one network former), free oxygen (an oxygen atom is not bonded to network former or H, marked as FO), molecular H$_2$O (H$_2$O$_m$), free hydroxyls (OH), and H$_3$O (an oxygen atom is bonded to three hydrogen atoms). Both the SiO$_2$ melt and NaAlSi$_3$O$_8$ melt are fully polymerized melts, and the NBO/T (T = Si, Al) of the SiO$_2$–H$_2$O and NaAlSi$_3$O$_8$–H$_2$O systems can increase from 0 (fully polymerized) to 4 (fully depolymerized) as the water content increases. We analysed in detail the oxygen species in the two systems (Figure 2) at different temperatures with increasing water content. At 3000 K, in the SiO$_2$–H$_2$O systems, BO decreases from 99.5% to 3.6% as the water content increases from 0 wt% to 70 wt% (Figure 2a). NBO initially increases to 51.3% as the water content increases to 40 wt% and then decreases to 32.2% as the water content increases to 70 wt%. The other oxygen species (FO, OH, H$_3$O and H$_2$O$_m$) increase to 64.2% as the water content increases to 70 wt%. The distributions of the oxygen species at 2600 K and 3500 K are basically the same as those at 3000 K in the SiO$_2$–H$_2$O systems. These features are also found in the NaAlSi$_3$O$_8$–H$_2$O systems (Figure 2c). The initial
increase in the ratio of NBO is due to the reaction between water and BO. As more water is added, not only is more FO produced, but also the NBO ratio is correspondingly reduced. NBO/T increases almost linearly from 0.01 to 3.27 as water content increases from 0.0 wt% to 70 wt%, in the SiO₂–H₂O systems (Figure 2b). Similarly, NBO/T increases linearly from 0.09 to 2.95 as water content increases from 0.0 wt% to 60 wt%, in the NaAlSi₃O₈–H₂O systems (Figure 2d).

**Hydrogen Speciation.** Hydrogen atoms in the SiO₂–H₂O systems and the NaAlSi₃O₈–H₂O systems mainly exist in the form of H₂Oₘ and Si–O–H (one H atom is bonded to the nonbridging oxygen, marked as NBO–H). In the two systems, both H₂Oₘ and NBO–H species show linear changes with increasing water content at all temperatures (Figure 3). The proportion of H₂Oₘ species gradually increases from 6.2% to 59.4% as water content increases from 10 wt% to 70 wt%, in the SiO₂–H₂O systems at 3000 K. Correspondingly, the proportion of NBO–H species gradually decreases from 79.7% to 28.8%. In the NaAlSi₃O₈–H₂O systems at 3000 K, the proportion of H₂Oₘ species increases from 6.9% to 51.4% as water content increases from 10 wt% to 60 wt%, and the proportion of NBO–H species decreases from 66.5% to 34.5%. Interestingly, in general, both H₂Oₘ and NBO–H species have a negative dependence on temperature. This is due to the presence of a small number of hydrogen species that have a positive dependence on temperature in the systems (Figures S2 and S3 in Supporting Information), including free protons (H), OH, bridging –O–H–O– (HO₂), H₃O, NBO–H₂ (two hydrogen atoms are bonded to the nonbridging oxygen) and BO–H (one H atom is bonded to the bridging oxygen). Some of these species are very unstable, such as H, OH and HO₂, and in most cases they exist for less than 10
fs (Figures S4 in Supporting Information). Since the time step used for the calculation is 0.5 fs, they can be identified during the transfer of H.

**Transport Properties**

**Diffusivities.** The calculated self-diffusivities for all elements in the SiO$_2$–H$_2$O systems and the NaAlSi$_3$O$_8$–H$_2$O systems at different temperatures are shown in Figure 4 and Figure 5, respectively (the corresponding MSD can be found in Figures S5 and S6 in Supporting Information). In the SiO$_2$–H$_2$O systems at 2600 K, $D_{\text{Si}}$ increases by two orders of magnitude as the water content increases from 10 wt% to 50 wt%. $D_{\text{O}}$ and $D_{\text{H}}$ increase by more than one order of magnitude. As the temperature increases to 3500 K, the increases in $D_{\text{Si}}$, $D_{\text{O}}$ and $D_{\text{H}}$ decrease with water content. This indicates that a higher temperature can weaken the enhancing effect of water on diffusivities of ions. In addition, the rate of increase in the diffusivities gradually decreases with increasing water content. The diffusivity sequence for the SiO$_2$–H$_2$O systems is $D_{\text{H}} > D_{\text{O}} > D_{\text{Si}}$. At 2600 K and 10 wt% H$_2$O, $D_{\text{H}}$ is 33 times and 9 times higher than $D_{\text{Si}}$ and $D_{\text{O}}$, respectively. At 3500 K and 10 wt% H$_2$O, $D_{\text{H}}$ is 9 times and 5 times larger than $D_{\text{Si}}$ and $D_{\text{O}}$, respectively. This shows that a higher temperature reduces the gap between $D_{\text{H}}$ and $D_{\text{Si}}$ or $D_{\text{O}}$. These phenomena are also observed in the NaAlSi$_3$O$_8$–H$_2$O systems. At 2000 K, $D_{\text{Na}}$, $D_{\text{O}}$ and $D_{\text{H}}$ increase by 3.4, 49.3 and 11.3 times, respectively, as the water content increases from 10 wt% to 50 wt%. At the same temperature, as the water content increases from 20 wt% to 50 wt%, $D_{\text{Al}}$ and $D_{\text{Si}}$ increase by 3.7 and 23.0 times, respectively. When the temperature rises to 3000 K, the increase in the diffusivities for all ions decreases with water content.
Viscosities. The calculated viscosities for the SiO$_2$–H$_2$O and NaAlSi$_3$O$_8$–H$_2$O systems are shown in Figure 6. Our results are consistent with the FPMD results of hydrous (with 8.25 wt% H$_2$O) SiO$_2$ liquid obtained by Karki and Stixrude (2010) and the FPMD results for the NaAlSi$_3$O$_8$ melt from Bajgain and Mookherjee (2020). We compared the viscosity of the NaAlSi$_3$O$_8$–H$_2$O systems with an experimental model derived from the fitting of experimental data at 873 – 1473 K (Audétat and Keppler, 2004). We found that the model of Audétat and Keppler (2004) can basically reproduce our viscosities at temperatures of up to 2500 K (Fig. 6b). And with increasing water content, characteristics of viscosity change obtained by Audétat and Keppler (2004) at 1073.15 K is in good agreement with our results (Figures S7 in Supporting Information). In the SiO$_2$–H$_2$O systems, the viscosity decreases by nearly 2 orders of magnitude as the water content increases from 10 wt% to 30 wt% at 2600 K (Figure 6a). At the same temperature, as the water content increases from 30 wt% to 50 wt%, the viscosity only decreases by a factor of 2. At 3000 K, the viscosity decreases exponentially in the first 40 wt% H$_2$O, and thereafter the change is roughly linear. A higher temperature weakens this sharp change in viscosity. At 3500 K, the viscosity basically decreases exponentially in the first 40 wt% H$_2$O, but the magnitude of the decrease is lower than that at lower temperatures. At a water content > 30 wt%, the viscosities of the SiO$_2$–H$_2$O systems at the three temperatures are very similar (inset of Figure 6a). When the water content exceeds 30 wt%, the viscosity approaches 0.0002 ~ 0.0008 Pa·s, that is even lower than the viscosity of liquid water (0.00089 Pa·s) under ambient pressure and temperature (Harris and Woolf, 2004). These changes in viscosity also occur in the NaAlSi$_3$O$_8$–H$_2$O systems. For example, at 3000 K, the viscosity decreases by a factor of 27 as the water content increases from 0 wt% to 30 wt%, while it only decreases by a factor of 3 from 30 wt% to 60 wt%. Similar to the SiO$_2$–H$_2$O system, the viscosities of the NaAlSi$_3$O$_8$–H$_2$O
systems at the three temperatures are very similar for water contents > 40 wt% (inset of Figure 6b).

DISCUSSION

Structures of Supercritical Fluids

A typical feature of supercritical fluids is that they are not only richer in silicates than aqueous fluids, but also maintain a low viscosity. This is mainly due to the structures of supercritical fluids. According to previous studies on the phase diagrams of the SiO$_2$–H$_2$O and NaAlSi$_3$O$_8$–H$_2$O systems (Hunt and Manning, 2012; Kennedy et al., 1962; Makhluf et al., 2020; Newton and Manning, 2008), the SiO$_2$–H$_2$O and NaAlSi$_3$O$_8$–H$_2$O systems with a water content of more than 30 wt% and 20 wt%, respectively, in this study can be regarded as supercritical fluids. In the supercritical SiO$_2$–H$_2$O and NaAlSi$_3$O$_8$–H$_2$O fluids, the proportion of Q$^n$ species depends on the water content. When the water content is relatively low (< 50 wt%), some Q$^4$ still exists in the supercritical fluids. As the water content continues to increase, Q$^4$ decreases until it disappears completely. Corresponding to it is the continuous increase of Q$^0$ (Figure 1). This is because the increase in water content promotes the depolymerization of silicate, causing a transition from higher Q$^n$ species to lower Q$^n$ species. Steele-MacInnis and Schmidt (2014) used Raman spectroscopy to study the silicate speciation in H$_2$O–Na$_2$O–SiO$_2$ fluids up to 873 K and 2 GPa. They found that as the SiO$_2$ concentration increases to 40 mol%, the proportion of Q$^0$ species decreases, and the proportions of Q$^1$ and Q$^2$ increase and then decrease. In their study, the maximum values for the proportions of Q$^1$ and Q$^2$ occur in the range of 7–15 mol% SiO$_2$ and 20–30 mol% SiO$_2$, respectively (Figure S10 in Supporting Information). This is consistent with the results of our calculation. We speculate that the maximum values for the proportions of Q$^1$,
Q₂, and Q³ occur in the range of 60–70 wt% H₂O, 30–40 wt% H₂O and 10–20 wt% H₂O, respectively. Experimental studies on quenched (from 1673.15 K at 1.5 GPa) hydrous Na-aluminosilicate melts also found that the Q³-abundance passes through a maximum in the 7 – 10 wt % H₂O with Al/(Al + Si) = 0.05 – 0.25 (Figure 1f), and the position of the maximum value has a positive correlation with Al/(Al + Si) (Mysen, 2007). In addition, we find that the effect of temperature on the NBO/T and average n of Q⁵ for supercritical fluids is weak (Figure 2 and Figure S11 in Supporting Information). Hydrogen atoms mainly exist in the form of molecular water and NBO–H, and both of them have a negative dependence on temperature (Figure 3). The addition of water not only depolymerizes the SiO₂ and NaAlSi₃O₈ melts, but also converts BO into NBO–H. Yuan et al. (2020) studied the effect of water on the depolymerized Mg²SiO₄ melt and found that with the increase of water content, the ratio of NBO–H increased linearly though NBO/T did not change much. Based on the results of this study and previous results (Mibe et al., 2008; Steele-MacInnis and Schmidt, 2014; Yuan et al., 2020), we believe that the presence of a large number of partially polymerized silicate units bonded to hydrogen is an important structural feature of supercritical fluids formed from the polymerized silicate melts (Figure 7). It can be speculated that the structural feature of supercritical fluids formed from depolymerized silicate melts is that they contain a large number of depolymerized silicate units bonded to hydrogen. Water will also bring about different changes in the viscosity of polymerized and depolymerized silicate melts, which we will discuss below.

### Self-diffusion of Hydrogen in Supercritical Fluids

In supercritical fluids, the transfer mechanism of H is different under different water content. When the water content is relatively low (< 40 wt%), the transfer of H occurs mainly through the
exchange of H between NBO and NBO–H: NBO–H ... NBO → NBO ... NBO–H. This is the same as the transfer mechanism of H in hydrous silicate melt (Karki and Stixrude, 2010). When the water content is relatively high (> 60 wt%), the main transfer mechanism of H occurs not only between NBO and NBO–H, but also between NBO and H$_2$O$_m$ and between different H$_2$O$_m$. In this case, a typical transfer of H is carried out like this: NBO–H ... H$_2$O$_m$ ... H$_2$O$_m$ ... NBO–H → NBO ... H$_3$O ... H$_2$O$_m$ ... NBO–H → NBO ... H$_2$O$_m$ ... H$_3$O ... NBO–H → NBO ... H$_2$O$_m$ ... H$_2$O$_m$ ... NBO–H. The free protons, free hydroxyls, H$_3$O, NBO–H$_2$, and BO–H can all play a role in the transfer of H, so we can also observe a small number of these hydrogen species in the supercritical fluids (Figures S2 and S3 in Supporting Information). The diffusivity sequence for the supercritical SiO$_2$–H$_2$O fluids is $D_H > D_O > D_{Si}$, and for the supercritical NaAlSi$_3$O$_8$–H$_2$O fluids, on the whole, is $D_{Na} = D_H > D_O > D_{Al} = D_{Si}$. Previous studies have found that in the hydrous (4.2 wt% H$_2$O) NaAlSi$_2$O$_6$ melt under low pressure (< 5 GPa), $D_H < D_{Na}$ (Bajgain et al., 2019). This is consistent with our results. When the water content is low (e.g., < 20 wt% H$_2$O, depending on composition and $P$-$T$ conditions), $D_H < D_{Na}$. With the increase of water content, $D_H$ will increase and approach or even exceed $D_{Na}$. This is because H mainly exists in the form of H$_2$O$_m$ and NBO–H (Figure 3), and the self-diffusivity of NBO–H species is affected by Si and O. Therefore, as the water content increases, the proportion of NBO–H species decreases and the proportion of H$_2$O$_m$ increases, leading to an increase in $D_H$ that approaches or even exceeds $D_{Na}$ at higher water content.

**Viscosities**

The viscosities of the silicate-H$_2$O systems are closely related to their structures. From the abovementioned results for the structure and transport properties, we can clearly observe the
evolution of these properties for the silicate-H\textsubscript{2}O systems as the water content increases. For the fully polymerized silicate melts, both silica and albite melts react with water and rapidly decompose: Si–O–Si + H\textsubscript{2}O → 2Si–OH. The bridging oxygen in the silicate melt is transformed into nonbridging oxygen (Figure 2). As the water content increases, the higher Q\textsuperscript{n} species transition to the lower Q\textsuperscript{n} species during dissolution: Q\textsuperscript{4} → Q\textsuperscript{3} → Q\textsuperscript{2} → Q\textsuperscript{1} → Q\textsuperscript{0} (Figure 1). This process results in a decrease in viscosity and an increase in diffusivity. In the SiO\textsubscript{2}–H\textsubscript{2}O systems, the viscosity decreases drastically in the first 30 wt% H\textsubscript{2}O at 2600 K, and thereafter, the change is slow. At 3000 K and 3500 K, a sharp drop in the viscosity occurs roughly in the first 40 wt% H\textsubscript{2}O. This corresponds to the sharp drop in the proportion of Q\textsuperscript{4} species in the first 30 ~ 40 wt% H\textsubscript{2}O. As the water content increases to 30 wt% (2600 K), 40 wt% (3000 K) and 40 wt% (3500 K), the proportion of Q\textsuperscript{4} species decreases to 8.0%, 3.2%, and 3.9%, respectively. This has also been observed in the NaAlSi\textsubscript{3}O\textsubscript{8}–H\textsubscript{2}O systems. The viscosity in the NaAlSi\textsubscript{3}O\textsubscript{8}–H\textsubscript{2}O systems decreases drastically in the first 40 wt% H\textsubscript{2}O, and thereafter the change is slow (inset of Figure 6b). When the water content increases to 40 wt%, the proportion of Q\textsuperscript{4} species at 2000 K, 2500 K and 3000 K decreases to 8.1%, 4.9% and 5.9%, respectively. At low water content, H\textsubscript{2}O\textsubscript{m} dissolves into the melts to form Si–OH and gradually breaks the network structure of the polymerized silicate melts until Q\textsuperscript{4} is almost exhausted. This leads to a sharp drop in the viscosity. As the water content further increases, the silicate solute continues to depolymerize, that is, Q\textsuperscript{3} → Q\textsuperscript{2} → Q\textsuperscript{1} → Q\textsuperscript{0}, while the viscosity of the silicate–H\textsubscript{2}O systems decreases slowly. Due to the continuous increase in molecular water in the systems, the viscosity tends to get close to the viscosity of water. The decomposition of the Q\textsuperscript{4} species means that the three-dimensional network structure of the polymerized silicate melts is destroyed, creating easy-to-flow partially polymerized silicate units (Bockris et al., 1955; Steele-MacInnis and Schmidt, 2014). Yuan et al.
(2020) found that both the ratio of NBO–H and the self-diffusion coefficient increased linearly as the water content increased from 0.0 wt% to 26.7 wt%. From the Eyring relation (Eyring, 1982), it can be speculated that the viscosity will also decrease linearly. This shows that a correlation exists between NBO–H and self-diffusion coefficient/viscosity, that is linear at least for the water content < 30 wt%. Why does the viscosity decrease exponentially in the SiO₂–H₂O and the NaAlSi₃O₈–H₂O systems? The same phenomenon was observed in the experimental study of the NaAlSi₃O₈–H₂O systems (Figure 6b) by Audétat and Keppler (2004). Here we can conclude that the reason is that the water not only generates a large amount of NBO–H, but also converts higher Qⁿ species to lower Qⁿ species, i.e. breaking the network structure in the polymerized silicate melts. Therefore, in the SiO₂–H₂O and NaAlSi₃O₈–H₂O systems, the superposition of these two effects leads to a sharp decrease in viscosity when Q⁴ species decreases sharply.

**IMPLICATIONS**

The structures and transport properties of supercritical fluids are key to understanding the role they play in mineralization processes at subduction zones. The speciation and transport properties of the SiO₂–H₂O and NaAlSi₃O₈–H₂O systems can reflect the characteristics of the silicate–H₂O system with NBO/T < 1 such as basaltic and picritic melts. Our results show that in supercritical fluids with high water content (> 60 wt% H₂O), network-forming elements mainly exists in the form of Q⁰, Q¹ and Q² species. While in the supercritical fluids with low water content (< 40 wt% H₂O), network-forming elements are mainly distributed in the forms of Q¹, Q² and Q³ species (Figure 1). If the supercritical fluids are formed from depolymerized silicate melts, their structures are dominated by Q⁰. Such Qⁿ distribution keeps the supercritical fluid rich in silicate and at the same time makes the fluid have partially polymerized structures and thus
low viscosity and high diffusivity. Therefore, supercritical fluids can transport elements that are hard to migrate in aqueous fluids (such as high field strength elements). The transport of dissolved species in supercritical fluids is determined by the transport properties and the solubility of the species involved. Audétat and Keppler (2004) found that the viscosities of supercritical fluids with different compositions at similar temperature and pressure are very close when measuring the viscosities of albite–H$_2$O systems, leucite–H$_2$O systems and pectolite–H$_2$O systems. Our results also show that when the water content exceeds 20 wt%, the viscosities of the SiO$_2$–H$_2$O systems at 3000 K are very similar to those of the NaAlSi$_3$O$_8$–H$_2$O systems at the same temperature (Figure S12 in Supporting Information). Although the pressures of the two systems are not exactly the same, a pressure difference of less than 1 GPa has a weak effect on the viscosity under high temperature conditions (Bajgain and Mookherjee, 2020; Karki et al., 2011). Therefore, the viscosity of supercritical fluids with different compositions at the same temperature and pressure may be similar. If this is the case, the element transport ability of supercritical fluids in the Earth’s interior may depend more on the solubility of that element. This problem still needs more research (especially supercritical fluids with different compositions) to confirm.

The next question to be solved is how do supercritical fluids transport elements that are hard to migrate in aqueous fluids? Our research indicate that the supercritical fluids have such potential, but the complexations of these elements in the supercritical fluids remain unclear. The self-diffusion coefficients of elements in the SiO$_2$–H$_2$O and the NaAlSi$_3$O$_8$–H$_2$O systems are given in this work. Combining these data with future self-diffusion data at low temperatures obtained through experiments or simulations, a diffusion model for supercritical fluids can be
established. According to this model, we can infer the migration rate of supercritical fluid to various elements under different conditions.

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metabasalt at the amphibolite to eclogite transition, with applications to TTG genesis.

American Mineralogist, 94(8-9), 1175-1186.


**FIGURE CAPTIONS**

**Figure 1.** Fraction of Q^n species in the SiO₂–H₂O systems and the NaAlSi₃O₈–H₂O systems at different temperatures as a function of water content. The green curves represent the average n for Q^n species, and the values correspond to the right y-axis in green. The filled triangles in (b) are the calculated Q⁰, Q¹, Q², Q³ and Q⁴ species (legend in the same color) in the SiO₂–H₂O system with 23.1 wt% H₂O at 3000 K (Spieckermann et al., 2016), and the average n for Q^n is shown by green filled diamond. The dashed curves in (f) represent the experimental Q¹, Q², Q³ and Q⁴ species in the hydrous [Na₂Si₄O₉–Na₂(NaAl)₄O₉] system with Al/(Al+Si) = 0.25 (Mysen, 2007). The filled triangles in (f) are the FPMD results of anhydrous (2.28 GPa) and hydrous (4.2 wt% H₂O, 2.03 GPa) NaAlSi₂O₆ melt at 3000 K (Bajgain et al., 2019).

**Figure 2.** Oxygen speciation and (oxygen species)/T with increasing water content. (a) Oxygen speciation in the SiO₂–H₂O systems at 2600 K (blue symbols), 3000 K (red symbols) and 3500 K (green symbols). The squares, diamonds and circles represent bridging oxygen (BO), nonbridging oxygen (NBO) and other oxygen species (FO, OH, H₂O, and H₂O₄⁻), respectively.
(b) NBO/T in the SiO$_2$–H$_2$O systems. (c) Oxygen speciation in the NaAlSi$_3$O$_8$–H$_2$O systems at 2000 K (yellow symbols), 2500 K (blue symbols) and 3000 K (red symbols). (d) NBO/T in the NaAlSi$_3$O$_8$–H$_2$O systems. The curves in (a) and (c) show the connecting lines for the 3000 K data in the corresponding systems. The lines in (b) and (d) show linear fits to the data at all temperatures. The open symbols in (a) and (b) are the FPMD results of the SiO$_2$–H$_2$O system with 23.1 wt% H$_2$O at 3000 K (Spiekermann et al., 2016). The larger open symbols in (c) and (d) are the FPMD results of the NaAlSi$_3$O$_8$ melt from Bajgain and Mookherjee (2020) at 2500 K (2.78 GPa) and 3000 K (3.31 GPa). The smaller open symbols in (c) and (d) are the FPMD results of anhydrous and hydrous (4.2 wt% H$_2$O) NaAlSi$_2$O$_6$ melt at 2500 K (3.21 GPa, 2.72 GPa) and 3000 K (2.28 GPa, 2.03 GPa) obtained by Bajgain et al. (2019).

**Figure 3.** Speciation of hydrogen in the (a) SiO$_2$–H$_2$O and (b) NaAlSi$_3$O$_8$–H$_2$O systems. The abundance of H$_2$O$_m$ species = the number of H$_2$O$_m$ species divided by the total number of all types of hydrogen species.

**Figure 4.** Water content and temperature dependence of the self-diffusion coefficients for Si, O and H in the SiO$_2$–H$_2$O systems. The FPMD results for hydrous (with 8.25 wt% H$_2$O) SiO$_2$ liquid (Karki and Stixrude, 2010) at 2500 K (~ 0 GPa), 3000 K (~ 4.08 GPa) and 3500 K (~ 0.61 GPa) are included for comparison.

**Figure 5.** Water content, and temperature dependence of the self-diffusion coefficients ($D$) for Na, Al, Si, O and H in the NaAlSi$_3$O$_8$–H$_2$O systems. The FPMD results of the NaAlSi$_3$O$_8$ melt
from Bajgain and Mookherjee (2020) at 2500 K (2.78 GPa) and 3000 K (3.31 GPa) and that from Kobsch and Caracas (2020) at 3000 K (~ 4.8 GPa) are included for comparison.

**Figure 6.** Viscosities of the SiO$_2$–H$_2$O and NaAlSi$_3$O$_8$–H$_2$O systems. The error bars indicate the mean absolute error. (a) The viscosities of the SiO$_2$–H$_2$O systems as a function of water content. The calculated viscosities ($\eta$) of the SiO$_2$–H$_2$O systems in this study at 2600 K (blue filled squares), 3000 K (red filled squares) and 3500 K (green filled squares) are shown. The FPMD results for hydrous (with 8.25 wt% H$_2$O) SiO$_2$ liquid (Karki and Stixrude, 2010) at 3000 K (~ 4.08 GPa) and 3500 K (~ 0.61 GPa) are included for comparison. (b) The viscosities of the NaAlSi$_3$O$_8$–H$_2$O systems as a function of water content. The calculated viscosities of the NaAlSi$_3$O$_8$–H$_2$O systems in this study at 2000 K (yellow filled circles), 2500 K (blue filled circles) and 3000 K (red filled circles) are shown. The FPMD results for the NaAlSi$_3$O$_8$ melt (Bajgain and Mookherjee, 2020) at 2500 K (2.78 GPa) and 3000 K (3.31 GPa) are included for comparison. The black dashed line and the blue dashed line show the results obtained from the experimental model of Audétat and Keppler (2004) at 2000 K and 2500 K, respectively. The insets show our viscosity data plotted with a linear y-axis. The corresponding stress ACF can be found in Figures S8 and S9 in Supporting Information.

**Figure 7.** Snapshot of the SiO$_2$–H$_2$O (left, 2600 K) and NaAlSi$_3$O$_8$–H$_2$O (right, 2000 K) systems with 50 wt% H$_2$O displayed by the 3D visualization program VESTA (Momma and Izumi, 2011). In addition to monomers, supercritical fluids contain various partially polymerized silicate units, including dimers, trimers and more polymerized species such as pentamers.
### TABLES

#### Table 1. The calculated pressures of SiO$_2$–H$_2$O systems. The error bars are calculated using the method of Flyvbjerg and Petersen (1989).

<table>
<thead>
<tr>
<th>H$_2$O (wt%)</th>
<th>System</th>
<th>Number of atoms</th>
<th>Pressure (GPa)</th>
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<td></td>
<td></td>
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<td>2600 K</td>
</tr>
<tr>
<td>0.00</td>
<td>60 SiO$_2$</td>
<td>180</td>
<td>—</td>
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<tr>
<td>70.94</td>
<td>7 SiO$_2$ + 57 H$_2$O</td>
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#### Table 2. The calculated pressures for the NaAlSi$_3$O$_8$–H$_2$O systems.

<table>
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<tr>
<th>H$_2$O (wt%)</th>
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<th>Pressure (GPa)</th>
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<td></td>
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<td>2000 K</td>
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<td>16 NaAlSi$_3$O$_8$</td>
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<td>10.27</td>
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<td>40.72</td>
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<td>2.03 ± 0.06</td>
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<td>50.75</td>
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<td>4 NaAlSi$_3$O$_8$ + 88 H$_2$O</td>
<td>316</td>
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</table>

### FIGURES
Figure 3

(a) SiO$_2$-H$_2$O
(b) NaAlSi$_3$O$_8$-H$_2$O

Abundance (%) vs. wt% H$_2$O

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Figure 4

(a) $D_{Si}(10^{-9}\text{ m}^2/\text{s})$ vs. wt% H$_2$O

(b) $D_{O}(10^{-9}\text{ m}^2/\text{s})$ vs. wt% H$_2$O

(c) $D_{H}(10^{-9}\text{ m}^2/\text{s})$ vs. wt% H$_2$O

Legend:
- 2600 K (This study)
- 3000 K (This study)
- 3500 K (This study)
- 2500 K, Karki & Stixrude (2010)
- 3500 K, Karki & Stixrude (2010)

Always consult and cite the final, published document. See http://www.minsocam.org or GeoscienceWorld
Figure 7