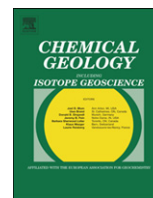




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Intrinsic proton dynamics in hydrous silicate melts as seen by quasielastic neutron scattering at elevated temperature and pressure



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ABSTRACT

We present quasielastic neutron scattering results on hydrous silica, sodium aluminosilicate, and sodium trisilicate melts with 10 mol% total water content, studied at high temperature under high pressure. Combining neutron time-of-flight spectrometry with neutron backscattering, intrinsic, microscopic proton dynamics is investigated on a time scale from 0.2 ps up to 1 ns between 850 K and 1250 K. All three hydrous silicate melts exhibit a relatively slow proton dynamics, although the melt viscosity is drastically reduced upon water dissolution. The self-diffusion coefficient of proton in the hydrous sodium trisilicate melt is on the order of $10^{-11} \text{ m}^2 \text{ s}^{-1}$, two orders of magnitude slower than the sodium dynamics in the corresponding anhydrous melt. The proton dynamics in hydrous silica and albite is not faster than that time scale. We show that the transport mechanism involves not only $-\text{OH}$ but also molecular water species. All protons are mobile during the transport of the water instead of diffusion of a specific water speciation. These characteristics of the proton structural relaxation in the melt can be attributed to a transport in a complex H-bonding environment.

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1. Introduction

The exsolution of volatiles is an important research issue in volcanology and has drawn enormous interests in the recent years. Among those, water is the dominant component in natural silicate melts. Several wt% of water can be stably dissolved in natural magma under a pressure of several kbars. The ascent and decompression of such a water bearing melt during explosive eruptions leads to bubble nucleation and growth in the melt, drives fragmentation of the magma (Gilbert and Sparks, 1998; Stebbins et al., 1995). Here, the knowledge of the water diffusion and the relation between the water content and the melt properties is essential to model these phenomena. Hence, the dissolution and transport mechanisms of water represent a key to understand many geological processes during volcanic eruption.

Upon its dissolution, it is now generally accepted that water reacts chemically with the Si-O network in silicate melts according to



resulting in both hydroxyl groups and molecular water. This can be identified by e.g. infrared spectroscopy (Stolper, 1982). The ratio between these two species is given by the extent of the reaction in Eq. (1), which depends on temperature, pressure and silicate melt composition (see e.g. Behrens and Nowak, 2003; Behrens and Yamashita, 2008, and a recent review by Zhang and Ni, 2010). The physical properties of the melt are non-linear functions of its water content. In particular, the melt viscosity could drop by several decades upon adding less than 1 wt% of water. In contrast, the change of the melt viscosity as function of water content is much shallower with further water dissolution. This can be generally understood by the depolymerisation of the Si-O network upon water addition (Dingwell et al., 1996).

However, the chemical equilibrium of Eq. (1) imposes many complications in the understanding of the water dissolution and its dynamics (Zhang and Ni, 2010). For conventional diffusion-couple experiments, the chemical diffusion of water in silicates must be

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treated as a multispecies diffusion case (Zhang and Ni, 2010; Zhang et al., 2007). Therefore, the role of each water species cannot be easily accessed. On the other hand, it also renders the quantification of the speciation itself a non-trivial task. For ex-situ experiments, since the water speciation changes with changing temperature, effects of quenching could be significant (Behrens and Nowak, 2003; Behrens and Yamashita, 2008). For in-situ experiment, the change of hydrogen bonding with respect to temperature, which is then reflected in e.g. the molar absorption coefficients in infrared spectroscopy, makes it difficult to isolate quantitatively the concentration changes of water species (Behrens and Nowak, 2003; Nowak and Behrens, 2001; Yamashita et al., 2008). Therefore, the water dissolution and diffusion mechanisms are still not well understood. Also, concerning the role of water in altering the macroscopic melt properties such as viscosity, it is difficult to relate the melt properties to a specific water speciation, which itself depends on the thermodynamic parameters and melt composition (Xue and Kanzaki, 2004).

Here we present our investigation on hydrous silicate melts employing quasielastic neutron scattering technique (QNS). In contrast to traditional diffusion couple or absorption/desorption experiments, QNS probes dynamics on a microscopic time and length scale. In addition, the intrinsic (self) proton dynamics of the melt is studied in a thermodynamic equilibrium state without the presence of chemical gradient. The momentum transfer q resolution of QNS allows detailed study of transport mechanisms. Thus, with this technique we intend to understand the elementary transport processes in hydrous silicate melts. In order to study hydrous silicates above their glass transition temperature, pressures around 100–200 MPa are necessary to keep the melt in equilibrium without water evaporation and bubble formation. Therefore, the neutron scattering experiments on the hydrous silicate melts were performed in a pressure cell made out of a niobium alloy. This benefits from the fact that neutrons have a relatively large penetration depth in metals, allowing the melts to be directly studied in the pressure cell with a wall thickness of about 15 mm. Moreover, the atomic scattering cross section of neutrons depends not only on the type of elements but also the type of isotopes, allowing a contrast variation via using different isotopes of the same element. Specifically here, proton (H) and deuterium (D) exhibit a large difference in their neutron scattering lengths and cross sections, makes it possible to access pure proton dynamics.

Three simple synthetic anhydrous silicate compositions were chosen for investigation: pure silica (SiO_2), sodium trisilicate ($\text{Na}_2\text{O} \cdot 3\text{SiO}_2$, NS3), and a sodium aluminosilicate composition ($\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$, albite), with a fixed water content of 10 mol%. The degree of the melt complexity increases from a single oxide component (SiO_2) to a three oxide components natural rock composition. Silica exhibits a melt structure of fully polymerised SiO_4 tetrahedrons. Upon addition of Na_2O the Si-O network is depolymerised, where the sodium ions are likely concentrated in the region of non-bridging oxygens (NBOs), charge compensating them. (Greaves, 1985; Kargl et al., 2006). For albite, by introducing another network-forming component Al_2O_3 , the network is again fully polymerised at the tectosilicate join ($\text{Na}_2\text{O}/\text{Al}_2\text{O}_3 = 1$), where all AlO_4 tetrahedrons are charge balanced by Na. Thus, influence of the degree of melt polymerisation and different network modifier/former on the water dynamics can be investigated. The hydrous melts were studied in a temperature range of 850–1250 K on two different neutron scattering instruments, covering a dynamics range from 0.2 picosecond (ps) up to 1 nanosecond (ns). This is necessary since it turns out that the proton dynamics is slow, extending beyond the ps time scale.

2. Material and methods

2.1. Sample preparation

Anhydrous glasses of NS3 and albite are prepared by fusion of pure powders of the corresponding oxides (Al_2O_3 , Alfa Aesar,

99.995%, and SiO_2 , Alfa Aesar, 99.995%, Suprasil) and sodium carbonate (Merck, 99.999%) at high temperatures under air in a Pt crucible. Batches of about 25–40 g anhydrous glasses were prepared to reduce the uncertainty in the sample composition. Melts were homogenised by annealing at 1500–1700 K for 12–24 h. For the albite composition, the dry melt is stirred additionally for 12 h with a Pt spindle at of about 1700 K to facilitate the homogenisation of the melt. Evaporation of components other than CO_2 during the complete preparation procedure was well below 1 wt%, verified by weighting the sample before and after each high temperature annealing step. The resulting homogeneous, transparent melt was quenched by pouring it on a stainless steel plate. The composition of the dry NS3 and albite glasses is checked with electron probe microanalyser (EMPA). The results are shown in Appendix A, and agree with the nominal composition within the measurement uncertainties.

Hydrous samples were synthesised in an internally heated pressure vessel under a constant pressure of 300 MPa (3 kbar) at 1500–1700 K. Both samples with H_2O and with D_2O were prepared for the purpose of contrast variation. The fixed total water content of 10 mol% was calculated by treating each oxide as one unit (Zhang, 1999). This corresponds to a weight fraction around 3%, listed for each glass composition in Appendix A. The proper amount of the anhydrous glass powder and water, typically 0.5–0.6 g anhydrous silicates with of about 20 mg H_2O / D_2O , were loaded in a Pt capsule and sealed gas tightly. The annealing time varies from 5 h to 12 h depending on the sample composition. For D_2O bearing samples, a small reservoir containing D_2O was put into the pressure vessel together with the samples to suppress H_2O contamination, from e.g. the Ar pressure medium. At the end of the annealing, as soon as the heating of the furnace was switched off, the sample was quenched adiabatically by driving it into a cold zone close to the bottom the pressure vessel. The cooling rate is estimated to be around 150–200 K/min when the melt passes its glass transition temperature, estimated from the temperature measured by a thermocouple attached to the sample. The capsule weight was carefully checked after each preparation step (before sealing, after sealing and heated to 120 °C, after annealing in the pressure vessel, and after opening and heated to 120 °C) to rule out the possibilities of any water loss and/or incomplete dissolution. Only samples with total capsule weight loss smaller than 1 mg were used for the scattering experiments. The uncertainty of the nominal water content is below ± 1 mol%, determined from the thermogravimetric analysis (TGA). The difference between the relative scattering intensity of H_2O and D_2O samples by of about a factor of 2.5 (c.f. Fig. 1) also supports such estimation. Water is also considered to be homogeneously distributed as fragments from different positions of a sample gave very similar TGA results. The proton dynamics of the sample is considered to be insensitive to such a small uncertainty at this total water content, as the macroscopic melt properties change only very little within this variation (see e.g. Dingwell et al., 1996). The measured glass transition temperature T_g of the hydrous NS3 and hydrous albite samples agrees very well with the reported literature values measured for similar total water content (Romano et al., 2001; Tomozawa et al., 1983; Zietka et al., 2007). For hydrous SiO_2 it was not possible to obtain T_g which is masked by foaming of the sample, which is however close to that reported T_g by Zietka et al. (2007) with a slightly lower water content.

The span of T_g s measured at different positions of a sample is smaller than 5 K for both protonated and deuterated NS3/albite compositions. The T_g of the D_2O bearing samples is however systematically higher than that of the H_2O samples by about 10 K. The difference in the water content larger than 10 % can be excluded. One possible reason might be that the cooling of the deuterated samples are slightly faster, since their position in the pressure vessel was slightly different due to the presence of the D_2O reservoir. For hydrous silica, the foaming temperatures measured are located around 950 K, which exhibits only a small spread.

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