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The dissolution mechanisms of water in silicate melts; a synthesis of recent data

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ABSTRACT

Dissolved water has significant effects on the physical and chemical properties of silicate melts. Some of the different approaches towards understanding these effects are reviewed here. Spectroscopic measurements on hydrous glasses quenched from melts provide good models for the structure of the melts at the glass transition temperature (T_g). Such measurements suggest that the mechanism of dissolution of water in silicate melts varies strongly with the bulk composition. In particular framework aluminosilicate compositions seem to have very different dissolution mechanisms from Al-free compositions. The water speciation reactions are temperature dependent, with some of the molecular water which is present in glasses at room temperature being converted to hydroxyl at high temperatures. This conversion probably occurs only above T_g . Data on the kinetics of the speciation reaction and the dynamics of microscopic processes in hydrous silicate melts are also discussed. Finally some important aims of future work on hydrous silicate melts are suggested.

KEYWORDS: dissolution mechanism, silicate melt, glass transition temperature.

Introduction

HYDROUS silicate melts are important in the Earth because of the central role they play in global processes such as partial melting of mantle rocks, differentiation of magmas, loss of volatiles from the Earth through time and explosive volcanic eruptions. The physical and chemical properties of such melts are a strong function of the amount of dissolved water, and a great deal of effort has been expended in systematically measuring water solubilities in melts and the effect of water on melt properties such as viscosity. As an example, the effect of small concentrations of water on the viscosity of a haplogranitic melt (Dingwell *et al.*, 1996) is shown in Fig. 1. Note the very large effect of the first 1% of water, which reduces viscosity by >6 orders of magnitude. The increase in viscosity which accompanies exsolution of water from a magma is considered to be a major factor in explosive volcanic eruptions. Water in

glass is also important in many technological applications of glass such as the chemical durability of nuclear waste glasses, the transmittance of optic fibres, the mechanical properties of glasses and the rheology of glass melts during fusion.

In order to be able to predict the effect of water on phase equilibria and melt properties, and to account for the effects of pressure, temperature and melt composition in complex multicomponent systems, it is crucial to understand the microscopic dissolution mechanisms of water. Some information on the mechanisms of dissolution of water in silicate melts may be obtained indirectly from phase equilibria (e.g. Kushiro, 1969; Pichavant *et al.*, 1992), calorimetry (e.g. Clemens and Navrotsky, 1987; Epel'baum *et al.*, 1995) and measurements of properties such as water solubility (e.g. Goranson, 1931; Holtz *et al.*, 1992, 1995a; Romano *et al.*, 1996) viscosity (e.g. Schulze *et al.*, 1996; Holtz *et al.* 1999), density (e.g. Burnham and Davis, 1971; Lange, 1994; Ochs and Lange, 1997), diffusion (e.g. Nowak and Behrens, 1997; Behrens and Nowak, 1997) and compressibility (e.g. Richet and Polian,

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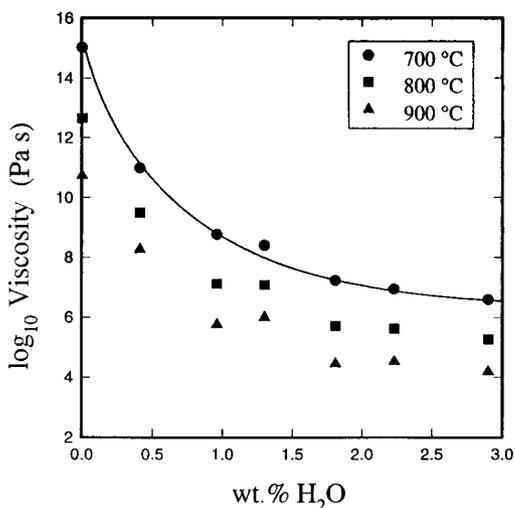
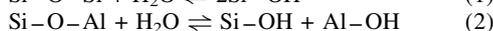
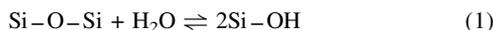


FIG. 1. The effect of dissolved water on the viscosity of the haplogranitic melt HPG8 at 1 bar (modified from Dingwell *et al.*, 1996).

1998). Such measurements were used in devising the thermodynamic model of Burnham (1975). This model and associated work (see Burnham, 1994 for a review) has generally been considered to be a useful tool in hydrous silicate melt thermodynamics. However, the structural basis of the model now appears to be in error; more sophisticated models are now required which take into account improved data for water solubility, viscosity, etc., and which embrace the substantial insights into water dissolution mechanisms which have come from spectroscopic and diffraction measurements on hydrous glasses and melts. It is these direct measurements of hydrous silicate glass and melt structures which will be the main subject of this review.

There is an enormous body of work on this subject which is distributed over the geology, glass technology, chemistry and physics literature and a comprehensive review is no longer feasible. My main aims here are to update the excellent review by McMillan (1994), and to provide a simple synthesis of the most important structural and spectroscopic data for non-specialists. The choice of these key data will inevitably be subjective to some extent, and a strong emphasis will be placed on NMR measurements, but it is to be hoped that this approach will serve as a useful starting point for more detailed surveys of the literature.

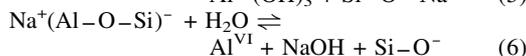
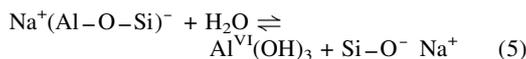
Many different dissolution mechanisms have been proposed for dissolution of water in silicate and aluminosilicate melts. The simplest are reactions involving rupture of a T-O-T bridge to give T-OH.



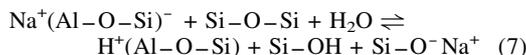
In reactions 2 and 3 the Al is tetrahedrally coordinated and charge balanced by a cation such as Na⁺ in both reactants and products. A modified version of reaction 2 involves breakage of Al-O-Si to give terminal hydroxyl Al-OH groups only, with no formation of Si-OH. A bridging Si-O-Si is thus formed. Again the Al is tetrahedrally coordinated and charge balanced by a cation such as Na⁺ in both reactants and products.



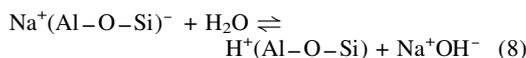
Much more complex mechanisms can also be proposed involving coordination changes, creation of anhydrous non-bridging oxygen and hydrous Al and/or Na complexes. The reactions 5 and 6 written below are the simplest way to convey these reactions (but note that they are not chemically balanced).



The mechanism invoked by Burnham (1975) also involves several reactions and can be summarized in equation 7 below. Replacement of Na⁺ by H⁺ as a charge balancing cation for AlO₄⁵⁻ is accompanied by rupture of one Si-O-Si bond to give Si-OH + Si-O⁻Na⁺. In the Burnham model further addition of water reacts via equation 1



Finally, a simple mechanism involving ion exchange of H⁺ as charge balancing cation for AlO₄⁵⁻ instead of Na⁺, with removal of Na to form a NaOH complex within the melt is possible. This charge balancing H can also be thought of as a bridging hydroxyl. Note that reaction 8 is the only one which does not involve rupture of T-O-T bonds.



Each of the reactions 1 to 8 represents an equilibrium between some type of hydroxyl as a product and molecular water as a reactant. Much of the spectroscopic data in the literature (mostly infrared) has focused on the position of the equilibrium, i.e. the $\text{OH}/\text{H}_2\text{O}_{\text{mol.}}$ ratio and there has been a tendency to overlook the need to establish the relative importance of the different possible reactions. In this review I will attempt to cover both the position of the hydroxyl/molecular water equilibrium and the relative importance of reactions such as 1 to 8 in melts of different compositions.

Sources of information on glass and melt structure

Infrared spectroscopy

Infrared (IR) spectroscopy has been used widely to provide information on the speciation of water in glasses, i.e. the $\text{OH}/\text{H}_2\text{O}_{\text{mol.}}$ ratio. However, quantitative measurement of water concentrations and speciation is subject to significant difficulties. Firstly, extinction coefficients (the proportionality constants which relate the intensity of an IR peak to the concentration of the species to which it is due) are often inadequately determined, because they may depend on glass composition, water concentration and temperature. Secondly, the method used to subtract the background, and differences between instruments make it difficult

to transfer extinction coefficients reliably from one study to another.

The O–H stretching fundamental at $\sim 3000\text{--}3600\text{ cm}^{-1}$ is not very useful for determining the speciation as it has contributions from hydroxyl and molecular water (although it can, in principle, be used to determine total water concentrations for glasses). The peaks which are generally used are those at 4500 cm^{-1} which is a combination band related to hydroxyl and 5200 cm^{-1} which is the bend-stretch combination of molecular water (Fig. 2). Stolper (1982) found that the weighted sum of the 4500 and 5200 cm^{-1} peaks was proportional to the total dissolved water concentration. Despite the widespread application of IR to measurement of water speciation in glasses, the exact origin of the 4500 cm^{-1} peak is not yet clear. It is usually described as a combination band between a vibration at $\sim 900\text{ cm}^{-1}$ and the fundamental O–H stretch at 3600 cm^{-1} . However as the nature of the 900 cm^{-1} vibration is not fully understood for aluminosilicate glasses the origin of the 4500 cm^{-1} band remains controversial. It should also be noted that the method used to subtract the background from the true peak intensities is crucial and different groups working in this area have used very different background subtraction methods. For example Stolper (1982) and Zhang *et al.* (1997b) used a curved baseline fit by eye, whereas Behrens *et al.* (1996) used a linear

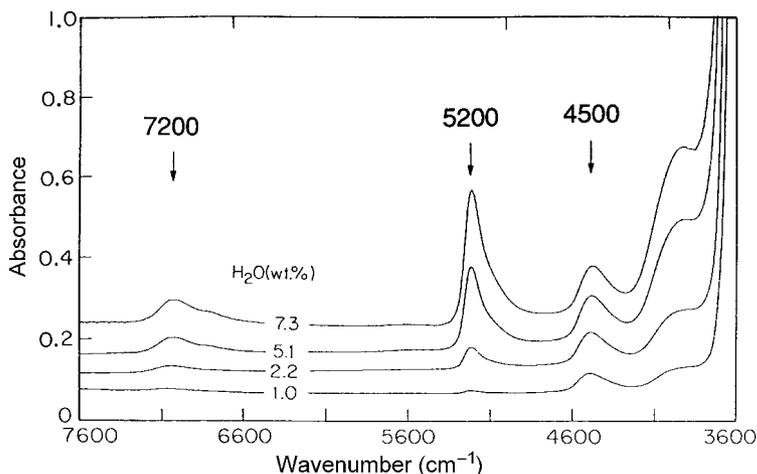


FIG. 2. Typical IR spectrum of a hydrous glass in the region $7600\text{--}3600\text{ cm}^{-1}$ (Silver and Stolper, 1989). The peak at 5200 cm^{-1} is related to dissolved molecular water and the peak at 4500 cm^{-1} is related to hydroxyl. The peak at 7200 cm^{-1} scales with the total water concentration of the glass.

extrapolation from a different part of the spectrum and removed a Gaussian peak at 4000 cm^{-1} . Both methods have their advantages, but this conflicting methodology leads to very different extinction coefficients for the peak. As a result many of the 'extinction coefficients' referred to in the literature are best considered simply as empirically derived constants as they may have little relationship to the physics of absorption of vibrational energy. Although it is perfectly valid to use these constants, they cannot be transferred reliably between IR instruments and any resulting water speciation data will be very susceptible to different data-processing methods. Another difference between different studies is that some have used linear extinction coefficients and measurements of peak heights whereas others have used integrated values and measurements of peak areas. The integrated area of the peaks should give more reliable values of water concentration, especially if peak shape is variable, but this method is more susceptible to errors in baseline subtraction, so the linear method is often used. Furthermore most workers have assumed that the extinction coefficients are independent of the water concentration of the glass, but Zhang *et al.* (1997b) have shown that the extinction coefficients do indeed vary as a function of water concentration. This is not a surprising result, because the local environment of any particular group (molecular water or hydroxyl) is likely to vary with total water concentration.

One very attractive feature of IR spectroscopy is that it is a sensitive technique. It is therefore suitable for samples with low water concentrations, and it can be used when good spatial resolution is required, e.g. for natural melt inclusions. This high sensitivity enables measurements to be made *in situ* at high pressures and temperatures using a small sample in a diamond anvil or similar cell.

Raman spectroscopy

Raman spectroscopy is complementary to IR in that it is a vibrational spectroscopic technique which is sensitive to different types of vibrations. Raman spectroscopy of glasses provides information mainly on the structure of the aluminosilicate part of the network. There is a series of bands at $\sim 800\text{--}1200\text{ cm}^{-1}$ which are better resolved in Raman spectroscopy than in IR. These bands have been assigned to stretching vibrations of silicate and aluminosilicate tetrahedra with varying

numbers of non-bridging oxygens (see McMillan, 1984; Mysen *et al.*, 1982). However, the origin of some bands in this region is still not fully understood, and the presence of Al in addition to Si reduces the resolution between the characteristic peaks. There are also bands at $400\text{--}700\text{ cm}^{-1}$ which appear to be related to intertetrahedral vibrations, and thus may contain information about intertetrahedral bond angles and ring sizes.

There are numerous Raman studies of hydrous glasses but the main limitations are that the complex spectra which are obtained are not fully assigned, and that overlapping peaks often necessitate the use of underdetermined spectral deconvolutions. Even if all the peaks in a Raman spectrum can be assigned, it is difficult to quantify the concentrations of species in a melt or glass from the intensities of the peaks. Consequently there have been disagreements over interpretations of spectra even amongst practitioners of the method.

Raman spectroscopy can be applied to high temperature and even simultaneous high pressure and high temperature conditions more easily than most of the other spectroscopic techniques. This is because the laser source can be focused to a small area and because the geometry of a diamond anvil cell is convenient for Raman. The timescale of the effect allows (in principle at least) changes in the abundances of silicate species to be measured well above T_g (e.g. Mysen, 1998). This is a major advantage over NMR for *in situ* high temperature measurements of silicate speciation (see below).

Nuclear magnetic resonance spectroscopy

Nuclear magnetic resonance (NMR) spectroscopy has provided some of the most important data with bearing on the structures of hydrous glasses. It is an element-specific technique, thereby enabling the local environment around each element of interest to be probed individually. Most of the elements of interest in understanding simple hydrous silicate melts have nuclei which are suitable for study using conventional techniques (e.g. ^1H , ^2H , ^{11}B , ^{17}O , ^{23}Na , ^{27}Al , ^{29}Si , ^{31}P) and thus a self-consistent and coherent picture of a glass structure can be constructed. The technique is intrinsically quantitative, with the area of a given peak being directly related to the abundance of the species from which it arises. There are also various methods of performing selective NMR experiments. One of the most

useful in the study of hydrous silicate glasses is cross-polarization from ^1H to ^{29}Si or other nuclei. The transfer of magnetization from ^1H to ^{29}Si increases the relative intensity of silicon atoms near hydrogen. By adjusting the parameters of the experiment detailed information about specific spatial relationships between pairs of elements can be obtained. In addition to providing information on static structures, NMR has the potential to probe a variety of dynamic processes on timescales ranging from several hours to microseconds (e.g. Stebbins, 1988; 1995). The most commonly used technique in studies of hydrous silicate glasses is magic angle spinning (MAS), a method which enables high resolution spectra to be obtained for solid samples. The method has been applied to study the local environments of Si, Al, Na and H. In this respect it is complementary to IR which is most useful for studies of the speciation of water.

A major application of NMR in anhydrous silicates has been *in situ* high temperature studies of dynamic processes. Processes such as exchange of Si between Q^3 and Q^4 environments in melts (where Q^n indicates a tetrahedral environment with n bridging oxygens and $4n$ non-bridging oxygens) are intimately related to the mechanism of viscous flow and are therefore of crucial importance (Stebbins, 1995). However, such measurements have not yet been performed for hydrous melts.

The major limitation of NMR is that it is generally unsuitable for samples containing iron or other paramagnetic cations. This has limited its use to simple synthetic analogue systems such as glasses in the Qz-Ab-Or system and alkali silicates rather than natural rhyolites and basalts. Furthermore, much larger samples are required than for IR or Raman spectroscopy and spatially resolved studies are not possible. A problem for the future is that it is much more difficult to devise an experimental procedure for high temperature and high pressure NMR (especially using MAS) than it is for IR and Raman. Therefore, NMR is likely to lag behind vibrational spectroscopy in *in situ* studies of hydrous silicate melts.

Optical absorption spectroscopy

Optical absorption spectroscopy has limited use in elucidating the dissolution mechanisms of water in silicate melts and glasses because it does not provide information on the environments of Si,

Al, Na, Ca, O, etc. However, it has been used to provide information on the environments of transition metals in hydrous glasses (e.g. Nowak and Keppler, 1998).

X-ray absorption spectroscopy (XAS)

In principal, XAS should be a very useful technique for obtaining structural information on hydrous glasses. However, most of the elements of interest have atomic numbers ≤ 14 , and the low X-ray energies involved make the measurements technically quite difficult. The main use of XAS so far has been to study the effect of dissolved water on the environments of transition metals and other heavy cations such as Mn and Sr (Kohn *et al.*, 1990), Mo (Siewert *et al.*, 1997), Ti and Zr (Farges and Brown, 1997).

X-ray and neutron diffraction

Although much of the early work on glass structure was done using X-ray diffraction, very few studies of hydrous glasses have been performed. X-ray diffraction can give a radial distribution function (RDF) which is the sum of the pair correlation functions of all the atoms in the glass. For complex compositions, this obviously makes it difficult to extract model-independent structural information. X-ray diffraction (XRD) is also limited in its application to hydrous glasses by the very low scattering factor of H. One example of the application of XRD to hydrous glasses is the work of Zotov *et al.* (1992), who observed changes in the first sharp diffraction peak in a series of hydrated rhyolites, but very little change in the RDF below 5.1 Å. The data were interpreted in terms of a model whereby water dissolution only affects medium range order. Neutron diffraction is a similar technique to XRD but it has the advantage that D is a strong coherent scatterer while H is a strong incoherent scatterer. Neutron diffraction has also been used with isotopic substitution of cations such as Ca and Ni to obtain partial radial distribution functions and thereby elucidate the nature of medium range order in anhydrous glasses (Gaskell *et al.*, 1991).

Hydrous glasses at ambient temperatures

For many years the only information which was available on the structure of hydrous silicate melts was obtained by spectroscopic and other studies at

ambient conditions of glasses quenched from melts at high pressure and temperature. Although it was always expected that there would be some changes in structure on quenching, there was until recently no way of testing the extent of this problem, and a large body of data on glasses was obtained with the assumption that the changes would be small. This assumption and the changes which occur in hydrous glass and melt structures as a function of temperature will be discussed in a later section; in summary it now appears that the structures of hydrous glasses in terms of (1) the aluminosilicate coordination and connectivity and (2) the water speciation, can be considered to be representative of the structures of the equivalent melts at T_g (Dingwell and Webb, 1990). The large database on hydrous glass structures collected under ambient conditions is therefore a crucial resource in understanding hydrous melts as long as it always remembered that large changes in structure may have occurred between the synthesis temperature of the sample and T_g . This is particularly important for hydrous melts where viscosity, and hence T_g , is such a strong function of water concentration.

Some early studies suggested that all water reacted with the melt structure and that molecular H_2O was not a dissolved species in glasses (e.g. Burnham, 1975). However, since the work of Stolper (1982) it has become clear that all glasses containing >1 wt.% water contain a significant concentration of H_2O_{mol} . The speciation in glasses is a strong function of water concentration, with high water concentrations having lower OH/ H_2O ratios. There have been a few studies of the effect of melt composition on speciation (e.g. Silver *et al.*, 1990) which suggest that there are significant differences. However, some of this variation may be due to differences in T_g for the different compositions. In reading the following sections, it should be remembered that in all compositions H_2O_{mol} becomes relatively more abundant compared to OH at high water concentrations; most of the following discussion will therefore concentrate on the nature of the species involved and the mechanisms of reaction.

SiO_2 glasses

The simplest possible hydrous silicate glass system is SiO_2-H_2O , and this system is therefore an important starting point in any consideration of more complex systems. Hydrous silica glasses have been studied by NMR (Farnan *et al.*, 1987;

Kohn *et al.*, 1989b), IR (McMillan and Remmele, 1986; Davis and Tomozawa, 1996) and Raman (Mysen and Virgo, 1996a; McMillan and Remmele, 1986; Holtz *et al.*, 1996) spectroscopy, and there is broad agreement between all studies. ^{29}Si MAS NMR gives very clear information on silicate speciation, because the ^{29}Si spectrum for dry SiO_2 glass consists of a relatively narrow peak at the position expected for Si with four Si next nearest neighbours (i.e. $Q^4(4Si)$). In hydrous SiO_2 glasses, the ^{29}Si MAS NMR spectra (Farnan *et al.*, 1987) show reasonably well resolved new peaks at more positive shifts (Fig. 3), showing unambiguously that Q^4 silicons are converted to Q^3-OH and, at high dissolved water concentrations, $Q^2-(OH)_2$. Farnan *et al.* (1987) measured the concentrations of these species for glasses with two different water concentrations, then by comparing these values with the expected values

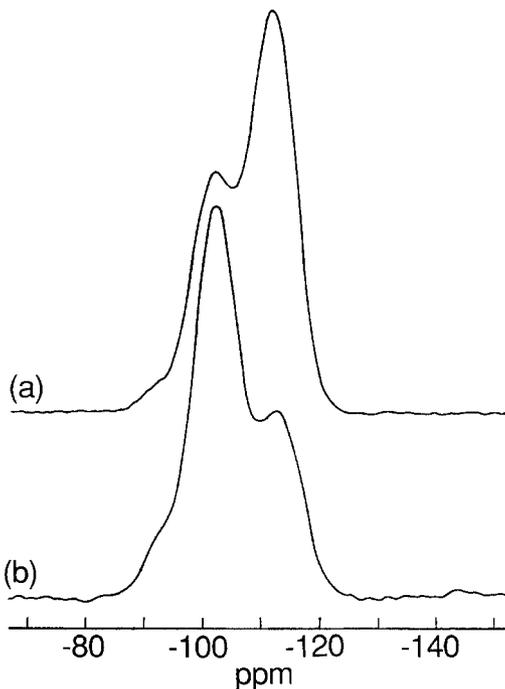


FIG. 3. ^{29}Si CP MAS NMR spectra of a hydrous SiO_2 glass containing 8.7 wt.% H_2O (Farnan *et al.*, 1987). The peaks at -111.1 , -100.5 and -91.5 ppm are due to Q^4 , Q^3-OH and $Q^2-(OH)_2$ silicons respectively. The spectrum in (a) was acquired using a contact time of 15 ms, compared with 500 μs for (b). The two spectra illustrate how the intensity of silicons close to H is enhanced by using short contact times.

for complete reaction via reaction 1 were able to calculate the $\text{OH}/\text{H}_2\text{O}_{\text{mol.}}$ ratio. Confirmation of the $\text{OH}/\text{H}_2\text{O}_{\text{mol.}}$ ratios for the same samples was obtained by ^1H MAS NMR (Kohn *et al.*, 1989*b*). The $\text{OH}/\text{H}_2\text{O}_{\text{mol.}}$ ratio is somewhat higher than that measured in compositions such as rhyolite and albite using IR (Silver *et al.*, 1990), an observation which may reflect a different dissolution mechanism, or may be related to T_g . An important feature of the Raman spectrum of hydrous SiO_2 glass is the appearance of a new peak at 970 cm^{-1} (Mysen and Virgo, 1986*a*) shown in Fig. 4. This peak moves to 950 cm^{-1} in deuterated samples, fully consistent with the assignment to a vibration of Si-OH.

Although the Q -species distribution and the $\text{OH}/\text{H}_2\text{O}_{\text{mol.}}$ ratio are fairly well constrained for

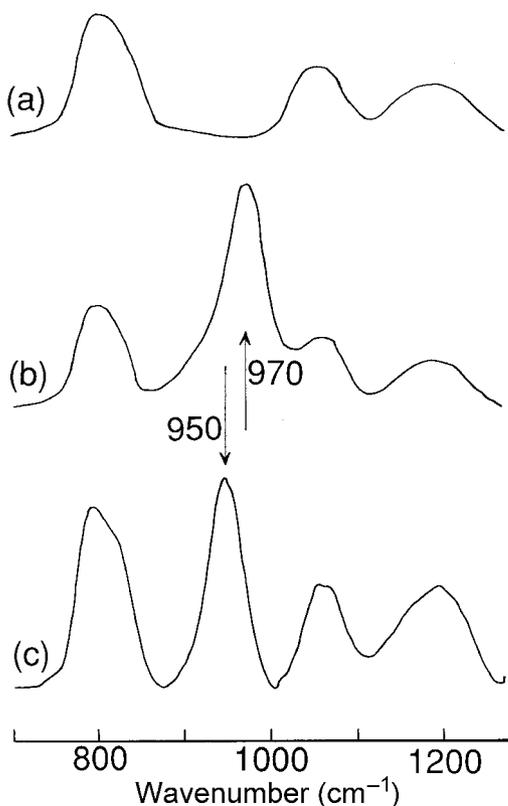


FIG. 4. Raman spectra of SiO_2 glasses (redrawn from data in Mysen and Virgo (1986*a*)). (a) dry SiO_2 glass; (b) $\text{SiO}_2 + 10\text{ wt.}\% \text{H}_2\text{O}$; (c) $\text{SiO}_2 + 5\text{ wt.}\% \text{D}_2\text{O}$. Notice the hydroxyl related band at 970 cm^{-1} in the H_2O bearing glass which moves to 950 cm^{-1} in the deuterated glass.

hydrous SiO_2 glass, there are other aspects of the dissolution mechanism which are more elusive. For example a substantial reduction in the intensity of the peaks at $\sim 605\text{ cm}^{-1}$ and 495 cm^{-1} , implies a reduction in the abundance of 'defect sites' such as 3- and 4-membered rings (McMillan and Remmele, 1986; Mysen and Virgo, 1986*a*) but the number of silicons in such environments is probably small, and a quantitative description of changes in ring size statistics is not yet possible. Another feature which needs to be clarified in future studies is whether Q^4 , Q^3 -OH and Q^2 -(OH) $_2$ species are distributed randomly within the structure, or are clustered in some way.

$\text{Na}_2\text{O-SiO}_2$ glasses

The next level of complexity comes from the addition of alkali or alkaline earth oxides. Most work has been done on $\text{Na}_2\text{O-SiO}_2$ glasses, but the limited data on other oxides such as Li_2O , SrO and BaO seem to suggest that these systems behave in a similar way. ^{29}Si MAS NMR studies of the dissolution of water in sodium tetrasilicate ($\text{Na}_2\text{Si}_4\text{O}_6$) glasses (Kümmerlen *et al.*, 1992) showed clearly that the concentration of Q^4 silicon is reduced relative to Q^3 by the presence of water (Fig. 5). At high water concentrations Q^2 silicon has a substantial abundance. Thus water dissolves in sodium tetrasilicate glass by essentially the same mechanisms as in silica glass, by breaking Si-O-Si bridges to give Si-OH, i.e. reaction 1. Recently, Zotov and Keppler (1998) combined Raman, IR and NMR data on hydrous sodium tetrasilicate glasses to confirm this picture. A reaction such as $\text{Si-O-Na} + \text{H}_2\text{O} \rightarrow \text{Si-OH} + \text{NaOH}$ may also occur. Similar results for lithium silicate gels were reported by Dupree *et al.* (1990). Infrared (McMillan and Remmele, 1986), ^1H MAS NMR (Kohn *et al.*, 1989*b*; Schaller and Sebald, 1995) and Raman (McMillan and Remmele, 1986) all show evidence for strongly hydrogen bonded hydroxyl, presumably via interaction with non-bridging oxygens.

Zotov *et al.* (1996) used changes in the shape of the first sharp diffraction peak in neutron diffraction data to suggest that hydrous sodium tetrasilicate glass has less medium range order than the equivalent dry glass. However, they noted that the Na coordination appears to be more ordered in the hydrous glass, and also confirmed that the hydrous glass is more depolymerized.

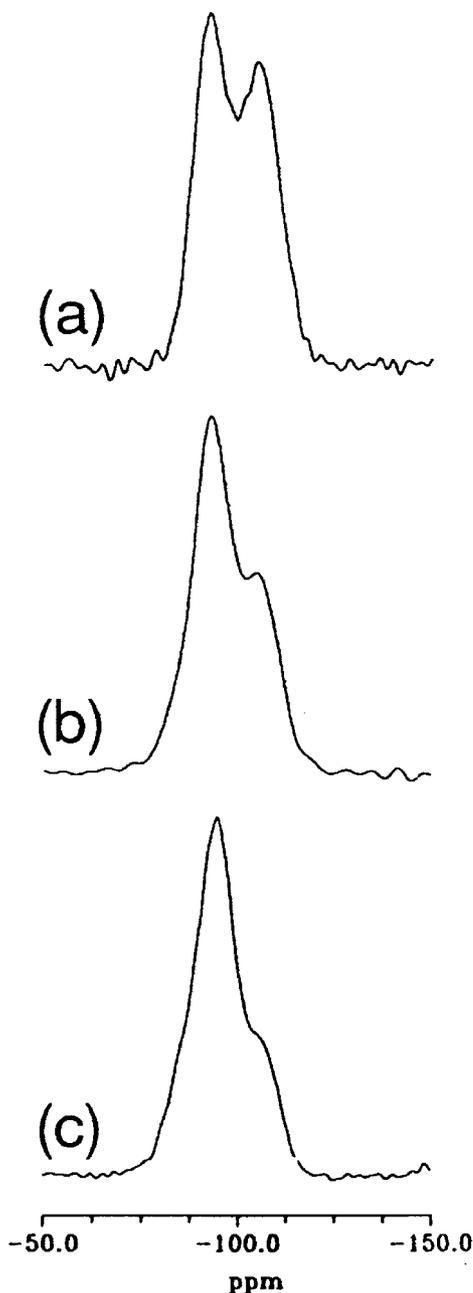


FIG. 5. ^{29}Si MAS NMR spectra of hydrous $\text{Na}_2\text{Si}_4\text{O}_9$ glasses (Kümmeler *et al.*, 1992). (a) dry glass; (b) 4.8 wt.% H_2O ; (c) 9.1 wt.% H_2O . The relative abundance of Q^3 (at -93 ± 1 ppm) is increased compared to Q^4 (-106 ± 1 ppm) upon water dissolution, and Q^2 (-83 ± 2 ppm) is present in substantial concentrations in the hydrous glasses.

In summary there is general agreement between different studies on the effect of water on silicon Q -species (i.e. short range order), but there are still rather few data on how these species are connected (an aspect of medium range order).

NaAlSi₃O₈ and other tectosilicate glasses containing aluminium

Virtually all natural silicate melts contain major element abundances of aluminium, therefore it is more important to understand water dissolution mechanisms in aluminosilicate melts than in simple systems such as SiO_2 and $\text{Na}_2\text{O-SiO}_2$. Unfortunately the dissolution mechanisms in aluminosilicate melts are much more controversial. Early studies concluded that there was no major distinction between the dissolution mechanism in silicate and aluminosilicate melts. However a multinuclear NMR study of hydrous albite glasses (Kohn *et al.*, 1989a) suggested that a completely different water dissolution mechanism from that in SiO_2 and alkali silicate glasses was occurring. One of the strongest pieces of evidence comes from ^{29}Si MAS NMR spectra of dry and hydrous albite glasses. Even when 60 mol.% H_2O is dissolved (on an 8 oxygen basis), there is no difference in the single pulse ^{29}Si NMR spectra. The $^1\text{H-}^{29}\text{Si}$ CP MAS spectra which showed major changes for hydrous SiO_2 glasses as a function of contact time also show only very small changes between glasses with low and high water concentration. The same observation has been made for glasses such as nepheline, $\text{An}_{50}\text{Qz}_{50}$ (Kohn *et al.*, 1992) and glasses on the feldspar-rich side of the Ab-Or-Qz system (Schmidt *et al.*, 1998, 2000 and unpublished data). The data for nepheline shown in Fig. 6 are particularly convincing as the linewidth in the anhydrous nepheline glass is as narrow as for SiO_2 glass. These data are therefore subject to less ambiguity than the broader peaks observed in compositions such as albite where a distribution of $Q^4(n\text{Al})$ environments coexist. These observations seem to rule out formation of large concentrations of Si-OH via reactions 1 or 2. They also suggest that 4 is not important, as a decrease in the number of Al next-nearest-neighbours implied by reaction 4 would also show up in changes in position and/or width of ^{29}Si MAS NMR spectra.

The interpretation of the ^{27}Al NMR data of Kohn *et al.* (1989a, 1992) is less certain because ^{27}Al is a quadrupolar nucleus, and the peaks are

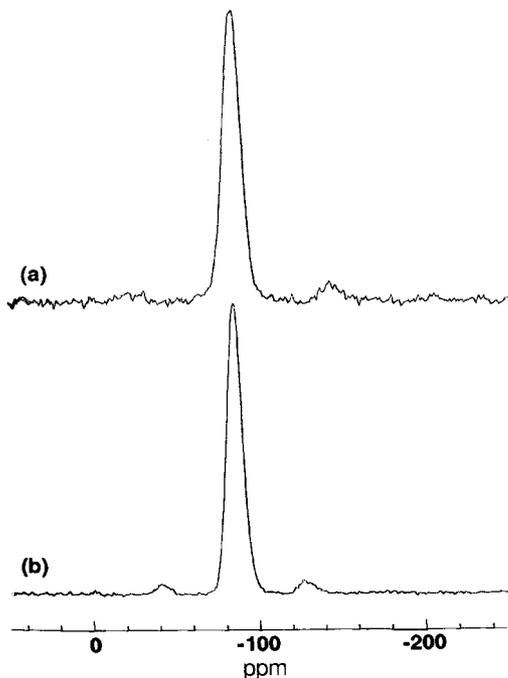


FIG. 6. (a) ^{29}Si MAS NMR spectra for anhydrous nepheline glass and (b) ^1H - ^{29}Si CP MAS NMR spectrum of hydrous nepheline glass containing 8.5 wt.% H_2O (Kohn *et al.*, 1992). The peaks in the spectra are at the same position strongly suggesting that Si-OH is not formed via reactions 1 or 2, that Si-O-Si is not formed via reaction 4 and that Si-O $^-\text{Na}^+$ is not formed via reactions 5 or 6. The peak in the hydrous glass is slightly narrower than in the dry glass, suggesting a more ordered structure.

broadened by electric field gradients (efg) at the nucleus. However, the absence of any intensity near 0 ppm in the spectra is strong evidence that the increases in Al coordination number suggested by equations 5 and 6 do not occur. The absence of octahedral Al is also suggested by XRD of hydrous albite glass (Okuno *et al.*, 1987). The isotropic chemical shift of the tetrahedral Al shows only small changes implying that large concentrations of Q^3 -OH are absent. Furthermore, there is a reduction in the distribution and mean value of the efg at Al. This also implies that tetrahedral Al-OH is absent because a Q^3 -OH group would be expected to have a larger efg than Q^4 (Kohn *et al.*, 1994). It can therefore be deduced that reactions 2, 3 and 4 are unimportant.

In contrast to the subtle changes in the Si and Al environments suggested by ^{29}Si and ^{27}Al

spectra there are major changes in the environment of Na in albite glasses as dissolved water concentration is increased. New data have recently been published (Kohn *et al.*, 1998) which supersede the ^{23}Na MAS NMR data of Kohn *et al.* (1989a) (the spinning speed in the earlier study was insufficient). Figure 7 shows a plot of centres of gravity of the ^{23}Na MAS NMR peaks plotted as a function of the inverse square of the Larmor frequency (Kohn *et al.*, 1998). The data are treated in this way because the intercept on the shift axis is equivalent to the mean isotropic chemical shift and the gradient is related to the mean quadrupole coupling constant (C_q). The isotropic chemical shift changes linearly with dissolved water concentration, approaching 0, the value for a hydrated sodium cation in aqueous solution. The nearly constant gradient implies that the average value of C_q is not dependent on dissolved water concentration (a conclusion supported by ^{23}Na nutation spectroscopy (Kohn *et al.*, 1998)). However, the distribution of C_q does change with water concentration, with a much smaller distribution of environments being present in the most hydrous glasses. Although it is not possible to describe the exact coordination environment on the basis of these ^{23}Na NMR data, it appears that whereas only subtle changes in Si and Al environment occur upon water dissolution, there are major changes in the local environments of Na. The original ^{23}Na data of Kohn *et al.* (1989a) were used by Sykes and Kubicki (1993) to suggest that a major change in dissolution mechanism occurs in albite melt at 30 mol.% dissolved H_2O . However, it is now known that the kink in the C_q data of Kohn *et al.* (1989a) was in error and the revised data of Kohn *et al.* (1998) which show no change in C_q between 0 and 60 mol.% dissolved H_2O argue against this aspect of the model. [As an aside, it should be mentioned that there have been several molecular orbital calculations of the stabilities of hydrated aluminosilicate species, and of NMR parameters and vibrational frequencies (e.g. Sykes and Kubicki, 1993; Sykes *et al.*, 1997; Tossell and Sàghi-Szabó, 1997). Such studies are an interesting complement to the spectroscopic data on glasses, but there are significant disagreements between studies from different groups, and at present are probably not sufficiently well developed to be considered as primary evidence.]

A further constraint on the dissolution mechanism of water in albite melt is provided

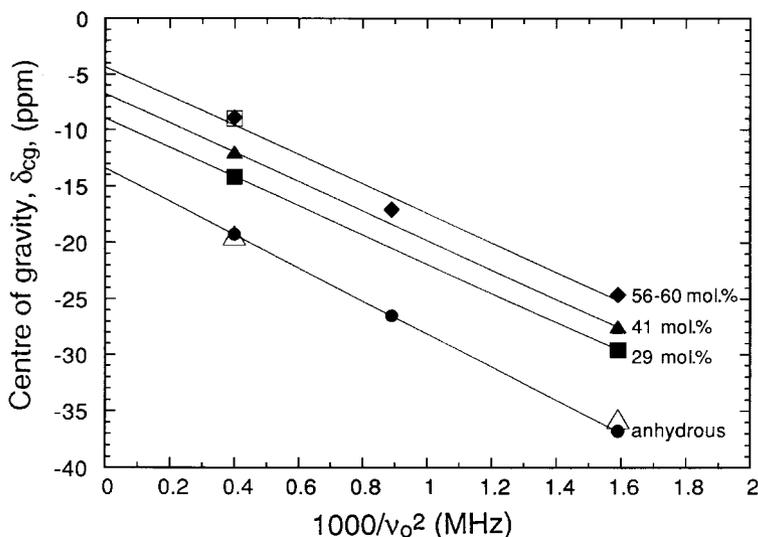


FIG. 7. The centre of gravity of ^{23}Na MAS NMR spectra for hydrous albite glasses plotted as a function of the inverse square of the Larmor frequency (Kohn *et al.*, 1998). In this plot the intercept on the shift axis is equivalent to the mean isotropic chemical shift, and the gradient is related to the mean electric field gradient at the ^{23}Na nuclei.

by ^{17}O multiple quantum (MQ) MAS NMR. In this type of experiment high resolution between different oxygen sites in glasses can be achieved, and data for dry albite glass (Dirken *et al.*, 1997) suggest that Al-O-Al linkages are essentially absent (Fig. 8). This observation rules out reaction 3 as an important component in the water dissolution mechanism in sharp contrast to the suggestion of Sykes and Kubicki (1993). ^{17}O MQ MAS NMR spectra of a hydrous albite glass are essentially identical to those for dry albite glass, with no significant change in the ratio of Si-O-Si:Si-O-Al (Kohn *et al.*, 1997). At first sight this is somewhat surprising, as $\text{H}_2\text{O}_{\text{mol}}$ and some sort of hydroxyl must be present. However, it is known that $\text{H}_2\text{O}_{\text{mol}}$ has a large C_q and because of the present limitations of MQ MAS NMR this type of oxygen would be expected to be absent from the spectrum. Similar arguments can be invoked for NaOH, Si-OH or Al-OH species if they are present. Nonetheless the constant value of the Si-O-Si:Si-O-Al ratio in both dry and hydrous glasses implies that a substantial role for reaction 4 in the water dissolution mechanism is very unlikely. A different ^{17}O NMR study of dry and hydrous glasses (Xu *et al.*, 1998) shows that the changes in the oxygen environments in albite are much less than for sodium tetrasilicate, but has suggested that small concentrations of Si-OH

can be detected. The discrepancy with the interpretation of Kohn *et al.* (1997) remains to be explained, but it should be emphasized that the differences between the spectra in the two studies are very small, and that the concentration of Si-OH in hydrous albite glass must be much less than in hydrous sodium tetrasilicate glass.

In addition to the range of NMR data discussed above, one of the key observations which has been discussed by many authors is the existence of a peak in the Raman spectrum of hydrous Ab glass at $\sim 900\text{ cm}^{-1}$. It has been suggested that the 900 cm^{-1} band results from vibration of Al-OH and that the 4500 cm^{-1} band is the combination between this vibration and AlO-H at 3600 cm^{-1} . The 900 cm^{-1} band would thus be the analogue of the 970 cm^{-1} band observed in hydrous SiO_2 glasses which is attributed to Si-OH. One problem with this interpretation is that the 900 cm^{-1} band shows no isotope effect when substituting H with D (Fig. 9a). This problem has been addressed by McMillan *et al.* (1993) who argued that the lack of an isotope effect does not preclude this peak being due to T-OH because of strong vibronic coupling. An alternative explanation is that the 900 cm^{-1} peak is due to $Q^2-(\text{O}^-)_2$, i.e. not attached to OH, formed by reactions like 5 and 6 (Mysen and Virgo, 1986b), but neither this explanation nor the presence of abundant Si-OH

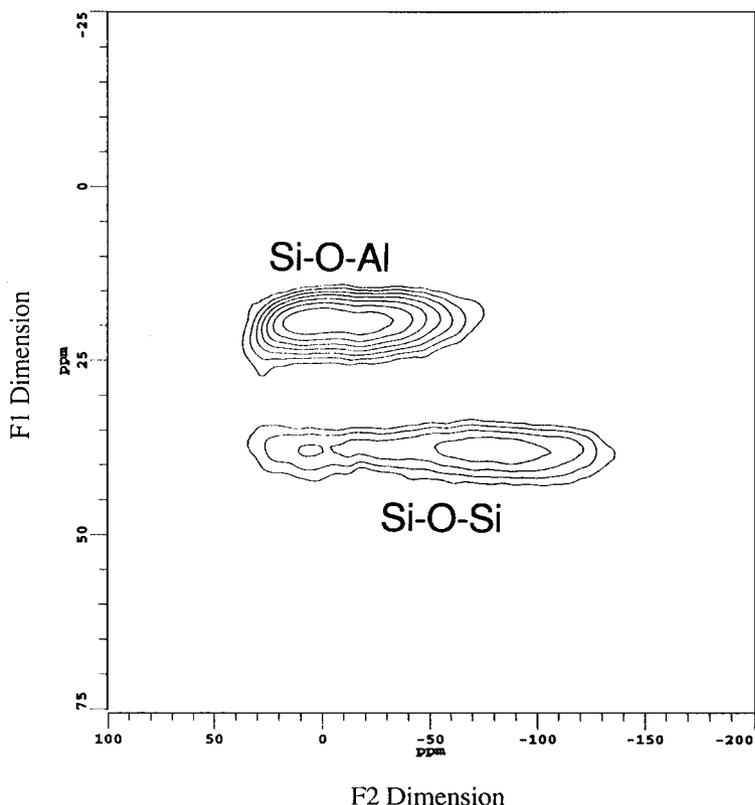


FIG. 8. ^{17}O triple quantum MAS NMR spectrum of anhydrous albite glass (Dirken *et al.*, 1997). The presence of Al-O-Si and Si-O-Si in equal concentrations and the absence of any peak for Al-O-Al effectively rules out any water dissolution mechanism which involves breakage of Al-O-Al bonds (reaction 3) as a major component.

or Al-OH appears to be consistent with the NMR data. Kohn *et al.* (1992) suggested that the 900 cm^{-1} band may be related to some sort of vibration of Si-O-Al modified by the presence of H on the bridging oxygen and recently new high pressure Raman data have been published which support the interpretation of the band as a vibration of the silicate framework (Sharma *et al.*, 1996, 1997). Sharma *et al.* (1996, 1997) suggest that the band at 900 cm^{-1} is due to an asymmetric mode of a T-O-T group. They suggest that this is the same motion as that responsible for the 1000 and 1100 cm^{-1} bands, and the appearance of a peak at 900 cm^{-1} in hydrous albite glass is due to lowering of symmetry of TO_4 cations because of the presence of H_3O^+ and H_2O in the glass. They suggest that pressurization restores the local symmetry of T cations and removes the asymmetry responsible for the 900 cm^{-1} peak (Fig. 9b).

As a final comment concerning the debate over the dissolution mechanisms of water in aluminosilicate melts it should be emphasized that identification of some specific group or complex in a glass is of limited value unless the concentration of that species can be reliably estimated. This is why the intrinsically quantitative nature of NMR is so important, and why the multinuclear NMR data must be fully accounted for in any structural model for hydrous glasses and melts. Thus there may be small concentrations of Si-OH or Al-OH in hydrous albite glasses, but their concentrations are far too small to be the products of the principal dissolution mechanisms.

A hierarchy of dissolution mechanisms?

The implication from the NMR and Raman data described above is that there is a change in water

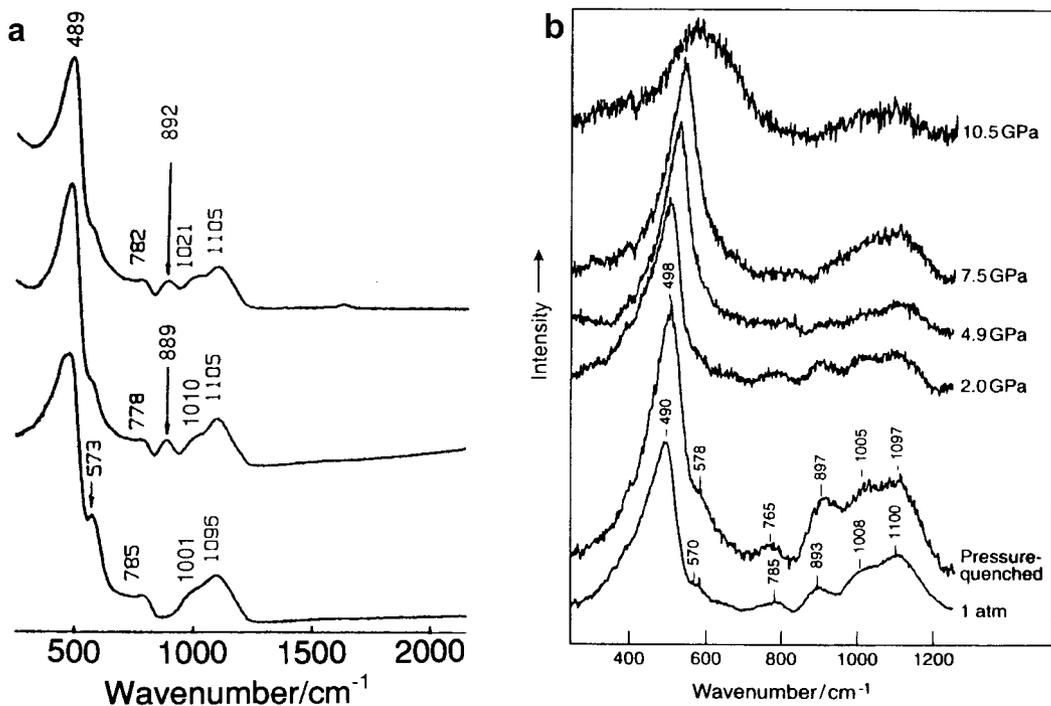


FIG. 9. (a) Raman spectra of dry (lowest), H₂O-bearing (uppermost) and D₂O-bearing (middle) albite glasses. Note the peak at 900 cm⁻¹ in the H₂O-bearing and D₂O-bearing glasses and the absence of an isotope shift (modified from McMillan *et al.*, 1993). (b) Disappearance of the 900 cm⁻¹ band in hydrous albite glass upon compression in a diamond anvil cell (Sharma *et al.*, 1996).

dissolution mechanism for tectosilicate glasses from a 'silica-like' dissolution mechanism for SiO₂-rich compositions to an 'albite-like' mechanism for more NaAlO₂-rich compositions. It therefore becomes important to investigate cases where a mixture of these melt components coexist to establish which mechanism is favoured. Data for samples with constant water concentrations, but varying compositions on the Ab-Qz join (Schmidt *et al.*, 2000) suggest that the Ab dissolution mechanism occurs first until the Ab component is exhausted; more silica rich compositions have a component of the Qz dissolution mechanism. Similar conclusions were reached by Holtz *et al.* (1995b) on the basis of trends in solubility and Raman data; the observation that Ab₃₇Qz₆₃ composition as well as Ab shows a negligible isotope shift for the 900 cm⁻¹ Raman peak (McMillan *et al.*, 1993) is also consistent with this idea. More work on peralkaline and peraluminous systems is required to establish the relative importance of different dissolution

mechanisms in compositions off the SiO₂-NaAlO₂ join. Mysen (1992) suggested that the relative importance of Si-OH is diminished and that of hydrated Na and Al complexes is enhanced with increasing NaAlO₂ component in the system Na₂Si₄O₉-Na₂(NaAl)₄O₉.

This concept of a 'hierarchy of dissolution mechanisms' is likely to be an oversimplification, but it may provide a simple framework within which a more sophisticated picture can be developed. Other data which have a bearing on such hierarchies are the data on the local environment of Ni in hydrous Ab melts (Nowak and Keppler, 1998). It was found that the environment of Ni was unchanged up to 5% dissolved water, then changed rapidly to a different coordination environment at higher water concentrations. Nowak and Keppler (1998) interpreted these data in terms of forming a complete hydration shell around Ni. An alternative explanation, however, is that the Ab component has a higher affinity for dissolved

water than the Ni, so the start of changes in Ni environment at 5 wt.% H₂O coincides with saturation of the Ab mechanism; it may be important that 5 wt.% water corresponds to a Na:H₂O ratio of ~1. In contrast the local environment of Co in albite glass is constant, suggesting that addition of water in excess of 5 wt.% dissolves by an alternative mechanism. The XAS data on trace elements in hydrous glasses also have a bearing on such hierarchies; some trace element environments are apparently modified by water, e.g. Mn and Sr (Kohn *et al.*, 1990), and Zr (Farges and Brown, 1997), whereas others such as Mo (Siewert *et al.*, 1997) and Ti (Farges and Brown, 1997) are not. However these studies are for different compositions and different water concentrations and may not be directly comparable.

Changes in hydrous glass and melt structure at elevated temperatures

Using diffraction and spectroscopic data for glasses to deduce high temperature melt structures has obvious drawbacks, but several early contributions suggested that the assumption of similar structures in glasses and melts was not too bad. For example Seifert *et al.* (1981) obtained Raman spectra for anhydrous sodium silicate and sodium aluminosilicate systems at temperatures of 100°C to 1200°C (well above the liquidus) and observed only minor changes. The comparison between glasses and melts is more difficult for hydrous systems because of problems with exsolution of water at 1 bar pressure, but an abstract published by Aines *et al.* (1983) which compared spectra for a glass containing 2 wt.% at 30°C and 750°C appeared to support the approach of quenching melts then making measurements under ambient conditions. Although significant changes in the apparent OH/H₂O_{mol.} ratio were observed, the kinetics of the interconversion appeared to be slow and it was therefore concluded that the OH/H₂O_{mol.} ratio, and hence presumably other aspects of the melt structure, could be preserved by rapid quenching. Further *in situ* measurements of hydrous melts were not reported for over 10 years.

Stolper (1989) attempted to determine the temperature dependence of speciation by annealing samples of natural hydrous obsidian, to reset the speciation, then quenching rapidly. He concluded that for a given total water concentration the OH/H₂O_{mol.} in the glass increases with increasing temperature. However, under the

conditions used, some samples were able to reach equilibrium but the speciation was not quenchable, whereas others were at temperatures too low to reach equilibrium in the time of the experiment. The energetics of the speciation are therefore difficult to quantify using this data set.

The next pieces of evidence for changes in speciation as a function of temperature came from the observation that hydrous melts quenched to glasses with different cooling rates preserved different speciation (Silver and Stolper, 1989). These data were interpreted by Dingwell and Webb (1990) in terms of the water speciation in the glasses being frozen at T_g , with the fast cooling rate corresponding to a higher T_g and the slower cooling rate corresponding to a lower T_g . The observation that samples with higher cooling rate had higher OH/H₂O_{mol.} ratio implied that the OH/H₂O_{mol.} increases with increasing T . The viscosity model of Shaw (1972) was used to calculate T_g for the different cooling rates and the variation of OH/H₂O_{mol.} with T_g was used to calculate the enthalpy of reaction 9 (which is essentially the same as reactions 1 to 8 where the details of the interaction are not defined) as 25 ± 5 kJ mol.⁻¹.



A more recent study of the effect of cooling rate on speciation (Fig. 10) was published by Zhang *et al.* (1997a). This study confirms the validity of the approach used by Dingwell and Webb (1990) and demonstrates that the temperature at which water speciation is frozen in (termed T_{ac}) is the same as the temperature of structural relaxation (T_g), i.e. no reequilibration of water speciation occurs below the structural T_g . The enthalpy of reaction 9 determined from measurements on annealed glasses is 25.9 kJ mol.⁻¹ (Zhang *et al.*, 1997b) in good agreement with the original estimate by Dingwell and Webb (1990). The development by Hess and Dingwell (1996) of an improved model for calculating the viscosities, and hence T_g , of rhyolite melts and glasses, has played an important role in establishing a consensus on these issues.

Romano *et al.* (1995) used an alternative approach to deduce the effect of temperature on speciation. They synthesized hydrous glasses along the Ab-Or join and measured both the water speciation in the glasses and T_g (using a fluid inclusion based approach on a parallel series of samples). They then plotted the equilibrium constant for reaction 9 against $1/T_g$ to obtain an

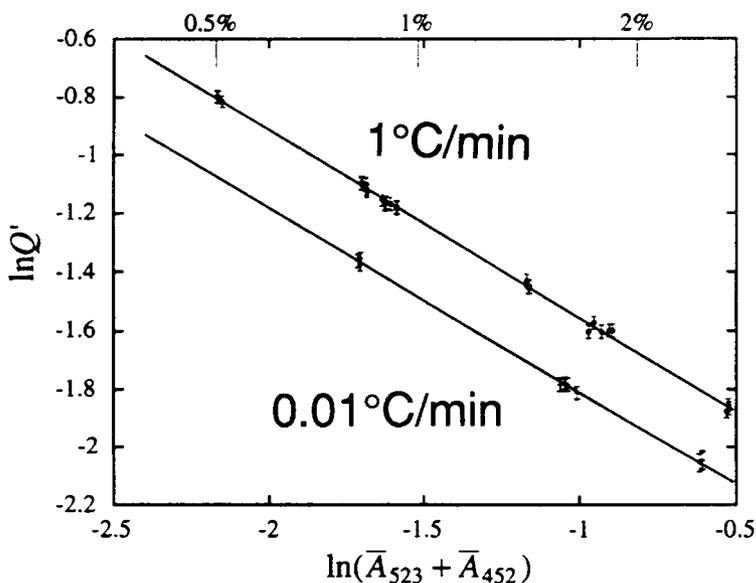


FIG. 10. The effect of quench rate on water speciation in glasses (modified from Zhang *et al.*, 1997). $\ln(A_{523} + A_{452}) \approx \ln(H_2O_{total})$ and $\ln Q' \approx \ln K$ where K is the equilibrium constant for reaction 9. The offset between the two quench rates indicates that the higher quench rate preserves a larger $OH/H_2O_{mol.}$ ratio.

enthalpy of the reaction of $36.5 \pm 5 \text{ kJ mol}^{-1}$. The linear arrangement of the data in such a plot led Romano *et al.* (1995) to conclude that the $K^+ \rightleftharpoons Na^+$ exchange has no effect on speciation; however, there is considerable scatter on the data and the accessible temperature range is only $422\text{--}515^\circ\text{C}$.

Direct experimental confirmation that water speciation was temperature dependent was published by Nowak and Behrens (1995) and Shen and Keppler (1995). These groundbreaking studies were performed *in situ* at simultaneous high pressures and temperatures. Both studies showed that speciation is strongly temperature dependent above T_g , with $H_2O_{mol.}$ being converted to OH with increasing temperature (Fig. 11) with an enthalpy of 30.3 kJ mol^{-1} (Shen and Keppler, 1995) or 33.6 kJ mol^{-1} (Nowak and Behrens, 1995) in fairly good agreement with earlier values deduced from the effect of T_g on speciation. The *in situ* data also appeared to show that some conversion of $H_2O_{mol.}$ to OH occurred on heating hydrous glasses from room temperature up to T_g with an enthalpy of reaction 9 of $1.5\text{--}1.6 \text{ kJ mol}^{-1}$ (Shen and Keppler, 1995; Nowak and Behrens, 1995); Both studies discussed whether or not the extinction coefficients vary as a function of temperature and concluded that they did not.

Other studies using different high P/T cells have now been performed (e.g. Mysen, 1998) and the possibility of using melt inclusions in minerals as

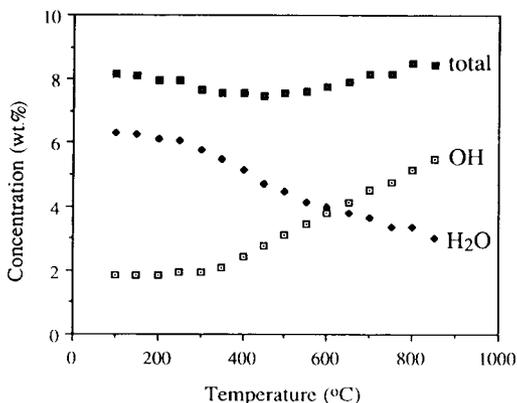


FIG. 11. Apparent water speciation as a function of temperature for a hydrous sodium aluminosilicate glass (Shen and Keppler, 1995). The water concentrations given assume constant integral extinction coefficients, an assumption which has been questioned in more recent studies. The small deviations in the apparent total water concentration obtained by summing the derived water concentrations for OH and $H_2O_{mol.}$ may reflect such changes.

pressure vessels for high P/T experiments is being explored (Pichavant *et al.*, 1997).

At about the same time as the studies of Shen and Keppler (1995) and Nowak and Behrens (1995) it began to become apparent that cylinders or chips of hydrous glass containing several wt.% H_2O could be heated to surprisingly high temperatures without nucleating bubbles or losing significant water by diffusion (Lejeune *et al.*, 1994). In these cases the melts are highly oversaturated in water, but experiments under these conditions allow high temperature spectroscopy to be performed without the need for complex high pressure apparatus. This observation has led to several studies of physical properties (Richet *et al.*, 1996; Dingwell *et al.*, 1996, 1998) and spectroscopic measurements (Holtz *et al.*, 1996; Sharma *et al.*, 1996; Grzechnik and McMillan, 1998; Behrens and Schmidt, 1998) being performed at high temperature but ambient pressure. The IR study of Grzechnik and McMillan (1998) on SiO_2 glass suggested that the linear extinction coefficient of the O-H fundamental at $\sim 3600\text{ cm}^{-1}$ is independent of temperature up to T_g . In contrast, some of the other studies appear to show that the extinction coefficients of the 4500 cm^{-1} and 5200 cm^{-1} bands are NOT independent of temperature. Raman spectra of silica glasses at 1 bar showed no change in the intensity of the 970 cm^{-1} band as a function of temperature up to 480°C (Holtz *et al.*, 1996), implying that the concentration of Si-OH is independent of temperature below T_g . Recent IR spectra of glasses (Behrens and Schmidt, 1998; Behrens *et al.*, 1998; Withers and Behrens, 1999) suggest that significant changes in extinction coefficients occur as a function of temperature. Thus the apparent changes in speciation below T_g observed by Nowak and Behrens (1995) and Shen and Keppler (1995) could in fact result solely from temperature dependent extinction coefficients. This also implies that the temperature dependence of the speciation reaction above T_g is less than that suggested by Nowak and Behrens (1995) and Shen and Keppler (1995) and the enthalpy of the reaction is slightly less than suggested earlier. At present there are no reliable data on the changes in extinction coefficients above T_g and any suggestions that they are constant or change in a particular way are largely guesswork. The current situation is that more systematic work must be done before the promise of quantitative *in situ* measurements can be realized.

Kinetics of OH/ H_2O_{mol} interconversion and the dynamics of microscopic processes in hydrous melts

The previous sections have discussed the structures of hydrous glasses quenched from melts and data on the position of the OH/ H_2O_{mol} equilibrium as a function of temperature. Additional aspects of dissolution of water in melts which are of importance are the rate at which equilibrium between OH and H_2O_{mol} species is approached and the rates of microscopic processes such as reorientation of water molecules and exchange of Si between different sites. One approach to measuring the kinetics of the water speciation reactions is to anneal glasses for long times at temperatures where speciation is quenchable (Dingwell and Webb, 1990). Using this method Zhang *et al.* (1995) determined both the position of equilibrium (see above) and the rate at which equilibrium is approached. Figure 12 shows how two samples with different speciation converge to a single value upon annealing at a given temperature. Notice that the rates of equilibration are not the same. The sample moving towards more negative values of $\ln Q$, i.e. $2OH$ going to H_2O_{mol} , approaches equilibrium more rapidly than the sample moving towards more positive values of $\ln Q$, i.e. H_2O_{mol} going to $2OH$. A detailed discussion of the implications of the kinetic data

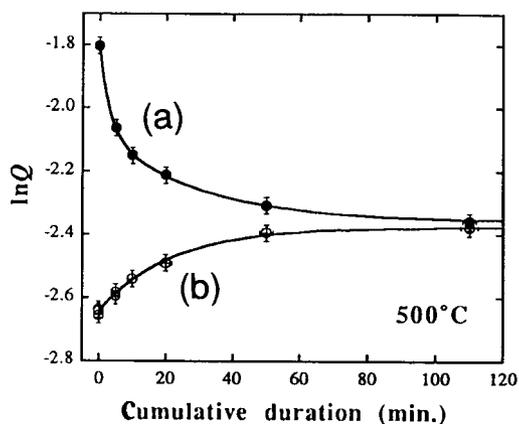


FIG. 12. The change in water speciation (expressed as $\ln Q$, where $Q = [OH]^2/[H_2O_{\text{mol}}][O]$) as a function of annealing time at 500°C for two samples previously equilibrated at either a higher temperature (curve a) or a lower temperature (curve b). Modified from Zhang *et al.* (1995).

to the reaction mechanism is given by Zhang *et al.* (1995). The existing data on the kinetics of OH/H₂O_{mol.} (Zhang *et al.*, 1995; 1997a) show that the original aim of using water speciation in natural glasses as a geothermometer (Stolper, 1989) is not generally viable, but that instead water speciation in natural glasses is a potentially valuable indicator of cooling rate (i.e. a geospeedometer).

The rate of interconversion of OH and H₂O_{mol.} is intimately related to local dynamics of hydrous species in the glass/melt system. Indeed an understanding of dynamics processes would provide important information on the nature of the OH groups, i.e. the roles of reactions such as 1–8. Much of this important information, such as the lifetimes of *Q*-species in hydrous melts, is not yet available, but some information on the mobility of dissolved water molecules has been reported. Eckert *et al.* (1987) used ²H NMR to study the motions of water molecules in hydrous rhyolite glasses. They showed that the water molecules flip about their 2-fold axis of symmetry on a timescale faster than 10⁻⁵s. This motion is progressively frozen out on reducing the temperature to 173 K. Rotations of water molecules at room temperature were also detected by Bezmen *et al.* (1991) using static ¹H NMR to study albite glasses with 50–60 mol.% dissolved water. Again the motion was observed to be gradually frozen out by cooling down to 150 K.

A very different dynamic phenomenon was observed by Keppler and Bagdassarov (1993). They performed IR spectroscopy on a rhyolite melt containing 300 ppm water at temperatures up to 1300°C. A new broad peak was observed at the highest temperatures which was attributed to highly mobile protons. Keppler and Bagdassarov (1993) suggested that under these conditions the distinction between OH and H₂O_{mol.} is lost. An alternative explanation was proposed by Dingwell (1995) who put these data in the context of other relaxation processes in hydrous melts and glasses. Figure 13 shows the simplified relaxation map proposed by Dingwell (1995). There are three different relaxation timescales; the slowest is the structural relaxation reflected by viscosity data; the second is water diffusion, which is thought to be dominated by the movement of molecular water and is thus decoupled from the strong aluminosilicate framework; the third is the timescale for electrical conductivity. The point corresponding to the timescale of the OH vibration and 1300°C (the temperature at which Keppler and Bagdassarov (1993) observed the

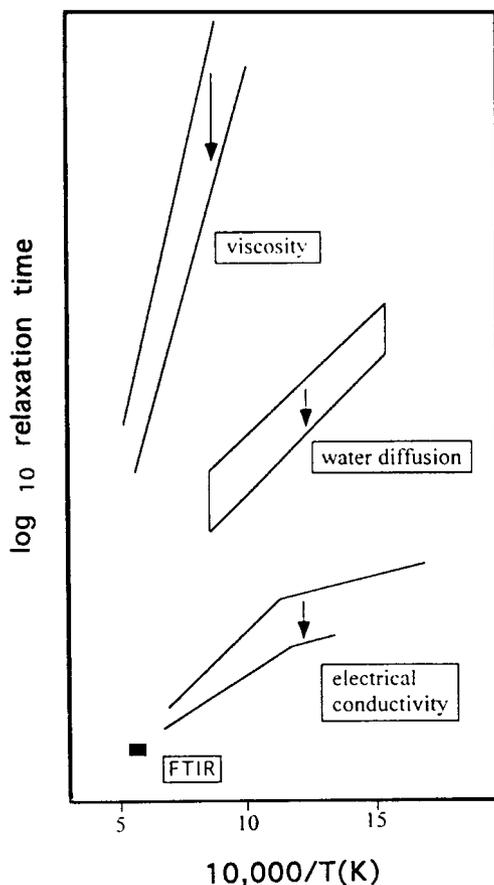


Fig. 13. Relaxation map for hydrous silicate melt/glass systems (Dingwell, 1995).

new peak) is marked on this map. It lies on the extrapolation of the trend for electrical conductivity, suggesting that the two effects are attributable to the same process, i.e. proton mobility. Thus the appearance of the new peak in the IR spectrum is due to mobility of protons rather than loss of distinction between oxygens, a process which is several orders of magnitude slower at this temperature (Dingwell, 1995).

Future directions

The two key questions for most petrologists and volcanologists are 'how can the effect of water on phase relations be modelled quantitatively?' and 'why does water have such a large effect on the viscosity of silicate melts?'. The first of these questions requires a thermodynamic model for

hydrous silicate melts to be established. Many of the early attempts to do this were not able to include melt structural data, the classic example being the work of Burnham (1975, 1994). More recently, some workers have started to use data from spectroscopic studies to constrain their models (Zeng and Nekvasil, 1996). In view of the continuing debate concerning even the major features of water dissolution mechanisms, much more spectroscopic work is required to provide a sound foundation for thermodynamic modelling. Integration of spectroscopic data with improved calorimetric data would also be very helpful.

To be able to answer the second question, the mechanism of viscous flow in dry and hydrous melts must be understood. There is still a widely held and erroneous view amongst the wider community of Earth Scientists that viscosity is related in a very direct way to polymerization via movement of large polymeric units. For anhydrous depolymerized melts, *in situ* high temperature ^{29}Si NMR has been used to show that viscous flow is related to Si–O bond breaking and local rearrangements, with the involvement of reactive intermediate complexes such as 5-coordinated Si. (Farnan and Stebbins, 1990, 1994). However, for nearly fully polymerized melts such as albite, the mechanism of flow is less well constrained. The data reviewed in this paper suggest that the dramatic effect of water in reducing viscosity is not related to ‘depolymerization’ in the usual sense of the word, but is more likely to be due to an enhanced stability for the activated complex involved in viscous flow. Thus, in contrast to most previous assertions, there is no necessity for water to depolymerize tectosilicate melts. The information needed to resolve this problem may come from a variety of sources. Firstly, more detailed studies of glass structure with emphasis on identifying and quantifying the minor species which are involved in the process of viscous flow. These species could be Al or Si with high coordination numbers, triclusters, or some specific ring conformation for example. New NMR techniques such as multiple quantum magic angle spinning are likely to play an important role in their detection. Secondly, studies of dynamic processes in hydrous melts and glasses around T_g using *in situ* high temperature and pressure NMR, and possibly using molecular dynamics calculations. Thirdly, calibration of IR extinction coefficients at high temperature, possibly using ^1H MAS NMR. This would allow truly quantitative high-temperature speciation

data to be obtained. Finally, an integrated view of the role of water in silicate melts will require an understanding of the coupling between viscous flow and $\text{OH}/\text{H}_2\text{O}_{\text{mol}}$ speciation and kinetics and the dynamics of microscopic processes.

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References

- Aines, R.D., Silver, L.A., Rossman, G.R., Stolper, E.M. and Holloway, J.R. (1983) Direct observation of water speciation in rhyolite at temperatures up to 850°C. *Geol. Soc. Am. Abstr. Prog.*, **15**, 512.
- Behrens, H. and Nowak, M. (1997) The mechanisms of water diffusion in polymerized silicate melts. *Contrib. Mineral. Petrol.*, **126**, 377–85.
- Behrens, H. and Schmidt, M.O. (1998) Infrared spectroscopy of hydrous silicic glasses at temperatures up to 600°C and implications for the incorporation and dynamics of water in glasses. *N. Jb. Miner. Abh.*, **172**, 203–26.
- Behrens, H., Romano, C., Nowak, M., Holtz, F. and Dingwell, D.B. (1996) Near-infrared spectroscopic determination of water species in glasses of the system MAlSi_3O_8 (M=Li, Na, K): an interlaboratory study. *Chem. Geol.*, **128**, 41–63.
- Behrens, H., Withers, A. and Zhang, Y. (1998) *In situ* spectroscopy on hydrous albitic and rhyolitic glasses and its implications for water speciation and water species reactions in silicate glasses and melts (extended abstract). *Mineral. Mag.*, **62A**, 139–40.
- Bezmen, N.I., Zharikov, V.A., Epelbaum, M.B., Zavel'sky, V.O., Dikov, Y.P., Suk, N.I. and Koshemchuk, S.K. (1991) the system $\text{NaAlSi}_3\text{O}_8\text{-H}_2\text{O-H}_2$ (1200°C, 2 kbar): the solubility and interaction mechanism of fluid species with melt. *Contrib. Mineral. Petrol.*, **109**, 89–97.
- Burnham, C.W. (1975) Water and magmas, a mixing

- model. *Geochim. Cosmochim. Acta*, **52**, 2659–69.
- Burnham, C.W. (1994) Development of the Burnham model for prediction of H₂O solubility in magmas. Pp. 123–9 in: *Volatiles in Magmas* (M.R. Carroll and J.R. Holloway, editors). Reviews in Mineralogy, **30**, Mineralogical Society of America, Washington D.C.
- Burnham, C.W. and Davis, N.F. (1971) The role of H₂O in silicate melts. I. PVT relations in the system NaAlSi₃O₈-H₂O to 10 kilobars and 1000°C. *Amer. J. Sci.*, **274**, 902–40.
- Clemens, J.D. and Navrotsky, A. (1987) Mixing properties of NaAlSi₃O₈ melt-H₂O: New calorimetric data and some geological implications. *J. Geol.*, **95**, 173–86.
- Davis, K.M. and Tomozawa, M. (1996) An infrared spectroscopic study of water-related species in silica glasses. *J. Non-cryst. Solids*, **201**, 177–98.
- Dingwell, D.B. (1995) Relaxation in silicate melts: some applications. Pp. 21–66 in: *Structures and Properties of Silicate Melts* (J.F. Stebbins, P.F. McMillan and D.B. Dingwell, editors). Reviews in Mineralogy, **32**, Mineralogical Society of America, Washington D.C.
- Dingwell D.B. and Webb S.L. (1990) Relaxation in silicate melts. *Eur. J. Mineral.*, **2**, 427–49.
- Dingwell, D.B., Romano, C. and Hess, K.U. (1996) The effect of water on the viscosity of a haplogranitic melt under P-T-X conditions relevant to silicic volcanism. *Contrib. Mineral. Petrol.*, **124**, 19–28.
- Dingwell, D.B., Hess, K.U. and Romano, C. (1998) Extremely fluid behavior of hydrous peralkaline rhyolites. *Earth Planet. Sci. Lett.*, **158**, 31–8.
- Dirken, P.J., Kohn, S.C., Smith, M.E. and van Eck, E.R.H. (1997) Complete resolution of Si-O-Si and Si-O-Al fragments in an aluminosilicate glass by ¹⁷O multiple quantum magic angle spinning NMR spectroscopy. *Chem. Phys. Lett.*, **266**, 568–74.
- Dupree, R., Holland, D., Mortuza, M.G., Smith, M.E., Chen, A. and James, P.F. (1990) Multinuclear magnetic resonance study of Li₂O-SiO₂ sol-gel glasses. *Mag. Res. Chem.*, **28**, s89–96.
- Eckert, H., Yesinowski, J.P., Stolper, E.M., Stanton, T.R. and Holloway, J. (1987) The state of water in rhyolitic glasses: A deuterium NMR study. *J. Non-Cryst. Solids*, **93**, 93–114.
- Epel'baum, M.B., Stolyarova, T.A. and Salova, T.P. (1995) Thermochemical studies on rhyolite glasses. *Geochem. Int.*, **32**, 11–20.
- Farges, F. and Brown, G.E. (1997) Effect of water on the speciation of high field strength cations in natural glasses. *Terra Nova (Abstract suppl. 1)*, **9**, 482.
- Farnan, I. and Stebbins, J.F. (1990) High-temperature ²⁹Si NMR investigation of solid and molten silicates. *J. Amer. Chem. Soc.*, **112**, 32–9.
- Farnan, I. and Stebbins, J.F. (1994) The nature of the glass-transition in a silica rich oxide melt. *Science*, **265**, 1206–9.
- Farnan, I., Kohn, S.C. and Dupree, R. (1987) A study of the structural role of water in hydrous silica glass using cross-polarisation magic angle spinning NMR. *Geochim. Cosmochim. Acta*, **51**, 2869–73.
- Gaskell, P.H., Eckersley, M.C., Barnes, A.C. and Chieux, P. (1991) Medium range order in the cation distribution of a calcium silicate glass. *Nature*, **350**, 675–7.
- Goranson, R.W. (1931) The solubility of water in granitic magmas. *Amer. J. Sci.*, **22**, 481–502.
- Grzechnik, A. and McMillan, P.F. (1998) Temperature dependence of the OH- absorption in SiO₂ glass and melt to 1975K. *Amer. Mineral.*, **83**, 331–8.
- Hess, K.-U. and Dingwell, D.B. (1996) Viscosities of hydrous leucogranitic melts: A non-Arrhenian model. *Amer. Mineral.*, **81**, 1297–300.
- Holtz, F., Behrens, H., Dingwell, D.B. and Taylor, R.P. (1992) Water solubility in aluminosilicate melts of haplogranite composition at 2 kbar. *Chem. Geol.*, **96**, 289–302.
- Holtz, F., Behrens, H., Dingwell, D.B. and Johannes, W. (1995a) H₂O solubility in haplogranitic melts: compositional, pressure, and temperature dependence. *Amer. Mineral.*, **80**, 94–108.
- Holtz, F., Beny, J.M., Roux, J., Pichavant, M. and Behrens, H. (1995b) Water in silica-rich and alkali feldspar glasses: evidence for two contrasting incorporation mechanisms. *Eos (Fall meeting suppl.)*, **76**, 648.
- Holtz, F., Beny, J.M., Mysen, B.O. and Pichavant, M. (1996) High-temperature raman-spectroscopy of silicate and aluminosilicate hydrous glasses – implications for water speciation. *Chem. Geol.*, **128**, 25–39.
- Holtz, F., Roux, J., Ohlhorst, S., Behrens, H. and Schulze, F. (1999) The effects of silica and water on the viscosity of hydrous quartzofeldspathic melts. *Amer. Mineral.*, **84**, 27–36.
- Keppler, H. and Bagdassarov, N.S. (1993) High-temperature FTIR spectra of H₂O in rhyolite melt to 1300°C. *Amer. Mineral.*, **78**, 1324–7.
- Kohn, S.C., Dupree, R., Smith, M.E. (1989a) A multinuclear magnetic resonance study of the structure of hydrous albite glasses. *Geochim. Cosmochim. Acta*, **53**, 2925–35.
- Kohn, S.C., Dupree, R., Smith, M.E. (1989b) ¹H NMR studies of hydrous silicate glasses. *Nature*, **337**, 539–41.
- Kohn, S.C., Charnock, J.M., Henderson, C.M.B. and Greaves, G.N. (1990) The structural environments of trace elements in dry and hydrous silicate glasses; a manganese and strontium K-edge X-ray absorption spectroscopic study. *Contrib. Mineral. Petrol.*, **105**, 359–368.
- Kohn, S.C., Dupree, R., Mortuza, M.G. (1992) The

- interaction between water and aluminosilicate magmas. *Chem. Geol.*, **96**, 399–409.
- Kohn, S.C., Smith, M.E. and Dupree, R. (1994) Comment on "A model for H₂O solubility mechanisms in albite melts from infrared spectroscopy and molecular orbital calculations." By D. Sykes and J.D. Kubicki. *Geochim. Cosmochim. Acta*, **58** 1377–80.
- Kohn, S.C., Smith, M.E., Van Eck, E.R.H. and Dirken, P.J. (1997) ¹⁷O NMR studies of water dissolution mechanisms in aluminosilicate glasses. *Terra Nova (Abstract suppl. 1)*, **9**, 478.
- Kohn, S.C., Smith, M.E., Dirken, P.J., Van Eck, E.R.H., Kentgens, A.P.M. and Dupree, R. (1998) Sodium environments in dry and hydrous albite glasses. Improved ²³Na solid state NMR data and their implications for water dissolution mechanisms. *Geochim. Cosmochim. Acta*, **62**, 79–87.
- Kümmerlen, J., Merwin, L.H., Sebald, A., and Keppler, H. (1992) Structural role of H₂O in sodium silicate glasses—results from ²⁹Si and ¹H NMR spectroscopy. *J. Phys. Chem.*, **96**, 6405–10.
- Kushiro, I. (1969) The system forsterite-diopside-silica with and without water at high-pressure. *Amer. J. Sci.*, **267**, 269–94.
- Lange, R.A. (1994) The effect of H₂O, CO₂ and F on the density and viscosity of silicate melts. *Rev. Mineral.*, **30**, 331–69.
- Lejeune, A.M., Holtz, F., Roux, J. and Richet, P. (1994) Rheology of an hydrous andesite: and experimental study at high viscosities. *Eos 75, (Fall meeting suppl.)*, 724.
- McMillan, P.F. (1984) Structural studies of silicate glasses and melts – applications and limitations of Raman spectroscopy. *Amer. Mineral.*, **69**, 622–44.
- McMillan, P.F. (1994) Water solubility and speciation models. *Rev. Mineral.*, **30**, 131–56.
- McMillan, P.F. and Remmele, R.L. (1986) Hydroxyl sites in SiO₂ glass: A note on infrared and Raman spectra. *Amer. Mineral.*, **71**, 772–8.
- McMillan, P.F., Poe, B.T., Stanton, T.R. and Remmele, R.L. (1993) A Raman spectroscopic study of H/D isotopically substituted hydrous aluminosilicate glasses. *Phys. Chem. Min.*, **19**, 454–9.
- Mysen, B. (1992) Peralkalinity, AlSi substitution, and solubility mechanisms of H₂O in aluminosilicate melts. *J. Petrol.*, **33**, 347–75.
- Mysen, B.O. (1998) Interaction between aqueous fluid and silicate melt in the pressure and temperature regime of the Earth's crust and upper mantle. *N. Jb. Miner. Abh.*, **172**, 227–44.
- Mysen, B.O. and Virgo, D. (1986a) Volatiles in silicate melts at high pressure and temperature. 1. Interaction between OH groups and Si⁴⁺, Al³⁺, Ca²⁺, Na⁺ and H⁺. *Chem. Geol.*, **57**, 303–31.
- Mysen, B.O. and Virgo, D. (1986b) Volatiles in silicate melts at high pressure and temperature. 2. Water in melts along the join NaAlO₂-SiO₂ and a comparison of solubility mechanisms of water and fluorine. *Chem. Geol.*, **57**, 333–58.
- Mysen, B.O., Virgo, D. and Seifert, F.A. (1982) The structure of silicate melts: implications for chemical and physical properties of natural magma. *Rev. Geophys. Space. Phys.*, **20**, 353–83.
- Nowak, M. and Behrens, H. (1995) The speciation of water in haplogranitic glasses and melts determined by in-situ near-infrared spectroscopy. *Geochim. Cosmochim. Acta*, **59**, 3445–50.
- Nowak, M. and Behrens, H. (1997) An experimental investigation on diffusion of water in haplogranitic melts. *Contrib. Mineral. Petrol.*, **126**, 365–76.
- Nowak, M. and Keppler, H. (1998) the influence of water on the environment of transition metals in glasses. *Amer. Mineral.*, **83**, 43–50.
- Ochs, F.A. and Lange, R.A. (1997) The partial molar volume, thermal expansivity and compressibility of H₂O in NaAlSi₃O₈ liquid: new measurements and an internally consistent model. *Contrib. Mineral. Petrol.*, **129**, 155–65.
- Okuno, M., Marumo, F., Morikawa, H., Nakashima, S. and Iiyama, J.T. (1987) Structures of hydrated glasses in the albite-anorthite-quartz system. *Mineral. J.*, **13**, 434–42.
- Pichavant, M., Holtz, F. and McMillan, P.F. (1992) Phase relations and compositional dependence of H₂O solubility in quartz-feldspar melts. *Chem. Geol.*, **96**, 303–19.
- Pichavant, M., Holtz, F., Beny, J.M., Clocchiatti, R. and Behrens, H. (1997) Minerals as natural pressure vessels: In situ spectroscopy using natural hydrous silicate melt inclusions. *Terra Nova (Abstract suppl. 1)*, **9**, 478.
- Richet, P. and Polian, A. (1998) Water as a dense icelike component in silicate glasses. *Science*, **281**, 396–8.
- Richet, P., Lejeune, A.M., Holtz, F. and Roux, J. (1996) Water and the viscosity of andesite melts. *Chem. Geol.*, **128**, 185–97.
- Romano, C., Dingwell, D.B. and Behrens, H. (1995) the temperature dependence of speciation of water in NaAlSi₃O₈-KAlSi₃O₈ melts: an application of fictive temperatures derived from synthetic fluid-inclusions. *Contrib. Mineral. Petrol.*, **122**, 1–10.
- Romano, C., Dingwell, D.B., Behrens, H. and Dolfi, D. (1996) Compositional dependence of H₂O solubility along the joins NaAlSi₃O₈-KAlSi₃O₈, NaAlSi₃O₈-LiAlSi₃O₈, and KAlSi₃O₈-LiAlSi₃O₈. *Amer. Mineral.*, **81**, 452–61.
- Schaller, T. and Sebald, A. (1995) One- and two-dimensional ¹H magic-angle spinning experiments on hydrous silicate glasses. *Solid State NMR*, **5**, 89–102.
- Schmidt, B.C., Riemer, T., Kohn, S.C. and Dupree, R. (1998) The effects of water on the structure of

- quartz-albite glasses quenched from hydrous melts at high P and T, an NMR spectroscopic study. *Terra Nova (Abstract suppl. 1)*, **10**, 55.
- Schmidt, B.C., Riemer, T., Kohn, S.C., Behrens, H. and Dupree, R. (2000) Different water solubility mechanisms in hydrous glasses along the Qz-Ab join. *Geochim. Cosmochim. Acta*, **64**, 513–26.
- Schulze, F., Behrens, H., Holtz, F., Roux, J. and Johannes, W. (1996) The influence of H₂O on the viscosity of a haplogranitic melt. *Amer. Mineral.*, **81**, 1155–65.
- Seifert, F.A., Mysen, B.O. and Virgo, D. (1981) Structural similarity between glasses and melts relevant to petrological processes. *Geochim. Cosmochim. Acta*, **45**, 1879–84.
- Sharma, S.K., Wang, Z. and van der Laan, S. (1996) Raman spectroscopy of oxide glasses at high pressure and high temperature. *J. Raman Spectrosc.*, **27**, 739–46.
- Sharma, S.K., Cooney, T.F., Wang, Z. and van der Laan, S. (1997) Raman band assignments of silicate and germanate glasses using high-pressure and high-temperature spectral data. *J. Raman Spectrosc.*, **28**, 697–709.
- Shaw, H.R. (1972) Viscosities of magmatic silicate liquids: An empirical method of prediction. *Amer. J. Sci.*, **272**, 870–93.
- Shen, A. and Keppler, H. (1995) Infrared-spectroscopy of hydrous silicate melts to 1000°C and 10 kbar – direct observation of H₂O speciation in a diamond-anvil cell. *Amer. Mineral.*, **80**, 1335–8.
- Siewert, R., Farges, F., Behrens, H., Buettner, H. and Brown, G.E. (1997) The effect of water on the coordination of Mo in albite glass. A high-resolution XANES spectroscopic study. *Eos (Fall meeting suppl.)*, **78**, F768.
- Silver, L. and Stolper, E. (1989) Water in albitic glasses. *J. Petrol.*, **30**, 667–709.
- Silver, L.A., Ihinger, P.D. and Stolper, E. (1990) The influence of bulk composition on the speciation of water in silicate glasses. *Contrib. Mineral. Petrol.*, **104**, 142–62.
- Stebbins, J.F. (1988) NMR spectroscopy and dynamic processes in mineralogy and geochemistry. Pp. 405–30 in: *Spectroscopic Methods in Mineralogy and Geology* (F.C. Hawthorne, editor). Reviews in Mineralogy, **18**, Mineralogical Society of America, Washington D.C.
- Stebbins, J.F. (1995) Dynamics and structure of silicate and oxide melts: nuclear magnetic resonance studies. Pp. 191–246 in: *Structure and Properties of Silicate Melts* (J.F. Stebbins, P.F. McMillan and D.B. Dingwell, editors). Reviews in Mineralogy, **32**, Mineralogical Society of America, Washington D.C.
- Stolper, E.M. (1982) Water in glasses: An infrared spectroscopic study. *Contrib. Mineral. Petrol.*, **81**, 1–17.
- Stolper, E.M. (1989) Temperature dependence of the speciation of water in rhyolitic melts and glasses. *Amer. Mineral.*, **74**, 1247–57.
- Sykes, D. and Kubicki, J.D. (1993) A model for H₂O solubility mechanisms in albite melts from infrared spectroscopy and molecular orbital calculations. *Geochim. Cosmochim. Acta*, **57**, 1039–52.
- Sykes, D., Kubicki, J.D. and Farrar, T.C. (1997) Molecular orbital calculation of ²⁷Al and ²⁹Si NMR parameters in Q(3) and Q(4) aluminosilicate molecules and implications for the interpretation of hydrous aluminosilicate glass NMR spectra. *J. Phys. Chem. A*, **101**, 2715–22.
- Tossell, J.A. and Sàghi-Szabó, G. (1997) Aluminosilicate and borosilicate single 4-rings: effects of counterions and water on structure, stability, and spectra. *Geochim. Cosmochim. Acta*, **61**, 1171–9.
- Withers, A.C. and Behrens, H. (1999) Temperature-induced changes in the NIR spectra of hydrous albitic and rhyolitic glasses between 300 and 100 K. *Phys. Chem. Min.*, **27**, 119–32.
- Xu, Z., Maekawa, H., Oglesby, J.V. and Stebbins, J.F. (1998) Oxygen speciation in hydrous silicate glasses—An oxygen-17 NMR study. *J. Amer. Chem. Soc.*, **120**, 9894–901.
- Zeng, Q.A., and Nekvasil, H. (1996) An associated solution model for albite-water melts. *Geochim. Cosmochim. Acta*, **60**, 59–73.
- Zhang, Y.X., Stolper, E.M. and Ihinger, P.D. (1995) Kinetics of the reaction H₂O+O=2OH in rhyolitic and albitic glasses: preliminary results. *Amer. Mineral.*, **80**, 593–612.
- Zhang, Y.X., Jenkins, J. and Xu, Z. (1997a) Kinetics of the reaction H₂O+O=2OH in rhyolitic glasses upon cooling: Geospeedometry and comparison with glass transition. *Geochim. Cosmochim. Acta*, **61**, 2167–73.
- Zhang, Y., Belcher, R., Ihinger, P.D., Wang, L., Xu, Z. and Newman, S. (1997b) New calibration of infrared measurement of dissolved water in rhyolitic glasses. *Geochim. Cosmochim. Acta*, **61**, 3089–100.
- Zotov, N. and Keppler, H. (1998) The influence of water on the structure of hydrous sodium tetrasilicate glasses. *Amer. Mineral.*, **83**, 823–34.
- Zotov, N., Yanev, Y., Epelbaum, M. and Konstantinov, L. (1992) Effect of water on the structure of hydrous rhyolite glasses – X-ray diffraction and Raman spectroscopy studies. *J. Non-cryst Solids*, **142**, 234–46.
- Zotov, N., Keppler, H., Hannon, A.C. and Soper, A.K. (1996) The effect of water on the structure of silicate-glasses – a neutron-diffraction study. *J. Non-cryst Solids*, **202**, 153–63.

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