Solubility mechanisms of H$_2$O in silicate melts at high pressures and temperatures: 
a Raman spectroscopic study

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Abstract

Raman spectroscopy has been employed to determine the solubility mechanisms of H$_2$O in
silicate melts. In melts that have a three-dimensional network structure (e.g., melts on the join
Na$_2$O-Al$_2$O$_3$-SiO$_2$), water reacts with bridging oxygens to form two OH groups per broken
oxygen bond. At the same time some of the three-dimensional network is broken down to
chain units, accompanied by the expulsion of Al$^{3+}$ from tetrahedral coordination. In melts
that have nonbridging oxygen (NBO), water reacts with both nonbridging oxygen and net-
work modifiers (e.g., Na$^+$) to form Si-OH bonds and M(OH) or M(OH)$_2$ complexes. The an-
hydrous portion of the network becomes more polymerized.

The formation of chain units at the expense of three-dimensional network units in melts
implies that the liquidus boundaries involving pyroxenes and silica minerals or feldspar min-
erals shift to higher silica contents. Liquidus fields of silica minerals or feldspar minerals are
depressed relative to those of pyroxene minerals. This prediction is supported by published
observations of phase relations in hydrous basalt and andesite systems. Similar logic can be
used to explain the formation of partial melts of andesitic bulk composition from hydrous pe-
ridotite in the upper mantle.

We propose that trace-element crystal-liquid partition coefficients involving highly polymer-
ized melts will decrease with increasing water content because of the formation of the less
polymerized chain units in the melt. Partition coefficients involving less polymerized melts
(e.g., picrite and komatiite) may increase because the degree of polymerization of the melt is
increased as a result of dissolved water.

Introduction

Water is one of the most important volatiles in
magmas. The presence of H$_2$O in the source region of
partial melts in the upper mantle results in a more
silica-rich liquid than in its absence (e.g., Kushiro et
reason, for example, water is required to produce an-
desitic partial melts from peridotite (Kushiro et al.,
1972; Mysen and Boettcher, 1975). Water in magma
also affects crystallization paths. The liquidus fields
of feldspars are depressed relative to those of pyro-
exenes, and the liquidus fields of pyroxenes relative to
those of olivine (Yoder, 1969, 1973; Eggler, 1972;
Kushiro, 1972). The redox equilibria of iron and
hence the phase equilibria of iron-bearing minerals
also depend on the water content of magma (Osborn,
1959).

Physical properties of magma such as viscosity and
electrical conductivity are affected by water (Lebedev
and Khitarov, 1964; Kushiro, 1978; Kushiro et al.,
1976). It has also been suggested that activity coeffi-
cients of trace elements and therefore crystal-liquid
partition coefficients depend on the water content of
the liquid (Drake and Holloway, 1977; Hart and
Davis, 1978).

As a result of the important petrological influence
of H$_2$O in silicate melts, the solubility behavior of
H$_2$O in a variety of melts and under a variety of
physical conditions has been studied extensively
(Goranson, 1931; Kennedy et al., 1962; Burnham,
1974, 1975; Burnham and Jahns, 1962; Burnham and
Davis, 1971, 1974; Hamilton et al., 1964; Eggler and
Rosenhauer, 1978). Solubility models of H$_2$O in sili-
cate melts based on solubility data and thermody-
namic properties of hydrous melts have been pro-
posed (Burnham, 1974, 1975).

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Despite the importance of H₂O in petrogenetic processes, data on the structural role of H₂O in silicate melts are scarce. Orlova (1964) and Velde and Kushiro (1976) determined that OH groups exist in highly polymerized, water-bearing melts on the join NaAlSiO₄–SiO₂. Hodges (1974) suggested that molecular water may occur as well. Data on the structural role of the OH groups in silicate melts are rare (Adams and Douglas, 1959). No data appear to exist for melts formed at both high temperature and high pressure. Such data are necessary to understand the influence of H₂O on chemical and physical processes of magma formation and evolution. In the present report, Raman spectroscopy has been used to determine (1) the chemical and structural forms of dissolved water in silicate melts and (2) the interaction between water-bearing structural units and the remaining anionic structure of silicate melts.

**Experimental methods**

The Raman spectra were acquired on small chips (~1 mm) of quenched melts. A discussion of the application of such data to the structures of melts was provided by Mysen et al. (1980). The problem was also discussed by Taylor and Brown (1979) and Sharma et al. (1978). They concluded that the structural features of liquids that are discernible with Raman spectroscopy can be quenched at least with the quenching rates employed here (250°–500°C/sec).

An added complexity in the present experiments is the mobility of H₂O in silicate melts and the tendency of water-bearing melts not to form a glass. Instead, minerals precipitate from the melt during quenching. In melts with a three-dimensional network structure [e.g., Na₂Si₆O₁₆ (Jd) and Na₂AlSi₂O₇ (Ab) compositions in the present study] it has been suggested that liquids with up to about 5 wt. percent H₂O can be quenched at high pressure (Burnham, 1975). No more than about 5 wt. percent H₂O was therefore added to these melts. Whether H₂O could be quenched in these melts was also assessed by monitoring the intensity of the Si–OH and HOH stretch bands in the Raman spectra (see below).

Less is known about melts that are less polymerized than those that have a three-dimensional network (NBO/T > 0).² In fact hydrous melts of meta-silicate composition cannot even be quenched to a glass. Di- and trisilicate of sodium [Na₂Si₉O₂₃ (NS2) and Na₂Si₂O₇ (NS3)] can be quenched to clear, bubble-free glass at least with water contents up to 4–5 wt. percent. Inasmuch as the intensity of Raman bands of Si–OH stretch vibrations of such melts increases with increasing H₂O content of the quenched melt, we conclude that in these melts (NS2 and NS3) the H₂O content can be quenched. Melts of Na₂Si₉O₂₃ and Na₂Si₂O₇ composition were used, therefore, to study solubility mechanisms of H₂O in silicate melts with a significant number of nonbridging oxygens.

The starting materials for high-pressure experiments were glasses made at 1 atm. The glasses were produced from spectroscopically pure (Johnson and Matthey) SiO₂ and Al₂O₃, and reagent-grade Na₂CO₃ (Fisher). Water was double-distilled H₂O, added to the samples with a microsyringe with 0.03 µl precision. Deuterium oxide (MSD isotope products, Canada) was 95 percent D₂O and 5 percent H₂O.

The samples were contained in sealed Pt capsules of 2 or 3 mm O.D. In order to ensure that the desired amount of water was in the charge during an experiment, the capsules were weighed before and after welding and again after 1–2 hr at 110°C. The accuracy of the amount of water reported is 4–7 percent (depending on the concentration of H₂O in the melt).

All experiments were carried out in solid-media, high-pressure apparatus (Boyd and England, 1960) using the piston-out technique with a −4 percent correction for friction (calibrated against the quartz-coesite transition). The temperatures were measured with Pt–Pt90Rh10 thermocouples. The uncertainties were ±1 kbar and ±6°–10°C (Eggler, 1977; Mao et al., 1971).

The Raman spectra were taken on small chips of quenched melt (about 0.5–1.0 mm cubes) free of bubbles. The spectra were recorded with a Jobin-Yvon optical system, holographic grating, double monochromator (HG25) with a photon-counting detection system. The spectra were recorded at 3 cm⁻¹/sec. The samples were excited with the 488.0 nm line of an Ar⁺ laser using laser power of 200–400 mW at the sample with 90° scattering geometry. Polarized spectra were obtained with the focused exciting beam parallel to the horizontal spectrometer slit and with the electric vector of the exciting radiation in a vertical orientation. A sheet of polarizer disk in front of an optical scrambler was used to record separately the parallel and perpendicular components of the scattered radiation.

Several of the high-frequency envelopes of the
Table 1. Raman spectroscopic data on the system Na₂O-SiO₂-D₂O-H₂O at 1300°C and 20 kbar

<table>
<thead>
<tr>
<th>Composition</th>
<th>Mole % H₂O (D₂O)</th>
<th>Wavenumber, cm⁻¹</th>
<th>r (1100)</th>
<th>r (1090)</th>
<th>r (950)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂Si₂O₅</td>
<td>8.1</td>
<td>573s,p, 763w,p</td>
<td>948m,p</td>
<td>...</td>
<td>1103s,p</td>
</tr>
<tr>
<td>Na₂Si₂O₅</td>
<td>33.6 (D₂O)</td>
<td>573s,p, 770w,p</td>
<td>948w,p</td>
<td>1057s,p</td>
<td>1098s,p</td>
</tr>
<tr>
<td>Na₂Si₂O₅</td>
<td>8.1</td>
<td>579s,p, 764w,p</td>
<td>939m,p</td>
<td>1061s,p</td>
<td>1098s,p</td>
</tr>
<tr>
<td>Na₂Si₂O₅</td>
<td>14.4</td>
<td>574s,p, 767w,p</td>
<td>960v,p</td>
<td>1070s,p</td>
<td>1100s,p</td>
</tr>
<tr>
<td>Na₂Si₃O₇</td>
<td>8.6</td>
<td>542s,p, 775w,p</td>
<td>942w,p</td>
<td>1065m,p</td>
<td>1093s,p</td>
</tr>
<tr>
<td>Na₂Si₃O₇</td>
<td>44.8 (D₂O)</td>
<td>538s,p, 760w,p</td>
<td>928w,p</td>
<td>1050s,p</td>
<td>1152m,p</td>
</tr>
<tr>
<td>Na₂Si₃O₇</td>
<td>8.6</td>
<td>539s,p, 777w,p</td>
<td>972w,p</td>
<td>1061m,p</td>
<td>1110s,p</td>
</tr>
<tr>
<td>Na₂Si₃O₇</td>
<td>24.3</td>
<td>546s,p, 773w,p</td>
<td>978m,p</td>
<td>1056s,p</td>
<td>1132m,p</td>
</tr>
<tr>
<td>Na₂Si₃O₇</td>
<td>37.9</td>
<td>546s,p, 773w,p</td>
<td>973m</td>
<td>1062s,p</td>
<td>1147m,p</td>
</tr>
</tbody>
</table>

Abbreviations: s, strong; m, medium; mw, medium to weak; w, weak; vw, very weak; (bd), broad; (sh), shoulder; p, polarized.
Band positions above 1200 cm⁻¹ not accurately measured. For detailed positions of such bands (H₂O and D₂O stretch bands), see Table 2.

spectra were attempted deconvoluted into individual peaks. The details of the procedures used are described by Mysen et al. (1980).

Results

Volatile-free melts

The structural interpretation of volatile-free, quenched NS2 and NS3 melts at 1 atm and at high pressure has been presented elsewhere (Brawer and White, 1975; Furukawa and White, 1980; Mysen et al., 1980). Only a summary of the band positions (Table 1) and interpretation of the Raman spectra are given here. The Raman spectrum of quenched NS2 melt consists of three polarized bands that are important for the present discussion. The strong band near 1100 cm⁻¹ is due to -O-Si-O Kelley stretching (diagnostic of sheet units in the melt). The band near 950 cm⁻¹ is due to -O-Si-O Kelley stretching (diagnostic of chain units), and that near 1060 cm⁻¹ is due to Si-O Kelley stretching (three-dimensional network unit). Other bands near 570 and 770 cm⁻¹, respectively, are due to Si-O Kelley rocking and bending motions.

In volatile-free melt of Na₂Si₂O₅ composition, the following expression can be used to describe the equilibrium between the anionic structural units of the melt (Mysen et al., 1980):

\[ 2\text{SiO}_2^{2-} (\text{sheet}) = \text{SiO}_2^{2-} (\text{chain}) + \text{SiO}_4 (3D) \]  

The same bands occur in volatile-free, quenched NS3 melt as in volatile-free NS2 melt (Table 1). Mysen et al. (1980) concluded, therefore, that quenched NS2 and NS3 melts contain the same structural units and that the equilibrium expressed with equation 1 applies to both melt compositions. The two melts differ, however, in that chain units are more dominant in NS2 than in NS3 melts, as indicated by the intensity ratios of diagnostic bands.

Virgo et al. (1980) found that analogous expressions could be derived for binary melts with greater NBO/Si than NS2. In those cases, the expressions were:

For NBO/Si between 1.0 and 2.0:

\[ 3\text{SiO}_2^{2-} (\text{chain}) = 2\text{SiO}_2^{2-} (\text{sheet}) + 2\text{SiO}_4^{2-} (\text{monomer}) \]  

and for NBO/Si between 4.0 and 2.0:

\[ 2\text{SiO}_2^{2-} (\text{dimer}) = \text{SiO}_2^{2-} (\text{chain}) + 2\text{SiO}_4^{2-} (\text{monomer}) \]  

Mysen et al. (1980) noted that the same expressions hold true regardless of the type of network-modifying cation. They also concluded that this structural model does not agree with models based on polymer theory, and presented arguments as to why this would be expected. This model is, however, consistent with rheological data on silicate melts (Bockris et al., 1956). The interested reader is referred to Mysen et al. (1980) for a complete discussion of the present and other models.

The distinct assignments to monomers, dimers, chain, and sheets were also discussed in some length by Mysen et al. (1980), and no further discussion of those assignments is presented here.

The anionic structures of the two melts with three-dimensional network structure at 20 kbar (Jd and Ab melt) are also known (Virgo et al., 1979a; Mysen et al., 1980). Only band positions of volatile-free,
Table 2. Band positions of Raman spectra from quenched melts in the system Na$_2$O–Al$_2$O$_3$–SiO$_2$–D$_2$O–H$_2$O at 1500°C and 20 kbar

| Composition | Mole % | Wavenumber, cm$^{-1}$ | r(1100) | f(1100) | r(1200) | r(1300) | r(1400) | r(1500) | r(1600) | r(1700) | r(1800) | r(1900) | r(2000) | r(2100) |
|-------------|--------|------------------------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| NaAlSiO$_5$ & $0.0$ | 470s, p | 566w, p | 784v, p | 950s, p | 1062s, p | 2175s | 2300v | 2500s | 2700v | 2900s | 3100s | 3300s | 3500s | 3700s |
| NaAlSiO$_5$ & $27.4$ | 480s, p | 570s, sh | 770v, p | 878s, dp | 983s, dp | 2180s | 2300v | 2500s | 2700v | 2900s | 3100s | 3300s | 3500s | 3700s |
| NaAlSiO$_5$ & $40.0$ | 465s, p | 563s, sh | 770v, p | 862v, dp | 985s, dp | 2180s | 2300v | 2500s | 2700v | 2900s | 3100s | 3300s | 3500s | 3700s |
| NaAlSiO$_5$ & $51.9$ | 465s, p | 563s, sh | 770v, p | 862v, dp | 985s, dp | 2180s | 2300v | 2500s | 2700v | 2900s | 3100s | 3300s | 3500s | 3700s |
| NaAlSiO$_5$ & $90.0$ | 480s, p | 570s, sh | 770v, p | 878s, dp | 983s, dp | 2180s | 2300v | 2500s | 2700v | 2900s | 3100s | 3300s | 3500s | 3700s |

Abbreviations and uncertainties as in Table 1.

*Present but not determined accurately.

quenched Jd and Ab melts are given (Table 2). Briefly, the high-frequency envelope consists of two (Si,Al)–O$^-$ stretch bands. Their frequencies are lowered with increasing Al content of the melt. The two stretch bands reflect two different three-dimensional network units in the melt. According to Mysen et al. (1980), these two units differ in average Si/(Si + Al), where the lowest frequency band is due to the most Si-rich unit. In addition, the Raman spectra show bands near 800, 570, and 470 cm$^{-1}$, which are due to Si–O$^-$ bending, decoupled defects, and Si–O$^-$ rocking, respectively (Bates et al., 1974; Stolen and Walrafen, 1976). The three bands at these positions are diagnostic of the presence of three-dimensional network units in the quenched melts (Virgo et al., 1979a).

In addition, the Raman spectra of all the samples, whether volatile-free or volatile-bearing, show two sharp bands near 2300 and 2200 cm$^{-1}$, respectively (Fig. 1). These two bands are due to N$_2$ and N$_2^*$ (Hartwig, 1977; Nakamoto, 1978) from air, and are of no consequence for the interpretation of the spectroscopic features under consideration. This observation is important because these two bands occur in the frequency region of Si–H stretching and could be misinterpreted as a result of such bonds. The two bands do not shift their frequency with composition, however, as would be expected if they were due to Si–H stretching (Lucovsky, 1979; Lucovsky et al., 1979). Furthermore, no Si–H bands could be detected in the frequency region between 800 and 900 cm$^{-1}$.

**Silicate melts with H$_2$O**

Before the spectra of H$_2$O-bearing silicate melts are discussed, it is instructive to discuss the D$_2$O-bearing samples, because Si–OH stretch vibrations are expected in the frequency region near 950 cm$^{-1}$ (Stolen and Walrafen, 1976). The Si–O stretch vibrations also occur in this frequency region. The analogous Si–OD bands are at frequencies that are lower than those of the OH vibrations by a factor of $\sqrt{2}$ (Van der Steen and Van den Boom, 1977; Hartwig, 1977).

The Raman spectrum of quenched Ab melt with 40.9 mole percent D$_2$O (calculated on the basis of 8 oxygens) is shown in Figure 1. The high-frequency envelope of this spectrum is compared with that of volatile-free and H$_2$O-bearing Ab melt in Figure 2. Detailed band positions are given in Table 2. The strong, broad, and asymmetric band near 2600 cm$^{-1}$ is due to D–O–D stretching (Van der Steen and Van den Boom, 1977). The two sharp bands on the low-frequency shoulder of the 2600 cm$^{-1}$ band are due to N$_2$ and N$_2^*$ from the air (see above). There is also a weak band near 3570 cm$^{-1}$, which is due to H–O–H stretching (e.g., Stolen and Walrafen, 1976). This band is expected because the D$_2$O also contained about 5 percent H$_2$O.

Several changes have occurred in the high-fre-
frequency envelope of the spectrum from Ab + D₂O compared with the envelope of volatile-free Ab melt (Figs. 1 and 2). The two (Si,Al)–O\(^{\circ}\) stretch bands remain in the same positions (about 1000 and 1100 cm\(^{-1}\)) as for the volatile-free melt. The intensity of the band near 1000 cm\(^{-1}\) is considerably weakened, however, relative to the 1100 cm\(^{-1}\) band \([I(1100)/I(1000)]\) is about 2.3 compared with 0.7 for volatile-free Ab melt; see also Table 2. We conclude, therefore, that the proportion of Si-rich, three-dimensional network unit (3D) in Ab melt has been substantially reduced as a result of dissolved D₂O. It is emphasized, however, that the average Si/(Si + Al) of the two three-dimensional units is the same. Only the proportion of the Si-rich unit has been reduced.

A new band at 886 cm\(^{-1}\) occurs in deuterated, quenched Ab melt at 20 kbar and 1500°C (Fig. 2, Table 2). The D₂O contains only a very small amount of H₂O and the position and intensity of the 886 cm\(^{-1}\) band do not change appreciably whether 40 mole percent H₂O or 40 mole percent D₂O (with 5 percent H₂O) has been dissolved in the melt. It is not likely, therefore, that this band is due to vibrations involving D, H, OH, or OD-groups, as their intensities and frequencies would depend on concentration and type of volatile component added to the melt. We conclude, therefore, that the 880 cm\(^{-1}\) band cannot be assigned to Si–H, Si–D, Al–H, Al–D, Si–OH, Si–OD, Al–OH, or Al–OD vibrations. In addition, there are other arguments in favor of another interpretation. The Al–H, Al–D, Si–H, and Si–D vibrations may have bands that occur in the frequency range between 700 and 900 cm\(^{-1}\) (e.g., Ryskin, 1974; Hartwig, 1977; Lucovsky, 1979; Lucovsky et al., 1979; Pei, 1966). The band near 880 cm\(^{-1}\) could be due to Al–O\(^{\circ}\), –O–(Si,Al)–O\(^{\circ}\) or –O–(Si,Al)–O\(^{-}\)-stretching. If it were due to Al–O\(^{\circ}\) stretch vibrations, clusters of AlO₄ tetrahedra without nonbridging oxygens would be expected in the melt. This hypothesis is ruled out for the following reasons. In vibrational spectra known to contain AlO₄ clusters, Al–O\(^{\circ}\) stretch vibrations result in one or more bands at 800 cm\(^{-1}\) or lower frequency (Tarte, 1967; Serna et al., 1977, 1979; Virgo and Seifert, unpublished data, 1979), and no such bands are found in the hydrated samples. It is not likely, therefore, that the 880 cm\(^{-1}\) band found in the Ab + D₂O spectrum results from AlO₄ clusters. The band between 750 and 800 cm\(^{-1}\) found in the spectra of quenched Ab and Jd melts (Table 2) also
occurs at this frequency in Al-free melts with three-dimensional network units. The band in the deuterated and hydrated melts is not significantly affected by D\textsubscript{2}O or H\textsubscript{2}O content. This band is assigned to Si–O\textsuperscript{0} bending, as also suggested by Bates et al. (1974) for quenched SiO\textsubscript{2} melt. No new bands occur in the spectral region below 800 cm\textsuperscript{-1} as a result of added volatiles. The presence of AlO\textsubscript{4} clusters is therefore ruled out.

The 880 cm\textsuperscript{-1} band changes its frequency with H\textsubscript{2}O and Al content (Table 2) and hence is most likely a coupled (Si,Al) vibration. The intensity of the band relative to the (Si,Al)–O\textsuperscript{0} stretch bands is so large, however, that it is unlikely that the 880 cm\textsuperscript{-1} band reflects vibrations of a bridging oxygen (see also Furukawa and White, 1980, for further discussion of such intensity considerations).

The 880 cm\textsuperscript{-1} band is polarized and thus is probably a symmetric –O–(Si,Al)–O– stretch vibration rather than an asymmetric –O–(Si,Al)–O\textsuperscript{0} stretch vibration. Mysen and Virgo (1979) noted that in quenched melts of NaCaAl\textsubscript{3}Si\textsubscript{2}O\textsubscript{8}, composition [Si/(Si + Al) = 0.33 as compared with 0.25 in NaAlSi\textsubscript{4}O\textsubscript{8} composition] the –O–Si–O– stretch band found near 950 cm\textsuperscript{-1} was shifted to near 900 cm\textsuperscript{-1} as a result of (Si,Al) coupling. In the system NaAlSi\textsubscript{4}O\textsubscript{8} + D\textsubscript{2}O, the average Si/(Si + Al) is greater than in Na CaAl\textsubscript{3}Si\textsubscript{2}O\textsubscript{8}. As discussed further below, the Si/(Si + Al) of the anhydrous portion of the melt is less than this average value, however, because some of the Si of the melt is no longer part of the anhydrous network (owing to the formation of Si–OH- or Si–OD-containing structural units in the melt). The Si–OD band (stretch) is expected near 600 cm\textsuperscript{-1}. This is a weak band, however (Stolen and Walrafen, 1976), and is unresolved beneath the asymmetric band with a maximum near 500 cm\textsuperscript{-1} (Fig. 2). As a result of these considerations, we conclude that the 880 cm\textsuperscript{-1} band in quenched Ab + D\textsubscript{2}O melt is due to symmetric –O–(Si,Al)–O– stretching. The (Si,Al) coupling is more extensive than indicated by the average Si/(Si + Al) of the melt. This band is, therefore, diagnostic of anhydrous (or undeuterated) chain units in the quenched Ab melt with 40.9 mole percent D\textsubscript{2}O in solution.

The Raman spectra of quenched Ab + H\textsubscript{2}O melt are shown in Figures 1 and 2, and band positions are given in Table 2. All spectra show the same features as the spectrum for Ab + D\textsubscript{2}O, except that the H–O–H and Si–OH vibrations occur at different frequencies because of the different mass of H compared with D (Van der Steen and Van den Boom, 1977). A broad, asymmetric band near 3520 cm\textsuperscript{-1} is assigned to H–O–H stretching (Stolen and Walrafen, 1976). The asymmetry toward lower frequency is probably due to weak OH–...O hydrogen bonds (Serratosa and Vinas, 1964; Peri, 1966). Hydrogen bonds between outer hydroxyl groups and neighboring oxygen are frequently observed in micas, for example (Serna et al., 1977, 1979).

There are no bands at higher frequency than the H–O–H band; thus the presence of molecular H\textsubscript{2} in the quenched Ab + H\textsubscript{2}O melt is ruled out (Lucovsky et al., 1979). The absence of a band near 1600 cm\textsuperscript{-1} rules out the possibility of a contribution of molecular H\textsubscript{2}O in solution in any of these melts (Lucovsky et al., 1979). The two sharp bands near 2200 and 2300 cm\textsuperscript{-1} are due to N\textsubscript{2} and N\textsubscript{2} from the air (see also above). The weak band near 1380 cm\textsuperscript{-1} (Fig. 2) is due to H–O–H bending (Ryskin, 1974).

We note that the intensity of the band near 570 cm\textsuperscript{-1} [due to defects (broken oxygen bridges) in the three-dimensional network structure (Bates et al., 1974; Stolen and Walrafen, 1976)] is lower in the spectra of melts with H\textsubscript{2}O (and D\textsubscript{2}O) than in those of melts without volatiles (Fig. 3). Stolen and Walrafen (1976) made similar observations in the system SiO\textsubscript{2}–H\textsubscript{2}O. They concluded that H\textsuperscript{+} reacted with defects in the three-dimensional network structure (Si–O–...Si–O–Si–) to form OH, thereby diminishing the intensity of this band. The same mechanism explains the reduced intensity of the 570 cm\textsuperscript{-1} band in the spectra shown here. Stolen and Walrafen (1976) noted, however, that only about 1000 ppm H\textsubscript{2}O can dissolve in fused SiO\textsubscript{2} according to this mechanism, and it is
therefore not considered the major mechanism for solution of several weight percent H₂O.

The band near 880 cm⁻¹ in quenched Ab + D₂O melt also occurs in quenched Ab + H₂O melt (Fig. 2) and is at nearly the same position (within experimental uncertainty).

The 1000 cm⁻¹ shoulder in Ab + H₂O spectra is stronger than in the spectrum from Ab + D₂O (Fig. 2). This higher intensity is caused by the presence of two bands in the frequency region near 1000 cm⁻¹. One is due to (Si,Al)-O⁰ stretching from the silica-rich, three-dimensional network unit (1000 cm⁻¹). The other band (near 980 cm⁻¹) is an Si-OH stretch vibration. It may be argued that the 980 cm⁻¹ band may also be due to Al-OH stretching. This possibility is considered unlikely because (1) the band occurs at the same frequency in Al-free samples (e.g., Stolen and Walrafen, 1976; see also below) and (2) several Al-OH bending and rocking vibrations would be expected in the frequency region between 950 and 750 cm⁻¹ (Ryskin, 1974). No such bands were found in our samples.

The 880 cm⁻¹ band may shift to slightly higher frequency with increasing water content of quenched Ab melt (Fig. 4). The frequencies of the 1000 and 1100 cm⁻¹ bands are not affected by the presence of water in the melt. The frequency increase of the 880 cm⁻¹ band with increasing water content indicates that the average Si/(Si+Al) of this structural unit in quenched Ab melt increases slightly with increasing H₂O content.

The intensities of both the 880 and 980 cm⁻¹ bands increase relative to those of the 1100 and 1000 cm⁻¹ (Al,Si)-O⁰ stretch bands as the water content of the Ab melt is increased (Fig. 5; see also Table 2). We conclude, therefore, that more chain units and Si-OH bands are formed as the water content of the melt is increased. Finally, the intensity ratio, I(1100)/I(1000), increases with increasing water content (Fig. 6). This increase implies that the Si-OH groups are formed as a result of interaction between the H₂O and the most silica-rich of the two three-dimensional network units in melt of NaAlSi₃O₈ composition.

The high-frequency envelope of the Raman spectra of quenched melts of NaAlSi₃O₈ and NaAl Si₂O₆ + H₂O composition are shown in Figure 7 (see also Table 2). The portions of these spectra at higher
and lower frequencies than those shown in Figure 7 are identical with the same regions in the spectra of quenched Ab + H$_2$O melt and are not included. The exact band positions from these regions are given in Table 2.

The structure of quenched anhydrous Jd melt at high pressure has been described by Mysen et al. (1980). Briefly, the structure closely resembles that of quenched anhydrous Ab melt except that the two three-dimensional network units are more Al-rich in the Jd than in the Ab melt. The proportion of the most Si-rich unit relative to the Al-rich unit is also smaller in Jd melt.

Addition of water to Jd melt results in the same changes in the high-frequency envelope of the Raman spectra as for Ab melt. A new, polarized band occurs near 860 cm$^{-1}$, which is analogous to the 880 cm$^{-1}$ band in quenched Ab + H$_2$O melt. This band is assigned to symmetric $\text{O}^\text{2-}(\text{Al,Si})-\text{O}^\text{2-}$ stretching, as in quenched Ab + H$_2$O melt. Its slightly lower frequency in Jd + H$_2$O melt is a result of the smaller Si/(Si + Al) of Jd compared with Ab melt. The intensity of this band relative to the (Si,Al)-O$^\text{2-}$ stretch bands increases with increasing water content of the melt, as was also the case for Ab + H$_2$O melt (Fig. 5). A new band near 980 cm$^{-1}$ is assigned to Si-OH stretching. This band most likely does not reflect Al-OH stretching, for the same reasons as outlined above for Ab + H$_2$O melt. Finally, the intensity ratio, $I(1060)/I(950)$, increases with increasing water content (Fig. 6). This intensity increase corresponds to the intensity increase of $I(1100)/I(1000)$ for Ab + H$_2$O melt, and is interpreted to mean that the proportion of the Si-rich, three-dimensional network unit decreases relative to the Al-rich unit as the water content of quenched Jd melt is increased.

In summary, solution of H$_2$O in melts of NaAlSi$_3$O$_8$ and NaAlSi$_2$O$_6$ has similar effects on the anionic structure of the melts. First, water is bound in the structure as Si-OH, resulting in a decrease in the average Si/(Si + Al) of the anhydrous portion of the melt. The three-dimensional network portion of the melt responds to this decrease by an increase in the proportion of the Al-rich unit relative to the Si-rich, three-dimensional network unit. Second, (Si,Al)-coupled chains of the type NaAlSi$_2$O$_6^-$ are formed. No OH groups are attached to the chain units. Third, aluminum is not attached to hydroxyl in any complex in the melt. Fourth, it is not possible to determine from the Raman spectra whether complexes involving Na$^+$ and OH$^-$ occur in the melt. This unidentified complex is referred to as Na(OH)$^0$ in the remainder of the text.

A comparison of the high-frequency envelopes of the Raman spectra of quenched melts of NaAlSi$_2$O$_8$ and NaAlSi$_3$O$_8$ is shown in Figure 8, and detailed data are given in Table 1. A comparison of the spectra of the volatile-free samples with the deuterated sample is conducted first, to avoid interferences from OH bands in the high-frequency envelope (see also above). Three features are evident from the comparison of the volatile-free and the deuterated samples. First, the 940 cm$^{-1}$ band diagnostic of chain units in anhydrous NS3 melt cannot be discerned in the deuterated sample. Second, a new band near 1150 cm$^{-1}$ is observed in the Raman spectrum of quenched NS3 + D$_2$O. We suggest that this is the band found at 1200 cm$^{-1}$ in quenched SiO$_2$ melt and assigned to Si-O$^0$ stretching (Bates et al., 1974). Brawer and White (1975, 1977) noted that this band shifts from 1200 cm$^{-1}$ to near 1150 cm$^{-1}$ as Na$_2$O is added to SiO$_2$ melt on the join Na$_2$O–SiO$_2$. The band disappears at...
Na$_2$O/SiO$_2$ = 1/3–1/4. The reappearance of this band with the addition of D$_2$O to quenched melt of NS3 composition (Na$_2$O/SiO$_2$ = 1/3) indicates that the proportion of bridging oxygen is greater in deuterated than in volatile-free melt of NS3 composition. Third, the intensity of the 1100 cm$^{-1}$ band (indicating that sheet units may be present in the melt; Mysen et al., 1980) relative to the intensity of the 1050 cm$^{-1}$ band (Si–O$^-$ antisymmetric stretch band; Furukawa and White, 1980; Mysen et al., 1980) has decreased. This observation also implies that deuterated NS3 melt is more polymerized than D$_2$O-free, quenched melt of Na$_2$Si$_2$O$_5$ composition.

The high-frequency envelopes of the Raman spectra of hydrated quenched NS3 melt are shown in Figure 9 (see also Table 1). When curves were fitted to the high-frequency envelope (see Mysen et al., 1980, for the fitting procedure), the bands near 1050, 1100, and 1150 cm$^{-1}$ were retained. In order to fulfill this requirement, a broad band near 970 cm$^{-1}$ also had to be included. This band becomes more intense with increasing water content, and because of this relation and its frequency, it is assigned to Si–OH stretching.

The intensity ratio of the 1100 and 1050 cm$^{-1}$ bands is plotted as a function of H$_2$O content of the melt in Figure 10. These data show that the 1050 cm$^{-1}$ band becomes more intense as the water content of the melt increases. This observation is interpreted to mean that the solution of H$_2$O in melt of Na$_2$Si$_2$O$_5$ composition results in the formation of Si–OH bonds with a concomitant decrease of NBO/Si of the melt.

The effect of dissolved H$_2$O and D$_2$O on the high-frequency envelope of the Raman spectra of quenched NS2 melt is shown in Figure 11. A comparison of the spectra of volatile-free, D$_2$O-bearing, and H$_2$O-bearing NS2 melt shows the same bands in all cases (940 cm$^{-1}$, SiO$_6^-$ chains; 1060 cm$^{-1}$, SiO$_2$ three-dimensional network; 1100 cm$^{-1}$, Si$_2$O$_5^-$ sheets). It is clear, however, that the intensity ratio $I$(1100)/$I$(1060) has decreased and $I$(1100)/$I$(940) has increased (Table 1; see also Fig. 10). As for hydrous melt of NS3 composition, these changes are interpreted to mean that the proportion of bridging oxygen in the melt has increased as water is dissolved. This change is reflected in an increased ratio of three-dimensional network units to sheet units, and an in-
crease of sheet units relative to chain units in the melt.

Addition of H$_2$O to quenched NS2 melt results in an additional change of the high-frequency envelope. A new band occurs near 980 cm$^{-1}$, which is the Si-OH stretch band also found in all the other compositions.

In summary, the influence of dissolved water on the structure of melts in the system Na$_2$O-SiO$_2$ appears similar for all compositions studied. Water is attached to the network with Si-OH bonds, and the hydroxyl-free portion of the network has become more polymerized. As in the systems Ab + H$_2$O and Jd + H$_2$O, it cannot be determined from the Raman spectra whether Na(OH)$^\circ$ occurs in the melts; however, mass-balance considerations require its presence. This conclusion contrasts with that for the other two compositions, in which Na(OH)$^\circ$ does not occur.

**Solubility mechanisms**

Even though H$_2$O reacts with silicate melts to form Si-OH bonds, two distinctly different solubility mechanisms are necessary to explain the spectroscopic observations, depending on whether the silicate melt contains nonbridging oxygen. Most solubility models for H$_2$O have been based on studies of melts with a three-dimensional network structure, and this type of melt is considered first.

The Raman spectra of hydrous Jd and Ab melt show the existence of four structural units. First, there are units that involve only Si and OH. Whether Si-O-Si bonds also exist in these structural units cannot be discerned from the Raman spectra. Second, there are chain units without OH but with both Si and Al. The Al$^{3+}$ must be locally charge-balanced with Na$^+$. The exact proportion of Si and Al in the chain unit cannot be determined. In the present discussion, the chain unit is described by the formula NaAlSiO$_4^+$, where Al, therefore, is in tetrahedral coordination. Third, a portion of the three-dimensional network units is not affected by the presence of H$_2$O in the melt. The proportion of the latter two units and the OH/Si of the hydroxylated silicate unit depends on the H$_2$O content of the melt. Fourth, Burnham (1975) noted that the equimolal solubility of H$_2$O in NaAlSiO$_4$ melt is about 10 percent greater than in SiO$_2$. This additional water is dissolved as OH$^-$, locally charge-balanced by Na$^+$. This configuration in the melt is referred to as Na(OH)$^\circ$ in this text. This notation is not meant to imply that such complexes actually occur in the melt.

A consequence of the formation of chain units from a three-dimensional network structure is the expulsion of some Al$^{3+}$ from tetrahedral coordination. There is no evidence that either this or any other Al$^{3+}$ is coordinated with OH groups. An equivalent amount of Na$^+$ must also be transformed from its charge-balancing role to become a network modifier.

The extra Al$^{3+}$ is referred to simply as Al$^{3+}$ in the
expressions below. This notation is meant to indicate the proportion of aluminum in the melt that is no longer in tetrahedral coordination. Instead, this proportion of the total amount of aluminum in the melt has become a network-modifier.

The formation of Si–OH bonds from bridging oxygen is visualized as follows:

\[-\text{Si–O–Si– (melt)} + \text{H}_2\text{O (vapor)} = \text{–Si–OH...HO–Si– (melt)}\]  
(4)

The principle illustrated with this expression was also proposed by Kurkjian and Russell (1957), Wassenburg (1957), Adams and Douglas (1959), and Uys and King (1963). The formation of two OH groups per molecule of H\(_2\)O was indicated by the fact that the H\(_2\)O solubility was proportional to \([\text{[H}_2\text{O}]]^{1/2}\) (Kurkjian and Russell, 1957).

In view of the above observations and discussion, an idealized expression that describes the solubility mechanism of H\(_2\)O in melt of NaAlSi\(_3\)O\(_8\) composition can be written:

\[\text{14NaAlSi}_3\text{O}_8 \text{ (melt) } + 13x\text{H}_2\text{O (vapor)} = 9\text{Si}_4\text{O}_{11}x\text{ (OH)}_2x \text{ (melt) } + 8\text{Na(OH)}_3x \text{ (melt)} + 8\text{Al}^{3+} \text{ (melt)} = 6\text{NaAlSiO}_4^{x-}\]  
(5)

The Al\(^{3+}\) in equation 5 reflects the proportion of aluminum that is now a network modifier. With \(x = 2, 4, 6,\) and \(8,\) the hydroxylated silicate is respectively a sheet, chain, dimer, and monomer. The corresponding amount of H\(_2\)O that can be dissolved in Ab melt with these values for \(x\) is given in Table 3. The results of the latter calculations (Table 3) show that in our quenched melts the hydroxylation probably did not proceed beyond sheets [Si\(_4\)O\(_{11}\)(OH)\(_x\)].

Fig. 9. High-frequency region of water-bearing, quenched melt of Na\(_2\)Si\(_3\)O\(_7\) composition.

<table>
<thead>
<tr>
<th>Mole % H(_2)O</th>
<th>Raman band intensity ratio, (I(1100)/I(1060),) of quenched NS3 and NS2 melts as a function of water content.</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.6 mole % H(_2)O</td>
<td>[\text{NS2} ]</td>
</tr>
<tr>
<td>24.3 mole % H(_2)O</td>
<td>[\text{NS3} ]</td>
</tr>
<tr>
<td>37.9 mole % H(_2)O</td>
<td>[\text{NS2} ]</td>
</tr>
</tbody>
</table>

Fig. 10. Raman band intensity ratio, \(I(1100)/I(1060),\) of quenched NS3 and NS2 melts as a function of water content.
The Raman spectra of quenched hydrated melt of NaAlSi\textsubscript{3}O\textsubscript{6} composition indicate that the solubility mechanism for H\textsubscript{2}O in such melts is similar to that in Ab melt. The analogous expression is

\[
28\text{NaAlSi}_3\text{O}_6 (\text{melt}) + 15x\text{H}_2\text{O} (\text{vapor}) = 11\text{Si}_6\text{O}_{8.5} (\text{OH})_{2x} (\text{melt}) + 16\text{Na(OH)}^\circ (\text{melt}) + 16\text{Al}^{3+} (\text{melt}) + 12\text{NaAlSi}_3\text{O}_6^- (\text{melt}) \tag{6}
\]

The maximum solubilities of H\textsubscript{2}O corresponding to \(x = 2, 4, 6,\) and 8 are shown in Table 3.

We suggest that analogous mechanisms control the solubility of H\textsubscript{2}O in melts with three-dimensional network structures but with other melt modifiers (e.g., K or alkaline earths) or amphoteric cations (e.g., Fe\textsuperscript{3+}). The solubility mechanisms of H\textsubscript{2}O in silicate melts with nonbridging oxygen indicate the formation of Si-OH bonds with a concomitant decrease in NBO/Si of the melt. The formation of an Si-OH bond from Si-O\textsuperscript{−} indicates that one H\textsuperscript{+} has taken the place of an Na\textsuperscript{+}. The Na\textsuperscript{+} released can be neutralized by forming Na(OH)\textsuperscript{0}, a model also advanced by Kurkjian and Russell (1957) on the basis of solubility studies on Na\textsubscript{2}O-SiO\textsubscript{2} melts. In fact, the formation of Na(OH)\textsuperscript{0} complexes is a consequence of the spectroscopic observation that Si\textsubscript{2}O\textsubscript{4}/Si\textsubscript{3}O\textsubscript{4} increases with increasing water content of the melts.

The complete reactions for melts of Na\textsubscript{2}Si\textsubscript{2}O\textsubscript{6} and Na\textsubscript{2}Si\textsubscript{3}O\textsubscript{6} compositions may be written:

\[
6\text{Na}_2\text{Si}_3\text{O}_7 (\text{melt}) + 5x\text{H}_2\text{O} (\text{vapor}) = 2\text{Si}_6\text{O}_{8.5} (\text{OH})_{2x} (\text{melt}) + 6\text{SiO}_2 (\text{melt}) + 12\text{Na(OH)}^\circ (\text{melt}) \tag{7}
\]

and

\[
6\text{Na}_2\text{Si}_3\text{O}_6 (\text{melt}) + 5x\text{H}_2\text{O} (\text{vapor}) = 2\text{Si}_6\text{O}_{8.5} (\text{OH})_{2x} (\text{melt}) + 4\text{SiO}_2 (\text{melt}) + 12\text{Na(OH)}^\circ (\text{melt}) \tag{8}
\]

The maximum water solubilities for given values of x (Table 3) show that for given x the water solubility increases with increasing Na\textsubscript{2}O/SiO\textsubscript{2}, as also concluded by Uys and King (1963) on the basis of water solubility studies on melts on alkali-silica joins.

We suggest that solution mechanisms similar to those shown in equations 7 and 8 also operate in
metasilicate melts. In those melts, chain units are the predominant units, and the hydroxylated units can be no more polymerized than that.

In summary, the Raman spectra of quenched hydrated melts with a three-dimensional network structure show that nonbridging oxygens are formed in addition to hydroxylated silicate units. In melts with nonbridging oxygen, the Raman spectra show an increase in the degree of polymerization of the network. Water is bonded in the structure as both Si–OH and complexes of the type M(OH)\(^n\), where M is a modifying cation.

Applications

Water affects the melting relations of silicate mineral assemblages. Kushiro (1969) has shown, for example, that in the system CaO–MgO–SiO\(_2\)–H\(_2\)O the pyroxene–silicate mineral liquidus boundary shifts significantly toward the silica-rich portion of the system with the addition of H\(_2\)O. This observation is understandable in the light of the solubility mechanisms for water in highly polymerized melts where \(X(T_2O_3)/X(TrO_5)\) increases as a function of increasing water content of the melt.\(^a\) If it is assumed that the relative changes of concentration of the structural units in the melt can be approximated with the relative changes of their activities (activity coefficient ratios are constant), the stability field of the most silica-rich mineral is reduced simply because \(X(T_2O_3)/[X(T_2O_3) + X(T_3O_5)]\) has decreased.

The plagioclase stability field shrinks at the expense of pyroxene stability fields as H\(_2\)O is added to natural and synthetic andesite systems (e.g., Kushiro, 1972; Eggler, 1972). These changes can also be directly related to the increased importance of TrO\(_6\) units in the melts with increasing water content.

Partial melts from hydrous peridotite in the upper mantle are more siliceous than those from anhydrous peridotite (e.g., Kushiro et al., 1972; Mysen and Boettcher, 1975). Carmichael et al. (1974) explained such observations by stating that the activity of silica in the hydrous partial melts is lower than in the anhydrous partial melts. The reason for this lowering of silica activity is the lowering of \(X(T_2O_3)/[X(T_2O_3) + X(T_3O_5)]\) as water is added to the system.

Melt structure (bulk composition) affects crystal–liquid partition coefficients (Watanabe, 1976, 1977; Hart and Davis, 1978; Mysen et al., 1979c). The most important feature of the melt structure affecting the partition coefficients is the ratio of nonbridging to bridging oxygen in the melt. The crystal–liquid partition coefficients of both transition metals and rare earth elements decrease with increasing NBO/T of the melt (Mysen et al., 1979c). Solution of H\(_2\)O in highly polymerized melts (e.g., basalt, andesite and granite) results in an increase of NBO/T. We suggest, therefore, that crystal–liquid partition coefficients will decrease with increasing water content. In melts with a large value of NBO/T (e.g., picrite, komatiite, and basanite), it is likely that solution of H\(_2\)O results in decreased NBO/T. In such cases, the relevant crystal–liquid partition coefficients (e.g., Ni between olivine and melt) will increase with increasing water content of the melt.

Iron is likely to play a similar role in silicate melts to aluminum (Seifert et al., 1979). That is, in hydrous basaltic melts some ferric iron is a network modifier and some is a network former. The proportion of ferric iron in tetrahedral coordination will depend on the water content of the melt. The activity of ferric iron complexed in octahedral coordination in melts is greater than when ferric iron is in tetrahedral coordination (Seifert et al., 1979; Mysen et al., 1979b). Consequently, the stability fields of iron oxides on the liquidus of hydrous basalt differ from those of anhydrous basaltic melts not only because water affects the fugacity of hydrogen (e.g., Osborn, 1959), but also because it affects the structural role of ferric iron in the melt.

Physical properties of silicate melts (e.g., electrical conductivity and viscosity) depend on their water content (Lebedev and Khitarov, 1964; Shaw, 1963; Kushiro, 1978; Kushiro et al., 1976). In anhydrous melts of basaltic and more acidic composition, NBO/T is less than 1 (Bottina and Weill, 1972; Scarfe et al., 1979; Mysen et al., 1979a). In such melts, the flow units during viscous flow are SiO\(_2\)-rich, three-dimensional clusters (Mysen et al., 1979a). The clusters are bonded with T–O bonds, where the T cation is tetrahedrally coordinated Al\(^{++}\), Ti\(^{++}\), and Fe\(^{++}\). The viscosity of such melts depends on the strength of the T–O bond (e.g., Taylor and Rindone, 1970). In melts with NBO/T > 1, the flow units are isolated SiO\(_4\) tetrahedra and modifying cations (e.g., Bockris et al., 1955). The viscosity of such melts depends on the number of oxygen bridges that must be broken to form the flow units. Furthermore, only a portion of the melt participates in the viscous flow at any given time. In this case, the viscosity of a melt with a sheet structure, for example, is greater than that of one

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\(^a\) The notations \(X(T_2O_3)\), \(X(T_2O_5)\) and \(X(T_3O_5)\), respectively, denote proportions of melt units with a three-dimensional network, sheet, and chain structure. The T cation can be Si\(^{++}\), Ti\(^{++}\), P\(^{++}\), (NaAl)\(^{++}\), (\(\frac{1}{2}\)CaAl)\(^{++}\), and (NaFe)\(^{++}\).
with a chain structure, and so on. The viscosity of such melts is also lower than in melts with three-di-
dimensional network structure because of the smaller size of the flow units. We suggest that viscous flow of hydrous basaltic and more silica-rich melts is controlled by the latter mechanism, whereas in the an-
hydrous equivalents the viscous flow is controlled by
the former mechanism. Hence hydrous melts are
more fluid than anhydrous, highly polymerized
melts.

We may also speculate that because H₂O in effect
increases NBO/T in less polymerized melts, the vis-
cosity of melts of picrite, komatiite, and basanite
composition may increase as a result of the dis-
solution of water.

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