

## Solubility mechanisms of water in basalt melt at high pressures and temperatures: NaCaAlSi<sub>2</sub>O<sub>7</sub>-H<sub>2</sub>O as a model

BJØRN O. MYSEN AND DAVID VIRGO

Geophysical Laboratory, Carnegie Institution of Washington  
Washington, D. C. 20008

### Abstract

The solubility mechanism of H<sub>2</sub>O in melt of NaCaAlSi<sub>2</sub>O<sub>7</sub> composition (Sm melt) has been determined at high pressures and temperatures by Raman spectroscopy. The NaCaAlSi<sub>2</sub>O<sub>7</sub> composition was chosen because its melt has an Al content and a ratio of nonbridging oxygen to tetrahedral cation (NBO/T = 0.67) similar to those in basalt (Al<sub>2</sub>O<sub>3</sub> = 13–18 wt. percent, NBO/T = 0.6–0.8).

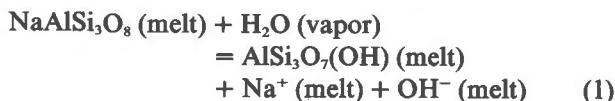
Water dissolves in Sm melt to form OH groups associated with Si<sup>4+</sup> and probably Na<sup>+</sup> or Ca<sup>2+</sup> or both. There is no spectroscopic evidence for Al–OH, Al–H, or Si–H bonds or for molecular H<sub>2</sub>O or H<sub>2</sub>.

The Raman spectra of both anhydrous and hydrous Sm melt indicate that both melts have structural units with an average NBO/T of 2, 1, and 0 (chains, sheets, and three-dimensional network). As the water content of the melt is increased, the chain and sheet units in the melt become more aluminous, whereas the three-dimensional network units show an increase of Si/(Si + Al). The bulk NBO/T of hydrous melt and, by implication, hydrous basalt melt has increased, however, relative to its anhydrous equivalent.

On the basis of the results on quenched melt of NaCaAlSi<sub>2</sub>O<sub>7</sub> + H<sub>2</sub>O and NaAlSi<sub>3</sub>O<sub>8</sub> + H<sub>2</sub>O compositions, we suggest that activity coefficients of cations that are sensitive to NBO/T of the melt (*e.g.*, transition metals and rare-earth trace elements) will decrease at a slower rate with increasing water content of basalt melt than if the melts were andesitic or granitic in composition. We also suggest that the viscosity of basalt melt is less sensitive to water content than the viscosity of more acidic melts (*e.g.*, andesite and granite).

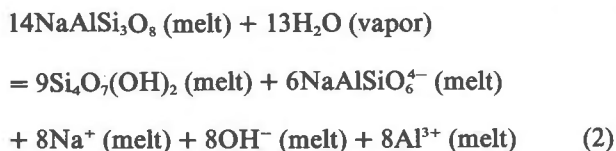
### Introduction

Water affects physical and chemical properties of silicate melts. It is known, for example, that the electrical conductivity, cation diffusion, and viscosity of granitic and andesitic melts are dramatically affected by dissolved H<sub>2</sub>O (*e.g.*, Orlova, 1964; Shaw, 1963; Kushiro, 1978; Watson, 1979). It has also been demonstrated that the activity of silica in highly polymerized melts is reduced as H<sub>2</sub>O is added (Eggler, 1972; Kushiro, 1969, 1972; see also Carmichael *et al.*, 1974). These observations have been related to depolymerization of the melt as a result of dissolved H<sub>2</sub>O (for solubility models see Wasserburg, 1957; Hamilton *et al.*, 1964; Burnham, 1975). The model of Burnham (1975), based on *P-V-T* data and solubility data in the system NaAlSi<sub>3</sub>O<sub>8</sub>-H<sub>2</sub>O, may be expressed by the equation



where the Na<sup>+</sup> and OH<sup>-</sup> are associated in the melt for local charge balance. On the basis of this model, many physical and chemical features of hydrous silicate melts may be explained. The model of Burnham (1975) also enables prediction of water-solubility in a variety of melt compositions (Burnham, 1975).

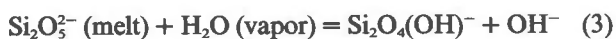
Recent Raman spectroscopic results (Mysen *et al.*, 1980a) have shown that in addition to the formation of OH groups in the melt, new nonbridging oxygens are, in fact, produced. Mysen *et al.* (1980a) also noted that the OH groups are attached to silicon and not to aluminum. For melt of NaAlSi<sub>3</sub>O<sub>8</sub> composition, the solubility mechanism proposed by Mysen *et al.* (1980a) can be expressed by the equation



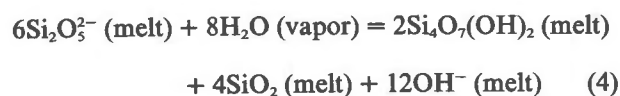
where NBO/T increases at a rate of 0.016 unit per mole percent dissolved  $\text{H}_2\text{O}$ .

The model expressed with equation 2 resembles that of Burnham (1975) in that it has retained the OH-replacement of some bridging oxygens and the exchange of some  $\text{Na}^+$  in the anhydrous, three-dimensional network with  $\text{H}^+$ . Mysen *et al.* (1980a) concluded that this exchange of  $\text{Na}^+$  would result in release of some  $\text{Al}^{3+}$  from tetrahedral coordination, because the Raman spectra of hydrous Ab melt indicated that Al-OH bonds do not exist. Consequently,  $\text{H}^+$  will not charge-balance  $\text{Al}^{3+}$  in the same fashion as alkali metals and alkaline earths (see Mysen *et al.*, 1980b, for discussion of charge balance of  $\text{Al}^{3+}$  in tetrahedral coordination).

The results indicated in equation 2 contrast with those for highly depolymerized melts. These are melts with a significant number of nonbridging oxygens per tetrahedral cation (NBO/T). It has been shown, for example, that binary, meta-, di- and trisilicate melts have a lower NBO/T as  $\text{H}_2\text{O}$  is dissolved (Kurkjian and Russell, 1957; Uys and King, 1963; Mysen *et al.*, 1980a). In such melts, nonbridging oxygens react with protons from  $\text{H}_2\text{O}$  to form OH groups. Excess  $\text{OH}^-$  from  $\text{H}_2\text{O}$  is neutralized with association of alkali or alkaline earth metals. In its simplest form, the solution mechanism may be expressed as



where NBO/T decreases by 0.02 unit per mole percent dissolved  $\text{H}_2\text{O}$ . In equation 3, excess  $\text{OH}^-$  from the water may associate with alkalis or alkaline earths for local charge-balance. Mysen *et al.* (1980a), using Raman spectroscopy, refined the original model. They found that new structural units with a lower ratio of nonbridging oxygens per tetrahedral cation (NBO/T) than in the anhydrous materials were most likely formed *e.g.*:



where NBO/T decreases by 0.018 unit per mole percent dissolved  $\text{H}_2\text{O}$ . In an expression such as that in equation 3, the NBO/T is lowered as a result of OH

formation from nonbridging oxygen. In equation 4, the latter effect is augmented by the formation of new three-dimensional network units in the melt (Mysen *et al.*, 1980a).

Basaltic melts have an average NBO/T between 0.6 and 0.8 ( $\text{T} = \text{Si}^{4+}, \text{Ti}^{4+}, \text{Al}^{3+}, \text{Fe}^{3+}, \text{and P}^{5+}$  with associated local charge balance) (Virgo *et al.*, 1979a). Such melts are also characterized by a large proportion of amphoteric oxides (*e.g.*,  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$ , which total 18–21 wt. percent; Chayes, 1975). Aluminum and ferric iron occupy tetrahedral coordination when charge-balanced with alkali metals or alkaline earths (Mysen *et al.*, 1979, 1980b; Seifert *et al.*, 1979). These cations may leave tetrahedral coordination, however, whenever the charge-balancing cation(s) become associated with OH groups (Mysen *et al.*, 1980a).

Basalt melts differ structurally from granitic melts in terms of their NBO/T (granite,  $\text{NBO/T} \leq 0.1$ ; andesite,  $\text{NBO/T} \leq 0.3$ ; see also Virgo *et al.*, 1979a) and from the simple binary melts with similar NBO/T (*e.g.*, trisilicate melt), in that basalt contains a large proportion of amphoteric cations, which may occur as both network modifier and network former in the melt. Our report is therefore oriented toward determination of the structural role of  $\text{H}_2\text{O}$  in silicate melts with a significant NBO/T and a large proportion of amphoteric cations. The  $\text{NaCaAlSi}_2\text{O}_7$  composition was chosen, rather than a natural basalt composition, because the chemical complexity of natural basalt melt results in considerable loss of spectroscopic resolution.

### Experimental methods

The starting material was a melt of  $\text{NaCaAlSi}_2\text{O}_7$  composition (Sm melt). The anhydrous Sm melt has  $\text{NBO/T} = 0.67$  (Mysen and Virgo, 1980), closely resembling that of basalt melt. Aluminum (19.74 wt. percent  $\text{Al}_2\text{O}_3$ ) is the amphoteric oxide. The aluminum content of Sm melt is slightly higher than that of most basaltic rocks (13–18 wt. percent; Chayes, 1975). It will be shown, however, that this difference in the  $\text{Al}_2\text{O}_3$  content of Sm melt and basalt melt does not appreciably affect the conclusions.

The  $\text{NaCaAlSi}_2\text{O}_7$  starting material was a glass made from spectroscopically pure  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{CaCO}_3$ , and reagent-grade  $\text{Na}_2\text{CO}_3$ . The  $\text{H}_2\text{O}$  was double-distilled and deionized. Deuterium oxide was provided by MSD Isotope Products, Canada.

Quenched hydrous Sm melts were formed in the solid-media, high-pressure apparatus (Boyd and England, 1960). The samples (about 20 mg Sm +

H<sub>2</sub>O) were contained in sealed Pt capsules of 3 mm O.D. in a Pyrex glass-sleeved furnace assembly of 0.5" O.D. The water content (1.6–5 wt. percent) was accurate to within 4–7 percent (depending on the amount of water added to the sample). The solubility of water in Sm melt at 20 kbar (the experimental pressure) is much greater than this amount (Mysen and Kushiro, unpublished data). All the quenched samples were therefore undersaturated with respect to water.

All aspects of the Raman spectroscopic techniques and the curve-fitting procedures have been presented and discussed by Mysen *et al.* (1980b).

Inasmuch as the spectra were taken on quenched hydrous melts and not liquid silicate, quenching problems must be considered. It has been shown (Sweet and White, 1969; Sharma *et al.*, 1978) that the anionic structure of melts and quenched melts on the join Na<sub>2</sub>O–SiO<sub>2</sub> is the same within the sensitivity of vibrational spectroscopy. For aluminum silicates with a three-dimensional network structure, Riebling (1968) and Taylor *et al.* (1980) obtained similar results. On this basis we conclude that the structural features of anhydrous Sm melt that can be discerned with Raman spectroscopy are quenchable.

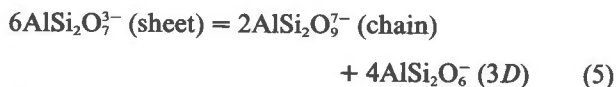
Hydrous melts tend to be more difficult to quench than the anhydrous equivalents. In fact, minerals often precipitate from the melt during quenching, and vapor may exsolve as small, densely-spaced bubbles. It has been shown (*e.g.*, Burnham and Davis, 1971, 1974) that quenching problems become increasingly severe with increasing water content of the melt. Burnham (1975) noted, for example, that no more than 5 wt. percent H<sub>2</sub>O can be quenched in melt of NaAlSi<sub>3</sub>O<sub>8</sub> composition. We found that melts with up to at least 5 wt. percent H<sub>2</sub>O quenched to clear glass, whereas melts with 8 wt. percent H<sub>2</sub>O appeared milky white as a result of numerous bubbles 1 μm or smaller in size.

Another criterion of retention of H<sub>2</sub>O in the quenched melt is a correlation between the intensity of Si–OH stretch bands in the Raman spectra and the amount of water added to the melt. As will be discussed further below, such a correlation does, in fact, exist in the water concentration range considered here. We conclude, therefore, that the spectra of hydrous quenched Sm melt discussed here reflect the structural features also present in the liquid state.

### Results

Raman spectroscopic data are shown in Figure 1 (see also Table 1), where spectroscopic changes as a

function of water content of the samples are depicted. The spectrum and deconvolution procedures of anhydrous quenched Sm melt are discussed elsewhere (Mysen and Virgo, 1980; Mysen *et al.*, 1980b), and only a brief summary of the results is given here. The 1013 cm<sup>-1</sup> band was interpreted (Mysen and Virgo, 1980) to be due to <sup>-</sup>O–(Al,Si)–O<sup>0</sup> stretching, the 990 cm<sup>-1</sup> band reflects <sup>0</sup>O–(Si,Al)–O<sup>0</sup> stretching, and the 907 cm<sup>-1</sup> band reflects <sup>-</sup>O–(Si,Al)–O<sup>-</sup> stretching. The 648 cm<sup>-1</sup> band reflects a deformation mode of the (Si,Al)–O polyhedra that show a stretch band at 907 cm<sup>-1</sup>. The band near 500 cm<sup>-1</sup> is a rocking band whose frequency is characteristic of Al-bearing, three-dimensional network units (Virgo *et al.*, 1979a; for discussion of terminology see also Bell and Dean, 1970, 1972, and Bates *et al.*, 1974). The corresponding stretch band is at 990 cm<sup>-1</sup>. The 567 cm<sup>-1</sup> band probably results from defects in three-dimensional network units (Stolen and Walrafen, 1976; Bell and Dean, 1972; Bates *et al.*, 1974). Mysen and Virgo (1980) suggested, therefore, that anhydrous melt of Sm composition consists of structural units with an average of 2, 1, and 0 nonbridging oxygens per tetrahedral cation. The tetrahedral cations in all the structural units are both Al<sup>3+</sup> and Si<sup>4+</sup>. The lowered frequency of the stretch bands relative to their positions in Al-free systems (Furukawa and White, 1980; Virgo *et al.*, 1980) is due to (Si,Al) coupling in all structural units. If it is assumed that there is no preference of Al<sup>3+</sup> for any of the structural units, an equation to express the equilibrium between them can be derived:



The stoichiometry of this equation will be altered if Al<sup>3+</sup> shows a preference for individual structural units.

Mysen *et al.* (1980a), in discussing possible interference of Si–OH, Al–OH, Si–H, and Al–H bands with the high-frequency envelope between 800 and 1200 cm<sup>-1</sup>, exchanged D<sub>2</sub>O for H<sub>2</sub>O with the assumption that the structural roles of H<sub>2</sub>O and D<sub>2</sub>O in silicate melts are similar. The deuterium bands occur at frequencies that are lower by a factor of 2<sup>-1/2</sup> compared with the analogous hydrogen bands (Van der Steen and Van den Boom, 1977). Hence, the analogous deuterium bands, if present, would occur at frequencies below 700 cm<sup>-1</sup>, and any possibility of interference with the oxygen stretch bands would be eliminated.

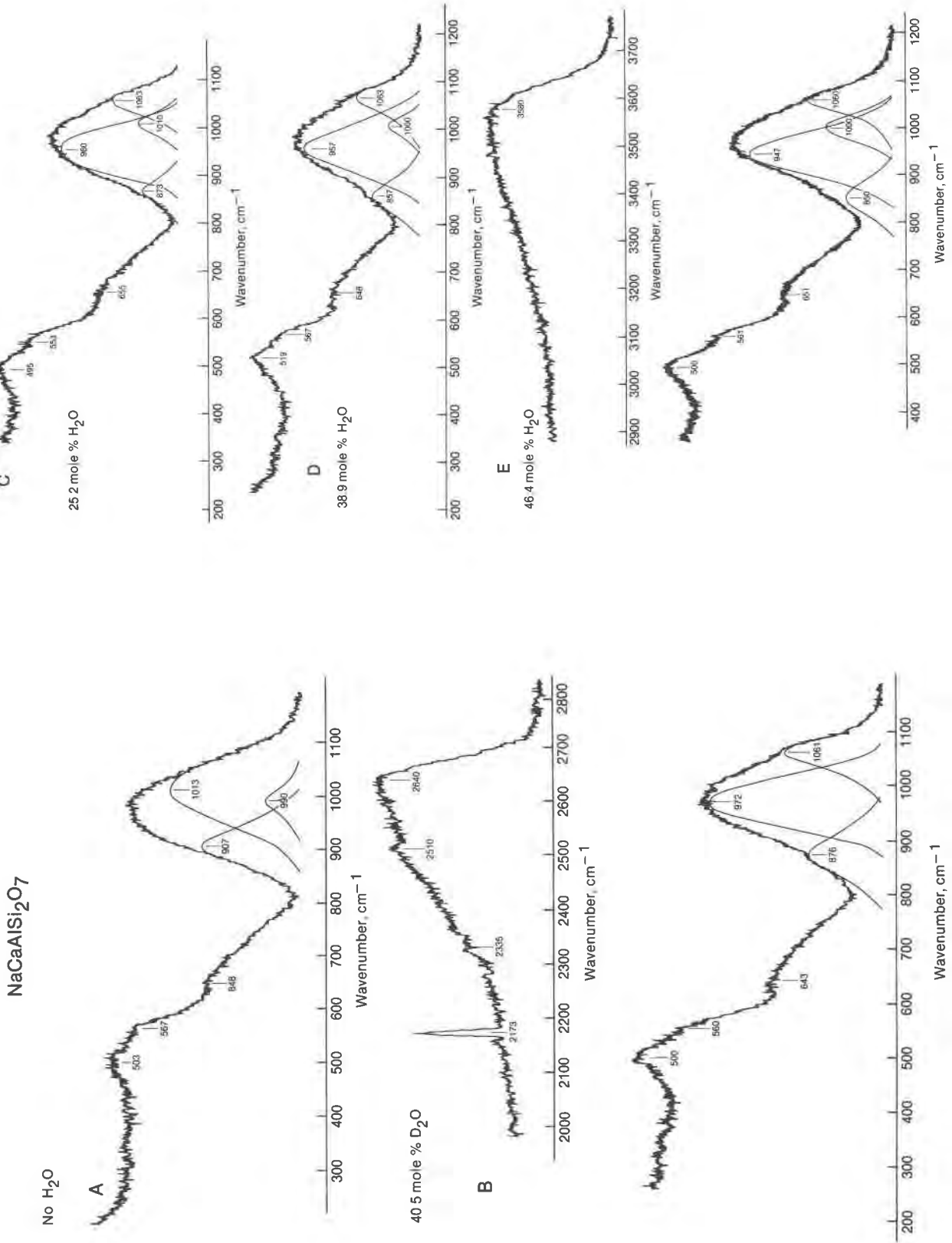


Fig. 1. Raman spectra of quenched melts in the system NaCaAlSi<sub>2</sub>O<sub>7</sub>-H<sub>2</sub>O-D<sub>2</sub>O. Mole percent H<sub>2</sub>O (D<sub>2</sub>O) calculated on the basis of 7 oxygens.

Table 1. Raman data on quenched melts in the system NaCaAlSi<sub>2</sub>O<sub>7</sub>-H<sub>2</sub>O-D<sub>2</sub>O\*

Composition	<i>T</i> , °C	<i>P</i> , kbar	Wavenumber, cm <sup>-1</sup>											
Sm	1450	20	503m(bd)†	567m(bd)	648w(bd)	907ms	990w(bd)	1013s	...	...‡	...	...	...	
Sm + 40.8 mole % D <sub>2</sub> O	1450	20	500m	560(sh)	643w(bd)	876m	1061m	972s	...	2173s	2335w	2510w	2640s(bd)	...
Sm + 25.7 mole % H <sub>2</sub> O	1450	20	495w	553(sh)	555w	873w	1063m	960s	1010w	...‡	...	...	...	...‡
Sm + 38.9 mole % H <sub>2</sub> O	1450	20	519m(bd)	567(sh)	648w(bd)	857m	1063m	957s	1000w	...‡	...	...	...	...‡
Sm + 46.4 mole % H <sub>2</sub> O	1450	20	500m	561(sh)	651w	850m	1060m	947s	1000w	2173s	...	...	...	3580s(bd)

\*Mole % H<sub>2</sub>O or D<sub>2</sub>O calculated on the basis of 7 oxygens. The uncertainty of each measurement is +5 cm<sup>-1</sup> except when bands are broad or occur as a shoulder. In the latter cases, the uncertainty is of the order of +20 cm<sup>-1</sup>.

†Abbreviations: *s*, strong; *ms*, medium to strong; *m*, medium; *w*, weak; (*bd*), broad; (*sh*), shoulder.

‡Present but not measured accurately.

The Raman spectrum of Sm + 40 mole percent D<sub>2</sub>O (5 wt. percent) (Fig. 1B) shows several new features compared with the anhydrous composition. There is a strong asymmetric band with a maximum near 2640 cm<sup>-1</sup>. This band is due to DOD stretching in the OD groups (Hartwig, 1977). The asymmetry of the band, as well as the weak superimposed bands near 2335 and 2510 cm<sup>-1</sup>, is ascribed to a combination of weak DO...D bonds and the possible existence of several geometrically distinct OD groups in quenched Sm + D<sub>2</sub>O melt (Hartwig, 1977; Serratos and Vinas, 1964; Peri, 1966). The sharp band near 2175 cm<sup>-1</sup> occurs whether or not H<sub>2</sub>O or D<sub>2</sub>O is present and is due to N<sub>2</sub><sup>+</sup> from air (Nakamoto, 1978; see also Mysen *et al.*, 1980a).

The high-frequency envelope of deuterated, quenched Sm melt has a sharp maximum near 970 cm<sup>-1</sup> with shoulders on both the high- and low-frequency limbs. Bands are fitted at 876, 972, and 1061 cm<sup>-1</sup>. All bands are polarized. When this spectrum was deconvoluted, bands were initially fitted to each shoulder and one to the maximum of the high-frequency envelope. The shape of the high- and low-frequency limbs, respectively, of the bands reflected in the shoulders was used as an initial guide of the band shape. These two bands were fitted with a third band near the maximum of the envelope so that the accumulative area of the three fitted bands equaled that of the entire envelope within the statistical uncertainty of the spectrum. Further details of this procedure are given by Mysen *et al.* (1980b). This portion of the spectrum is identical with that found for Al-free metasilicate melts (Mysen *et al.*, 1980b). In addition to the three bands in the high-frequency envelope,

there is a weak band near 640 cm<sup>-1</sup>, a strong band at 500 cm<sup>-1</sup>, and a shoulder near 560 cm<sup>-1</sup>. Furthermore, the three Si-O stretch bands in the high-frequency envelope occur at lower frequency in such melts than in quenched D<sub>2</sub>O-free Sm melt. The 640 cm<sup>-1</sup> band in deuterated, quenched Sm melt is much weaker than that in metasilicate melt relative to the 970 cm<sup>-1</sup> band as well. Note also that the stretch bands shift to lower frequency whenever (Si,Al) coupling is involved. Inasmuch as Sm melt has Si/(Si + Al) = 0.67, such coupling is expected, as already noted by Virgo *et al.* (1979a), and also considered briefly above for anhydrous Sm melt. Consequently, if the deuterated, quenched Sm melt consisted of monomer, chain, and sheet units such as found in metasilicate melts, the stretch bands reflecting chain and sheet units would be at lower frequencies than those found in Al-free metasilicate melts. Inasmuch as the frequencies considered here are the same as those for Al-free metasilicate melt, we conclude that the structural units resulting in the three stretch bands differ from those found in Al-free metasilicate melt. Despite the superficial resemblance to metasilicate melts, an interpretation of the Raman spectrum of Sm + D<sub>2</sub>O melt similar to that of metasilicate melts is not considered viable.

The existence of a band near 500 cm<sup>-1</sup> in aluminosilicate melts is characteristic of the presence of three-dimensional network units in the melt (Virgo *et al.*, 1979). The attendant Si-O<sup>0</sup> stretch band occurs at 1061 cm<sup>-1</sup> in quenched, deuterated Sm melt (Fig. 1B). The frequency of this band has increased compared with that of the D<sub>2</sub>O-free sample (Figs. 1A and 1B), probably as a result of diminished (Si,Al) cou-

pling. The  $640\text{ cm}^{-1}$  band is characteristic of O–Si–O deformation in a structural unit with an average of 2 NBO/T (Mysén and Virgo, 1980; Virgo *et al.*, 1980). The associated stretch band is at  $876\text{ cm}^{-1}$  in quenched Sm + 40 mole percent  $\text{D}_2\text{O}$  melt. Its frequency is lowered compared with the position in anhydrous Sm melt (Figs. 1A and 1B); thus more extensive (Si,Al) coupling is indicated. The main band in the high-frequency envelope occurs at  $972\text{ cm}^{-1}$  (Fig. 1B). This band most likely is the (Si,Al)–O stretch band reflecting the presence of a sheet unit in the melt. The lowering of its frequency compared with that of  $\text{D}_2\text{O}$ -free Sm melt is a result of more extensive (Si,Al) coupling.

In summary, the Raman spectra of quenched, deuterated Sm melt are interpreted to indicate that this melt consists of the same structural units as  $\text{D}_2\text{O}$ -free, quenched Sm melt. The deuterated sample differs, however, in the lower Si/(Si + Al) of the two structural units with nonbridging oxygens and the higher Si/(Si + Al) of the three-dimensional network unit. It also appears that the structural unit with NBO/T = 0 has become more prevalent relative to the other structural units in the melt.

The Raman spectra of hydrous, quenched Sm melt are shown in Figures 1C–E (see also Table 1). There is a broad, asymmetric band with a maximum at  $3580\text{ cm}^{-1}$ . The presence of this band indicates the existence of OH groups in quenched Sm +  $\text{H}_2\text{O}$  melt. The asymmetry of this band could be due to several geometrically different OH groups or weak hydrogen bonds between OH groups or both (Hartwig, 1977; Serna *et al.*, 1977, 1979). There are no bands at higher frequency. The presence of molecular  $\text{H}_2$  is therefore ruled out (Lucovsky *et al.*, 1979). Because of the absence of a band near  $1600\text{ cm}^{-1}$ , the presence of molecular  $\text{H}_2\text{O}$  in quenched Sm +  $\text{H}_2\text{O}$  melt (Lucovsky *et al.*, 1979) is also considered unlikely.

The Raman spectra of quenched Sm +  $\text{H}_2\text{O}$  in the frequency region below  $1200\text{ cm}^{-1}$  resemble that of quenched Sm +  $\text{D}_2\text{O}$ . The bands in the high-frequency envelope were therefore fitted with the results from Sm +  $\text{D}_2\text{O}$  in mind. The same three stretch bands should occur, therefore, in the high-frequency envelopes of both Sm +  $\text{D}_2\text{O}$  and Sm +  $\text{H}_2\text{O}$  melt. Their exact frequencies may vary as a result of variable Si/(Si + Al) of the structural units as a function of  $\text{H}_2\text{O}$  content of the melt. The latter feature was also observed in hydrous quenched melts of  $\text{NaAlSi}_3\text{O}_8$  and  $\text{NaAlSi}_2\text{O}_6$  composition (Mysén *et al.*, 1980b). The fitting procedure (see also Mysén *et al.*, 1980b, and Mysén and Virgo, 1980, for more de-

tailed discussion) results in an additional band near  $1000\text{ cm}^{-1}$ , which is most likely due to Si–OH stretching (Stolen and Walrafen, 1976). There are no new bands in the frequency region between 950 and  $800\text{ cm}^{-1}$ , where Al–OH stretch bands would be expected (Ryskin, 1974). Bonds of Al–H and Si–H type are also ruled out because there are no new bands in the frequency region between 900 and  $700\text{ cm}^{-1}$  (e.g., Peri, 1966; Ryskin, 1974; Hartwig, 1977; Lucovsky, 1979; Lucovsky *et al.*, 1979). We conclude, therefore, that  $\text{H}_2\text{O}$  is dissolved in Sm melt through the formation of OH groups. Some of these OH groups are bonded directly to  $\text{Si}^{4+}$ . Whether OH groups are also associated with alkali metals or alkaline earths, as suggested by Burnham (1975) and Mysén *et al.* (1980a) for  $\text{H}_2\text{O}$  in  $\text{NaAlSi}_3\text{O}_8$  melt, cannot be determined. Such bands are likely to be weak and will occur in the low-frequency region in the Raman spectra, where they are easily masked by the Rayleigh tail.

The three bands at about 850, 950, and  $1060\text{ cm}^{-1}$  are probably due to stretching of (Si,Al)–O in structural units with an average of 2, 1, and 0 NBO/T. There are no bands in the frequency region between 700 and  $800\text{ cm}^{-1}$  that could be assigned to Al–O stretching in tetrahedral Al–O clusters. The frequency of the  $1060\text{ cm}^{-1}$  band is independent of the  $\text{H}_2\text{O}$  content of the quenched Sm +  $\text{H}_2\text{O}$  melt, whereas the 850 and  $950\text{ cm}^{-1}$  bands shift to lower frequency with increasing  $\text{H}_2\text{O}$  content (Fig. 2). These shifts indicate that the Si/(Si + Al) of the two structural units with NBO/T > 0 decreases with increasing water content of the melt, whereas the Si/(Si + Al) of the unit with no nonbridging oxygens is independent of the  $\text{H}_2\text{O}$  content.

It cannot be determined from the Raman spectra whether the  $1060\text{ cm}^{-1}$  band stems from Si–O<sup>o</sup> stretch vibrations in a hydroxylated complex where only some of the bridging oxygens have been replaced by OH groups or whether the  $1060\text{ cm}^{-1}$  band results from a fully polymerized, OH-free structural unit.

The intensity ratios of the stretch bands give an indication of the relative proportions of the structural units in quenched Sm melt. The data in Figure 3 show that the intensity of the  $1060\text{ cm}^{-1}$  band increases at the expense of the  $950\text{ cm}^{-1}$  band as the  $\text{H}_2\text{O}$  content of the quenched Sm +  $\text{H}_2\text{O}$  melt is increased. On this basis, we conclude that the proportion of structural units with NBO/T = 0 increases at the expense of units with NBO/T = 1 as a function of  $\text{H}_2\text{O}$  content of the melt.

In summary, solution of  $\text{H}_2\text{O}$  in melt of Na

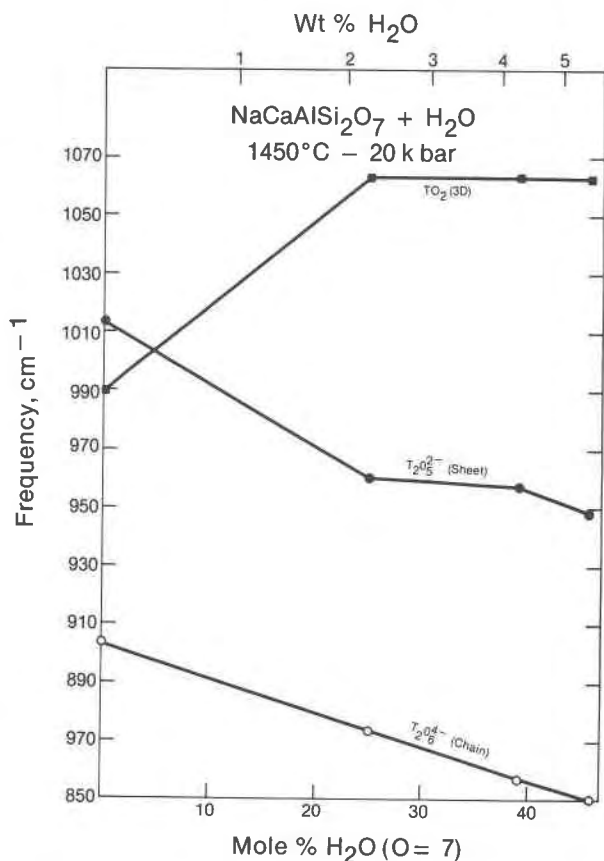


Fig. 2. Frequency shifts ( $\text{cm}^{-1}$ ) of important Raman bands as a function of  $\text{H}_2\text{O}$  content of quenched  $\text{NaCaAlSi}_2\text{O}_7$ .

$\text{CaAlSi}_2\text{O}_7$  composition at 20 kbar results in the formation of Si–OH bonds in the melt. This reaction is associated with a decrease of the Si/(Si + Al) of the chain and sheet units and an increase of the Si/(Si + Al) of the units with NBO/T = 0.

#### Solution mechanisms

As in all other melt compositions studied so far (Kurkjian and Russell, 1957; Uys and King, 1963; Burnham, 1975; Velde and Kushiro, 1976; Orlova, 1964; Mysen *et al.*, 1980a),  $\text{H}_2\text{O}$  is dissolved through the formation of OH groups. There is no evidence for molecular  $\text{H}_2\text{O}$  or  $\text{H}_2$  and no hydrogen–cation bonds with the possible exception of weak hydrogen bonds in the OH groups. The OH groups are bonded to  $\text{Si}^{4+}$ , but not to  $\text{Al}^{3+}$ . Excess  $\text{OH}^-$  may be associated with metal cations (alkalies and alkaline earths) in the melt in order to maintain local charge balance. There is, however, no negative or positive spectroscopic evidence for such complexes. In these respects, the solution mechanism of  $\text{H}_2\text{O}$  in Sm melt resembles

that of  $\text{H}_2\text{O}$  in fully polymerized silicate melts (Burnham, 1975; Mysen *et al.*, 1980a).

Burnham (1975) commented that not only does the solubility of  $\text{H}_2\text{O}$  in  $\text{NaAlSi}_3\text{O}_8$  melt imply the presence of hydroxylated silicate (as previously suggested by Wasserburg, 1957, and Hamilton *et al.*, 1954) but some  $\text{OH}^-$  must also be associated with  $\text{Na}^+$  in the melt. Solubility data for  $\text{H}_2\text{O}$  in  $\text{CaMgSi}_2\text{O}_6$  melt at high pressures and temperatures led Egger and Rosenhauer (1978) to a similar conclusion for  $\text{Ca}^{2+}$  and  $\text{OH}^-$  in such melts and Kurkjian and Russell (1957) for  $\text{Na}^+$  in melts on the join  $\text{Na}_2\text{O}$ – $\text{SiO}_2$ . The existence of such complexes is assumed in the present melts although there is no spectroscopic evidence to support this assumption.

It has been shown elsewhere (*e.g.*, Virgo *et al.*, 1980; Seifert *et al.*, 1979; Mysen *et al.*, 1979b; Mysen and Virgo, 1980) that whenever local charge balance of  $\text{Al}^{3+}$  with alkali metals or alkaline earths is not satisfied, the  $\text{Al}^{3+}$  is no longer in tetrahedral coordination. Thus, if some  $\text{Na}^+$  is associated with  $\text{OH}^-$ , an equivalent amount of  $\text{Al}^{3+}$  will leave the network. There is no evidence in the Raman spectra to indicate that this  $\text{Al}^{3+}$  forms Al–O clusters (with Al in four-fold coordination), as there are no stretch bands in the Raman spectra of  $\text{NaCaAlSi}_2\text{O}_7 + \text{H}_2\text{O}$  (and  $\text{NaAlSi}_3\text{O}_8$  and  $\text{NaAlSi}_2\text{O}_6 + \text{H}_2\text{O}$ ; Mysen *et al.*,

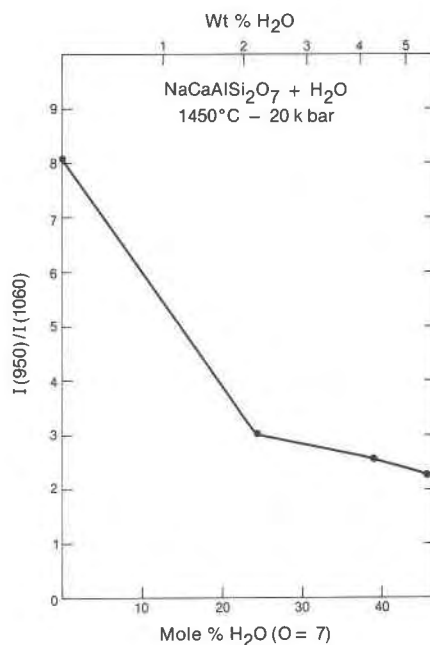
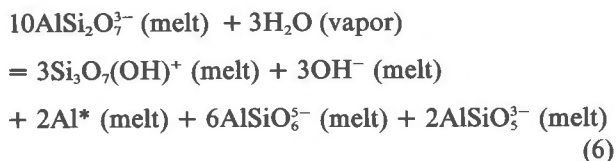


Fig. 3. Intensity ratio,  $I(950)/I(1060)$ , of Raman spectra of quenched melts in the system  $\text{NaCaAlSi}_2\text{O}_7$ – $\text{H}_2\text{O}$  as a function of water content.

1980a) to indicate its presence. We conclude, therefore, that provided some  $\text{OH}^-$  is associated with alkalis or alkaline earths, an equivalent amount of Al has become a network modifier.

The spectroscopic data indicate the presence of two different structural units in the melt with averages of 1 and 2 NBO/T. The  $\text{Si}/(\text{Si} + \text{Al})$  of these two units is lower in hydrous than in anhydrous Sm melt. Finally, the Raman spectra are interpreted to indicate an increase in the proportion of structural units with  $\text{NBO}/\text{T} = 0$  relative to structural units with  $\text{NBO}/\text{T} = 1$ . We suggest that the units with  $\text{NBO}/\text{T} = 0$  are of the type  $\text{Si}_2\text{O}_7(\text{OH})^+$ .

In the following equation,  $\text{Si}/(\text{Si} + \text{Al})$  of the chain and sheet units of hydrous Sm melt is set equal to 0.5. The proportion of Al that is no longer in tetrahedral coordination is denoted  $\text{Al}^*$ . The expression is



According to the stoichiometry of equation 6, the NBO/T increases by 0.014 unit per mole percent dissolved  $\text{H}_2\text{O}$ . This increase compares with 0.016 unit per mole percent dissolved  $\text{H}_2\text{O}$  in completely polymerized melts such as that of  $\text{NaAlSi}_3\text{O}_8$  composition. This reduction of rate of increase of NBO/T with water content reflects the presence of some NBO/T in anhydrous Sm melt compared with the  $\text{NBO}/\text{T} = 0$  for anhydrous melt of  $\text{NaAlSi}_3\text{O}_8$  composition.

### Applications

Virgo *et al.* (1980) have shown that the NBO/T of basalt melts is between 0.6 and 0.8, a conclusion also reached by Bottinga and Weill (1972). The NBO/T of  $\text{NaCaAlSi}_2\text{O}_7$  melt is 0.67, falling within the range of basaltic melts. The  $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$  of basaltic rocks is between 18 and 21 wt. percent (Chayes, 1975). Inasmuch as  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  frequently have similar structural roles in silicate melts (Virgo *et al.*, 1979, 1980; Seifert *et al.*, 1979; Brown *et al.*, 1978),  $\text{Al}^{3+}$  may be considered an analogue for  $\text{Fe}^{3+}$ . Consequently, both NBO/T and the bulk amphoteric oxide content of  $\text{NaCaAlSi}_2\text{O}_7$  and basalt melt are similar. The solubility behavior of  $\text{H}_2\text{O}$  in Sm melt is therefore expected to mimic that of basalt melt.

On the basis of the solution mechanisms expressed by equation 2 and 6 for model granite and basalt

melts, respectively, we conclude that solution of  $\text{H}_2\text{O}$  in melts ranging from granite to basalt results in an increase of NBO/T. It is likely, however, that the influence of  $\text{H}_2\text{O}$  on the melt structure becomes less pronounced the greater the value of NBO/T of the anhydrous melt. Inasmuch as NBO/T of melts increases as they become more basic, the influence of  $\text{H}_2\text{O}$  on melt structure becomes less pronounced as the melts become more basic.

A number of physical and chemical properties of melts can be related to NBO/T. Melt viscosities tend to decrease with increasing NBO/T, for example (Mysen *et al.*, 1980b). On the basis of the present experiments and those of Mysen *et al.* (1980a), we conclude that the viscosity of basaltic melts is less sensitive to water content than the viscosity of andesitic and granitic melts.

Mysen (1979) has shown that the activity coefficients of important trace elements in melts (transition metals and rare earth elements) decrease with increasing NBO/T. Mysen and Virgo (in preparation, 1980) have shown a linear relation between the value of such activity coefficients and the NBO/T of the melt. On the basis of the present data and those of Mysen *et al.* (1980a), we suggest that crystal-liquid trace-element partition coefficients involving basic melts are less sensitive to the water contents of the melt than those involving andesitic and granitic melts.

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