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Melting, Crystallization and the Glass transition:
Toward a Unified Description for Silicate Phase Transitions

H. Wayne Nesbitt¹, G. Michael Bancroft², Grant, S. Henderson³, Pascal Richet⁴, Cedrick O’Shaughnessy³

¹Dept. of Earth Sciences, Univ. of Western Ontario, London On., N6A 5B7 Canada
²Dept. of Chemistry, Univ. of Western Ontario, London On., N6A 5B7 Canada
³Dept. of Earth Science, Univ. of Toronto, Toronto On., M5S 3B1 Canada
⁴Institut de Physique du Globe de Paris, 1 Rue Jussieu, F-75252 Paris, France

Corresponding Author:
H. Wayne Nesbitt, Tel: (519) 661-2100 ext. 83194, e-mail: hwn@uwo.ca
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ABSTRACT

The melting mechanism of Na$_2$SiO$_3$, a crystal with pyroxene structure, includes three distinct reactions. All are driven by heating with each reaction commencing at a different temperature. The first two reactions proceed within the crystal at temperatures well below the melting point and are expressed by distinctive crystallographic, calorimetric and Raman spectroscopic changes in the crystal. With the reactions identified and explained for Na$_2$SiO$_3$(c) and the melting mechanism elucidated, the Na$_2$SiO$_3$ system becomes the ‘Rosetta Stone’ by which to decipher the melting mechanisms of all pyroxenes and other silicate minerals.

The first reaction produces itinerant Na$^+$ within the crystal. Itinerancy results from dissociation of some NBO-Na bonds due to heating, with dissociation commencing at ~770 K. The reaction proceeds according to:

$$\text{Si-O-Na} \rightarrow \text{Si-O}^- + \text{Na}^+$$

The Si-O$^-$ moiety remains attached to its SiO$_3$ chain and it is charged because one of its NBO atoms has no associated Na ion. The second reaction is characterized by the appearance of a Q$^3$ band in Raman spectra of the crystal at temperatures >770 K. It is produced via a polymerization reaction involving the Si-O$^-$ species, a product of the first reaction, and a Q$^2$ species of an adjacent SiO$_3$ chain according to:

$$\text{Na}_2\text{-Q}^2 + (\text{Na}_1\text{-Q}^2)^- \rightarrow 2\text{Na}_1\text{-Q}^3 + \text{Na}^+ + \text{O}^{2-}$$

Na atoms are included with each Q species to preserve mass balances and (Na$_1$-Q$^2$)$^-$ is equivalent to the Si-O$^-$ species. The produced Q$^3$ species form cross-chain linkages which affect the crystallographic properties of the crystal. They are responsible for the cessation of thermal
expansion of the Na$_2$SiO$_3$ unit cell in the ‘a’-‘b’ axial plane at T > 770 K, and the near-constancy of ‘a’ and ‘b’ unit cell parameters between ~770 K and ~1300 K. The presence of Q$^3$ species in Raman spectra and the inhibited expansion in the ‘a’-‘b’ axial plane provide exceedingly strong evidence for this reaction. The third reaction commences at ~1200 K where Q$^1$ Raman band first appears. It can be produced only through depolymerization of Q$^2$ chains according to:

$$2\text{Na}_2\text{Q}^2 + 2\text{Na}^+ + \text{O}^{2-} \rightarrow 2\text{Na}_3\text{Q}^1$$

where Na$^+$ and O$^{2-}$ are itinerant species produced by the second reaction. With conversion of Q$^2$ to Q$^1$ species, SiO$_3$ chains are ruptured, long range order is lost and melt is produced at 1362 K.

The last two reactions proceed by nucleophilic substitution where Si centers are attacked to form 5-fold coordinated activated complexes. Si-O$^-$ acts as nucleophile in the second reaction (producing Q$^3$ species), and O$^{2-}$ acts as nucleophile in the third reaction (producing Q$^1$). Taken in reverse, these mechanisms describe the formation of nuclei in crystallizing melts and in addition provide insight into the elusive changes that occur at the glass transition. Elucidation of the melting mechanism could thus provide a unified framework within which melting, crystallization and the glass transition can be understood.

**INTRODUCTION**

From practical and theoretical perspectives, melting and crystallization are the most important phase transitions. Silicates have a special importance in this respect as the concentric structure of the Earth with a core, a mantle and a crust, the existence of SiO$_2$-rich, buoyant continents and, thus, the subsequent emergence of life, are processes that were all ultimately determined by melting and crystallization reactions. Today these reactions are also of utmost importance as they are at the roots of the basic industries with annual production of nearly 3x10$^9$ tons of cement, 4x10$^8$ tons of iron and steel slags and about 10$^8$ tons of glass. A comprehensive
theoretical framework within which to interpret melting, crystallization and vitrification consequently would be of great benefit to Earth and materials scientists. We propose such a framework by developing a melting mechanism applicable to numerous silicate minerals. It is based in experimental results, thermodynamic constraints and on chemical kinetics principles. The experimental results for Na$_2$SiO$_3$ are critically important to the development of the melting mechanism. Our first objective consequently is to review the crystallographic, calorimetric and Raman spectroscopic properties of Na$_2$SiO$_3$ between 298 K and its melting temperature (Richet et al., 1996; McMillan, 1984; McDonald and Cruickshank, 1967). Once analysed and the changes to the crystal elucidated, our second and most important objective, is to develop a melting mechanism applicable to many silicate minerals through application of chemical kinetics principles (Laidler, 1965) using the experimental results to constrain its development.

Physicists and chemists, for over a century, have studied the melting phenomenon for by employing mostly physical principles, including vibrational instability, vanishing shear moduli and defect production (Lindemann, 1910; Brillouin, 1938; Born. 1939; Lennard-Jones and Devonshire, 1939; Frenkel, 1955; Eyring et al., 1958). None explains successfully the melting of compositionally and structurally complex silicate minerals as emphasized by Wolf and Jeanloz, (1984). There is, therefore, little or no understanding of how these silicates minerals melt. The reason their melting is so poorly understood is that melting is too abrupt, and crystallization begins with nuclei too small to be readily investigated by techniques available today. There are, however, a few special cases whereby these reactions are more amenable to experimental investigation. These manifest themselves in crystals with extensive premelting regions, which may extend over tens to hundreds of degrees. (e.g., Thiéblot et al., 1999; Richet et al., 1996; 1994). Na$_2$SiO$_3$ is one such case. Crystalline sodium metasilicate (Na$_2$SiO$_3$) displays a large
premelting region of ~160 degrees and its structure is simple (Richet et al., 1996) making detailed structural, calorimetric and spectroscopic studies possible over a wide range of temperature (Figs. 1a, 1b). From such results we identify three reactions which are necessary precursors to the melting of Na$_2$SiO$_3$. Perhaps most importantly, each reaction is initiated at a different temperature permitting detailed investigation of each without appreciable overlap or interference from the other reactions. Taken in reverse, the same reactions account for the formation of nuclei in melts and subsequent crystallization. The steps are also applicable to changes that occur at the glass transition, including structural relaxation and viscous flow, thus providing a unified description and theory of these phenomena.

**STRUCTURE OF Na$_2$SiO$_3$**

The Si-O structural arrangements of crystalline Na$_2$SiO$_3$ are identical to those of the pyroxene group of minerals. It consists of chains of Si tetrahedra (McDonald and Cruickshank 1967; Ching et al., 1983) where two apical oxygen atoms bridge two Si atoms (bridging oxygens or BO) to produce Si-O-Si moieties and to form SiO$_3$ chains parallel to the c axis as shown schematically in Figure 2a. The two other oxygen atoms of each tetrahedron are bonded to a Si and a Na atom to produce the Si-O-Na moiety whose oxygen is referred to as non-bridging (NBO). Na atoms are encased in oxygen bipyramids and are located between the chains binding them together. The crystal’s cell parameters increase systematically with temperature to ~770 K (Fig. 1a). The ‘c’ cell parameter continues to increase without inflection to at least 1300 K (Richet et al., 1994; 1996). The ‘a’ and ‘b’ cell parameters, by contrast, remain effectively constant between about ~770 K and ~1300 K (Fig. 1a). There is also a change in space group at ~850 K from $Cmc\text{$_2$1}$ to a lower symmetry, probably to $Pmc\text{$_2$1}$ (Richet et al., 1996). With transition to lower symmetry, there is loss of a Na position in the ‘a’-‘b’ axial plane.
The mean heat capacities \((C_m)\) for four crystalline phases are plotted against temperature in Figure 1b, where \(C_m\) is defined as \((H_T-H_{273})/(T-273)\) with \(H\) being enthalpy (Richet and Fiquet, 1991). The heat capacities of all crystals initially change as expected with respect to temperature, due primarily to acoustic vibrational contributions but on approach to the melting point, each displays a dramatic increase in \(C_m\). The inflection in \(C_m\) for \(Na_2SiO_3(c)\) occurs at ~1200 K and the region between the inflection and the melting point (1362 K) is defined as the premelting region. Many other minerals display premelting regions (Bouhifd et al., 2002; Thiébaut et al., 1999; George et al., 1998; Richet et al., 1998; 1996; 1994; 1993). The \(^{23}\text{Na}\) NMR study of George et al. (1998) demonstrate cation itinerancy within the premelting region of \(Na_2SiO_3\). They note that “\(Na^+\) site hopping appears to involve a more liquid-like behavior, implying exchange occurred among many sites (i.e., itinerancy) with different orientations, and in a disordered fashion”. \(Na^+\) itinerancy in crystals apparently is analogous to \(Na^+\) mobility in glass as simulated by Cormack et al. (2002) where they monitored alkali ion ‘jumps’ to adjacent empty sites of variable potential energy. The data of George et al. (1998) are conclusive but a question arises concerning the temperature at which itinerancy is initiated. The structural data, particularly thermal expansion characteristics (Fig. 1a), indicates a significant change in crystal properties at ~770 K and this may reflect the onset of itinerancy. The suggestion is reinforced by loss of a \(Na\) position in the ‘a’-‘b’ axial plane at ~850 K.

The temperature at which \(Na^+\) itinerancy is initiated must relate to the weakness of \(Na-O\) bonds. Crystalline \(Li_2SiO_3\) and \(Na_2SiO_3\), for example, share the same structure but upon heating there is no indication of \(Li^+\) itinerancy, and no change in space group in the temperature range 298 K to the melting point. The \(Na-O\) bond dissociation energy is 257 kJ/mol whereas that of Li-
O is 341 kJ/mol (Speight, 2005). With heating and vibrational excitation, Na-O bonds are therefore expected to dissociate at lower temperatures than Li-O bonds (and to greater extent at the same temperature). Dissociation may be represented by the reaction:

$$\text{Si-O-Na} \rightarrow \text{Si-O}^- + \text{Na}^+$$  \hspace{1cm} (1a)

To maintain mass balances, Na atoms attached to each Q species should be included so that:

$$\text{Na}_2\text{-Q}^2 \rightarrow (\text{Na}_1\text{-Q}^2)^- + \text{Na}^+$$ \hspace{1cm} (1b)

where a Si-O-Na moiety incorporated into the Na$_2$-Q$^2$ species dissociates yielding a charged (Na$_1$-Q$^2$)$^-$ species and Na$. In summary, it is established that Na-O dissociation occurs (George et al., 1998; Richet et al., 1996) and structural changes to the crystal (e.g., Fig. 1a) suggest that it commences at ~770 K. Increased temperature drives Reaction (1) to the right thus increasing itinerancy and promoting structural change such as that evident at ~850 K where there is loss of an Na position in the ‘a’-‘b’ axial plane of the crystal (Richet et al., 1996).

Dissociation of each Na-O bond necessarily produces a Si-O$^-$ moiety which, while still attached to a chain, should undergo librations unavailable to the Si-O-Na moiety due to the loss of a bonding partner (Na) and to the presence of an ‘exposed’ negative charge on the NBO. Additional librations in the premelting region were confirmed by $^{29}$Si NMR results of George et al. (1998) where partial averaging of low temperature biaxial chemical shifts occur, “suggesting some kind of extensive, librational motion of SiO$_4$ tetrahedra”. In addition, progressive heating causes many weak, low to intermediate frequency Raman Na-O bands to broaden or merge into the spectral background (Richet et al., 1996). The Si-O$^-$ species is negatively charged and may act as a nucleophile in chemical reactions, as emphasized subsequently.

**RAMAN SPECTRA OF Na$_2$SiO$_3$**

Previously published $^{29}$Si NMR and Raman spectra of Na$_2$SiO$_3$ crystal and glass (Figs.
3a, 3b, 3c) contain valuable information concerning reactions that occur in the crystal during heating to the melting point. This was not realized previously because the spectral similarities between crystal and glass had not been recognized (spectra from Nesbitt et al., 2011; Richet et al., 1996; Frantz and Mysen, 1995). We emphasize these similarities and begin by addressing the $^{29}$Si MAS NMR and Raman spectra of Na$_2$SiO$_3$ glass (Figs. 3a, 3b) followed by interpretation of the Raman spectrum of crystalline Na$_2$SiO$_3$ (Fig. 3c).

**Na$_2$SiO$_3$ Glass Spectra.**

**Assignment of Bands.** The $^{29}$Si MAS NMR spectrum of the glass (Fig. 3a) was fit by Nesbitt et al. (2011) employing three symmetric 100% Gaussian peaks. Once the spectrum was fit, the peaks were assigned to Q$^1$, Q$^2$ and Q$^3$ species based on peak position. Maekawa et al. (1991) arrived at precisely the same assignments. The two studies demonstrate that there are three major contributions to the glass spectrum, the Q$^1$, Q$^2$ and Q$^3$ species signals and also demonstrate that no other Q species makes major contribution to the glass spectrum.

Comparison of Figures 3a and 3b reveal similarities between the $^{29}$Si MAS NMR and Raman spectra of Na$_2$SiO$_3$ glass (Nesbitt et al., 2011; Frantz and Mysen, 1995; Maekawa et al., 1991). Each displays a strong central peak with a shoulder on the high frequency side of the central peak, and a weak peak on the low frequency side. The similarity is expected because the signals for both spectra arise from the same sources, the Q species; that is, the three Q species observed in the $^{29}$Si NMR spectrum of Figure 3a must also contribute to the Raman spectrum of Figure 3b. It is therefore reassuring that the two figures have similar characteristics. The results of Brawer and White (1975) provide the information needed to identify the approximate location of the three Q species contributions in the Raman spectrum of the glass (Fig. 3b). These authors collected Raman spectra of crystalline and vitreous Na$_2$SiO$_3$ at ambient temperature. The crystal
contains only the Q$^2$ species whose peak is centered at 975 cm$^{-1}$. Their glass spectrum displays its most intense peak at 985 cm$^{-1}$. At this composition the Q$^2$ band is expected to be the most intense. On this basis, and on the similarity of peak positions in crystal and glass, we propose that the Q$^2$ species is the major contributor to the 985 cm$^{-1}$ peak of their Na$_2$SiO$_3$ glass (i.e., Q$^2$ species is assigned to the 985 cm$^{-1}$ band).

Turning to Figure 3b and focussing on the experimental results (dots), we find that the most intense experimental signal is centred at ~966 cm$^{-1}$. By comparison with the glass spectrum of Brawer and White (1975), and based on peak position and intensity, we assign the Q$^2$ signal to the 966 cm$^{-1}$ band. With its position established, the other contributions to Figure 3b can be assigned. Brawer and White (1975) observe a peak at 855 cm$^{-1}$ in their glass spectrum, which is located at ~130 cm$^{-1}$ lower frequency than the Q$^2$ band. Figure 3b has a peak at ~842 cm$^{-1}$. It is ~124 cm$^{-1}$ lower in frequency than the Q$^2$ band. McMillan (1984) locates the Q$^1$ band at ~50-100 cm$^{-1}$ lower frequency than the Q$^2$ band. Thus the 842 cm$^{-1}$ peak of Figure 3b is assigned to the Q$^1$ species. McMillan (1984) also notes that the Q$^3$ band is located at ~50-100 cm$^{-1}$ greater frequency than the Q$^2$ band, thus the Q$^3$ band of Figure 3b should be present at ~1015-1065 cm$^{-1}$, and within the pronounced shoulder on the high frequency side of the Q$^2$ band. A better estimate of the location of the Q$^3$ peak can be obtained by fitting parts of the spectrum.

**Partial Fit to the Spectrum.** The Raman spectrum (Fig. 3b) was fit using 100% Gaussian lineshapes. The shape may not be optimum but it is sufficient for our purpose. A Q$^1$ peak was introduced and centered at ~842 cm$^{-1}$. Its FWHM was adjusted manually to fit as closely as possible the experimental peak. The fitted peak has a linewidth of ~36 cm$^{-1}$. We then added a Q$^2$ peak, the position and Full Width at Half Maximum (FWHM) of which were constrained to fit the high frequency side of the most intense peak. The resulting peak position is ~966 cm$^{-1}$ and its
FWHM is \( \sim 41 \text{ cm}^{-1} \). The positions of the Q\(^1\) and Q\(^2\) peaks are consistent with those quoted by McMillan (1984). We introduced a third peak to represent the Q\(^3\) (highest frequency) band. Its intensity, FWHM and location were constrained as follows. The Q\(^3\) intensity of the \( ^{29}\text{Si} \) MAS NMR spectrum (Fig. 3a) is 5.2 times more intense than that of the Q\(^1\) peak. Assuming the Raman scattering factors for the Q\(^1\) and Q\(^3\) peaks are similar (i.e., 1:1 ratio) we constrained the Raman Q\(^3\) band of Figure 3b to have an intensity 5.2 times greater than that of the Q\(^1\) band of the Raman spectrum. There is no detectable Q\(^4\) signal in the NMR spectrum of Na\(_2\)SiO\(_3\) glass (Fig. 3a) so that the Q\(^3\) species is considered the highest frequency contribution to Figure 3b. The linewidth of the Q\(^3\) peak was therefore adjusted to fit the highest-frequency portion of the spectrum while maintaining the appropriate peak intensity, thus yielding the peak represented by the solid curve of Figure 3b. It is centered at \( \sim 1030 \text{ cm}^{-1} \) with FWHM of 94 cm\(^{-1}\) and is consistent with the Q\(^3\) peak position quoted by McMillan (1984).

The greatest uncertainty related to fitting the Q\(^3\) peak is the assumption that scattering factors are the same for the Q\(^1\) and Q\(^3\) bands. To determine the sensitivity of this assumption, we alternatively employed the scattering factors of Koroleva et al. (2013), which are 1.53 for Q\(^1\) and 1.0 for Q\(^3\). From the Q\(^1\) and Q\(^3\) areas of Figure 3a and these scattering factors, the Q\(^3\) peak area should be 3.5 greater than the Q\(^1\) peak area in Figure 3b. With this constraint, the resulting best fit for the Q\(^3\) band is shown as the dashed curve centered at \( \sim 1048 \text{ cm}^{-1} \) (FWHM \( \sim 81 \text{ cm}^{-1} \)). The Q\(^3\) peak position of the glass therefore is reasonably well established to reside between \( \sim 1030 \) cm\(^{-1}\) and \( \sim 1050 \text{ cm}^{-1} \) regardless of the scattering factors used. The position is consistent with the Q\(^3\) position noted by McMillan (1984). The approximate locations of the three Q species have been ascertained. Additional contributions to the Raman spectrum are required to complete the fit, which will be provided in a future publication. (e.g., Fig. 4 of Koroleva et al., 2013; Fig. 12 of this lecture notes).
of Richet et al., 1996). Although our fit is not complete, three important conclusions nevertheless can be drawn from the partial fit: (1) the peak assignments are consistent with the $^{29}$Si NMR spectra of Maekawa et al. (1991) and Nesbitt et al., (2011) as apparent in Figure 3a; (2) the Raman Q species peak positions are reasonably well established and agree with those previously reported by McMillan (1984); (3) the intensity of the $Q^3$ band is greater than that of the $Q^1$ band.

### Crystalline Na$_2$SiO$_3$ Spectrum.

**Introduction.** Raman spectra for crystalline Na$_2$SiO$_3$ (e.g., Fig. 3c) were collected at temperatures ranging from 298 K to the melting point (1362 K) by Richet et al. (1996). The 298 K spectrum displays an exceedingly intense band representing the Si-O symmetric stretch of the $Q^2$ species. The band is located at $\sim$965 cm$^{-1}$, has a FWHM of 6 cm$^{-1}$ and its shape is strongly Lorentzian (Richet et al., 1996). The spectrum in Figure 3c is that of crystalline Na$_2$SiO$_3$ collected at 1348 K (just below its melting point). With heating a new band appears at $\sim$770 K which is centered at $\sim$1030 cm$^{-1}$ (Richet et al., 1996). The band becomes more intense with temperature and is most intense in the premelting region. At $\sim$1200 K, another band develops at $\sim$900 cm$^{-1}$. Its intensity increases with temperature but it never approaches the intensity of the band at $\sim$1030 cm$^{-1}$.

**Fitting the Spectrum.** Following Richet et al. (1996), three entirely *unconstrained*, 100% Lorentzian peaks were introduced to fit the spectrum. The resulting least squares fit is shown in Figure 3c. The most intense fitted peak, centered at 959 cm$^{-1}$, represents the $Q^2$ signal (Richet et al., 1996). Its FWHM is $\sim$37 cm$^{-1}$ and it represents $\sim$68% of the spectral intensity. McMillan (1984) states that the $Q^3$ signal is situated at 50-100 cm$^{-1}$ greater frequency than the $Q^2$ signal in the glass, and if present in Figure 3c, it should be located between about $\sim$1010 cm$^{-1}$ and $\sim$1060 cm$^{-1}$. The *unconstrained*, fitted peak centred at $\sim$1031 cm$^{-1}$ is entirely consistent with it being a
Q³ signal and we interpret it as such. The location of the Q³ peak for the glass (Fig. 3b) and the crystal (Fig. 3c) is similar, reinforcing the Q³ species assignment. The Q³ peak of the crystal has a FWHM of ~86 cm⁻¹ and its intensity constitutes ~22% of the total signal.

The third unconstrained peak fitted to the spectrum is centered at ~905 cm⁻¹. It has a FWHM of 65.4 cm⁻¹ and constitutes ~10% of the total signal. McMillan (1984) states that the Q¹ signal is located at 50 to 100 cm⁻¹ lower frequency than the Q² band, thus the peak centred at ~905 cm⁻¹ is consistent with it being a Q¹ peak and we interpret it as such. The Q³ peak intensity is appreciably greater than the Q¹ intensity and it remains to explain how Q³ and Q¹ species are produced in the crystalline chain silicate Na₂SiO₃ near its melting point. With the three Q species contributing to the crystal reasonably well established, insight into the reactions occurring within the crystal in response to thermal input can be evaluated.

**THE MECHANISM – STEP I: Q³ AND O²⁻ PRODUCTION**

The implications of the similarities between the Raman spectra of crystalline and vitreous Na₂SiO₃ (Figs. 3b and 3c) are now addressed in more detail than originally provided (Richet et al., 1996). Between ambient temperature and ~770K only a strong Q² peak is observed in the Raman spectrum of Na₂SiO₃ (Richet et al., 1996, their Fig. 6). Above ~770 K a Q³ band appears and its intensity increases dramatically within the premelting region. There is no Q¹ band present in spectra collected below ~1200 K and in the absence of a Q¹ band, the only means to produce Q³ species in the crystal, without producing an equal amount of Q¹ species, is via a polymerization reaction involving Q² species. If (Na₁-Q²⁻) (or alternatively Si-O⁻) produced by reaction (1) were to react with another Q² species (i.e., Na₂-Q²⁻) then:

\[(Na₁-Q²⁻) + Na₂-Q²⁻ \rightarrow 2Na₁-Q³^+ + Na⁺ + O²⁻\]  \hspace{1cm} (2a)

The (Na₁-Q²⁻)⁻ moiety is a nucleophilic agent and is likely to react with Si centers as explained...
subsequently in the ‘Reaction Mechanism’ section. The reaction produces an itinerant Na\(^+\) and itinerant O\(^2-\). The reaction obviously requires structural changes to the crystal to accommodate the Q\(^3\) species.

**Structural Effects.** As observed in double chain silicates (e.g., amphiboles, Deer et al., 2013), the Q\(^3\) species in Na\(_2\)SiO\(_3\) likely form cross-chain linkages in the ‘a’–‘b’ axial plane as shown schematically in Figure 2b. These cross-chain linkages should inhibit or prevent expansion of the Na bipyramids along their polar axes in the ‘a’–‘b’ axial plane but they should not inhibit expansion along the ‘c’ polar axis. The formation of Q\(^3\) cross-chain linkages consequently provides the explanation for the unusual changes observed in the unit cell thermal expansion coefficients of Figure 1a; that is, all three a, b and c cell parameters increase as expected up to ~770 K. Once Q\(^3\) species begin to form there is minimal increase in the ‘a’ and ‘b’ cell parameters but the ‘c’ cell parameter continues to increase without inflection at ~770 K.

The Si-O-Si and O-Si-O bond angles may be distorted due to Q\(^3\) cross-chain linkages but they need not disrupt the structure of the crystal. Indeed, the pyroxene structure of Na\(_2\)SiO\(_3\) is maintained to its melting temperature (George et al., 1998; Richet et al., 1996). If formed randomly along the chains, the cross linkages would not be detectable by X-ray diffraction methods. The effects of Reactions (1) and (2) on structure thus are elucidated and the relationships between Q\(^3\) production and properties of the unit cell parameters are established.

**Reaction Mechanism.** The Si-O bonds of the Si-O-Si and Si-O-Na moieties have substantially different bonding character as evident from O 1s X-Ray Photoelectron spectroscopy (XPS) results for Na\(_2\)SiO\(_3\) glass where O 1s photoelectrons derived from BO and NBO differ by ~1.8 eV in binding energy (Nesbitt et al., 2011; 2015a). The valence electron density over NBO is consequently greater than over BO so that NBO has the greater ionic character. Oxygen is
more electronegative than Na\(^+\) so that upon Na-O bond dissociation, NBO retains its negative charge. With retention of the charge, the (Na\(_1\)-Q\(^2\))\(^-\) or Si-O\(^-\) moiety produced by Reaction (1a) becomes a strong *nucleophile*. Si tetrahedra are Si sp\(^3\) hybridized and nucleophilic substitution commonly occurs on sp\(^3\) hybridized species (Huheey et al., 1993; Chuit et al., 1993; Corriu, 1990). At high temperature, the nucleophile, Si-O\(^-\), likely attacks Si of Q\(^2\) tetrahedra in adjacent SiO\(_3\) chains to form a 5-coordinate Si-O moiety (Chuit et al., 1993; Corriu, 1990). In support of the suggestion, Si-O pentahedra are observed in some zeolites at ambient temperature (Fyfe et al., 2002), in K and Na silicate glasses at ambient temperature and pressure (Stebbins, 1991) and in Na-silicate melts subjected to high pressure (Wolf et al., 1990). We propose that the Q\(^3\) species observed in the Raman spectra of Na\(_2\)SiO\(_3\) are produced by a nucleophilic substitution reaction. It occurs through attack of a charged Q\(^2\) species, (Na\(_1\)-Q\(^2\))\(^-\), produced by Reaction (1) on a Si center of a Q\(^2\) species according to:

\[
Na_2\text{-}Q^2 + (Na_1\text{-}Q^2)^- \rightleftharpoons [(Si\text{-}O)-Q^2]^\ddagger \rightarrow 2Na_1\text{-}Q^3 + Na^+ + O^{2-} \tag{2b}
\]

where [(Si-O)-Q\(^2\)]\(^\ddagger\) is the transition state (activated) complex illustrated schematically in Fig. 2c. Reaction (2a) is the stoichiometric equivalent of Reaction (2b). The activated complex may decompose to its reactants (indicated by ⇋) but occasionally it may proceed to the final products, namely, Na\(^+\), O\(^{2-}\) and Q\(^3\) (Fig. 2b). The leaving species (Na\(^+\) + O\(^{2-}\)), along with the itinerant Na\(^+\) produced by Reaction (1), yield two itinerant Na\(^+\) and an itinerant O\(^{2-}\) as products. Si-O\(^-\) is generated by Na-O dissociation and its abundance increases with temperature, driving Reaction (2b) to the right. Steric hindrance may inhibit nucleophilic attack but the reaction is promoted at high temperature by the short lifetime of Si-O bonds (Farnan and Stebbins, 1990).

The hypothesis is corroborated by molecular-dynamics (MD) simulations of Na\(_2\)SiO\(_3\) melt at 2000 K. According to Berezhnoi and Boiko (2005), when two Si tetrahedra approach, the
non-bridging oxygen (Si-O’) of one tetrahedron attacks the Si center of another tetrahedron to form a 5-fold coordinated Si pentahedron (the activated complex of Reaction 2b and Fig. 2c). Immediately, one of the other Si-O bonds is severed to reform a tetrahedrally coordinated Si center. The details of the mechanism by which Reaction (2b) proceeds is uncertain but likely follows a SN2 mechanism (Laidler, 1965), although this remains to be proved. The mechanism involves an elementary (single step), bi-molecular reaction the details of which are lucidly presented by Laidler (1965, p. 144-163).

THE MECHANISM – STEP II: Q1 PRODUCTION AND MELTING

Melting of Na2SiO3 requires rupture of the Si-O-Si bonds of its SiO3 chains. With a bond dissociation energy of 798 kJ/mol (Speight, 2005) Si-O bonds are unlikely to be ruptured unless they undergo nucleophilic attack (Corriu, 1990). Above ~770 K, Reaction (2) is active and itinerant O2− is present in the crystal. Free oxygen is a stronger nucleophile than Si-O’ and is less affected by steric hindrance due to its smaller size. Furthermore, the O2− produced by Reaction (2) finds no available structural site in crystalline Na2SiO3; it is itinerant and available for nucleophilic attack on tetrahedrally coordinated, sp3 hybridized Si centres (Corriu, 1990; Chuit et al., 1993). Nucleophilic attack forms a 5-coordinate transition state (activated) complex (SiO5‡) as shown in Figures 4a and 4c. The activated complex, SiO5‡, once formed may occasionally decompose to form Q1 species via Reaction (3) through rupture of a Si-BO bond of the activated complex (SiO5‡); production of Q1 species, necessarily fragments the SiO3 chain (Fig. 4b). With sufficient O2−, formation of Q1 continues and the SiO3 chains eventually lose their integrity, long-range structure is lost, and melt is produced (illustrated in Figure 4). The reaction is:

\[ 2\text{Na}_2\text{-Q}^2 + 2\text{Na}^+ + \text{O}^2- \rightleftharpoons \text{Q}^2\text{-SiO}_5^{\ddagger} \rightarrow 2\text{Na}_3\text{-Q}^1 \]  

and omitting the activated complex:
\[ 2\text{Na}_2\text{Q}^2 + 2\text{Na}^+ + \text{O}^2^- \rightarrow 2\text{Na}_3\text{Q}^1 \] \hspace{1cm} (3b)

Na atoms are associated with the Q species to maintain mass balances. The Raman spectrum of Figure 3c was collected in the premelting region of Na$_2$SiO$_3$ where the crystal still retained its structural integrity, yet a small Q$^1$ signal is apparent. Within the premelting region, the intensity of this band increases with temperature (Richet et al., 1996, their Fig. 6). The weak Q$^1$ signal suggests that SiO$_3$ chains have been ruptured in a few places prior to melting, but not in sufficient quantity to destroy long-range order, possibly because the Q$^3$ cross linkages already formed help to stabilize the few segmented chains. The Q$^1$ band (Fig. 3c) is strong evidence that Reaction (3) occurs while Na$_2$SiO$_3$ is crystalline. There can be little doubt that this reaction also proceeds at its melting point. With production of sufficient Q$^1$ species, the long range order of the crystal must be lost and a melt produced. We conclude that destruction of the SiO$_3$ chains and melting of crystalline Na$_2$SiO$_3$ occur through nucleophilic attack on Si centers by the very strong nucleophile, O$^{2-}$. Involvement of O$^{2-}$ and (Na$_1$-Q$^3$)$^-$ in Reaction (2) likely occurs through a SN2 mechanism (Laidler, 1965). Molecular dynamics simulations on Na$_2$SiO$_5$ melt (Berezhnoi and Boiko, 2005) support strongly such a mechanism as they reveal the presence of O$^{2-}$, which attacks Si centers of tetrahedral chains as proposed for the melting by Reaction (3).

Effects prior to melting are exceedingly important in that the strong nucleophile, O$^{2-}$, is produced beginning at \( \sim 770 \) K (Rxn 2) at a rate that depends ultimately on the strength of the Na-O bond and temperature. The cation becomes itinerant, cross-linking of chains becomes feasible with production of Si-NBO$^-$ and, thanks to such cross-linking, O$^{2-}$ is produced via Reaction (2). As temperature increases, the itinerant O$^{2-}$ builds until a sufficient concentration is achieved to sustain the production of SiO$_5^-$ and, ultimately, the production of Q$^1$ and rupture of the SiO$_3$ chains. At melting, a steady state is achieved because production of O$^{2-}$ (via Rxn. 2) is...
balanced by its consumption (via Rxn 3). The stoichiometric reaction at the melting point then is:

$$2Q^2 \rightarrow Q^1 + Q^3$$  \hspace{1cm} (4)

where the $O^{2-}$ concentration is constant as melting proceeds. Free oxygen ($O^{2-}$) is a critical constituent in the proposed mechanism. This exceptionally strong nucleophile is the primary agent causing depolymerization of the SiO$_3$ chains and ultimately melting. It is generated in the crystal through formation of cross-chain linkages (Rxn 2) as revealed by the presence of $Q^3$ species in high temperature Raman spectra of Na$_2$SiO$_3$(c) (Richet et al., 1996). Involvement of free oxygen in melting is proved by its presence at the mol% level in binary silicate melts and their quenched glasses (Nesbitt et al., 2015a; 2015b; 2015c; 2011; Retsinas et al., 2014; Al-Hasni and Mountjoy, 2014; Sawyer et al., 2012; 2015; Nasikas et al., 2012; 2011; Davis et al., 2011; 2009; Kalampounias et al., 2009; Sen and Tangeman, 2008). The amount of $O^{2-}$ present in the melt will dependent on the equilibrium constants of Reactions (2) and (3).

**MELTING OF OTHER SILICATES**

Lithium metasilicate is isostructural with Na$_2$SiO$_3$ but bond distances are shorter and Li is tetrahedrally coordinated with oxygen (Richet et al., 1996). Extending the arguments derived from the Na$_2$SiO$_3$(c) Raman spectrum (Fig. 3c), we note that the Li$_2$SiO$_3$(c) includes a weak $Q^3$ band in its Raman spectrum collected just below its melting point indicating the formation of cross-chain linkages and production of itinerant Li$^+$ and $O^{2-}$ (Richet et al., 1996, their Fig. 12). Because of the greater dissociation energy of Li-O (341 kJ/mol) compared to that of Na-O (257 kJ/mol), lithium mobility is lower in the Li$_2$SiO$_3$ crystal, thus no phase transition takes place, and no nucleophilic agent (e.g., Si-O$^-$ or O$^{2-}$) is produced until the premelting region is encountered (which extends ~10 K below the melting point). All of Reactions (1), (2) and (3) are thus constrained to a very small thermal window of ~10 K. Within this window, the reactions are
initiated and melting occurs over such a small temperature range that they cannot be followed experimentally. Thus melting of Li$_2$SiO$_3$ is sharper than that of Na$_2$SiO$_3$ (Téqui et al., 1992). In summary, the greater dissociation energy of Li-O (341 kJ/mol) relative to Na-O (257 kJ/mol) confines all reactions, and the associated melting mechanisms, to a span of a few degrees. The melting of Li$_2$SiO$_3$ thus is a counterpoint to Na$_2$SiO$_3$ whose reactions occur over an extended temperature range.

Pseudowollastonite (CaSiO$_3$) contains 3-membered rings of $Q^2$ species (Seryotkin, 2012) and it displays a premelting region extending from ~1570 K to its melting point of 1820 K (Fig. 1a; Richet et al., 1998). Ca-O bond lengths vary from ~2.28 to ~2.68 Å (Yang and Prewitt, 1999). With heating, Ca associated with the longest bonds may become itinerant allowing an analog of Reaction (1) to occur. As evidence, Bouhifd et al. (2002) observed an increase in Ca self-diffusion within the crystal beginning at ~1570 K which implies initiation of Ca-O bond dissociation and Ca itinerancy. Raman spectra of CaSiO$_3$ (Richet et al., 1998, their Fig. 10) collected within its premelting region indicates development a $Q^3$ band as observed for Na$_2$SiO$_3$ (Fig. 3c). These observations are taken as evidence that a reaction analogous to Reaction (2) occurs in the premelting region whereby $Q^3$, Ca$^{2+}$ and O$^{2-}$ are produced with the $Q^3$ species forming linkages connecting adjacent rings. The cross linkages seem to affect most the ‘b’ polar dimension because the ‘b’ cell parameter ceases to expand (and may contract) within the premelting region (Richet et al., 1998, their Fig. 2). With production of O$^{2-}$, a reaction analogous to Reaction (3) likely occurs, producing $Q^1$ species, dismemberment of the rings, and melt.

Diopside (CaMgSi$_2$O$_6$) melts much like Na$_2$SiO$_3$ and CaSiO$_3$. Dimanov and Ingrin (1995) demonstrated that upon heating, a substantial change in Ca self-diffusion occurred within diopside beginning at ~1515 K (melts at 1670 K). The enhanced mobility of Ca may represent
the onset of Ca-O bond dissociation and production of itinerant Ca. Diopside premelting begins at ~1530 K (Fig. 1b) and a weak signal develops on the high frequency side of the Q\(^2\) peak as the melting temperature (1670 K) is approached (Richet et al., 1998, their Fig. 6). Its location is consistent with the Q\(^3\) band frequency in Raman spectra of Na\(_2\)SiO\(_3\) (e.g., Fig. 3c) and its presence provides evidence that a reaction equivalent to Reaction (2) occurs in the premelting region of diopside. The reaction produces O\(^2-\) and with its presence, a reaction equivalent to Reaction (3) may cause rupture of Q\(^2\) chains and melting. Melting of diopside is, however, slightly incongruent and is more complex than here portrayed.

Protoenstatite (MgSiO\(_3\)) melts congruently but metastably at ~1816 K and demonstrates a premelting region beginning at ~ 1700 K (Thiéblot et al., 1999). Thiéblot et al. (1999) note that onset of premelting correlates with enhanced Mg mobility (itinerancy) implying that some Mg-O bond dissociation occurs with necessary production of SiO\(_3^–\), which in turn allows for production of Q\(^3\) cross linkages and O\(^2-\) production via Reaction (2). Protoenstatite may undergo melting by the same mechanism as the other pyroxenes.

A different situation obtains for orthosilicates such as olivine, which consist of Q\(^0\) species. A reaction analogous to Reaction (3) cannot occur for lack of O\(^2-\). Similarly, these mechanisms are inapplicable to SiO\(_2\) polymorphs and tectosilicates in which alkalis have a very low mobility as a result of their charge-compensating role for aluminum in tetrahedral coordination (Richet and Mysen, 1999). These minerals do not undergo premelting, and melting and precipitation are sluggish (Bourova et al., 2006; Schairer and Bowen, 1956). A surface melting mechanism rather than a bulk melting mechanism has been described for quartz and cristobalite (Wagstaff, 1969; Ainslie et al., 1961). These crystals lack a simple mechanism to produce free oxygen thus they provide circumstantial evidence for the critical role of the anion
DISCUSSION WITH IMPLICATIONS

At the congruent melting point the fusion and crystallization reactions are by definition reversible. This macroscopic reversibility implies that the mechanisms involved in the solid-liquid transformation are also reversible, in agreement with the fact that the relevant constituents such as Q species, itinerant cations and O\textsuperscript{2-} species are present in both Na\textsubscript{2}SiO\textsubscript{3} crystals and melts (Fig. 3). The first consequence is that determination of long-range order within growing nuclei would bring little information on the actual crystallization mechanisms at play, which involve instead complex, short-range order rearrangements. The second is that, even with current technology, it would be a formidable task to investigate the relevant reactions and the ensuing variations of short-range order within nanoscale nuclei that represent a negligible volume fraction of the system at the onset of crystallization. To obviate this problem, monitoring the abundances of critical species such as the Q species and O\textsuperscript{2-} during slow cooling of a melt might be a more fruitful approach. In the favorable cases where premelting is significant, however, the most straightforward way to study crystallization is to investigate instead fusion through premelting and melting reactions which, their sense notwithstanding, are the same whether the material is heated or cooled. Finally, the complete failure of nucleation theories to predict nucleation rates, which can be 10\textsuperscript{20}-10\textsuperscript{50} times greater than observed, has been repeatedly stated (Fokin et al., 2006). In this respect a major source of discrepancy could be the neglect of such reactions as (1-4) rather than the roughness of the liquid-nuclei interface, variations of surface energy with temperature and the size of nuclei, or initial nucleation of metastable crystals.

These suggestions have bearing on the other major solidification process, namely, vitrification. At the glass transition, variations in second-order thermodynamic properties occur
when the configuration of the silicate framework becomes frozen in (Richet and Neuville, 1992). By contrast the mobility of network-modifier cations, hence electrical conduction, is much less affected at the transition (Bouhifd et al., 2002; Gruener et al., 2001). The experimental results for the alkali metasilicate crystals point to this conclusion in that only the rates of Reactions (2) and (3) involving Q species increase markedly at the onset of premelting while network-modifier cations remain highly mobile across the transition.

That the analogy is even deeper is indicated by the role played in these reactions by five-coordinate Si atoms. Activated complexes are essential to the proposed melting and crystallization mechanisms and they are a key factor in the configurational rearrangements involved in viscous flow (Fokin et al., 2006). Reactions of the kind described here likely contribute to the configurational changes characteristic of the liquid phase, and particularly to their calorimetric effects. A connection between melting and viscosity mechanisms has been drawn recently (Buchenau et al., 2014) from a reformulation of Lindemann criterion (in terms of shear moduli) without, however, making room for distinct reaction steps such as proposed here. Insights may also be gained from theoretical and molecular dynamics simulations if they were to incorporate the properties of the three types of reaction and the bonds in chain silicates (e.g., Na-O, Si-NBO, Si-O in Na$_2$SiO$_3$). A consistent description of melting, crystallization and glass transition seems possible, combining kinetic, thermodynamic, transport and structural properties.

To understand better the melting, crystallization and vitrification of silicates, chemical species and their abundances should be monitored as a function of temperature above and below melting points. Melting, crystallization and vitrification of compositionally complex silicates are better addressed via chemical mechanisms and orbital hybridization (Richet and Ottonello, 2014; Koroleva et al., 2013) than via mechanical mechanisms (e.g., vibrational instability).
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**Figure Captions**
Fig. 1. Changes to unit cell parameters for Na$_2$SiO$_3$ and heat capacities of numerous crystals as a function of temperature (T). (a) Changes to the ‘a’, ‘b’ and ‘c’ unit cell parameters of Na$_2$SiO$_3$ as a function of T, cast as ratios, a/a$_0$, b/b$_0$ and c/c$_0$. The denominator represents the value of the cell parameter at the lowest temperature measured. For clarity, the a/a$_0$ ratios are displaced to a lower value by 0.005 units. (b) Mean heat capacity (C$_m$) of crystals versus T where C$_m$ = (H$_T$-H$_{273}$)/(T-273) with H being heat content (Richet and Fiquet, 1991). The premelting region extends from the inflection in C$_m$ to the melting point (e.g., ~1200 to 1362 K for Na$_2$SiO$_3$). Dashed curves are extrapolations of fits to the C$_m$ data, excluding measurements in the premelting range. The diopside data are displaced upward by one unit. Fig. 2. Schematic of the structural consequences of Reaction (1a) where two, initially separate SiO$_3$ chains shown in (a), undergo reaction to produce a cross-chain linkage through production of a Q$^3$ species, as shown in (b). A schematic of the activated complex is illustrated in (c).

Fig. 3. $^{29}$Si MAS NMR and Raman spectra of Na$_2$SiO$_3$ for glass and crystal. Experimental data are represented by dots in each diagram. Solid curves represent the introduced Q$^1$, Q$^2$ and Q$^3$ species peaks. The sum of the Q species contributions are also represented by solid curves. (a) NMR spectrum of the glass collected at ambient temperature. The data, fit and Q species abundances are taken from Nesbitt et al. (2011). (b) Raman spectrum of the glass collected at 298 K. The experimental data are represented by dots and are taken from Frantz and Mysen (1995, their Fig. 9). Peak assignments and the partial fit are discussed in the text. The fit is not intended to be complete but was performed solely to establish the approximate locations of the major Q species peaks for comparison with those of the crystal. (c) Raman spectrum of the crystal collected just below the melting
temperature (data from Richet et al., 1996). The fit is entirely unconstrained. Peak
assignments and fit are discussed in the text.

Fig. 4. Schematic diagram of the melting of Na$_2$SiO$_3$(c). (a) Illustrates the attack of O$^{2-}$ on a Si
center to form a transition state complex (dotted oval) according to Reaction (3b). (b) Schematic diagram showing the products of Reaction (3b), which are two Q$^1$ species
terminating two SiO$_3$ chains and destroying the chain structure to produce melt. (c) a
pseudo 3-dimensional rendering of the activated complex.
Fig. 1

(a) Cell parameter ratio \( p/p_0 = a/a_0, b/b_0 \) or \( c/c_0 \) as a function of temperature (K).

(b) Cm of Crystalline Phases (J/g atom K) vs. temperature (K).

- \( \text{Na}_2\text{SiO}_3 \) (crystal)
- diopside
- akermanite
- pseudo-wollastonite

data from Richet et al. (1996) and Richet et al. (1994).
Fig. 2

Reaction (2)

2O²⁻ → 2O³⁻ + 2Na⁺ + O²⁻

or

2NBO⁻ → BO + O²⁻
Fig. 3
Fig. 4

The Melting Reaction

\[ 2Q^2 + O^{2-} \rightarrow SiO_5^2 \rightarrow 2Q^1 \]

SiO_5^2 = the activated complex