1   **REVISION II (FINAL)**

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3   **Melting, Crystallization and the Glass transition:**

4   **Toward a Unified Description for Silicate Phase Transitions**

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27 ^{29}Si NMR and Raman spectra of glasses and melts

28 **ABSTRACT**

29   The melting mechanism of Na_2SiO_3, a crystal with pyroxene structure, includes three

30 distinct reactions. All are driven by heating with each reaction commencing at a different

31 temperature. The first two reactions proceed within the crystal at temperatures well below the

32 melting point and are expressed by distinctive crystallographic, calorimetric and Raman

33 spectroscopic changes in the crystal. With the reactions identified and explained for $Na_2SiO_3(c)$

34 and the melting mechanism elucidated, the Na_2SiO_3 system becomes the 'Rosetta Stone' by

35 which to decipher the melting mechanisms of all pyroxenes and other silicate minerals.

36   The first reaction produces itinerant Na^+ within the crystal. Itinerancy results from

37 dissociation of some NBO-Na bonds due to heating, with dissociation commencing at ~770 K.

38 The reaction proceeds according to:

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

40 The Si-O$^-$ moiety remains attached to its SiO_3 chain and it is charged because one of its NBO

41 atoms has no associated Na ion. The second reaction is characterized by the appearance of a Q^3

42 band in Raman spectra of the crystal at temperatures >770 K. It is produced via a polymerization

43 reaction involving the Si-O$^-$ species, a product of the first reaction, and a Q^2 species of an

44 adjacent SiO_3 chain according to:

45      $1Na_2\text{-}Q^2 + 1(Na_1\text{-}Q^2)^- \rightarrow 2Na_1\text{-}Q^3 + Na^+ + O^{2-}$
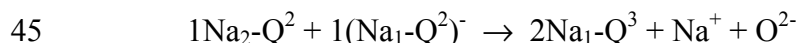
46 Na atoms are included with each Q species to preserve mass balances and $(Na_1\text{-}Q^2)^-$ is equivalent

47 to the Si-O$^-$ species. The produced Q^3 species form cross-chain linkages which affect the

48 crystallographic properties of the crystal. They are responsible for the cessation of thermal

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49   expansion of the Na_2SiO_3 unit cell in the 'a'-'b' axial plane at T >770 K, and the near-constancy

50   of 'a' and 'b' unit cell parameters between ~770 K and ~1300 K. The presence of Q^3 species in

51   Raman spectra and the inhibited expansion in the 'a'-'b' axial plane provide exceedingly strong

52   evidence for this reaction. The third reaction commences at ~1200 K where Q^1 Raman band first

53   appears. It can be produced *only* through depolymerization of Q^2 chains according to:

54    $$2Na_2\text{-}Q^2 + 2Na^+ + O^{2-} \rightarrow 2Na_3\text{-}Q^1$$
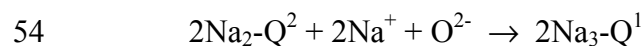
55   where Na^+ and O^{2-} are itinerant species produced by the second reaction. With conversion of Q^2

56   to Q^1 species, SiO_3 chains are ruptured, long range order is lost and melt is produced at 1362 K.

57   The last two reactions proceed by nucleophilic substitution where Si centers are attacked

58   to form 5-fold coordinated activated complexes. $Si\text{-}O^-$ acts as nucleophile in the second reaction

59   (producing Q^3 species), and O^{2-} acts as nucleophile in the third reaction (producing Q^1). Taken in

60   reverse, these mechanisms describe the formation of nuclei in crystallizing melts and in addition

61   provide insight into the elusive changes that occur at the glass transition. Elucidation of the

62   melting mechanism could thus provide a unified framework within which melting, crystallization

63   and the glass transition can be understood.

INTRODUCTION

65   From practical and theoretical perspectives, melting and crystallization are the most

66   important phase transitions. Silicates have a special importance in this respect as the concentric

67   structure of the Earth with a core, a mantle and a crust, the existence of SiO_2-rich, buoyant

68   continents and, thus, the subsequent emergence of life, are processes that were all ultimately

69   determined by melting and crystallization reactions. Today these reactions are also of utmost

70   importance as they are at the roots of the basic industries with annual production of nearly 3×10^9

71   tons of cement, 4×10^8 tons of iron and steel slags and about 10^8 tons of glass. A comprehensive

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72 theoretical framework within which to interpret melting, crystallization and vitrification

73 consequently would be of great benefit to Earth and materials scientists. We propose such a

74 framework by developing a melting mechanism applicable to numerous silicate minerals. It is

75 based in experimental results, thermodynamic constraints and on chemical kinetics principles.

76 The experimental results for Na_2SiO_3 are critically important to the development of the melting

77 mechanism. Our first objective consequently is to review the crystallographic, calorimetric and

78 Raman spectroscopic properties of Na_2SiO_3 between 298 K and its melting temperature (Richet

79 et al., 1996; McMillan, 1984; McDonald and Cruickshank, 1967). Once analysed and the

80 changes to the crystal elucidated, our second and most important objective, is to develop a

81 melting mechanism applicable to many silicate minerals through application of chemical kinetics

82 principles (Laidler, 1965) using the experimental results to constrain its development.

83   Physicists and chemists, for over a century, have studied the melting phenomenon for by

84 employing mostly physical principles, including vibrational instability, vanishing shear moduli

85 and defect production (Lindemann, 1910; Brillouin, 1938; Born. 1939; Lennard-Jones and

86 Devonshire, 1939; Frenkel, 1955; Eyring et al., 1958). None explains successfully the melting of

87 compositionally and structurally complex silicate minerals as emphasized by Wolf and Jeanloz,

88 (1984). There is, therefore, little or no understanding of how these silicates minerals melt. The

89 reason their melting is so poorly understood is that melting is too abrupt, and crystallization

90 begins with nuclei too small to be readily investigated by techniques available today. There are,

91 however, a few special cases whereby these reactions are more amenable to experimental

92 investigation. These manifest themselves in crystals with extensive premelting regions, which

93 may extend over tens to hundreds of degrees. (e.g., Thiéblot et al., 1999; Richet et al., 1996;

94 1994). Na_2SiO_3 is one such case. Crystalline sodium metasilicate (Na_2SiO_3) displays a large

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95   premelting region of ~160 degrees and its structure is simple (Richet et al., 1996) making

96   detailed structural, calorimetric and spectroscopic studies possible over a wide range of

97   temperature (Figs. 1a, 1b). From such results we identify three reactions which are *necessary*

98   *precursors* to the melting of Na_2SiO_3. Perhaps most importantly, each reaction is initiated at a

99   different temperature permitting detailed investigation of each without appreciable overlap or

100   interference from the other reactions. Taken in reverse, the same reactions account for the

101   formation of nuclei in melts and subsequent crystallization. The steps are also applicable to

102   changes that occur at the glass transition, including structural relaxation and viscous flow, thus

103   providing a unified description and theory of these phenomena.

104   **STRUCTURE OF Na_2SiO_3**

105   The Si-O structural arrangements of crystalline Na_2SiO_3 are identical to those of the

106   pyroxene group of minerals. It consists of chains of Si tetrahedra (McDonald and Cruickshank

107   1967; Ching et al., 1983) where two apical oxygen atoms bridge two Si atoms (bridging oxygens

108   or BO) to produce Si-O-Si moieties and to form SiO_3 chains parallel to the c axis as shown

109   schematically in Figure 2a. The two other oxygen atoms of each tetrahedron are bonded to a Si

110   and a Na atom to produce the Si-O-Na moiety whose oxygen is referred to as non-bridging

111   (NBO). Na atoms are encased in oxygen bipyramids and are located between the chains binding

112   them together. The crystal's cell parameters increase systematically with temperature to ~770 K

113   (Fig. 1a). The 'c' cell parameter continues to increase without inflection to at least 1300 K

114   (Richet et al., 1994; 1996). The 'a' and 'b' cell parameters, by contrast, remain effectively

115   constant between about ~770 K and ~1300 K (Fig. 1a). There is also a change in space group at

116   ~850 K from *Cmc* 2_1 to a lower symmetry, probably to *Pmc* 2_1 (Richet et al., 1996). With

117   transition to lower symmetry, there is loss of a Na position in the 'a'-'b' axial plane.

118   **Na_2SiO_3 HEAT CAPACITY AND ITINERANT Na^+**

119   The mean heat capacities (C_m) for four crystalline phases are plotted against temperature

120   in Figure 1b, where C_m is defined as $(H_T-H_{273})/(T-273)$ with H being enthalpy (Richet and

121   Fiquet, 1991). The heat capacities of all crystals initially change as expected with respect to

122   temperature, due primarily to acoustic vibrational contributions but on approach to the melting

123   point, each displays a dramatic increase in C_m. The inflection in C_m for Na_2SiO_3(c) occurs at

124   ~1200 K and the region between the inflection and the melting point (1362 K) is defined as the

125   *premelting region*. Many other minerals display premelting regions (Bouhifd et al., 2002;

126   Thiéblot et al., 1999; George et al., 1998; Richet et al., 1998; 1996; 1994; 1993). The ^{23}Na NMR

127   study of George et al. (1998) demonstrate cation itinerancy within the premelting region of

128   Na_2SiO_3. They note that "Na^+ site hopping appears to involve a more liquid-like behavior,

129   implying exchange occurred among many sites (i.e., itinerancy) with different orientations, and

130   in a disordered fashion". Na^+ itinerancy in crystals apparently is analogous to Na^+ mobility in

131   glass as simulated by Cormack et al. (2002) where they monitored alkali ion 'jumps' to adjacent

132   empty sites of variable potential energy. The data of George et al. (1998) are conclusive but a

133   question arises concerning the temperature at which itinerancy is initiated. The structural data,

134   particularly thermal expansion characteristics (Fig. 1a), indicates a significant change in crystal

135   properties at ~770 K and this may reflect the onset of itinerancy. The suggestion is reinforced by

136   loss of a Na position in the 'a'-'b' axial plane at ~850 K.

137   The temperature at which Na^+ itinerancy is initiated must relate to the weakness of Na-O

138   bonds. Crystalline Li_2SiO_3 and Na_2SiO_3, for example, share the same structure but upon heating

139   there is no indication of Li^+ itinerancy, and no change in space group in the temperature range

140   298 K to the melting point. The Na-O bond dissociation energy is 257 kJ/mol whereas that of Li-

141 O is 341 kJ/mol (Speight, 2005). With heating and vibrational excitation, Na-O bonds are

142 therefore expected to dissociate at lower temperatures than Li-O bonds (and to greater extent at

143 the same temperature). Dissociation may be represented by the reaction:

144 $\quad$ Si-O-Na $\rightarrow$ Si-O$^-$ + Na$^+$ $\hfill$ (1a)

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

146 $\quad$ Na$_2$-Q^2 $\rightarrow$ (Na$_1$-Q^2)$^-$ + Na$^+$ $\hfill$ (1b)

147 where a Si-O-Na moiety incorporated into the Na$_2$-Q^2 species dissociates yielding a charged

148 (Na$_1$-Q^2)$^-$ species and Na$^+$. In summary, it is established that Na-O dissociation occurs (George et

149 al., 1998; Richet et al., 1996) and structural changes to the crystal (e.g., Fig. 1a) suggest that it

150 commences at ~770 K. Increased temperature drives Reaction (1) to the right thus increasing

151 itinerancy and promoting structural change such as that evident at ~850 K where there is loss of

152 an Na position in the 'a'-'b' axial plane of the crystal (Richet et al., 1996).

153 $\quad$ Dissociation of each Na-O bond necessarily produces a Si-O$^-$ moiety which, while still

154 attached to a chain, should undergo librations unavailable to the Si-O-Na moiety due to the loss

155 of a bonding partner (Na) and to the presence of an 'exposed' negative charge on the NBO.

156 Additional librations in the premelting region were confirmed by ^{29}Si NMR results of George et

157 al. (1998) where partial averaging of low temperature biaxial chemical shifts occur, "suggesting

158 some kind of extensive, librational motion of SiO$_4$ tetrahedra". In addition, progressive heating

159 causes many weak, low to intermediate frequency Raman Na-O bands to broaden or merge into

160 the spectral background (Richet et al., 1996). The Si-O$^-$ species is negatively charged and may

161 act as a nucleophile in chemical reactions, as emphasized subsequently.

162 $\qquad$ **RAMAN SPECTRA OF Na$_2$SiO$_3$**

163 $\quad$ Previously published ^{29}Si NMR and Raman spectra of Na$_2$SiO$_3$ crystal and glass (Figs.

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164 3a, 3b, 3c) contain valuable information concerning reactions that occur in the crystal during

165 heating to the melting point. This was not realized previously because the spectral similarities

166 between crystal and glass had not been recognized (spectra from Nesbitt et al., 2011; Richet et

167 al., 1996; Frantz and Mysen, 1995). We emphasize these similarities and begin by addressing the

168 ^{29}Si MAS NMR and Raman spectra of Na_2SiO_3 glass (Figs. 3a, 3b) followed by interpretation of

169 the Raman spectrum of crystalline Na_2SiO_3 (Fig. 3c).

170 **Na_2SiO_3 Glass Spectra.**

171 **Assignment of Bands.** The ^{29}Si MAS NMR spectrum of the glass (Fig. 3a) was fit by Nesbitt et

172 al. (2011) employing three symmetric100% Gaussian peaks. Once the spectrum was fit, the

173 peaks were assigned to Q^1, Q^2 and Q^3 species based on peak position. Maekawa et al. (1991)

174 arrived at precisely the same assignments. The two studies demonstrate that there are three major

175 contributions to the glass spectrum, the Q^1, Q^2 and Q^3 species signals and also demonstrate that

176 no other Q species makes major contribution to the glass spectrum.

177 Comparison of Figures 3a and 3b reveal similarities between the ^{29}Si MAS NMR and

178 Raman spectra of Na_2SiO_3 glass (Nesbitt et al., 2011; Frantz and Mysen, 1995; Maekawa et al.,

179 1991). Each displays a strong central peak with a shoulder on the high frequency side of the

180 central peak, and a weak peak on the low frequency side. The similarity is expected because the

181 signals for both spectra arise from the same sources, the Q species; that is, the three Q species

182 observed in the ^{29}Si NMR spectrum of Figure 3a must also contribute to the Raman spectrum of

183 Figure 3b. It is therefore reassuring that the two figures have similar characteristics. The results

184 of Brawer and White (1975) provide the information needed to identify the approximate location

185 of the three Q species contributions in the Raman spectrum of the glass (Fig. 3b). These authors

186 collected Raman spectra of crystalline and vitreous Na_2SiO_3 at ambient temperature. The crystal

187 contains only the Q^2 species whose peak is centered at 975 cm^{-1}. Their glass spectrum displays

188 its most intense peak at 985 cm^{-1}. At this composition the Q^2 band is expected to be the most

189 intense. On this basis, and on the similarity of peak positions in crystal and glass, we propose

190 that the Q^2 species is the major contributor to the 985 cm^{-1} peak of their Na_2SiO_3 glass (i.e., Q^2

191 species is assigned to the 985 cm^{-1} band).

192   Turning to Figure 3b and focussing on the experimental results (dots), we find that the

193 most intense experimental signal is centred at ~966 cm^{-1}. By comparison with the glass spectrum

194 of Brawer and White (1975), and based on peak position and intensity, we assign the Q^2 signal to

195 the 966 cm^{-1} band. With its position established, the other contributions to Figure 3b can be

196 assigned. Brawer and White (1975) observe a peak at 855 cm^{-1} in their glass spectrum, which is

197 located at ~130 cm^{-1} lower frequency than the Q^2 band. Figure 3b has a peak at ~842 cm^{-1}. It is

198 ~124 cm^{-1} lower in frequency than the Q^2 band. McMillan (1984) locates the Q^1 band at ~50-100

199 cm^{-1} lower frequency than the Q^2 band. Thus the 842 cm^{-1} peak of Figure 3b is assigned to the Q^1

200 species. McMillan (1984) also notes that the Q^3 band is located at ~50-100 cm^{-1} greater

201 frequency than the Q^2 band, thus the Q^3 band of Figure 3b should be present at ~1015-1065 cm^{-1},

202 and within the pronounced shoulder on the high frequency side of the Q^2 band. A better estimate

203 of the location of the Q^3 peak can be obtained by fitting parts of the spectrum.

204 **Partial Fit to the Spectrum.** The Raman spectrum (Fig. 3b) was fit using 100% Gaussian

205 lineshapes. The shape may not be optimum but it is sufficient for our purpose. A Q^1 peak was

206 introduced and centered at ~842 cm^{-1}. Its FWHM was adjusted manually to fit as closely as

207 possible the experimental peak. The fitted peak has a linewidth of ~36 cm^{-1}. We then added a Q^2

208 peak, the position and Full Width at Half Maximum (FWHM) of which were constrained to fit

209 the high frequency side of the most intense peak. The resulting peak position is ~966 cm^{-1} and its

210   FWHM is ~41 cm^{-1}. The positions of the Q^1 and Q^2 peaks are consistent with those quoted by

211   McMillan (1984). We introduced a third peak to represent the Q^3 (highest frequency) band. Its

212   intensity, FWHM and location were constrained as follows. The Q^3 intensity of the ^{29}Si MAS

213   NMR spectrum (Fig. 3a) is 5.2 times more intense than that of the Q^1 peak. Assuming the Raman

214   scattering factors for the Q^1 and Q^3 peaks are similar (i.e., 1:1 ratio) we constrained the Raman

215   Q^3 band of Figure 3b to have an intensity 5.2 times greater than that of the Q^1 band of the

216   Raman spectrum. There is no detectable Q^4 signal in the NMR spectrum of Na_2SiO_3 glass (Fig.

217   3a) so that the Q^3 species is considered the highest frequency contribution to Figure 3b. The

218   linewidth of the Q^3 peak was therefore adjusted to fit the highest-frequency portion of the

219   spectrum while maintaining the appropriate peak intensity, thus yielding the peak represented by

220   the solid curve of Figure 3b. It is centered at ~1030 cm^{-1} with FWHM of 94 cm^{-1} and is

221   consistent with the Q^3 peak position quoted by McMillan (1984).

222   The greatest uncertainty related to fitting the Q^3 peak is the assumption that scattering

223   factors are the same for the Q^1 and Q^3 bands. To determine the sensitivity of this assumption, we

224   alternatively employed the scattering factors of Koroleva et al. (2013), which are 1.53 for Q^1 and

225   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

226   should be 3.5 greater than the Q^1 peak area in Figure 3b. With this constraint, the resulting best

227   fit for the Q^3 band is shown as the dashed curve centered at ~1048 cm^{-1} (FWHM ~81 cm^{-1}). The

228   Q^3 peak position of the glass therefore is reasonably well established to reside between ~1030

229   cm^{-1} and ~1050 cm^{-1} regardless of the scattering factors used. The position is consistent with the

230   Q^3 position noted by McMillan (1984). The approximate locations of the three Q species have

231   been ascertained. Additional contributions to the Raman spectrum are required to complete the

232   fit, which will be provided in a future publication. (e.g., Fig. 4 of Koroleva et al., 2013; Fig. 12

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233   of Richet et al., 1996). Although our fit is not complete, three important conclusions nevertheless

234   can be drawn from the partial fit: (1) the peak assignments are consistent with the ^{29}Si NMR

235   spectra of Maekawa et al. (1991) and Nesbitt et al., (2011) as apparent in Figure 3a; (2) the

236   Raman Q species peak positions are reasonably well established and agree with those previously

237   reported by McMillan (1984); (3) the intensity of the Q^3 band is greater than that of the Q^1 band.

238   **Crystalline Na$_2$SiO$_3$ Spectrum.**

239   **Introduction.** Raman spectra for crystalline Na$_2$SiO$_3$ (e.g., Fig. 3c) were collected at

240   temperatures ranging from 298 K to the melting point (1362 K) by Richet et al. (1996). The 298

241   K spectrum displays an exceedingly intense band representing the Si-O symmetric stretch of the

242   Q^2 species. The band is located at ~965 cm^{-1}, has a FWHM of 6 cm^{-1} and its shape is strongly

243   Lorentzian (Richet et al., 1996). The spectrum in Figure 3c is that of crystalline Na$_2$SiO$_3$

244   collected at 1348 K (just below its melting point). With heating a new band appears at ~770 K

245   which is centered at ~1030 cm^{-1} (Richet et al., 1996). The band becomes more intense with

246   temperature and is most intense in the premelting region. At ~1200 K, another band develops at

247   ~900 cm^{-1}. Its intensity increases with temperature but it never approaches the intensity of the

248   band at ~1030 cm^{-1}.

249   **Fitting the Spectrum.** Following Richet et al. (1996), three entirely *unconstrained*, 100%

250   Lorentzian peaks were introduced to fit the spectrum. The resulting least squares fit is shown in

251   Figure 3c. The most intense fitted peak, centered at 959 cm^{-1}, represents the Q^2 signal (Richet et

252   al., 1996). Its FWHM is ~37 cm^{-1} and it represents ~68% of the spectral intensity. McMillan

253   (1984) states that the Q^3 signal is situated at 50-100 cm^{-1} greater frequency than the Q^2 signal in

254   the glass, and if present in Figure 3c, it should be located between about ~1010 cm^{-1} and ~1060

255   cm^{-1}. The *unconstrained*, fitted peak centred at ~1031 cm^{-1} is entirely consistent with it being a

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256   Q^3 signal and we interpret it as such. The location of the Q^3 peak for the glass (Fig. 3b) and the

257   crystal (Fig. 3c) is similar, reinforcing the Q^3 species assignment. The Q^3 peak of the crystal has

258   a FWHM of ~86 cm^{-1} and its intensity constitutes ~22% of the total signal.

259   The third *unconstrained* peak fitted to the spectrum is centered at ~905 cm^{-1}. It has a

260   FWHM of 65.4 cm^{-1} and constitutes ~10% of the total signal. McMillan (1984) states that the Q^1

261   signal is located at 50 to 100 cm^{-1} lower frequency than the Q^2 band, thus the peak centred at

262   ~905 cm^{-1} is consistent with it being a Q^1 peak and we interpret it as such. The Q^3 peak intensity

263   is appreciably greater than the Q^1 intensity and it remains to explain how Q^3 and Q^1 species are

264   produced in the crystalline chain silicate Na_2SiO_3 near its melting point. With the three Q species

265   contributing to the crystal reasonably well established, insight into the reactions occurring within

266   the crystal in response to thermal input can be evaluated.

267   **THE MECHANISM – STEP I: Q^3 AND O^{2-} PRODUCTION**

268   The implications of the similarities between the Raman spectra of crystalline and vitreous

269   Na_2SiO_3 (Figs. 3b and 3c) are now addressed in more detail than originally provided (Richet et

270   al., 1996). Between ambient temperature and ~770K only a strong Q^2 peak is observed in the

271   Raman spectrum of Na_2SiO_3 (Richet et al., 1996, their Fig. 6). Above ~770 K a Q^3 band appears

272   and its intensity increases dramatically within the premelting region. There is *no* Q^1 band present

273   in spectra collected below ~1200 K and in the absence of a Q^1 band, the *only means to produce*

274   *Q^3 species* in the crystal, without producing an equal amount of Q^1 species, is via a

275   polymerization reaction involving Q^2 species. If $(Na_1-Q^2)^-$ (or alternatively Si-O$^-$) produced by

276   reaction (1) were to react with another Q^2 species (i.e., Na_2-Q^2) then:

277       $(Na_1-Q^2)^- + Na_2-Q^2 \rightarrow 2Na_1-Q^3 + Na^+ + O^{2-}$ (2a)

278   The $(Na_1-Q^2)^-$ moiety is a nucleophilic agent and is likely to react with Si centers as explained

279   subsequently in the 'Reaction Mechanism' section. The reaction produces an itinerant Na^+ *and*

280   itinerant O^{2-}. The reaction obviously requires structural changes to the crystal to accommodate

281   the Q^3 species.

282   **Structural Effects.** As observed in double chain silicates (e.g., amphiboles, Deer et al.,

283   2013), the Q^3 species in Na_2SiO_3 likely form cross-chain linkages in the 'a'–'b' axial plane as

284   shown schematically in Figure 2b. These cross-chain linkages should inhibit or prevent

285   expansion of the Na bipyramids along their polar axes in the 'a'-'b' axial plane but they should

286   not inhibit expansion along the 'c' polar axis. The formation of Q^3 cross-chain linkages

287   consequently provides the explanation for the unusual changes observed in the unit cell thermal

288   expansion coefficients of Figure 1a; that is, all three a, b and c cell parameters increase as

289   expected up to ~770 K. Once Q^3 species begin to form there is minimal increase in the 'a' and

290   'b' cell parameters but the 'c' cell parameter continues to increase without inflection at ~770 K.

291   The Si-O-Si and O-Si-O bond angles may be distorted due to Q^3 cross-chain linkages but

292   they need not disrupt the structure of the crystal. Indeed, the pyroxene structure of Na_2SiO_3 is

293   maintained to its melting temperature (George et al., 1998; Richet et al., 1996). If formed

294   randomly along the chains, the cross linkages would not be detectable by X-ray diffraction

295   methods. The effects of Reactions (1) and (2) on structure thus are elucidated and the

296   relationships between Q^3 production and properties of the unit cell parameters are established.

297   **Reaction Mechanism.** The Si-O bonds of the Si-O-Si and Si-O-Na moieties have

298   substantially different bonding character as evident from O 1s X-Ray Photoelectron spectroscopy

299   (XPS) results for Na_2SiO_3 glass where O 1s photoelectrons derived from BO and NBO differ by

300   ~1.8 eV in binding energy (Nesbitt et al., 2011; 2015a). The valence electron density over NBO

301   is consequently greater than over BO so that NBO has the greater ionic character. Oxygen is

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302   more electronegative than Na^+ so that upon Na-O bond dissociation, NBO retains its negative

303   charge. With retention of the charge, the $(Na_1-Q^2)^-$ or $Si-O^-$ moiety produced by Reaction (1a)

304   becomes a strong *nucleophile*. Si tetrahedra are Si sp^3 hybridized and nucleophilic substitution

305   commonly occurs on sp^3 hybridized species (Huheey et al., 1993; Chuit et al., 1993; Corriu,

306   1990). At high temperature, the nucleophile, $Si-O^-$, likely attacks Si of Q^2 tetrahedra in adjacent

307   SiO_3 chains to form a 5-coordinate Si-O moiety (Chuit et al., 1993; Corriu, 1990). In support of

308   the suggestion, Si-O pentahedra are observed in some zeolites at ambient temperature (Fyfe et

309   al., 2002), in K and Na silicate glasses at ambient temperature and pressure (Stebbins, 1991) and

310   in Na-silicate melts subjected to high pressure (Wolf et al., 1990). We propose that the Q^3

311   species observed in the Raman spectra of Na_2SiO_3 are produced by a nucleophilic substitution

312   reaction. It occurs through attack of a charged Q^2 species, $(Na_1-Q^2)^-$, produced by Reaction (1)

313   on a Si center of a Q^2 species according to:

314         $Na_2-Q^2 + (Na_1-Q^2)^- \leftrightarrows [(Si-O)^- -Q^2]^{\ddagger} \rightarrow 2Na_1-Q^3 + Na^+ + O^{2-}$ (2b)
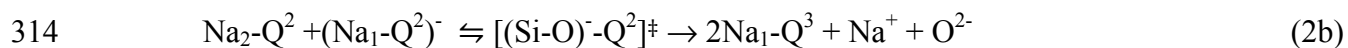
315   where $[(Si-O)^- -Q^2]^{\ddagger}$ is the transition state (activated) complex illustrated schematically in Fig. 2c.

316   Reaction (2a) is the stoichiometric equivalent of Reaction (2b). The activated complex may

317   decompose to its reactants (indicated by $\leftrightarrows$) but occasionally it may proceed to the final products,

318   namely, Na^+, O^{2-} and Q^3 (Fig. 2b). The leaving species ($Na^+ + O^{2-}$), along with the itinerant Na^+

319   produced by Reaction (1), yield two itinerant Na^+ and an itinerant O^{2-} as products. $Si-O^-$ is

320   generated by Na-O dissociation and its abundance increases with temperature, driving Reaction

321   (2b) to the right. Steric hindrance may inhibit nucleophilic attack but the reaction is promoted at

322   high temperature by the short lifetime of Si-O bonds (Farnan and Stebbins, 1990).

323   The hypothesis is corroborated by molecular-dynamics (MD) simulations of Na_2SiO_3

324   melt at 2000 K. According to Berezhnoi and Boiko (2005), when two Si tetrahedra approach, the
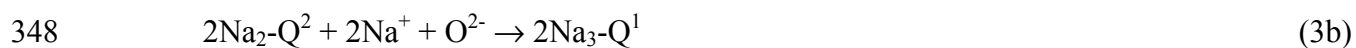
14

325   non-bridging oxygen (Si-O⁻) of one tetrahedron attacks the Si center of another tetrahedron to

326   form a 5-fold coordinated Si pentahedron (the activated complex of Reaction 2b and Fig. 2c).

327   Immediately, one of the other Si-O bonds is severed to reform a tetrahedrally coordinated Si

328   center. The details of the mechanism by which Reaction (2b) proceeds is uncertain but likely

329   follows a S_N2 mechanism (Laidler, 1965), although this remains to be proved. The mechanism

330   involves an elementary (single step), bi-molecular reaction the details of which are lucidly

331   presented by Laidler (1965, p. 144-163).

THE MECHANISM – STEP II: Q^1 PRODUCTION AND MELTING

333   Melting of Na_2SiO_3 requires rupture of the Si-O-Si bonds of its SiO_3 chains. With a bond

334   dissociation energy of 798 kJ/mol (Speight, 2005) Si-O bonds are unlikely to be ruptured unless

335   they undergo nucleophilic attack (Corriu, 1990). Above ~770 K, Reaction (2) is active and

336   itinerant O^{2-} is present in the crystal. Free oxygen is a stronger nucleophile than Si-O⁻ and is less

337   affected by steric hindrance due to its smaller size. Furthermore, the O^{2-} produced by Reaction

338   (2) finds no available structural site in crystalline Na_2SiO_3; it is itinerant and available for

339   nucleophilic attack on tetrahedrally coordinated, sp^3 hybridized Si centres (Corriu, 1990; Chuit et

340   al., 1993). Nucleophilic attack forms a 5-coordinate transition state (activated) complex ($SiO_5‡$)

341   as shown in Figures 4a and 4c. The activated complex, $SiO_5‡$, once formed may occasionally

342   decompose to form Q^1 species via Reaction (3) through rupture of a Si-BO bond of the activated

343   complex ($SiO_5‡$); production of Q^1 species, *necessarily* fragments the SiO_3 chain (Fig. 4b). With

344   sufficient O^{2-}, formation of Q^1 continues and the SiO_3 chains eventually lose their integrity, long-

345   range structure is lost, and melt is produced (illustrated in Figure 4). The reaction is:

346   $$2Na_2\text{-}Q^2 + 2Na^+ + O^{2-} \leftrightharpoons Q^2\text{-}SiO_5‡ \rightarrow 2Na_3\text{-}Q^1 \tag{3a}$$
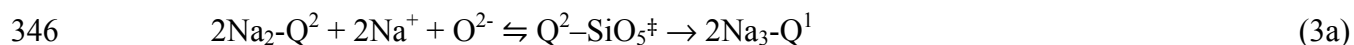
347   and omitting the activated complex:

348         $2Na_2-Q^2 + 2Na^+ + O^{2-} \rightarrow 2Na_3-Q^1$ (3b)

349   Na atoms are associated with the Q species to maintain mass balances. The Raman spectrum of

350   Figure 3c was collected in the premelting region of Na_2SiO_3 where **the crystal** still retained its

351   structural integrity, yet a small Q^1 signal is apparent. Within the premelting region, the intensity

352   of this band increases with temperature (Richet et al., 1996, their Fig. 6). The weak Q^1 signal

353   suggests that SiO_3 chains have been ruptured in a few places prior to melting, but not in

354   sufficient quantity to destroy long-range order, possibly because the Q^3 cross linkages already

355   formed help to stabilize the few segmented chains. The Q^1 band (Fig. 3c) is strong evidence that

356   Reaction (3) occurs while Na_2SiO_3 is crystalline. There can be little doubt that this reaction also

357   proceeds at its melting point. With production of sufficient Q^1 species, the long range order of

358   the crystal must be lost and a melt produced. We conclude that destruction of the SiO_3 chains and

359   melting of crystalline Na_2SiO_3 occur through nucleophilic attack on Si centers by the very strong

360   nucleophile, O^{2-}. Involvement of O^{2-} and $(Na_1-Q^2)^-$ in Reaction (2) likely occurs through a S_N2

361   mechanism (Laidler, 1965). Molecular dynamics simulations on Na_2SiO_5 melt (Berezhnoi and

362   Boiko, 2005) support strongly such a mechanism as they reveal the presence of O^{2-}, which

363   attacks Si centers of tetrahedral chains as proposed for the melting by Reaction (3).

364   Effects prior to melting are exceedingly important in that the strong nucleophile, O^{2-}, is

365   produced beginning at ~770 K (Rxn 2) at a rate that depends ultimately on the strength of the

366   Na-O bond and temperature. The cation becomes itinerant, cross-linking of chains becomes

367   feasible with production of $Si-NBO^-$ and, thanks to such cross-linking, O^{2-} is produced via

368   Reaction (2). As temperature increases, the itinerant O^{2-} builds until a sufficient concentration is

369   achieved to sustain the production of $SiO_5^{\ddagger}$ and, ultimately, the production of Q^1 and rupture of

370   the SiO_3 chains. At melting, a steady state is achieved because production of O^{2-} (via Rxn. 2) is

371   balanced by its consumption (via Rxn 3). The stoichiometric reaction *at the melting point* then is:

372         $2Q^2 \rightarrow Q^1 + Q^3$ (4)

373   where the O^{2-} concentration is constant as melting proceeds. Free oxygen (O^{2-}) is a critical

374   constituent in the proposed mechanism. This exceptionally strong nucleophile is the primary

375   agent causing depolymerization of the SiO_3 chains and ultimately melting. It is generated in the

376   crystal through formation of cross-chain linkages (Rxn 2) as revealed by the presence of Q^3

377   species in high temperature Raman spectra of $Na_2SiO_3(c)$ (Richet et al., 1996). Involvement of

378   free oxygen in melting is proved by its presence at the mol% level in binary silicate melts and

379   their quenched glasses (Nesbitt et al., 2015a; 2015b; 2015c; 2011; Retsinas et al., 2014; Al-Hasni

380   and Mountjoy, 2014; Sawyer et al., 2012; 2015; Nasikas et al., 2012; 2011; Davis et al., 2011;

381   Sen et al., 2009; Kalampounias et al., 2009; Sen and Tangeman, 2008). The amount of O^{2-}

382   present in the melt will dependent on the equilibrium constants of Reactions (2) and (3).

MELTING OF OTHER SILICATES

384   Lithium metasilicate is isostructural with Na_2SiO_3 but bond distances are shorter and Li is

385   tetrahedrally coordinated with oxygen (Richet et al., 1996). Extending the arguments derived

386   from the $Na_2SiO_3(c)$ Raman spectrum (Fig. 3c), we note that the $Li_2SiO_3(c)$ includes a weak Q^3

387   band in its Raman spectrum collected just below its melting point indicating the formation of

388   cross-chain linkages and production of itinerant Li^+ and O^{2-} (Richet et al., 1996, their Fig. 12).

389   Because of the greater dissociation energy of Li-O (341 kJ/mol) compared to that of Na-O (257

390   kJ/mol), lithium mobility is lower in the Li_2SiO_3 crystal, thus no phase transition takes place, and

391   no nucleophilic agent (e.g., Si-O⁻ or O^{2-}) is produced until the premelting region is encountered

392   (which extends ~10 K below the melting point). All of Reactions (1), (2) and (3) are thus

393   constrained to a very small thermal window of ~10 K. Within this window, the reactions are

17

394   initiated and melting occurs over such a small temperature range that they cannot be followed

395   experimentally. Thus melting of Li_2SiO_3 is sharper than that of Na_2SiO_3 (Téqui et al., 1992). In

396   summary, the greater dissociation energy of Li-O (341 kJ/mol) relative to Na-O (257 kJ/mol)

397   confines all reactions, and the associated melting mechanisms, to a span of a few degrees. The

398   melting of Li_2SiO_3 thus is a counterpoint to Na_2SiO_3 whose reactions occur over an extended

399   temperature range.

400   Pseudowollastonite ($CaSiO_3$) contains 3-membered rings of Q^2 species (Seryotkin, 2012)

401   and it displays a premelting region extending from ~1570 K to its melting point of 1820 K (Fig.

402   1a; Richet et al., 1998). Ca-O bond lengths vary from ~2.28 to ~2.68 Å (Yang and Prewitt,

403   1999). With heating, Ca associated with the longest bonds may become itinerant allowing an

404   analog of Reaction (1) to occur. As evidence, Bouhifd et al. (2002) observed an increase in Ca

405   self-diffusion within the crystal beginning at ~1570 K which implies initiation of Ca-O bond

406   dissociation and Ca itinerancy. Raman spectra of $CaSiO_3$ (Richet et al., 1998, their Fig. 10)

407   collected within its premelting region indicates development a Q^3 band as observed for Na_2SiO_3

408   (Fig. 3c). These observations are taken as evidence that a reaction analogous to Reaction (2)

409   occurs in the premelting region whereby Q^3, Ca^{2+} and O^{2-} are produced with the Q^3 species

410   forming linkages connecting adjacent rings. The cross linkages seem to affect most the 'b' polar

411   dimension because the 'b' cell parameter ceases to expand (and may contract) within the

412   premelting region (Richet et al., 1998, their Fig. 2). With production of O^{2-}, a reaction analogous

413   to Reaction (3) likely occurs, producing Q^1 species, dismemberment of the rings, and melt.

414   Diopside ($CaMgSi_2O_6$) melts much like Na_2SiO_3 and $CaSiO_3$. Dimanov and Ingrin (1995)

415   demonstrated that upon heating, a substantial change in Ca self-diffusion occurred within

416   diopside beginning at ~1515 K (melts at 1670 K). The enhanced mobility of Ca may represent

18

417   the onset of Ca-O bond dissociation and production of itinerant Ca. Diopside premelting begins

418   at ~1530 K (Fig. 1b) and a weak signal develops on the high frequency side of the Q^2 peak as the

419   melting temperature (1670 K) is approached (Richet et al., 1998, their Fig. 6). Its location is

420   consistent with the Q^3 band frequency in Raman spectra of Na_2SiO_3 (e.g., Fig. 3c) and its

421   presence provides evidence that a reaction equivalent to Reaction (2) occurs in the premelting

422   region of diopside. The reaction produces O^{2-} and with its presence, a reaction equivalent to

423   Reaction (3) may cause rupture of Q^2 chains and melting. Melting of diopside is, however,

424   slightly incongruent and is more complex than here portrayed.

425   Protoenstatite ($MgSiO_3$) melts congruently but metastabily at ~1816 K and demonstrates

426   a premelting region beginning at ~ 1700 K (Thiéblot et al., 1999). Thiéblot et al. (1999) note that

427   onset of premelting correlates with enhanced Mg mobility (itinerancy) implying that some Mg-O

428   bond dissociation occurs with necessary production of SiO_3^-, which in turn allows for production

429   of Q^3 cross linkages and O^{2-} production via Reaction (2). Protoenstatite may undergo melting by

430   the same mechanism as the other pyroxenes.

431   A different situation obtains for orthosilicates such as olivine, which consist of Q^0

432   species. A reaction analogous to Reaction (3) cannot occur for lack of O^{2-}. Similarly, these

433   mechanisms are inapplicable to SiO_2 polymorphs and tectosilicates in which alkalis have a very

434   low mobility as a result of their charge-compensating role for aluminum in tetrahedral

435   coordination (Richet and Mysen, 1999). These minerals do not undergo premelting, and melting

436   and precipitation are sluggish (Bourova et al., 2006; Schairer and Bowen, 1956). A surface

437   melting mechanism rather than a bulk melting mechanism has been described for quartz and

438   cristobalite (Wagstaff, 1969; Ainslie et al., 1961). These crystals lack a simple mechanism to

439   produce free oxygen thus they provide circumstantial evidence for the critical role of the anion

440   (O^{2-}) in melting and crystallization of the chain silicates.

441   **DISCUSION WITH IMPLICATIONS**

442   At the congruent melting point the fusion and crystallization reactions are by definition

443   reversible. This macroscopic reversibility implies that the mechanisms involved in the solid-

444   liquid transformation are also reversible, in agreement with the fact that the relevant constituents

445   such as Q species, itinerant cations and O^{2-} species are present in both Na_2SiO_3 crystals and

446   melts (Fig. 3). The first consequence is that determination of long-range order within growing

447   nuclei would bring little information on the actual crystallization mechanisms at play, which

448   involve instead complex, short-range order rearrangements. The second is that, even with current

449   technology, it would be a formidable task to investigate the relevant reactions and the ensuing

450   variations of short-range order within nanoscale nuclei that represent a negligible volume

451   fraction of the system at the onset of crystallization. To obviate this problem, monitoring the

452   abundances of critical species such as the Q species and O^{2-} during slow cooling of a melt might

453   be a more fruitful approach. In the favorable cases where premelting is significant, however, the

454   most straightforward way to study crystallization is to investigate instead fusion through

455   premelting and melting reactions which, their sense notwithstanding, are the same whether the

456   material is heated or cooled. Finally, the complete failure of nucleation theories to predict

457   nucleation rates, which can be 10^{20}-10^{50} times greater than observed, has been repeatedly stated

458   (Fokin et al., 2006). In this respect a major source of discrepancy could be the neglect of such

459   reactions as (1-4) rather than the roughness of the liquid-nuclei interface, variations of surface

460   energy with temperature and the size of nuclei, or initial nucleation of metastable crystals.

461   These suggestions have bearing on the other major solidification process, namely,

462   vitrification. At the glass transition, variations in second-order thermodynamic properties occur

463   when the configuration of the silicate framework becomes frozen in (Richet and Neuville, 1992).

464   By contrast the mobility of network-modifier cations, hence electrical conduction, is much less

465   affected at the transition (Bouhifd et al., 2002; Gruener et al., 2001). The experimental results for

466   the alkali metasilicate crystals point to this conclusion in that only the rates of Reactions (2) and

467   (3) involving Q species increase markedly at the onset of premelting while network-modifier

468   cations remain highly mobile across the transition.

469   That the analogy is even deeper is indicated by the role played in these reactions by five-

470   coordinate Si atoms. Activated complexes are essential to the proposed melting and

471   crystallization mechanisms and they are a key factor in the configurational rearrangements

472   involved in viscous flow (Fokin et al., 2006). Reactions of the kind described here likely

473   contribute to the configurational changes characteristic of the liquid phase, and particularly to

474   their calorimetric effects. A connection between melting and viscosity mechanisms has been

475   drawn recently (Buchenau et al., 2014) from a reformulation of Lindemann criterion (in terms of

476   shear moduli) without, however, making room for distinct reaction steps such as proposed here.

477   Insights may also be gained from theoretical and molecular dynamics simulations if they were to

478   incorporate the properties of the three types of reaction and the bonds in chain silicates (e.g., Na-

479   O, Si-NBO, Si-O in Na_2SiO_3). A consistent description of melting, crystallization and glass

480   transition seems possible, combining kinetic, thermodynamic, transport and structural properties.

481   To understand better the melting, crystallization and vitrification of silicates, chemical

482   species and their abundances should be monitored as a function of temperature above *and* below

483   melting points. Melting, crystallization and vitrification of compositionally complex silicates are

484   better addressed via chemical mechanisms and orbital hybridization (Richet and Ottonello, 2014;

485   Koroleva et al., 2013) than via mechanical mechanisms (e.g., vibrational instability).

ACKNOWLEDGMENTS

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646   **Figure Captions**

647   Fig. 1. Changes to unit cell parameters for Na_2SiO_3 and heat capacities of numerous crystals as a

648   function of temperature (T). (a) Changes to the 'a', 'b' and 'c' unit cell parameters of

649   Na_2SiO_3 as a function of T, cast as a ratios, a/a_o, b/b_o and c/c_o. The denominator

650   represents the value of the cell parameter at the lowest temperature measured. For clarity,

651   the a/a_o ratios are displaced to a lower value by 0.005 units. (b) Mean heat capacity (C_m)

652   of crystals versus T where $C_m = (H_T-H_{273})/(T-273)$ with H being heat content (Richet and

653   Fiquet, 1991). The premelting region extends from the inflection in C_m to the melting

654   point (e.g., ~1200 to 1362 K for Na_2SiO_3). Dashed curves are extrapolations of fits to the

655   C_m data, excluding measurements in the premelting range. The diopside data are

656   displaced upward by one unit. Fig. 2. Schematic of the structural consequences of

657   Reaction (1a) where two, initially separate SiO_3 chains shown in (a), undergo reaction to

658   produce a cross-chain linkage through production of a Q^3 species, as shown in (b). A

659   schematic of the activated complex is illustrated in (c).

660   Fig. 3. ^{29}Si MAS NMR and Raman spectra of Na_2SiO_3 for glass and crystal. Experimental data

661   are represented by dots in each diagram. Solid curves represent the introduced Q^1, Q^2 and

662   Q^3 species peaks. The sum of the Q species contributions are also represented by solid

663   curves. (a) NMR spectrum of the glass collected at ambient temperature. The data, fit and

664   Q species abundances are taken from Nesbitt et al. (2011). (b) Raman spectrum of the

665   glass collected at 298 K. The experimental data are represented by dots and are taken

666   from Frantz and Mysen (1995, their Fig. 9). Peak assignments and the partial fit are

667   discussed in the text. The fit is not intended to be complete but was performed solely to

668   establish the approximate locations of the major Q species peaks for comparison with

669   those of the crystal. (c) Raman spectrum of the crystal collected just below the melting

670   temperature (data from Richet et al., 1996). The fit is entirely unconstrained. Peak

671   assignments and fit are discussed in the text.

672   Fig. 4. Schematic diagram of the melting of Na_2SiO_3(c). (a) Illustrates the attack of O^{2-} on a Si

673   center to form a transition state complex (dotted oval) according to Reaction (3b). (b)

674   Schematic diagram showing the products of Reaction (3b), which are two Q^1 species

675   terminating two SiO_3 chains and destroying the chain structure to produce melt. (c) a

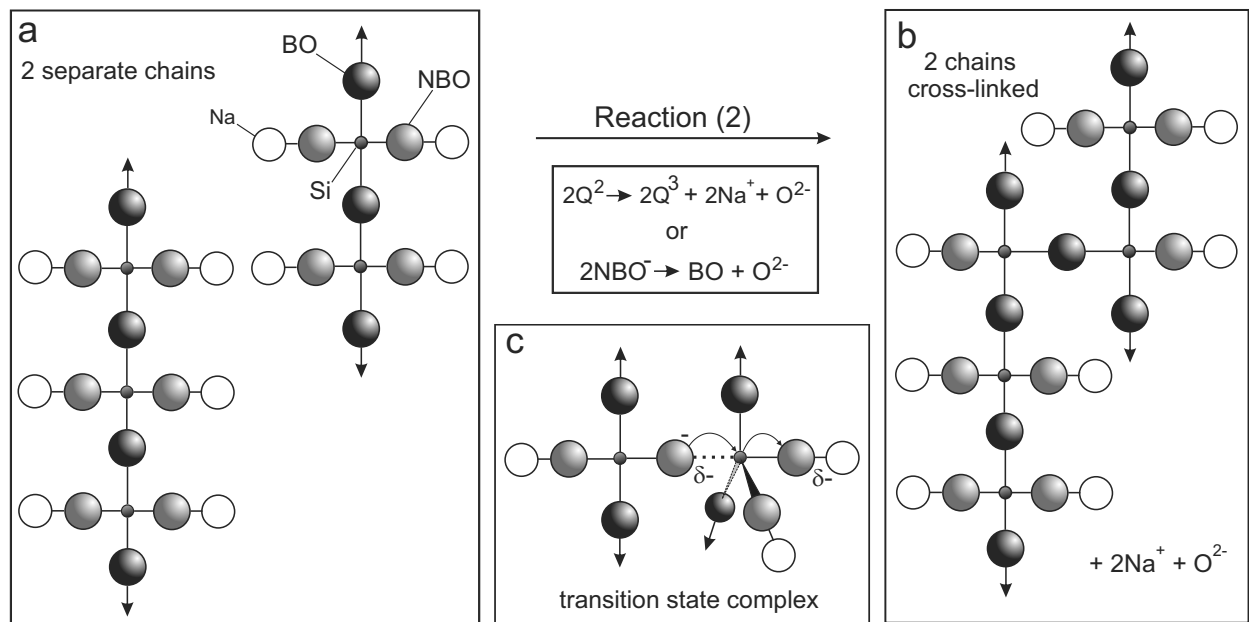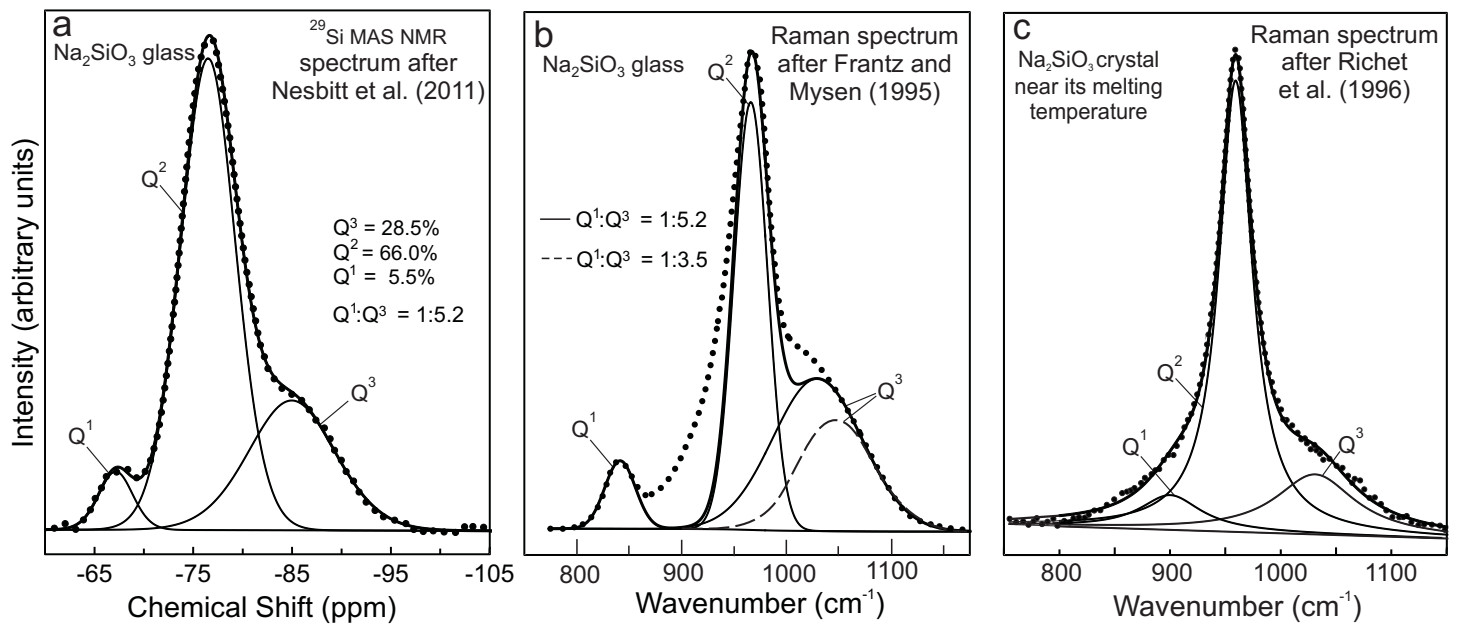676   pseudo 3-dimensional rendering of the activated complex.

30

Fig. 1

Fig. 2

Fig. 3

Fig. 4