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Defect Contributions to the Heat Capacities and Stabilities of Some Chain,

Ring and Sheet Silicates, with Implications for Mantle Minerals

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ABSTRACT

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26   At temperatures less than ~1500K, previously published C_p data demonstrate that the heat

27 capacities of orthoenstatite, proto-enstatite, diopside and pseudowollastonite include primarily

28 Debye type vibrational and anharmonic contributions whereas the alkali chain, sheet and ring

29 silicates, Na_2SiO_3, Li_2SiO_3, K_2SiO_3 and $Na_2Si_2O_5$ include a third contribution. The third

30 contribution to C_p arises from defect formation due to the mobility Na, K, Li, and O^{2-}. The

31 contribution becomes apparent at temperatures above 700-800K for Na and K silicates, and above

32 900-1000K for Li metasilicate. With strong thermal agitation, alkali-non-bridging oxygen (NBO)

33 bonds are ruptured with the cations exiting their structural sites to occupy interstitial sites, thereby

34 producing intrinsic Frenkel defects which contribute to the C_p of the alkali silicates. The

35 magnitudes of the C_p defect contributions correlate inversely with cation-oxygen bond strengths, as

36 measured by bond dissociation energies. K-O and Na-O bond strengths are weak (239 and 257

37 kJ/mol) and defect contributions are large for these alkali chain, ring and sheet silicates. The

38 greater bond strength of Li-O (341 kJ/mol) correlates with a weaker defect contribution to the C_p

39 of Li_2SiO_3. Mg-O and Ca-O bonds are stronger still (394 and 464 kJ/mol) and no C_p defect

40 contributions are observed for the pyroxenes and pseudowollastonite up to ~1500K.

41   Above ~800K a polymerization reaction occurs in Na_2SiO_3 which produces some Q^3

42 species and free oxygen (O^{2-} or oxide ion). The polymerization reaction annihilates an oxygen

43 structural site so that the O^{2-} produced must reside on non-structural sites thus producing intrinsic

44 anionic defects. The same reactions likely occur in $Na_2Si_2O_5$ and K_2SiO_3. Raman spectra of

45 Na_2SiO_3 indicate >10% of Na^+ and ~1.7% of O^{2-} on interstitial sites at 1348K.

46   Ca- and Mg-bearing mantle minerals subjected to temperature greater than ~1500K

47 experience the destabilizing effects of disordering (Frenkel defect formation). The minerals may

48 respond either by changing their composition or by changing phase. An abundance of Ca and Na

49 defects in pyroxenes, for example, likely promote production of new components (e.g., $CaAl_2SiO_6$,

50 $NaAlSi_2O_6$) in pyroxenes. By their production, Ca and Na defect concentrations are reduced

51 thereby stabilizing the phases. Mg-O bond dissociation and production of intrinsic Mg^{2+} and O^{2-}

52 point defects within olivine likely destabilize it and promote the phase transition to wadsleyite at

53 the base of the upper mantle.

54 **Keywords:** heat capacity of silicate minerals, Frenkel defects in silicates, Cation Disorder, Silicate
55 mineral stability, stability of mantle minerals
56

57   **INTRODUCTION**

58   Richet et al. (1996) compared the temperature dependence of the heat capacities (C_p) of the

59 isostructural chain silicates Li_2SiO_3(c) and Na_2SiO_3(c), and noted that C_p of Na_2SiO_3(c) was

60 consistently greater than that of Li_2SiO_3(c), regardless of temperature. The differing values below

61 ~600K may be due to different Debye Temperatures (θ) of the phases because θ affects mostly the

62 low temperature C_p values of a phase. At higher temperatures, θ values have minimal effect on

63 heat capacity at constant volume (C_v), or on C_p, in that C_v approaches the universal value of 3nR

64 regardless of θ values. Richet et al. (1996) explored these differences at both low and high

65 temperatures using sophisticated C_p models (e.g., Kieffer, 1982; 1980), which included

66 anharmonic effects, and they summarized the situation by stating that the excess C_p of Na_2SiO_3

67 remained unexplained. We address this conundrum by evaluating previously published

68 contributions to C_p of eight chain, ring and sheet silicates, orthoenstatite ($MgSiO_3$), proto-enstatite

69 ($MgSiO_3$), diopside ($MgCaSi_2O_6$), pseudowollastonite ($CaSiO_3$), Na_2SiO_3, $Na_2Si_2O_5$, K_2SiO_3 and

70 Li_2SiO_3. All crystals contain Q^2 species (silicate chains or rings) except $Na_2Si_2O_5$ which is a sheet

71 silicate consisting of Q^3 species (where Q represents a Si tetrahedron and the superscript indicates

                                                      3

72   the number of bridging oxygen atoms bonded to the central Si atom of the tetrahedron).

73   Cations of some crystals, heated to high temperature, may become mobile through rupture

74   of oxygen-cation bonds (e.g., Nesbitt et al., 2017; George et al., 1998) thereby contributing to

75   disorder by forming intrinsic defects (e.g., Frenkel defects). There is overwhelming evidence for

76   high temperature alkali and alkaline earth cation disorder in chain and ring silicates (Courtial et al.,

77   2000; Thiéblot et al., 1999; Richet et al., 1998, 1996, 1993; George et al., 1998; Dimanov and

78   Jaoul, 1998; Dimanov and Ingrin, 1995). George et al. (1998), for example, conducted a study of

79   Na_2SiO_3 and Li_2SiO_3 by collecting ^{7}Li, ^{23}Na and ^{29}Si NMR spectra as a function of temperature.

80   The study indicated limited Li mobility at high temperature. For Na_2SiO_3, motional averaging

81   commenced at ~700-800K and at ~900-1000K, Na^+ was sufficiently mobile to behave in a liquid-

82   like, disordered manner, residing on both structural and non-structural sites (George et al., 1998).

83   Recently, Nesbitt et al. (2017) emphasized that Na^+ and O^{2-} disorder occurred in Na_2SiO_3 crystals

84   at temperatures as low as 700-800K, and well *before* the premelting region of the crystal was

85   encountered (Fig. 1a).

86   An appreciation for the problem to be addressed is gained by plotting C_p of Na_2SiO_3 against

87   temperature (Fig. 1a). Three sets of C_p data are plotted and they are reasonably consistent

88   (addressed subsequently). An obvious aspect is the rapid increase in C_p within the premelting

89   region (e.g., Richet et al., 1994) beginning at ~1200K. A less obvious aspect is the almost linear

90   increase in C_p between ~400K and ~1200K, the slope of which is appreciably steeper than

91   expected considering that the rule of Dulong and Petit (Slater, 1963) requires the heat capacity to

92   reach a high temperature limit of 3nR (~149 $Jmol^{-1}K^{-1}$ for Na_2SiO_3). To emphasize this aspect, C_p

93   of Na_2SiO_3 has been normalized to the number of atoms 'n' in the formula unit (n=6 for Na_2SiO_3)

94   to yield a "normalized C_p" (i.e., C_p/n). The normalized experimental data are plotted against

95   temperature in Figure 1b as is the heat capacity (C_v) calculated using the Debye Function where

96   the Debye Temperature (θ) = 750K (Fig. 1b, dashed curve and Table 1). The Debye Function (i.e.,

97   C_v) reproduces reasonably well the normalized C_p data in the range 300K to 600K but C_v deviates

98   from experiment between ~700K and 1200K. It may result from anharmonic contributions to C_p

99   but Richet et al. (1996) concluded that C_v and anharmonic contributions alone cannot account for

100   the discrepancy. We address this discrepancy and attempt to explain it.

101   **THERMODYNAMICS ASPECTS**

102   Heat capacity includes at least two major contributions between ~300K and the premelting

103   region of a crystal. One is the heat capacity at constant volume (C_v or Debye Function) which

104   derives from the 'Debye elastic continuum' (Ghose et al., 1991; Keifer, 1980; Debye, 1912; Born

105   and von Kármán, 1912; Einstein, 1907). Anharmonic contributions constitute the second

106   contribution arising from the nature of site potentials within a crystal, which give rise to thermal

107   expansion. The two contributions allow calculation of C_p according to:

108            $C_p = C_v + [\alpha_V^2 V/\beta)]T$ (1)

109   where V is the volume of the phase, α_V is the volume coefficient of thermal expansion, β is the

110   compressibility and T is temperature. With V, α and β of a crystal known, the anharmonic term,

111   $([\alpha_V^2 V/\beta)]T)$, can be evaluated and C_p calculated as a function of temperature (provided C_v is

112   known). Equation (1) can be simplified using a relationship elucidated by Grüneisen (1912; 1926):

113            $\alpha_V V/\beta = \gamma C_v$ (2)

114   where γ is the thermal Grüneisen parameter (Slater, 1963, p. 238). Substitution of Equation (2) into

115   Equation (1) and rearrangement yields:

116            $C_p = (1 + \alpha_V \gamma T)C_v$ (3)

117   Estimates of the Grüneisen parameter for chain silicates range from 0.88 to 1.3 (Table 2; see also

                                             5

118   Angel and Jackson, 2002) with the average value being 1.1 (n = 7, σ = 0.15). The average is used

119   in subsequent calculations. The γ parameter is largely independent of temperature (Slater, 1963, p.

120   219) and is similar for all silicates studied here (Angel and Jackson, 2002; Hofmeister and Mao,

121   2002; Ita and Stixrude, 1992; Jeanloz and Thompson, 1983).

122   The volume of crystalline Na_2SiO_3 is illustrated in Figure 2a where the solid circles

123   represent volumes from 298 to ~1200K and the open circles represent measurements within the

124   premelting region. A linear least squares best fit to the solid circles was performed and the fit is

125   plotted on the figure. The slope, (dV/dT) is effectively constant at $~1.43 \times 10^{-2}$ ($Å^3$/K). The

126   coefficient of thermal expansion is defined as:

127           $\alpha_V = (dV/dT)_p/V$ (4)

128   where 'p' denotes constant pressure. Because dV/dT is effectively constant, calculation of α_V

129   requires only that it be divided by V at the temperature of interest. The resulting α_V values for

130   Na_2SiO_3 are plotted on Figure 2b and α_V is effectively linear in T. The same procedure was used to

131   obtain α_V for other crystals studied and the results are illustrated in Figures 2c to 2f.

132   Accurate calculation of C_v for silicate crystals is complex (e.g., Ghose et al., 1991; Keiffer,

133   1982; 1980) but as noted in the Introduction, reasonable estimates of C_v can be obtained using the

134   Debye Function or a modification of it. The Debye Function (e.g, Table 1) employs only one

135   adjustable parameter, the Debye Temperature (θ), which can be evaluated from elastic or other

136   properties of the crystal (Grimvall, 2001). In the approach used here, the Debye Temperature is

137   treated as a fit parameter. To obtain approximate C_v values for a crystal, the Debye Temperature is

138   adjusted to provide a good fit to the heat capacity *in a specified temperature range* (here 300-600

139   K). The same θ value necessarily yields reasonable estimates of C_v at high temperature because the

140   Debye Function (C_v) approaches 3nR regardless of the value of θ. Treating θ as a fit parameter has

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141   the advantage that the calculation of C_v may accommodate other moderate temperature lattice

142   contributions such as some optical modes (Ghose et al., 1991; Kieffer, 1980). Highly accurate

143   estimates of C_v are not required for this exercise, and the Debye Function is used to calculate C_v.

144   **CALCULATED AND EXPERIMENTAL C_P DATA**

145   **Orthoenstatite and Proto-enstatite**

146   Three sets of experimental C_p data are plotted on Figure 3a. The large open and shaded

147   circles represent, respectively, C_p of orthoenstatite and proto-enstatite. The values are derived from

148   relative enthalpies (heat contents) reported by Thiéblot et al. (1999). They measured the heat

149   evolved upon cooling a sample from a temperature T to a reference temperature (T* = 273 K). The

150   heat evolved is the *difference* in enthalpy (H) at the two temperatures (H_T - H_{T*}). A finite

151   difference approach was used to estimate an average C_p (i.e., $C_p(av)$) over the temperature range of

152   any two measurements. Subtracting two heat content measurements (one at T_2 and one at T_1)

153   yields ($H_{T2} - H_{T1)}$ and dividing it by the difference in the two temperatures ($T_2 - T_1$) gives $C_p(av)$:

154     $$C_p(av) \; = \; (H_{T2} - H_{T1})/(T_2 - T_1) \; = \; \Delta H/\Delta T \tag{5}$$

155   The $C_p(av)$ value represents the average C_p over the interval T_1 to T_2 and may be plotted on Fig. 3

156   at $T(av) = (T_2 - T_1)/2$. T_1 need not be T* and may be any temperature at which a heat content

157   measurement has been made. The original relative enthalpies of Thiéblot et al. (1999) for

158   orthoenstatite and proto-enstatite are reproduced in Table 3 and were used to calculate $C_p(av)$,

159   which were, in turn, normalized to 'n' to obtain $C_p(av)/n$ (n=5 for $MgSiO_3$). Heat capacities

160   derived from relative enthalpies commonly are of lower precision than those obtained by other

161   techniques due to subtraction of two large numbers. The resulting values are, however, devoid of

162   assumptions and propagation of errors, and may be more accurate than techniques which include

163   assumptions and propagation of errors. Use of $C_p(av)$ to approximate C_p introduces minimal

164 uncertainty in C_p above about 700K, as now shown. The average value of T_2-T_1 of Table 3 is

165 ~100K so that the temperature range associated with each $C_p(av)$ is about $\pm 50K$. Uncertainty of

166 this magnitude does not affect the conclusions drawn subsequently.

167 The small circles of Figure 3a represent experimental $C_p(av)/n$ values for a synthetic

168 orthoenstatite. The large open and shaded circles represent $C_p(av)/n$ data for orthoenstatite and

169 proto-enstatite, respectively. The small and large circles merge between ~450K and 800K,

170 substantiating the accuracy of both sets of data. There is a group of measurements between 850K

171 and 1000K (Fig. 3a, small circles) which is offset to slightly greater C_p values relative to the other

172 data. These 'offset' data are not considered in the following discussion.

173 A Debye Temperature of 875K was used to calculate C_v for both enstatites and C_v is plotted

174 in Figure 3a as the dashed curve. The expression for α_V provided in Figure 2c and the Grüneisen

175 parameter (=1.1) were employed to calculate C_p according to Equation (3). The result is illustrated

176 by the solid curve of Figure 3a. The solid curve reproduces (within experimental uncertainty) the

177 orthoenstatite and proto-enstatite experimental values up to ~1650K and the difference between the

178 solid curve and the dashed curve represents the anharmonic contribution to C_p. Clearly there are

179 only two major contributions to C_p of the enstatites between ~300K and the premelting region of

180 proto-enstatite. Moreover, the α_V and Grüneisen parameter used in the calculations are reasonable

181 for both enstatites. Finally, the conformity of the calculated and experimental C_p values indicates

182 that the Debye Function provides reasonable estimates of C_v for the enstatites.

183 **Diopside**

184 Two sets of experimental C_p data for diopside ($CaMgSi_2O_6$) are plotted on Figure 3b and

185 they merge smoothly. With a Debye Temperature of 900K, the α_V expression of Figure 2b and a

186 Grüneisen parameter of 1.1, the C_p values for diopside were calculated (Eq. 3) and plotted as the

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187   solid curve of Figure 3b. The solid curve conforms closely to the experimental data up to ~1500K,

188   beyond which premelting and Ca disorder commences (Dimanov and Jaoul, 1998; Richet et al.,

189   1998; Dimanov and Ingrin, 1995; Richet et al., 1994; Richet and Fiquet, 1991). As for

190   orthoenstatite and proto-enstatite, there are two major contributions to the C_p of diopside, C_v and

191   an anharmonic contribution. Diopside is structurally different from the enstatite polymorphs but

192   the same Grüneisen parameter (1.1) allows reasonable estimates of C_p for the three crystals.

Pseudowollastonite

194   The C_p/n (n= 5) values calculated for two sets of experimental data are plotted on Figure

195   3c. The C_v of pseudowollastonite ($CaSiO_3$) was calculated with θ = 900K and plotted on Figure 3c

196   (dashed curve). The expression for α_V (Fig. 2f) and a Grüneisen parameter = 1.1 were used to

197   calculate the effect of anharmonicity (Eq. 3) and the solid curve represents the result. The essential

198   agreement between experiment and calculation indicates that within the temperature range ~300K

199   to ~1500K, its C_p includes only C_v and anharmonic contributions. The Grüneisen parameter for the

200   pyroxenes and this ring silicate are effectively the same, demonstrating that structural variability

201   has no appreciable effect on the parameter.

Li_2SiO_3

203   The crystal is an orthorhombic chain silicate with Si_2O_6 chains linked by LiO_4 polyhedra

204   (Hesse, 1977). Experimental $C_p(av)/n$ values (n = 6) of Téqui et al. (1992) are plotted on Figure 3d

205   (open circles). The C_v contribution was calculated with θ = 950K (Fig. 3d, dashed curve) and C_p

206   was calculated (Eq. 3) with α_V given in Figure 2e and a Grüneisen parameter = 1.1 (Fig. 3d, solid

207   curve). It conforms to the experimental data between ~500K and ~700K but systematically

208   underestimates C_p at 900K and greater temperatures. There are three likely reasons for the

209   discrepancy; the value for α_V or C_v is incorrect at high temperature, or γ is greater than 1.1. An

210   incorrect α_V is unlikely in that it was accurately measured and behaves systematically with

211   temperature (Fig. 2e). That C_v would be incorrect at temperatures greater than ~900K also seems

212   unlikely because all C_v values tend toward the same 3nR limit (i.e., θ has little effect on C_v at high

213   temperature). This leaves the Grüneisen parameter. An extreme value of 1.3 was adopted for the

214   Grüneisen parameter (Table 2) and C_p was recalculated with the results plotted as a dotted curve

215   on Figure 3d. The C_p discrepancy is diminished but nevertheless remains at temperatures greater

216   than ~1000K. Noting that $\gamma = 1.1$ for the previously treated metasilicates, there is no reason to

217   expect a different value for Li_2SiO_3 and we suggest that there is a third, weak contribution to C_p of

218   Li_2SiO_3 at high temperature. We return to this aspect subsequently.

219   **Na_2SiO_3**

220   Na_2SiO_3 is a chain silicate isostructural with Li_2SiO_3. The crystal undergoes a polymorphic

221   transition (from *Cmc* 2_1 symmetry to *Pmc* 2_1 symmetry) at ~850K involving Na-O polyhedra but

222   the Q^2 chains are unaffected (Richet et al., 1996). Heat content data from three sources are plotted

223   on Figure 3e. Naylor (1945) used T* = 298.15 whereas Richet et al. (1984) used T* = 273.15 and

224   their different procedures resulted in a systematic difference in $C_p(av)$. To standardize the data,

225    $C_p(av)$ was calculated for both sets of data and the difference between them was 15 $Jmol^{-1}K^{-1}$ at

226   ~1080K. The Richet et al. (1984) $C_p(av)$ values were increased by this amount making the two sets

227   of data remarkably consistent (Fig. 3e). They are also consistent with those reported by Kelley

228   (1960).

229   Na_2SiO_3 C_v values were obtained using $\theta = 750K$ (Fig. 3e, dashed curve) and C_p was

230   calculated via Equation (3) using α_V provided in Figure 2b and a Grüneisen parameter = 1.1. (Fig.

231   3e, solid curve). The calculated and experimental C_p values are consistent between ~300 and

232   ~700K but they diverge beyond ~700K. At ~1200K the C_p discrepancy is ~15% relative to the

233   experimental value. There is no obvious effect on C_p at the polymorphic transition (~850K) as

234   shown in Figures 2b or 3e so that any effect of the transition on C_p is within experimental

235   uncertainty. It is concluded that there is a third contribution to the C_p of Na_2SiO_3 with onset at

236   ~700K and this contribution increases systematically with temperature.

237   **K_2SiO_3**

238   K_2SiO_3, like pseudowollastonite, consists of three-membered rings (Si_3O_9), with potassium

239   polyhedra linking them to produce a monoclinic unit cell (Werthmann and Hoppe, 1981). The heat

240   contents of Beyer et al. (1979) were employed to calculate $C_p(av)/n$ values and these are plotted on

241   Figure 3f (crosses). The results mimic the experimental data for Na_2SiO_3 (Fig. 3f, circles). The

242   melting temperature of K_2SiO_3 is 1195K and the $C_p(av)/n$ experimental datum point at 1150K is

243   much greater than the value at 1100K, which may indicate a premelting region for K_2SiO_3. A $\theta_D =$

244   750 was employed to calculate C_v of the crystal and it fits reasonably the $C_p(av)/n$ experimental

245   result at ~500K (Fig. 3f) but underestimates $C_p(av)/n$ at greater temperatures. No value for α_V was

246   found for K_2SiO_3 so that C_p could not be calculated and the α_V value of Na_2SiO_3 was used as a

247   proxy, yielding the solid curve of Figure 3f. The agreement with the experimental data in the range

248   ~450-700K indicates that the α_V proxy is reasonable but the calculated C_p/n values underestimate

249   experimental values at temperatures greater than ~700K. No reasonable value of α_V can reproduce

250   the experimental data at high temperature and apparently there is a third contribution to C_p of

251   K_2SiO_3 which is similar in character and magnitude to that of the Na_2SiO_3 C_p discrepancy.

252   **EXPLANATION FOR C_p DISCREPANCIES**

253   **Introduction**

254   Free translation of atoms through crystals is unlikely and electronic contributions to C_p of

255   insulators are similarly unimportant in the temperature range ~300K to 1500K (Slater, 1963; Borg

256   and Dienes, 1992). Substitutional disorder resulting from exchange of cations on different

257   structural sites is also impossible for Na_2SiO_3, K_2SiO_3, $Na_2Si_2O_5$ or Li_2SiO_3 unless Si sites are

258   involved, which is highly unlikely. The C_p discrepancies observed for these alkali-bearing crystals

259   therefore arise from other contributions. Heat capacity is the sum of numerous internal and

260   configurational contributions (Grimvall, 2001):

261          $C_p(crystal) = C_p(vibration) + C_p(defect) + C_p(rotation) + C_p(libration)$ (6)

262   Lattice vibrations and anharmonic contributions are here accounted for by Equation (3). There are

263   no structural changes to Li_2SiO_3 or K_2SiO_3 from 298K to their premelting regions, hence there is

264   no contribution to their C_p resulting from polymorphism. Na_2SiO_3 undergoes a transition at ~850K

265   from orthorhombic (*Cmc* 2_1) to a lower symmetry, possibly *Pmc*2_1 (Richet et. al., 1996). There is,

266   however, no discontinuity evident in the C_p trend at this temperature (Fig. 3e) so that any resulting

267   C_p contribution is within the uncertainty associated with the measurements of C_p. The effects of

268   dislocations on C_p are well known to experimentalists, and care special is taken to avoid samples

269   with high dislocation densities through sample selection and treatment (e.g., Richet et al., 1996;

270   Naylor, 1945). This leaves configurational contributions such as point defects and rotation/libration

271   as the most likely causes of the C_p discrepancies.

272   Whether intrinsic defect formation or rotation/libration contributions are responsible for the

273   C_p discrepancies can be assessed by reference to crystalline $Na_2Si_2O_5$, a sheet silicate consisting of

274   Q^3 species. Naylor (1945) reports $Na_2Si_2O_5$ heat contents from which $C_p(av)/n$ values were

275   calculated and the results are plotted on Figure 4 (filled circles). The $C_p(av)/n$ data for Na_2SiO_3 are

276   also plotted (Fig. 4, open and shaded circles). The $Na_2Si_2O_5$ and Na_2SiO_3 experimental data are

277   effectively coincident from ~300K to ~1000K and the Debye Function reproduces well the

278   experimental C_p data for $Na_2Si_2O_5$ between 300 and 600K with $\theta_D = 750$ (Fig. 4, dashed curve).

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279   The anharmonic contribution to C_p of $Na_2Si_2O_5$ could not be calculated for lack of a α_V value and

280   the Na_2SiO_3 value (Fig. 2b) was used as a proxy to obtain the solid curve of Figure 4. The C_p/n vs.

281   T trend described by the $Na_2Si_2O_5$ experimental data is too steep to be accounted for by Equation

282   (3) using a reasonable value for α_V. We conclude that $Na_2Si_2O_5$ displays a C_p discrepancy of the

283   same magnitude as that for Na_2SiO_3.

284   The structures of the two crystals are different (chain vs sheet) and the Q^2 and Q^3 tetrahedra

285   of the respective crystals should make different rotational or librational contributions to C_p due to

286   their different linkages. There is, nevertheless a remarkable similarity in the C_p of the two crystals

287   and in their C_p discrepancies. We conclude that rotation and libration are unlikely to be responsible

288   for the similarities in their C_p discrepancies. Instead, the essentially coincidence of the $Na_2Si_2O_5$

289   and Na_2SiO_3 C_p trends relate to their common cation, and specifically to intrinsic cation defect

290   formation in both phases. Although rotation and libration occur in some silicates (Voronko et al.,

291   2006; George et al., 1998; Ghose et al., 1986; Massa et al., 1983) defect formation is the cause of

292   C_p discrepancies in these crystals.

293   **Cation Mobility, Disorder and Relationship to C_p**

294   **Li Mobility in Li_2SiO_3.** There is experimental evidence for Li mobility in Li_2SiO_3 where

295   subjected to strong thermal agitation. George et al. (1998) conclude from their ^{7}Li NMR results

296   that: "Li^+ site hopping is clearly observed in Li_2SiO_3 by a partial averaging of the [7]Li quadrupolar

297   peak shape, requiring exchange among a few, ordered orientations of LiO4 tetrahedra". Clearly, Li

298   is not sufficiently mobile, even at 1420K, to have a completely averaged, isotropic environment.

299   With Li-O bond dissociation at high temperature, the majority of mobile Li^+ alight on previously

300   vacated structural sites and re-establish Li-O bonds, which results in no net change to C_p. The

301   spectroscopic results do not preclude, however, a small fraction of mobile Li^+ from having

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302   alighted, fleetingly, on interstitial sites to form a few intrinsic (Frenkel) defects. The fraction

303   should increase with temperature as more Li become mobile.

304   **Na Mobility in Na_2SiO_3.** George et al. (1998) observe that Na is strongly mobile in

305   Na_2SiO_3 at high temperatures. Quoting George et al. (1998): "From ^{23}Na NMR results, Na^+ site

306   hopping in Na_2SiO_3 appears to involve a more liquid-like behavior, implying exchange among

307   many sites with different orientations in a disordered fashion". The disordering probably results

308   from a fraction of mobile Na^+ alighting on interstitial sites to create intrinsic Frenkel defect pairs,

309   as observed for Ca^{2+} in diopside and pseudowollastonite (see next section). These defects increase

310   the C_p of the crystal in proportion to the number of mobile ions at any instant.

311   Insight into the high temperature 'liquid-like' behaviour of Na^+ in Na_2SiO_3 may be gleaned

312   by analogy with Na^+ behaviour in Na-silicate glass. Although there is some ambiguity in

313   distinguishing different types of cationic sites in the glass, Cormack et al. (2002) nevertheless

314   distinguish 'cationic sites' from more energetic 'transitional sites', the distinction being dependent

315   on the residence time of the cation on each type of site. Consider, in an energetic sense, the

316   'cationic sites' of the glass to be analogous to the cationic structural sites of the crystal and the

317   'transitional sites' of the glass to be analogous to interstitial sites of the crystal. Cormack et al.

318   (2002) note that Na^+ of the glass mostly occupies 'cationic sites', but during transit from one

319   cationic site to another, the cation may occupy, fleetingly, 'transitional sites' (i.e., in Fig. 5 of

320   Cormack et al., 2002; the Na^+ atom in cation site 1 migrates to a transitional site with its 3rd step).

321   The potential energy minima of 'transitional sites' almost certainly are shallower than the minima

322   of the 'cationic sites'. Occupation of 'transitional sites' consequently increases C_p of the glass by

323   an amount proportional to the number of transitional sites occupied at any instant, just as

324   occupation of interstitial (defect) sites in the crystal increases its C_p in proportion to the number of

325   defects present at any instant.

326   **Ca Mobility in Diopside and Pseudowollastonite.** There is very strong experimental

327   evidence for Ca mobility in diopside and pseudowollastonite at temperatures greater than ~1500K

328   (Bouhfid et al., 2002; Dimanov and Jaul, 1998; Dimanov and Ingrin, 1995). Based on Rutherford

329   Backscattering analysis Dimanov and Ingrin (1995) observed a high temperature intrinsic diffusion

330   regime in diopside which "takes place near the onset of premelting as detected in calorimetric

331   measurements and can be interpreted in terms of enhanced formation of Frenkel defects". The

332   premelting region commences at 1500-1600K. These results were confirmed by Dimanov and Jaul

333   (1998) who also concluded that Ca self-diffusion may involve Ca-Frenkel point defects. The

334   Raman and conductivity experiments of Bouhfid et al. (2002) demonstrated the mobility of Ca in

335   both pseudowollastonite and gehlenite, where mobility of Ca in the two phases occurs at

336   temperatures greater than ~1500K. The Ca-Frenkel defects formed will contribute to the C_p of

337   these crystals but only at temperatures above ~1500K (i.e., in their premelting regions).

338   **C_p Discrepancies and Cation-O Bond Strengths**

339   The mobility of cations and the abundance of intrinsic cation defects increase with

340   temperature because thermal agitation promotes rupture of cation-oxygen bonds. There may be,

341   therefore, a relationship between cation-oxygen bond dissociation energies, cation mobility, defect

342   formation and C_p-discrepancies. K-O and Na-O bond dissociation energies are weak at 239 kJ/mol

343   and 257 kJ/mol respectively whereas the Li-O bond is somewhat stronger at 341 kJ/mol (Speight,

344   2005). The alkaline earth-oxygen bond dissociation energies are stronger still, ranging between

345   394 and 563 kJ/mol. From these values we conclude that dissociation of K-O and Na-O bonds

346   should occur at comparatively low temperatures, Li-O dissociation at somewhat greater

347   temperature and Mg-O and Ca-O bond dissociation should occur at still greater temperatures. The

348   Na and K metasilicate and disilicate C_p discrepancies commence at ~700-800K and their C_p

349   discrepancies are the most pronounced (Figs. 3, 4). The Li metasilicate C_p discrepancy (Fig. 3d)

350   commences at greater temperature (900-1000 K), and it is less pronounced than the discrepancies

351   for Na and K silicates (Figs. 3d 3e, 3f). Finally, no C_p discrepancies are apparent up to 1500K for

352   the alkaline earth metasilicates (Figs. 3a, 3b, 3c). Bond dissociation energies correlate well with

353   the temperatures at which C_p discrepancies are initiated and with the strength of the discrepancies.

354   We propose that bond dissociation, resulting from strong thermal agitation, promotes cation

355   mobility, cation (Frenkel) defect formation and production of the C_p discrepancies of the alkali

356   metasilicates (Figs. 3 and 4). The same order of bond strength ($K_2O<Na_2O<Li_2O<MgO/CaO$) is

357   obtained from Coulombic interaction considerations using effective ionic radii (Huheey et al.,

358   1993, Chap. 4).

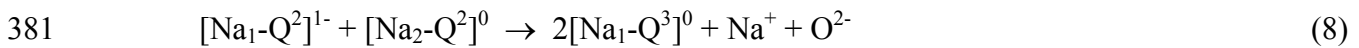359   **Reactions Producing Defects and C_p Discrepancies**

360   **Cationic Defects.** We have concluded that Na-NBO bond dissociation is observed in

361   crystalline Na_2SiO_3 above ~700-800K (se also Nesbitt et al., 2017) and the reaction proceeds

362   according to:

363        $[Na_2\text{-}Q^2]^0 \rightarrow [Na_1\text{-}Q^2]^{1-} + Na^+$ (7)

364   where $[Na_2\text{-}Q^2]^0$ is a Q^2 species with a Na atom bonded to each NBO, and $[Na_1\text{-}Q^2]^{1-}$ represents a

365   Q^2 species where one NBO has no associated Na atom. With NBO-M bond dissociation, the cation

366   (M) vacates its structural site and migrates to a non-structural (interstitial) site. The escape of Na^+

367   from a structural site creates a vacancy, and together with the occupation of a non-structural site,

368   creates a *Frenkel* defect pair. Creation of these defects increases the C_p of the crystal (i.e., the C_p

369   discrepancy) and consequently increases the entropy of the crystal (Courtial et al., 2000; Richet et

370   al., 1998; Dimanov and Ingrin, 1995). These contributions are *configurational* in nature, and are a

371   major contributor to the C_p discrepancies observed in Figures 3d, 3e, 3f and 4. The cation defects

372   must be located between the Q^2 chains thus weakening forces binding the chains together.

373   **Anionic Defects.** With formation of a $[Na_1\text{-}Q^2]^{1-}$ moiety via Reaction (7), the tetrahedron

374   becomes 'unpinned' at its NBO⁻ apex (i.e., the apex with no associated Na^+). Due to thermal

375   agitation it may undergo librations different from, and more severe than, 'pinned' $[Na_2\text{-}Q^2]^0$

376   moieties. George et al. (1998) corroborate the effects of thermal agitation, noting that there is

377   "some kind of extensive, librational motion of SiO_4 tetrahedral" in crystalline Na_2SiO_3 at high

378   temperature. As emphasized by Nesbitt et al. (2017), the $[Na_1\text{-}Q^2]^{1-}$ moiety produced by Reaction

379   (7) is a nucleophile which may attack Si centers of Q^2 species resident on adjacent chains. The

380   reaction produces Q^3 species ($[Na_1\text{-}Q^3]^0$) according to:

381        $$[Na_1\text{-}Q^2]^{1-} + [Na_2\text{-}Q^2]^0 \rightarrow 2[Na_1\text{-}Q^3]^0 + Na^+ + O^{2-} \tag{8}$$

382   where O^{2-} is free oxygen or the oxide ion (Nesbitt et al., 2017, their Rxn 2b). The presence of Q^3

383   species in the Raman spectra of Na_2SiO_3 confirms that Reaction (8) occurs at temperatures as low

384   as 774K (Richet et al., 1996). The O^{2-} produced must also form anionic Frenkel pairs because

385   Reaction (8) annihilates a tetrahedral oxygen site through formation of BO. Wherever O^{2-} alights it

386   will occupy an interstitial site. It may reside on sites with weak potential energy minima associated

387   with cationic polyhedra (located between Q^2 chains) or it may react with other moieties of the

388   crystal, as discussed in the next paragraph. The abundance of cationic Frenkel defects is at least

389   double the abundance of anionic Frenkel defects (see Eqns. 7 and 8)

390   The strong nucleophile, O^{2-}, is a highly reactive, strong nucleophile and some O^{2-} may

391   attack Q species to produce Si-pentahedra (SiO_5) such as observed in alkali silicate glasses and

392   melts (e.g., Berezhnoi and Boiko, 2005; Stebbins, 1991). The SiO_5 moiety then becomes the

393   defect. At high temperatures the lifetimes of all Si tetrahedra are short (Farnan and Stebbins, 1990)

17

394   as will be the lives of the SiO_5 moieties. The activation energy associated with formation of the

395   SiO_5 moiety may inhibit its production at low temperatures. Nevertheless, the anionic defects O^{2-}

396   or SiO_5 necessarily contribute to C_p(config.).

397   **Defects in Other Alkali Silicate Crystals.** The K-O bond dissociation energy is less than

398   that of Na-O so that reactions equivalent to (7) and (8) likely occur in crystalline K_2SiO_3 (and

399    $K_2Si_2O_5$). By analogy with Na-NBO bond dissociation in Na_2SiO_3, K-NBO dissociation should

400   occur at ~700-800K with intrinsic cationic point defects forming in the K-silicate crystals, thus

401   explaining the C_p deficiency observed in Figure 3f. The Li-O bond strength is greater than Na-O

402   bond strength so that Li cation point defect formation should be inhibited in Li_2SiO_3 relative to

403   Na_2SiO_3. The prediction holds in that Li_2SiO_3 displays a weaker C_p discrepancy than Na_2SiO_3 and

404   the discrepancy is restricted to higher temperatures, commencing at ~900-1000K (Fig. 3d). There

405   is no evidence that Reaction (2) occurs in Li_2SiO_3 (Richet et al., 1996), hence there is no evidence

406   for appreciable O^{2-} disorder in Li_2SiO_3. Finally, based on Na disorder in Na_2SiO_3, Na-O bond

407   dissociation and cation defects formation probably occurs in $Na_2Si_2O_5$ above ~700K, accounting

408   for the C_p discrepancy observed in Figure 4.

409   **Defect Abundances in Na_2SiO_3**

410   Creation of Q^3 species via Reaction (2) annihilates Na and O structural sites and the

411   displaced atoms must reside on other sites, here considered 'defect' sites. Production of Q^1 species

412   creates new Na and O structural sites by establishment of additional Si-NBO-Na moieties (Nesbitt

413   et al., 2017, their Reaction 3). The 1348K Raman spectrum of Na_2SiO_3 collected by Richet et al.

414   (1996) was fit by Nesbitt et al. (2017) to obtain ~10% Q^1 species, ~68% Q^2 species and ~22% Q^3

415   species. These Q species abundances were used to calculate the abundance of O^{2-}, yielding ~1.7

416   mol% O^{2-} or X_{O2-} = 0.017 (see Sawyer et al., 2015, Appendix A for calculation). Considering that

417 there are 3 moles of O per unit formula, there exists 0.051 (3x0.017) moles of O^{2-} in the crystal.

418 Reactions (7) and (8) combined indicate twice the moles of 'defect' Na (i.e., Na*) as O^{2-}, requiring

419 0.102 moles of Na* in the crystal at 1348K. But there are two moles of Na per unit formula so that

420 X_{Na*} = 0.051. Richet et al. (1996) also collected and fit Na_2SiO_3 Raman spectra at 1217K and

421 965K. Q^1 species were absent and Q^3 species were present at ~10% and ~5% respectively (visual

422 estimates), indicating that X_{Na*} ~0.025 and X_{O2-} ~0.016 at 1217K, and X_{Na*} ~0.012 and X_{O2-}

423 ~0.008 at 965K. The Q^3 signal is undetectable in Raman spectra below 774K (Richet et al., 1996),

424 the implication being that Na* and O^{2-} are negligible below this temperature.

425   Reaction (7) creates a cationic vacancy and interstitial site (i.e., a Frenkel pair) whereas

426 Reaction (8) annihilates a cationic site by a different mechanism (Nesbitt et al., 2017). Thus the

427 abundance of Frenkel pairs is that produced by Reaction (7), which represents half the X_{Na*}

428 calculated in the previous paragraph. The values of X_{Na*} therefore were halved to obtain the

429 number of Frenkel pairs produced by Reaction (7) and these are plotted on Figure 5 (solid circles).

430 The equation appropriate to prediction of Frenkel pairs is (Borg and Dienes, 1992):

431     $$Ln(X_{Na*}) = -E*/(2RT) \tag{3}$$

432 where E* is the energy required to create the vacancy site-interstitial site pair, R is the gas constant

433 and T is temperature (K). With E* = -84560 J/mol, the calculated increase in X_{Na*} as a function of

434 temperature is illustrated by the solid curve (Fig. 5), which agrees reasonably with the

435 experimental values at 965K, 1217K and 1348K (Fig. 5, solid circles). The calculation indicates

436 that X_{Na*} ~0.001 at 700K. The calculation indicates that a C_p discrepancy for Na_2SiO_3 should be

437 vanishingly small up to ~700K (Fig. 3e). Beyond 700K Na* concentrations increase rapidly with

438 temperatures, as does the C_p discrepancy of Na_2SiO_3. The calculations are consistent with the

439 Raman spectral results (Richet et al., 1996) and with C_p measurements (Fig. 3e). Raman spectra of

440 Li$_2$SiO$_3$ reveal no obvious Q^3 species up to 1465K (Richet et al., 1996), indicating an absence of

441 O^{2-}. The very weak C$_p$ discrepancy beginning at ~900-1000K (Fig. 3d) likely is attributed solely to

442 minor Li disorder (e.g., Frenkel pair formation). There are insufficient experimental data to

443 calculate cation defect abundances for the other alkali silicates.

IMPLICATIONS FOR MANTLE MINERALS

445 The observations and deductions concerning C$_p$ indicate that alkali-O bond dissociation and

446 defect formation occur in alkali metasilicate and disilicate crystals due primarily to thermal

447 agitation. Alkali-O bond dissociation energies are low compared with alkaline earth-O bond

448 dissociation energies, implying that greater thermal agitation is required for the latter bonds to be

449 ruptured. The very high temperatures of the mantle may be sufficient to cause alkaline earth-O

450 bond dissociation and to produce defects in pyroxenes and olivines. Dimanov and Ingrin, (1995)

451 Richet et al. (1998), Dimanov and Jaoul (1998) and Bouhifd et al. (2002) documented the

452 enhanced mobility (disorder) of Ca in pseudowollastonite, diopside and gehlenite, where disorder

453 commences at ~1500-1600K in the first two phases and ~1800K for the last. In addition, Mg

454 disordering, hence Mg-O bond dissociation, probably occurs within the premelting region of

455 enstatite and forsterite (Richet et al., 1993; Thiéblot et al., 1999), and likely occurs within the

456 premelting regions of most minerals subjected to mantle temperatures (Richet et al., 1998; 1994;

457 Richet and Fiquet, 1991). Where Ca or Mg disordering occurs in pyroxenes, reactions entirely

458 analogous to Reactions (7) and (8) may occur (with Ca or Mg substituted for 2Na) thus promoting

459 formation of intrinsic, Frenkel type, defects in the minerals. Two implications for mantle minerals

460 follow.

461 The onset of premelting of diopside and proto-enstatite occurs at ~1550K and ~1700K

462 respectively, resulting in cation disorder and formation of Frenkel type cationic defects (Thiéblot

463   et al., 1999; Richet et al. 1998; Dimanov and Ingrin 1995). As here emphasized, the defects tend to

464   destabilize the minerals by increasing their C_p, entropy and free energy values. In response, the

465   minerals may change structure or composition to produce a more stable phase. Structural changes

466   driven by defect formation may include creation of 'new' sites which incorporate previously

467   disordered cations. These new structural sites may be accompanied by other changes such as

468   incorporation of Al into octahedral or tetrahedral sites, which should stabilize the minerals at high

469   temperature (Al-O bond dissociation energy is ~512 kJ/mol). Through such changes, the

470   abundance of point defects should decrease, thereby stabilizing pyroxenes against the effects of

471   thermal agitation. The Ca-Tschermak ($CaAl_2SiO_6$) and $NaAlSi_2O_6$ components are likely examples

472   of pyroxene components produced through minimization of cationic defects. We suggest that

473   elimination of defects through changes to composition and structure play an important role in

474   stabilizing pyroxenes against extreme thermal agitation.

475   Richet et al. (1993) suggests that Mg undergoes disordering within the premelting region of

476   forsterite (~2050-2163 K) which spans the temperature range of the wadsleyite stability field

477   (Frost, 2008; Katsura et al., 2004). Mg-O bond dissociation and production of Frenkel defects

478   should contribute to the instability of olivine and to formation of wadsleyite by converting the

479   highly energetic Mg Frenkel defects of olivine to more stable edge-sharing Mg^{2+} octahedral

480   structural sites of wadsleyite (Ashbrook et al., 2005). In addition, Mg-O bond dissociation

481   necessarily produces a negatively charged $[Q^0]^-$ moiety within the crystal (e.g., Nesbitt et al.,

482   2017). The moiety is a strong nucleophile and due to thermal agitation it may encounter and react

483   with adjacent Q^0 species to produce a $[Si_2O_6]$ moiety and O^{2-} according to:

484        $2[Q^0]^- \rightarrow 2[Q^1] + O^{2-}$ (4)

485   The reaction is analogous to Reaction (4) and occurs in Mg_2SiO_4 glass and melt in which Q^1

486 species are observed (Nesbitt et al., 2015; Sen and Tangeman, 2008; Voronko et al., 2006). The

487 products of Reaction (4), Q^1 and O^{2-}, are essential constituents of wadsleyite, β-Mg_2SiO_4,

488 (Ashbrook et al., 2005) and the reaction should promote its formation at the expense of olivine.

489 The presence of wadsleyite in the mantle may have as much to do with Mg-O bond dissociation

490 (through thermal instability) and production of Q^1 species and O^{2-} in olivine as it has to do with

491 pressure.

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636   **Figure Captions**

637   **Fig. 1:** (a) Illustrates the heat capacity (at constant pressure) of crystalline and liquid Na$_2$SiO$_3$ as a

638   function of temperature. The vertical dotted line represents initiation of the premelting region of

639   the crystal the dotted, curved arrow indicates the trend in C$_p$ within the premelting region. The

640   vertical solid arrow indicates the melting point. (b) Illustrates the normalized heat (C$_p$/n) of the

641   crystal as a function of temperature (n = no. of atoms in the unit formula). The dashed curve

642   represents C$_v$ (Debye Function) calculated assuming the Debye Temperature = 750K and the

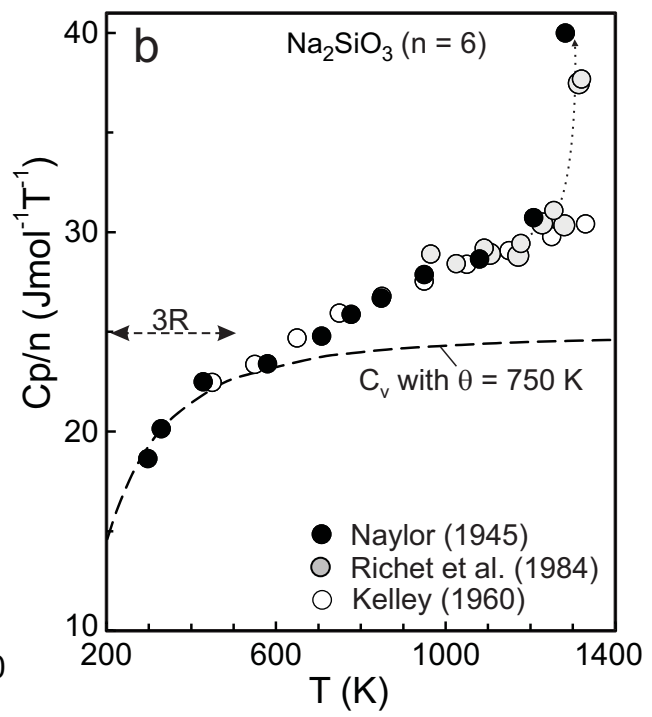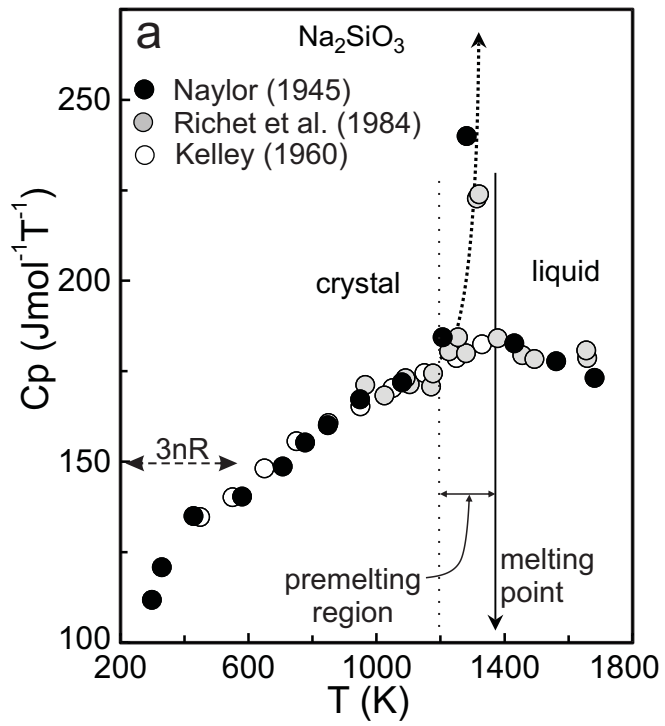643   dotted arrow indicates the premelting trend.

644   **Fig. 2:** Illustrates volumetric properties of some chain and ring silicates as a function of

645   temperature. (a) volume of Na$_2$SiO$_3$(c) as a function of temperature. The straight line is the least

646   squares best fit to the solid circles. The arrow indicates onset of the premelting region. (b), (c), (d),

28

647   (e) and (f) Illustrates the volume coefficient of thermal expansion (α_V) of the indicated crystal as a

648   function of temperature. The solid curves are a least squares best fit to the solid circles. The best fit

649   equation and the source of the data are provided in each diagram.

650   **Fig. 3:** Illustrates the experimental and calculated 'normalized' C_p results for the indicated crystals

651   (normalized $C_p = C_p/n$ where n = no. of atoms per unit formula). The solid curve in each diagram

652   represents the C_p calculated from Equation (3). The dashed curves represent C_v calculated using

653   the Debye Temperature indicated in the diagram. The short arrow (labelled m.p. in some diagrams)

654   indicates the melting point. The dotted curves indicate the C_p trends within the premelting regions

655   of the crystals. See text for details. (a) C_p/n values for orthoenstatite (small and large circles) and

656   proto-enstatite (shaded circles); (b) C_p/n values for diopside.; (c) C_p/n values for

657   pseudowollastonite (p-CaSiO$_3$); (d) C_p/n for Li$_2$SiO$_3$(c). The dotted curve represents C_p/n values

658   calculated assuming that the Grüneisen parameter = 1.3. (e) C_p/n of Na$_2$SiO$_3$(c); (f) C_p/n for

659   K$_2$SiO$_3$(c) is indicated by crosses and the C_p/n data for Na$_2$SiO$_3$ are indicated by open and shaded

660   circles.

661   **Fig. 4:** Illustrates the experimental C_p/n values for Na$_2$Si$_2$O$_5$ (solid circles). The experimental C_p/n

662   values for Na$_2$SiO$_3$ are plotted for comparison (open and shaded circles). The dashed curve

663   represents the Debye Function and the two dotted arrows indicate C_p/n trends within the

664   premelting regions of Na$_2$Si$_2$O$_5$ and Na$_2$SiO$_3$.

665   **Fig. 5:** Defect concentrations of Na (X_{Na^*}) determined from experiment (dots) and the calculated

666   Frenkel pair defect concentrations (solid curve) using the activation energy shown in the diagram.

667   Details are provided in the text.

a Na$_2$SiO$_3$

dV/dT = 1.431x10^{-2} (Å^3/T)

Volume (Å^3)

premelting region

data: Richet et al., 1996

b Na$_2$SiO$_3$

data: Richet et al., 1996

α (1/T)

α_V = -2.091x10^{-9}T+4.723x10^{-5}

c MgSiO$_3$

α (1/T)

data: Jackson et al., 2003

α_V = -1.198x10^{-9}T+3.567x10^{-5}

d Ca$_{0.5}$Mg$_{0.5}$SiO$_3$

α (1/T)

data: Pandolfo et al., 2015

α_V = -9.688x10^{-10}T+3.183x10^{-5}

e Li$_2$SiO$_3$

α (1/T)

data: Richet et al., 1996

α_V = -3.563x10^{-9}T+6.300x10^{-5}

f CaSiO$_3$

α (1/T)

data: Richet et al., 1998

α_V = -9.525x10^{-10}T+3.162x10^{-5}

Fig. 2

Fig. 3

Fig. 4

E* = -84560 J/mol

Fig. 5

Table 1: The Debye Function[1]

θ/T	T (K)	Cv
	750	J/mol^{-1}T^{-1}
0.10	0.0	24.89
0.20	0.0	24.85
0.30	0.0	24.81
0.40	0.0	24.73
0.50	0.0	24.60
0.60	0.0	24.48
0.70	0.0	24.31
0.80	0.0	24.14
0.90	0.0	23.93
1.00	0.0	23.72
1.50	0.0	22.34
2.00	0.0	20.59
2.50	0.0	18.62
3.00	0.0	16.53
3.50	0.0	14.48
4.00	0.0	12.55
5.00	0.0	9.20
6.00	0.0	6.61

1 Pitzer and Brewer (1961),
   Table A5-1, p. 660.

Table 2: Gruneisen Parameter (γ) for Chain Silicates

Phase	Composition	γ	Error	References
Orthopyroxene	$(Mg,Fe)SiO_3$	1.1	±0.1	Jeanloz and Thompson, 1983
Orthopyroxene	$FeSiO_3$	1.1	?	Anderson, 1967
Orthopyroxene	$(Mg,Fe)SiO_3$	0.87	±0.04	Yang and Ghose, 1994
Orthopyroxene	$(Mg,Fe)SiO_3$	1.28	±0.05	Chopelas, 2000
Orthopyroxene	$(Mg,Fe)SiO_3$	1.05	?	Zhao et al., 1995
Orthopyroxene	$MgSiO_3$	1.3	?	Hofmeister and Mao, 2002
Clinopyroxene	$Ca(MgFe)Si_2O_6$	1.1	±0.05	Jeanloz and Thompson, 1983
Average:		1.1		
Standard Dev.		0.15		

Table 3: Enstatite Cp(av) Values Calculated from Relative Enthalpies[1]

Exptl. Run	T_2 (K)	$H_{T2}-H_{T1}$[2] kJ/mol	T_1 (K)	$\Delta T=(T_2-T_1)$ (K)	$T(av)$[3] (K)	$Cp(av)$[4] $Jmol^{-1}T^{-1}$	$Cp(av)/n$[5] $Jmol^{-1}T^{-1}$
Orthoenstatite							
	273.15	0.0					
EE12-B	415.6	12.64	273.15	142.45	344.38	88.73	17.75
EE1-B	513.7	22.87	415.6	98.1	464.65	104.28	20.86
EE11-B	514.1	22.73	415.6	98.5	464.85	102.44	20.49
EE4-B	638.5	36.54	514.1	124.4	576.30	111.01	22.20
EE2-B	696.6	43.3	638.5	58.1	667.55	116.35	23.27
EE20-B	724.1	46.75	638.5	85.6	681.30	119.28	23.86
EE5-B	771.7	52.16	696.6	75.1	734.15	117.98	23.60
EE13-B	849.6	61.7	771.7	77.9	810.65	122.46	24.49
EE6-B	907.9	68.89	849.6	58.3	878.75	123.33	24.67
EE8-B	968.4	76.51	907.9	60.5	938.15	125.95	25.19
EE9-B	1051.8	86.96	968.4	83.4	1010.10	125.30	25.06
EE10-B	1168.6	101.85	1051.8	116.8	1110.20	127.48	25.50
EE17	1225.4	109.51	1051.8	173.6	1138.60	129.90	25.98
Proto-enstatite							
EX17	1366	129.17					
EX11	1427	136.84	1366	61	1396.70	126.15	25.23
EX4	1481	143.47	1366	115	1423.65	124.67	24.93
EX2	1575	155.98	1481	94	1527.80	133.65	26.73
EX3	1683	169.66	1575	109	1628.85	126.08	25.22
EX26	1740	177.16	1683	57	1711.50	132.04	26.41
EX16	1745	177.83	1683	62	1714.00	132.20	26.44
EX5	1773	182.56	1683	90	1728.15	143.17	28.63
EX15	1787	184.77	1745	47	1763.60	160.55	32.11
EX10	1811	191.86	1745	67	1778.15	210.98	42.20

1 Relative enthalpies (heat content) are from Thieblot et al. (1999)

2 Values may have large errors where ΔT values are less than 70 K.

3 $\Delta H = (H_{T2} - H_{T1})$; $\Delta T = (T_2 - T_1)$; $T(av) = (T_2 + T_1)/2$

4 $Cp(av) = (H_{T2} - H_{T1})/(T_2 - T_1) = \Delta H/\Delta T$. Cp(av) is plotted at T(av).

5 Cp/n = Cp normalized to 'n', the number of atoms in the unit formula