Defect Contributions to the Heat Capacities and Stabilities of Some Chain,  
Ring and Sheet Silicates, with Implications for Mantle Minerals

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At temperatures less than ~1500K, previously published $C_p$ data demonstrate that the heat capacities of orthoenstatite, proto-enstatite, diopside and pseudowollastonite include primarily Debye type vibrational and anharmonic contributions whereas the alkali chain, sheet and ring silicates, $\text{Na}_2\text{SiO}_3$, $\text{Li}_2\text{SiO}_3$, $\text{K}_2\text{SiO}_3$ and $\text{Na}_2\text{Si}_2\text{O}_5$ include a third contribution. The third contribution to $C_p$ arises from defect formation due to the mobility Na, K, Li, and $\text{O}^{2-}$. The contribution becomes apparent at temperatures above 700-800K for Na and K silicates, and above 900-1000K for Li metasilicate. With strong thermal agitation, alkali-non-bridging oxygen (NBO) bonds are ruptured with the cations exiting their structural sites to occupy interstitial sites, thereby producing intrinsic Frenkel defects which contribute to the $C_p$ of the alkali silicates. The magnitudes of the $C_p$ defect contributions correlate inversely with cation-oxygen bond strengths, as measured by bond dissociation energies. K-O and Na-O bond strengths are weak (239 and 257 kJ/mol) and defect contributions are large for these alkali chain, ring and sheet silicates. The greater bond strength of Li-O (341 kJ/mol) correlates with a weaker defect contribution to the $C_p$ of $\text{Li}_2\text{SiO}_3$. Mg-O and Ca-O bonds are stronger still (394 and 464 kJ/mol) and no $C_p$ defect contributions are observed for the pyroxenes and pseudowollastonite up to ~1500K.

Above ~800K a polymerization reaction occurs in $\text{Na}_2\text{SiO}_3$ which produces some $Q^3$ species and free oxygen ($\text{O}^{2-}$ or oxide ion). The polymerization reaction annihilates an oxygen structural site so that the $\text{O}^{2-}$ produced must reside on non-structural sites thus producing intrinsic anionic defects. The same reactions likely occur in $\text{Na}_2\text{Si}_2\text{O}_5$ and $\text{K}_2\text{SiO}_3$. Raman spectra of $\text{Na}_2\text{SiO}_3$ indicate >10% of $\text{Na}^+$ and ~1.7% of $\text{O}^{2-}$ on interstitial sites at 1348K.

Ca- and Mg-bearing mantle minerals subjected to temperature greater than ~1500K experience the destabilizing effects of disordering (Frenkel defect formation). The minerals may
respond either by changing their composition or by changing phase. An abundance of Ca and Na
defects in pyroxenes, for example, likely promote production of new components (e.g., CaAl$_2$SiO$_6$,
NaAlSi$_2$O$_6$) in pyroxenes. By their production, Ca and Na defect concentrations are reduced
thereby stabilizing the phases. Mg-O bond dissociation and production of intrinsic Mg$^{2+}$ and O$^{2-}$
point defects within olivine likely destabilize it and promote the phase transition to wadsleyite at
the base of the upper mantle.

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

**INTRODUCTION**

Richet et al. (1996) compared the temperature dependence of the heat capacities ($C_p$) of the
isostructural chain silicates Li$_2$SiO$_3$ (c) and Na$_2$SiO$_3$ (c), and noted that $C_p$ of Na$_2$SiO$_3$ (c) was
consistently greater than that of Li$_2$SiO$_3$ (c), regardless of temperature. The differing values below
~600K may be due to different Debye Temperatures ($\theta$) of the phases because $\theta$ affects mostly the
low temperature $C_p$ values of a phase. At higher temperatures, $\theta$ values have minimal effect on
heat capacity at constant volume ($C_v$), or on $C_p$, in that $C_v$ approaches the universal value of 3nR
regardless of $\theta$ values. Richet et al. (1996) explored these differences at both low and high
temperatures using sophisticated $C_p$ models (e.g., Kieffer, 1982; 1980), which included
anharmonic effects, and they summarized the situation by stating that the excess $C_p$ of Na$_2$SiO$_3$
remained unexplained. We address this conundrum by evaluating previously published
contributions to $C_p$ of eight chain, ring and sheet silicates, orthoenstatite (MgSiO$_3$), proto-enstatite
(MgSiO$_3$), diopside (MgCaSi$_2$O$_6$), pseudowollastonite (CaSiO$_3$), Na$_2$SiO$_3$, Na$_2$Si$_2$O$_5$, K$_2$SiO$_3$ and
Li$_2$SiO$_3$. All crystals contain $Q^2$ species (silicate chains or rings) except Na$_2$Si$_2$O$_5$ which is a sheet
silicate consisting of $Q^3$ species (where Q represents a Si tetrahedron and the superscript indicates
the number of bridging oxygen atoms bonded to the central Si atom of the tetrahedron).

Cations of some crystals, heated to high temperature, may become mobile through rupture of oxygen-cation bonds (e.g., Nesbitt et al., 2017; George et al., 1998) thereby contributing to disorder by forming intrinsic defects (e.g., Frenkel defects). There is overwhelming evidence for high temperature alkali and alkaline earth cation disorder in chain and ring silicates (Courtial et al., 2000; Thiéblot et al., 1999; Richet et al., 1998, 1996, 1993; George et al., 1998; Dimanov and Jaoul, 1998; Dimanov and Ingrin, 1995). George et al. (1998), for example, conducted a study of Na$_2$SiO$_3$ and Li$_2$SiO$_3$ by collecting $^7$Li, $^{23}$Na and $^{29}$Si NMR spectra as a function of temperature. The study indicated limited Li mobility at high temperature. For Na$_2$SiO$_3$, motional averaging commenced at ~700-800K and at ~900-1000K, Na$^+$ was sufficiently mobile to behave in a liquid-like, disordered manner, residing on both structural and non-structural sites (George et al., 1998).

Recently, Nesbitt et al. (2017) emphasized that Na$^+$ and O$^{2-}$ disorder occurred in Na$_2$SiO$_3$ crystals at temperatures as low as 700-800K, and well before the premelting region of the crystal was encountered (Fig. 1a).

An appreciation for the problem to be addressed is gained by plotting $C_p$ of Na$_2$SiO$_3$ against temperature (Fig. 1a). Three sets of $C_p$ data are plotted and they are reasonably consistent (addressed subsequently). An obvious aspect is the rapid increase in $C_p$ within the premelting region (e.g., Richet et al., 1994) beginning at ~1200K. A less obvious aspect is the almost linear increase in $C_p$ between ~400K and ~1200K, the slope of which is appreciably steeper than expected considering that the rule of Dulong and Petit (Slater, 1963) requires the heat capacity to reach a high temperature limit of 3nR (~149 Jmol$^{-1}$K$^{-1}$ for Na$_2$SiO$_3$). To emphasize this aspect, $C_p$ of Na$_2$SiO$_3$ has been normalized to the number of atoms ‘n’ in the formula unit (n=6 for Na$_2$SiO$_3$) to yield a “normalized $C_p$” (i.e., $C_p$/n). The normalized experimental data are plotted against
temperature in Figure 1b as is the heat capacity \((C_v)\) calculated using the Debye Function where

the Debye Temperature \((\theta) = 750K\) (Fig. 1b, dashed curve and Table 1). The Debye Function (i.e., \(C_v\)) reproduces reasonably well the normalized \(C_p\) data in the range 300K to 600K but \(C_v\) deviates from experiment between ~700K and 1200K. It may result from anharmonic contributions to \(C_p\) but Richet et al. (1996) concluded that \(C_v\) and anharmonic contributions alone cannot account for the discrepancy. We address this discrepancy and attempt to explain it.

**THERMODYNAMICS ASPECTS**

Heat capacity includes at least two major contributions between ~300K and the premelting region of a crystal. One is the heat capacity at constant volume \((C_v\) or Debye Function) which derives from the ‘Debye elastic continuum’ (Ghose et al., 1991; Keifer, 1980; Debye, 1912; Born and von Kármán, 1912; Einstein, 1907). Anharmonic contributions constitute the second contribution arising from the nature of site potentials within a crystal, which give rise to thermal expansion. The two contributions allow calculation of \(C_p\) according to:

\[
C_p = C_v + [\alpha V^2 V/\beta]T
\]

where \(V\) is the volume of the phase, \(\alpha\) is the volume coefficient of thermal expansion, \(\beta\) is the compressibility and \(T\) is temperature. With \(V\), \(\alpha\) and \(\beta\) of a crystal known, the anharmonic term, \([\alpha V^2 V/\beta]T\), can be evaluated and \(C_p\) calculated as a function of temperature (provided \(C_v\) is known). Equation (1) can be simplified using a relationship elucidated by Grüneisen (1912; 1926):

\[
\alpha V/\beta = \gamma C_v
\]

where \(\gamma\) is the thermal Grüneisen parameter (Slater, 1963, p. 238). Substitution of Equation (2) into Equation (1) and rearrangement yields:

\[
C_p = (1 + \alpha V \gamma T)C_v
\]

Estimates of the Grüneisen parameter for chain silicates range from 0.88 to 1.3 (Table 2; see also
Angel and Jackson, 2002) with the average value being 1.1 ($n = 7$, $\sigma = 0.15$). The average is used in subsequent calculations. The $\gamma$ parameter is largely independent of temperature (Slater, 1963, p. 219) and is similar for all silicates studied here (Angel and Jackson, 2002; Hofmeister and Mao, 2002; Ita and Stixrude, 1992; Jeanloz and Thompson, 1983).

The volume of crystalline Na$_2$SiO$_3$ is illustrated in Figure 2a where the solid circles represent volumes from 298 to ~1200K and the open circles represent measurements within the premelting region. A linear least squares best fit to the solid circles was performed and the fit is plotted on the figure. The slope, $(dV/dT)$ is effectively constant at $\sim 1.43 \times 10^{-2}$ (Å$^3$/K). The coefficient of thermal expansion is defined as:

$$\alpha_V = \frac{(dV/dT)_p}{V}$$  \hspace{1cm} (4)

where ‘p’ denotes constant pressure. Because $dV/dT$ is effectively constant, calculation of $\alpha_V$ requires only that it be divided by $V$ at the temperature of interest. The resulting $\alpha_V$ values for Na$_2$SiO$_3$ are plotted on Figure 2b and $\alpha_V$ is effectively linear in $T$. The same procedure was used to obtain $\alpha_V$ for other crystals studied and the results are illustrated in Figures 2c to 2f.

Accurate calculation of $C_V$ for silicate crystals is complex (e.g., Ghose et al., 1991; Keiffer, 1982; 1980) but as noted in the Introduction, reasonable estimates of $C_V$ can be obtained using the Debye Function or a modification of it. The Debye Function (e.g, Table 1) employs only one adjustable parameter, the Debye Temperature ($\theta$), which can be evaluated from elastic or other properties of the crystal (Grimvall, 2001). In the approach used here, the Debye Temperature is treated as a fit parameter. To obtain approximate $C_V$ values for a crystal, the Debye Temperature is adjusted to provide a good fit to the heat capacity in a specified temperature range (here 300-600 K). The same $\theta$ value necessarily yields reasonable estimates of $C_V$ at high temperature because the Debye Function ($C_V$) approaches $3nR$ regardless of the value of $\theta$. Treating $\theta$ as a fit parameter has
the advantage that the calculation of $C_v$ may accommodate other moderate temperature lattice
contributions such as some optical modes (Ghose et al., 1991; Kieffer, 1980). Highly accurate
estimates of $C_v$ are not required for this exercise, and the Debye Function is used to calculate $C_v$.

CALCULATED AND EXPERIMENTAL $C_p$ DATA

Orthoenstatite and Proto-enstatite

Three sets of experimental $C_p$ data are plotted on Figure 3a. The large open and shaded
circles represent, respectively, $C_p$ of orthoenstatite and proto-enstatite. The values are derived from
relative enthalpies (heat contents) reported by Thiéblot et al. (1999). They measured the heat
evolved upon cooling a sample from a temperature $T$ to a reference temperature ($T^* = 273$ K). The
heat evolved is the difference in enthalpy ($H$) at the two temperatures ($H_T - H_{T^*}$). A finite
difference approach was used to estimate an average $C_p$ (i.e., $C_p(\text{av})$) over the temperature range of
any two measurements. Subtracting two heat content measurements (one at $T_2$ and one at $T_1$)
yields $(H_{T_2} - H_{T_1})$ and dividing it by the difference in the two temperatures ($T_2 - T_1$) gives $C_p(\text{av})$:

$$C_p(\text{av}) = (H_{T_2} - H_{T_1})/(T_2 - T_1) = \Delta H/\Delta T$$

(5)

The $C_p(\text{av})$ value represents the average $C_p$ over the interval $T_1$ to $T_2$ and may be plotted on Fig. 3
at $T(\text{av}) = (T_2 - T_1)/2$. $T_1$ need not be $T^*$ and may be any temperature at which a heat content
measurement has been made. The original relative enthalpies of Thiéblot et al. (1999) for
orthoennstatite and proto-enstatite are reproduced in Table 3 and were used to calculate $C_p(\text{av})$,
which were, in turn, normalized to ‘n’ to obtain $C_p(\text{av})/n$ ($n=5$ for MgSiO$_3$). Heat capacities
derived from relative enthalpies commonly are of lower precision than those obtained by other
techniques due to subtraction of two large numbers. The resulting values are, however, devoid of
assumptions and propagation of errors, and may be more accurate than techniques which include
assumptions and propagation of errors. Use of $C_p(\text{av})$ to approximate $C_p$ introduces minimal
uncertainty in $C_p$ above about 700K, as now shown. The average value of $T_2-T_1$ of Table 3 is 
$\sim100$K so that the temperature range associated with each $C_p(\text{av})$ is about $\pm50$K. Uncertainty of 
this magnitude does not affect the conclusions drawn subsequently.

The small circles of Figure 3a represent experimental $C_p(\text{av})/n$ values for a synthetic 
orthoenstatite. The large open and shaded circles represent $C_p(\text{av})/n$ data for orthoenstatite and 
proto-enstatite, respectively. The small and large circles merge between $\sim450$K and 800K, 
substantiating the accuracy of both sets of data. There is a group of measurements between 850K 
and 1000K (Fig. 3a, small circles) which is offset to slightly greater $C_p$ values relative to the other 
data. These ‘offset’ data are not considered in the following discussion.

A Debye Temperature of 875K was used to calculate $C_V$ for both enstatites and $C_V$ is plotted 
in Figure 3a as the dashed curve. The expression for $\alpha_V$ provided in Figure 2c and the Grüneisen 
parameter (=1.1) were employed to calculate $C_p$ according to Equation (3). The result is illustrated 
by the solid curve of Figure 3a. The solid curve reproduces (within experimental uncertainty) the 
orthoenstatite and proto-enstatite experimental values up to $\sim1650$K and the difference between the 
solid curve and the dashed curve represents the anharmonic contribution to $C_p$. Clearly there are 
only two major contributions to $C_p$ of the enstatites between $\sim300$K and the premelting region of 
proto-enstatite. Moreover, the $\alpha_V$ and Grüneisen parameter used in the calculations are reasonable 
for both enstatites. Finally, the conformity of the calculated and experimental $C_p$ values indicates 
that the Debye Function provides reasonable estimates of $C_V$ for the enstatites.

**Diopside**

Two sets of experimental $C_p$ data for diopside ($\text{CaMgSi}_2\text{O}_6$) are plotted on Figure 3b and 
they merge smoothly. With a Debye Temperature of 900K, the $\alpha_V$ expression of Figure 2b and a 
Grüneisen parameter of 1.1, the $C_p$ values for diopside were calculated (Eq. 3) and plotted as the
solid curve of Figure 3b. The solid curve conforms closely to the experimental data up to ~1500K, beyond which premelting and Ca disorder commences (Dimanov and Jaoul, 1998; Richet et al., 1998; Dimanov and Ingrin, 1995; Richet et al., 1994; Richet and Fiquet, 1991). As for orthoenstatite and proto-enstatite, there are two major contributions to the $C_p$ of diopside, $C_v$ and an anharmonic contribution. Diopside is structurally different from the enstatite polymorphs but the same Grüneisen parameter (1.1) allows reasonable estimates of $C_p$ for the three crystals.

**Pseudowollastonite**

The $C_p/n$ ($n=5$) values calculated for two sets of experimental data are plotted on Figure 3c. The $C_v$ of pseudowollastonite (CaSiO$_3$) was calculated with $\theta = 900K$ and plotted on Figure 3c (dashed curve). The expression for $\alpha_V$ (Fig. 2f) and a Grüneisen parameter = 1.1 were used to calculate the effect of anharmonicity (Eq. 3) and the solid curve represents the result. The essential agreement between experiment and calculation indicates that within the temperature range ~300K to ~1500K, its $C_p$ includes only $C_v$ and anharmonic contributions. The Grüneisen parameter for the pyroxenes and this ring silicate are effectively the same, demonstrating that structural variability has no appreciable effect on the parameter.

**Li$_2$SiO$_3$**

The crystal is an orthorhombic chain silicate with Si$_2$O$_6$ chains linked by LiO$_4$ polyhedra (Hesse, 1977). Experimental $C_p(\text{av})/n$ values ($n=6$) of Téqui et al. (1992) are plotted on Figure 3d (open circles). The $C_v$ contribution was calculated with $\theta = 950K$ (Fig. 3d, dashed curve) and $C_p$ was calculated (Eq. 3) with $\alpha_V$ given in Figure 2e and a Grüneisen parameter = 1.1 (Fig. 3d, solid curve). It conforms to the experimental data between ~500K and ~700K but systematically underestimates $C_p$ at 900K and greater temperatures. There are three likely reasons for the discrepancy; the value for $\alpha_V$ or $C_v$ is incorrect at high temperature, or $\gamma$ is greater than 1.1. An
incorrect $\alpha_V$ is unlikely in that it was accurately measured and behaves systematically with
temperature (Fig. 2e). That $C_v$ would be incorrect at temperatures greater than $\sim$900K also seems
unlikely because all $C_v$ values tend toward the same 3nR limit (i.e., $\theta$ has little effect on $C_v$ at high
temperature). This leaves the Grüneisen parameter. An extreme value of 1.3 was adopted for the
Grüneisen parameter (Table 2) and $C_p$ was recalculated with the results plotted as a dotted curve
on Figure 3d. The $C_p$ discrepancy is diminished but nevertheless remains at temperatures greater
than $\sim$1000K. Noting that $\gamma = 1.1$ for the previously treated metasilicates, there is no reason to
expect a different value for Li$_2$SiO$_3$ and we suggest that there is a third, weak contribution to $C_p$ of
Li$_2$SiO$_3$ at high temperature. We return to this aspect subsequently.

Na$_2$SiO$_3$

Na$_2$SiO$_3$ is a chain silicate isostructural with Li$_2$SiO$_3$. The crystal undergoes a polymorphic
transition (from $Cmc\text{ }2_1$ symmetry to $Pmc\text{ }2_1$ symmetry) at $\sim$850K involving Na-O polyhedra but
the Q$^2$ chains are unaffected (Richet et al., 1996). Heat content data from three sources are plotted
on Figure 3e. Naylor (1945) used $T^* = 298.15$ whereas Richet et al. (1984) used $T^* = 273.15$ and
their different procedures resulted in a systematic difference in $C_p(\text{av})$. To standardize the data,
$C_p(\text{av})$ was calculated for both sets of data and the difference between them was 15 Jmol$^{-1}$K$^{-1}$ at
$\sim$1080K. The Richet et al. (1984) $C_p(\text{av})$ values were increased by this amount making the two sets
of data remarkably consistent (Fig. 3e). They are also consistent with those reported by Kelley
(1960).

Na$_2$SiO$_3$ $C_v$ values were obtained using $\theta = 750K$ (Fig. 3e, dashed curve) and $C_p$ was
calculated via Equation (3) using $\alpha_V$ provided in Figure 2b and a Grüneisen parameter $= 1.1$. (Fig.
3e, solid curve). The calculated and experimental $C_p$ values are consistent between $\sim$300 and
$\sim$700K but they diverge beyond $\sim$700K. At $\sim$1200K the $C_p$ discrepancy is $\sim$15% relative to the
experimental value. There is no obvious effect on $C_p$ at the polymorphic transition (~850K) as shown in Figures 2b or 3e so that any effect of the transition on $C_p$ is within experimental uncertainty. It is concluded that there is a third contribution to the $C_p$ of Na$_2$SiO$_3$ with onset at ~700K and this contribution increases systematically with temperature.

**K$_2$SiO$_3$**

K$_2$SiO$_3$, like pseudowollastonite, consists of three-membered rings (Si$_3$O$_9$), with potassium polyhedra linking them to produce a monoclinic unit cell (Werthmann and Hoppe, 1981). The heat contents of Beyer et al. (1979) were employed to calculate $C_p$(av)/n values and these are plotted on Figure 3f (crosses). The results mimic the experimental data for Na$_2$SiO$_3$ (Fig. 3f, circles). The melting temperature of K$_2$SiO$_3$ is 1195K and the $C_p$(av)/n experimental datum point at 1150K is much greater than the value at 1100K, which may indicate a premelting region for K$_2$SiO$_3$. A $\theta_D$ = 750 was employed to calculate $C_v$ of the crystal and it fits reasonably the $C_p$(av)/n experimental result at ~500K (Fig. 3f) but underestimates $C_p$(av)/n at greater temperatures. No value for $\alpha_V$ was found for K$_2$SiO$_3$ so that $C_p$ could not be calculated and the $\alpha_V$ value of Na$_2$SiO$_3$ was used as a proxy, yielding the solid curve of Figure 3f. The agreement with the experimental data in the range ~450-700K indicates that the $\alpha_V$ proxy is reasonable but the calculated $C_p$/n values underestimate experimental values at temperatures greater than ~700K. No reasonable value of $\alpha_V$ can reproduce the experimental data at high temperature and apparently there is a third contribution to $C_p$ of K$_2$SiO$_3$ which is similar in character and magnitude to that of the Na$_2$SiO$_3$ $C_p$ discrepancy.

**EXPLANATION FOR $C_p$ DISCREPANCIES**

**Introduction**

Free translation of atoms through crystals is unlikely and electronic contributions to $C_p$ of insulators are similarly unimportant in the temperature range ~300K to 1500K (Slater, 1963; Borg
Substitutional disorder resulting from exchange of cations on different structural sites is also impossible for Na$_2$SiO$_3$, K$_2$SiO$_3$, Na$_2$Si$_2$O$_5$ or Li$_2$SiO$_3$ unless Si sites are involved, which is highly unlikely. The $C_p$ discrepancies observed for these alkali-bearing crystals therefore arise from other contributions. Heat capacity is the sum of numerous internal and configurational contributions (Grimvall, 2001):

$$C_p(\text{crystal}) = C_p(\text{vibration}) + C_p(\text{defect}) + C_p(\text{rotation}) + C_p(\text{libration})$$

(6)

Lattice vibrations and anharmonic contributions are here accounted for by Equation (3). There are no structural changes to Li$_2$SiO$_3$ or K$_2$SiO$_3$ from 298K to their premelting regions, hence there is no contribution to their $C_p$ resulting from polymorphism. Na$_2$SiO$_3$ undergoes a transition at ~850K from orthorhombic ($Cmc$ 2$_1$) to a lower symmetry, possibly $Pmc2_1$ (Richet et al., 1996). There is, however, no discontinuity evident in the $C_p$ trend at this temperature (Fig. 3e) so that any resulting $C_p$ contribution is within the uncertainty associated with the measurements of $C_p$. The effects of dislocations on $C_p$ are well known to experimentalists, and care special is taken to avoid samples with high dislocation densities through sample selection and treatment (e.g., Richet et al., 1996; Naylor, 1945). This leaves configurational contributions such as point defects and rotation/libration as the most likely causes of the $C_p$ discrepancies.

Whether intrinsic defect formation or rotation/libration contributions are responsible for the $C_p$ discrepancies can be assessed by reference to crystalline Na$_2$Si$_2$O$_5$, a sheet silicate consisting of Q$^3$ species. Naylor (1945) reports Na$_2$Si$_2$O$_5$ heat contents from which $C_p(\text{av})/n$ values were calculated and the results are plotted on Figure 4 (filled circles). The $C_p(\text{av})/n$ data for Na$_2$SiO$_3$ are also plotted (Fig. 4, open and shaded circles). The Na$_2$Si$_2$O$_5$ and Na$_2$SiO$_3$ experimental data are effectively coincident from ~300K to ~1000K and the Debye Function reproduces well the experimental $C_p$ data for Na$_2$Si$_2$O$_5$ between 300 and 600K with $\theta_D = 750$ (Fig. 4, dashed curve).
The anharmonic contribution to $C_p$ of Na$_2$Si$_2$O$_5$ could not be calculated for lack of a $\alpha_V$ value and the Na$_2$SiO$_3$ value (Fig. 2b) was used as a proxy to obtain the solid curve of Figure 4. The $C_p/n$ vs. $T$ trend described by the Na$_2$Si$_2$O$_5$ experimental data is too steep to be accounted for by Equation (3) using a reasonable value for $\alpha_V$. We conclude that Na$_2$Si$_2$O$_5$ displays a $C_p$ discrepancy of the same magnitude as that for Na$_2$SiO$_3$.

The structures of the two crystals are different (chain vs sheet) and the $Q^2$ and $Q^3$ tetrahedra of the respective crystals should make different rotational or librational contributions to $C_p$ due to their different linkages. There is, nevertheless a remarkable similarity in the $C_p$ of the two crystals and in their $C_p$ discrepancies. We conclude that rotation and libration are unlikely to be responsible for the similarities in their $C_p$ discrepancies. Instead, the essentially coincidence of the Na$_2$Si$_2$O$_5$ and Na$_2$SiO$_3$ $C_p$ trends relate to their common cation, and specifically to intrinsic cation defect formation in both phases. Although rotation and libration occur in some silicates (Voronko et al., 2006; George et al., 1998; Ghose et al., 1986; Massa et al., 1983) defect formation is the cause of $C_p$ discrepancies in these crystals.

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

**Li Mobility in Li$_2$SiO$_3$.** There is experimental evidence for Li mobility in Li$_2$SiO$_3$ where subjected to strong thermal agitation. George et al. (1998) conclude from their $^7$Li NMR results that: “Li$^+$ site hopping is clearly observed in Li$_2$SiO$_3$ by a partial averaging of the $^7$Li quadrupolar peak shape, requiring exchange among a few, ordered orientations of LiO$_4$ tetrahedra”. Clearly, Li is not sufficiently mobile, even at 1420K, to have a completely averaged, isotropic environment. With Li-O bond dissociation at high temperature, the majority of mobile Li$^+$ alight on previously vacated structural sites and re-establish Li-O bonds, which results in no net change to $C_p$. The spectroscopic results do not preclude, however, a small fraction of mobile Li$^+$ from having
alighted, fleetingly, on interstitial sites to form a few intrinsic (Frenkel) defects. The fraction should increase with temperature as more Li become mobile.

**Na Mobility in Na$_2$SiO$_3$.** George et al. (1998) observe that Na is strongly mobile in Na$_2$SiO$_3$ at high temperatures. Quoting George et al. (1998): “From $^{23}$Na NMR results, Na$^+$ site hopping in Na$_2$SiO$_3$ appears to involve a more liquid-like behavior, implying exchange among many sites with different orientations in a disordered fashion”. The disordering probably results from a fraction of mobile Na$^+$ alighting on interstitial sites to create intrinsic Frenkel defect pairs, as observed for Ca$^{2+}$ in diopside and pseudowollastonite (see next section). These defects increase the $C_p$ of the crystal in proportion to the number of mobile ions at any instant.

Insight into the high temperature ‘liquid-like’ behaviour of Na$^+$ in Na$_2$SiO$_3$ may be gleaned by analogy with Na$^+$ behaviour in Na-silicate glass. Although there is some ambiguity in distinguishing different types of cationic sites in the glass, Cormack et al. (2002) nevertheless distinguish ‘cationic sites’ from more energetic ‘transitional sites’, the distinction being dependent on the residence time of the cation on each type of site. Consider, in an energetic sense, the ‘cationic sites’ of the glass to be analogous to the cationic structural sites of the crystal and the ‘transitional sites’ of the glass to be analogous to interstitial sites of the crystal. Cormack et al. (2002) note that Na$^+$ of the glass mostly occupies ‘cationic sites’, but during transit from one cationic site to another, the cation may occupy, fleetingly, ‘transitional sites’ (i.e., in Fig. 5 of Cormack et al., 2002; the Na$^+$ atom in cation site 1 migrates to a transitional site with its 3rd step). The potential energy minima of ‘transitional sites’ almost certainly are shallower than the minima of the ‘cationic sites’. Occupation of ‘transitional sites’ consequently increases $C_p$ of the glass by an amount proportional to the number of transitional sites occupied at any instant, just as occupation of interstitial (defect) sites in the crystal increases its $C_p$ in proportion to the number of
defects present at any instant.

**Ca Mobility in Diopside and Pseudowollastonite.** There is very strong experimental evidence for Ca mobility in diopside and pseudowollastonite at temperatures greater than ~1500K (Bouhfid et al., 2002; Dimanov and Jaul, 1998; Dimanov and Ingrin, 1995). Based on Rutherford Backscattering analysis Dimanov and Ingrin (1995) observed a high temperature intrinsic diffusion regime in diopside which “takes place near the onset of premelting as detected in calorimetric measurements and can be interpreted in terms of enhanced formation of Frenkel defects”. The premelting region commences at 1500-1600K. These results were confirmed by Dimanov and Jaul (1998) who also concluded that Ca self-diffusion may involve Ca-Frenkel point defects. The Raman and conductivity experiments of Bouhfid et al. (2002) demonstrated the mobility of Ca in both pseudowollastonite and gehlenite, where mobility of Ca in the two phases occurs at temperatures greater than ~1500K. The Ca-Frenkel defects formed will contribute to the $C_p$ of these crystals but only at temperatures above ~1500K (i.e., in their premelting regions).

**C$_p$ Discrepancies and Cation-O Bond Strengths**

The mobility of cations and the abundance of intrinsic cation defects increase with temperature because thermal agitation promotes rupture of cation-oxygen bonds. There may be, therefore, a relationship between cation-oxygen bond dissociation energies, cation mobility, defect formation and $C_p$-discrepancies. K-O and Na-O bond dissociation energies are weak at 239 kJ/mol and 257 kJ/mol respectively whereas the Li-O bond is somewhat stronger at 341 kJ/mol (Speight, 2005). The alkaline earth-oxygen bond dissociation energies are stronger still, ranging between 394 and 563 kJ/mol. From these values we conclude that dissociation of K-O and Na-O bonds should occur at comparatively low temperatures, Li-O dissociation at somewhat greater temperature and Mg-O and Ca-O bond dissociation should occur at still greater temperatures. The
Na and K metasilicate and disilicate \( C_p \) discrepancies commence at \( \sim 700-800 \) K and their \( C_p \) discrepancies are the most pronounced (Figs. 3, 4). The Li metasilicate \( C_p \) discrepancy (Fig. 3d) commences at greater temperature (900-1000 K), and it is less pronounced than the discrepancies for Na and K silicates (Figs. 3d 3e, 3f). Finally, no \( C_p \) discrepancies are apparent up to 1500K for the alkaline earth metasilicates (Figs. 3a, 3b, 3c). Bond dissociation energies correlate well with the temperatures at which \( C_p \) discrepancies are initiated and with the strength of the discrepancies.

We propose that bond dissociation, resulting from strong thermal agitation, promotes cation mobility, cation (Frenkel) defect formation and production of the \( C_p \) discrepancies of the alkali metasilicates (Figs. 3 and 4). The same order of bond strength (\( K_2O < Na_2O < Li_2O < MgO/CaO \)) is obtained from Coulombic interaction considerations using effective ionic radii (Huheey et al., 1993, Chap. 4).

**Reactions Producing Defects and \( C_p \) Discrepancies**

**Cationic Defects.** We have concluded that Na-NBO bond dissociation is observed in crystalline \( Na_2SiO_3 \) above \( \sim 700-800 \) K (se also Nesbitt et al., 2017) and the reaction proceeds according to:

\[
[Na_2\cdot Q^2]^0 \rightarrow [Na_1\cdot Q^2]^- + Na^+ \quad (7)
\]

where \([Na_2\cdot Q^2]^0\) is a \( Q^2 \) species with a Na atom bonded to each NBO, and \([Na_1\cdot Q^2]^-\) represents a \( Q^2 \) species where one NBO has no associated Na atom. With NBO-M bond dissociation, the cation (M) vacates its structural site and migrates to a non-structural (interstitial) site. The escape of Na\(^+\) from a structural site creates a vacancy, and together with the occupation of a non-structural site, creates a *Frenkel* defect pair. Creation of these defects increases the \( C_p \) of the crystal (i.e., the \( C_p \) discrepancy) and consequently increases the entropy of the crystal (Courtial et al., 2000; Richet et al., 1998; Dimanov and Ingrin, 1995). These contributions are *configurational* in nature, and are a
major contributor to the $C_p$ discrepancies observed in Figures 3d, 3e, 3f and 4. The cation defects must be located between the $Q^2$ chains thus weakening forces binding the chains together.

**Anionic Defects.** With formation of a $[\text{Na}_1-\text{Q}^2]^{1-}$ moiety via Reaction (7), the tetrahedron becomes ‘unpinned’ at its NBO apex (i.e., the apex with no associated $\text{Na}^+$). Due to thermal agitation it may undergo librations different from, and more severe than, ‘pinned’ $[\text{Na}_2-\text{Q}^2]^0$ moieties. George et al. (1998) corroborate the effects of thermal agitation, noting that there is “some kind of extensive, librational motion of SiO$_4$ tetrahedral” in crystalline Na$_2$SiO$_3$ at high temperature. As emphasized by Nesbitt et al. (2017), the $[\text{Na}_1-\text{Q}^2]^{1-}$ moiety produced by Reaction (7) is a nucleophile which may attack Si centers of $Q^2$ species resident on adjacent chains. The reaction produces $Q^3$ species ($[\text{Na}_1-\text{Q}^3]^0$) according to:

$$[\text{Na}_1-\text{Q}^2]^{1-} + [\text{Na}_2-\text{Q}^2]^0 \rightarrow 2[\text{Na}_1-\text{Q}^3]^0 + \text{Na}^+ + \text{O}^{2-}$$  \hspace{1cm} (8)$$

where $\text{O}^{2-}$ is free oxygen or the oxide ion (Nesbitt et al., 2017, their Rxn 2b). The presence of $Q^3$ species in the Raman spectra of Na$_2$SiO$_3$ confirms that Reaction (8) occurs at temperatures as low as 774K (Richet et al., 1996). The $\text{O}^{2-}$ produced must also form anionic Frenkel pairs because Reaction (8) annihilates a tetrahedral oxygen site through formation of BO. Wherever $\text{O}^{2-}$ alights it will occupy an interstitial site. It may reside on sites with weak potential energy minima associated with cationic polyhedra (located between $Q^2$ chains) or it may react with other moieties of the crystal, as discussed in the next paragraph. The abundance of cationic Frenkel defects is at least double the abundance of anionic Frenkel defects (see Eqns. 7 and 8)

The strong nucleophile, $\text{O}^{2-}$, is a highly reactive, strong nucleophile and some $\text{O}^{2-}$ may attack $Q$ species to produce Si-pentahedra (SiO$_5$) such as observed in alkali silicate glasses and melts (e.g., Berezhnoi and Boiko, 2005; Stebbins, 1991). The SiO$_5$ moiety then becomes the defect. At high temperatures the lifetimes of all Si tetrahedra are short (Farnan and Stebbins, 1990)
as will be the lives of the SiO$_5$ moieties. The activation energy associated with formation of the SiO$_5$ moiety may inhibit its production at low temperatures. Nevertheless, the anionic defects O$^{2-}$ or SiO$_5$ necessarily contribute to $C_p$(config).

Defects in Other Alkali Silicate Crystals. The K-O bond dissociation energy is less than that of Na-O so that reactions equivalent to (7) and (8) likely occur in crystalline K$_2$SiO$_3$ (and K$_2$Si$_2$O$_5$). By analogy with Na-NBO bond dissociation in Na$_2$SiO$_3$, K-NBO dissociation should occur at ~700-800K with intrinsic cationic point defects forming in the K-silicate crystals, thus explaining the $C_p$ deficiency observed in Figure 3f. The Li-O bond strength is greater than Na-O bond strength so that Li cation point defect formation should be inhibited in Li$_2$SiO$_3$ relative to Na$_2$SiO$_3$. The prediction holds in that Li$_2$SiO$_3$ displays a weaker $C_p$ discrepancy than Na$_2$SiO$_3$ and the discrepancy is restricted to higher temperatures, commencing at ~900-1000K (Fig. 3d). There is no evidence that Reaction (2) occurs in Li$_2$SiO$_3$ (Richet et al., 1996), hence there is no evidence for appreciable O$^{2-}$ disorder in Li$_2$SiO$_3$. Finally, based on Na disorder in Na$_2$SiO$_3$, Na-O bond dissociation and cation defects formation probably occurs in Na$_2$Si$_2$O$_5$ above ~700K, accounting for the $C_p$ discrepancy observed in Figure 4.

Defect Abundances in Na$_2$SiO$_3$

Creation of Q$^3$ species via Reaction (2) annihilates Na and O structural sites and the displaced atoms must reside on other sites, here considered ‘defect’ sites. Production of Q$^1$ species creates new Na and O structural sites by establishment of additional Si-NBO-Na moieties (Nesbitt et al., 2017, their Reaction 3). The 1348K Raman spectrum of Na$_2$SiO$_3$ collected by Richet et al. (1996) was fit by Nesbitt et al. (2017) to obtain ~10% Q$^1$ species, ~68% Q$^2$ species and ~22% Q$^3$ species. These Q species abundances were used to calculate the abundance of O$^{2-}$, yielding ~1.7 mol% O$^{2-}$ or $X_{O2-} = 0.017$ (see Sawyer et al., 2015, Appendix A for calculation). Considering that
there are 3 moles of O per unit formula, there exists 0.051 (3x0.017) moles of O\textsuperscript{2-} in the crystal.

Reactions (7) and (8) combined indicate twice the moles of ‘defect’ Na (i.e., Na\textsuperscript{*}) as O\textsuperscript{2-}, requiring 0.102 moles of Na\textsuperscript{*} in the crystal at 1348K. But there are two moles of Na per unit formula so that \(X_{\text{Na}\textsuperscript{*}} = 0.051\). Richet et al. (1996) also collected and fit Na\textsubscript{2}SiO\textsubscript{3} Raman spectra at 1217K and 965K. \(Q^1\) species were absent and \(Q^3\) species were present at \(\sim 10\%\) and \(\sim 5\%\) respectively (visual estimates), indicating that \(X_{\text{Na}\textsuperscript{*}} \sim 0.025\) and \(X_{\text{O}2}\sim 0.016\) at 1217K, and \(X_{\text{Na}\textsuperscript{*}} \sim 0.012\) and \(X_{\text{O}2}\sim 0.008\) at 965K. The \(Q^3\) signal is undetectable in Raman spectra below 774K (Richet et al., 1996), the implication being that Na\textsuperscript{*} and O\textsuperscript{2-} are negligible below this temperature.

Reaction (7) creates a cationic vacancy and interstitial site (i.e., a Frenkel pair) whereas Reaction (8) annihilates a cationic site by a different mechanism (Nesbitt et al., 2017). Thus the abundance of Frenkel pairs is that produced by Reaction (7), which represents half the \(X_{\text{Na}\textsuperscript{*}}\) calculated in the previous paragraph. The values of \(X_{\text{Na}\textsuperscript{*}}\) therefore were halved to obtain the number of Frenkel pairs produced by Reaction (7) and these are plotted on Figure 5 (solid circles).

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

\[
\ln(X_{\text{Na}\textsuperscript{*}}) = \frac{-E^*}{2RT} \quad (3)
\]

where \(E^*\) is the energy required to create the vacancy site-interstitial site pair, \(R\) is the gas constant and \(T\) is temperature (K). With \(E^* = -84560\) J/mol, the calculated increase in \(X_{\text{Na}\textsuperscript{*}}\) as a function of temperature is illustrated by the solid curve (Fig. 5), which agrees reasonably with the experimental values at 965K, 1217K and 1348K (Fig. 5, solid circles). The calculation indicates that \(X_{\text{Na}\textsuperscript{*}} \sim 0.001\) at 700K. The calculation indicates that a \(C_p\) discrepancy for Na\textsubscript{2}SiO\textsubscript{3} should be vanishingly small up to \(\sim 700\)K (Fig. 3e). Beyond 700K Na\textsuperscript{*} concentrations increase rapidly with temperatures, as does the \(C_p\) discrepancy of Na\textsubscript{2}SiO\textsubscript{3}. The calculations are consistent with the Raman spectral results (Richet et al., 1996) and with \(C_p\) measurements (Fig. 3e). Raman spectra of
Li$_2$SiO$_3$ reveal no obvious Q$^3$ species up to 1465K (Richet et al., 1996), indicating an absence of O$^2$. The very weak C$_p$ discrepancy beginning at ~900-1000K (Fig. 3d) likely is attributed solely to minor Li disorder (e.g., Frenkel pair formation). There are insufficient experimental data to calculate cation defect abundances for the other alkali silicates.

**IMPLICATIONS FOR MANTLE MINERALS**

The observations and deductions concerning C$_p$ indicate that alkali-O bond dissociation and defect formation occur in alkali metasilicate and disilicate crystals due primarily to thermal agitation. Alkali-O bond dissociation energies are low compared with alkaline earth-O bond dissociation energies, implying that greater thermal agitation is required for the latter bonds to be ruptured. The very high temperatures of the mantle may be sufficient to cause alkaline earth-O bond dissociation and to produce defects in pyroxenes and olivines. Dimanov and Ingrin, (1995) Richet et al. (1998), Dimanov and Jaoul (1998) and Bouhifd et al. (2002) documented the enhanced mobility (disorder) of Ca in pseudowollastonite, diopside and gehlenite, where disorder commences at ~1500-1600K in the first two phases and ~1800K for the last. In addition, Mg disordering, hence Mg-O bond dissociation, probably occurs within the premelting region of enstatite and forsterite (Richet et al., 1993; Thiéblot et al., 1999), and likely occurs within the premelting regions of most minerals subjected to mantle temperatures (Richet et al., 1998; 1994; Richet and Fiquet, 1991). Where Ca or Mg disordering occurs in pyroxenes, reactions entirely analogous to Reactions (7) and (8) may occur (with Ca or Mg substituted for 2Na) thus promoting formation of intrinsic, Frenkel type, defects in the minerals. Two implications for mantle minerals follow.

The onset of premelting of diopside and proto-enstatite occurs at ~1550K and ~1700K respectively, resulting in cation disorder and formation of Frenkel type cationic defects (Thiéblot
et al., 1999; Richet et al. 1998; Dimanov and Ingrin 1995). As here emphasized, the defects tend to destabilize the minerals by increasing their $C_p$, entropy and free energy values. In response, the minerals may change structure or composition to produce a more stable phase. Structural changes driven by defect formation may include creation of ‘new’ sites which incorporate previously disordered cations. These new structural sites may be accompanied by other changes such as incorporation of Al into octahedral or tetrahedral sites, which should stabilize the minerals at high temperature (Al-O bond dissociation energy is ~512 kJ/mol). Through such changes, the abundance of point defects should decrease, thereby stabilizing pyroxenes against the effects of thermal agitation. The Ca-Tschermak (CaAl$_2$SiO$_6$) and NaAlSi$_2$O$_6$ components are likely examples of pyroxene components produced through minimization of cationic defects. We suggest that elimination of defects through changes to composition and structure play an important role in stabilizing pyroxenes against extreme thermal agitation.

Richet et al. (1993) suggests that Mg undergoes disordering within the premelting region of forsterite (~2050-2163 K) which spans the temperature range of the wadsleyite stability field (Frost, 2008; Katsura et al., 2004). Mg-O bond dissociation and production of Frenkel defects should contribute to the instability of olivine and to formation of wadsleyite by converting the highly energetic Mg Frenkel defects of olivine to more stable edge-sharing Mg$^{2+}$ octahedral structural sites of wadsleyite (Ashbrook et al., 2005). In addition, Mg-O bond dissociation necessarily produces a negatively charged [$Q^0$]$^-$ moiety within the crystal (e.g., Nesbitt et al., 2017). The moiety is a strong nucleophile and due to thermal agitation it may encounter and react with adjacent $Q^0$ species to produce a [Si$_2$O$_6$] moiety and O$^{2-}$ according to:

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

The reaction is analogous to Reaction (4) and occurs in Mg$_2$SiO$_4$ glass and melt in which $Q^1$
species are observed (Nesbitt et al., 2015; Sen and Tangeman, 2008; Voronko et al., 2006). The
products of Reaction (4), $Q^1$ and $O^{2-}$, are essential constituents of wadsleyite, $\beta$-Mg$_2$SiO$_4$,
(Ashbrook et al., 2005) and the reaction should promote its formation at the expense of olivine.
The presence of wadsleyite in the mantle may have as much to do with Mg-O bond dissociation
(through thermal instability) and production of $Q^1$ species and $O^{2-}$ in olivine as it has to do with
pressure.

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**Figure Captions**

**Fig. 1:** (a) Illustrates the heat capacity (at constant pressure) of crystalline and liquid Na$_2$SiO$_3$ as a function of temperature. The vertical dotted line represents initiation of the premelting region of the crystal the dotted, curved arrow indicates the trend in $C_p$ within the premelting region. The vertical solid arrow indicates the melting point. (b) Illustrates the normalized heat ($C_p/n$) of the crystal as a function of temperature ($n$ = no. of atoms in the unit formula). The dashed curve represents $C_v$ (Debye Function) calculated assuming the Debye Temperature = 750K and the dotted arrow indicates the premelting trend.

**Fig. 2:** Illustrates volumetric properties of some chain and ring silicates as a function of temperature. (a) volume of Na$_2$SiO$_3$(c) as a function of temperature. The straight line is the least squares best fit to the solid circles. The arrow indicates onset of the premelting region. (b), (c), (d),
(e) and (f) Illustrates the volume coefficient of thermal expansion (\(\alpha_V\)) of the indicated crystal as a function of temperature. The solid curves are a least squares best fit to the solid circles. The best fit equation and the source of the data are provided in each diagram.

**Fig. 3:** Illustrates the experimental and calculated ‘normalized’ \(C_p\) results for the indicated crystals (normalized \(C_p = C_p/n\) where \(n = \) no. of atoms per unit formula). The solid curve in each diagram represents the \(C_p\) calculated from Equation (3). The dashed curves represent \(C_V\) calculated using the Debye Temperature indicated in the diagram. The short arrow (labelled m.p. in some diagrams) indicates the melting point. The dotted curves indicate the \(C_p\) trends within the premelting regions of the crystals. See text for details. (a) \(C_p/n\) values for orthoenstatite (small and large circles) and proto-enstatite (shaded circles); (b) \(C_p/n\) values for diopside.; (c) \(C_p/n\) values for pseudowollastonite (p-CaSiO\(_3\)); (d) \(C_p/n\) for Li\(_2\)SiO\(_3\)(c). The dotted curve represents \(C_p/n\) values calculated assuming that the Grüneisen parameter = 1.3. (e) \(C_p/n\) of Na\(_2\)SiO\(_3\)(c); (f) \(C_p/n\) for 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 circles.

**Fig. 4:** Illustrates the experimental \(C_p/n\) values for Na\(_2\)Si\(_2\)O\(_5\) (solid circles). The experimental \(C_p/n\) values for Na\(_2\)SiO\(_3\) are plotted for comparison (open and shaded circles). The dashed curve represents the Debye Function and the two dotted arrows indicate \(C_p/n\) trends within the premelting regions of Na\(_2\)Si\(_2\)O\(_5\) and Na\(_2\)SiO\(_3\).

**Fig. 5:** Defect concentrations of Na (\(X_{Na^+}\)) determined from experiment (dots) and the calculated Frenkel pair defect concentrations (solid curve) using the activation energy shown in the diagram. Details are provided in the text.
Na$_2$SiO$_3$

- Naylor (1945)
- Richet et al. (1984)
- Kelley (1960)

- Crystal
- Premelting region
- Melting point
- Liquid

3nR

C$_p$ with $\theta = 750$ K

$C_p$ with $\theta = 750$ K
Fig. 2
Fig. 4
Fig. 5

$E^* = -84560 \text{ J/mol}$

![Graph showing the relationship between $X_{Na^*}$ and temperature (K).](graph.png)
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1 Pitzer and Brewer (1961), Table A5-1, p. 660.
### Table 2: Gruneisen Parameter ($\gamma$) for Chain Silicates

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Table 3: Enstatite Cp(avg) Values Calculated from Relative Enthalpies

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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 ΔH = (H<sub>T2</sub> - H<sub>T1</sub>); ΔT = (T<sub>2</sub>-T<sub>1</sub>); T(avg) = (T<sub>2</sub>+T<sub>1</sub>)
4 Cp(avg) = (H<sub>T2-H1</sub>)/(T<sub>2</sub>-T<sub>1</sub>) = ΔH/ΔT. Cp(avg) is plotted at T(avg).
5 Cp/n = Cp normalized to 'n', the number of atoms in the unit formula