



AperTO - Archivio Istituzionale Open Access dell'Università di Torino

# Volume thermal expansion along the jadeite-diopside join

This is the author's manuscript
Original Citation:
Availability:
This version is available http://hdl.handle.net/2318/153763 since
Published version:
DOI:10.1007/s00269-014-0694-9
Terms of use:
Open Access
Anyone can freely access the full text of works made available as "Open Access". Works made available under a Creative Commons license can be used according to the terms and conditions of said license. Use of all other works requires consent of the right holder (author or publisher) if not exempted from copyright protection by the applicable law.

(Article begins on next page)



# UNIVERSITÀ DEGLI STUDI DI TORINO

This is an author version of the contribution published on:

Pandolfo F, Camara F, Domeneghetti MC, Alvaro M, Nestola F, Karato S-I, Amulele G Volume thermal expansion along the jadeite-diopside join PHYSICS AND CHEMISTRY OF MINERALS (2015) 42 DOI: 10.1007/s00269-014-0694-9

The definitive version is available at: http://link.springer.com/content/pdf/10.1007/s00269-014-0694-9

# Volume thermal expansion along the jadeite-diopside join

FRANCESCO PANDOLFO<sup>1</sup>, FERNANDO CÁMARA<sup>2,†</sup>,

M. CHIARA DOMENEGHETTI<sup>1</sup>, MATTEO ALVARO<sup>3\*</sup>, FABRIZIO NESTOLA<sup>3</sup>, SHUN-ICHIRO KARATO<sup>4</sup>, GEORGE

AMULELE<sup>4</sup>

<sup>1</sup>Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia, via Ferrata 1, I-27100 Pavia, Italy <sup>2</sup>Dipartimento di Scienze della Terra, Università degli Studi di Torino, via Valperga Caluso 35, I-10125 Torino, Italy <sup>3</sup>Dipartimento di Geoscienze, Università di Padova, via Gradenigo 6, I-35131 Padova, Italy <sup>4</sup>Department of Geology and Geophysics, Yale University, New Haven, CT, USA <sup>†</sup>CrisDi, Interdepartmental Centre for Crystallography, Torino, Italy

\*E-mail: matteo.alvaro@unipd.it

#### ABSTRACT

20 An in situ single-crystal high temperature X-ray diffraction study was performed on clinopyroxene crystals along the 21 jadeite, (NaAlSi<sub>2</sub>O<sub>6</sub>Jd) – diopside (CaMgSi<sub>2</sub>O<sub>6</sub>Di) join. In particular, natural samples of jadeite, diopside, P2/n22 omphacite and three  $C_2/c$  synthetic samples with intermediate composition (i.e.  $Jd_{80}$ ,  $Jd_{60}$ ,  $Jd_{40}$ ) were investigated. In 23 order to determine the unit-cell volume thermal expansion coefficient ( $\alpha_{\rm V}$ ) the unit-cell parameters for all these 24 compositions have been measured up to c.a. 1073 K. The evolution of the unit-cell volume thermal expansion 25 coefficient ( $\alpha_v$ ) along the Jd - Di join at different temperatures has been calculated by using a modified version of 26 the equation proposed by Holland and Powell 1998). The equation  $a_{V(303K,1bar)} = 2.68(3) \times 10^{-5} + [1.1(1) \times 10^{-5}]$  $10^{-8} \times X_{Id}$ ] - [7.1(1.7) ×  $10^{-10} \times X_{Id}^2$ ] obtained from the  $\alpha_V$  at room-*T* (i.e.  $\alpha_{V303K,1bar}$ ), allows us to predict the 27 28 room-T volume thermal expansion for Fe-free C2/c clinopyroxenes with intermediate composition along the binary 29 join Jd-Di. The observed  $\alpha_V$  value for P2/n omphacite  $\alpha_{V(303K,1bar)} = 2.58(5) \times 10^{5} \text{K}^{-1}$  was compared with that recalculated for disordered C2/c omphacite published by Pandolfo et al 2012 [ $\alpha_{V(303K,1bar)} = 2.4(5) \times 10^{-5} K^{-1}$ ]. Despite 30 31 the large e.s.d.'s for the latter, the difference of both values at room T is small, indicating that convergent ordering 32 has practically no influence on the room-T thermal expansion. However, at high-T the smaller thermal expansion 33 coefficient for the C2/c sample with respect to the P2/n one with identical composition could provide further 34 evidence for its reduced stability relative to the ordered one. 35

36

37 38

39 KEYWORDS: jadeite; diopside; omphacite; thermal expansion; high temperature; single-crystal X-ray diffraction.

40

# **INTRODUCTION**

43	Clinopyroxenes are major constituents of the upper mantle and they are involved in a
44	wide range of geological environments. The construction of a reliable model for upper-mantle
45	behavior requires data on their thermodynamic properties like the bulk modulus and thermal
46	expansion. In particular, "for most upper mantle depths the thermal diffusivity of the pyroxene is
47	$\sim$ 70% greater than that of the olivine making up the bulk of the surrounding mantle" (Hunt et al.
48	2011). Due to the complex compositional variability of clinopyroxenes, thermodynamic data are
49	necessary not only for the end-members but also for intermediate samples and for the complete
50	solid solutions, for which data are very often poorly determined or absent. Several different
51	studies have been performed to determine the high-temperature behavior of clinopyroxenes, most
52	of them concerning the end-member compositions. A review was provided by Yang and Prewitt
53	2000, although numerous studies have recently been performed on sodic and lithium
54	clinopyroxenes (see Redhammer et al. 2010, and references therein).
55	The volume thermal expansion coefficients ( $\alpha_V$ ) along the jadeite (Jd) – diopside (Di) join
56	are available almost exclusively for composition close to the end-members. In particular,
57	Cameron et al. 1973 reported data on the high-temperature behavior of natural samples of jadeite
58	and diopside studied using <i>in-situ</i> single crystal X-ray diffraction in the range 24-1000°C. These
59	authors obtained an $\alpha_V$ value, calculated using a linear equation (no dependence of $\alpha$ on <i>T</i> ), of
60	$2.47 \times 10^{-5}$ K <sup>-1</sup> for jadeite and of $3.33 \times 10^{-5}$ K <sup>-1</sup> for diopside. Finger and Ohashi 1976 studied the
61	thermal expansion of a natural diopside up to 800°C and performed an intensity data collection at
62	700°C. The authors reported a linear thermal expansion value ( $\alpha_V$ ) of 3.1(3)×10 <sup>-5</sup> K <sup>-1</sup> . Richet et
63	al. 1998 investigated synthetic diopside using powder X-ray diffraction technique obtaining an
64	$\alpha_V = 9.263 \times 10^{-6} + 42.7 \times 10^{-9} T - 7.215 \times 10^{-12} T^2$ ( <i>T</i> in K) by considering $\alpha$ as a polynomial function

of temperature, thus yielding  $2.16 \times 10^{-5}$  K<sup>-1</sup> at 300K and  $5.91 \times 10^{-5}$  K<sup>-1</sup> at 1600K. Tribaudino et al. 65 66 2008 studied the thermal expansion of jadeite up to 800°C using single-crystal X-ray diffraction 67 technique (SC-XRD) fitting the unit-cell volume with a linear equation obtaining  $\alpha_V =$  $2.54(6) \times 10^{-5}$  K<sup>-1</sup>. Zhao et al. 1997 reported the thermoelastic equation of state (*T*-EoS) of jadeite 68 69 and diopside obtained by an in situ synchrotron X-ray powder diffraction study at simultaneous 70 high-T and high-P conditions. The thermal expansion coefficients obtained by fitting their data assuming a linear dependence of  $\alpha$  with  $T(\alpha = a + bT)$  are 2.64×10<sup>-5</sup> K<sup>-1</sup> and 2.89×10<sup>-5</sup> K<sup>-1</sup> for Jd 71 72 and Di, respectively.

73 According to our knowledge the only available thermal expansion data for omphacite 74 samples are those by Pavese et al. 2000. These authors studied a natural chemically quasi-ideal 75 ordered *P2/n* omphacite up to 1000°C by *in-situ* high temperature SC-XRD; by fitting a linear function of the data on heating they obtained an  $\alpha_V$  value of 2.76(4)×10<sup>-5</sup>K<sup>-1</sup> while the fitting of 76 the data on cooling provided an  $\alpha_V$  value of 2.51(3)×10<sup>-5</sup>K<sup>-1</sup>. The authors suggested that the 77 78 discrepancies between heating and cooling (10%) are mainly due to order-disorder reaction in 79 the sample. Very recently, Pandolfo et al. 2012 investigated a natural disordered omphacite 80 (space group  $C^{2}/c$ ) using the same experimental technique but fitting the data following the equation proposed by Berman 1988 (expressed in the form where  $\alpha_{V,Tr} = a_0 + 2a_1(T-T_r)$ ]) 81 obtaining an  $\alpha_{V303K}$  value of 2.64(2)×10<sup>-5</sup>K<sup>-1</sup>. 82

It is evident that data in literature are broadly scattered, mainly because of the different
methods adopted to estimate α values. It is therefore crucial to carefully determine the unit-cell
volume thermal expansions because of their application for thermodynamic calculation of
equilibrium reaction in rocks (see by instance Gottschalk 1997, Berman 1988, Holland and
Powell 1998, 2011).

88 In this study we will: i) better constrain the  $\alpha_{\rm V}$  evolution along the jadeite – diopside 89 binary join investigating the thermal expansion behavior of the end-members as well as that of 90 synthetic samples along the join, by using the very same device in order to avoid any effect due 91 to changes in the experimental set up or temperature calibration of the device; ii) evaluate the 92 effect of the convergent ordering on the  $\alpha_V$  value, by investigating the thermal expansion 93 behavior of a P2/n omphacite and comparing it with that obtained on a disordered C2/c sample 94 (Pandolfo et al. 2012). 95 96 **EXPERIMENTAL METHODS** 97 a. Samples 98 The experimental work was performed on natural and synthetic samples with composition 99 along the join jadeite (NaAlSi<sub>2</sub> $O_6$ ) – diopside (CaMgSi<sub>2</sub> $O_6$ ). The end members jadeite and 100 diopside (labelled Jd<sub>100</sub>, and Di, respectively) and the omphacite [sample 74AM33, with 101 composition ca.  $(Ca,Na)(Mg,Al)Si_2O_6$ ] are natural samples already well characterized by Boffa 102 Ballaran et al. 1998. The jadeite pure end-member comes from serpentine rocks (New Idria, 103 California, US) and the diopside pure end-member from the Dekald country (New York State, 104 US; Mineral collection Dept. of Earth Sciences Cambridge, UK); the 74AM33 omphacite sample 105 is from an eclogitic rock (Münchberg Mass, Bavaria). The omphacite crystal of this study 106 labelled N5 has P2/n symmetry. The samples with intermediate compositions,  $Jd_{80}$ ,  $Jd_{60}$ ,  $Jd_{40}$ , 107 all  $C_{2/c}$ , have been synthesized at the Department of Geology and Geophysics at the Yale 108 University (Conneticut, USA) using a multi-anvil press. 109 **b.** Syntheses

110 The glasses for the syntheses experiments were prepared using dried MgO,  $Al_2O_3$ , 111 CaCO<sub>3</sub>, Na and SiO<sub>2</sub> (provided by Alpha Aesar Company) as starting material. After weighing, 112 the oxide mixture was ground under ethanol with an agate mortar. The dried mixture was placed 113 into a platinum crucible and decarbonated by heating up to 1400 °C and then glassed by 114 quenching into cold water; after quenching the glassed sample was grounded again to powder as 115 described before. This process of melting, quenching and grinding was performed in order to 116 ensure the homogeneity of the powered samples. The powder was then loaded into platinum foil 117 capsules welded in both sides. Tungsten carbide anvils of 11 mm truncation edge length with 118 standard 18 mm edge length octahedra were used. The capsule was placed in a graphite furnace 119 surrounded by an MgO sleeve and spacers. The temperature was monitored with a D-type 120 thermocouple inserted within an alumina sleeve, with the junction in contact with the top of the 121 capsule (Nishihara et al. 2006). Experiments were performed at 5 GPa between 1300 and 1350 122 °C for periods of 6-9 hrs in a 1000-ton Kawai-type multi anvil press. The quenching was 123 performed by switching off the furnace following a decompression profile that allowed to reach 124 room *P*,*T* conditions in 10-12 hours. The obtained capsules contained single crystals with sizes 125 ranging between 40-100  $\mu$ m with presence of oxides or glasses.

126

### 127 c. Electron microprobe analysis (EMPA)

The crystals studied by X-ray diffraction were embedded in epoxy and polished. Electron microprobe analysis (EMPA) were carried out at the Dipartimento di Geoscienze (University of Padova, Italy) using a CAMECA- SX 50 electron microprobe operating in wavelength dispersive mode with a fine-focused beam (~1 mm diameter), an acceleration voltage of 20 kV and a beam current of 10 nA, with 10 s counting times for both peak and total background. X-ray counts

133	were converted to oxide wt.% using the PAP correction program supplied by CAMECA
134	(Pouchou and Pichoir 1991). For standards, spectral lines, and analytical crystals used were
135	albite (Na–Ka, TAP), wollastonite (Si, Ca–Kα, TAP), olivine (Mg–Kα, TAP), Al <sub>2</sub> O <sub>3</sub> (Al– Kα,
136	TAP), MnTiO <sub>3</sub> (Mn–Kα, LiF; Ti–Kα, PET), Cr <sub>2</sub> O <sub>3</sub> (Cr–Kα, LiF) and Fe <sub>2</sub> O <sub>3</sub> (Fe– Kα, LiF). The
137	oxide wt.% reported in Table 1 were obtained by averaging 15 microprobe analyses and the
138	reported formulae was normalized on the basis of 6 oxygen atoms

139

## 140 d. X-Ray diffraction at ambient conditions

141 Single crystal X-ray diffraction (SCXRD) intensity data at room-T have been collected at 142 the Dipartimento di Scienze della Terra e dell'Ambiente (Università degli Studi di Pavia, Italy) 143 using a three-circle Bruker AXS SMART APEX diffractometer, equipped with a CCD detector 144 (graphite-monocrhomatized MoKα radiation, 50 kV, 30 mA) and a 0.3 mm monocap collimator. 145 The Bruker SMART v. 5.625 software package was used for collecting a total of 3360 frames 146 (frame resolution 512×512 pixels) with four different goniometer settings using the  $\omega$ -scan mode 147 (scan width: 0.2 ° $\omega$ ; exposure time: 10 s; detector sample distance 4.02 cm) up to  $2\theta = 78^{\circ}$ . The 148 Bruker SAINT+ v. 6.45 software was used for data reduction, including intensity integration and 149 background and Lorentz-Polarization corrections. The semi-empirical absorption correction of 150 Blessing 1995, based on the determination of transmission factors for equivalent reflections, was 151 applied using the program SADABS (Sheldrick 1996). The intensity data at room-T for the 152 sample Di have been collected using a Philips PW1100 four-circle automated diffractometer 153 equipped with a point detector (graphite-monocrhomatized MoK $\alpha$  radiation at 30 mA/50 kV) and 154 using a 0.5 mm collimator, and operated with FEBO software (local developed control software) 155 up to  $67.9^{\circ} 2\theta$ . The intensity data were merged for the monoclinic Laue group 2/m.

156 The structure refinements were carried out using the program SHELX-97 (Sheldrick 157 2008) starting from the atom coordinates by Boffa Ballaran et al. 1998, for samples with space 158 group C2/c and by Pavese et al. 2000 for the N5-P2/n omphacite sample. Neutral versus ionized 159 scattering factors were used to refine occupancy for all sites that are not involved in chemical 160 substitutions (O and Si) (Hawthorne et al. 1995) and ionized scattering factors were used for 161 cationic sites. Scattering curves were taken from the *International Tables for X-ray* 162 *Crystallography* (Wilson 1995). The anisotropic displacement parameters were refined for all 163 atoms in all the studied crystals. The unit-cell parameters of the crystals at room-T (collected 164 using the Philips PW1100 four-circle diffractometer; before and after the *in-situ* annealing for 165 the P2/n sample), the statistics values (i.e. the agreement factors  $R_1$ , w $R_2$  etc...) as well as other 166 details from the structure refinement of the samples studied are reported in Table 2. The structure 167 models (CIF files) are available as supplementary electronic material<sup>1</sup>. 168 For the P2/n sample N5, once the structure refinement reached convergence, a structure 169 refinement with chemical constraints was carried out using the data from the electron microprobe 170 analysis with  $1\sigma$  error in order to obtain reliable site partitioning that allowed to calculate the 171 order degree (see Pandolfo et al. 2012 for details about the refinement procedure). For the same 172 sample the mean atomic numbers calculated for the octahedral sites  $[m.a.n._{M1+M11+M2+M21}]$  by 173 SCXRD (before introducing the chemical constraints) and by EMPA are in agreement within 174 their errors. In Table 3 the mean atomic number, the mean bond lengths for the M1 and M2 sites before and after the *in-situ* annealing, the order parameters  $Q^{\text{occ}}$  and  $Q^{\text{dist}}$  (Carpenter et al. 1990) 175 176 calculated using the site population, are listed together. In the same table the Ca-site occupancies 177 of M2 and M21 sites and the octahedral mean bond distances from omphacite data reported by

<sup>&</sup>lt;sup>1</sup> CIF file are available as supplementary material.

Pavese et al. 2000 [labeled here as Omp50] are shown. The  $O^{\text{dist}}$  and  $O^{\text{occ}}$  values for M1 and M2 178 179 sites have been calculated starting from the data by Pavese et al. 2000 using the equations 180

181

#### 182 e. High temperature X-ray diffraction experiments

proposed by Carpenter et al. 1990)

183 High-temperature single crystal X-ray diffraction (HT-SC-XRD) experiments were 184 carried out at the Dipartimento di Scienze della Terra e dell'Ambiente (Università di Pavia, Italy) 185 using a Philips PW1100 four-circle automated diffractometer and a point detector, working with 186 the same experimental conditions as described above, and equipped with a microfurnace for *in*-187 situ high-temperature experiments consisting of a H-shaped Pt-Rh resistance and a Pt:Pt-Rh 188 thermocouple inside a steel cylindrical cage 1 inch wide closed with a Kapton film. The device 189 allows the X-ray diffraction data to be collected up to  $\theta_{max}=29^\circ$ . Each crystal was loaded in a 0.3 190 mm inner diameter 26 mm long quartz vial closed at the top by using oxy-methane flame after alternately washing with Ar flux and vacuuming (4 x  $10^{-2}$  mbar). In order to avoid any 191 192 mechanical stress, each crystal was kept in position within the vial using quartz wool. A small 193 piece of an iron wire, used as a buffer to avoid Fe oxidation during annealing, was loaded inside 194 the vial together with the crystal (crystal-iron wire distance c.a. 1.5 mm). 195 The temperature calibration of the microfurnace was undertaken as described in Cámara et al. 196 (2012), Ferrari et al. (2014) and Gatta et al. (2014). The high temperature device and the 197 calibration equation used for these experiments are detailed described in Pandolfo et al. (2012). 198 Preliminary cell centring using horizontal and vertical slits was performed on 24 intense 199 reflections over the  $2\theta$  interval 15–30°. Accurate and precise lattice constants were then 200 determined using the Philips LAT procedure on the 60 most intense reflactions (see Cannillo et

201 al. 1983 Cámara et al. 2012 for further details). The same set of selected reflections was used for 202 each temperature measurement. In order to avoid temperature fluctuation during the centring 203 procedure reflections were ordered by  $\gamma$  values reducing therefore the changes in  $\gamma$  angles 204 between consecutive reflections. Lattice parameters were collected in the temperature range 303-205 1073 K at intervals of 50 K with increasing and decreasing temperature. The only exception are 206 the data of the P2/n omphacite sample N.5 collected during cooling with steps of 100 K. Higher 207 temperatures (1173 K) were reached only for the measurement performed on Di sample. Each 208 standard experiment was conducted in about 110 hrs. For the P2/n sample N.5, the high-T data 209 (in the interval between 873 K - 1073 K) were collected in not more than 15 hrs in order to 210 hamper the ordering kinetic effects. Moreover the intensities for selected reflections with h + k =211 2n + 1 ( $\overline{1}$  0 1, 0 5 0) and h + k = 2n ( $\overline{2}$  0 2, 0 6 0) were measured at each temperature. The 212 presence of *b*-type reflections (i.e. h + k = 2n + 1) with intensities  $I > 3\sigma$  during temperature 213 increasing and decreasing ensured that the crystal maintained the same degree of order for the 214 entire experiment. This is also confirmed by the comparison between the Q parameters 215 calculated from the site occupancies and the mean bond distances obtained from the structural 216 refinement performed before and after the heating experiments (see Table 3). 217 The measured unit-cell volumes as a function of temperature for all samples are reported in 218 Table 4. Lattice parameters as a function of temperature have been deposited as electronic 219 supplementary material (Table 5a,b,c,d). Unfortunately we have not been able to complete the 220 cooling experiment for the crystals N5 and Di because of the break of the vial. 221 222 **RESULTS AND DISCUSSION** 223 224 *Lattice thermal expansion behavior* 

225	At room- $Tb$ lattice parameters as well as unit-cell volumes are clearly controlled by the
226	composition as shown in Figure 1a and Figure 1b. The change in composition along the Jd-Di
227	join has a strong effect on the volumes of the $M$ polyhedra (see Tribaudino and Mantovani, 2014)
228	for further details) that are basically able to accommodate the compositional changes only along
229	[010]. Moreover, the O3-O3-O3 kinking angle contributes in a lesser extent to accommodate the
230	compositional change along the <b>b</b> and <b>c</b> lattice directions (Figure 1b). The larger is the expansion
231	along [010], the narrower is the O3-O3-O3 angle of the tetrahedral chain. It is evident that
232	samples with wider O3-O3-O3 angles can accommodate less deformation with respect to those
233	with narrower O3-O3-O3 angles (Figures 1a, b). Such behavior has already been shown for
234	different composition samples by several studies mainly devoted to the high- $P$ and high- $T$
235	structural investigation (Alvaro et al. 2010; Alvaro et al. 2011a; Alvaro et al. 2011b; Cámara et
236	al. 2003; Nestola et al. 2008; Redhammer et al. 2010; Tribaudino 1996; Tribaudino et al. 2008
237	and Tribaudino and Mantovani, 2014)
238	The room-T unit-cell volume data allowed us to extrapolate the equation
239	$V(\text{\AA}^3) = 439.0(2) - 0.369(4) X_{\text{Jd}}$ (equation 1)
240	that describes the unit cell volume changes as a function of composition within diopside - jadeite
241	join.
242	The unit-cell parameters expand almost linearly with increasing $T$ for all the
243	compositions studied in this work (Di, Jd40, Jd60, Jd80, Jd100 and Jd55 N. 5 $P2/n$ ) as shown in
244	Figure 2.
245	The <i>b</i> lattice, being the softest direction mostly affected by the compositional changes,
246	undergoes the largest expansion with temperature compared with the other lattice parameters (i.e.
247	<i>a</i> , <i>c</i> and $\beta$ , see Figure 2 a, b, c, d), accommodating more than a half of the total volume

248 expansion. For example, in diopside a, c and  $\beta$  expand by 0.68%, 0.61% and 0.14% respectively 249 (in 870 K) whereas b expands by 1.53%, with an overall volume expansion of 2.77%. This 250 observation is clearly in agreement with previous data in other clinopyroxenes (Tribaudino et al. 251 2002; Cámara et al. 2003; Redhammer et al. 2010; Alvaro et al. 2011a; Mantovani et al. 2013). It 252 is interesting to note that the slope of the b lattice expansion as well as the  $\beta$  angle increase 253 within the Jd-Di solid solution, while very similar rates of expansion are observed for both a and 254 c lattice parameters. Therefore the different volume thermal expansion within the solid solution 255 is the consequence of an increased thermal expansion along [010] and shear within the (010)256 plane.

257 In Figure 3a the volume-temperature data obtained for the end-members C2/c samples of 258 this study  $[Di, Jd_{100}]$  are reported together with those available from literature, in particular three 259 diopside samples from Finger and Ohashi 1976 ( $Di_{Fn}$ ), Richet et al. 1998 ( $Di_{Rt}$ ), and Cameron et 260 al. 1973 (Di<sub>Cr</sub>) and the two jadeite samples from Cameron et al. 1973 (Jd<sub>Cr</sub>) and Tribaudino et al. 261 2008 (Jd<sub>Tr</sub>). For diopside the small room-T unit-cell volume discrepancies between our data and 262 those by Finger and Ohashi 1976, Richet et al. 1998 and Cameron et al. 1973 could be ascribed 263 to small differences in composition, mainly due to the lower Ca content of our samples. Data by 264 Richet et al. 1998 show a change in the slope at high T, which the authors ascribe to pre-melting 265 starting at ca. 1500 K. For the end-member jadeite the unit cell volume at room and high-T of our 266 sample (Jd<sub>100</sub>) is very close to that reported in literature by Cameron et al. 1973 and Tribaudino 267 et al. 2008. In Figure 3b the volume-temperature data obtained for the intermediate composition 268 C2/c and P2/n samples of this work (Jd<sub>40</sub>, Jd<sub>60</sub>, Jd<sub>80</sub>, Jd<sub>55</sub> N.5 P2/n) are reported together with 269 those available from literature, in particular  $Jd_{55}$  N.2 C2/c from Pandolfo et al. 2012 and Omp 270 P2/n from Pavese et al. 2000.

The cell volume increases almost linearly for all intermediate compositions with increasing temperature with a very similar increasing rate for all the *C*2/*c* samples, while the slope of the *V*,*T* data is slightly different for the *P*2/*n* samples (Figure 3b) that increases at two different rates. It is very interesting to notice that the three samples close to the 50% of Jd (Jd<sub>55</sub> N.2 *C*2/*c* and Jd<sub>55</sub> N.5 *P*2/*n* with 55% Jd; and Omp *P*2/*n* with 50%Jd) show volume differences larger than 1 e.s.d.'s at room-*T* while are almost undistinguishable (differences within 1 e.s.d.'s) at high-*T* (above 850K).

278

# 279 Thermal expansion coefficients behavior

To a first approximation, the coefficient of volume thermal expansion can be considered as being *T*-independent, and therefore the variation of the unit-cell volume with *T* could be fitted by least-squares with the equation proposed by Gottschalk 1997 where  $V(T) = V_{o(Pr:Tr)} e^{\alpha_o(T-Tr)}$ 

with  $V_0$ ,  $P_r$  and  $T_r$  being the reference volume, pressure and temperatures, respectively.

However, most ionic or mixed ionic-covalent compounds show a dependence of  $\alpha$  with *T* (see by instance values reported by Fei, 1995), and a strong increase of  $\alpha$  with *T* and a saturation effect at

high values of *T*. Therefore, the temperature-dependence of  $\alpha$  is expected to be limited above the

287 Debye temperature (Anderson et al. 1992). A physical model valid for ionic compounds

involving the vibrational density of states (Anderson et al. 1992) or a quasi-harmonic Einstein's

289 model as described by Knight 1996 would require high quality data collected well below room-*T* 

290 (see also Tribaudino et al. 2010 for further discussions on different thermal expansion model and

- 291 naming). However empirical fits can be adopted to quantify such limited but still present
- temperature dependence. For instance the second-order polynomial equation proposed by

293 Berman 1988, where  $V_{0T} = V_{00} \left( 1 + \alpha_0 (T - T_{ref}) + \frac{1}{2} \alpha_1 (T - T_{ref})^2 \right)$  [from which

294  $\partial V / \partial T = \alpha \approx \alpha_0 + \alpha_1 (T - T_{ref})$ ] allows for a linear dependence of  $\alpha$  on *T*. As a consequence, we 295 obtain better fitting results at both the highest and lowest *T* than those obtained with the model 296 assuming  $\alpha$  being independent form *T*. In addition, the saturation of  $\alpha_V$  at high temperature can 297 be considered using the equation proposed by Holland and Powell 1998 where

298 
$$V_{0T} = V_{00} \left( 1 + \alpha_0 (T - T_{ref}) - 2\alpha_1 \left( \sqrt{T} - \sqrt{T_{ref}} \right) \right) \text{ [from which } \partial V / \partial T = \alpha = \alpha_0 - \alpha_1 \left( \sqrt{T} - \sqrt{T_{ref}} \right) \text{] as}$$

- well as the one modified by Pawley et al. 1996 where the authors simplified the equation taking into account the experimental evidences by which  $a_1=10(2)a_0$  [from which
- 301  $\partial V / \partial T = \alpha = \alpha_0 (1 10\sqrt{T_{ref}})$ . To be noticed is that in order to accommodate this simplification
- 302 in a simple manner EosFit7c (Angel et al. 2014) is coded with a modified equation

303 
$$V_{0(\text{Pr},Tr)} = V_{00} \left( 1 + \alpha_0 (T - T_r) - 2 \left( 10\alpha_0 + \alpha_1 \right) \left( \sqrt{T} - \sqrt{T_r} \right) \right) \text{ where the entire term } \left( 10\alpha_0 + \alpha_1 \right) \text{ of this}$$

equation is in actual fact equal to the  $\alpha_1$  coefficient reported in the simplified equation by Pawley et al. (1996). Thus, when  $\alpha_1$  is fixed at zero the whole term  $(10\alpha_0 + \alpha_1)$  becomes equal to  $10\alpha_0$ and the simplified equation proposed by Pawley et al. (1996), and used in Holland and Powell (1998), is obtained.

308 Therefore all the volume-temperature data were fitted with the four abovementioned 309 empirical equations, Gottschalk 1997; Berman 1988; and the two form of Holland and Powell 310 1998; using the program EosFit7c, and weighting scheme for volume sigmas, in order to choose 311 the fitting model most representative for all of our datasets. An example is given in Figure 4a 312 where the experimental data for  $Jd_{100}$  are reported together with the volume calculated at each 313 temperature with the different fitting equations considered (Berman 1988; Holland and Powell 314 1998 and Gottschalk 1997). In Figure 4b the  $\delta Vs$  (difference between calculated and observed 315 volume) are shown versus temperatures. As it is clearly shown in Figures 4a and 4b that the

fitting equation modified from that proposed by Holland and Powell 1998 is the one betterdescribing our experimental datasets.

For an easier comparison among the different fitting models and the different compositions, including the literature data, the  $\alpha_V$  values, the room temperature volume ( $V_{303K}$ ) and the fitting coefficients are reported together in Table 6 a and b. The axial thermal expansions coefficients for the four approaches were calculated for all compositions and have been deposited as electronic supplementary material (Table 7a and b).

In order to be consistent and perform a reliable comparison with the literature data by Cameron et al. (1973) ( $Jd_{Cr}$ ); Finger and Ohashi (1976) ( $Di_{Fn}$ ); Pandolfo et al. (2012) ( $Jd_{55}$  N.2); Pavese et al. (2000) ( $Omp_{50}$ ); Richet et al. (1998) ( $Di_{Rt}$ ); Tribaudino et al. (2008) ( $Jd_{Tr}$ ) we have re-calculated the thermal expansion coefficient at 303K using the published *V*,*T* experimental data. As explained above, also for these samples we have used the equation by Holland and Powell 1998 that resulted to be the best fitting model for our data. The fitting results are reported in Table 6 a and b and Figures 5a,b,c,d.

Fitting data on  $\alpha_{V0}$  obtained for our *C*2/*c* samples versus composition in terms of Jd content yielded the following equation

332  $a_{V(303K,1bar)} = 2.68(3) * 10^{-5} + [1.1(1) * 10^{-8} * X_{Id}] - [7.1(1.7) * 10^{-10} * X_{Id}^2]$  (equation 2)

333 (where  $X_{Jd}$  is given in mol%) that describes the evolution of  $\alpha_V$  with the composition at room 334 temperature and pressure (303K, 1bar). This equation will allow to obtain the room *T* thermal 335 expansion for any given composition within the Di - Jd join.

336 As shown in Figure 5a and b the  $\alpha_{V0}$  values obtained for  $Jd_{Cr}$  and  $Jd_{Tr}$  are overlapped 337 within their e.s.d.'s and are very close to those obtained for our jadeite sample. The  $\alpha_{V0}$  values 338 for  $Di_{Fn}$  and  $Di_{Rt}$  are very similar, while the  $\alpha_{V0}$  value for  $Di_{Cr}$  is in agreement with the others 339 only considering the remarkable error bar obtained from the data fit. Without considering the 340 data on the two diopsides by Cameron et al. 1973; Richet et al. 1998 it is therefore clear that the 341 unit-cell volume thermal expansion coefficient ( $\alpha_{V0}$ ) shows small but significant variations 342 (larger than 1 e.s.d.'s) with composition along the entire join. The small discrepancies between 343 our  $\alpha_{V0}$  values and those from literature are probably due to our slight underestimation of the 344 unit-cell volume at room P,T conditions. Despite these small discrepancies, it remains clear that 345 the reciprocal relationship between different compositions obtained on our data is still in good 346 agreement with the data obtained from literature.

347 The unit-cell volume thermal expansion behavior with temperature for the different 348 composition samples and the thermal expansion coefficients  $\alpha_{V,T}$  were calculated for each 349 temperature in the T range investigated in this work. The results are reported in Figure 5c where 350 the  $\alpha_{V,T}$  evolution with temperature are shown for each of the studied compositions. As it is 351 evident from this Figure, if we do not consider the samples with composition close to 50 Jd 352 mol.% (Jd<sub>55</sub> P2/n and Jd<sub>55</sub> C2/c) that are within the stability field of the P2/n omphacite 353 (Carpenter 1979), the unit-cell volume thermal expansion coefficient  $\alpha_{V,T}$  gradually decreases 354 with increasing Jd% with a convex upward curve at room T (see equation 2). However as the 355 temperature increases, the trend firstly becomes linear at 573 K and then at higher T it describes 356 a concave downward curve. This change in the thermal expansion behavior with composition is 357 also showed in Figure 5d where the  $\alpha_{V,T}$  value are shown against temperature. It is evident from 358 both Figures that the unit-cell volume thermal expansion coefficient  $\alpha_{V,T}$  increases from Jd<sub>100</sub> to 359 diopside, but  $Jd_{100}$  and Di showed a much higher increasing rate with respect to  $Jd_{40}$  and  $Jd_{80}$ . 360 The different  $\alpha_{V,T}$  increasing rate with temperature showed in Figure 5c (where the  $\alpha$  normalized with respect to the room *P*,*T* value are shown) makes the thermal expansion coefficient of  $Jd_{80}$ and  $Jd_{100}$  undistinguishable at high *T* (as also seen in Figure 5d, being  $2.8(1) \times 10^{-5}$  K<sup>-1</sup> and 2.8(1) $\times 10^{-5}$  K<sup>-1</sup> at 1073 K, respectively) whereas it increases the differences between Di and Jd<sub>40</sub>

364 (being  $3.3(1) \times 10^{-5}$  K<sup>-1</sup> and  $3.0(2) \times 10^{-5}$  K<sup>-1</sup> at 1073 K, respectively).

365 Approaching the 50% Jd the two C2/c samples Jd<sub>55</sub> N.2 C2/c, and Jd<sub>60</sub> C2/c samples at room-T showed slightly smaller unit-cell volume thermal expansion coefficients,  $2.58(5) \times 10^{-5}$ 366  $K^{-1}$  and 2.47(9)  $\times 10^{-5} K^{-1}$  at 303 K, respectively, with respect to the join trend described with the 367 368 abovementioned equation 2. However at high-T the two Jd<sub>55</sub> N.2 C2/c and Jd<sub>60</sub> C2/c samples showed the largest  $\alpha_{VT}$  values  $[3.31(8) \times 10^{-5} \text{ K}^{-1} \text{ and } 3.2(1) \times 10^{-5} \text{ K}^{-1} \text{ at } 1073 \text{ K}$ , respectively] 369 very close to that of diopside  $[3.3(1) \times 10^{-5} \text{ K}^{-1} \text{ at } 1073 \text{ K}]$ . On the other hand it is clear from 370 371 Figure 5c that while at room-T the P2/n Jd<sub>55</sub> N.5 shows higher thermal expansion coefficient 372 compared with the C2/c samples with identical composition, at high-T  $\alpha_V$  for the P2/n sample is 373 much lower than the C2/c one. 374 This thermal expansion excess of the C2/c intermediate composition samples at high-T 375 seems to be consistent with the observation by Ballaran 2003; Carpenter et al. 1999; Carpenter

376 2002. They firstly interpreted the sharpening of some FTIR absorption bands (i.e.  $\Delta corr150$ ) as

- 377 substantial local decrease of strain heterogeneity, on the basis of the elastic trace element
- 378 substitution model proposed by Blundy and Wood 1994; van Westrenen et al. 2003; van
- 379 Westrenen et al. 2001.
- 380
- 381
- 382

383

384

ACKNOWLEDGEMENTS
Roberto Gastoni CNR-Pavia is thanked for sample preparation for EMPA analyses, and R. Carampin of CNR
Padova is thanked for help with the WDS electron microprobe facilities. M.C. Domeneghetti was funded by the
Italian grant PRIN EARRRZ_005 (2010); M. Alvaro was funded by ERC starting Grant No. 307322 to F. Nestola
and F. Cámara was supported by "Progetti di ricerca finanziati dall'Università degli Studi di Torino (ex 60%)" -
year 2012.

413 414	REFERENCES
415	Alvaro M, Nestola F, Ballaran TB, Cámara F, Domeneghetti MC, Tazzoli V (2010) High-
416	pressure phase transition of a natural pigeonite. Am Mineral 95 (2-3):300-311.
417	doi:10.2138/am.2010.3175
418	Alvaro M, Cámara F, Domeneghetti M, Nestola F, Tazzoli V (2011a) HT P2 <sub>1</sub> /c-C2/c phase
419	transition and kinetics of Fe <sup>2+</sup> –Mg order–disorder of an Fe-poor pigeonite: implications
420	for the cooling history of ureilites. Contrib Mineral Petrol 162 (3):599-613.
421	Alvaro M, Nestola F, Cámara F, Domeneghetti MC, Tazzoli V (2011b) High-pressure displacive
422	phase transition of a natural Mg-rich pigeonite. Phys Chem Minerals 38 (5):379-385
423	Anderson OL, Isaak D, Oda H (1992) High-temperature elastic constant data on minerals
424	relevant to geophysics. Rev Geophys 30 (1):57-90
425	Angel RJ, Gonzalez-Platas J, Alvaro M (2014) EosFit7c and a Fortran module (library) for
426	equation of state calculations. Z Kristallogr 229(5):405-419
427	Boffa Ballaran T, Carpenter MA, Domeneghetti MC, Tazzoli V (1998) Structural mechanisms of
428	solid solution and cation ordering in augite-jadeite pyroxenes; I, A macroscopic
429	perspective. Am Mineral 83 (5-6):419
430	Boffa Ballaran T (2003) Line broadening and enthalpy: Some empirical calibrations of solid
431	solution behaviour from IR spectra. Phase Transitions: A Multinational Journal 76 (1-
432	2):137-154
433	Berman RG (1988) Internally-Consistent Thermodynamic Data for Minerals in the System
434	Na <sub>2</sub> O-K <sub>2</sub> O-CaO-MgO-FeO-Fe <sub>2</sub> O <sub>3</sub> -Al <sub>2</sub> O <sub>3</sub> -SiO <sub>2</sub> -TiO <sub>2</sub> -H <sub>2</sub> O-CO <sub>2</sub> . J Petrol 29 (2):445-522
435	Blessing RH (1995) An empirical correction for absorption anisotropy. Acta Crystallogr, Sect A
436	51 (1):33-38
437	Blundy J, Wood B (1994) Prediction of crystal- melt partition coefficients from elastic moduli.
438	Nature 372 (6505):452-454
439	Cámara F, Carpenter MA, Domeneghetti MC, Tazzoli V (2003) Coupling between non-
440	convergent ordering and transition temperature in the $C2/c <-> P2_1/c$ phase transition in
441	pigeonite. Am Mineral 88 (7):1115-1128
442	Cámara F, Gatta GD, Meven M, and Pasqual D (2012) Thermal expansion and high temperature
443	structure evolution of zoisite by single-crystal X-ray and neutron diffraction. Phys. Chem
444	Mineral 39(1):27-45.
445	Cameron M, Sueno S, Prewitt CT, Papike JJ (1973) High-Temperature Crystal Chemistry of
446	Acmite, Diopside, Hedenbergite, Jadeite, Spodumene, and Ureyite. Am Mineral 58:594-
447	618
448	Cannillo E, Germani G, and Mani F, (1983) Nuovo software cristallografico per il diffrattometro
449	a cristallo singolo Philips PW1100 (New crystallographic software for Philips PW1100
450	single crystal diffractometer) Internal Report 2 C.N.R. Centro di Studio per la
451	Cristallografia Strutturale
452	Carpenter MA (1979) Omphacites from Greece, Turkey, and Guatemala; composition limits of
453	cation ordering. Am Mineral 64 (1-2):102-108

454 Carpenter MA (2002): Microscopic strain, macroscopic strain and the thermodynamics of phase 455 transitions in minerals. In Gramaccioli, C.M. (ed.): Energy modelling in minerals. EMU 456 Notes Mineral., 4. Budapest: Eötvös Univ. Press, 311-346 457 Carpenter MA, Domeneghetti MC, Tazzoli V (1990) Application of Landau Theory to Cation 458 Ordering in Omphacite .1. Equilibrium Behavior. Eur J Mineral 2 (1):7-18 459 Carpenter MA, Ballaran TB, Atkinson A (1999) Microscopic strain, local structural 460 heterogeneity and the energetics of silicate solid solutions. Phase Transitions: A 461 Multinational Journal 69 (1):95-109 Ferrari S., Nestola F., Massironi M., Maturilli A., Helbert J., Alvaro M., Domeneghetti M. C., 462 463 and Zorzi F. 2014. In-situ high-temperature emissivity spectra and thermal expansion of 464 C2/c pyroxenes: implications for the surface of Mercury. Am Mineral 99(4):786-792. 465 Finger LW, Ohashi Y (1976) The thermal expansion of diopside to 800°C and a refinement of 466 the crystal structure at 700°C. Am Mineral 61:303-310 467 Gatta G. D., Comboni D., Alvaro M., Lotti P., Cámara F., and Domeneghetti M. C. 2014. 468 Thermoelastic behavior and dehydration process of cancrinite. Phys Chem Mineral 469 41(5):373-386. 470 Gottschalk M (1997) Internally consistent thermodynamic data for rock-forming minerals in the 471 system SiO<sub>2</sub>-TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-CaO-MgO-FeO-K<sub>2</sub>O-Na<sub>2</sub>OH<sub>2</sub>O-CO<sub>2</sub>. Eur J Mineral 9 (1):175-472 223 473 Hawthorne FC, Ungaretti L, Oberti R (1995) Site populations in minerals; terminology and 474 presentation of results of crystal-structure refinement. Can Mineral 33 (4):907-911 475 Holland TB (1990) Activities of components in omphacitic solid solutions. Contrib Mineral 476 Petrol 105 (4):446-453 477 Holland TJB, Powell R (1998) An internally consistent thermodynamic data set for phases of 478 petrological interest. J Metamorph Geol 16 (3):309-343 479 Holland TJB, Powell R (2011) An improved and extended internally consistent thermodynamic 480 dataset for phases of petrological interest, involving a new equation of state for solids. J 481 Metamorph Geol 29 (3):333-383 482 Hunt SA, Walker AM, McCormack RJ, Dobson DP, Wills AS, Li L (2011) The effect of 483 pressure on thermal diffusivity in pyroxenes. Mineral Mag 75 (5):2597-2610 484 Knight KS (1996) A neutron powder diffraction determination of the thermal expansion tensor of 485 crocoite (PbCrO<sub>4</sub>) between 60 K and 290 K. Mineral Mag 60:9 Mantovani L, Tribaudino M, Mezzadri F, Calestani G, Bromiley G (2013) The structure of 486 (Ca,Co)CoSi<sub>2</sub>O<sub>6</sub> pyroxenes and the Ca- $M^{2+}$  substitution in (Ca, $M^{2+}$ ) $M^{2+}$ Si<sub>2</sub>O<sub>6</sub> pyroxenes 487  $(M^{2+} = Co, Fe, Mg)$ . Am Mineral 98:241-1252 488 489 Nestola F, Ballaran TB, Liebske C, Thompson R, Downs RT (2008) The effect of the 490 hedenbergitic substitution on the compressibility of jadeite. Am Mineral 93 (7):1005-491 1013 492 Nishihara Y, Matsukage KN, Karato SI (2006) Effects of metal protection coils on thermocouple 493 EMF in multi-anvil high-pressure experiments. Am Mineral 91 (1):111-114

494 Ohashi Y, Burnham CW (1973) Clinopyroxene Lattice Deformations: The Roles of Chemical 495 Substitution and Temperature. Am Mineral 58:843-849 Pandolfo F. Nestola F. Cámara F. Domeneghetti MC (2012) New thermoelastic parameters of 496 497 natural C2/c omphacite. Phys Chem Minerals:1-10 498 Pavese A, Bocchio R, Ivaldi G (2000) In situ high temperature single crystal X-ray diffraction 499 study of a natural omphacite. Mineral Mag 64 (6):983-993 500 Pawley AR, Redfern SAT, Holland TJB (1996) Volume behavior of hydrous minerals at high 501 pressure and temperature: I. Thermal expansion of lawsonite, zoisite, clinozoisite, and 502 diaspore. Am Mineral 81 (3):335-340 503 Pouchou JL, Pichoir F (1991) Quantitative analysis of homogeneous or stratified microvolumes applying the model "PAP". Electron probe quantitation:31-75 504 505 Redhammer GJ, Cámara F, Alvaro M, Nestola F, Tippelt G, Prinz S, Simons J, Roth G, 506 Amthauer G (2010) Thermal expansion and high-temperature  $P2_1/c-C2/c$  phase 507 transition in clinopyroxene-type LiFeGe<sub>2</sub> $O_6$  and comparison to NaFe(Si,Ge)<sub>2</sub> $O_6$ . Phys 508 Chem Minerals 37 (10):685-704 509 Richet P, Mysen BO, Ingrin J (1998) High-temperature X-ray diffraction and Raman 510 spectroscopy of diopside and pseudowollastonite. Phys Chem Minerals 25 (6):401-414 Sheldrick GM (1996) Sadabs, University of Göttingen Germany, 511 512 Sheldrick GM (2008) A short history of SHELX. Acta Crystallogr, Sect A 64:112-122 513 Tribaudino M (1996) High-temperature crystal chemistry of C2/c clinopyroxenes along the join 514 CaMgSi<sub>2</sub>O<sub>6</sub>-CaAl<sub>2</sub>SiO<sub>6</sub>. Eur J Mineral 8 (2):273-279 515 516 Tribaudino M, Nestola F, Cámara F, Domeneghetti MC (2002) The high-temperature  $P2_1/c$ -C2/c517 phase transition in Fe-free pyroxene (Ca<sub>0.15</sub>Mg<sub>1.85</sub>Si<sub>2</sub>O<sub>6</sub>): Structural and thermodynamic 518 behavior. Am Mineral 87 (5-6):648-657 519 Tribaudino M, Nestola F, Bruno M, Ballaran TB, Liebske C (2008) Thermal expansion along the NaAlSi<sub>2</sub>O<sub>6</sub>-NaFe<sup>3+</sup>Si<sub>2</sub>O<sub>6</sub> and NaAlSi<sub>2</sub>O<sub>6</sub>-CaFe<sup>2+</sup>Si<sub>2</sub>O<sub>6</sub> solid solutions. Phys Chem 520 521 Minerals 35 (5):241-248 522 Tribaudino M, Angel RJ, Cámara F, Nestola F, Pasqual D, and Margiolaki I (2010) Thermal 523 expansion of plagioclase feldspars. Contrib Mineral Petrol 160: 899-908. 524 Tribaudino M, Mantovani L (2014) Thermal expansion in C2/c pyroxenes: a review and new 525 high temperature structural data on a pyroxene of composition  $(Na_{0.53}Ca_{0.47})($ 526  $Al_{0.53}Fe_{0.47}$ )Si<sub>2</sub>O<sub>6</sub> (Jd<sub>53</sub>Hd<sub>47</sub>). Mineral Mag (in press) 527 van Westrenen W, Wood B, Blundy J (2001) A predictive thermodynamic model of garnet-melt 528 trace element partitioning. Contrib Mineral Petrol 142 (2):219-234 529 van Westrenen W, Allan NL, Blundy JD, Lavrentiev MY, Lucas BR, Purton JA (2003) Trace 530 element incorporation into pyrope–grossular solid solutions: an atomistic simulation 531 study. Phys Chem Minerals 30 (4):217-229. doi:10.1007/s00269-003-0307-5 532 Wilson AJC (1995) International tables for crystallography. Volume C. . Kluwer Academic 533 Publishers, Dordrecht, The Netherlands.,

534 535	Yang H, Prewitt CT (2000) Chain and layer silicates at high temperatures and pressures. Rev Mineral Geochem 41 (1):211-255
536 537 538 539	Zhao Y, Von Dreele RB, Shankland TJ, Weidner DJ, Ianzhong Zhang J, Wang Y, Gasparik T (1997) Thermoelastic equation of state of jadeite NaAlSi <sub>2</sub> 0 <sub>6</sub> : An energy-dispersive Reitveld refinement study of low symmetry and multiple phases diffraction. Geophys Res Lett 24 (1):5-8
540 541 542 543 544	
545 546 547 548 549	
550 551 552 553 554 555	
556 557 558 559 560	
561 562 563 564 565 566	
567 568 569 570 571	
572 573 574 575 576	
577 578 579 580 581 582	
583 584 585 586	

587	TABLES AND FIGURE CAPTIONS
588	
589	<b>Table 1.</b> Electron microprobe analysis and formula in atoms per formula unit (apfu) based on six oxygen
590	atoms.
591	Table 2. Unit cell parameters and information on data collection and structure refinement obtained on
592	natural and annealed samples.
593	Table 3. Site populations, electron number, mean bond distances and order parameters obtained from
594	structure refinements using chemical constraints. $(12)$
595	<b>Table 4.</b> Unit cell volume (V, expressed in A <sup>+</sup> ) as a function of temperature (K).
596	<b>Table 5a.</b> Lattice parameter ( <i>a</i> expressed in A) as a function of temperature (K). (supplementary material)
597	Table 5b. Lattice parameter (b expressed in A) as a function of temperature (K). (supplementary
598	material)
599	<b>Table 5c.</b> Lattice parameter ( $c$ expressed in A) as a function of temperature (K). (supplementary material)
600	<b>Table 5d.</b> Lattice angle ( $\beta$ , expressed in °) as a function of temperature (K). (supplementary material)
601	Table 6a. Unit cell volume thermal equation of state fitting results
602	Table 6b. Unit cell volume thermal equation of state fitting results
603	Table 7a. Lattice parameters thermal equation of state fitting results
604	Table 7b. Lattice parameters thermal equation of state fitting results
605	
606	
607	<b>Figure 1a.</b> Room temperature volume for all the samples discussed in the manuscript as a function of
608	composition (Jd%). Filled circles represent all our $C2/c$ data. Open symbols represent literature data:
609	diopside from Finger and Ohashi (1976) – squares; diopside from Richet et al. (1998) - diamonds;
610	diopside and jadeite from Cameron et al. (1973) upward and downward triangles respectively; jadeite by
611	Tribaudino et al. (2008) circles; Jd55 N.2 ( $C2/c$ ) from Pandolto et al., (2012) – right-pointing triangles;
612	P2/n Omp from Pavese et al., (2000) – left-pointing triangles.
613	Figure 1b. Room T variation of the b lattice versus O3-O3-O3 kinking angle for all the $C2/c$ samples
614	with different compositions studied in this work.
615	Figure 2a. Unit-cell parameters a relative variation $(a_T/a_{To})$ with increasing T for all the C2/c samples
616	studied in this work.
617	Figure 2b. Unit-cell parameters b relative variation ( $\mathbf{b}_T/\mathbf{b}_{T_0}$ ;) with increasing T for all the C2/c samples
618	studied in this work.
619	Figure 2c. Unit-cell parameters c relative variation ( $c_T/c_{To}$ ) with increasing T for all the C2/c samples
620	studied in this work.
621	Figure 2d. Beta angle relative variation ( $\beta_T/\beta_{T_0}$ ) with increasing T for all the C2/c samples studied in this
622	WORK.
623	Figure 3a. Volume variations with temperature for the end-member $C^2/c$ samples of this study together
624	with those from literature. Filled symbols (this work): Di - downward triangles; $Jd_{100}$ – squares. Open
625	symbols (literature data): diopside from Finger and Ohashi (1976) – squares; diopside from Richet et al.
626	(1998) - diamonds; diopside and jadeite from Cameron et al. (1973) upward and downward triangles
627	respectively; jadeite from Tribaudino et al. (2008) circles.
628	Figure 3b. Volume variations with temperature for the intermediate composition samples of this study
629	together with those from literature. Filled symbols (this work): $Jd_{40}$ – upward triangles; $Jd_{60}$ – circles; $Jd_{80}$

- 630 diamonds; Jd<sub>55</sub> N.5 (*P*2/*n*) hexagons. Open symbols (literature data): Jd55 N.2 (C2/c) from Pandolfo et
- 631 al., (2012) right-pointing triangles; Omp (P2/n) from Pavese et al., (2000) left-pointing triangles.
- **Figure 4a**. Volume variation for  $Jd_{100}$ . In figure are shown the 4 fitting models considered in this
- 633 manuscript. Dot line represents the fitting of the Jd100 data performed using Gottschalk (2004) equation.
- **Figure 4b.** Delta Volume variations calculated as described in the text for Jd<sub>100</sub>. The solid line represents
- the measured volume; open triangles represent data fitted following the equation by Berman (1988); filled
- triangles represent the data fitted following the equation by Holland and Powell (1998) modified by
- Pawley et al., (1996); filled circles represent data fitted following the equation by Holland and Powell
- 638 (1998); open circle represent data fitted following the equation by Gottschalk (1997). The shadowed area 639 covers the e.s.d.'s interval  $(\pm 1\sigma)$  for the volume at each temperature.
- **640** Figure 5a. Room temperature volume thermal expansion coefficients ( $\alpha_{V_0}$ ) for all the samples discussed
- 641 in the manuscript as a function of composition (Jd%). Filled circles represent all our C2/c data. Open
- 642 symbols represent literature data: diopside from Finger and Ohashi (1976) squares; diopside from
- 643 Richet et al. (1998) diamonds; diopside and jadeite from Cameron et al. (1973) upward and downward
- triangles respectively; jadeite by Tribaudino et al. (2008) circles; Jd55 N.2 (C2/c) from Pandolfo et al.,
- 645 (2012) right-pointing triangles; Omp from Pavese et al., (2000) left-pointing triangles. The dashed
- 646 line represents the equation fitted for the C2/c samples of this work.
- **Figure 5b.** Normalized volume thermal expansion coefficients ( $\alpha_V$ ), calculated as  $\alpha_{V,T}/\alpha_0$  (where  $\alpha_0$  is the
- 648 volume thermal expansion coefficient at room-*T*) for all C2/c samples of this work. Diopside downward
- $\label{eq:constraint} 649 \qquad triangles; Jd_{40} upward \ triangles; Jd_{60} circles; Jd_{80} diamonds; jd_{100} squares.$
- **Figure 5c.** Volume thermal expansion coefficients ( $\alpha_v$ ) as a function of composition (Jd%) at selected
- temperature steps for all samples of this work. For an easier representation the  $Jd_{55}$  (*C*2/*c*) sample with
- Jd% = 55 has been moved slightly to the left (towards 50% of Jd) to distinguish it from  $Jd_{55} P2/n$  (empty
- 653 symbols) with identical Jd contents.
- **Figure 5d.** Volume thermal expansion coefficients ( $\alpha_V$ ) as a function of temperature (K) for all the *C*2/*c*
- 655 samples of this work. Diopside downward triangles;  $Jd_{40}$  upward triangles;  $Jd_{60}$  circles;  $Jd_{80}$  -
- 656 diamonds;  $Jd_{100}$  squares.