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Original Citation:

Availability:

This version is available <http://hdl.handle.net/2318/153763> since

Published version:

DOI:10.1007/s00269-014-0694-9

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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

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ABSTRACT

An *in situ* single-crystal high temperature X-ray diffraction study was performed on clinopyroxene crystals along the jadeite, (NaAlSi₂O₆Jd) – diopside (CaMgSi₂O₆Di) join. In particular, natural samples of jadeite, diopside, *P2/n* omphacite and three *C2/c* synthetic samples with intermediate composition (i.e. Jd₈₀, Jd₆₀, Jd₄₀) were investigated. In order to determine the unit-cell volume thermal expansion coefficient (α_V) the unit-cell parameters for all these compositions have been measured up to c.a. 1073 K. The evolution of the unit-cell volume thermal expansion coefficient (α_V) along the Jd - Di join at different temperatures has been calculated by using a modified version of the equation proposed by Holland and Powell 1998). The equation $\alpha_{V(303K,1bar)} = 2.68(3) \times 10^{-5} + [1.1(1) \times 10^{-8} \times X_{Jd}] - [7.1(1.7) \times 10^{-10} \times X_{Jd}^2]$ obtained from the α_V at room-*T* (i.e. $\alpha_{V303K,1bar}$), allows us to predict the room-*T* volume thermal expansion for Fe-free *C2/c* clinopyroxenes with intermediate composition along the binary join Jd-Di. The observed α_V value for *P2/n* omphacite $\alpha_{V(303K,1bar)} = 2.58(5) \times 10^{-5} K^{-1}$ 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 the large e.s.d.'s for the latter, the difference of both values at room *T* is small, indicating that convergent ordering has practically no influence on the room-*T* thermal expansion. However, at high-*T* the smaller thermal expansion coefficient for the *C2/c* sample with respect to the *P2/n* one with identical composition could provide further evidence for its reduced stability relative to the ordered one.

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

INTRODUCTION

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Clinopyroxenes are major constituents of the upper mantle and they are involved in a wide range of geological environments. The construction of a reliable model for upper-mantle behavior requires data on their thermodynamic properties like the bulk modulus and thermal expansion. In particular, “for most upper mantle depths the thermal diffusivity of the pyroxene is ~70% greater than that of the olivine making up the bulk of the surrounding mantle” (Hunt et al. 2011). Due to the complex compositional variability of clinopyroxenes, thermodynamic data are necessary not only for the end-members but also for intermediate samples and for the complete solid solutions, for which data are very often poorly determined or absent. Several different studies have been performed to determine the high-temperature behavior of clinopyroxenes, most of them concerning the end-member compositions. A review was provided by Yang and Prewitt 2000, although numerous studies have recently been performed on sodic and lithium clinopyroxenes (see Redhammer et al. 2010, and references therein).

The volume thermal expansion coefficients (α_V) along the jadeite (Jd) – diopside (Di) join are available almost exclusively for composition close to the end-members. In particular, Cameron et al. 1973 reported data on the high-temperature behavior of natural samples of jadeite and diopside studied using *in-situ* single crystal X-ray diffraction in the range 24-1000°C. These authors obtained an α_V value, calculated using a linear equation (no dependence of α on T), of $2.47 \times 10^{-5} \text{ K}^{-1}$ for jadeite and of $3.33 \times 10^{-5} \text{ K}^{-1}$ for diopside. Finger and Ohashi 1976 studied the thermal expansion of a natural diopside up to 800°C and performed an intensity data collection at 700°C. The authors reported a linear thermal expansion value (α_V) of $3.1(3) \times 10^{-5} \text{ K}^{-1}$. Richet et al. 1998 investigated synthetic diopside using powder X-ray diffraction technique obtaining an $\alpha_V = 9.263 \times 10^{-6} + 42.7 \times 10^{-9} T - 7.215 \times 10^{-12} T^2$ (T in K) by considering α as a polynomial function

65 of temperature, thus yielding $2.16 \times 10^{-5} \text{ K}^{-1}$ at 300K and $5.91 \times 10^{-5} \text{ K}^{-1}$ at 1600K. Tribaudino et al.
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 $\alpha_V =$
68 $2.54(6) \times 10^{-5} \text{ K}^{-1}$. Zhao et al. 1997 reported the thermoelastic equation of state (*T*-EoS) of jadeite
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
71 assuming a linear dependence of α with *T* ($\alpha = a + bT$) are $2.64 \times 10^{-5} \text{ K}^{-1}$ and $2.89 \times 10^{-5} \text{ K}^{-1}$ for Jd
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
76 function of the data on heating they obtained an α_V value of $2.76(4) \times 10^{-5} \text{ K}^{-1}$ while the fitting of
77 the data on cooling provided an α_V value of $2.51(3) \times 10^{-5} \text{ K}^{-1}$. The authors suggested that the
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 *C2/c*) using the same experimental technique but fitting the data following the
81 equation proposed by Berman 1988 (expressed in the form where $\alpha_{V,T} = a_0 + 2a_1(T - T_r)$)
82 obtaining an $\alpha_{V,303K}$ value of $2.64(2) \times 10^{-5} \text{ K}^{-1}$.

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

88 In this study we will: i) better constrain the α_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 α_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 ($\text{NaAlSi}_2\text{O}_6$) – diopside ($\text{CaMgSi}_2\text{O}_6$). The end members jadeite and
100 diopside (labelled Jd_{100} , and Di , respectively) and the omphacite [sample 74AM33, with
101 composition ca. $(\text{Ca},\text{Na})(\text{Mg},\text{Al})\text{Si}_2\text{O}_6$] 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 $C2/c$, have been synthesized at the Department of Geology and Geophysics at the Yale
108 University (Connecticut, USA) using a multi-anvil press.

109 ***b. Syntheses***

110 The glasses for the syntheses experiments were prepared using dried MgO, Al₂O₃,
111 CaCO₃, Na and SiO₂ (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 powdered 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 μm with presence of oxides or glasses.

126

127 *c. Electron microprobe analysis (EMPA)*

128 The crystals studied by X-ray diffraction were embedded in epoxy and polished. Electron
129 microprobe analysis (EMPA) were carried out at the Dipartimento di Geoscienze (University of
130 Padova, Italy) using a CAMECA- SX 50 electron microprobe operating in wavelength dispersive
131 mode with a fine-focused beam (~1 mm diameter), an acceleration voltage of 20 kV and a beam
132 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–K α , TAP), wollastonite (Si, Ca–K α , TAP), olivine (Mg–K α , TAP), Al₂O₃ (Al– K α ,
136 TAP), MnTiO₃ (Mn–K α , LiF; Ti–K α , PET), Cr₂O₃ (Cr–K α , LiF) and Fe₂O₃ (Fe– K α , 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-monochromatized MoK α radiation, 50 kV, 30 mA) and a 0.3 mm moncap 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 ω -scan mode
147 (scan width: 0.2 ° ω ; 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-monochromatized MoK α 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° 2 θ . 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 , wR_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 material¹.
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 1σ 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
175 before and after the *in-situ* annealing, the order parameters Q^{occ} and Q^{dist} (Carpenter et al. 1990)
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

¹ CIF file are available as supplementary material.

178 Pavese et al. 2000 [labeled here as Omp50] are shown. The Q^{dist} and Q^{occ} values for $M1$ and $M2$
179 sites have been calculated starting from the data by Pavese et al. 2000 using the equations
180 proposed by Carpenter et al. 1990)

181

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

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 $\theta_{\text{max}}=29^\circ$. 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
191 alternately washing with Ar flux and vacuuming (4×10^{-2} mbar). In order to avoid any
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 2θ interval $15\text{--}30^\circ$. Accurate and precise lattice constants were then
200 determined using the Philips LAT procedure on the 60 most intense reflections (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 χ values reducing therefore the changes in χ 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 $2n + 1$ ($\bar{1} 0 1, 0 5 0$) and $h + k = 2n$ ($\bar{2} 0 2, 0 6 0$) 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- T b 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 \mathbf{b} and \mathbf{c} 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
$$V (\text{\AA}^3) = 439.0(2) - 0.369(4) X_{\text{Jd}} \text{ (equation 1)}$$

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 b 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 a , c and β , 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 β 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 β 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, Jd₁₀₀] 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_{Cr}) and the two jadeite samples from Cameron et al. 1973 (Jd_{Cr}) and Tribaudino et al.
261 2008 (Jd_{Tt}). 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 (Jd₁₀₀) 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 (Jd₄₀, Jd₆₀, Jd₈₀, Jd₅₅ N.5 $P2/n$) are reported together with
269 those available from literature, in particular Jd₅₅ N.2 $C2/c$ from Pandolfo et al. 2012 and Omp
270 $P2/n$ from Pavese et al. 2000.

271 The cell volume increases almost linearly for all intermediate compositions with
272 increasing temperature with a very similar increasing rate for all the *C2/c* samples, while the
273 slope of the *V,T* data is slightly different for the *P2/n* samples (Figure 3b) that increases at two
274 different rates. It is very interesting to notice that the three samples close to the 50% of Jd (Jd₅₅
275 N.2 *C2/c* and Jd₅₅ N.5 *P2/n* with 55% Jd; and Omp *P2/n* with 50%Jd) show volume differences
276 larger than 1 e.s.d.'s at room-*T* while are almost undistinguishable (differences within 1 e.s.d.'s)
277 at high-*T* (above 850K).

278

279 *Thermal expansion coefficients behavior*

280 To a first approximation, the coefficient of volume thermal expansion can be considered
281 as being *T*-independent, and therefore the variation of the unit-cell volume with *T* could be fitted
282 by least-squares with the equation proposed by Gottschalk 1997 where $V(T) = V_{o(P_r;T_r)} e^{\alpha_o(T-T_r)}$
283 with V_o , P_r and T_r being the reference volume, pressure and temperatures, respectively.
284 However, most ionic or mixed ionic-covalent compounds show a dependence of α with *T* (see by
285 instance values reported by Fei, 1995), and a strong increase of α with *T* and a saturation effect at
286 high values of *T*. Therefore, the temperature-dependence of α is expected to be limited above the
287 Debye temperature (Anderson et al. 1992). A physical model valid for ionic compounds
288 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
292 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 α 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 α being independent form T . In addition, the saturation of α_v at high temperature can
 297 be considered using the equation proposed by Holland and Powell 1998 where

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

299 well as the one modified by Pawley et al. 1996 where the authors simplified the equation taking
 300 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 $V_{0(P_r, T_r)} = V_{00} \left(1 + \alpha_0(T - T_r) - 2(10\alpha_0 + \alpha_1)(\sqrt{T} - \sqrt{T_r}) \right)$ where the entire term $(10\alpha_0 + \alpha_1)$ of this

304 equation is in actual fact equal to the α_1 coefficient reported in the simplified equation by Pawley
 305 et al. (1996). Thus, when α_1 is fixed at zero the whole term $(10\alpha_0 + \alpha_1)$ becomes equal to $10\alpha_0$
 306 and the simplified equation proposed by Pawley et al. (1996), and used in Holland and Powell
 307 (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 δV_s (difference between calculated and observed
 315 volume) are shown versus temperatures. As it is clearly shown in Figures 4a and 4b that the

316 fitting equation modified from that proposed by Holland and Powell 1998 is the one better
317 describing our experimental datasets.

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

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

330 Fitting data on α_{V0} obtained for our $C2/c$ samples versus composition in terms of Jd
331 content yielded the following equation

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

333 (where X_{Jd} is given in mol%) that describes the evolution of α_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 α_{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 α_{V0} values

338 for Di_{Fn} and Di_{Rt} are very similar, while the α_{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 (α_{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 α_{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.% ($\text{Jd}_{55} P2/n$ and $\text{Jd}_{55} C2/c$) 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_{100} 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 α normalized

361 with respect to the room P, T value are shown) makes the thermal expansion coefficient of Jd_{80}
362 and Jd_{100} undistinguishable at high T (as also seen in Figure 5d, being $2.8(1) \times 10^{-5} \text{ K}^{-1}$ and $2.8(1)$
363 $\times 10^{-5} \text{ K}^{-1}$ at 1073 K, respectively) whereas it increases the differences between Di and Jd_{40}
364 (being $3.3(1) \times 10^{-5} \text{ K}^{-1}$ and $3.0(2) \times 10^{-5} \text{ K}^{-1}$ at 1073 K, respectively).

365 Approaching the 50% Jd the two $C2/c$ samples $Jd_{55} \text{ N.2 } C2/c$, and $Jd_{60} \text{ } C2/c$ samples at
366 room- T showed slightly smaller unit-cell volume thermal expansion coefficients, $2.58(5) \times 10^{-5}$
367 K^{-1} and $2.47(9) \times 10^{-5} \text{ K}^{-1}$ at 303 K, respectively, with respect to the join trend described with the
368 abovementioned equation 2. However at high- T the two $Jd_{55} \text{ N.2 } C2/c$ and $Jd_{60} \text{ } C2/c$ samples
369 showed the largest $\alpha_{v,T}$ values [$3.31(8) \times 10^{-5} \text{ K}^{-1}$ and $3.2(1) \times 10^{-5} \text{ K}^{-1}$ at 1073K, respectively]
370 very close to that of diopside [$3.3(1) \times 10^{-5} \text{ K}^{-1}$ at 1073K]. On the other hand it is clear from
371 Figure 5c that while at room- T the $P2/n \text{ } Jd_{55} \text{ N.5}$ shows higher thermal expansion coefficient
372 compared with the $C2/c$ samples with identical composition, at high- T α_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. $\Delta\text{corr150}$) 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.

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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.

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TABLES AND FIGURE CAPTIONS

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588
589 **Table 1.** 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
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606
- 607 **Figure 1a.** 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 Pandolfo et al., (2012) – right-pointing triangles;
612 $P2/n$ Omp from Pavese et al., (2000) – left-pointing triangles.
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618 studied in this work.
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622 work.
- 623 **Figure 3a.** Volume variations with temperature for the end-member $C2/c$ samples of this study together
624 with those from literature. Filled symbols (this work): Di - downward triangles; Jd₁₀₀ – 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): Jd₄₀ – upward triangles; Jd₆₀ – circles; Jd₈₀

630 – diamonds; Jd₅₅ N.5 (*P2/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.

632 **Figure 4a.** Volume variation for Jd₁₀₀. 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.

634 **Figure 4b.** Delta Volume variations calculated as described in the text for Jd₁₀₀. The solid line represents
635 the measured volume; open triangles represent data fitted following the equation by Berman (1988); filled
636 triangles represent the data fitted following the equation by Holland and Powell (1998) modified by
637 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 (α_{v0}) 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
644 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.

647 **Figure 5b.** Normalized volume thermal expansion coefficients (α_v), calculated as $\alpha_{v,T}/\alpha_0$ (where α_0 is the
648 volume thermal expansion coefficient at room-*T*) for all *C2/c* samples of this work. Diopside - downward
649 triangles; Jd₄₀ - upward triangles; Jd₆₀ - circles; Jd₈₀ – diamonds; jd₁₀₀ – squares.

650 **Figure 5c.** Volume thermal expansion coefficients (α_v) as a function of composition (Jd%) at selected
651 temperature steps for all samples of this work. For an easier representation the Jd₅₅ (*C2/c*) sample with
652 Jd% = 55 has been moved slightly to the left (towards 50% of Jd) to distinguish it from Jd₅₅ *P2/n* (empty
653 symbols) with identical Jd contents.

654 **Figure 5d.** Volume thermal expansion coefficients (α_v) as a function of temperature (K) for all the *C2/c*
655 samples of this work. Diopside - downward triangles; Jd₄₀ - upward triangles; Jd₆₀ - circles; Jd₈₀ –
656 diamonds; Jd₁₀₀ – squares.