Volume thermal expansion along the jadeite-diopside join

DOI:10.1007/s00269-014-0694-9

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

Volume thermal expansion along the jadeite-diopside join

Francesco Pandolfo[1], Fernando Cámara[2,†],
M. Chiara Domeneghetti[1], Matteo Alvaro[3*], Fabrizio Nestola[3], Shun-Ichiro Karato[4], George Amulele[4]
[1]Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia, via Ferrata 1, I-27100 Pavia, Italy
[2]Dipartimento di Scienze della Terra, Università degli Studi di Torino, via Valperga Caluso 35, I-10125 Torino, Italy
[3]Dipartimento di Geoscienze, Università di Padova, via Gradenigo 6, I-35131 Padova, Italy
[4]Department of Geology and Geophysics, Yale University, New Haven, CT, USA
[†]CrisDi, Interdepartmental Centre for Crystallography, Torino, Italy

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

ABSTRACT

An *in situ* single-crystal high temperature X-ray diffraction study was performed on clinopyroxene crystals along the jadeite, ($NaAlSi_2O_6$ Jd) – diopside ($CaMgSi_2O_6$ Di) join. In particular, natural samples of jadeite, diopside, *P*2/*n* omphacite and three *C*2/*c* synthetic samples with intermediate composition (i.e. Jd_{80}, Jd_{60}, Jd_{40}) 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 $a_{V(303K,1bar)} = 2.68(3) \times 10^{-5} + [1.1(1) \times 10^{-8} \times X_{Jd}] - [7.1(1.7) \times 10^{-10} \times X_{Jd}^2]$ 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 *C*2/*c* clinopyroxenes with intermediate composition along the binary join Jd-Di. The observed α_V value for *P*2/*n* omphacite $\alpha_{V(303K,1bar)} = 2.58(5) \times 10^{-5} K^{-1}$ was compared with that recalculated for disordered *C*2/*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

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 2.47×10^{-5} K^{-1} for jadeite and of 3.33×10^{-5} 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 $3.1(3)\times10^{-5}$ K^{-1}. Richet et al. 1998 investigated synthetic diopside using powder X-ray diffraction technique obtaining an $\alpha_V = 9.263\times10^{-6} + 42.7\times10^{-9}T - 7.215\times10^{-12}T^2$ (T in K) by considering α as a polynomial function of temperature, thus yielding 2.16×10^{-5} K^{-1} at 300K and 5.91×10^{-5} K^{-1} at 1600K. Tribaudino et al. 2008 studied the thermal expansion of jadeite up to 800°C using single-crystal X-ray diffraction technique (SC-XRD) fitting the unit-cell volume with a linear equation obtaining α_V = $2.54(6)\times10^{-5}$ K^{-1}. Zhao et al. 1997 reported the thermoelastic equation of state (*T*-EoS) of jadeite and diopside obtained by an in situ synchrotron X-ray powder diffraction study at simultaneous high-*T* and high-*P* conditions. The thermal expansion coefficients obtained by fitting their data assuming a linear dependence of α with *T* ($\alpha = a + bT$) are 2.64×10^{-5} K^{-1} and 2.89×10^{-5} K^{-1} for Jd and Di, respectively.

According to our knowledge the only available thermal expansion data for omphacite samples are those by Pavese et al. 2000. These authors studied a natural chemically quasi-ideal ordered *P*2/*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 α_V value of $2.76(4)\times10^{-5}K^{-1}$ while the fitting of the data on cooling provided an α_V value of $2.51(3)\times10^{-5}K^{-1}$. The authors suggested that the discrepancies between heating and cooling (10%) are mainly due to order-disorder reaction in the sample. Very recently, Pandolfo et al. 2012 investigated a natural disordered omphacite (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 $\alpha_{V,T_r} = a_o + 2a_1(T\text{-}T_r)$]) obtaining an $\alpha_{V,303K}$ value of $2.64(2)\times10^{-5}K^{-1}$.

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).

In this study we will: i) better constrain the α_V evolution along the jadeite – diopside binary join investigating the thermal expansion behavior of the end-members as well as that of synthetic samples along the join, by using the very same device in order to avoid any effect due to changes in the experimental set up or temperature calibration of the device; ii) evaluate the effect of the convergent ordering on the α_V value, by investigating the thermal expansion behavior of a *P*2/*n* omphacite and comparing it with that obtained on a disordered *C*2/*c* sample (Pandolfo et al. 2012).

EXPERIMENTAL METHODS

a. Samples

The experimental work was performed on natural and synthetic samples with composition along the join jadeite ($NaAlSi_2O_6$,) – diopside ($CaMgSi_2O_6$). The end members jadeite and diopside (labelled $Jd_{100,}$ and Di, respectively) and the omphacite [sample 74AM33, with composition ca. $(Ca,Na)(Mg,Al)Si_2O_6$] are natural samples already well characterized by Boffa Ballaran et al. 1998. The jadeite pure end-member comes from serpentine rocks (New Idria, California, US) and the diopside pure end-member from the Dekald country (New York State, US; Mineral collection Dept. of Earth Sciences Cambridge, UK); the 74AM33 omphacite sample is from an eclogitic rock (Münchberg Mass, Bavaria). The omphacite crystal of this study labelled N5 has *P*2/*n* symmetry. The samples with intermediate compositions, Jd_{80}, Jd_{60}, Jd_{40}, all *C*2/*c,* have been synthesized at the Department of Geology and Geophysics at the Yale University (Conneticut, USA) using a multi-anvil press.

b. *Syntheses*

The glasses for the syntheses experiments were prepared using dried MgO, Al_2O_3, $CaCO_3$, Na and SiO_2 (provided by Alpha Aesar Company) as starting material. After weighing, the oxide mixture was ground under ethanol with an agate mortar. The dried mixture was placed into a platinum crucible and decarbonated by heating up to 1400 °C and then glassed by quenching into cold water; after quenching the glassed sample was grounded again to powder as described before. This process of melting, quenching and grinding was performed in order to ensure the homogeneity of the powered samples. The powder was then loaded into platinum foil capsules welded in both sides. Tungsten carbide anvils of 11 mm truncation edge length with standard 18 mm edge length octahedra were used. The capsule was placed in a graphite furnace surrounded by an MgO sleeve and spacers. The temperature was monitored with a D-type thermocouple inserted within an alumina sleeve, with the junction in contact with the top of the capsule (Nishihara et al. 2006). Experiments were performed at 5 GPa between 1300 and 1350 °C for periods of 6-9 hrs in a 1000-ton Kawai-type multi anvil press. The quenching was performed by switching off the furnace following a decompression profile that allowed to reach room *P*,*T* conditions in 10-12 hours. The obtained capsules contained single crystals with sizes ranging between 40-100 μm with presence of oxides or glasses.

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 were converted to oxide wt.% using the PAP correction program supplied by CAMECA (Pouchou and Pichoir 1991). For standards, spectral lines, and analytical crystals used were albite (Na–Ka, TAP), wollastonite (Si, Ca–*K*α, TAP), olivine (Mg–*K*α, TAP), Al_2O_3 (Al– *K*α, TAP), $MnTiO_3$ (Mn–*K*α, LiF; Ti–*K*α, PET), Cr_2O_3 (Cr–*K*α, LiF) and Fe_2O_3 (Fe– *K*α, LiF). The oxide wt.% reported in Table 1 were obtained by averaging 15 microprobe analyses and the reported formulae was normalized on the basis of 6 oxygen atoms. .

d. X-Ray diffraction at ambient conditions

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

The structure refinements were carried out using the program SHELX-97 (Sheldrick 2008) starting from the atom coordinates by Boffa Ballaran et al. 1998, for samples with space group *C*2/*c* and by Pavese et al. 2000 for the N5-*P*2/*n* omphacite sample. Neutral versus ionized scattering factors were used to refine occupancy for all sites that are not involved in chemical substitutions (O and Si) (Hawthorne et al. 1995) and ionized scattering factors were used for cationic sites. Scattering curves were taken from the *International Ta***b***les for X-ray Crystallography* (Wilson 1995). The anisotropic displacement parameters were refined for all atoms in all the studied crystals. The unit-cell parameters of the crystals at room-*T* (collected using the Philips PW1100 four-circle diffractometer; before and after the *in-situ* annealing for the *P*2/*n* sample), the statistics values (i.e. the agreement factors $R_{1,}$ wR_2 etc…) as well as other details from the structure refinement of the samples studied are reported in Table 2. The structure models (CIF files) are available as supplementary electronic material[1].

For the *P*2/*n* sample N5, once the structure refinement reached convergence, a structure refinement with chemical constraints was carried out using the data from the electron microprobe analysis with 1σ error in order to obtain reliable site partitioning that allowed to calculate the order degree (see Pandolfo et al. 2012 for details about the refinement procedure). For the same sample the mean atomic numbers calculated for the octahedral sites [$\text{m.a.n.}_{M1+M11+M2+M21}$] by SCXRD (before introducing the chemical constraints) and by EMPA are in agreement within their errors. In Table 3 the mean atomic number, the mean bond lengths for the *M*1 and *M*2 sites before and after the *in-situ* annealing, the order parameters Q^{occ} and Q^{dist} (Carpenter et al. 1990) calculated using the site population, are listed together. In the same table the Ca-site occupancies of *M*2 and *M*21 sites and the octahedral mean bond distances from omphacite data reported by

---

[1] CIF file are available as supplementary material.

Pavese et al. 2000 [labeled here as Omp50] are shown. The Q^{dist} and Q^{occ} values for *M*1 and *M*2 sites have been calculated starting from the data by Pavese et al. 2000 using the equations proposed by Carpenter et al. 1990)

e. High temperature X-ray diffraction experiments

High-temperature single crystal X-ray diffraction (HT-SC-XRD) experiments were carried out at the Dipartimento di Scienze della Terra e dell'Ambiente (Università di Pavia, Italy) using a Philips PW1100 four-circle automated diffractometer and a point detector, working with the same experimental conditions as described above, and equipped with a microfurnace for *in-situ* high-temperature experiments consisting of a H-shaped Pt-Rh resistance and a Pt:Pt-Rh thermocouple inside a steel cylindrical cage 1 inch wide closed with a Kapton film. The device allows the X-ray diffraction data to be collected up to θ_{max}=29°. Each crystal was loaded in a 0.3 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 mechanical stress, each crystal was kept in position within the vial using quartz wool. A small piece of an iron wire, used as a buffer to avoid Fe oxidation during annealing, was loaded inside the vial together with the crystal (crystal-iron wire distance c.a. 1.5 mm).

The temperature calibration of the microfurnace was undertaken as described in Cámara et al. (2012), Ferrari et al. (2014) and Gatta et al. (2014). The high temperature device and the calibration equation used for these experiments are detailed described in Pandolfo et al. (2012).

Preliminary cell centring using horizontal and vertical slits was performed on 24 intense reflections over the 2θ interval 15–30°. Accurate and precise lattice constants were then determined using the Philips LAT procedure on the 60 most intense reflactions (see Cannillo et al. 1983 Cámara et al. 2012 for further details). The same set of selected reflections was used for each temperature measurement. In order to avoid temperature fluctuation during the centring procedure reflections were ordered by χ values reducing therefore the changes in χ angles between consecutive reflections. Lattice parameters were collected in the temperature range 303-1073 K at intervals of 50 K with increasing and decreasing temperature. The only exception are the data of the *P*2/*n* omphacite sample N.5 collected during cooling with steps of 100 K. Higher temperatures (1173 K) were reached only for the measurement performed on Di sample. Each standard experiment was conducted in about 110 hrs. For the *P*2/*n* sample N.5, the high-*T* data (in the interval between 873 K – 1073 K) were collected in not more than 15 hrs in order to hamper the ordering kinetic effects. Moreover the intensities for selected reflections with $h + k = 2n + 1$ ($\bar{1}$ 0 1, 0 5 0) and $h + k = 2n$ ($\bar{2}$ 0 2, 0 6 0) were measured at each temperature. The presence of *b*-type reflections (i.e. $h + k = 2n + 1$) with intensities $I > 3\sigma$ during temperature increasing and decreasing ensured that the crystal maintained the same degree of order for the entire experiment. This is also confirmed by the comparison between the *Q* parameters calculated from the site occupancies and the mean bond distances obtained from the structural refinement performed before and after the heating experiments (see Table 3).

The measured unit-cell volumes as a function of temperature for all samples are reported in Table 4. Lattice parameters as a function of temperature have been deposited as electronic supplementary material (Table 5a,b,c,d). Unfortunately we have not been able to complete the cooling experiment for the crystals N5 and Di because of the break of the vial.

RESULTS AND DISCUSSION

Lattice thermal expansion behavior

At room-*T* *b* lattice parameters as well as unit-cell volumes are clearly controlled by the composition as shown in Figure 1a and Figure 1b. The change in composition along the Jd-Di join has a strong effect on the volumes of the *M* polyhedra (see Tribaudino and Mantovani, 2014 for further details) that are basically able to accommodate the compositional changes only along [010]. Moreover, the O3-O3-O3 kinking angle contributes in a lesser extent to accommodate the compositional change along the **b** and **c** lattice directions (Figure 1b). The larger is the expansion along [010], the narrower is the O3-O3-O3 angle of the tetrahedral chain. It is evident that samples with wider O3-O3-O3 angles can accommodate less deformation with respect to those with narrower O3-O3-O3 angles (Figures 1a, b). Such behavior has already been shown for different composition samples by several studies mainly devoted to the high-*P* and high-*T* structural investigation (Alvaro et al. 2010; Alvaro et al. 2011a; Alvaro et al. 2011b; Cámara et al. 2003; Nestola et al. 2008; Redhammer et al. 2010; Tribaudino 1996; Tribaudino et al. 2008 and Tribaudino and Mantovani, 2014)

The room-*T* unit-cell volume data allowed us to extrapolate the equation

$$V\ (\text{Å}^3) = 439.0(2) - 0.369(4)\ X_{\text{Jd}} \quad (\textit{equation 1})$$

that describes the unit cell volume changes as a function of composition within diopside - jadeite join.

The unit-cell parameters expand almost linearly with increasing *T* for all the compositions studied in this work (Di, Jd40, Jd60, Jd80, Jd100 and Jd55 N. 5 *P*2/*n*) as shown in Figure 2.

The *b* lattice, being the softest direction mostly affected by the compositional changes, undergoes the largest expansion with temperature compared with the other lattice parameters (i.e. *a*, *c* and *β*, see Figure 2 a, b, c, d), accommodating more than a half of the total volume expansion. For example, in diopside *a*, *c* and β expand by 0.68%, 0.61% and 0.14% respectively (in 870 K) whereas *b* expands by 1.53%, with an overall volume expansion of 2.77%. This observation is clearly in agreement with previous data in other clinopyroxenes (Tribaudino et al. 2002; Cámara et al. 2003; Redhammer et al. 2010; Alvaro et al. 2011a; Mantovani et al. 2013). It is interesting to note that the slope of the *b* lattice expansion as well as the β angle increase within the Jd-Di solid solution, while very similar rates of expansion are observed for both *a* and *c* lattice parameters. Therefore the different volume thermal expansion within the solid solution is the consequence of an increased thermal expansion along [010] and shear within the (010) plane.

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

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 $V(T) = V_{o(Pr;Tr)}\, e^{\alpha_{\circ}(T-Tr)}$ with V_o, 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 α with *T* (see by instance values reported by Fei, 1995), and a strong increase of α with *T* and a saturation effect at high values of *T*. Therefore, the temperature-dependence of α is expected to be limited above the 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 model as described by Knight 1996 would require high quality data collected well below room-*T* (see also Tribaudino et al. 2010 for further discussions on different thermal expansion model and 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 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

$\partial V / \partial T = \alpha \approx \alpha_0 + \alpha_1 \left(T - T_{ref}\right)$] allows for a linear dependence of α on *T*. As a consequence, we obtain better fitting results at both the highest and lowest *T* than those obtained with the model assuming α being independent form *T*. In addition, the saturation of α_V at high temperature can be considered using the equation proposed by Holland and Powell 1998 where $V_{0T} = V_{00}\left(1 + \alpha_0 (T - T_{ref}) - 2\alpha_1\left(\sqrt{T} - \sqrt{T_{ref}}\right)\right)$ [from which $\partial V / \partial T = \alpha = \alpha_0 - \alpha_1\left(\sqrt{T} - \sqrt{T_{ref}}\right)$] 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 $\partial V / \partial T = \alpha = \alpha_0 (1 - 10\sqrt{T_{ref}}$]. To be noticed is that in order to accommodate this simplification in a simple manner EosFit7c (Angel et al. 2014) is coded with a modified equation $V_{0(\mathrm{Pr},Tr)} = V_{00}\left(1 + \alpha_0 (T - T_r) - 2\left(10\alpha_0 + \alpha_1\right)\left(\sqrt{T} - \sqrt{T_r}\right)\right)$ where the entire term $\left(10\alpha_0 + \alpha_1\right)$ of this equation is in actual fact equal to the α_1 coefficient reported in the simplified equation by Pawley et al. (1996). Thus, when α_1 is fixed at zero the whole term $\left(10\alpha_0 + \alpha_1\right)$ 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.

Therefore all the volume-temperature data were fitted with the four abovementioned empirical equations, Gottschalk 1997; Berman 1988; and the two form of Holland and Powell 1998; using the program EosFit7c, and weighting scheme for volume sigmas, in order to choose the fitting model most representative for all of our datasets. An example is given in Figure 4a where the experimental data for Jd_{100} are reported together with the volume calculated at each temperature with the different fitting equations considered (Berman 1988; Holland and Powell 1998 and Gottschalk 1997). In Figure 4b the δVs (difference between calculated and observed 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 better describing our experimental datasets.

For an easier comparison among the different fitting models and the different compositions, including the literature data, the α_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 α_{V0} obtained for our *C*2/*c* samples versus composition in terms of Jd content yielded the following equation

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

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

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

The unit-cell volume thermal expansion behavior with temperature for the different composition samples and the thermal expansion coefficients $\alpha_{V,T}$ were calculated for each temperature in the *T* range investigated in this work. The results are reported in Figure 5c where the $\alpha_{V,T}$ evolution with temperature are shown for each of the studied compositions. As it is evident from this Figure, if we do not consider the samples with composition close to 50 Jd mol.% (Jd_{55} *P*2/*n* and Jd_{55} *C*2/*c*) that are within the stability field of the *P*2/*n* omphacite (Carpenter 1979), the unit-cell volume thermal expansion coefficient $\alpha_{V,T}$ gradually decreases with increasing Jd% with a convex upward curve at room *T* (see equation 2). However as the temperature increases, the trend firstly becomes linear at 573 K and then at higher *T* it describes a concave downward curve. This change in the thermal expansion behavior with composition is also showed in Figure 5d where the $\alpha_{V,T}$ value are shown against temperature. It is evident from both Figures that the unit-cell volume thermal expansion coefficient $\alpha_{V,T}$ increases from Jd_{100} to diopside, but Jd_{100} and Di showed a much higher increasing rate with respect to Jd_{40} and Jd_{80}. The different $\alpha_{V,T}$ increasing rate with temperature showed in Figure 5c (where the α 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^{-1} and $2.8(1) \times 10^{-5}$ K^{-1} at 1073 K, respectively) whereas it increases the differences between Di and Jd_{40} (being $3.3(1) \times 10^{-5}$ K^{-1} and $3.0(2) \times 10^{-5}$ K^{-1} at 1073 K, respectively).

Approaching the 50% Jd the two *C*2/*c* samples Jd_{55} N.2 *C*2/*c*, and Jd_{60} *C*2/*c* samples at room-*T* showed slightly smaller unit-cell volume thermal expansion coefficients, $2.58(5) \times 10^{-5}$ K^{-1} and $2.47(9) \times 10^{-5}$ K^{-1} at 303 K, respectively, with respect to the join trend described with the abovementioned equation 2. However at high-*T* the two Jd_{55} N.2 *C*2/*c* and Jd_{60} *C*2/*c* samples showed the largest $\alpha_{V,T}$ values [$3.31(8) \times 10^{-5}$ K^{-1} and $3.2(1) \times 10^{-5}$ K^{-1} at 1073K, respectively] very close to that of diopside [$3.3(1) \times 10^{-5}$ K^{-1} at 1073K]. On the other hand it is clear from Figure 5c that while at room-T the *P*2/*n* Jd_{55} N.5 shows higher thermal expansion coefficient compared with the *C*2/*c* samples with identical composition, at high-*T* α_V for the *P*2/*n* sample is much lower than the *C*2/*c* one.

This thermal expansion excess of the *C*2/*c* intermediate composition samples at high-*T* seems to be consistent with the observation by Ballaran 2003; Carpenter et al. 1999; Carpenter 2002. They firstly interpreted the sharpening of some FTIR absorption bands (i.e. Δcorr150) as substantial local decrease of strain heterogeneity, on the basis of the elastic trace element substitution model proposed by Blundy and Wood 1994; van Westrenen et al. 2003; van Westrenen et al. 2001.

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.

REFERENCES

Alvaro M, Nestola F, Ballaran TB, Cámara F, Domeneghetti MC, Tazzoli V (2010) High-pressure phase transition of a natural pigeonite. Am Mineral 95 (2-3):300-311. doi:10.2138/am.2010.3175

Alvaro M, Cámara F, Domeneghetti M, Nestola F, Tazzoli V (2011a) H*T* $P2_1/c$–$C2/c$ phase transition and kinetics of Fe^{2+}–Mg order–disorder of an Fe-poor pigeonite: implications for the cooling history of ureilites. Contrib Mineral Petrol 162 (3):599-613.

Alvaro M, Nestola F, Cámara F, Domeneghetti MC, Tazzoli V (2011b) High-pressure displacive phase transition of a natural Mg-rich pigeonite. Phys Chem Minerals 38 (5):379-385

Anderson OL, Isaak D, Oda H (1992) High-temperature elastic constant data on minerals relevant to geophysics. Rev Geophys 30 (1):57-90

Angel RJ, Gonzalez-Platas J, Alvaro M (2014) EosFit7c and a Fortran module (library) for equation of state calculations. Z Kristallogr 229(5):405-419

Boffa Ballaran T, Carpenter MA, Domeneghetti MC, Tazzoli V (1998) Structural mechanisms of solid solution and cation ordering in augite-jadeite pyroxenes; I, A macroscopic perspective. Am Mineral 83 (5-6):419

Boffa Ballaran T (2003) Line broadening and enthalpy: Some empirical calibrations of solid solution behaviour from IR spectra. Phase Transitions: A Multinational Journal 76 (1-2):137-154

Berman RG (1988) Internally-Consistent Thermodynamic Data for Minerals in the System Na_2O-K_2O-CaO-MgO-FeO-Fe_2O_3-Al_2O_3-SiO_2-TiO_2-H_2O-CO_2. J Petrol 29 (2):445-522

Blessing RH (1995) An empirical correction for absorption anisotropy. Acta Crystallogr, Sect A 51 (1):33-38

Blundy J, Wood B (1994) Prediction of crystal– melt partition coefficients from elastic moduli. Nature 372 (6505):452-454

Cámara F, Carpenter MA, Domeneghetti MC, Tazzoli V (2003) Coupling between non-convergent ordering and transition temperature in the $C2/c$ <-> $P2_1/c$ phase transition in pigeonite. Am Mineral 88 (7):1115-1128

Cámara F, Gatta GD, Meven M, and Pasqual D (2012) Thermal expansion and high temperature structure evolution of zoisite by single-crystal X-ray and neutron diffraction. Phys. Chem Mineral 39(1):27-45.

Cameron M, Sueno S, Prewitt CT, Papike JJ (1973) High-Temperature Crystal Chemistry of Acmite, Diopside, Hedenbergite, Jadeite, Spodumene, and Ureyite. Am Mineral 58:594-618

Cannillo E, Germani G, and Mani F, (1983) Nuovo software cristallografico per il diffrattometro a cristallo singolo Philips PW1100 (New crystallographic software for Philips PW1100 single crystal diffractometer) Internal Report 2 C.N.R. Centro di Studio per la Cristallografia Strutturale

Carpenter MA (1979) Omphacites from Greece, Turkey, and Guatemala; composition limits of cation ordering. Am Mineral 64 (1-2):102-108

Carpenter MA (2002): Microscopic strain, macroscopic strain and the thermodynamics of phase transitions in minerals. In Gramaccioli, C.M. (ed.): Energy modelling in minerals. EMU Notes Mineral., 4. Budapest: Eötvös Univ. Press, 311–346

Carpenter MA, Domeneghetti MC, Tazzoli V (1990) Application of Landau Theory to Cation Ordering in Omphacite .1. Equilibrium Behavior. Eur J Mineral 2 (1):7-18

Carpenter MA, Ballaran TB, Atkinson A (1999) Microscopic strain, local structural heterogeneity and the energetics of silicate solid solutions. Phase Transitions: A Multinational Journal 69 (1):95-109

Ferrari S., Nestola F., Massironi M., Maturilli A., Helbert J., Alvaro M., Domeneghetti M. C., and Zorzi F. 2014. In-situ high-temperature emissivity spectra and thermal expansion of C2/c pyroxenes: implications for the surface of Mercury. Am Mineral 99(4):786-792.

Finger LW, Ohashi Y (1976) The thermal expansion of diopside to 800°C and a refinement of the crystal structure at 700°C. Am Mineral 61:303-310

Gatta G. D., Comboni D., Alvaro M., Lotti P., Cámara F., and Domeneghetti M. C. 2014. Thermoelastic behavior and dehydration process of cancrinite. Phys Chem Mineral 41(5):373-386.

Gottschalk M (1997) Internally consistent thermodynamic data for rock-forming minerals in the system SiO_2-TiO_2-Al_2O_3-CaO-MgO-FeO-K_2O-Na_2OH_2O-CO_2. Eur J Mineral 9 (1):175-223

Hawthorne FC, Ungaretti L, Oberti R (1995) Site populations in minerals; terminology and presentation of results of crystal-structure refinement. Can Mineral 33 (4):907-911

Holland TB (1990) Activities of components in omphacitic solid solutions. Contrib Mineral Petrol 105 (4):446-453

Holland TJB, Powell R (1998) An internally consistent thermodynamic data set for phases of petrological interest. J Metamorph Geol 16 (3):309-343

Holland TJB, Powell R (2011) An improved and extended internally consistent thermodynamic dataset for phases of petrological interest, involving a new equation of state for solids. J Metamorph Geol 29 (3):333-383

Hunt SA, Walker AM, McCormack RJ, Dobson DP, Wills AS, Li L (2011) The effect of pressure on thermal diffusivity in pyroxenes. Mineral Mag 75 (5):2597-2610

Knight KS (1996) A neutron powder diffraction determination of the thermal expansion tensor of crocoite ($PbCrO_4$) between 60 K and 290 K. Mineral Mag 60:9

Mantovani L, Tribaudino M, Mezzadri F, Calestani G, Bromiley G (2013) The structure of (Ca,Co)$CoSi_2O_6$ pyroxenes and the Ca-M^{2+} substitution in (Ca,M^{2+})$M^{2+}Si_2O_6$ pyroxenes (M^{2+} = Co, Fe, Mg). Am Mineral 98:241-1252

Nestola F, Ballaran TB, Liebske C, Thompson R, Downs RT (2008) The effect of the hedenbergitic substitution on the compressibility of jadeite. Am Mineral 93 (7):1005-1013

Nishihara Y, Matsukage KN, Karato SI (2006) Effects of metal protection coils on thermocouple EMF in multi-anvil high-pressure experiments. Am Mineral 91 (1):111-114

Ohashi Y, Burnham CW (1973) Clinopyroxene Lattice Deformations: The Roles of Chemical Substitution and Temperature. Am Mineral 58:843-849

Pandolfo F, Nestola F, Cámara F, Domeneghetti MC (2012) New thermoelastic parameters of natural *C*2/*c* omphacite. Phys Chem Minerals:1-10

Pavese A, Bocchio R, Ivaldi G (2000) In situ high temperature single crystal X-ray diffraction study of a natural omphacite. Mineral Mag 64 (6):983-993

Pawley AR, Redfern SAT, Holland TJB (1996) Volume behavior of hydrous minerals at high pressure and temperature: I. Thermal expansion of lawsonite, zoisite, clinozoisite, and diaspore. Am Mineral 81 (3):335-340

Pouchou JL, Pichoir F (1991) Quantitative analysis of homogeneous or stratified microvolumes applying the model "PAP". Electron probe quantitation:31-75

Redhammer GJ, Cámara F, Alvaro M, Nestola F, Tippelt G, Prinz S, Simons J, Roth G, Amthauer G (2010) Thermal expansion and high-temperature $P2_1/c$–$C2/c$ phase transition in clinopyroxene-type $LiFeGe_2O_6$ and comparison to $NaFe(Si,Ge)_2O_6$. Phys Chem Minerals 37 (10):685-704

Richet P, Mysen BO, Ingrin J (1998) High-temperature X-ray diffraction and Raman spectroscopy of diopside and pseudowollastonite. Phys Chem Minerals 25 (6):401-414

Sheldrick GM (1996) Sadabs, University of Göttingen Germany,

Sheldrick GM (2008) A short history of SHELX. Acta Crystallogr, Sect A 64:112-122

Tribaudino M (1996) High-temperature crystal chemistry of *C*2/*c* clinopyroxenes along the join $CaMgSi_2O_6$-$CaAl_2SiO_6$. Eur J Mineral 8 (2):273-279

Tribaudino M, Nestola F, Cámara F, Domeneghetti MC (2002) The high-temperature $P2_1/c$-$C2/c$ phase transition in Fe-free pyroxene ($Ca_{0.15}Mg_{1.85}Si_2O_6$): Structural and thermodynamic behavior. Am Mineral 87 (5-6):648-657

Tribaudino M, Nestola F, Bruno M, Ballaran TB, Liebske C (2008) Thermal expansion along the $NaAlSi_2O_6$-$NaFe^{3+}Si_2O_6$ and $NaAlSi_2O_6$-$CaFe^{2+}Si_2O_6$ solid solutions. Phys Chem Minerals 35 (5):241-248

Tribaudino M, Angel RJ, Cámara F, Nestola F, Pasqual D, and Margiolaki I (2010) Thermal expansion of plagioclase feldspars. Contrib Mineral Petrol 160: 899-908.

Tribaudino M, Mantovani L (2014) Thermal expansion in *C*2/*c* pyroxenes: a review and new high temperature structural data on a pyroxene of composition $(Na_{0.53}Ca_{0.47})(Al_{0.53}Fe_{0.47})Si_2O_6$ ($Jd_{53}Hd_{47}$). Mineral Mag (in press)

van Westrenen W, Wood B, Blundy J (2001) A predictive thermodynamic model of garnet-melt trace element partitioning. Contrib Mineral Petrol 142 (2):219-234

van Westrenen W, Allan NL, Blundy JD, Lavrentiev MY, Lucas BR, Purton JA (2003) Trace element incorporation into pyrope–grossular solid solutions: an atomistic simulation study. Phys Chem Minerals 30 (4):217-229. doi:10.1007/s00269-003-0307-5

Wilson AJC (1995) International tables for crystallography. Volume C. . Kluwer Academic Publishers, Dordrecht, The Netherlands., Yang H, Prewitt CT (2000) Chain and layer silicates at high temperatures and pressures. Rev Mineral Geochem 41 (1):211-255

Zhao Y, Von Dreele RB, Shankland TJ, Weidner DJ, Ianzhong Zhang J, Wang Y, Gasparik T (1997) Thermoelastic equation of state of jadeite $NaAlSi_20_6$: An energy-dispersive Reitveld refinement study of low symmetry and multiple phases diffraction. Geophys Res Lett 24 (1):5-8

TABLES AND FIGURE CAPTIONS

Table 1. Electron microprobe analysis and formula in atoms per formula unit (apfu) based on six oxygen atoms.

Table 2. Unit cell parameters and information on data collection and structure refinement obtained on natural and annealed samples.

Table 3. Site populations, electron number, mean bond distances and order parameters obtained from structure refinements using chemical constraints.

Table 4. Unit cell volume (V, expressed in Å^3) as a function of temperature (K).

Table 5a. Lattice parameter (*a* expressed in Å) as a function of temperature (K). (supplementary material)

Table 5b. Lattice parameter (**b** expressed in Å) as a function of temperature (K). (supplementary material)

Table 5c. Lattice parameter (*c* expressed in Å) as a function of temperature (K). (supplementary material)

Table 5d. Lattice angle (β, expressed in °) as a function of temperature (K). (supplementary material)

Table 6a. Unit cell volume thermal equation of state fitting results

Table 6b. Unit cell volume thermal equation of state fitting results

Table 7a. Lattice parameters thermal equation of state fitting results

Table 7b. Lattice parameters thermal equation of state fitting results

Figure 1a. Room temperature volume for all the samples discussed in the manuscript as a function of composition (Jd%). Filled circles represent all our *C*2/*c* data. Open symbols represent literature data: diopside from Finger and Ohashi (1976) – squares; diopside from 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 (*C*2/*c*) from Pandolfo et al., (2012) – right-pointing triangles; *P*2/*n* Omp from Pavese et al., (2000) – left-pointing triangles.

Figure 1b. Room *T* variation of the b lattice versus O3-O3-O3 kinking angle for all the *C*2/*c* samples with different compositions studied in this work.

Figure 2a. Unit-cell parameters *a* relative variation (a_T/a_{To})with increasing *T* for all the *C*2/*c* samples studied in this work.

Figure 2b. Unit-cell parameters **b** relative variation ($\mathbf{b}_T/\mathbf{b}_{To}$;) with increasing *T* for all the *C*2/*c* samples studied in this work.

Figure 2c. Unit-cell parameters *c* relative variation (c_T/c_{To}) with increasing *T* for all the *C*2/*c* samples studied in this work.

Figure 2d. Beta angle relative variation (β_T/β_{To}) with increasing *T* for all the *C*2/*c* samples studied in this work.

Figure 3a. Volume variations with temperature for the end-member *C*2/*c* samples of this study together with those from literature. Filled symbols (this work): Di - downward triangles; Jd_{100} – squares. Open symbols (literature data): diopside from Finger and Ohashi (1976) – squares; diopside from Richet et al. (1998) - diamonds; diopside and jadeite from Cameron et al. (1973) upward and downward triangles respectively; jadeite from Tribaudino et al. (2008) circles.

Figure 3b. Volume variations with temperature for the intermediate composition samples of this study together with those from literature. Filled symbols (this work): Jd_{40} – upward triangles; Jd_{60} – circles; Jd_{80}

– diamonds; Jd$_{55}$ N.5 (*P*2/*n*) - hexagons. Open symbols (literature data): Jd55 N.2 (C2/c) from Pandolfo et al., (2012) – right-pointing triangles; Omp (*P*2/*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 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$_{100}$. 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 (1998); open circle represent data fitted following the equation by Gottschalk (1997). The shadowed area covers the e.s.d.'s interval (± 1σ) for the volume at each temperature.

Figure 5a. Room temperature volume thermal expansion coefficients (α_{Vo}) for all the samples discussed in the manuscript as a function of composition (Jd%). Filled circles represent all our C2/c data. Open symbols represent literature data: diopside from Finger and Ohashi (1976) – squares; diopside from 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., (2012) – right-pointing triangles; Omp from Pavese et al., (2000) – left-pointing triangles. The dashed line represents the equation fitted for the *C*2/*c* samples of this work.

Figure 5b. Normalized volume thermal expansion coefficients (α_V), calculated as $\alpha_{V,T}/\alpha_0$ (where α_0 is the volume thermal expansion coefficient at room-*T*) for all C2/c samples of this work. Diopside - downward triangles; Jd$_{40}$ - upward triangles; Jd$_{60}$ - circles; Jd$_{80}$ – diamonds; jd$_{100}$ – squares.

Figure 5c. Volume thermal expansion coefficients (α_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 symbols) with identical Jd contents.

Figure 5d. Volume thermal expansion coefficients (α_V) as a function of temperature (K) for all the *C*2/*c* samples of this work. Diopside - downward triangles; Jd$_{40}$ - upward triangles; Jd$_{60}$ - circles; Jd$_{80}$ – diamonds; Jd$_{100}$ – squares.