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High-pressure behavior of *P2/n* omphacite

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ABSTRACT

High-pressure and room-temperature single-crystal X-ray diffraction (XRD) study has been performed using diamond-anvil cell on a crystal of *P2/n* natural omphacite sample with composition very close to $\text{Jd}_{52}\text{Ag}_{48}$ and with high degree of order in the cation distribution. Unit-cell parameters were determined at 13 different pressures up to about 7.5 GPa. A third-order Birch-Murnaghan equation of state (BM3-EoS) fit to the *P-V* data yielded $V_0 = 421.43(4) \text{ \AA}^3$, $K_{T0} = 122(1)$ GPa and $K' = 5.1(3)$. The K_{T0} value for this sample lies between the data obtained for the two end-members jadeite and diopside, describing a slight positive curvature trend.

During the same experiment, intensity data were collected and crystal structures were refined at 5 pressures up to 7.3 GPa. Both M1 and M2 polyhedra volumes showed a slight but significant change in slope at about 4 GPa. Such behavior cannot be explained in terms of bond lengths compression anomaly but much likely in terms of tilt angle variation of TA and TB tetrahedral, which also showed a change in slope with pressure.

Keywords: pyroxene, omphacite, high-pressure, single crystal XRD, crystal structures, diamond-anvil cell, Equation of State.

29 **INTRODUCTION**

30 Several recent X-ray diffraction studies have been focused on the behavior under high-pressure con-
31 ditions of clinopyroxene with different compositions (Downs 2003; Origlieri et al. 2003; Thompson
32 et al. 2005; Bindi et al. 2006; McCarty et al. 2008; Nestola et al. 2005, 2006, 2007, 2008a, 2010;
33 Gavrilenko et al. 2010). Such large number of investigations is likely due to the very wide range of
34 geological high-pressure environments in which this mineral is found, from methamorphic rocks to
35 meteorites and also as inclusions in diamonds (e.g. Nestola et al. 2007; Koch-Mueller et al. 2004).
36 In particular, clinopyroxenes are significantly abundant in the upper mantle, and most mineralogical
37 and geophysical investigations have been concentrated on shedding light on the extremely complex
38 geodynamic processes occurring at that depth (e.g. Agee 1999). The knowledge of the
39 compressional and thermal behavior of clinopyroxenes is fundamental for understanding the
40 geological environments in which these silicates play a crucial role. Concerning the high-pressure
41 behavior of Na-clinopyroxene, X-ray diffraction studies have been performed both on jadeite,
42 aegirine, hedenbergite end-members and on jadeite - aegirine and jadeite – hedenbergite solid
43 solutions (Nestola et al. 2006; Nestola et al. 2007; Nestola et al. 2008a). The compressional
44 behavior of omphacite (solid solution between $\text{CaMgSi}_2\text{O}_6$, Di – $\text{NaAlSi}_2\text{O}_6$, Jd, end-members) was
45 investigated for the disordered phase with $C2/c$ space group by McCormick et al. (1989) by single-
46 crystal X-ray diffraction and by Nishihara et al. (2003) using an in situ multi anvil apparatus by X-
47 ray synchrotron radiation; for the ordered phase, with $P2/n$ space group, it was studied by Pavese et
48 al. (2001) on powder material by X-ray synchrotron radiation. However no studies on the structural
49 behavior at high pressure have been performed so far on this mineral. The aim of this work is to
50 define for the first time the crystal structure evolution as a function of pressure and the pressure –
51 volume equation of state for a natural ordered omphacite $P2/n$ with low Fe content by single-crystal
52 X-ray diffraction (SCXRD). This work is part of a wider project focused on the high-pressure and
53 high-temperature behavior of natural and synthetic Na-bearing pyroxenes.

55 **Key-words:** omphacite, high-pressure, single-crystal, X-ray, diffraction

56

57 **EXPERIMENTAL METHODS**

58 *Sample*

59 The sample investigated at high-pressure in this work comes from the same crystal suite studied by
60 **Boffa Ballaran et al. (1998)** and in particular it is labeled as their sample 74AM33. The chemical
61 analysis of this sample is reported in Table 1. The sample has been selected for its very low Fe
62 content in order to avoid the effect of iron on the Di-Jd solid solution. This sample also presents the
63 highest degree of order for a natural omphacite among the samples studied by Boffa Ballaran et al.
64 (1998). From this sample we picked up a single crystal, labeled as N.4, suitable for the high-
65 pressure experiments due to its sharp optical extinction, sharp diffraction profiles, absence of
66 twinning and evident defects and appropriate crystal size (0.17 x 0.12 x 0.05 mm).

67 *Chemistry*

68 Chemical analysis was performed on the same crystal used for the high-pressure work. After
69 extracting crystal from the DAC it was embedded in epoxy resin and polished for electron
70 microprobe analysis (EMPA), which were carried out at the Dipartimento di Geoscienze (Uni-
71 versity of Padova) using a CAMECA-CAMEBAX electron microprobe operating in wavelength
72 dispersive mode with a fine-focused beam (~1 mm diameter), an acceleration voltage of 20 kV and
73 a beam current of 10 nA, with 10 s counting times for both peak and total background. X-ray counts
74 were converted to oxide wt.% using the PAP correction program supplied by CAMECA (**Pochou**
75 **and Pichoir, 1991**). Standards, spectral lines, and analytical crystals used were: albite (Na-Ka,
76 TAP), wollastonite (Si, Ca-Ka, TAP), olivine (Mg-Ka, TAP), Al₂O₃ (Al-Ka, TAP), MnTiO₃ (Mn-
77 Ka, LiF; Ti- Ka, PET), Cr₂O₃ (Cr-Ka, LiF), Fe₂O₃ (Fe-Ka, LiF). The oxide wt.% obtained by
78 averaging 15 microprobe analyses are reported in Table 1.

79 *Single-crystal on air X-ray diffraction*

80 The on air intensity data collection was collected at the University of Pavia on a three-circle Bruker
81 AXS SMART APEX diffractometer, equipped with a CCD detector (graphite-monochromatized
82 MoK α radiation $\lambda=0.71073$ Å, 55 kV, 30 mA) and a monocarp collimator. The Bruker SMART
83 software package was used. A total of 3360 frames (frame resolution 512x512 pixels) were
84 collected with four different goniometer settings using the ω -scan mode (scan width: 0.2 $^\circ\omega$;
85 exposure time: 10 s; detector sample distance 4.02 cm). A total of 10337 reflections were collected.
86 Completeness of the measured data was achieved up to 78 $^\circ$ θ . The Bruker SAINT+ software was
87 used for data reduction, including intensity integration and background and Lorentz-Polarization
88 corrections. The semi-empirical absorption correction of [Blessing \(1995\)](#), based on the
89 determination of transmission factors for equivalent reflections, was applied using the program
90 SADABS ([Sheldrick 1996](#)) and the monoclinic Laue group $2/m$. The intensity data were refined in
91 the $P2/n$ space group using program SHELX-97 ([Sheldrick 2008](#)) starting from the atom
92 coordinates by ([Pavese et al. 2000](#)). Scattering curves were taken from the *International Tables for*
93 *X-ray Crystallography* ([Wilson 1995](#)). Neutral versus ionized scattering factors were used to refine
94 occupancy for all sites that are not involved in chemical substitutions (O and Si) ([Hawthorne et al.](#)
95 [1995](#)) and ionized scattering factors were used for cationic sites. When the refinement reached
96 convergence, full-matrix least-squares were carried out using the data from the electron microprobe
97 analysis (with 1 σ error) as chemical constraints to obtain the site partitioning. The following
98 restraints were introduced into the refinement: (1) all structural sites were considered fully
99 occupied; (2) Al $^{3+}$ was distributed between T, M11 and M1; (3) Mn $^{2+}$ was ordered in M1 while Cr
100 and Ti were considered ordered in M11; (4) Fe $^{2+}$ and Mg were considered as present in both M1
101 and M11, while Fe $^{2+}$ only in M2 and Mg in M21; 5) charge balance was ensured by the equation
102 $X_{Na}^{M2} + X_{Na}^{M21} = X_{Al^{3+}} + X_{Al}^{M11} + X_{Al}^{M1} + 2X_{Ti} + X_{Cr}$; (6) additional equations based on the $\langle M1-O \rangle$
103 and $\langle M11-O \rangle$ observed mean bond distances were used to better constrain the site partitioning of
104 Mg and Al in M1 and M11 sites. These equations are $\langle M1-O \rangle = 2.077Mg_{M1} + 1.928Al_{M1} +$
105 $2.130Fe_{M1}^{2+} + 2.173Mn_{M1}$ and $\langle M11-O \rangle = 2.077Mg_{M11} + 1.928Al_{M11} + 2.130Fe_{M11}^{2+} + 1.990Ti_{M11}$

106 + 2.01Cr_{M11}. The values of mean bond distances for Mg, Al and Fe²⁺ are from Boffa Ballaran et al.
107 (1998), values for Mn, Ti and Cr are from Zema et al. (1997). The mean atomic numbers calculated
108 for the octahedral sites [m.a.n._{M1+M11+M2+M21}] by EMPA [28.87(13)] and by SCXRD [28.74(31)] are
109 in agreement within their errors. The unit-cell parameters of the crystal in air are reported in Table
110 2, the values of the conventional agreement factor R1 as well as other details from the chemical
111 constrained structure refinement are reported in Table 3. The site populations obtained from this
112 refinement are reported in Table 4, fractional coordinates and displacement parameters in Table 5,
113 bond lengths and angles in Table 6. The full structural data are also been deposited as cif¹.

114

115 *Single-crystal High-pressure X-ray diffraction*

116 The high-pressure SCXRD experiments were carried out at the Dipartimento di Geoscienze,
117 Università di Padova. Crystal N.4 was loaded in an ETH-type DAC (Miletich et al. 2000) using a
118 steel gasket (T301), pre-indented to a thickness of 110 µm and with a 250 µm diameter hole. A
119 single crystal of quartz was used as internal diffraction pressure standard (Angel et al. 1997) and a
120 16:3:1 mixture of methanol:ethanol:water was used as hydrostatic pressure medium, which remains
121 hydrostatic up to about 9.5-10 GPa (Angel et al. 2007). Unit-cell parameters were determined at 13
122 different pressures up to about 7.5 GPa using a STOE STADI-IV four-circle diffractometer
123 (operating at 50 kV and 40 mA) automated by SINGLE software (Angel and Finger 2011). The
124 unit-cell parameters were measured centering about 20 reflections for each high-pressure
125 experiment. Full details of the instrument and the peak-centering algorithms are provided by Angel
126 (2001). During the centering procedure the effects of crystal offsets and diffractometer aberrations
127 were eliminated from refined peak positions by the eight-position centering method of King and
128 Finger (1979). Unit-cell parameters, obtained by vector least-squares (Ralph and Finger 1982) are
129 reported for each pressure step in Table 2. The intensity data were collected every about 2 GPa
130 using a second STOE STADI-IV single-crystal diffractometer equipped with a CCD detector

131 located in the same Department (graphite monochromated MoK α radiation, Oxford Diffraction).
132 The intensity data were collected in the $5 \leq 2\theta \leq 60^\circ$ range using a 1° ω -scan and an exposure time
133 of 60 s per frame. The sample detector distance was 60 mm. The program CrysAlis RED (Oxford
134 Diffraction) was used to integrate the intensity data, applying the Lorentz-polarization correction.
135 ABSORB 6.0 (Angel 2004) program was adopted to correct for absorption and also take into
136 account the effect of gasket shadowing (Angel 2001). The package SHELX-97 (Sheldrick 2008)
137 was used for structure refinements, which were performed in space group $P2/n$, starting from the
138 atomic coordinates of Pavese et al. (2000). The atomic scattering curves were taken from the
139 *International Tables for X-ray Crystallography* (Wilson 1995). Isotropic displacement parameters
140 were considered for all atoms. For each high pressure refinement the site occupancies were
141 constrained to the values obtained from the on air refinement (see Table 4). The values of the
142 conventional agreement factor R_1 as well as other details from every pressure step refinement are
143 reported in Table 3. Fractional coordinates and displacement parameters are reported in Table 5,
144 bond lengths and angles in Table 6. The full structural data are also been deposited as cifs¹.

145

146 ¹ Cif deposit items are available via the MSA web site at <http://www.minsocam.org>, go to the
147 American Mineralogist Contents, find the table of contents for the specific volume/issue wanted,
148 and then click on the deposit link there.

149

150 **RESULTS**

151 *Order degree*

152 The site population (Table 4) was used to calculate the order parameters Q_{M1} and Q_{M2} of the M1
153 and M2 sites using equations (2) and (3) provided by Carpenter et al. (1990) expressed as Eqn. 1 and
154 Eqn. 2. They resulted to be: $Q_{M1}^{occ} = 0.896$ and $Q_{M2}^{occ} = 0.499$. These values are in agreement with
155 those reported by Boffa Ballaran (1998) for the same 74AM33 sample. The order parameters
156 expressed in terms of mean bond lengths were calculated using Eqn.3 and Eqn.4 provided by

157 Carpenter et al. (1990), which yielded: $Q_{M1}^{dist} = 0.0689$ and $Q_{M2}^{dist} = 0.0161$ (Table 4). The
158 correlation between the two parameters confirms the low aegirine content for N4 sample (see Fig. 2
159 by Carpenter et al. 1990).

160

161 *Evolution of the unit-cell parameters with pressure and pressure – volume equation of state*

162 The evolutions of the unit-cell parameters and unit-cell volume with pressure are shown in Figure
163 1a and 1b. A continuous decrease of a , b , c , β angle and volume, V , is observed as a function of
164 pressure with no evidence of a phase transition up to the maximum pressure reached. The a , b , c
165 lattice parameters decrease by about 1.8, 2.0 and 1.9% up to 7.5 GPa, respectively, β by 0.7% and
166 the unit-cell volume decreases by about 5.2%.

167 In order to define the best equation of state that adequately describes the pressure-volume trend for
168 the sample here studied an F_E - f_E plot was constructed following Angel (2001) and is shown in
169 Figure 2. The plot shows that data lie on a positively inclined straight line indicating that a Birch-
170 Murnaghan equation of state truncated at the third-order (BM3-EoS, Birch 1947) must be used to fit
171 the experimental pressure-volume data. Thus, using EoS-FIT 5.2 software (Angel 2002) it was
172 possible to refine simultaneously to a BM3 the volume, V_0 , the bulk modulus K_{T0} , and its first
173 pressure derivative K' obtaining the following coefficients: $V_0 = 421.43(4) \text{ \AA}^3$, $K_{T0} = 122(1) \text{ GPa}$, K'
174 $= 5.1(3)$. The quality of the experimental data is demonstrated by the small differences between the
175 EoS coefficients obtained by the refinement and by the F_E - f_E plot of Figure 2 ($K_{T0} = 122.9(6) \text{ GPa}$,
176 $K' = 4.9(2)$); the intercept corresponds to the bulk modulus whereas the slope of the straight line
177 provides the first pressure derivative as in Angel (2001).

178 A parameterized form of the BM3 EoS was used to determine the axial moduli of a , b , and c again
179 using EoS-FIT5.2. Equation-of-state coefficients together with the relative axial compressibilities
180 are reported in Table 7. The anisotropy scheme, using the data reported in Table 7, is $K_c \leq K_a \leq K_b$,
181 with an anisotropy ratio 1.04:1.00:1.07.

182

183 *Crystal-structure evolution with pressure*

184 Figure 3 and Figure 4 show the evolution of the polyhedral volumes for M1, M11, M2 and M21
185 sites as a function of pressure. Relatively to the M2 and M21 polyhedra we observe a continuous
186 decrease of volume with pressure by about 6.4 and 6.9%, respectively (Fig. 4). The M2 polyhedron
187 shows a large deformation: the M2-O31 bond length shows a strong decrease close to 4.5% (see
188 Table 6); for the M21 polyhedron the M21-O32 bond length decreases even more with a reduction
189 by about 5.7% (see Table 6). This strong difference could explain the slightly greater volumetric
190 reduction of the M21 polyhedron.

191 The M1 and M11 polyhedra show lower volume decrease (by about 5.7 and 6.1%, respectively)
192 than M2 sites. The M11 polyhedron is slightly softer than M1 and this should be due to the greater
193 compressibility of the two bond lengths M1-O11 and M1-O22, which show a decrease by 2 and
194 3.3%, respectively, against the M11-O21 and M11-O12, which decrease by 1.2 and 3%,
195 respectively (see Table 6). In Figure 3 and Figure 4 it is possible to note that both M1 and M2
196 polyhedra show a slight but significant change in slope at about 4 GPa. Such a behavior cannot be
197 explained in terms of bond lengths compression anomaly but much likely to the tilt angle [defined
198 as the out-of-plane tilting of the basal face of the tetrahedral with respect to the plane (100) (see
199 [Cameron et al. 1973](#))] variation as a function of pressure. In fact, in Figure 5 both the tilt angles of
200 TA and TB show a slope change between 2 and 4 GPa.

201 Concerning the TA and TB tetrahedra, they show a small decrease up to the maximum pressure
202 reached during the experiments, as expected for such usually very rigid polyhedra as a function of
203 pressure. However, a slight difference in compressibility between TA and TB is found (2.2 and
204 0.9%, respectively, up to 7.3 GPa).

205 The O3-O3-O3 angle, defining the tetrahedral chain kinking, linearly decreases by about 1.7% up to
206 6 GPa and then it seems to remain constant up to the maximum pressure reached.

207

208

209 **DISCUSSION**

210 The value of K_{T0} of our sample, obtained using a BM3-EoS, was plotted versus composition
211 expressed in molar percentage of jadeite in Figure 6. In this Figure, pure value for jadeite is from
212 Nestola et al. (2006), which is very close to McCarty et al. (2008) value. We decided to use Nestola
213 et al. (2006) data because their data have been obtained using the same experimental techniques as
214 those used in this work and thus the data are reliably comparable. Diopside is from Gavrilenko et al.
215 (2010). Their data are the most recent on diopside compressibility and were calculated with the
216 same experimental techniques used in this work (and using a BM3-EoS). These authors investigated
217 two diopside samples: a first sample, Di₀ with K_{T0} (GPa) = 106(1) shows a not pure diopside
218 composition (e.g. a limited excess of Mg) while a second sample, Di₆₀₀ with K_{T0} (GPa) = 108(1) is
219 hydrated (e.g. 600 ppm). However, it appears clear that both samples, in spite of their non purity, do
220 not show any significant bulk modulus deviation from synthetic diopside by Tribaudino et al.
221 (2000), K_{T0} (GPa) = 105.1(9), from the of value of K_{T0} (GPa) = 108 GPa computed from the
222 adiabatic bulk modulus reported by Levien et al. (1979), and from the value extrapolated by Boffa
223 Ballaran et al. (2009) on a pure diopside, K_{T0} (GPa) = 107.4(1). In Figure 6, the data referring to
224 Jd₁₀₀Di₀, Jd₅₀Di₅₀ and Jd₀Di₁₀₀ lie on a well defined bulk modulus vs. composition trend, which
225 shows a clear curvature at intermediate composition. Along the jadeite-diopside solid solution the
226 bulk modulus K_{T0} decreases by about 9% from 134.0(7) GPa for jadeite to the value of 122(1) GPa
227 for our sample down to 106(1) GPa for diopside with a total decrease of about 21%. The value of
228 bulk modulus from Pavese et al. (2001), lies very close to the trend in Figure 6. In the same figure
229 the data from Nishihara et al. (2003), K_{T0} (GPa) = 126(1), and from sample SBB-1, K_{T0} (GPa) =
230 129(3), and SDC-1 K_{T0} (GPa) = 139(4) by McCormick et al. (1989) are also reported. They are not
231 strictly relative to a Jd₅₀Di₅₀ composition and were calculated using a BM2-EoS with K' assumed to
232 be 4. The recalculation of their data, using a BM3-EoS for purpose of comparison with our data led
233 to a negative value of K' . Moreover, sample SBB-1 by McCormick et al. (1989) and sample by

234 Nishihara et al. (2003) contain 13 and 9% of Ca-Eskola ($\text{Ca}_{0.5}\square_{0.5}\text{AlSi}_2\text{O}_6$, vacancy-rich end-
235 member) respectively. Regarding samples by McCormick et al. (1989), as already observed by the
236 authors “there is a significant difference in the compression of the two omphacites, with the
237 vacancy-rich pyroxene (SBB-1) being more compressible than the vacancy-poor pyroxene (SDC-
238 1)”. At any rate, the effect on the compressibility of the presence of Ca-Ts ($\text{CaAl}_2\text{Si}_2\text{O}_6$ end
239 member) cannot be neglected. In fact the samples that more deviate from the trend are those
240 containing the greater percentage of Ca-Ts: 6.2% and 4.6% for SDC-1 and Nishihara et al. (2003)
241 samples, respectively. The influence of tetrahedral Al on the bulk-modulus was already evidenced
242 by Nestola et al. (2008b) for an aluminum-rich orthopyroxene, where significant stiffening was
243 reported.

244 Concerning the first pressure derivative, K' , it increases nearly linearly as a function of the diopside
245 content from 4.4(1) of jadeite, Nestola et al. (2006) to 5.1(3) (our study) to pure diopside 6.1(5)
246 (Gavrilenko et al. 2010) as found for jadeite – hedenbergite join (Nestola et al. 2008a). It is well
247 known (see Angel 2001) that the bulk modulus and its first pressure derivative strongly correlate to
248 more than 95%; such correlation often covers the real errors in determining both the parameters as
249 during the least squares refinement they are considered as two independent parameters. In this light,
250 in order to better understand the K_{T0} - K' correlation along the Jd-Di join a series of confidence
251 ellipses in the parameter space was constructed following Angel (2001) and shown in Figure 7. The
252 confidence ellipse was calculated for our sample, as well as for diopside (Gavrilenko et al. 2010),
253 omphacite (Pavese et al. 2001) and jadeite (Nestola et al. 2006) for a 68.3% confidence level. In this
254 figure it is possible to note that for all the four samples a negative correlation is present and that,
255 considering the extension of the ellipses, the errors on the K_{T0} and K' must be reconsidered for all
256 samples: for jadeite (Nestola et al. 2006) the errors in K_{T0} and K' increase only slightly from 0.7
257 GPa and 0.1 to 1 GPa and 0.3, respectively; for diopside (Gavrilenko et al. 2010) the errors in K_{T0}
258 and K' increase from 1 GPa and 0.5 to 2 GPa and 0.7, respectively; for our omphacite samples the
259 errors in K_{T0} and K' increase from 1 GPa and 0.3 to 2 GPa and 0.5, respectively; finally for the

260 omphacite sample by Pavese et al. (2001) the errors increase from 2.5 GPa and 0.6 to 4 GPa and
261 1.0, respectively, suggesting that some non hydrostaticity could be the cause of such strong increase
262 in the K_{T0} and K' errors due to their correlation. In fact Pavese et al. (2001) obtained their EoS by
263 X-ray powder diffraction up to 13 GPa using synchrotron radiation and nitrogen as a pressure
264 medium. As demonstrated by Angel et al. (2007) nitrogen is a non hydrostatic pressure medium for
265 pressures above 2-3 GPa.

266 In order to explain the difference in compressibility along the jadeite – diopside solid solution the
267 structural deformation mechanisms along the join has to be taken into account. As mentioned by
268 Thompson and Downs (2008) and Nestola et al. (2008a) the main three deformation mechanisms
269 can be described as following: isotropic scaling of the structure, tetrahedral chain kinking and
270 narrowing of the M1 chain along the **b** direction. For our omphacite sample, we observed the
271 following high-pressure behavior: i) concerning the isotropic scaling of the structure, as reported in
272 Table 7, the axial bulk modulus anisotropy is relatively limited with differences lower than 7%; ii)
273 the tetrahedral chain shows a significant contraction of about 0.47°/GPa, thus affecting the M2-O31
274 bond length, which shows the strongest contraction compared with the other bond lengths (by about
275 0.017 Å/GPa); iii) the angle between O21-O22-O21, which can be used as an indication of the
276 narrowing of the M1 chain (see Figure 8) increases by 1.3° up to 7.34 GPa. (Table 6).

277 In order to verify if we could find any systematic structural deformation mechanism along the
278 diopside-jadeite join we compared our sample with the two end-members diopside and jadeite
279 (Thompson and Downs 2008 and Nestola et al. 2008a). In particular, relatively to the contraction of
280 the tetrahedral chain and the M1 chain narrowing, we did not find a significant different behavior of
281 our sample compared to that of the end-members. Taking into account the linear compressibility
282 [expressed as $\beta = ((V-V_0)/V_0)/\Delta P$] of the structural M1 and M2 polyhedra, a possible comparison of
283 our $P2/n$ omphacite with the two end members can be performed on the basis of the site population
284 of the structural sites. Regarding the M1 polyhedra, in an ordered $P2/n$ omphacite, the M11 of
285 omphacite is similar to the M1 of jadeite due to its aluminum content ($X_{M11}^{Al} = 0.957$) while M1 for

286 | its Mg content ($X_{M1}^{Mg} = 0.837$) is similar to M1 of diopside. Concerning M2 polyhedra, the
287 | comparison of M2 in omphacite to M2 of jadeite and M21 polyhedron to M2 of diopside is more
288 | questionable due to the partial order of Na and Ca in the structural sites of the ordered omphacite.
289 | The linear compressibility of M2 of omphacite shows the same value than that of jadeite ($\beta_{M2} =$
290 | 0.0088 GPa^{-1} and $\beta_{M2} = 0.0090 \text{ GPa}^{-1}$, respectively) whereas its M11 linear compressibility is
291 | greater (β_{M11} of omphacite = 0.0083 GPa^{-1} , β_{M1} of jadeite = 0.0065 GPa^{-1}). This supports the
292 | evidence of a lower bulk modulus for the *P2/n* omphacite (K_{T0} omphacite is 122 GPa with respect
293 | to the K_{T0} of 134 for jadeite). However, similar relationships has not been found comparing
294 | omphacite and diopside. In fact, whereas the M1 linear compressibility is identical for both samples
295 | ($\beta_{M1} = 0.0077 \text{ GPa}^{-1}$), the value of M21 of omphacite is significantly greater than that of M2 of
296 | diopside ($\beta_{M21} = 0.0094 \text{ GPa}^{-1}$ and $\beta_{M2} = 0.0080 \text{ GPa}^{-1}$ respectively). This is in contrast with the
297 | evidence of a greater bulk modulus for the *P2/n* omphacite with respect to diopside ($K_{T0} = 106$).

298 | If the variation of the M1 and M2 polyhedral volumes with pressure, as reported in Figure 3 and
299 | Figure 4, is considered, a linear fitting can be used. With this approach, regarding the M1
300 | polyhedra, the coefficient that describes the slope of the straight line confirms the similar behavior
301 | of M11 of omphacite with M1 of jadeite [0.079(9) vs. 0.061(8), respectively] and of M1 of
302 | omphacite and diopside [0.093(7) vs. 0.091(2), respectively]. Concerning the M2 polyhedra, the
303 | same coefficient does confirm the similarity between the M2 of omphacite and jadeite [0.22(2) vs.
304 | 0.22(3), respectively] but shows the same contrast between M21 of omphacite and M2 of diopside
305 | [0.25(2) vs. 0.205(7), respectively] already observed above. It seems apparent that while about 25%
306 | of Ca in M2 of omphacite does not affect the compressibility of this polyhedron with respect to that
307 | of jadeite, the same amount of Na in M21 of omphacite makes the compressibility of the
308 | polyhedron to increase with respect to that of M2 of diopside. It is remarkable that the averaged
309 | effect of the various polyhedra is, by all means, intermediate between those of Jd and Di (reported
310 | also in Figs. 3 and 4) as it is for the bulk modulus.

312

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317

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426

427 **Table and Figure captions**

428 **Table 1.** Electron microprobe analysis and formula in atoms per formula unit (apfu) based on six
429 oxygen atoms for omphacite crystal N.4 (average of 15 spots)

430 **Table 2.** Unit-cell parameters at different pressure values for crystal N.4

431 **Table 3.** Structure refinement details (the relative unit-cell parameters are reported in Table 2) for
432 crystal N.4

433 **Table 4.** Site populations and degree of order of crystal N4 in air.

434 **Table 5.** Fractional coordinates and displacement parameters for the crystal N4

435 **Table 6.** Selected bond lengths (Å) and angles (°) in *P2/n* structure for the sample studied in this
436 work.

437 **Table 7.** Equation of state coefficients for N4 using a third order Birch-Murnaghan equation.

438

439 **Figure 1.** Evolution of the **a)** unit-cell parameters and **b)** unit-cell volume as a function of pressure
440 for all the samples investigated. The symbols used are larger than the errors. The curve plotted in **b)**
441 is the real Equation of State for the sample.

442 **Figure 2.** $F_E - f_E$ plot $\{F_E = P/3 \times f_E \times (1 + 2f_E)^{5/2}$ and $f_E = [(V_0/V)^{2/3} - 1]/2$, see Angel 2000} for
443 the sample studied in this work.

444 **Figure 3.** Evolution of M1 polyhedral volumes as a function of pressure.

445 **Figure 4.** Evolution of M2 polyhedral volumes as a function of pressure.

446 **Figure 5.** Evolution of the tilt angle as a function of pressure for the two tetrahedral chains TA and
447 TB.

448 **Figure 6.** Evolution of K_{T0} as a function of composition along the diopside-jadeite join.

449 **Figure 7.** Confidence ellipse for the equation of state of the sample studied in this work and for
450 other samples studied along the diopside-jadeite join.

451 **Figure 8.** Part of the crystal-structure of the sample studied in this work viewed along the [100]
452 direction. The octahedral M1 and M11 sites are showed. The black line corresponds to the O21-
453 O22-O21 angle.

454

455 Equations

456 **Eqn. 1** $Q_{M1}^{occ} = \frac{\left| \frac{(Al+Fe^{3+})_{M1} - (Al+Fe^{3+})_{M11}}{\Sigma(Al+Fe^{3+})} \right| + \left| \frac{(Mg+Fe^{2+})_{M1} - (Mg+Fe^{2+})_{M11}}{\Sigma(Mg+Fe^{2+})} \right|}{2}$

457 **Eqn. 2** $Q_{M2}^{occ} = \frac{\left| \frac{Na_{M2} - Na_{M21}}{\Sigma Na} \right| + \left| \frac{Ca_{M2} - Ca_{M21}}{\Sigma Ca} \right|}{2}$

458

459 **Eqn. 3** $Q_{M1}^{dist} = \left| \frac{\langle M1-O \rangle - \langle M11-O \rangle}{\frac{1}{2}(\langle M1-O \rangle + \langle M11-O \rangle)} \right|$

460 **Eqn. 4** $Q_{M2}^{dist} = \left| \frac{\langle M2-O \rangle - \langle M21-O \rangle}{\frac{1}{2}(\langle M2-O \rangle + \langle M21-O \rangle)} \right|$

461

462

Table 1. Electron microprobe analysis and formula in atoms per formula unit (apfu) based on six oxygen atoms for omphacite crystal N.4 (average of 15 spots)

% oxides		<i>a.p.f.u.</i>	
SiO ₂	56.1(4)	Si	1.968(7)
TiO ₂	0.11(2)	Al ^{IV}	0.032(7)
Al ₂ O ₃	13.1(2)	Al ^{VI}	0.510(9)
Cr ₂ O ₃	0.03(3)	Fe ³⁺	0.002(3)
FeO	2.33(6)	Fe ²⁺	0.067(4)
MnO	0.03(2)	Mg	0.448(8)
MgO	8.6(1)	Mn	0.0009(6)
CaO	13.0(2)	Ti	0.0030(6)
Na ₂ O	6.9(2)	Cr	0.0009(9)
K ₂ O	0.004(5)	Ca	0.490(7)
<i>total</i>	100.3(5)	Na	0.47(1)
		K	0.0002(2)
		<i>total</i>	3.99(1)

Table 2. Unit-cell parameters at different pressure values for crystal N.4

<i>P</i> (GPa)	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	β (Å)	<i>V</i> (Å ³)
<i>in air</i>	9.5613(4)	8.7578(4)	5.2543(2)	106.953(1)	420.85(3)
0.00010(1)	9.568(1)	8.7608(15)	5.2561(8)	106.995(10)	421.36(9)
0.449(6)	9.5541(5)	8.7481(7)	5.2482(3)	106.895(4)	419.71(4)
1.245(8)	9.5346(5)	8.7292(7)	5.2376(4)	106.809(5)	417.30(4)
1.78(1)	9.5198(4)	8.715(1)	5.2296(6)	106.744(8)	415.48(7)
2.74(1)	9.4973(4)	8.6914(6)	5.2163(3)	106.630(4)	412.57(4)
3.41(1)	9.4810(5)	8.6745(6)	5.2078(3)	106.567(4)	410.52(4)
4.14(1)	9.4645(4)	8.6576(6)	5.1981(3)	106.497(4)	408.40(3)
5.02(1)	9.4452(6)	8.6368(9)	5.187(4)	106.412(6)	405.89(5)
5.89(1)	9.4278(6)	8.6165(7)	5.1769(4)	106.334(5)	403.57(4)
6.456(9)	9.4156(6)	8.6044(8)	5.1695(4)	106.228(5)	402.00(4)
7.11(2)	9.403(5)	8.5913(7)	5.162(3)	106.234(4)	400.37(4)
7.34(2)	9.3992(6)	8.5857(7)	5.1593(3)	106.216(5)	399.79(4)
7.55(2)	9.3949(6)	8.5832(9)	5.1574(5)	106.210(6)	399.35(5)

Table 3. Structure refinement details (the relative unit-cell parameters are reported in Table 2) for crystal N.4

P (GPa)	<i>in air</i>	0	1.78	4.14	5.89	7.34
2θ max (°)	78	60	60	60	60	60
$R1$ (%)	2.38	8.4	8.31	9.14	8.25	10.38
n. of $I/\sigma > 4$	2068	315	307	306	301	285
n. relf. tot.	2164	534	519	512	514	497
ref. param.	110	45	45	45	45	45
GooF	1.151	1.193	1.159	1.222	1.196	1.223
WR^2 (%)	6.1	21.5	23.0	24.2	23.0	28.6

Table 4. site populations and degree of order of crystal N4 in air

T	Si	1.9639	M2	Ca	0.2531
	Al	0.0361		Na	0.7365
				Fe	0.0104
M1	Mg	0.8370	M21	Ca	0.7128
	Fe	0.0921		Na	0.2309
	Al	0.0693		Mg	0.0563
	Mn	0.0016			
M11	Mg	0.0157	Q^{occ}_{M1}		0.8956
	Fe	0.0199			
	Al	0.9572	Q^{occ}_{M2}		0.4993
	Ti	0.0058			
	Cr	0.0015	Q^{dist}_{M1}		0.0689
		Q^{dist}_{M2}			0.0161

Table 7. Equation of state coefficients for N4 using a third order Birch-Murnaghan equation.

a₀	9.5685(5)	b₀	8.7618(7)	c₀	5.2558(3)	V₀	421.43(4)
Ka₀	112(2)	Kb₀	107(2)	Kc₀	115(2)	K_{TO}	122(1)
K'	7.6(5)	K'	3.9(5)	K'	4.9(5)	K'	5.1(3)

Table 5. Fractional coordinates and displacement parameters for the crystal N4

<i>P</i> (GPa)		<i>in air</i>	0	1.77	4.14	5.89	7.34
M1	x	0.25	0.25	0.25	0.25	0.25	0.25
	y	0.15953(4)	0.1592(5)	0.1600(5)	0.1599(5)	0.1607(5)	0.1560(6)
	z	0.25	0.25	0.25	0.25	0.25	0.25
M11	Uiso	0.0069(1)	0.012(1)	0.012(1)	0.009(1)	0.009(1)	0.010(1)
	x	0.25	0.25	0.25	0.25	0.25	0.25
	y	0.34753(4)	0.3481(5)	0.3471(5)	0.3465(5)	0.3461(5)	0.3451(6)
M2	z	0.75	0.75	0.75	0.75	0.75	0.75
	Uiso	0.0058(1)	0.007(1)	0.008(1)	0.009(1)	0.009(1)	0.012(1)
	x	0.25	0.25	0.25	0.25	0.25	0.25
M21	y	0.55220(5)	0.5521(6)	0.5532(6)	0.5541(6)	0.5548(6)	0.5553(6)
	z	0.25	0.25	0.25	0.25	0.25	0.25
	Uiso	0.0103(1)	0.016(1)	0.014(1)	0.015(1)	0.014(1)	0.013(1)
Si1	x	0.25	0.25	0.25	0.25	0.25	0.25
	y	0.95046(3)	0.9502(4)	0.9491(4)	0.9474(4)	0.9470(4)	0.9470(5)
	z	0.75	0.75	0.75	0.75	0.75	0.75
Si2	Uiso	0.01079(9)	0.013(1)	0.013(1)	0.013(1)	0.012(1)	0.013(1)
	x	0.53939(2)	0.5390(3)	0.5390(4)	0.5390(4)	0.5393(4)	0.5392(5)
	y	0.34783(2)	0.3485(3)	0.3493(3)	0.3484(4)	0.3490(3)	0.3495(4)
O11	z	0.22638(4)	0.2261(5)	0.2256(5)	0.2256(5)	0.2252(6)	0.2253(6)
	Uiso	0.00528(6)	0.0099(8)	0.0093(8)	0.0083(9)	0.0084(9)	0.010(1)
	x	0.53731(2)	0.5368(3)	0.5378(4)	0.5376(4)	0.5375(4)	0.5378(5)
O12	y	0.16263(2)	0.1632(3)	0.1628(3)	0.1613(4)	0.1609(3)	0.1608(4)
	z	0.73036(4)	0.7307(5)	0.7308(5)	0.7303(5)	0.7291(6)	0.7293(6)
	Uiso	0.00510(6)	0.0086(8)	0.0085(8)	0.0084(9)	0.0095(9)	0.010(1)
O21	x	0.36286(6)	0.3626(8)	0.3631(8)	0.3627(9)	0.3616(9)	0.361(1)
	y	0.33887(7)	0.3358(8)	0.3374(8)	0.3390(8)	0.3398(7)	0.3392(8)
	z	0.1199(1)	0.118(1)	0.119(1)	0.122(1)	0.119(1)	0.120(1)
O22	Uiso	0.0075(1)	0.011(2)	0.011(2)	0.007(2)	0.007(2)	0.004(2)
	x	0.36109(6)	0.3623(7)	0.3618(8)	0.3606(9)	0.3610(9)	0.362(1)
	y	0.17821(7)	0.1769(8)	0.1762(8)	0.1758(8)	0.1749(9)	0.175(1)
O31	z	0.6483(1)	0.649(1)	0.650(1)	0.649(1)	0.650(1)	0.653(2)
	Uiso	0.0073(1)	0.010(2)	0.010(2)	0.011(2)	0.015(2)	0.016(2)
	x	0.61503(7)	0.6168(9)	0.6154(9)	0.6164(9)	0.6157(9)	0.617(1)
O32	y	0.51010(7)	0.5109(8)	0.5103(8)	0.5137(9)	0.5135(8)	0.517(1)
	z	0.3090(1)	0.310(1)	0.312(1)	0.312(1)	0.314(1)	0.315(1)
	Uiso	0.0086(1)	0.013(2)	0.013(2)	0.012(2)	0.012(2)	0.012(2)
O33	x	0.60598(7)	0.6050(8)	0.6051(9)	0.6054(9)	0.6061(9)	0.607(1)
	y	0.99774(7)	0.9984(8)	0.9975(8)	0.9944(8)	0.9941(8)	0.9926(9)
	z	0.8048(1)	0.804(1)	0.806(1)	0.809(1)	0.811(1)	0.813(1)
O34	Uiso	0.0097(1)	0.011(2)	0.011(2)	0.009(2)	0.010(2)	0.012(2)
	x	0.60675(6)	0.6069(8)	0.6079(8)	0.6072(8)	0.6071(9)	0.607(1)
	y	0.26646(7)	0.2662(8)	0.2683(8)	0.2693(8)	0.2712(8)	0.2719(9)
O35	z	0.0041(1)	0.004(1)	0.002(1)	0.000(1)	_0.002(1)	_0.003(1)
	Uiso	0.0075(1)	0.009(2)	0.010(2)	0.008(2)	0.010(2)	0.010(2)
	x	0.59781(6)	0.5970(8)	0.5995(8)	0.6004(9)	0.6010(9)	0.600(1)
O36	y	0.24041(7)	0.2387(8)	0.2379(8)	0.2356(8)	0.2345(8)	0.235(1)
	z	0.4972(1)	0.498(1)	0.495(1)	0.494(1)	0.492(1)	0.491(1)
	Uiso	0.0081(1)	0.011(2)	0.011(2)	0.009(2)	0.012(2)	0.013(2)

Table 6. Selected bond lengths (Å) and angles (°) in *P2/n* structure for the sample studied in this work.

P(GPa)	<i>in air</i>	0.00	1.78	4.14	5.89	7.34
T1-O11	1.6178(6)	1.620(8)	1.609(8)	1.603(9)	1.612(9)	1.614(10)
T1-O21	1.5962(6)	1.606(8)	1.585(8)	1.612(8)	1.598(7)	1.618(9)
T1-O31	1.6510(6)	1.657(8)	1.654(8)	1.640(9)	1.630(9)	1.624(10)
T1-O32	1.6608(6)	1.675(6)	1.673(6)	1.666(7)	1.665(7)	1.652(8)
<T1 - O>	1.631(30)	1.640(32)	1.630(40)	1.630(28)	1.626(29)	1.627(17)
Volume (Å ³)	2.210(2)	2.24(2)	2.20(2)	2.20(2)	2.19(2)	2.19(3)
TQE	1.0059	1.0077	1.0077	1.0064	1.0065	1.0066
TAV (°)	25.6262	34.1313	33.8249	28.2997	28.1005	27.9951
TILT (°)	3.50(2)	3.9(2)	3.2(2)	3.2(2)	3.0(2)	2.3(3)
T2-O12	1.6185(6)	1.603(8)	1.610(8)	1.612(9)	1.603(10)	1.593(11)
T2-O22	1.5873(7)	1.585(8)	1.580(8)	1.588(8)	1.584(7)	1.594(9)
T2-O31	1.6670(6)	1.663(6)	1.660(6)	1.658(7)	1.663(7)	1.652(8)
T2-O32	1.6471(6)	1.637(7)	1.644(8)	1.641(8)	1.635(8)	1.632(10)
<T2 - O>	1.630(35)	1.622(35)	1.624(36)	1.625(31)	1.621(35)	1.618(29)
Volume (Å ³)	2.207(2)	2.18(2)	2.18(2)	2.19(2)	2.17(2)	2.16(3)
TQE	1.0051	1.0044	1.0041	1.0043	1.0046	1.0047
TAV (°)	21.556	18.5843	17.0801	18.0703	19.3477	19.9658
TILT (°)	1.92(2)	2.0(2)	1.6(2)	1.4(2)	1.3(2)	1.4(3)
M1-O11	2.1281(7)	2.144(8)	2.109(8)	2.094(9)	2.084(8)	2.073(9)
M1-O12	2.0587(6)	2.065(5)	2.061(5)	2.044(6)	2.045(7)	2.055(8)
M1-O22	2.0267(7)	2.036(9)	2.026(9)	1.998(9)	1.991(9)	1.968(10)
<M1 - O>	2.071(46)	2.072(35)	2.065(37)	2.045(43)	2.040(42)	2.032(50)
Volume (Å ³)	11.603(7)	11.62(7)	11.51(7)	11.19(7)	11.10(8)	10.96(8)
TQE	1.0144	1.0139	1.0135	1.0134	1.0137	1.0143
TAV (°)	46.7793	46.1522	44.5324	43.4855	44.4995	45.5613
M11-O11	1.9299(6)	1.924(5)	1.920(5)	1.927(6)	1.906(6)	1.903(7)
M11-O12	1.9859(6)	2.004(8)	1.986(8)	1.967(8)	1.960(9)	1.944(10)
M11-O21	1.8840(6)	1.866(9)	1.878(9)	1.844(9)	1.848(9)	1.825(10)
<M11 - O>	1.933(46)	1.931(62)	1.928(49)	1.913(56)	1.905(50)	1.891(54)
Volume (Å ³)	9.546(6)	9.51(6)	9.48(6)	9.24(7)	9.13(7)	8.93(7)
TQE	1.0066	1.0073	1.0065	1.0072	1.0067	1.0066
TAV (°)	21.3266	22.1401	20.631	22.0344	21.2417	20.2871
M2-O11	2.3564(7)	2.381(8)	2.365(8)	2.334(9)	2.323(8)	2.316(9)
M2-O21	2.3640(6)	2.358(6)	2.347(6)	2.343(6)	2.331(6)	2.326(7)
M2-O31	2.6919(7)	2.695(8)	2.649(8)	2.617(9)	2.586(9)	2.57(10)
M2-O32	2.4603(7)	2.475(8)	2.458(8)	2.454(8)	2.448(8)	2.441(9)
<M2 - O>	2.47(14)	2.48(14)	2.45(13)	2.45(12)	2.42(11)	2.41(11)
Volume (Å ³)	24.63(1)	24.8(1)	24.2(1)	23.8(1)	23.4(1)	23.2(2)
M21-O12	2.3924(7)	2.390(8)	2.376(8)	2.366(8)	2.350(9)	2.34(10)
M21-O22	2.3866(7)	2.391(6)	2.380(6)	2.366(6)	2.351(6)	2.336(7)
M21-O31	2.4743(7)	2.471(7)	2.468(7)	2.457(7)	2.462(7)	2.468(9)
M21-O32	2.77506	2.773(8)	2.723(7)	2.672(8)	2.643(8)	2.64(10)
<M21 - O>	2.51(17)	2.51(17)	2.49(15)	2.46(13)	2.45(13)	2.45(13)
Volume (Å ³)	25.92(1)	26.0(1)	25.4(1)	24.7(1)	24.4(1)	24.2(2)
O31-O32-O31	169.46(04)	168.7(4)	167.9(4)	166.9(4)	165.9(4)	166.0(5)
O21-O22-O21	63.19(01)	63.19(13)	63.24(14)	63.95(14)	64.01(13)	64.52(15)

bond length and volume data from IVTON program

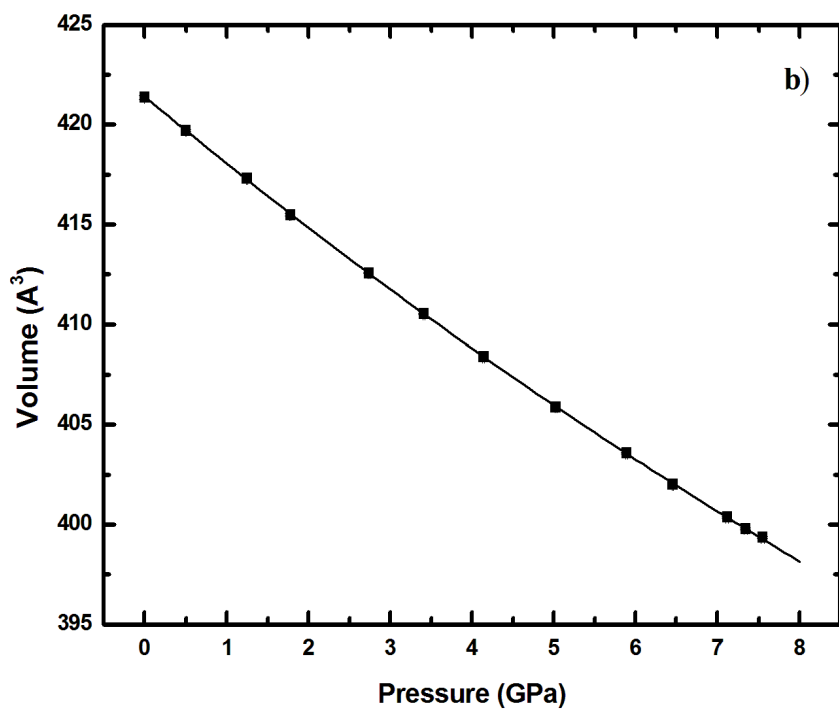
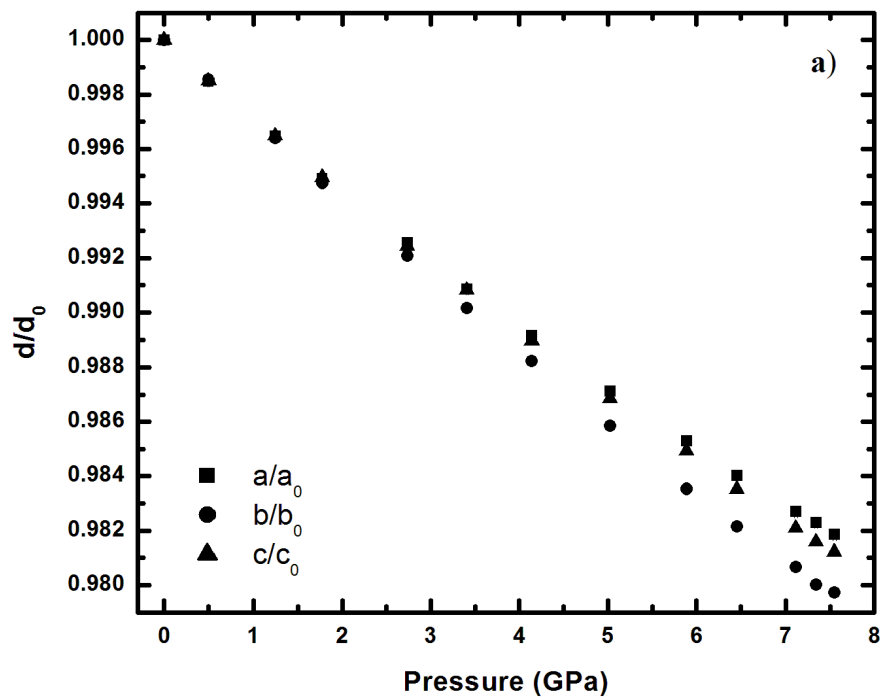


Figure 1. Evolution of the **a)** unit-cell parameters and **b)** unit-cell volume as a function of pressure for all the samples investigated. The symbols used are larger than the errors. The curve plotted in **b)** is the real Equation of State for the sample.

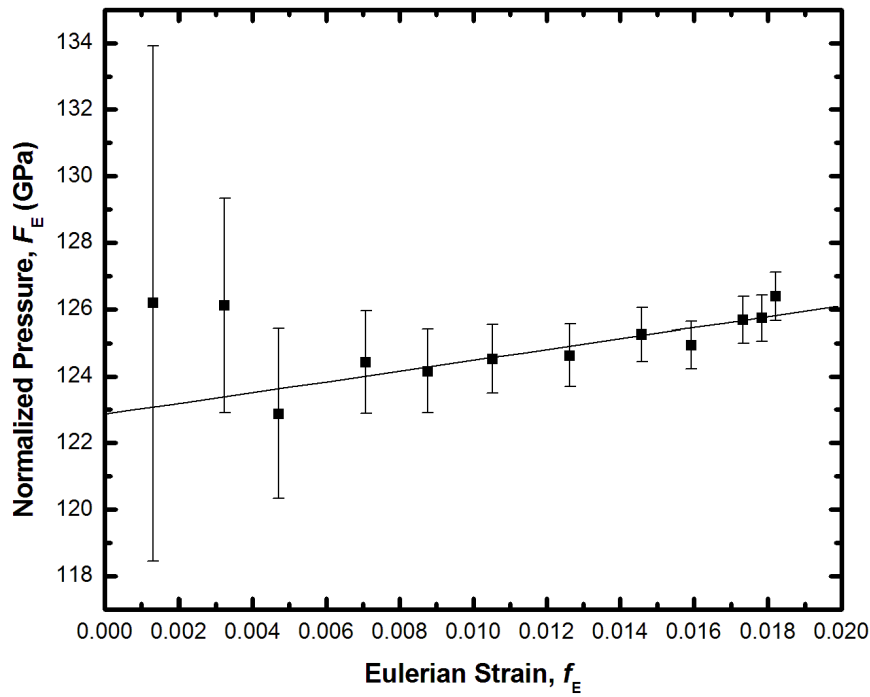


Figure 2. $F_E - f_E$ plot $\{F_E = P/3 \times f_E \times (1 + 2f_E)5/2$ and $f_E = [(V_0/V)^{2/3} - 1]/2$, see Angel 2000} for the sample studied in this work

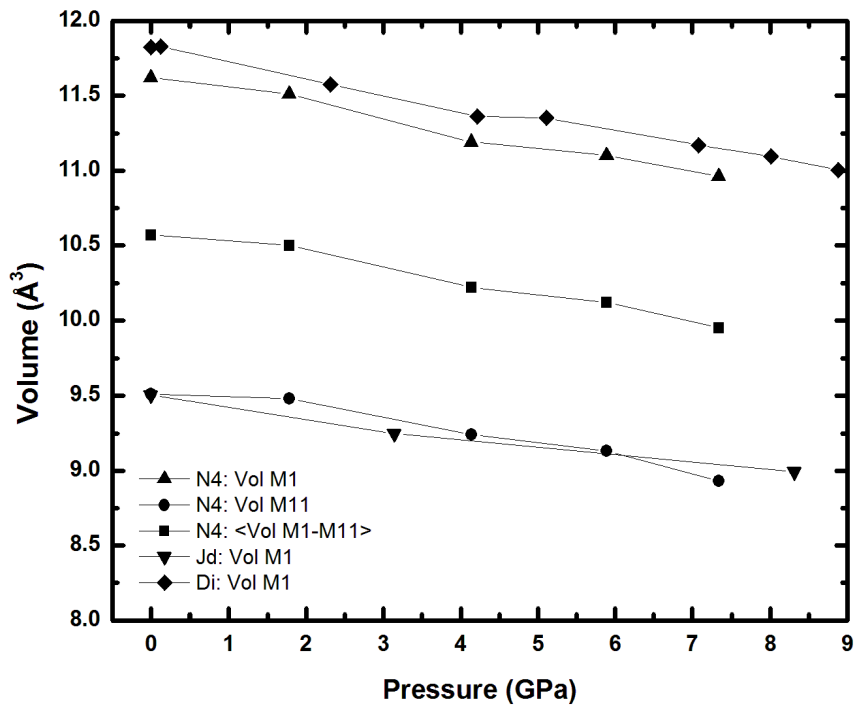


Figure 3. Evolution of M1 polyhedral volumes as a function of pressure.

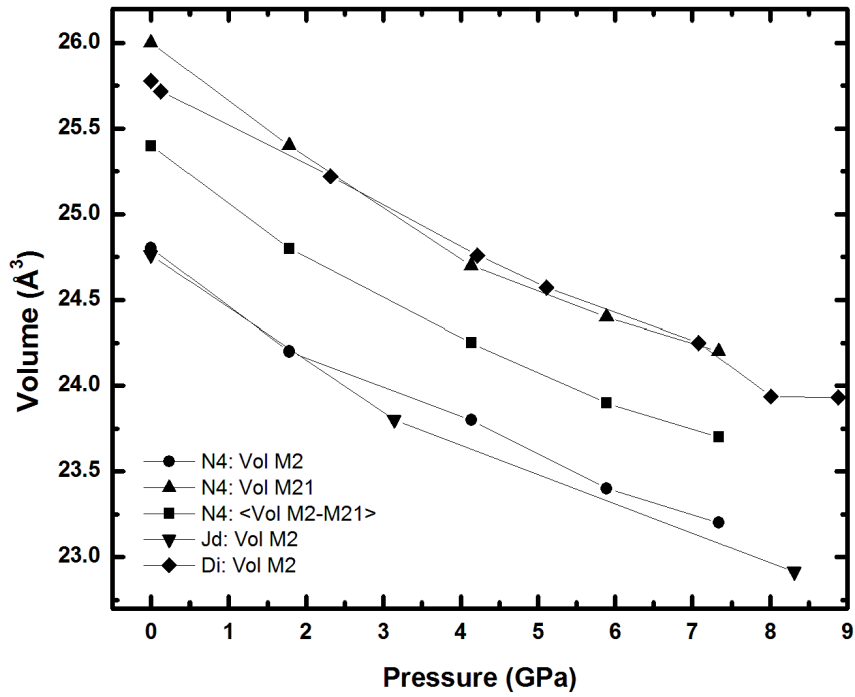


Figure 4. Evolution of M2 polyhedral volumes as a function of pressure.

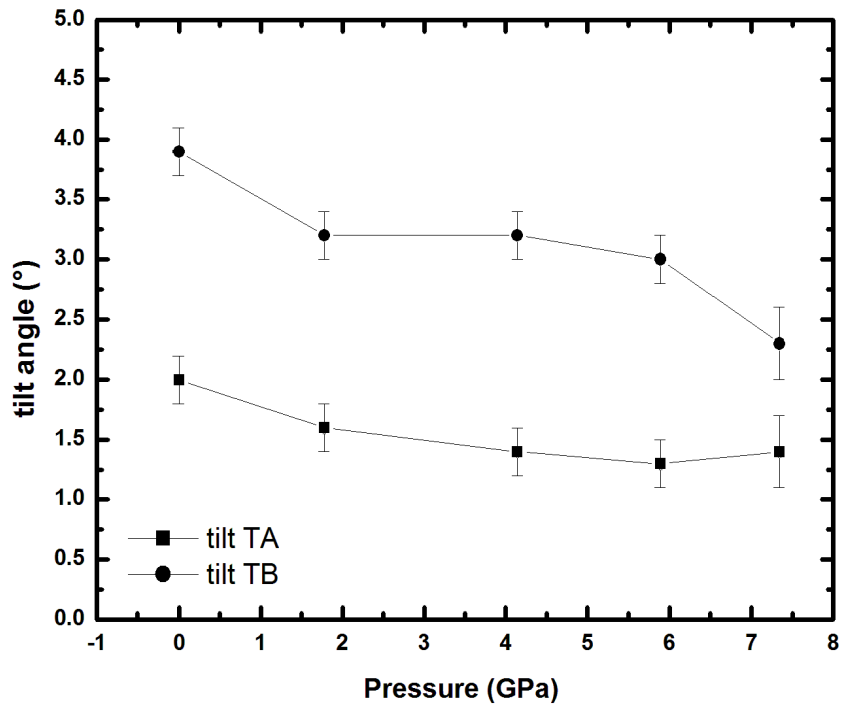


Figure 5. Evolution of the tilt angle as a function of pressure for the two tetrahedral chains TA and TB.

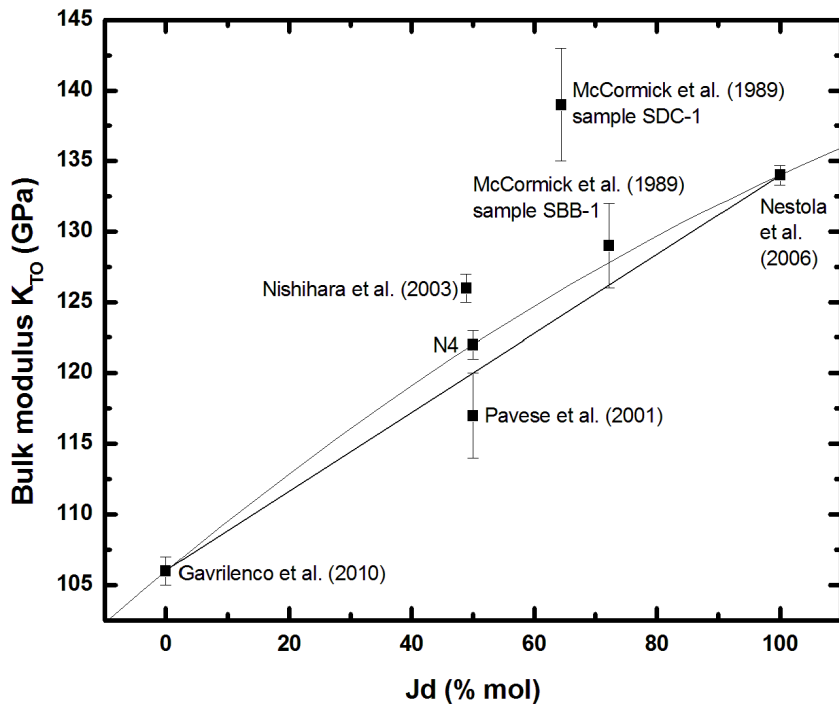


Figure 6. Evolution of K_{T0} as a function of composition along the diopside-jadeite join.

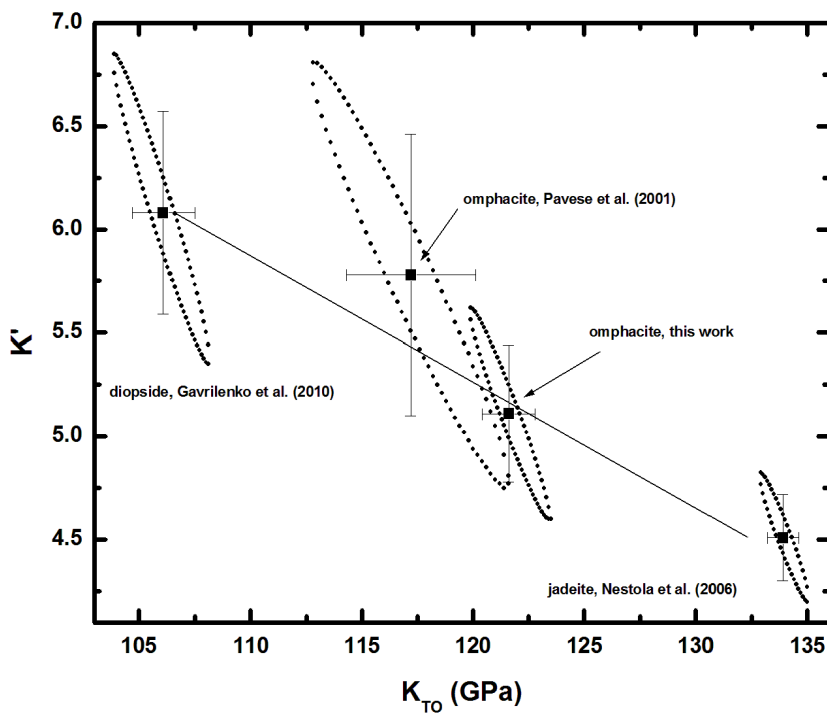


Figure 7. Confidence ellipse for the equation of state of the sample studied in this work and for other samples studied along the diopside-jadeite join.

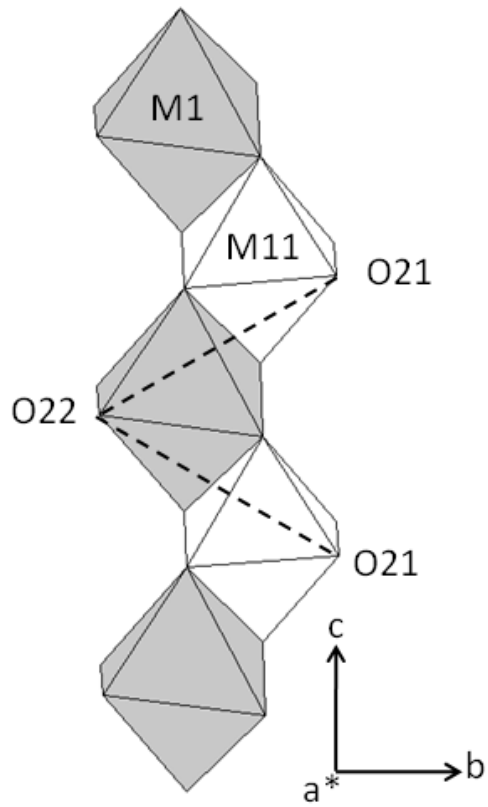


Figure 8. Part of the crystal-structure of the sample studied in this work viewed along the [100] direction. The octahedral M1 and M11 sites are showed. The black line corresponds to the O21-O22-O21 angle.