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High-pressure study of a natural cancrinite

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Abstract

The high-pressure behavior and the P -induced structure evolution of a natural cancrinite from Cameroun ($\text{Na}_{6.59}\text{Ca}_{0.93}[\text{Si}_6\text{Al}_6\text{O}_{24}](\text{CO}_3)_{1.04}\text{F}_{0.41}\cdot 2\text{H}_2\text{O}$, $a = 12.5976(6)$ Å, $c = 5.1168(2)$ Å, space group: $P6_3$) were investigated by *in situ* single-crystal X-ray diffraction under hydrostatic conditions up to 6.63(2) GPa with a diamond anvil cell. The P - V data were fitted with an isothermal Birch-Murnaghan-type equation of state (BM EoS) truncated to the 3rd-order. Weighted fit (by the uncertainty in P and V) gave the following elastic parameters: $V_0 = 702.0(7)$ Å³, $K_{V0} = 51(2)$ GPa and $K_V' = 2.9(4)$. Linearized BM EoS was used to fit the a - P and c - P data, giving the following refined parameters: $a_0 = 12.593(5)$ Å, $K_{a0} = 64(4)$ GPa, $K_a' = 4.5(9)$, for the a -axis, and $c_0 = 5.112(3)$ Å, $K_{c0} = 36(1)$ GPa, $K_c' = 1.9(3)$ for the c -axis (elastic anisotropy: $K_{a0}:K_{c0} = 1.78:1$). A subtle change of the elastic behavior appears to occur at $P > 4.62$ GPa, and so the elastic behavior was also described on the basis of BM EoS valid between 0.0001 – 4.62 and 5.00 – 6.63 GPa, respectively. The high-pressure structure refinements allowed the description of the main deformation mechanisms responsible for the anisotropic compression of cancrinite on (0001) and along [0001]. A comparative analysis of the structure evolution in response of the applied pressure and temperature of isotopic materials with cancrinite-like topology is carried out.

Keywords: cancrinite, zeolites, high pressure, compressibility, structure evolution.

Introduction

Cancrinite is a feldspathoid with ideal chemical formula $(\text{Na,Ca})_{7-8}[\text{Al}_6\text{Si}_6\text{O}_{12}](\text{CO}_3)_{1.2-1.7}\cdot 2\text{H}_2\text{O}$, which can form as a primary phase in low- SiO_2 alkaline rocks in the late hydrothermal stages or as the

55 alteration product of nepheline- or sodalite-group minerals. It is the parent member of a group
56 including about 20 minerals (Bonaccorsi and Merlino 2005; Cámara et al. 2005; Rastvetaeva et al.
57 2007; Cámara et al. 2010; Bonaccorsi et al. 2012), among which the most common are davyne and
58 vishnevite.

59 Cancrinite has an open-framework structure (framework density = $16.9 \text{ T}/1000 \text{ \AA}^3$, Baerlocher
60 et al. 2007), with CAN topology. Its framework is built up by 12-, 6- and 4-membered rings of
61 tetrahedra in a way that planes of 6-membered rings perpendicular to [0001] (hereafter 6mRs \perp [0001])
62 are stacked according to an $\cdots\text{ABAB}\cdots$ close-packing sequence (Fig. 1). The resulting framework
63 consists of columns of base-sharing cages (Fig. 1), the so-called cancrinite, or undecahedral or ϵ cages
64 (Baerlocher et al. 2007), and iso-oriented 12mRs-channels parallel to [0001] (Figs. 1, 2). Cages and
65 channels are connected by distorted 6mRs windows parallel to [0001] (hereafter 6mR//[0001]) (Fig. 2).
66 Moreover, 4mRs form *double zigzag chains* (Baerlocher et al. 2007) running parallel to [0001] (Fig. 1).
67 The topological symmetry of the CAN framework type is $P6_3/mmc$, with idealized lattice constants $a =$
68 12.494 \AA and $c = 5.254 \text{ \AA}$ (Baerlocher et al. 2007).

69 The cancrinite structure was first described by Pauling (1930) and then refined by Jarchow
70 (1965) in the space group $P6_3$, due to the full Si/Al-ordering in the tetrahedral framework. The extra-
71 framework population consists of $\cdots\text{Na}-\text{H}_2\text{O}-\text{Na}-\text{H}_2\text{O}\cdots$ chains lying in the cancrinite cages and by
72 CO_3^{2-} groups lying in two mutually exclusive and partially occupied positions in the center of the
73 12mRs-channels, occupied also by mixed Na/Ca sites near the channel wall (Figs. 3 and 4). In
74 cancrinite the $\cdots\text{Na}-\text{H}_2\text{O}-\text{Na}\cdots$ chains show one shorter and one longer Na-H₂O bond distances. In
75 contrast, in the isotypic davyne or microsommite (Bonaccorsi and Merlino 2005), $\cdots\text{Ca}-\text{Cl}\cdots$ chains
76 show constant bond lengths. In the 12mRs-channel, different anions (*e.g.* SO_4^{2-} , NO_3^- , Cl^- , OH^-) or H₂O
77 molecules can replace CO_3^{2-} in natural or synthetic cancrinites (*e.g.* Grundy and Hassan 1982; Hassan
78 and Grundy 1984; Bresciani-Pahor et al. 1982; Hassan and Grundy 1991; Buhl et al. 2000; Fechtelkord
79 et al. 2001; Ballirano and Maras 2005).

80 Over the last forty years, cancrinite-like materials have been extensively studied for their
81 structure-related properties. Many studies have been devoted to the superstructures reflections often
82 found in cancrinites, governed by the ordering of the carbonate groups and their vacancies along [0001]
83 (*e.g.* Grundy and Hassan 1982; Brown and Cesbron 1973; Foit et al. 1973; Hassan and Buseck 1992),
84 but also for the occurrence and use of cancrinite in many technological processes: *e.g.* as final product

85 of Na-aluminosilicates precipitation from liquor during the Bayer process for the refining of bauxite
86 (Gerson and Zheng 1997; Barnes et al. 1999) or as a precipitation product in nuclear waste tanks at the
87 Hanford site (WA, USA), and as product of the reaction between simulated leaked waste fluids and
88 quartz- or kaolinite-bearing sediments at the same site (Buck and McNamara 2004; Bickmore et al.
89 2001; Zhao et al. 2004). Moreover, Zhao et al. (2004) reported a sorption capacity for Cs⁺ ions in waste
90 fluids, whereas Poborchii (1994) and Poborchii et al. (2002) studied the optical properties of Se₂²⁻ and
91 Se₂⁻ in the cancrinite channels.

92 Only a few studies have been devoted to the behavior of cancrinite under non-ambient
93 conditions. Hassan et al. (2006) performed an *in-situ* high-temperature X-ray powder diffraction study
94 up to 1255 K, and reported: 1) a phase transition with loss of the superstructure reflections at ~777 K,
95 2) a continuous dehydration process toward a full dehydration at 898 K coupled with 3) a minimal loss
96 of CO₂. The results of an *in-situ* high-temperature single-crystal X-ray diffraction study up to 673 K
97 were reported by Isupova et al. (2010), whereas the description of the elastic behavior and structure
98 evolution at low-temperature (LT) conditions (down to 100 K) was recently provided by Gatta et al.
99 (2011) by *in-situ* LT single-crystal X-ray diffraction. Gatta and Lee (2008) described the elastic
100 behavior and the pressure-induced structure evolution of Na₆Cs₂Ga₆Ge₆O₂₄·Ge(OH)₆, a synthetic
101 compound isotypic with cancrinite, by means of *in-situ* high pressure (HP) synchrotron powder
102 diffraction up to 5.01 GPa. However, to the best of our knowledge, no study has to date been devoted
103 to the HP behavior of a natural cancrinite. In this light, the aim of this study is to describe the elastic
104 behavior and the *P*-induced structure evolution of a natural cancrinite, with no evidence of
105 superstructure reflections at ambient conditions, by *in-situ* single-crystal X-ray diffraction under
106 hydrostatic conditions. The formulation of the isothermal equation of state, along with the description
107 of the main deformation mechanisms of the tetrahedral framework and the behavior of the extra-
108 framework population will be provided. Furthermore, a comparative analysis of the structure evolution
109 in response of the applied pressure of the natural cancrinite here investigated and of
110 Na₆Cs₂Ga₆Ge₆O₂₄·Ge(OH)₆ (Gatta and Lee 2008) will be carried out.

111

112 **Materials and methods**

113 The single-crystal X-ray diffraction experiments were performed on a platy crystal of natural cancrinite
114 free of defects under the polarized microscope, collected from the same gem-quality sample from

115 Cameroun used by Della Ventura et al. (2009), for a single-crystal neutron diffraction experiment and
116 polarized infra-red spectroscopy, and by Gatta et al. (2011), for a *LT* single-crystal X-ray diffraction
117 study. Cancrinite crystals from this sample do not show any evidence of superstructure reflections. The
118 chemical composition, obtained by electron microprobe analysis in wavelength dispersive mode, is
119 $\text{Na}_{6.59}\text{Ca}_{0.93}[\text{Si}_6\text{Al}_6\text{O}_{24}](\text{CO}_3)_{1.04}\text{F}_{0.41}\cdot 2\text{H}_2\text{O}$ ($Z = 1$) (Della Ventura et al. 2009).

120 An intensity data collection with the crystal in air was first performed using an Xcalibur -
121 Oxford Diffraction diffractometer equipped with a CCD detector, operating at 50 kV and 40 mA with a
122 monochromatised $\text{MoK}\alpha$ radiation source and a detector-sample distance fixed at 80 mm. A
123 combination of ω and φ scans was chosen to maximize data coverage and redundancy. The step scan
124 was $1^\circ/\text{frame}$ along with an exposure time of 60 s/frame (Table 1). A total number of 19,933
125 reflections, out of which 1933 unique for symmetry, were collected up to $2\theta_{\text{max}}=70^\circ$, showing a
126 metrically hexagonal lattice with systematic extinctions consistent with the space group $P6_3$ (Table 1).
127 The refined unit-cell parameters were: $a = 12.5976(6)$ Å, $c = 5.1168(2)$ Å and $V = 703.2(1)$ Å³ (Table
128 1). Intensities were then integrated, corrected for Lorentz-polarization (Lp) and for absorption effects
129 (analytical absorption corrections by Gaussian integration based upon the physical description of the
130 crystal) using the CrysAlis software package (Oxford Diffraction 2010). Further details pertaining to
131 the data collection strategy are in Table 1. A hydrogen-free structure refinement of cancrinite was then
132 performed with the Shelx-97 program (Sheldrick 1997), starting from the atomic coordinates of Della
133 Ventura et al. (2009) in the space group $P6_3$. Neutral atomic scattering factors for Si, Al, Na, Ca, C and
134 O from the *International Tables of Crystallography* (Wilson and Prince 1999) were used. A mixed
135 scattering curve of Na and Ca was used to model the *Na2* site, and the site occupancy factors of *C1* and
136 *C2* were constrained to be equal to that of *Oc1* and *Oc2*, respectively. The H_2O oxygen site (*Ow*), lying
137 off the 3-fold axis in three symmetry-related and mutually exclusive positions, was modeled with a site
138 occupancy factor (s.o.f.) of 1/3. The *C-Oc* bond lengths were restrained to 1.300 ± 0.005 Å, on the
139 basis of the neutron refinement reported by Della Ventura et al. (2009). In the last cycles of the
140 refinement, the displacement parameters of all the atomic sites were refined anisotropically; only *C*, *Oc*
141 and *Ow* sites were refined isotropically, due to a significant correlation among the refined parameters
142 likely ascribable to the positional disorder of the carbonate groups and H_2O molecules (Grundy and
143 Hassan 1982; Della Ventura et al. 2009). The refinement converged to an agreement factor R_1 of 5.6%
144 for 1092 reflections with $F_o > 4\sigma(F_o)$. At the end of the refinement, no significant correlation was
145 observed in the variance-covariance matrix and the residual peaks in the difference-Fourier function of

146 the electron density were between $+0.77/-0.55 e^-/\text{\AA}^3$. Further details pertaining to the structure
147 refinement are in Table 1.

148 An ETH-type diamond anvil cell (DAC, Miletich et al. 2000), was used for the high-pressure
149 experiments. A T301 steel foil, 0.250 mm thick, was used as a gasket, which was pre-indented to a
150 thickness of about 0.110 mm before drilling a micro-hole (~ 0.300 mm in diameter) by spark-erosion.
151 The same crystal of cancrinite previously investigated at ambient conditions was placed into the gasket
152 hole along with some ruby chips and a single-crystal of quartz used as *P*-standards (Mao et al. 1986;
153 Angel et al. 1997). A 4:1 mixture of methanol:ethanol was used as hydrostatic pressure-transmitting
154 medium (Angel et al. 2007). Lattice parameters were measured between 0.0001 and 6.63(2) GPa (Table
155 2), using 42 Bragg reflections with a KUMA KM4 point-detector diffractometer, operating at 50 kV
156 and 40 mA with a graphite monochromatized $\text{MoK}\alpha$ radiation source. Ten intensity data collections
157 between 0.0001 GPa (with crystal in the DAC without any pressure medium) and 6.63(3) GPa (Table
158 1) were performed with an Xcalibur - Oxford Diffraction diffractometer equipped with a CCD
159 (graphite-monochromatized $\text{MoK}\alpha$ radiation). A combination of ω and ϕ scans was used, with step of
160 $0.5^\circ/\text{frame}$ and an exposure time of 60 s/frame (Table 1). No violations of the reflection conditions
161 expected for the space group $P6_3$ were observed within the *P*-range investigated. Integrated intensity
162 data were corrected for L_p and absorption effects due to the crystal and the DAC using the ABSORB
163 computer program (Angel 2004). The *HP* structure refinements based on the intensity data collected
164 with the crystal in the DAC were performed with the Shelx-97 program (Sheldrick 1997). The number
165 of the refined parameters was reduced to 45: all the occupancy factors were constrained to the values
166 refined with the crystal in air and the atomic displacement parameters (a.d.p.s.) were all refined
167 isotropically. In addition, the *C1-C2* and *Oc1-Oc2* a.d.p.s. were, respectively, constrained to be equal.
168 As for the structure model at room conditions, the *C-Oc* bond lengths were restrained to 1.300 ± 0.005
169 \AA . The refinements converged for all the *HP* datasets with R_1 always lower than 8.9%, with no
170 significant correlation between the refined parameters and residual peaks in the difference-Fourier
171 maps lower than $\pm 0.96 e^-/\text{\AA}^3$.

172 Atomic fractional coordinates, site occupancy factors and atomic displacement parameters
173 pertaining to the structure refinements at room-*P* and *HP* are given in Table 3; bond distances and
174 angles are listed in Table 4. Refined anisotropic displacement parameters are available in the CIF
175 (deposited).

176 **Results**

177 *Elastic behavior*

178 The evolution of the unit-cell parameters of cancrinite up to 6.63(2) GPa is shown in Fig. 5. The
179 unit-cell parameters measured in decompression showed that the pressure-induced structural evolution
180 of up to ~6.6 GPa is completely reversible.

181 The P - V between 0.0001 and 6.63 GPa data were first fitted with an isothermal Birch-
182 Murnaghan-type equation of state truncated to the 3rd-order (BM-III EoS, Birch 1947), using the EoS-
183 Fit v5.2 program (Angel 2000). Weighted fit (by the uncertainty in P and V) gives the following elastic
184 parameters: $V_0 = 702.0(7) \text{ \AA}^3$, $K_{V0} = 51(2) \text{ GPa}$ and $K_V' = 2.9(4)$. The evolution of the Eulerian strain
185 vs. the normalized pressure within the entire P -range investigated (fe - Fe plot, $f_e = [(V_0/V)^{2/3} - 1]/2$ and
186 $F_e = P/[3f_e(1+2f_e)^{5/2}]$, Angel 2000) is shown in Fig. 5, suggesting that the isothermal volume
187 compression in cancrinite can be described with a 3rd-order BM EoS, giving a bulk modulus at room-
188 P of $Fe(0) = 50(1)$ and its P -derivative of 3.2(3). A “linearized” BM-III equation of state was used to
189 fit the a - P and c - P data (Angel 2000), giving the following refined parameters: $a_0 = 12.593(5) \text{ \AA}$, $K_{a0} =$
190 $64(4) \text{ GPa}$, $K_a' = 4.5(9)$, $c_0 = 5.112(3) \text{ \AA}$, $K_{c0} = 36(1) \text{ GPa}$, $K_c' = 1.9(3)$. The elastic anisotropy at room
191 pressure is then: $K_{a0}:K_{c0} = 1.78:1$.

192 When one EoS is used over the entire P -range investigated, a modest misfit is observed for the
193 a -axis and the unit-cell volume, respectively, suggesting a potential change of the compressional
194 behaviors between 4.62 – 5.00 GPa. On this basis, two different BM EoS fits were used to model the
195 elastic behavior along the a -axis and for the unit-cell volume between 0.0001 – 4.62 and 5.00 – 6.63
196 GPa, respectively. The refined parameters are: $a_0 = 12.603(7) \text{ \AA}$, $K_{a0} = 52(6) \text{ GPa}$ and $K_a' = 11(4)$, and
197 $V_0 = 703.3(7) \text{ \AA}^3$, $K_{V0} = 45(2) \text{ GPa}$ and $K_V' = 6(1)$ between 0.0001 and 4.62 GPa; $a_0 = 12.63(2) \text{ \AA}$, $K_{a0} =$
198 $58(4) \text{ GPa}$ and $K_a' = 4$ (fixed), and $V_0 = 715(4) \text{ \AA}^3$, $K_{V0} = 40(2) \text{ GPa}$ and $K_V' = 4$ (fixed) between 5.00
199 and 6.63 GPa. A further fe - Fe plot is shown in Fig. 5 with the refined V_0 obtained by the BM-III EoS fit
200 (0.0001 – 4.62 GPa) and by the BM-II EoS fit (5.00 – 6.63 GPa), respectively.

201

202

203

204 *Structure refinements*

205 The structure refinement of cancrinite at room-*P* confirms the framework and extraframework
206 configuration previously described (*e.g.* Della Ventura et al. 2009), with the ϵ cages stuffed by $\cdots\text{Na}-$
207 $\text{H}_2\text{O}-\text{Na}-\text{H}_2\text{O}\cdots$ chains and the 12mRs-channels with cation sites close to the channel walls (*Na*2),
208 partially occupied by Na (85.4(6)%) and Ca (14.6(6)%), and CO_3^{2-} groups in the center of the channel
209 in two mutually exclusive positions (*i.e.* *C*1 and *O**c*1 s.o.f. = 42.1(7)%; *C*2 and *O**c*2 s.o.f = 45.9(6)%;
210 Table 3) (Figs. 3, 4). The chemical formula deduced on the basis of the structure refinement is:
211 $\text{Na}_{7.04}\text{Ca}_{0.88}[\text{Al}_6\text{Si}_6\text{O}_{24}](\text{CO}_3)_{1.76}\cdot 2\text{H}_2\text{O}$, and if we consider the amount of F obtained on the basis of the
212 EMPA-EDS (*i.e.* 0.41 atoms per formula unit, Della Ventura et al. 2009), we obtain (after a
213 recalculation of the C/F s.o.f.): $\text{Na}_{7.04}\text{Ca}_{0.88}[\text{Al}_6\text{Si}_6\text{O}_{24}](\text{CO}_3)_{1.15}\text{F}_{0.41}\cdot 2\text{H}_2\text{O}$. This chemical formula
214 shows a slightly higher amount of Na and a lower amount of Ca with respect to the formula reported by
215 Della Ventura et al. (2009). In fact, the sum of the electrons ascribable to the extraframework cations
216 (Na and Ca) from the structure refinement is 95.4 e^- , slightly higher than 91.1 e^- from the experimental
217 chemical analysis ($\Delta e^- \sim 4.5\%$).

218 The *HP* structure refinements showed that the general configuration of framework and
219 extraframework population was maintained within the *P*-range investigated; the main deformation
220 mechanisms of the tetrahedral framework and of the channel and cage content are described below.

221

222 *High-pressure framework behavior*

223 At high pressure, the structure refinements show that the 6-membered rings perpendicular to [0001]
224 ($6\text{mRs}\perp[0001]$) experience a ditrigonalization process, with the opening of the ω_1 angle (*O*1-*O*2-*O*1)
225 and the closure of ω_2 angle (*O*2-*O*1-*O*2) (Fig. 2; Table 4). A linear increasing of the ditrigonal rotation
226 angle α (Fig. 6; Table 4) [$\alpha = 1/6 \cdot \sum_i |120^\circ - \theta_i|/2$, where θ_i is the angle between the basal edges of
227 neighboring tetrahedra articulated in the six membered ring; Brigatti and Guggenheim 2002] is
228 observed. This unit is also compressed in response to the applied pressure as shown by the shortening
229 of the *O*1-*O*2 distance and the reduction of the ditrigonal area subtended by the oxygen atoms (Fig. 2;
230 Table 4). Moreover, we observed a decrease of the (A,B)-plane corrugation [defined as $\Delta z = [z(\text{O})_{\text{max}} -$
231 $z(\text{O})_{\text{min}}] \cdot c$, where $z(\text{O})_{\text{max}}$ is the maximum z coordinate of the oxygen atoms belonging to the plane,
232 $z(\text{O})_{\text{min}}$ the minimum one and c is the unit-cell edge length; Brigatti and Guggenheim 2002)] (Table 4).

233 The 4mR joint-unit shows a compression along the $O3-O4$ diameter (Figs. 2 and 6; Table 4),
234 whereas an expansion is shown along $O2-O2$, giving as overall effect a reduction of the area subtended
235 by the four oxygen corners (Fig. 2; Table 4). In the 12mR-channel, an almost constant value of the six
236 symmetrically related $O3-O4$ distances is observed with pressure, along with a shortening of the six
237 symmetrical $O1-O1$ distances (*i.e.* $\sim 5.7\%$; Figs. 2 and 6; Table 4). The 6mR-windows connecting
238 channels and cages (6mR//[0001]) show a strong ditrigonalization with a shortening of the $O1-O1$
239 diameter (*i.e.* the c edge of unit-cell), and a less pronounced contraction of the $O3-O3$ and $O4-O4$
240 diameters (Fig. 2; Table 4). The cancrinite cage shows a pronounced flattening along [0001], governed
241 by the closure of the κ angle ($O2-O2-O2$) (Figs. 2 and 6; Table 4), whereas the maximum width on the
242 (0001) plane, defined by the three symmetry-related diameters $O2-O2$ (dashed lines in Fig. 2), is
243 constant within the P -range investigated (Table 4).

244 The evolution of the channel volume (modeled as $V_{\text{ch}} = D \cdot c$; with $D = (O1-O1 + O3-O4)/2$,
245 where $O1-O1$ and $O3-O4$ are the independent diameters of the 12mR; Fig. 2, Table 4) and of the ε -cage
246 volume (modeled as $V_{\text{cg}} = (V_{\text{cell}} - V_{\text{ch}})/2$) with P was studied. Both the $V_{\text{ch}}-P$ and $V_{\text{cg}}-P$ data (Table 4)
247 were fitted with a truncated BM-III equation of state, fixing V_0 to the experimental value at P_0 . The
248 refined elastic parameters are: $K_{0\text{ch}} = 52(3)$ GPa, $K'_{\text{ch}} = 1.4(1.0)$ for the 12mR channel, and $K_{0\text{cg}} =$
249 $53(4)$ GPa, $K'_{\text{cg}} = 4(2)$ for the ε -cage.

250

251 *High-pressure extraframework behavior*

252 The $Na1$ site, which lies in the ε cage, coordinates the neighboring 6mR's oxygen and two H_2O
253 molecules (ditrigonal bipyramid coordination shell) (Fig. 3). The distortion of this polyhedron is
254 strictly governed by the framework deformation. With increasing pressure, we observe a contraction of
255 the $Na1-O2$ and an expansion of the $Na1-O1$ bond lengths (Table 4). The two $Na1-O_w$ distances of the
256 coordination polyhedron are symmetrically independent and both show a shortening with pressure
257 (Table 4).

258 The sum of the refined site occupancies of the mutually exclusive carbonate groups is lower
259 than 1 (Table 3), reflecting site vacancy. The absence of any superstructure reflections suggests that
260 these vacancies are randomly distributed along the 12mR channels. Three combinations of subsequent

261 CO₃ groups are possible: C1-C2 (3.85(7) Å at room-*P*), C1-C1 and C2-C2 (both spaced by $c/2$,
262 2.542(2) Å at room-*P*) (Fig. 4; Table 4).

263 The Na2 site is coordinated by 5 framework oxygen atoms on a side and up to 3 carbonate
264 oxygen atoms on the opposite side (Fig. 3). With increasing pressure, we observe a decrease of the
265 shorter Na2-O3', Na2-O4' and Na2-O1 bond lengths and an expansion of the longer Na2-O3'' and Na2-
266 O4'', whereas no significant change occurs for the Na2-O_c distances (Table 4).

267

268 Discussion

269 Elastic behavior

270 The refined isothermal bulk modulus at room-*P* (*i.e.* $K_{V0} = 45\text{-}52$ GPa) is similar to that of other
271 microporous materials which share with cancrinite the presence of “6-membered rings” of tetrahedra as
272 “secondary building units” (*sensu* Baerlocher et al. 2007) (Gatta 2008), among those: sodalite (*i.e.* K_{V0}
273 = 51(1) GPa; Hazen and Sharp 1988), levyne (*i.e.* $K_{V0} = 56(4)$ GPa for $P < 1$ GPa, 46(1) GPa for $P > 1$
274 GPa; Gatta et al. 2005), and chabazite (*i.e.* $K_{V0} = 35(5)$ GPa for $P \leq 1$ GPa, 62(1) GPa for $P \geq 1.4$ GPa;
275 Leardini et al. 2010). The stiffer open-framework silicates show bulk moduli of 60-70 GPa (*e.g.*
276 philippsite $K_{V0} = 67(2)$ GPa, Gatta and Lee 2007; gismondine $K_{V0} = 63.8(2)$, Ori et al. 2008), whereas
277 for the softest the range is 18-40 GPa (*e.g.* Na-ZSM-5 $K_{V0} = 18.2(6)$ GPa, Arletti et al. 2011; H-ZSM-5
278 $K_{V0} = 23.7(4)$ GPa, Quartieri et al. 2011; zeolite-A $K_{V0} = 22.1(3)$, Arletti et al. 2003; heulandite $K_{V0} =$
279 27.5(2), Gatta et al. 2003; mordenite $K_{V0} = 41(2)$ GPa, Gatta and Lee 2006).

280 A subtle change in the elastic behavior of cancrinite appears to occur at $P > 4.6$ GPa (Fig. 5).
281 However, the accuracy and precision of our data, along with the *P*-range investigated, do not allow to
282 have a unique picture of the elastic behavior. In addition, a potential change of the compressional
283 mechanisms at $P > 4.6$ GPa is not supported by the deformation mechanisms deduced on the basis of
284 the HP structure refinements, by any change of the symmetry or by any evidence of satellite reflections
285 (Fig. 6, Table 4).

286 The elastic behavior of the natural cancrinite here investigated differs significantly from that of
287 the isotypic Na₆Cs₂Ga₆Ge₆O₂₄·Ge(OH)₆. The compressional behavior of the synthetic analogue was
288 fitted with a Murnaghan-type equation of state (Murnaghan 1937) by Gatta and Lee (2008), giving: K_{V0}

289 = 36(2) GPa and $K_V' = 9(1)$ GPa. Possible reasons for the higher compressibility at room- P , along with
290 the higher stiffness rate of the synthetic compound, can be found in the compression of the (Ga,Ge)
291 tetrahedra, which is already significant in response to moderate pressure (*i.e.* $P < 5$ GPa) if compared to
292 the almost rigid behavior of the (Si,Al) tetrahedra of the natural sample (Table 4), and in the different
293 nature of the extraframework population.

294

295 *High-pressure framework behavior*

296 The main deformation mechanism in the cancrinite framework in response to the applied pressure is the
297 anti-cooperative rotation of adjacent tetrahedra belonging to the $6mR_s \perp [0001]$. This mechanism
298 requires that for a given tetrahedron belonging to the A plane which shows a clockwise rotation, the
299 four adjacent vertex-sharing tetrahedra (three on the same A plane and one on the next B plane) will
300 show an anti-clockwise rotation (Fig. 2). The $6mR_s \perp [0001]$ ditrigonalization is the main effect of the
301 anti-cooperative rotation mechanism, leading to the 12mR-channels contraction along the $O1-O1$
302 distances (Figs. 2 and 6). The ($O1-O1/O3-O4$) ratio decreases with P from 1.038(3) at 0.0001 GPa to
303 0.989(2) at 6.63 GPa (Table 4). The shortest free diameter of the channels (*i.e.* $O3-O4$) is nearly
304 constant up to ~ 5.3 - 5.4 GPa and then decreases at higher pressure. On the whole, *a*) the channel $O1-O1$
305 shortening coupled with *b*) the 4mR joint-units compression along the $O3-O4$ direction and *c*) the
306 $6mR_s \perp [0001]$ compression (described by the $O1-O2$ shortening, Table 4) are the mechanisms
307 responsible for the P -driven contraction on the (0001) plane (Figs. 2 and 6), whereas the compression
308 along the c axis is accommodated by *a*) the ϵ -cage flattening, *b*) the decrease of the (A,B)-planes
309 corrugation and *c*) the ditrigonal distortion of the $6mR_s // [0001]$ windows connecting channels and
310 cages (Figs. 2 and 6; Table 4).

311 The elastic parameters obtained from the compressional behavior of the 12mR-channel and of
312 the ϵ cage (Table 4) show that these units have similar bulk moduli at room- P , but cage becomes stiffer
313 with increasing pressure, likely for the presence of the $\cdots Na-H_2O \cdots$ chains as cage-population which
314 can hinder the compression of the cage.

315 The isotypic $Na_6Cs_2Ga_6Ge_6O_{24} \cdot Ge(OH)_6$ variant (Gatta and Lee 2008), despite the significant
316 differences in the nature of framework and extraframework population, shows the same P -induced
317 main deformation mechanisms found in natural cancrinite. On this basis, we believe that the main

318 deformation mechanisms here described might be intrinsically governed by the CAN framework
319 topology. As a matter of fact, a comparison with the structural evolution of a natural cancrinite at high-
320 temperature conditions, on the basis of the data reported by Hassan et al. (2006), shows the same
321 deformation mechanisms, but opposite in sign, here observed at high pressure.

322

323

324 *High-pressure extraframework behavior*

325 At high pressure, the *Na1* to framework-oxygen bond lengths variation appears to be the effect of the
326 $6mR_s \perp [0001]$ ditrigonalization, whereas the compression along $[0001]$ governs the bond lengths
327 shortening along the $\cdots Na-H_2O-Na-H_2O \cdots$ chains (Fig. 3; Table 4).

328 Different coordination shells, with maximum coordination number (C.N.) of 8, are possible for
329 the Na/Ca mixed *Na2* site, due to the different CO_3 ordering but with a fixed coordination with 5
330 framework oxygen (Fig. 3). At high pressure, the expansion of the longer *Na2-O3'* and *Na2-O4'* bond
331 lengths leads an increasingly weaker interaction with these atoms, suggesting an actual C.N. = 6 at
332 these conditions.

333 The contraction of the short *C1-C1* and *C2-C2* distances (equal to $c/2$) at high pressure suggests
334 an increasing instability for these stacking configurations in favor of the longer *C1-C2* one (~ 3.85 Å at
335 room-*P*), if we consider the C-C distance in aragonite (~ 2.87 Å) as the shortest reported in carbonates
336 (Bonaccorsi and Merlino 2005). However, previous structure refinements of natural cancrinites from
337 X-ray and neutron diffraction data (*e.g.* Ballirano and Maras 2005; Della Ventura et al. 2009, Gatta et
338 al. 2011) showed anisotropic displacement parameters of the CO_3 group significantly elongated along
339 $[0001]$, likely due to a positional disorder aimed to optimize the C-C distances at a local scale toward
340 an energetically less costly configuration.

341 The role of the extraframework population on the high-pressure structure evolution of natural
342 cancrinite appears to be only secondary, suggesting that the *P*-induced structure response is mainly
343 governed by the framework deformation mechanisms, which, in turn, are likely controlled by the CAN
344 topology.

345

346

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353

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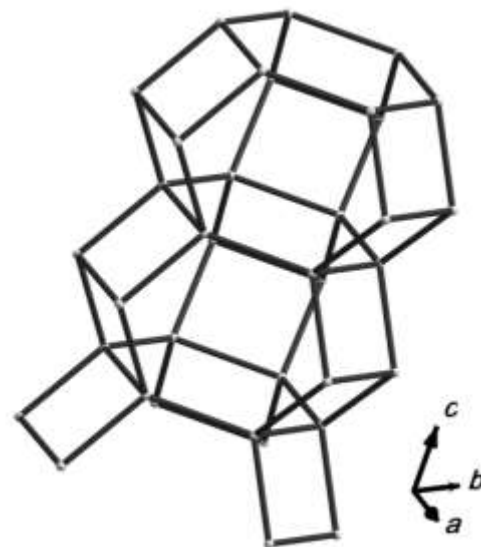
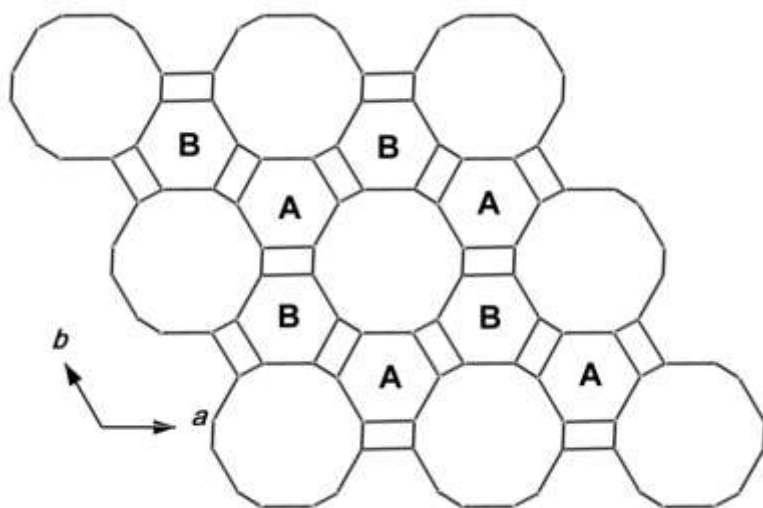
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487

488 Figure 1. (*Left side*) The building scheme of the CAN framework: planes of 6-membered rings of
489 tetrahedra perpendicular to $[0001]$ are stacked according to an ABAB close-packing sequence. (*Right*
490 *side*) A column, parallel to $[0001]$, of base-sharing ϵ cages. Three *double zigzag chains* run along the
491 column.



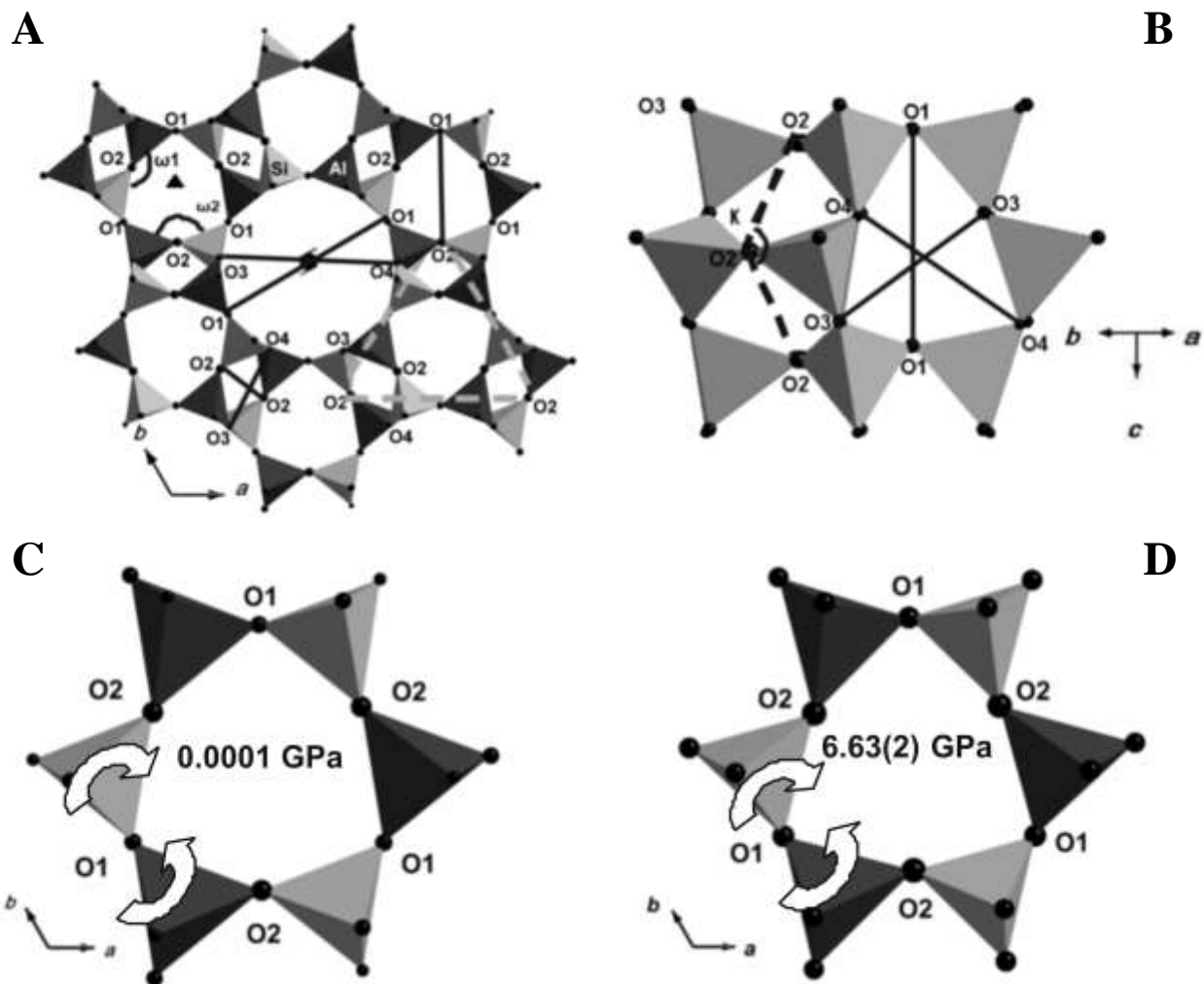
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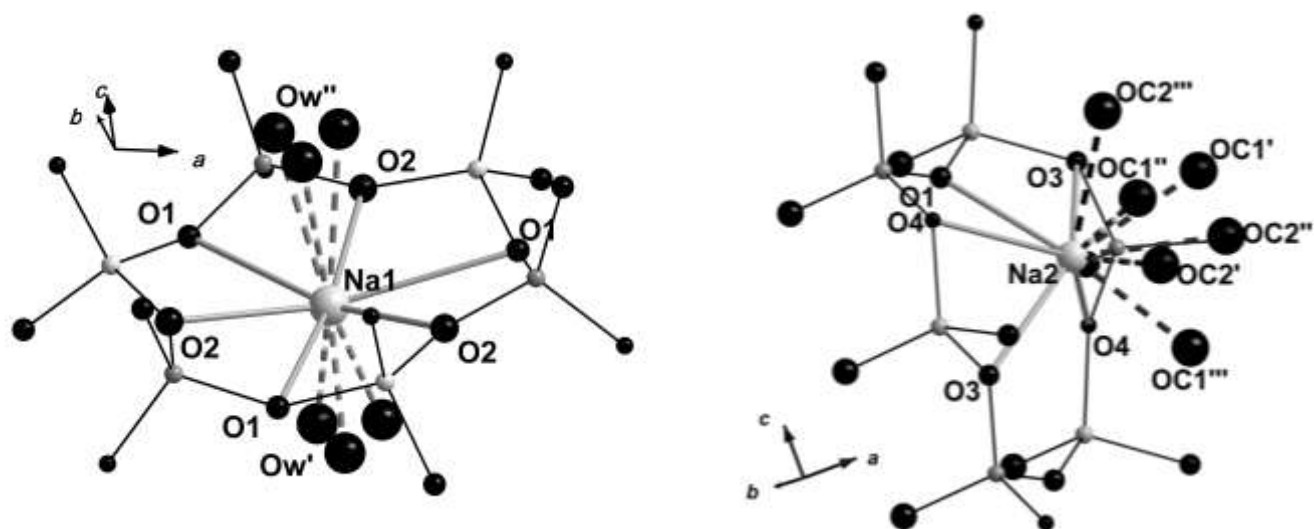
494 Figure 2. (A) The cancrinite framework viewed down [0001]. (B) The ϵ cage, with a view of the κ angle (O2-O2-O2) and of the $6mR//[0001]$ window's diameters. (C and D) The $6mR\perp[0001]$ at room- P
 495 (C) and at 6.63 GPa (D). P -induced anti-cooperative rotation of adjacent tetrahedra (ditrigonalization)
 496 (C) and at 6.63 GPa (D). P -induced anti-cooperative rotation of adjacent tetrahedra (ditrigonalization)
 497 is shown.

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500 Figure 3. (*Left side*) The coordination shell of the Na1 site. Dashed lines represent mutually exclusive
501 Na-Ow bond lengths. (*Right side*) The coordination shell of the Na2 site (*i.e.* 5 framework oxygen on a
502 side and up to three carbonate oxygen on the opposite side, maximum C.N. = 8).



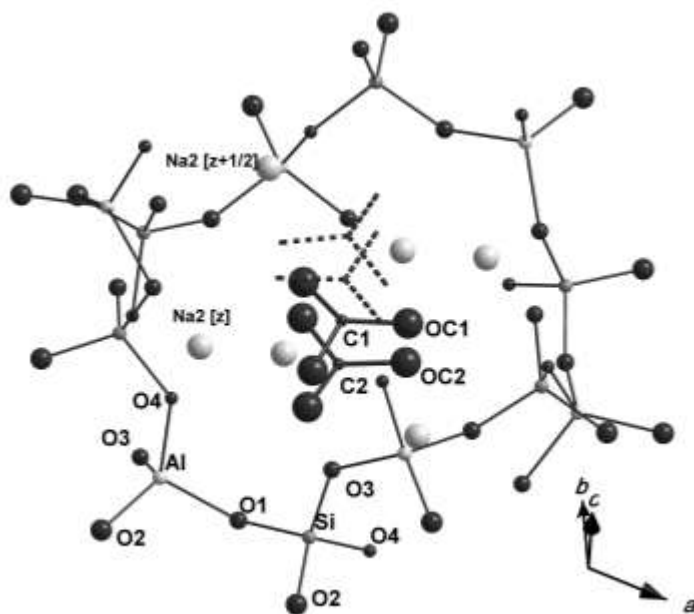
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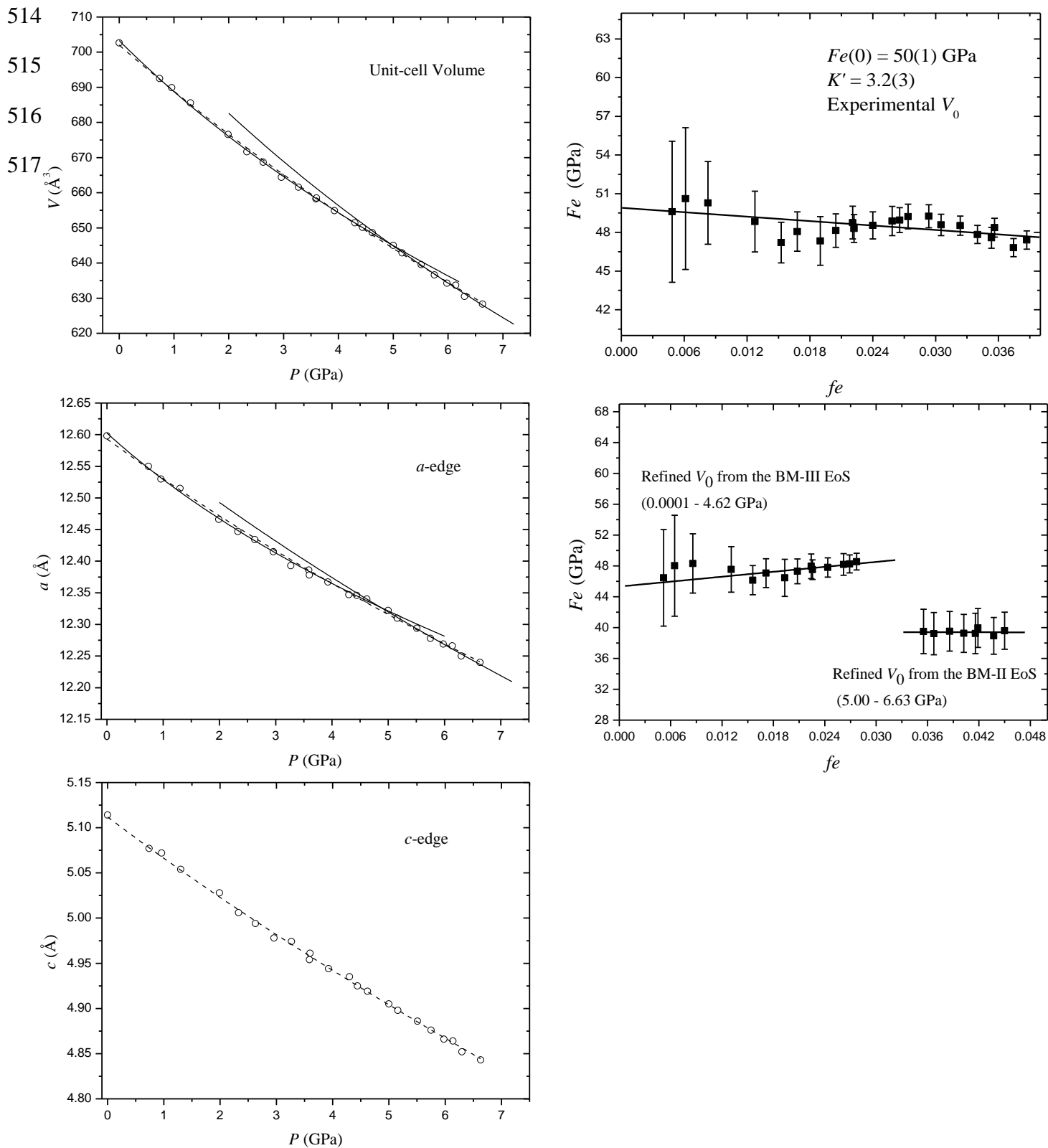
505 Figure 4. The extraframework population of the 12mR channel, with the Na2 site close to the wall and
506 the carbonate anions lying at the center. Different stacking sequences of the CO_3^{2-} groups and their
507 vacancies are possible.

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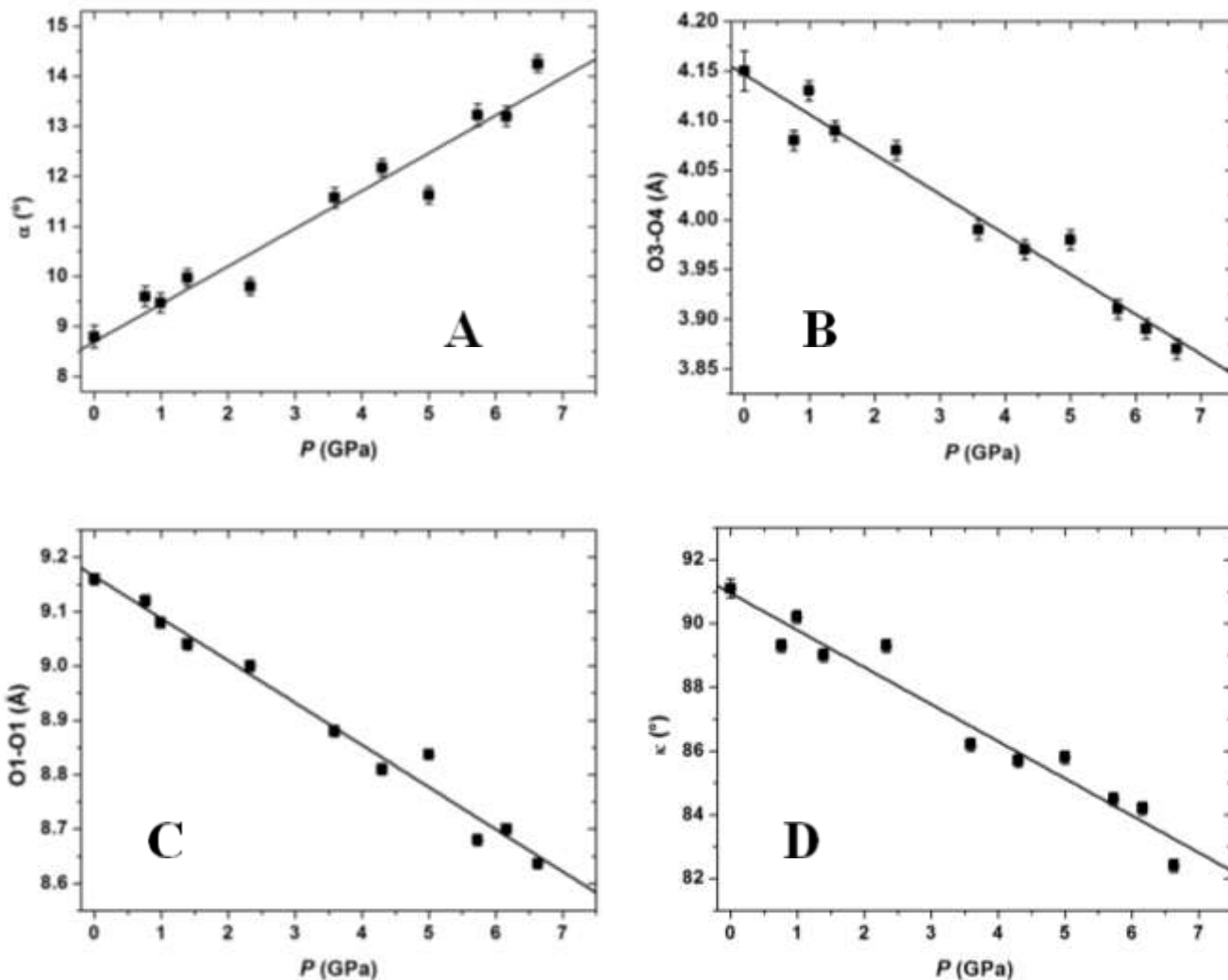
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510 Figure 5. Variation of the unit-cell parameters of cancrinite with pressure and Eulerian finite strain *vs* normalized stress plot
 511 (*fe-Fe* plot). For the unit-cell parameters *vs. P* plots, the dotted lines represent the axial and volume BM-EoS fits between
 512 0.0001 and 6.63 GPa, whereas the solid lines represents the BM-EoS fit between 0.0001- 4.62 GPa and 5.00-6.63 GPa,
 513 respectively (see text for further details). The *e.s.s.* are of the same size of the symbols.



518 Figure 6. Evolution with P of: (A) the ditrigonal rotation angle α of the $6mR \perp [0001]$ unit, (B) the O3-
519 O4 diameter of the $4mR$ unit, (C) the O1-O1 diameter of the $12mR$ unit, and (D) the κ angle (O2-O2-
520 O2) of the ϵ cage. The weighted linear fits through the data points are shown.



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528 Table 1. Details of the data collection strategy and structure refinement of cancrinite at different pressures.

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| <i>P</i> (GPa) | 0.0001 | 0.0001* | 0.76(2) | 0.99(2) | 1.39(2) | 2.33(2) | 3.59(2) | 4.30(3) | 5.00(2) | 5.73(3) | 6.16(2) | 6.63(3) |
|--|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| X-ray radiation | Mo-K α | Mo-K α | Mo-K α | Mo-K α | Mo-K α | Mo-K α | Mo-K α | Mo-K α | Mo-K α | Mo-K α | Mo-K α | Mo-K α |
| Scan width (°/frame) | 1 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| <i>a</i> (Å) | 12.5976(6) | 12.620(9) | 12.580(9) | 12.530(9) | 12.514(9) | 12.447(5) | 12.386(3) | 12.347(6) | 12.322(4) | 12.278(2) | 12.266(3) | 12.240(4) |
| <i>c</i> (Å) | 5.1168(2) | 5.083(4) | 5.058(3) | 5.072(5) | 5.034(2) | 5.006(2) | 4.954(2) | 4.935(3) | 4.905(2) | 4.876(1) | 4.864(2) | 4.843(2) |
| Maximum 2 θ (°) | 69.96 | 60.91 | 64.02 | 64.05 | 64.05 | 64.05 | 63.42 | 63.64 | 63.96 | 63.66 | 64.00 | 63.85 |
| Measured reflections | 19,933 | 1,545 | 1,858 | 1,932 | 2,034 | 1,838 | 1,937 | 2,238 | 2,019 | 2,000 | 2,111 | 1,945 |
| Unique reflections | 1,980 | 685 | 789 | 769 | 771 | 722 | 728 | 834 | 780 | 752 | 799 | 704 |
| Unique reflections with $F_0 > 4\sigma(F_0)$ | 1,092 | 327 | 374 | 396 | 356 | 343 | 325 | 402 | 350 | 337 | 373 | 327 |
| R_{int} | 0.0581 | 0.1068 | 0.0958 | 0.1177 | 0.0936 | 0.0964 | 0.1088 | 0.0961 | 0.0900 | 0.0972 | 0.0884 | 0.0995 |
| N. of refined parameters | 87 | 45 | 45 | 45 | 45 | 45 | 45 | 45 | 45 | 45 | 45 | 45 |
| R_1 , $F_0 > 4\sigma(F_0)$ | 0.0560 | 0.0833 | 0.0888 | 0.0777 | 0.0656 | 0.0549 | 0.0634 | 0.0696 | 0.0606 | 0.0733 | 0.0830 | 0.0694 |
| wR^2 | 0.0634 | 0.0925 | 0.1025 | 0.1192 | 0.0946 | 0.0775 | 0.0890 | 0.0958 | 0.0855 | 0.1045 | 0.0958 | 0.0881 |
| GooF | 1.073 | 1.096 | 1.036 | 1.117 | 1.095 | 1.285 | 1.098 | 1.079 | 1.080 | 1.062 | 1.029 | 1.024 |
| Residuals ($e^-/\text{Å}^3$) | +0.77/ -0.55 | +0.71/ -0.85 | +0.65/ -0.74 | +0.66/ -0.72 | +0.70/ -0.73 | +0.77/ -0.51 | +0.66/ -0.69 | +0.60/ -0.87 | +0.61/ -0.63 | +0.79/ -0.96 | +0.76/ -0.80 | +0.89/ -0.72 |

* With the crystal in the DAC without any *P*-medium. At any pressure: ω/φ scan type, 60 s exposure time, $P6_3$ space group.

$$R_{\text{int}} = \frac{\sum |F_{\text{obs}}^2 - F_{\text{obs}}^2(\text{mean})|}{\sum [F_{\text{obs}}^2]}; R_1 = \frac{\sum (|F_{\text{obs}}| - |F_{\text{calc}}|)/\sum |F_{\text{obs}}|}{\sum |F_{\text{obs}}|}; wR_2 = \frac{[\sum [w(F_{\text{obs}}^2 - F_{\text{calc}}^2)^2]/\sum [w(F_{\text{obs}}^2)^2]]^{0.5}}{\sum [w(F_{\text{obs}}^2) + (0.01 * P)^2]}; P = (\text{Max}(F_{\text{obs}}^2, 0) + 2 * F_{\text{calc}}^2)/3$$

531

532 Table 2. Unit-cell parameters of cancrinite at different pressures measured using a KUMA
 533 diffractometer.

534

535

| <i>P</i> (GPa) | <i>a</i> (Å) | <i>c</i> (Å) | <i>V</i> (Å ³) |
|----------------|--------------|--------------|----------------------------|
| 0.0001* | 12.598(8) | 5.114(4) | 702.6(8) |
| 0.74(2) | 12.550(7) | 5.077(3) | 692.5(7) |
| 0.96(2) | 12.530(9) | 5.072(5) | 690.0(9) |
| 1.30(2) | 12.515(6) | 5.054(3) | 685.6(6) |
| 1.99(2) | 12.466(8) | 5.028(4) | 676.6(8) |
| 2.33(2) | 12.447(5) | 5.006(2) | 671.7(5) |
| 2.63(2) | 12.434(6) | 4.994(2) | 668.7(5) |
| 2.96(2) | 12.415(7) | 4.978(7) | 664.0(9) |
| 3.27(2) | 12.393(5) | 4.974(3) | 661.6(5) |
| 3.59(2) | 12.386(3) | 4.954(2) | 658.3(3) |
| 3.60(2) | 12.378(6) | 4.961(3) | 658.5(6) |
| 3.93(2) | 12.367(4) | 4.944(2) | 654.9(4) |
| 4.30(3) | 12.347(6) | 4.935(3) | 651.5(6) |
| 4.44(2) | 12.346(4) | 4.925(2) | 650.1(4) |
| 4.62(3) | 12.340(3) | 4.919(2) | 648.6(3) |
| 5.00(2) | 12.322(4) | 4.905(2) | 645.0(4) |
| 5.16(2) | 12.310(3) | 4.898(2) | 642.9(3) |
| 5.51(2) | 12.294(2) | 4.886(1) | 639.6(2) |
| 5.75(2) | 12.278(2) | 4.876(1) | 636.6(2) |
| 5.98(2) | 12.269(5) | 4.866(3) | 634.2(5) |
| 6.14(2) | 12.266(3) | 4.864(2) | 633.7(3) |
| 6.30(3) | 12.250(3) | 4.852(2) | 630.5(3) |
| 6.63(3) | 12.240(4) | 4.843(2) | 628.3(4) |

* With the crystal in the DAC without any *P*-medium.

Note: Unit-cell parameters measured with a KUMA point-detector diffractometer.

553

554

555

556 Table 3. Atomic fractional coordinates, site occupancy factors (s.o.f.), and thermal displacement
 557 parameters (\AA^2) at different pressures.

| Sites occupancies at P_0 -AIR | | | | | |
|---|-------------------------|------------|------------|-----------|--------------------------------|
| Site | s.o.f. | Site | s.o.f. | Site | s.o.f. |
| Si | 1.0 | O4 | 1.0 | Oc1 | 0.421(7) |
| Al | 1.0 | Na1 | 0.960(9) | C2 | 0.459(6) |
| O1 | 1.0 | Na2(Na) | 0.854(6) | Oc2 | 0.459(6) |
| O2 | 1.0 | Na2(Ca) | 0.146(6) | Ow | 1.0 |
| O3 | 1.0 | C1 | 0.421(7) | | |
| Site fractional coordinates and displacement parameters | | | | | |
| P (GPa) | Site | x | y | z | $U_{\text{iso}}/U_{\text{eq}}$ |
| 0.0001 (P_0 -AIR) | Si | 0.08267(7) | 0.41096(7) | 0.7338(2) | 0.0090(2) |
| | Al | 0.33709(7) | 0.41224(7) | 0.7342(2) | 0.0087(2) |
| | O1 | 0.2014(2) | 0.4043(2) | 0.6419(4) | 0.0155(5) |
| | O2 | 0.1145(2) | 0.5507(2) | 0.7109(5) | 0.0198(5) |
| | O3 | 0.0443(2) | 0.3588(2) | 0.0276(4) | 0.0164(6) |
| | O4 | 0.3212(2) | 0.3508(2) | 0.0442(4) | 0.0148(6) |
| | Na1 | 2/3 | 1/3 | 0.1159(5) | 0.0294(9) |
| | Na2 | 0.8742(1) | 0.7516(1) | 0.7764(2) | 0.0287(5) |
| | C1 | 0 | 0 | 0.914(4) | 0.048(6) |
| | OC1 | 0.0562(7) | 0.1184(4) | 0.888(2) | 0.052(3) |
| | C2 | 0 | 0 | 0.649(3) | 0.021(4) |
| | OC2 | 0.0639(5) | 0.1196(3) | 0.664(1) | 0.030(2) |
| | Ow | 0.315(1) | 0.6171(6) | 0.171(1) | 0.048(3) |
| | 0.0001 (P_0 -DAC) | Si | 0.0824(3) | 0.4106(3) | 0.7244(8) |
| Al | | 0.3372(3) | 0.4126(3) | 0.7231(9) | 0.0087(9) |
| O1 | | 0.2007(7) | 0.4027(7) | 0.634(1) | 0.013(2) |
| O2 | | 0.1140(6) | 0.5520(7) | 0.698(2) | 0.019(2) |
| O3 | | 0.0462(8) | 0.3590(8) | 0.020(2) | 0.012(3) |
| O4 | | 0.3199(8) | 0.3517(7) | 0.036(1) | 0.007(2) |
| Na1 | | 2/3 | 1/3 | 0.108(2) | 0.038(3) |
| Na2 | | 0.8746(4) | 0.7519(4) | 0.7673(5) | 0.027(1) |
| C1 | | 0 | 0 | 0.91(1) | 0.006(9) |
| OC1 | | 0.058(2) | 0.1182(8) | 0.881(6) | 0.038(5) |
| C2 | | 0 | 0 | 0.652(9) | 0.006(9) |
| OC2 | | 0.062(2) | 0.1190(5) | 0.662(4) | 0.038(5) |
| Ow | | 0.316(4) | 0.617(2) | 0.173(4) | 0.039(9) |
| 0.76(2) | | Si | 0.0828(3) | 0.4112(3) | 0.7347(7) |
| | Al | 0.3373(3) | 0.4126(3) | 0.7348(9) | 0.0111(8) |
| | O1 | 0.2009(7) | 0.4022(7) | 0.639(1) | 0.015(2) |
| | O2 | 0.1175(6) | 0.5542(6) | 0.704(1) | 0.019(2) |
| | O3 | 0.0491(7) | 0.3632(7) | 0.034(2) | 0.014(2) |
| | O4 | 0.3212(7) | 0.3540(7) | 0.048(2) | 0.010(2) |
| | Na1 | 2/3 | 1/3 | 0.112(1) | 0.041(3) |
| | Na2 | 0.8754(4) | 0.7517(4) | 0.7779(6) | 0.032(1) |
| | C1 | 0 | 0 | 0.90(2) | 0.04(1) |
| | OC1 | 0.061(2) | 0.1190(8) | 0.883(6) | 0.048(5) |

| | | | | | |
|---------|-----|-----------|-----------|-----------|-----------|
| | C2 | 0 | 0 | 0.672(4) | 0.04(1) |
| | OC2 | 0.062(2) | 0.1193(5) | 0.672(4) | 0.048(5) |
| | Ow | 0.306(4) | 0.613(2) | 0.181(4) | 0.054(9) |
| 0.99(2) | Si | 0.0826(3) | 0.4108(3) | 0.7376(6) | 0.0139(7) |
| | Al | 0.3374(2) | 0.4121(3) | 0.7389(7) | 0.0133(8) |
| | O1 | 0.2000(7) | 0.4017(7) | 0.644(1) | 0.020(2) |
| | O2 | 0.1163(6) | 0.5513(6) | 0.707(1) | 0.020(2) |
| | O3 | 0.0457(7) | 0.3588(7) | 0.034(1) | 0.015(2) |
| | O4 | 0.3191(7) | 0.3512(7) | 0.053(1) | 0.017(2) |
| | Na1 | 2/3 | 1/3 | 0.115(1) | 0.036(2) |
| | Na2 | 0.8733(3) | 0.7497(4) | 0.7820(6) | 0.032(1) |
| | C1 | 0 | 0 | 0.91(1) | 0.05(1) |
| | OC1 | 0.056(3) | 0.119(1) | 0.864(7) | 0.069(6) |
| | C2 | 0 | 0 | 0.66(1) | 0.05(1) |
| | OC2 | 0.063(2) | 0.1200(5) | 0.657(5) | 0.069(6) |
| | Ow | 0.309(3) | 0.608(2) | 0.173(4) | 0.05(1) |
| 1.39(2) | Si | 0.0829(2) | 0.4109(2) | 0.7342(6) | 0.0105(7) |
| | Al | 0.3372(2) | 0.4121(3) | 0.7356(7) | 0.0112(7) |
| | O1 | 0.2004(6) | 0.4006(7) | 0.635(1) | 0.017(2) |
| | O2 | 0.1180(5) | 0.5533(6) | 0.702(1) | 0.022(2) |
| | O3 | 0.0484(6) | 0.3620(6) | 0.035(1) | 0.013(2) |
| | O4 | 0.3183(6) | 0.3535(6) | 0.054(1) | 0.015(2) |
| | Na1 | 2/3 | 1/3 | 0.110(1) | 0.040(2) |
| | Na2 | 0.8743(3) | 0.7508(3) | 0.7784(5) | 0.032(1) |
| | C1 | 0 | 0 | 0.90(1) | 0.028(9) |
| | OC1 | 0.058(2) | 0.1200(6) | 0.886(6) | 0.052(5) |
| | C2 | 0 | 0 | 0.671(4) | 0.028(9) |
| | OC2 | 0.063(2) | 0.1203(5) | 0.671(4) | 0.052(5) |
| | Ow | 0.305(3) | 0.614(2) | 0.178(4) | 0.056(8) |
| 2.33(2) | Si | 0.0829(2) | 0.4111(2) | 0.7340(7) | 0.0103(6) |
| | Al | 0.3369(2) | 0.4123(3) | 0.7357(8) | 0.0092(7) |
| | O1 | 0.2004(6) | 0.4010(7) | 0.634(1) | 0.016(2) |
| | O2 | 0.1174(5) | 0.5525(5) | 0.699(1) | 0.021(2) |
| | O3 | 0.0494(6) | 0.3629(7) | 0.0390(1) | 0.014(2) |
| | O4 | 0.3181(6) | 0.3529(6) | 0.058(1) | 0.016(2) |
| | Na1 | 2/3 | 1/3 | 0.107(1) | 0.042(2) |
| | Na2 | 0.8749(3) | 0.7524(3) | 0.7792(5) | 0.0283(9) |
| | C1 | 0 | 0 | 0.90(1) | 0.032(8) |
| | OC1 | 0.052(2) | 0.1193(7) | 0.870(5) | 0.053(5) |
| | C2 | 0 | 0 | 0.655(9) | 0.032(8) |
| | OC2 | 0.067(2) | 0.1198(6) | 0.672(3) | 0.053(5) |
| | Ow | 0.319(4) | 0.617(2) | 0.176(3) | 0.047(6) |
| 3.59(2) | Si | 0.0831(3) | 0.4112(3) | 0.7360(7) | 0.0101(7) |
| | Al | 0.3367(3) | 0.4124(3) | 0.7393(8) | 0.0105(7) |
| | O1 | 0.1988(7) | 0.3977(7) | 0.631(1) | 0.017(2) |
| | O2 | 0.1232(6) | 0.5556(6) | 0.697(1) | 0.020(2) |
| | O3 | 0.0529(7) | 0.3664(6) | 0.047(1) | 0.014(2) |
| | O4 | 0.3189(6) | 0.3581(6) | 0.062(1) | 0.015(2) |

| | | | | | |
|---------|-----|-----------|-----------|-----------|-----------|
| | Na1 | 2/3 | 1/3 | 0.100(1) | 0.038(2) |
| | Na2 | 0.8755(3) | 0.7523(3) | 0.7785(6) | 0.028(1) |
| | C1 | 0 | 0 | 0.91(1) | 0.05(1) |
| | OC1 | 0.066(3) | 0.119(1) | 0.860(5) | 0.054(5) |
| | C2 | 0 | 0 | 0.686(9) | 0.05(1) |
| | OC2 | 0.057(2) | 0.1210(6) | 0.664(4) | 0.054(5) |
| | Ow | 0.308(3) | 0.615(2) | 0.159(3) | 0.031(7) |
| 4.30(3) | Si | 0.0835(2) | 0.4111(3) | 0.7345(7) | 0.0120(6) |
| | Al | 0.3369(2) | 0.4126(3) | 0.7366(8) | 0.0125(7) |
| | O1 | 0.1981(6) | 0.3957(7) | 0.628(1) | 0.019(2) |
| | O2 | 0.1243(5) | 0.5566(6) | 0.691(1) | 0.020(2) |
| | O3 | 0.0539(6) | 0.3675(6) | 0.046(1) | 0.015(2) |
| | O4 | 0.3181(6) | 0.3579(6) | 0.063(1) | 0.017(2) |
| | Na1 | 2/3 | 1/3 | 0.095(1) | 0.040(2) |
| | Na2 | 0.8754(3) | 0.7523(3) | 0.7756(6) | 0.0291(9) |
| | C1 | 0 | 0 | 0.90(1) | 0.026(8) |
| | OC1 | 0.055(2) | 0.1204(9) | 0.867(5) | 0.053(5) |
| | C2 | 0 | 0 | 0.682(7) | 0.026(8) |
| | OC2 | 0.067(2) | 0.1216(5) | 0.669(4) | 0.053(5) |
| | Ow | 0.311(3) | 0.617(2) | 0.155(2) | 0.031(6) |
| 5.00(2) | Si | 0.0841(2) | 0.4116(2) | 0.7369(7) | 0.0127(6) |
| | Al | 0.3372(2) | 0.4131(3) | 0.7384(8) | 0.0123(7) |
| | O1 | 0.1984(6) | 0.3978(6) | 0.626(1) | 0.016(2) |
| | O2 | 0.1235(6) | 0.5554(6) | 0.691(1) | 0.024(2) |
| | O3 | 0.0546(7) | 0.3666(6) | 0.048(1) | 0.014(2) |
| | O4 | 0.3182(6) | 0.3584(6) | 0.067(1) | 0.017(2) |
| | Na1 | 2/3 | 1/3 | 0.094(1) | 0.039(2) |
| | Na2 | 0.8757(3) | 0.7527(3) | 0.7795(6) | 0.0276(9) |
| | C1 | 0 | 0 | 0.918(9) | 0.025(8) |
| | OC1 | 0.054(2) | 0.118(1) | 0.857(5) | 0.050(4) |
| | C2 | 0 | 0 | 0.659(8) | 0.025(8) |
| | OC2 | 0.065(2) | 0.1218(5) | 0.665(4) | 0.050(4) |
| | Ow | 0.314(3) | 0.614(2) | 0.151(3) | 0.045(8) |
| 5.73(3) | Si | 0.0839(3) | 0.4118(3) | 0.7377(8) | 0.0123(7) |
| | Al | 0.3377(3) | 0.4137(3) | 0.7415(9) | 0.0131(8) |
| | O1 | 0.1955(7) | 0.3916(8) | 0.625(1) | 0.020(2) |
| | O2 | 0.1259(7) | 0.5560(7) | 0.686(1) | 0.027(2) |
| | O3 | 0.0574(8) | 0.3702(6) | 0.058(1) | 0.014(2) |
| | O4 | 0.3196(7) | 0.3617(7) | 0.072(2) | 0.017(2) |
| | Na1 | 2/3 | 1/3 | 0.085(2) | 0.049(3) |
| | Na2 | 0.8760(4) | 0.7531(4) | 0.7764(7) | 0.030(1) |
| | C1 | 0 | 0 | 0.90(1) | 0.024(9) |
| | OC1 | 0.060(3) | 0.121(1) | 0.855(6) | 0.047(5) |
| | C2 | 0 | 0 | 0.67(1) | 0.024(9) |
| | OC2 | 0.064(2) | 0.1226(5) | 0.668(4) | 0.047(5) |
| | Ow | 0.308(4) | 0.614(2) | 0.151(3) | 0.048(9) |
| 6.16(2) | Si | 0.0842(3) | 0.4119(3) | 0.7387(8) | 0.0130(6) |
| | Al | 0.3375(2) | 0.4139(3) | 0.7405(9) | 0.0125(7) |

| | | | | | |
|---------|-----|-----------|-----------|-----------|-----------|
| | O1 | 0.1960(7) | 0.3931(7) | 0.627(1) | 0.020(2) |
| | O2 | 0.1267(6) | 0.5590(6) | 0.686(1) | 0.027(2) |
| | O3 | 0.0578(7) | 0.3721(6) | 0.055(1) | 0.014(2) |
| | O4 | 0.3193(6) | 0.3613(6) | 0.070(1) | 0.017(2) |
| | Na1 | 2/3 | 1/3 | 0.084(1) | 0.047(2) |
| | Na2 | 0.8761(3) | 0.7530(3) | 0.7774(7) | 0.031(1) |
| | C1 | 0 | 0 | 0.92(1) | 0.016(8) |
| | OC1 | 0.060(2) | 0.119(1) | 0.853(5) | 0.045(4) |
| | C2 | 0 | 0 | 0.676(7) | 0.016(8) |
| | OC2 | 0.062(2) | 0.1228(5) | 0.666(4) | 0.045(4) |
| | Ow | 0.311(3) | 0.614(2) | 0.146(3) | 0.048(9) |
| 6.63(3) | Si | 0.0841(2) | 0.4123(3) | 0.7392(8) | 0.0126(6) |
| | Al | 0.3373(2) | 0.4142(3) | 0.7424(9) | 0.0137(7) |
| | O1 | 0.1959(6) | 0.3910(7) | 0.626(1) | 0.022(2) |
| | O2 | 0.1302(6) | 0.5576(6) | 0.687(1) | 0.027(2) |
| | O3 | 0.0572(7) | 0.3721(6) | 0.061(1) | 0.018(2) |
| | O4 | 0.3199(6) | 0.3620(6) | 0.073(1) | 0.019(2) |
| | Na1 | 2/3 | 1/3 | 0.077(2) | 0.065(3) |
| | Na2 | 0.8762(3) | 0.7527(3) | 0.7758(7) | 0.034(1) |
| | C1 | 0 | 0 | 0.90(1) | 0.031(8) |
| | OC1 | 0.061(4) | 0.121(1) | 0.854(5) | 0.055(4) |
| | C2 | 0 | 0 | 0.684(8) | 0.031(8) |
| | OC2 | 0.062(3) | 0.1225(6) | 0.661(4) | 0.055(4) |
| | Ow | 0.308(3) | 0.615(2) | 0.141(3) | 0.045(9) |

558

559

560 Table 4. Relevant bond distances (Å), ring “diameters” (Å), angles (°), areas (Å²), volumes (Å³) and
 561 the (0001)-plane corrugation (Δz , Å) at different pressures.

562

| <i>P</i> (GPa) | 0.0001 | 0.76(2) | 0.99(2) | 1.39(2) | 2.33(2) | 3.59(2) | 4.30(3) | 5.00(2) | 5.73(3) | 6.16(2) | 6.63(3) |
|------------------------------|----------------------------|----------|----------|----------|----------|----------|----------|----------|-----------|----------|----------|
| | <i>P</i> ₀ -DAC | | | | | | | | | | |
| Si-O1 | 1.613(9) | 1.620(8) | 1.603(8) | 1.618(7) | 1.610(7) | 1.611(8) | 1.607(7) | 1.598(7) | 1.604(9) | 1.596(8) | 1.610(7) |
| Si-O2 | 1.627(8) | 1.631(8) | 1.600(7) | 1.617(7) | 1.599(6) | 1.607(8) | 1.619(7) | 1.601(7) | 1.598(8) | 1.629(7) | 1.595(7) |
| Si-O3 | 1.612(8) | 1.604(8) | 1.611(7) | 1.610(6) | 1.617(7) | 1.621(8) | 1.609(7) | 1.603(7) | 1.624(8) | 1.597(8) | 1.616(8) |
| Si-O4 | 1.628(8) | 1.624(9) | 1.615(8) | 1.622(7) | 1.602(7) | 1.615(8) | 1.615(7) | 1.613(7) | 1.604(9) | 1.612(8) | 1.603(8) |
| <Si-O> | 1.620 | 1.620 | 1.607 | 1.617 | 1.607 | 1.613 | 1.613 | 1.604 | 1.608 | 1.609 | 1.606 |
| Al-O1 | 1.725(8) | 1.723(8) | 1.728(8) | 1.721(7) | 1.711(7) | 1.709(8) | 1.706(7) | 1.716(7) | 1.723(8) | 1.716(8) | 1.703(7) |
| Al-O2 | 1.701(9) | 1.701(8) | 1.723(7) | 1.713(7) | 1.708(6) | 1.719(7) | 1.711(7) | 1.711(7) | 1.719(8) | 1.687(8) | 1.730(7) |
| Al-O3 | 1.752(9) | 1.755(9) | 1.741(8) | 1.736(8) | 1.727(7) | 1.729(8) | 1.727(8) | 1.734(8) | 1.729(9) | 1.734(8) | 1.718(8) |
| Al-O4 | 1.734(8) | 1.718(8) | 1.734(8) | 1.731(7) | 1.742(7) | 1.704(8) | 1.715(8) | 1.716(8) | 1.708(9) | 1.702(8) | 1.697(9) |
| <Al-O> | 1.728 | 1.724 | 1.732 | 1.725 | 1.722 | 1.715 | 1.715 | 1.719 | 1.720 | 1.710 | 1.712 |
| Na1-O1 (x 3) | 2.888(8) | 2.883(8) | 2.879(8) | 2.886(7) | 2.867(7) | 2.894(7) | 2.902(7) | 2.874(7) | 2.931(8) | 2.914(7) | 2.932(7) |
| Na1-O2 (x 3) | 2.441(7) | 2.397(6) | 2.403(6) | 2.38(6) | 2.374(6) | 2.312(6) | 2.286(7) | 2.291(6) | 2.262(7) | 2.252(6) | 2.219(6) |
| Na1-Ow' | 2.28(2) | 2.26(2) | 2.34(2) | 2.25(2) | 2.23(2) | 2.25(1) | 2.24(1) | 2.25(1) | 2.19(2) | 2.20(2) | 2.18(1) |
| Na1-Ow'' | 2.92(2) | 2.94(2) | 2.90(2) | 2.91(2) | 2.90(2) | 2.83(1) | 2.81(1) | 2.79(1) | 2.82(2) | 2.79(2) | 2.79(1) |
| Na2-O1 | 2.515(9) | 2.479(8) | 2.467(8) | 2.432(7) | 2.425(6) | 2.371(7) | 2.353(7) | 2.337(6) | 2.294(8) | 2.301(7) | 2.280(7) |
| Na2-O3' | 2.436(9) | 2.426(9) | 2.419(8) | 2.406(7) | 2.397(6) | 2.357(7) | 2.351(7) | 2.334(7) | 2.310(8) | 2.329(7) | 2.308(7) |
| Na2-O4' | 2.429(9) | 2.437(8) | 2.390(8) | 2.375(7) | 2.359(6) | 2.355(7) | 2.327(7) | 2.324(7) | 2.315(8) | 2.316(7) | 2.308(7) |
| Na2-O3'' | 2.930(10) | 2.980(9) | 2.902(8) | 2.947(8) | 2.949(8) | 2.995(8) | 2.999(8) | 2.985(8) | 3.040(10) | 3.043(9) | 3.051(9) |
| Na2-O4'' | 2.903(9) | 2.905(9) | 2.884(8) | 2.910(7) | 2.902(7) | 2.940(7) | 2.940(7) | 2.937(7) | 2.976(8) | 2.960(7) | 2.964(8) |
| Na2-Oc1' | 2.40(3) | 2.42(3) | 2.34(4) | 2.38(3) | 2.26(3) | 2.44(3) | 2.27(3) | 2.25(3) | 2.30(3) | 2.30(3) | 2.31(5) |
| Na2-Oc1'' | 2.44(3) | 2.38(3) | 2.41(3) | 2.43(3) | 2.46(3) | 2.23(3) | 2.14(3) | 2.39(3) | 2.32(3) | 2.31(3) | 2.29(5) |
| Na2-Oc1''' | 2.42(3) | 2.44(3) | 2.56(3) | 2.42(3) | 2.48(2) | 2.50(3) | 2.43(3) | 2.49(2) | 2.45(3) | 2.47(2) | 2.44(3) |
| Na2-Oc2' | 2.39(2) | 2.37(2) | 2.41(3) | 2.38(2) | 2.29(2) | 2.41(3) | 2.28(3) | 2.31(2) | 2.30(3) | 2.33(2) | 2.33(4) |
| Na2-Oc2'' | 2.43(2) | 2.43(2) | 2.46(3) | 2.42(2) | 2.45(2) | 2.34(3) | 2.42(3) | 2.40(2) | 2.36(3) | 2.34(2) | 2.34(4) |
| Na2-Oc2''' | 2.45(2) | 2.44(2) | 2.37(2) | 2.42(2) | 2.40(2) | 2.34(2) | 2.37(2) | 2.32(2) | 2.32(2) | 2.31(2) | 2.29(2) |
| C1↔C1, C2↔C2 | 2.542(2) | 2.529(2) | 2.538(3) | 2.517(1) | 2.503(1) | 2.477(1) | 2.468(2) | 2.453(1) | 2.438(1) | 2.432(1) | 2.422(1) |
| C1↔C2 | 3.85(7) | 3.8(1) | 3.81(9) | 3.63(7) | 3.71(7) | 3.55(8) | 3.56(6) | 3.72(6) | 3.59(8) | 3.60(6) | 3.46(7) |
| 6mR₁[0001] | | | | | | | | | | | |
| ω ₁ | 136.0(5) | 137.5(5) | 137.4(4) | 138.2(4) | 137.9(4) | 141.4(5) | 142.7(4) | 141.5(4) | 144.9(5) | 144.9(5) | 146.9(4) |
| ω ₂ | 100.8(4) | 99.1(3) | 99.5(4) | 98.3(3) | 98.7(3) | 95.1(3) | 94.0(3) | 95.0(3) | 92.0(4) | 92.1(3) | 89.9(3) |
| α | 8.8(2) | 9.6(2) | 9.5(2) | 10.0(2) | 9.8(2) | 11.6(2) | 12.2(2) | 11.6(2) | 13.2(2) | 13.2(2) | 14.3(2) |
| O1↔O2 | 5.29(1) | 5.24(1) | 5.24(1) | 5.23(1) | 5.20(1) | 5.15(1) | 5.14(1) | 5.119(9) | 5.14(1) | 5.11(1) | 5.08(1) |
| Area | 18.2(4) | 17.8(4) | 17.8(4) | 17.7(4) | 17.5(4) | 17.1(4) | 17.0(4) | 16.8(4) | 16.9(4) | 16.7(4) | 16.5(4) |
| 4mR | | | | | | | | | | | |

| | | | | | | | | | | | |
|-----------------------------------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| O3↔O4 | 4.15(1) | 4.08(1) | 4.13(1) | 4.09(1) | 4.07(1) | 3.99(1) | 3.97(1) | 3.98(1) | 3.91(1) | 3.89(1) | 3.87(1) |
| O2↔O2 | 3.56(1) | 3.60(1) | 3.584(9) | 3.591(9) | 3.563(8) | 3.625(8) | 3.63(8) | 3.604(8) | 3.625(9) | 3.629(9) | 3.677(9) |
| Area | 7.39(6) | 7.34(4) | 7.40(4) | 7.34(4) | 7.25(3) | 7.23(3) | 7.21(3) | 7.17(3) | 7.09(4) | 7.06(4) | 7.11(4) |
| 12mR | | | | | | | | | | | |
| O1↔O1 | 9.16(1) | 9.12(1) | 9.08(1) | 9.04(1) | 9.00(1) | 8.88(1) | 8.81(1) | 8.837(9) | 8.68(1) | 8.70(1) | 8.636(9) |
| O3↔O4 | 8.48(1) | 8.51(2) | 8.41(1) | 8.432(9) | 8.388(8) | 8.405(8) | 8.380(8) | 8.351(8) | 8.377(9) | 8.386(8) | 8.379(8) |
| (O1↔O1)/(O3↔O4) | 1.038(3) | 1.030(4) | 1.037(3) | 1.030(2) | 1.031(2) | 1.015(2) | 1.009(2) | 1.017(2) | 0.994(2) | 0.996(2) | 0.989(2) |
| 6mR//[0001] | | | | | | | | | | | |
| O3↔O3 | 4.97(1) | 4.98(1) | 4.94(1) | 4.95(1) | 4.93(1) | 4.92(1) | 4.91(1) | 4.88(1) | 4.89(1) | 4.90(1) | 4.89(1) |
| O4↔O4 | 4.95(1) | 4.95(1) | 4.92(1) | 4.91(1) | 4.88(1) | 4.89(1) | 4.87(1) | 4.86(1) | 4.86(1) | 4.85(1) | 4.85(1) |
| ϵ cage | | | | | | | | | | | |
| κ (O2-O2-O2) | 91.1(3) | 89.3(2) | 90.2(2) | 89.0(2) | 89.3(2) | 86.2(2) | 85.7(2) | 85.8(2) | 84.5(2) | 84.2(2) | 82.4(2) |
| O2↔O2 | 8.47(1) | 8.51(1) | 8.45(1) | 8.47(1) | 8.42(1) | 8.48(1) | 8.48(1) | 8.44(1) | 8.46(1) | 8.46(1) | 8.51(1) |
| Δz | 0.90(2) | 0.86(2) | 0.88(1) | 0.84(1) | 0.80(1) | 0.74(1) | 0.72(1) | 0.70(1) | 0.62(1) | 0.64(1) | 0.61(1) |
| V_{ch} | 298(1) | 296(1) | 292(1) | 289.4(8) | 285.0(7) | 278.7(7) | 274.6(8) | 273.0(7) | 267.1(7) | 267.5(7) | 264.1(7) |
| V_{cg} | 157(3) | 155(2) | 154(3) | 153(2) | 151(2) | 150(2) | 150(2) | 147(2) | 149(2) | 147(2) | 148(2) |

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