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1 **Revision_1**

2 **High-pressure behavior of intermediate scapolite:**
3 **compressibility, structure deformation and phase transition**

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Abstract

Scapolites are common volatiles-bearing minerals in metamorphic rocks. In this study, the high-pressure behavior of an intermediate member of the scapolite solid solution series (Me_{47}), chemical formula $(\text{Na}_{1.86}\text{Ca}_{1.86}\text{K}_{0.23}\text{Fe}_{0.01})(\text{Al}_{4.36}\text{Si}_{7.64})\text{O}_{24}[\text{Cl}_{0.48}(\text{CO}_3)_{0.48}(\text{SO}_4)_{0.01}]$, has been investigated up to 17.79 GPa, by means of in situ single-crystal synchrotron X-ray diffraction. The isothermal elastic behavior of the studied scapolite has been described by a III-order Birch-Murnaghan equation of state, which provided the following refined parameters: $V_0 = 1110.6(7) \text{ \AA}^3$, $K_{V0} = 70(2) \text{ GPa}$ ($\beta_{V0} = 0.0143(4) \text{ GPa}^{-1}$) and $K' = 4.8(7)$. The refined bulk modulus is intermediate between those previously reported for Me_{17} and Me_{68} scapolite samples, confirming that the bulk compressibility among the solid solution increases with the Na content. A discussion on the P -induced structure deformation mechanisms of tetragonal scapolite at the atomic scale is provided, along with the implications of the reported results for the modelling of scapolite stability. In addition, a single-crystal to single-crystal phase transition, which is displacive in character, has been observed toward a triclinic polymorph at 9.87 GPa. The high-pressure triclinic polymorph was found to be stable up to the highest pressure investigated.

Keywords: scapolite, compressibility, phase transition, synchrotron X-ray diffraction.

29 **1. Introduction**

30 Scapolite represents a non-binary solid solution series, which members can be rock-forming
31 minerals in crustal igneous and metamorphic environments. The general chemical formula of
32 scapolite can be written as $M_4[T_{12}O_{24}]A$, where: M is a monovalent or divalent cation, usually Na^+ ,
33 Ca^{2+} (major components), K^+ , Sr^{2+} , Ba^{2+} or Fe^{2+} ; T represents Si^{4+} and Al^{3+} (less commonly Fe^{3+}) in
34 tetrahedral coordination; A is an anion, usually Cl^- , CO_3^{2-} or SO_4^{2-} . Three end-members have been
35 reported: marialite, $Na_4Al_3Si_9O_{24}Cl$, and meionite, $Ca_4Al_6Si_6O_{24}(CO_3)$, are long-time known (Shaw
36 1960), whereas silvialite, $Ca_4Al_6Si_6O_{24}(SO_4)$, the sulfate analogue of meionite, has been described
37 only recently (Teerstra et al. 1999). A common symbolism adopted to define the scapolite
38 composition is that of meionite content, Me_x , which, in its broadest definition, is $Me_x =$
39 $\frac{\Sigma(M^{2+})}{\Sigma(M^+ + M^{2+})}$. The complex substitution mechanisms operating across the solid solution
40 series have been thoroughly studied. Evans et al. (1969) proposed two substitutional schemes:
41 between marialite (Me_0) and Me_{75} and between Me_{75} and meionite (Me_{100}). The same substitutional
42 schemes have been reported by Chamberlain et al. (1985) and Hassan and Buseck (1988). Zolotarev
43 (1993, 1996), based on new chemical analyses of scapolite samples and on revision of the literature
44 data, proposed the existence of three binary solid solutions among the end members marialite and
45 meionite: 1) from $Na_4Al_3Si_9O_{24}Cl$ to $CaNa_3Al_4Si_8O_{24}Cl$, 2) from $CaNa_3Al_4Si_8O_{24}Cl$ to
46 $NaCa_3Al_5Si_7O_{24}CO_3$ and 3) from $NaCa_3Al_5Si_7O_{24}CO_3$ to $Ca_4Al_6Si_6O_{24}CO_3$. The existence of three
47 binary solid solution series was later confirmed by means of spectroscopic (NMR), powder and
48 single-crystal X-ray diffraction analyses (Sokolova et al. 1996; Sheriff et al. 1998, 2000; Sokolova
49 and Hawthorne 2008). As noted by Sokolova and Hawthorne (2008), due to the complex
50 substitution mechanisms within the scapolite series, the Me_x symbolism reported above is not
51 formally correct, but is effective to roughly define the scapolite composition and valid at a first
52 approximation. For this reason, it will be adopted hereafter to refer to samples of this and previous
53 studies. A further complex feature of scapolite minerals concerns their symmetry: the compounds

54 close to the marialite end member, on one side, and to the meionite end member, on the other side,
55 are usually found to crystallize with a structure described in the $I4/m$ space group, whereas the
56 intermediate members have $P4_2/n$ symmetry. Hawthorne and Sokolova (2008) placed the
57 occurrence of the phase transitions at Me_{20} and Me_{75} , respectively, and ascribed it to the coupling of
58 the short range order between the $[(Si,Al)_{12}O_{24}]$ and $\{Na,Ca\}\{Cl,(CO_3)\}$ frameworks.

59 The crystal structure of scapolite was first solved by Pauling (1930) and Schiebold and Seumel
60 (1932) and refined by several authors (e.g. Papike and Stephenson 1966; Lin and Burley 1973a). In
61 the $I4/m$ space group, two independent tetrahedral sites occur, T1 and T2, which give rise to an
62 open-framework analogue to that of feldspathoids and zeolites (Figure 1). In the $P4_2/n$ structure, T2
63 splits into two independent sites, i.e. T2 and T3. In the $I4/m$ members close to the marialite side of
64 the series, Al is strongly ordered at the T2 site, whereas at the composition corresponding to the
65 phase transition to $P4_2/n$, Al is strongly concentrated at T2 and depleted at T3. With increasing
66 meionite content, Al fills both T1 and T3, until a similar content at T2 and T3 is reached and the
67 $I4/m$ structure is recovered, close to the meionite-rich side of the series, where a preferential
68 ordering of Al at T2, with respect to T1, is still preserved (Sokolova and Hawthorne 2008). The
69 (Si,Al)-tetrahedra give rise to two different four-membered rings: type-I (hereafter 4mR-I), made by
70 the T1 tetrahedra, and type-II (hereafter 4mR-II), made by T2/T3 tetrahedra (Figure 1). Their
71 interconnection along the [001] direction builds up columns of five-membered rings of tetrahedra.
72 The latter and the 4mR-I define a large structural cage, centered on the four-fold axis and hosting
73 the anions (either Cl, CO_3 or SO_4) (Figure 1). The access to the cage is granted by four symmetry-
74 related eight-membered rings of tetrahedra (Figure 1). Along the direction parallel to the c axis, i.e.
75 [001], every cage is surrounded by four symmetry-related highly elliptical channels defined by
76 eight-membered rings of tetrahedra (hereafter 8mR_[001], Figure 1). These channels host the cations,
77 occupying, both in $I4/m$ and $P4_2/n$, one independent site (Figure 1). Every anion in the cage is,
78 therefore, surrounded by four cations, whereas every cation is bonded to seven framework oxygens

79 (Figure 2) and to one anion (one bond with Cl, one or two bonds with the carbonate or sulfate
80 oxygens).

81 In Nature, scapolites are typical minerals of metamorphic environments. CO₃⁻ and SO₄⁻-rich
82 members are commonly reported as constituents of metamorphic rocks in amphibolite and granulite
83 facies (Oterdoom and Wenk 1983; Satish-Kumar et al. 2006; Porter and Austrheim 2017; Hammerli
84 et al. 2017), but are also reported to be unstable during the regression to lower grade metamorphic
85 facies (Satish-Kumar et al. 2006; Porter and Austrheim 2017; Hammerli et al. 2017). Cl-rich
86 scapolites are reported in a broader range of metamorphic environments, from greenschist to
87 eclogite facies (Frietsch et al. 1997; Kullerud and Erambert 1999; Satish-Kumar et al. 2006;
88 Katongo et al. 2011), including contact (Arranz et al. 2002; Mazhari et al. 2011) and hydrothermal
89 metamorphism (Frietsch et al. 1997; Bernal et al. 2017). Although less commonly, scapolites of
90 magmatic origin have also been reported (Smith et al. 2008) and is noteworthy to mention that
91 scapolite has also been found within a melt inclusion in olivine from a martian meteorite (Filiberto
92 et al. 2014). Overall, scapolites usually form at non-ambient temperature and pressure conditions in
93 presence of plagioclase and fluids carrying Cl⁻, CO₃²⁻ and/or SO₄²⁻ anions. Therefore, scapolite has
94 been reported in the literature as an important reservoir of volatiles within the Earth's crust (e.g.
95 Satish-Kumar et al. 2006; Porter and Austrheim 2017; Hammerli et al. 2017). In addition, Cl-rich
96 scapolites of hydrothermal origin are often associated with ore minerals deposits (Frietsch et al.
97 1997; Katongo et al. 2011; Almeida and Jenkins 2017), whereas the destabilization of SO₄-rich
98 scapolites during metamorphic regression may release a significant amount of sulfur, which, in turn,
99 may influence the fractionation and concentration of calcophile elements (Porter and Austrheim
100 2017; Hammerli et al. 2017). For these reasons, several experimental investigations have been
101 devoted to understand the relative stability of scapolite with respect to plagioclase, halite, calcite
102 and/or volatiles-bearing fluids (e.g. Orville 1975; Ellis 1978; Baker and Newton 1995; Almeida and
103 Jenkins 2017). At the same time, the quantitative characterization of the elastic and structural

104 behavior of the members across the scapolite series, at varying temperature and pressure conditions,
105 is equally important for understanding the stability and occurrence of these minerals in
106 metamorphic environments. Levien and Papike (1976), Graziani and Lucchesi (1982) and Baker
107 (1994) reported the high-temperature behavior (at ambient P) of several members of the scapolite
108 series, remarking a significant elastic anisotropy and the role played by the chemical composition.
109 Hazen and Sharp (1988) and Comodi et al. (1990) reported the high-pressure behavior (at ambient
110 T) of three members of the solid solution (Me_{88} , Me_{68} and Me_{17}) up to ca. 4 GPa, pointing out that
111 an increase in the meionite content is coupled with a decrease in the bulk compressibility.

112 In this study, we have investigated the high- P (and ambient- T) behavior of an intermediate scapolite
113 (Me_{47}) up to ca. 18 GPa, by means of in situ high- P single-crystal synchrotron X-ray diffraction,
114 using diamond anvil cells. A comparative analysis with the literature data (Hazen and Sharp 1988;
115 Comodi et al. 1990) is provided. In addition, we report, for the first time, the occurrence a
116 tetragonal-to-triclinic phase transition at ca. 9.5 GPa.

117 **2. Materials and experimental methods**

118 A gem-quality and transparent single crystal of scapolite from Madagascar, ca. 1 cm in diameter,
119 belonging to a private mineralogical collection, has been chosen for this experiment. Several
120 fragments of the starting single crystal were recovered and investigated under the polarized
121 microscope to check the absence of optical defects and inclusions.

122 Four of the largest fragments were selected for the chemical analysis, which was performed using a
123 Jeol JXA-8200 electron microprobe, operating in wavelength-dispersive mode (EPMA-WDS), at
124 the Earth Sciences Department of the University of Milano (ESD-MI), Italy. The system was
125 operated with an accelerated voltage of 15 kV, a beam current of 5 nA, a counting time of 30 s on
126 the peaks and 10 s on the backgrounds and a beam diameter of 3 μm . Natural samples have been
127 used as standards for calibration: grossular for Si, Al and Ca, omphacite for Na, K-feldspar for K,

128 celestite for Sr, fayalite for Fe, galena for S and marialitic scapolite for Cl. The results of chemical
129 analysis are reported in Table 1.

130 A single-crystal fragment, ca. $300 \times 200 \times 200 \mu\text{m}^3$ in size, was selected for a single-crystal X-ray
131 diffraction data collection at ambient conditions using an Oxford Diffraction Xcalibur four-circle
132 diffractometer at the ESD-MI, equipped with a Mo-K α X-ray tube, a graphite monochromator and a
133 CCD detector, and operating at 50 kV and 30 mA. A combination of φ and ω scans, with $1^\circ/\text{frame}$
134 step width and 20 s/frame exposure time, was adopted to maximize the reciprocal lattice coverage.
135 Indexing of the diffraction peaks, refinement of the unit-cell parameters and intensity data reduction
136 were performed using the CrysAlisPro version 1.171.38.46 software system (Rigaku Oxford
137 Diffraction 2018). Corrections for the crystal absorption were applied by the semiempirical
138 ABSPACK routine implemented in CrysAlisPro.

139 The in situ high-pressure single-crystal X-ray diffraction experiments were performed, using a
140 diamond anvil cell, at the former ID09A beamline of the European Synchrotron Radiation Facility
141 (ESRF, Grenoble, France). A monochromatic X-ray beam ($E = 30 \text{ keV}$, $\lambda = 0.4138 \text{ \AA}$) has been
142 focused to the samples (beam size = $30 \times 30 \mu\text{m}^2$) and the X-ray diffraction patterns have been
143 collected by a MAR555 flat panel detector at 250 mm from the sample position. A description of
144 the beamline experimental setup can be found in Merlini and Hanfland (2013). A single crystal
145 fragment, ca $30 \times 20 \times 20 \mu\text{m}^3$ in size was selected for the experiment and loaded in the P -chamber
146 obtained, by electro spark erosion (hole diameter = $250 \mu\text{m}$), in a pre-indented (to $\sim 70 \mu\text{m}$) steel
147 foil gasket. A mixture of methanol:ethanol:water (16:3:1, hereafter *mew*) was used as P -transmitting
148 medium (Angel et al. 2007) and the ruby-fluorescence method (Mao et al. 1986; Chervin et al.
149 2001) was adopted for pressure calibration. A remotely controlled membrane-driven diamond anvil
150 cell, with Boehler-Almax designed diamonds (culet diameter = $600 \mu\text{m}$) was used. Eighteen
151 intensity data collections (two of which in decompression) were performed at different pressures
152 from ambient conditions (crystal in the DAC without P -medium) up to 10.23 GPa. The same

153 collection strategy was always applied: an ω -scan from -30 to $+30^\circ$, with 1° step width and 1 s
154 exposure time per frame.

155 Since a phase transition was detected between 9.23 and 9.87 GPa (see section 4.4), which is close to
156 the hydrostatic limit of the adopted P -transmitting fluid mixture (Angel et al. 2007), a second high-
157 pressure ramp was performed using helium as P -transmitting medium. The same experimental
158 conditions as those reported above were adopted using a single-crystal fragment of similar size and
159 shape, except for the following: a pre-indented (to $\sim 45 \mu\text{m}$) rhenium foil was used as a gasket and a
160 hole, $100 \mu\text{m}$ in diameter, was drilled by spark-erosion to serve as P -chamber, as Boehler-Almax
161 designed diamonds with $300 \mu\text{m}$ culet size were used. Nineteen intensity data collections (one of
162 which in decompression) were performed at different pressures from 0.20 up to 17.79 GPa using the
163 same ω -scan strategy described above. For both the HP-ramps, indexing, refinement of the unit-cell
164 parameters and intensity data reduction were performed using the **CrysAlisPro software (Rigaku**
165 **Oxford Diffraction 2018)**. Corrections for absorption of the DAC components was performed using
166 the ABSPACK routine implemented in **CrysAlisPro**. Unit-cell parameters pertaining to both the P -
167 ramps are reported in **Tables S1 and S2 (deposited as supplementary materials)**.

168 **3. Structure refinements**

169 All the structure refinements have been performed using the JANA2006 software (Petříček et al.
170 2014).

171 Scapolites with compositions **between $\sim \text{Me}_{20}$ and Me_{75}** are always reported to crystallize in the
172 tetragonal space group $P4_2/n$ (**cf. Lin and Burley, 1973b, 1975; Sherriff et al., 1998; Sokolova and**
173 **Hawthorne, 2008)**. However, our single-crystal X-ray diffraction data, collected both at ambient
174 conditions using a conventional diffractometer and at high pressure using synchrotron radiation
175 (section 2), always showed the occurrence of systematic extinctions consistent with an I -centered
176 lattice (Figure 3). A discussion on this point is given in the section 5.1. For this reason, according to

177 the observed systematic extinctions, the structure refinement based on the intensity data collected at
178 ambient conditions at the ESD-MI was performed in the $I4/m$ space group, starting from the
179 framework coordinates of the S6 sample reported by Sokolova and Hawthorne (2008). The cations
180 and anions sites have been, subsequently, detected by the position of residual peaks in the
181 difference-Fourier maps of the electron density. In the final cycles of the refinement all, but the
182 anions sites, have been refined using anisotropic displacement parameters (hereafter adp's). The X-
183 ray scattering curve of Si was assigned to the T1 and T2 tetrahedral sites. The Na, Ca and K sites
184 were restrained to share the same coordinates and adp's and their fractional occupancies were
185 restrained so that their sum would be one. The refinement of the Cl^- and CO_3^{2-} anions in the
186 structural cage was less straightforward, due to the strong correlations arising by their close
187 positions in the average structure model. Therefore, in order to minimize correlations, the Cl, C and
188 the three Oc sites were restrained to share the same isotropic displacement parameter (hereafter
189 idp), the C and Oc sites to share the same fractional occupancy, the C-O bond lengths were
190 restrained to $1.30 \pm 0.02 \text{ \AA}$ and the O-C-O bond angles of the carbonate group were restrained to
191 $120 \pm 2^\circ$. The final cycles converged with no significant correlations among the refined parameters.
192 Statistical parameters pertaining to the structure refinement are reported in Table 2. Fractional
193 coordinates, occupancies and dp's are reported in Table 3. Selected structural parameters are
194 reported in Table 4 and Table S3 (deposited as supplementary material).

195 The structure refinements based on the intensity data collected at high- P before the phase transition
196 (i.e. low- P polymorph) were performed in the $I4/m$ space group, starting from the model described
197 above. In addition to the same restrictions previously reported, the occupancies of the Ca, Na, K, Cl,
198 C and Oc sites have been constrained according to the measured chemical composition (Table 1).
199 The refinements based on the high- P data in *mew* were performed restraining the displacement
200 parameter of the O2 atom to be isotropic, as any attempt of anisotropic refinement failed, likely for

201 insufficient information due to the shadowing of portions of the reciprocal lattice by the DAC
202 components (see e.g. Miletich et al. 2000).

203 The structure refinements of the high-pressure polymorph were performed in the triclinic *I*-1
204 subgroup (see section 4.4), based on the intensity data collected in He at 10.08, 11.06, 12.30, 13.39
205 and 14.61 GPa. At higher pressures, a dramatic reduction in the number of observed reflections (*i.e.*
206 $F^2_{hkl}/\sigma(F^2_{hkl}) \geq 3$) prevented robust and reliable structure refinements. In order to compensate the
207 increase in the number of independent variables, due to symmetry reduction, all the independent
208 atomic positions have been refined with idp's. Fractional occupancies of cationic and anionic sites
209 were constrained according to the measured chemical composition and assumed to be identical
210 among the independent sites with a common parent site in *I4/m*. In addition, the same restraints
211 previously described were applied.

212 Statistical parameters on the structure refinements based on high-*P* data are reported in [Table 2](#),
213 whereas fractional coordinates, occupancies and dp's from selected pressures are reported in [Table](#)
214 [3](#). Selected structural parameters are reported in [Tables 4 and S3](#). The volumes of coordination
215 polyhedra have been calculated using the tools implemented in the software *Vesta* (Momma and
216 Izumi 2011).

217 **4. Results**

218 **4.1 Chemical composition**

219 The chemical composition of four fragments of the large single-crystal selected for this experiment,
220 determined by EPMA-WDS, is reported in Table 1. For any fragment, the reported mass fractions
221 have been averaged from 5 point analyses. The chemical formula has been calculated, according to
222 the method proposed by Teerstra and Sheriff (1997), normalizing to Si + Al = 12 atoms per formula
223 unit (apfu). The CO₂ content, following the protocol of Teerstra and Sheriff (1997), has been
224 calculated assuming that: 1) it is the amount necessary to compensate the excess positive charge

225 obtained subtracting the framework and anions (Cl^- and SO_4^{2-}) negative charges from the sum of
226 cations charge, and 2) the investigated scapolite sample is anhydrous,.

227 As there is no significant difference among the compositions of the investigated fragments, an
228 average chemical formula can be calculated:

229 $(\text{Na}_{1.86}\text{Ca}_{1.86}\text{K}_{0.23}\text{Fe}_{0.01})(\text{Al}_{4.36}\text{Si}_{7.64})\text{O}_{24}[\text{Cl}_{0.48}(\text{CO}_3)_{0.48}(\text{SO}_4)_{0.01}]$. The chemical analysis shows that
230 the investigated sample is intermediate between the end-members marialite and meionite, with an
231 insignificant amount of sulfate anions. According to the symbolism of meionite content reported in
232 section 1, the sample of this study can be classified as Me_{47} .

233 The cations composition from the structure refinement based on the data collected in air at the ESD-
234 MI (Table 3) shows an overestimation in K and an underestimation in Ca, which can be attributed to
235 their similar X-ray scattering factors. Nevertheless, the calculated electrons content (per unit
236 formula) from cations based on the structure refinement (i.e. $61.72 e^-$), is in fair agreement to that
237 calculated from the experimental chemical formula (i.e. $62.29 e^-$). For this reason, the cations
238 occupancies in the structure refinements based on the high- P data have been fixed to the values
239 derived from the chemical analysis (Tables 1 and 3).

240 **4.2 High-pressure elastic behavior of tetragonal scapolite**

241 The P -induced evolution of the unit-cell parameters of the tetragonal polymorph of scapolite,
242 obtained from both the P -ramps in *mew* and He, are reported in Table S1 and in Figure 4, from
243 which a different elastic behavior along the **a** and **c** axes is observed. At ambient conditions, the
244 compressibility is highest within the (001) plane and lowest along the direction parallel to the 4-fold
245 axis, i.e. [001]. However, if a stiffening is observed with pressure along the **a** axis, a softening
246 affects the **c** axis at $P > 2.00$ - 2.50 GPa, as confirmed by the P -induced behavior of the c/a ratio
247 reported in Figure 4 and Table S1. In addition, a sudden increase in compressibility affects the

248 structure along both the crystallographic directions and, in turn, the bulk elastic behavior at $P > 8.50$
249 GPa, likely ascribable to the impending phase transition (see section 4.4).

250 An isothermal Birch-Murnaghan equation of state, truncated to the third order (hereafter III-BM
251 EoS), which is widely used to model the isothermal bulk elastic behavior of minerals (Birch 1947,
252 Duffy and Wang 1998, Angel 2000), has been fitted to the experimental V - P data of tetragonal
253 scapolite in the range 0.0001-8.49 GPa (i.e. excluding the points showing the anomalous increase in
254 compressibility at $P > 8.50$ GPa), using the *EoSFit7_GUI* software (Angel et al. 2014, Gonzalez-
255 Platas et al. 2016). The obtained refined parameters are: $V_0 = 1110.6(7) \text{ \AA}^3$, $K_{V0} = 70(2) \text{ GPa}$ ($\beta_{V0} =$
256 $0.0143(4) \text{ GPa}^{-1}$) and $K_{V'} = 4.8(7)$, where $K_{V0} = 1/\beta_{V0}$, $\beta_{V0} = -1/V \cdot (\partial V/\partial P)_T$ and $K_{V'} = \partial K_V/\partial P$. A fit
257 of the V - P data with a BM EoS truncated to the second order (II-BM EoS), for which $K_{V'}$ is fixed to
258 4, has also been performed, for an ease of comparison with the literature data: $V_0 = 1110.1(5) \text{ \AA}^3$
259 and $K_{V0} = 72.4(7) \text{ GPa}$.

260 **4.3 P -induced structure deformation of tetragonal scapolite**

261 The P -induced bulk compression of open-framework silicates, both zeolites and feldspathoids, is
262 usually accommodated by the tilting of the rigid framework tetrahedra (see e.g.: Gatta and Lee
263 2014; Lotti et al. 2015a, 2015b, 2016; Gatta and Lotti 2016; Comboni et al. 2017; Gatta et al. 2018)
264 and this is the main mechanism operating also in the investigated sample of scapolite. However, a
265 slight compression of the independent T1 and T2 tetrahedra can also be observed (Table 4).
266 Interestingly, a subtle increase in the compressibility of the T2 tetrahedron (Figure 5) can be
267 detected at $P > 4$ GPa. The main deformation mechanism which accommodate compression and
268 expansion in the plane perpendicular to the tetragonal axis, i.e. (001), is governed by the
269 cooperative rotation of the 4mRs around the shared O4 oxygen hinges (Figure 1), as previously
270 reported by Levien and Papike (1976) and Comodi et al. (1990). This mechanism leads to a
271 decrease in ellipticity of the $8mR_{[001]}$ with temperature and an increase in ellipticity with pressure. A

272 comparative analysis of the refined structure models, based on the high- P data from both the ramps
273 in *mew* and He, shows that such a cooperative rotation, described by the closure of the O1-O4-O3
274 intertetrahedral angle (Figures 1 and 5, Table 4), induces an increase in ellipticity, mainly governed
275 by the compression of the shortest O4-O4 diameter of the 8mR_[001] channels (Figures 1 and 5, Table
276 4). However, at $P > 4$ GPa a sudden increase in the compressibility of the longest O4-O4 diameter
277 is also observed (Figures 1 and 5, Table 4). The compression within the (001) plane is also partly
278 accommodated by the internal compression of the 4mRs-II (Figure 1), which can be described by
279 the shortening of the O3-O3 diameter (Figure 1, Table 4). On the other hand, the 4mR-I apparently
280 undergoes an internal compression (shortening of O1-O1) only at pressures close to the
281 destabilization of the tetragonal polymorph of scapolite (Figure 1 and Table 4). It is interesting to
282 note that the 4mR-I delimits, in the plane perpendicular to [001], the cage hosting the anionic
283 groups. The access to that cage in the plane parallel to [001] is defined by 8mRs (Figure 1), which
284 height corresponds to the **c** unit-cell axis and, therefore, undergoes an increase in compressibility at
285 P ca. > 2 GPa. Overall, the high- P behavior of the structure along the **c** unit-cell axis (Figure 5,
286 Table S1) and of the 4mR-I (Table 4) imply a continuous increase in the compressibility of the
287 structural cage hosting the anionic groups.

288 The cations filling the 8mR channels are bonded to 7 oxygen atoms (Figure 2). Hereafter, the
289 notation “Ca” will be adopted to refer to the cation site, shared by either Ca, Na, or K. The high-
290 pressure behavior of the Ca-O bonds is reported in Figure 5 and Table S3, where it is shown that a
291 linear compression of the Ca-O3 and Ca-O4'' bonds occurs within the entire range of stability of the
292 tetragonal scapolite, whereas the Ca-O2 and Ca-O4' bonds undergo a saturation at $P > 4$ GPa. A
293 perfect linear compressibility, within the stability range of the tetragonal polymorph, is also shown
294 by the Ca-Cl bonds (Figure 2 and Table S3). On the other hand, we avoided any description of the
295 high- P behavior of the interatomic bonds between the cations and the oxygens of the carbonate
296 group, due the potential bias induced the significant restraints applied to the C and Oc sites.

297 **4.4 Phase transition from tetragonal to triclinic scapolite**

298 A phase transition, displacive in character and apparently of the first order, from the starting
299 tetragonal scapolite towards a polymorph with triclinic symmetry has been observed both in the *P*-
300 ramp in *mew*, between 9.23 and 9.87 GPa, and in the ramp in He, between 9.02 and 10.08 GPa. For
301 an ease of comparison with the tetragonal *I4/m* crystal structure, the triclinic polymorph has not
302 been described in the primitive reduced cell, but in the $I\bar{1}$ space group, as in this way the
303 tetragonal and triclinic unit cells are directly comparable. For both the *P*-ramps, the data collections
304 performed in decompression showed that the tetragonal-to-triclinic phase transition is fully
305 reversible.

306 Following the phase transition, the T1 and T2 tetrahedral sites split into two (T1_1 and T1_3) and
307 four (T2_1, T2_2, T2_3 and T2_4) independent crystallographic sites, respectively. However, the
308 three-dimensional framework may still be described as made by one 4mR defined by the T1
309 tetrahedra (4mR-I) and one 4mR defined by the T2 tetrahedra (4mR-II, Figure 6), but the symmetry
310 reduction removes the constraints induced by the four-fold axis. As a consequence, both the rings
311 are significantly distorted in the triclinic polymorph, being the 4mR-I approximately elongated
312 along the **a** axis and the 4mR-II along the **b** axis, respectively (Figure 6). The symmetry reduction
313 makes different (i.e. not equivalent) the 8mR_[001] channels. In the triclinic polymorph, two sets of
314 independent channels exist: one set roughly elongated along [100] and the second set roughly
315 elongated along [010] (Figure 6). Each set of channels is made by the alternation of two
316 independent 8mRs and, therefore, in the $I\bar{1}$ scapolite four independent 8mR_[001] exist. The
317 structural cage is delimited by the distorted 4mR-I in the plane roughly perpendicular to [001] and
318 by two sets of independent 8mR channels, roughly perpendicular to the [100] and [010] directions,
319 respectively (Figure 6), and is characterized by a significant deformation.

320 The Cl atom still occupies one independent site in the triclinic polymorph, whereas the CO₃ sites
321 have been derived according to the $I4/m \rightarrow I\bar{1}$ group-subgroup relationships, as any trial to locate
322 them by means of difference-Fourier syntheses failed. The cation site splits into two independent
323 positions: Ca₁ occupies the channels roughly elongated along [100], whereas Ca₃ is located in
324 the channels approximately elongated along [010] (Figure 6). With respect to the tetragonal
325 polymorph, cations in Ca₁ also make seven bonds with the framework oxygens, but after losing a
326 bond with one of the farther O4'' atoms and gaining a bond with O1₁ (Figure 6); Ca₃ only loses a
327 bond with one of the farther O4'' atoms and is, therefore, bonded to six framework oxygens only
328 (Figure 6).

329 **4.5 High-pressure behavior of triclinic scapolite**

330 The *P*-induced evolution of the unit-cell parameters of triclinic scapolite is reported in Table S2 and
331 Figure 4. The bulk compression is mainly accommodated along the **b and c** crystallographic axes,
332 whereas the **a** axis is apparently less affected by pressure. However, the compression along the
333 [100] and [001] directions significantly increases in the higher pressure range (Figure 4 and Table
334 S2). As a consequence, a change in the *V*-*P* pattern can be observed between 12.30 and 13.39 GPa,
335 as confirmed by the change in the *P*-induced behaviors of the α and β crystallographic angles
336 (Table S2). For this reason, no fit of the high-*P* behavior of the triclinic scapolite by an isothermal
337 equation of state has been performed. The calculated average volume compressibility, $\bar{\beta}_V = -1/(\bar{V}$
338 $) \cdot [(P_{\max} - P_{\min}) / (V_{P_{\max}} - V_{P_{\min}})]$, is 0.0193 GPa⁻¹, in the *P*-range 10.08-12.30 GPa, and 0.0203 GPa⁻¹,
339 in the range 13.39-17.79 GPa, respectively. A comparative analysis of the *P*-induced structure
340 evolution of the triclinic scapolite, based on the structure refinements performed in the $I\bar{1}$ space
341 group, is hindered by the high uncertainties of the refined parameters.

342 **5. Discussion**

343 5.1 Crystal chemistry and structure of the investigated scapolite

344 The results of the chemical analysis (Table 1) show that the investigated sample of scapolite has a
345 composition intermediate between the end-members marialite and meionite, with a ratio $(\text{Na}+\text{K})/\text{Si}$,
346 which follows the compositional trend reported by Teerstra and Sheriff (1997). In addition, unit-cell
347 parameters at ambient conditions also follow the trends reported by Sokolova and Hawthorne
348 (2008) for the scapolite solid solution series. Unfortunately, no precise information on the origin of
349 the investigated sample are available, but its chemical composition is quite close to those of sample
350 “5” of Graziani and Lucchesi (1982) and sample “MAD” of Sheriff et al. (1998), both also from
351 Madagascar. From the literature data (e.g. Teerstra and Sheriff 1997; Sheriff et al. 1998; Sokolova
352 and Hawthorne 2008; Hawthorne and Sokolova 2008 and references therein), scapolites of
353 intermediate composition are reported to crystallize in the primitive $P4_2/n$ tetragonal space group.
354 However, the X-ray diffraction data collected on the single-crystal fragments of this study, using
355 both conventional and synchrotron X-ray sources, do not show any evidence of violation of the I -
356 centered reciprocal lattice (Figure 3). From the structure refinement based on the intensity data
357 collected with the crystal in air at the ESD-MI, the following average T-O bond distances can be
358 calculated: 1.625(3) and 1.670(3) Å, for the T1 and T2 sites, respectively (Table 4). These values
359 confirm that Al is preferentially ordered at the T2 site, but a minor fraction of this element also
360 occupies the T1 site.

361 Transmission electron microscopy and electron diffraction data of primitive samples have shown
362 the common occurrence of anti-phase domains of different size (e.g. Phakey and Ghose 1972;
363 Oterdoom and Wenk 1983; Hassan and Buseck 1988; Seto et al. 2004). Oterdoom and Wenk (1983)
364 suggest that, at an anti-phase boundary, a reversal of the ordering of the T2 and T3 sites, and of the
365 related Si and Al distribution, occurs. Oterdoom and Wenk (1983) also suggest that anti-phase
366 domains may form due to a transition from a disordered (i.e. $I4/m$) towards an ordered structure, or
367 during the crystal growth. Seto et al. (2004) support the hypothesis that the anti-phase domains

368 result from an $I4/m$ -to- $P4_2/n$ phase transition induced by cooling, which implies that primitive
369 scapolites of intermediate composition may crystallize in the I -centered space group at high
370 temperature. The authors also suggest that a fast cooling may possibly lead to the persistence of a
371 metastable $I4/m$ scapolite at low temperatures, also at compositions where a primitive structure is
372 expected. Hawthorne and Sokolova (2008) suggested that the size of the anti-phase domains would
373 be a function of the cooling rate, where a faster cooling would lead to smaller domains, potentially
374 undetectable by X-ray diffraction.

375 If the single-crystal fragments here investigated are the result of a significantly fast cooling,
376 according to what suggested by Seto et al. (2004) and Hawthorne and Sokolova (2008), they would
377 be characterized by very small anti-phase domains, with a reverse T2 and T3 ordering and a $P4_2/n$
378 structure. Due to the small size, these domains would not be detected by X-ray diffraction data,
379 which will bear information of the average $I4/m$ crystal structure. However, based on the collected
380 data, we have no experimental basis to assert that the investigated sample is characterized by anti-
381 phase domains with $P4_2/n$ structure, nor that, following the hypothesis of Seto et al. (2004), it is a
382 metastable form of the $I4/m$ structure preserved by a very fast cooling. For this reason, since a
383 structure model based on the $P4_2/n$ space group would not be supported by the experimental X-ray
384 diffraction data, the structure refinements of tetragonal scapolite have been performed in the $I4/m$
385 space group. Nevertheless, the choice of the $I4/m$ structure model does not induce any significant
386 bias to the scopes of this study, i.e.: 1) the determination of the isothermal elastic parameters of
387 intermediate scapolite and 2) the description of the main mechanisms of structure deformation.

388 **5.2 High-pressure behavior of intermediate scapolite**

389 Hazen and Sharp (1988) first reported the isothermal elastic behavior of a meionitic scapolite
390 (Mess), with a bulk modulus of 90 GPa and an almost isotropic compressibility. The authors
391 suggested that with an increasing Na content, the bulk compressibility would be significantly

392 increased because of the higher compressibility of the Na-O bonds with respect to the Ca-O ones.
393 Later, Comodi et al. (1990) reported the isothermal elastic behavior of two more sodic members,
394 Me₁₇ and Me₆₈, which bulk moduli were refined to be 60 and 86 GPa, respectively, confirming the
395 hypothesis of Hazen and Sharp (1988). In addition, if the bulk compression of Me₆₈ was found to be
396 almost isotropic, like Me₈₈, in Me₁₇ the structure along the **a** axis was clearly more compressible
397 than along the **c** axis. The scapolite sample here investigated (Me₄₇) has a bulk modulus (70(2)
398 GPa) that is intermediate between those of Me₁₇ and Me₆₈ (Figure 4). In addition, the elastic
399 anisotropy of our scapolite is also intermediate between Me₁₇ and Me₆₈, further confirming that the
400 Na content, which induce a channel expansion at ambient conditions (Papike and Stephenson 1966),
401 favors the compression within the (001) plane and, therefore, the bulk compressibility of scapolite.
402 Presently, our knowledge of the isothermal elastic parameters within the scapolite solid solution is
403 limited to four members only and it is difficult to speculate on the deviation from the linear K_V vs
404 %Me trend shown by either Me₆₈ or Me₈₈ (Figure 4). Further investigations should be performed on
405 the members of the scapolite solid solution series, with a special focus on samples close to the
406 marialite and meionite end-members, in order to provide a robust description of the relationship
407 between volume compressibility (β_V) and chemical composition.

408 The main deformation mechanism, which acts at the atomic scale, is the same already reported by
409 Comodi et al. (1990) at high pressure, by Levien and Papike (1976) and Graziani and Lucchesi
410 (1982) at high temperature and by Papike and Stephenson (1966) at varying chemical composition,
411 i.e. the rotation of the 4mRs around the shared O4 hinge, which induces the compression of the
412 shorter diameter of the 8mR_[001] channels and, as a consequence, an increase in their ellipticity
413 (Figures 1 and 5, Table 4). Coupled with the internal compression of the 4mR-II (Figure 5, Table
414 4), this mechanism accommodates the bulk compression within the stability range of tetragonal
415 scapolite. However, the saturating trend of these mechanisms is compensated, at $P > 4$ GPa, by the
416 compression of the longest diameter of the 8mR_[001] channels (Figures 1 and 5, Table 4) and, partly,

417 by the compression of the T2 tetrahedra. It is noteworthy to report that, at the same time, a
418 saturation in the compressibility of the Ca-O2 and Ca-O4' bonds is observed (Figures 2 and 5, **Table**
419 **S3**). In addition to the increase in compressibility along the **c** crystallographic axis at $P > 2$ GPa, the
420 observed deformation mechanisms suggest a destabilization of the tetragonal structure with
421 increasing pressure, which leads to the phase transition to the triclinic polymorph. The structural
422 cages hosting the anions were confirmed to act as relatively rigid units, as previously observed by
423 Comodi et al. (1990), even if their compressibility increases with pressure, following the c vs. P
424 behavior (see sections 4.2 and 4.3).

425 Comodi et al. (1990) reported that the compressibility of the cation polyhedron increases with the
426 Na content, being 68 GPa in Me₆₈ and 46 GPa in Me₁₇, respectively. Due to the significant
427 restrictions applied to the refinement of the CO₃ positions, we have calculated a fictive volume,
428 defined as the cube of the average <Ca-Of> bond length, which P -evolution (**Table S3**), at a first
429 approximation, provides information on the compressibility of the cation polyhedron. A fit of the V -
430 P data with a BM-EoS truncated to the second order, performed using the *EoS-Fit7_GUI* software
431 (Angel et al. 2014; Gonzalez-Platas et al. 2016), leads to the following refined bulk modulus: $K_{V0} =$
432 56(15) GPa, which is also intermediate between the values reported for Me₁₇ and Me₆₈,
433 respectively, by Comodi et al. (1990).

434 The $I4/m$ -to- $I\bar{1}$ phase transition, due to the symmetry lowering, provides more degrees of freedom
435 to the scapolite structure to accommodate compression, which is reflected by a slight increase in the
436 bulk compressibility (Figure 4). The bulk compression of the triclinic polymorph is mainly
437 accommodated along the **b and c** crystallographic directions, which suggests a different behavior of
438 the independent **8mRs**. Unfortunately, the large uncertainties of the refined structural models do not
439 allow an unambiguous comparative analysis of the structure deformation. The increase in
440 compressibility at $P > 12.30$ GPa suggests an impending destabilization of the triclinic structure.

441 Overall, the anomalous elastic behavior of the $\overline{I1}$ scapolite and the high pressure at which the
442 phase transition occurs (at ambient temperature), apparently suggest that the triclinic polymorph is
443 unlikely to occur in Nature. In addition, based on the described deformation mechanisms acting at
444 the atomic scale and on the elastic behavior of the tetragonal polymorph, a structural instability at P
445 > 2.0 - 2.5 GPa (at ambient temperature) can be suggested. However, the absence of amorphization
446 phenomena, at least up to 17.79 GPa, highlights the significant flexibility of the scapolite structure,
447 which helps to understand why this mineral is so commonly found in rocks of different T and P
448 origin, especially in the metamorphic realm.

449 6. Conclusions

450 Scapolites are volatiles-bearing minerals widespread in metamorphic environments. Understanding
451 the relative stability of scapolite in a mineral assemblage at varying pressure and temperature may
452 allow to reconstruct the formation conditions (e.g. Kullerud and Erambert 1999; Satish-Kumar et al.
453 2006; Hammerli et al. 2017). Modelling the stability of a mineral assemblage requires the
454 knowledge of several thermodynamic parameters of the involved mineral phases, including the
455 volume thermal expansivity, α_V , and compressibility, β_V (e.g. Almeida and Jenkins 2017). For what
456 concerns scapolites, this requires an experimental determination of these parameters across the solid
457 solution series. In this work, we report the bulk volume compressibility (at ambient T) of a Me_{47}
458 scapolite, which was found to be intermediate between the values reported in the literature for the
459 Me_{17} and Me_{68} members (Comodi et al. 1990). Adopting the bulk modulus refined from the II-BM
460 EoS, for ease of comparison with the literature data, a linear fit through the bulk moduli of Me_{17} ,
461 Me_{47} , Me_{68} and Me_{88} is possible. Taking into account all the limitations due to a linear fit based on
462 four experimental points only, a rough extrapolation of the bulk moduli of the scapolite members in
463 the range Me_{17-88} is provided by the following equation: K_{V0} (GPa) = $53(2) + 0.45(4)*(\% \text{Me})$ [or β_V
464 (GPa^{-1}) = $0.0179(6) - 0.00008(1)*(\% \text{Me})$], where $17 \leq \% \text{Me} \leq 88$. Further mapping of the

465 isothermal elastic behavior across the intermediate members of the scapolite solid solution is
466 needed for better constraining the bulk modulus (and its pressure derivatives) as a function of the
467 chemical composition, as provided, e.g., by Angel (2004) for plagioclase feldspars. Further
468 investigations, are also required for the compositions close to the marialite and meionite end
469 members, in order to observe possible deviations from the linear trend (cfr. Figure 4). The
470 experimental findings of this study also show an increase in the axial compressibility along the **c**
471 axis at $P > 2.5$ GPa, which is followed by a re-arrangement in the structure deformation
472 mechanisms at $P > 4$ GPa. Based on these data, a pressure limit (at room T) for the structural
473 stability of scapolite may be inferred. However, robust extrapolations of the experimental structural
474 data would be possible if further investigations on the behavior of scapolite solid solution members
475 at high- (P,T) conditions will be provided and a comparative analysis would be possible.

476 From a broader point of view, the extrapolation of the elastic parameters as a function of the
477 chemical composition may be applied to other solid solution series of minerals. In fact, the reported
478 results further confirm that the substitution of Na by Ca in solid solutions of (open-)framework
479 silicates is responsible for a decrease in the bulk compressibility at ambient conditions. This
480 relationship has been experimentally observed across the plagioclase series by Angel (1988), but
481 can also be observed in the group of fibrous zeolites (Gatta 2005), where Ca-rich scolecite ($K_{V0} =$
482 $54.6(6)$ GPa) is stiffer than Na-rich natrolite ($K_{V0} = 43(2)$ GPa), and in the group of sodalite, where
483 the bulk modulus increases from the Na-rich ($52(8)$ GPa; Hazen and Sharp 1988) to the Ca-rich end
484 members ($69(6)$ GPa; Hargis et al. 2014).

485

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639 **Fig. 1** (*Up.*) View of the scapolite crystal structure (in the $I4/m$ space group) along the **c**
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642 **Fig. 2** View of the coordination environment of the cation site in the tetragonal polymorph of
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644 **Fig. 3** Reconstructions of selected reciprocal lattice planes of the tetragonal polymorph of scapolite,
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648 **Fig. 4** (A.) High-pressure evolution of the unit-cell volume of tetragonal scapolite, based on the data
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657 evolution of the $8mR_{[001]}$ channel diameters. (C.) The $8mR_{[001]}$ channel ellipticity (defined as $O4_{short}/O4_{long}$)
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660 scapolite.

661 **Fig. 6** (A.) Crystal structure of the triclinic polymorph of scapolite viewed down the **c**
662 crystallographic axis. (B.) The structural cage hosting the anions in triclinic scapolite. (C and D.)
663 View of the coordination environment of the Ca₁ and Ca₃ cation sites of triclinic scapolite.
664

665 **Table 1.** Composition of four selected fragments from the investigated single-crystal sample of
 666 scapolite. The composition of each fragment is based on five point analyses.

wt.%	#1	s.d.(#1)	#2	s.d.(#2)	#3	s.d.(#3)	#4	s.d.(#4)
SiO ₂	51.97	0.41	51.56	0.43	50.43	0.27	51.65	0.39
Al ₂ O ₃	24.61	0.26	24.95	0.14	25.37	0.11	24.63	0.17
FeO	0.05	0.03	0.05	0.03	0.04	0.02	0.04	0.02
CaO	11.48	0.44	11.49	0.18	12.37	0.08	11.25	0.05
MgO	0.01	0.01	0.02	0.01	0.01	0.01	0.02	0.01
BaO	0.01	0.01	0.01	0.01	0.04	0.02	0.01	0.01
SrO	0.08	0.05	0.04	0.02	0.03	0.01	0.04	0.02
MnO	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Na ₂ O	6.61	0.23	6.49	0.06	6.10	0.07	6.57	0.10
K ₂ O	1.24	0.08	1.25	0.03	1.10	0.02	1.27	0.01
SO ₃	0.08	0.01	0.07	0.02	0.08	0.05	0.07	0.03
Cl	1.87	0.01	1.94	0.02	1.72	0.02	1.92	0.04
O = Cl	-0.43		-0.45		-0.40		-0.46	
<i>Sum</i>	98.01		97.43		96.90		97.02	
CO ₂ *	2.71		2.24		2.53		2.26	
a.p.f.u.								
Si	7.70		7.64		7.53		7.68	
Al	4.30		4.36		4.47		4.32	
Fe	0.01		0.01		0.01		0.01	
Ca	1.82		1.83		1.98		1.79	
Mg	0.00		0.00		0.00		0.00	
Ba	0.00		0.00		0.00		0.00	
Sr	0.01		0.00		0.00		0.00	
Mn	0.00		0.00		0.00		0.00	

Na	1.90	1.87	1.77	1.89
K	0.23	0.24	0.21	0.24
S	0.01	0.01	0.01	0.01
Cl	0.48	0.50	0.45	0.50
C	0.51	0.45	0.52	0.46

* Calculated according to the protocol of Teerstra and Sheriff (1997), assuming that 1) it is the amount necessary to compensate the excess positive charge obtained subtracting the framework and anions negative charges from the sum of cations charges, and 2) the investigated sample is anhydrous.

667

668

Table 2. Details pertaining to the structure refinements of the tetragonal and triclinic polymorphs of scapolite, at different pressures.

<i>P</i> (GPa)	0.0001	0.0001*	0.15(2)	0.67(2)	1.29(2)	1.83(2)	2.46(2)	3.24(2)	3.80(2)	4.48(2)	5.27(2)
Experiment	Air ESD-MI	HP- <i>mew</i>									
Space group	<i>I4/m</i>										
$\min \leq h, k, l \leq \max$	$-16 \leq h \leq 16$	$-19 \leq h \leq 19$	$-18 \leq h \leq 19$	$-19 \leq h \leq 18$	$-19 \leq h \leq 18$	$-18 \leq h \leq 19$	$-19 \leq h \leq 18$	$-19 \leq h \leq 18$	$-19 \leq h \leq 18$	$-18 \leq h \leq 19$	$-19 \leq h \leq 18$
	$-16 \leq k \leq 16$	$-18 \leq k \leq 19$	$-17 \leq k \leq 17$	$-17 \leq k \leq 17$	$-17 \leq k \leq 17$	$-17 \leq k \leq 16$	$-16 \leq k \leq 17$	$-17 \leq k \leq 16$			
	$-9 \leq l \leq 10$	$-4 \leq l \leq 4$	$-5 \leq l \leq 4$								
Unique reflections	765	466	469	467	432	460	421	424	421	443	412
Observed reflections $F_o^2/\sigma(F_o^2) > 3$	703	366	377	378	351	367	348	347	349	362	335
R_{int} (all)	0.0242	0.0502	0.0534	0.0519	0.0438	0.0448	0.0443	0.0416	0.0417	0.0454	0.0510
Refined param.	63	58	58	58	58	58	58	58	58	58	58
R_1 (obs)	0.0380	0.0565	0.0471	0.0701	0.0500	0.0514	0.0575	0.0603	0.0550	0.0551	0.0718
R_1 (all)	0.0427	0.0710	0.0593	0.0806	0.0612	0.0606	0.0678	0.0731	0.0655	0.0659	0.0830
wR_1 (obs)	0.0591	0.0659	0.0542	0.0773	0.0581	0.0575	0.0643	0.0685	0.0615	0.0622	0.0786
Residuals ($e/\text{\AA}^3$)	+0.68 -1.01	+0.63 -0.74	+0.61 -0.62	+1.04 -1.13	+0.78 -0.78	+0.79 -0.91	+0.83 -0.77	+0.90 -0.88	+0.94 -0.82	+0.96 -0.70	+1.18 -1.05
<i>P</i> (GPa)	6.03	6.75	7.63	8.49	9.23	1.34 ^d	0.20	1.09	2.02	3.06	3.97
Experiment	HP- <i>mew</i>	HP-He	HP-He	HP-He	HP-He	HP-He					
Space group	<i>I4/m</i>										
$\min \leq h, k, l \leq \max$	$-18 \leq h \leq 19$	$-19 \leq h \leq 18$	$-19 \leq h \leq 18$	$-19 \leq h \leq 18$	$-18 \leq h \leq 18$	$-17 \leq h \leq 18$	$-7 \leq h \leq 10$	$-10 \leq h \leq 9$	$-8 \leq h \leq 10$	$-9 \leq h \leq 8$	$-8 \leq h \leq 9$
	$-17 \leq k \leq 16$	$-16 \leq k \leq 17$	$-16 \leq k \leq 17$	$-16 \leq k \leq 16$	$-16 \leq k \leq 17$	$-16 \leq k \leq 17$	$-17 \leq k \leq 16$	$-16 \leq k \leq 16$	$-16 \leq k \leq 17$	$-16 \leq k \leq 17$	$-17 \leq k \leq 16$
	$-5 \leq l \leq 4$	$-5 \leq l \leq 3$	$-7 \leq l \leq 8$	$-6 \leq l \leq 8$	$-7 \leq l \leq 8$	$-7 \leq l \leq 8$	$-7 \leq l \leq 8$				
Unique reflections	440	439	399	388	424	415	477	420	478	477	464
Observed reflections $F_o^2/\sigma(F_o^2) > 3$	357	356	322	304	294	374	359	330	374	364	317
R_{int} (all)	0.0577	0.0509	0.0344	0.0373	0.0385	0.0804	0.0385	0.0376	0.0430	0.0325	0.0353
Refined param.	58	58	58	58	58	58	61	61	61	61	61
R_1 (obs)	0.0600	0.0593	0.0562	0.0560	0.0599	0.0876	0.0490	0.0462	0.0535	0.0455	0.0526

R_1 (all)	0.0721	0.0717	0.0688	0.0690	0.0832	0.0916	0.0625	0.0589	0.0663	0.0611	0.0779
wR_1 (obs)	0.0675	0.0661	0.0643	0.0622	0.0654	0.1065	0.0614	0.0534	0.0675	0.0572	0.0574
Residuals ($e/\text{\AA}^3$)	+1.08 -0.92	+1.00 -0.83	+0.92 -0.93	+0.76 -0.77	+0.78 -0.74	+1.21 -1.32	+0.70 -0.72	+0.57 -0.65	+0.68 -0.83	+0.60 -0.78	+0.64 -0.61
P (GPa)	5.09(2)	6.12(2)	7.00(2)	8.17(2)	9.02(2)	10.08(2)	11.06(2)	12.30(2)	13.39(2)	14.61(2)	0.28 ^d (2)
Experiment	HP-He	HP-He	HP-He	HP-He	HP-He	HP-He	HP-He	HP-He	HP-He	HP-He	HP-He
Space group	$I4/m$	$I4/m$	$I4/m$	$I4/m$	$I4/m$	$\bar{1}$	$\bar{1}$	$\bar{1}$	$\bar{1}$	$\bar{1}$	$I4/m$
$\min \leq h,k,l \leq \max$	$-10 \leq h \leq 9$ $-17 \leq k \leq 16$ $-9 \leq l \leq 7$	$-9 \leq h \leq 8$ $-16 \leq k \leq 17$ $-7 \leq l \leq 8$	$-8 \leq h \leq 9$ $-17 \leq k \leq 16$ $-7 \leq l \leq 8$	$-8 \leq h \leq 9$ $-16 \leq k \leq 16$ $-9 \leq l \leq 7$	$-8 \leq h \leq 9$ $-16 \leq k \leq 16$ $-7 \leq l \leq 8$	$-9 \leq h \leq 10$ $-16 \leq k \leq 16$ $-7 \leq l \leq 7$	$-9 \leq h \leq 10$ $-16 \leq k \leq 15$ $-7 \leq l \leq 7$	$-9 \leq h \leq 10$ $-16 \leq k \leq 15$ $-7 \leq l \leq 7$	$-8 \leq h \leq 10$ $-16 \leq k \leq 15$ $-7 \leq l \leq 7$	$-9 \leq h \leq 10$ $-16 \leq k \leq 15$ $-6 \leq l \leq 7$	$-9 \leq h \leq 10$ $-17 \leq k \leq 17$ $-7 \leq l \leq 8$
Unique reflections	506	453	451	439	429	385	498	446	439	423	464
Observed reflections $F_o^2/\sigma(F_o^2) > 3$	388	343	343	319	295	269	324	346	346	289	309
R_{int} (all)	0.0371	0.0315	0.0444	0.0340	0.0407	0.1033	0.1059	0.1057	0.0672	0.0428	0.0547
Refined param.	61	61	61	61	61	106	106	106	106	106	61
R_1 (obs)	0.0466	0.0512	0.0543	0.0514	0.0610	0.1116	0.1222	0.1254	0.1117	0.1215	0.0695
R_1 (all)	0.0586	0.0676	0.0716	0.0709	0.0845	0.1564	0.1606	0.1478	0.1310	0.1496	0.0918
wR_1 (obs)	0.0596	0.0596	0.0649	0.0578	0.0660	0.1150	0.1355	0.1358	0.1254	0.1318	0.0703
Residuals ($e/\text{\AA}^3$)	+0.72 -0.78	+0.79 -0.85	+0.82 -0.80	+0.61 -0.86	+0.77 -0.84	+0.55 -0.53	+0.73 -0.64	+0.62 -0.73	+0.49 -0.46	+0.53 -0.46	+0.65 -0.68

670

671

672 **Table 3.** Site occupancy factors (*s.o.f.*), coordinates and isotropic or equivalent displacement

673 parameters (\AA^2) from selected structure refinements of tetragonal and triclinic scapolite.

Tetragonal scapolite							
Site	Experiment	<i>P</i> (GPa)	<i>s.o.f.</i>	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} / <i>U</i> _{eq}
Ca	Air – ESD-MI	0.0001	0.35(8)	0.3605(1)	0.28524(9)	0	0.0276(4)
	HP - He	0.20(2)	0.465	0.3616(2)	0.2858(2)	0	0.0286(9)
	HP – He	5.09(2)	“	0.3652(2)	0.2878(2)	0	0.0279(8)
	HP - He	9.02(2)	“	0.3689(3)	0.2907(2)	0	0.047(1)
Na	Air – ESD-MI	0.0001	0.49(8)	*	*	*	*
	HP - He	0.20(2)	0.465	*	*	*	*
	HP – He	5.09(2)	“	*	*	*	*
	HP - He	9.02(2)	“	*	*	*	*
K	Air – ESD-MI	0.0001	0.16(8)	*	*	*	*
	HP - He	0.20(2)	0.058	*	*	*	*
	HP – He	5.09(2)	“	*	*	*	*
	HP - He	9.02(2)	“	*	*	*	*
T1	Air – ESD-MI	0.0001	1.0	0.16120(7)	0.09055(8)	0	0.0068(3)
	HP - He	0.20(2)	“	0.1611(2)	0.0911(2)	0	0.0063(6)
	HP – He	5.09(2)	“	0.1597(2)	0.0974(2)	0	0.0081(5)
	HP - He	9.02(2)	“	0.1589(2)	0.1001(2)	0	0.0187(8)
T2	Air – ESD-MI	0.0001	1.0	0.16000(6)	0.41420(6)	0.2069(1)	0.0096(2)
	HP - He	0.20(2)	“	0.1610(1)	0.4140(1)	0.2067(2)	0.0092(5)
	HP – He	5.09(2)	“	0.1607(1)	0.4087(1)	0.2070(2)	0.0113(4)
	HP - He	9.02(2)	“	0.1605(2)	0.4071(2)	0.2075(3)	0.0242(7)
O1	Air – ESD-MI	0.0001	1.0	0.0419(2)	0.1500(2)	0	0.0147(7)
	HP - He	0.20(2)	“	0.0423(4)	0.1497(5)	0	0.015(2)
	HP – He	5.09(2)	“	0.0381(4)	0.1541(4)	0	0.018(2)
	HP - He	9.02(2)	“	0.0365(5)	0.1552(6)	0	0.045(3)
O2	Air – ESD-MI	0.0001	1.0	0.1901(2)	0.3767(2)	0	0.0157(8)
	HP - He	0.20(2)	“	0.1898(5)	0.3760(5)	0	0.014(2)
	HP – He	5.09(2)	“	0.1877(4)	0.3675(4)	0	0.018(2)
	HP - He	9.02(2)	“	0.1868(6)	0.3623(5)	0	0.034(3)
O3	Air – ESD-MI	0.0001	1.0	0.1506(2)	0.5515(2)	0.2112(3)	0.0182(6)
	HP - He	0.20(2)	“	0.1502(3)	0.5515(3)	0.2120(6)	0.017(1)
	HP – He	5.09(2)	“	0.1535(3)	0.5488(3)	0.2059(5)	0.020(1)
	HP - He	9.02(2)	“	0.1543(4)	0.5474(4)	0.2034(8)	0.040(2)
O4	Air – ESD-MI	0.0001	1.0	0.2309(2)	0.1309(2)	0.1736(3)	0.0177(6)
	HP - He	0.20(2)	“	0.2312(4)	0.1318(3)	0.1735(5)	0.016(1)
	HP – He	5.09(2)	“	0.2293(3)	0.1387(3)	0.1758(5)	0.021(1)

	HP - He	9.02(2)	"	0.2287(5)	0.1419(4)	0.1768(7)	0.042(2)
Cl	Air – ESD-MI	0.0001	0.44(1)	0.5	0.5	0	0.061(2)
	HP - He	0.20(2)	0.48	0.5	0.5	0	0.055(3)
	HP – He	5.09(2)	"	0.5	0.5	0	0.042(2)
	HP - He	9.02(2)	"	0.5	0.5	0	0.043(3)
C	Air – ESD-MI	0.0001	0.14(1)	0.515(2)	0.513(2)	0	**
	HP - He	0.20(2)	0.12	0.525(4)	0.502(7)	0	**
	HP – He	5.09(2)	"	0.527(3)	0.502(4)	0	**
	HP - He	9.02(2)	"	0.523(4)	0.506(5)	0	**
Oc1	Air – ESD-MI	0.0001	0.14(1)	0.470(3)	0.608(3)	0	**
	HP - He	0.20(2)	0.12	0.469(6)	0.593(10)	0	**
	HP – He	5.09(2)	"	0.460(4)	0.588(6)	0	**
	HP - He	9.02(2)	"	0.454(5)	0.593(9)	0	**
Oc2	Air – ESD-MI	0.0001	0.14(1)	0.424(3)	0.544(4)	0	**
	HP - He	0.20(2)	0.12	0.406(10)	0.523(9)	0	**
	HP – He	5.09(2)	"	0.399(5)	0.512(6)	0	**
	HP - He	9.02(2)	"	0.403(7)	0.516(8)	0	**
Oc3	Air – ESD-MI	0.0001	0.14(1)	0.493(3)	0.620(3)	0	**
	HP - He	0.20(2)	0.12	0.494(4)	0.632(4)	0	**
	HP – He	5.09(2)	"	0.482(4)	0.636(3)	0	**
	HP - He	9.02(2)	"	0.476(4)	0.633(3)	0	**

* Ca, Na and K restrained to share the same coordinates and anisotropic dp 's;

** Cl, C, Oc1, Oc2 Oc3 restrained to share the same isotropic dp 's;

see section 3 for further details

Triclinic scapolite							
Site	Experiment	P (GPa)	s.o.f.	x	y	z	U_{iso}/U_{eq}
Ca_1	HP - He	10.08(2)	0.465	0.379(3)	0.2935(8)	0.057(3)	0.052(3)
Na_1	HP - He	10.08(2)	0.465	#	#	#	#
K_1	HP - He	10.08(2)	0.058	#	#	#	#
Ca_3	HP - He	10.08(2)	0.465	-0.289(3)	0.3686(9)	-0.013(3)	0.062(4)
Na_3	HP - He	10.08(2)	0.465	##	##	##	##
K_3	HP - He	10.08(2)	0.058	##	##	##	##
T1_1	HP - He	10.08(2)	1.0	0.159(2)	0.1030(7)	-0.003(2)	0.027(2)
T1_3	HP - He	10.08(2)	1.0	-0.090(2)	0.1588(6)	0.017(2)	0.029(2)
T2_1	HP - He	10.08(2)	1.0	0.144(2)	0.4214(7)	0.195(2)	0.039(3)
T2_2	HP - He	10.08(2)	1.0	-0.176(2)	-0.3953(7)	0.208(2)	0.034(3)
T2_3	HP - He	10.08(2)	1.0	-0.397(2)	0.1469(7)	0.200(2)	0.033(2)
T2_4	HP - He	10.08(2)	1.0	0.417(2)	-0.1724(7)	0.207(2)	0.035(3)
O1_1	HP - He	10.08(2)	1.0	0.045(2)	0.165(2)	0.064(4)	0.035(6)
O1_3	HP - He	10.08(2)	1.0	-0.137(4)	0.031(1)	0.028(5)	0.032(6)
O2_1	HP - He	10.08(2)	1.0	0.195(4)	0.361(2)	0.011(3)	0.044(6)

O2_3	HP - He	10.08(2)	1.0	-0.352(3)	0.186(2)	-0.001(3)	0.056(8)
O3_1	HP - He	10.08(2)	1.0	0.128(7)	0.562(1)	0.170(7)	0.040(6)
O3_2	HP - He	10.08(2)	1.0	-0.180(3)	-0.538(1)	0.214(4)	0.029(5)
O3_3	HP - He	10.08(2)	1.0	-0.535(2)	0.135(2)	0.212(5)	0.048(7)
O3_4	HP - He	10.08(2)	1.0	0.556(2)	-0.162(2)	0.208(4)	0.063(9)
O4_1	HP - He	10.08(2)	1.0	0.257(3)	0.117(3)	0.154(5)	0.11(2)
O4_2	HP - He	10.08(2)	1.0	-0.208(4)	-0.152(2)	0.192(5)	0.040(6)
O4_3	HP - He	10.08(2)	1.0	-0.148(3)	0.242(2)	0.171(4)	0.049(7)
O4_4	HP - He	10.08(2)	1.0	0.122(3)	-0.213(1)	0.186(3)	0.58(8)
Cl_1	HP - He	10.08(2)	0.48	0.5	0.5	0	0.049(9)
C_1	HP - He	10.08(2)	0.12	0.54(3)	0.50(2)	0.01(5)	###
Oc1_1	HP - He	10.08(2)	0.12	0.48(2)	0.59(3)	0.02(7)	###
Oc2_1	HP - He	10.08(2)	0.12	0.47(3)	0.43(1)	0.15(3)	###
Oc3_1	HP - He	10.08(2)	0.12	0.58(3)	0.62(2)	0.14(4)	###
C_3	HP - He	10.08(2)	0.12	-0.49(3)	0.57(1)	0.02(3)	###
Oc1_3	HP - He	10.08(2)	0.12	-0.56(2)	0.49(1)	0.09(4)	###
Oc2_3	HP - He	10.08(2)	0.12	-0.51(5)	0.40(3)	-0.06(7)	###
Oc3_3	HP - He	10.08(2)	0.12	-0.64(3)	0.51(2)	-0.09(4)	###

Ca_1, Na_1 and K_1 restrained to share the same coordinates and isotropic dp 's;

Ca_3, Na_3 and K_3 restrained to share the same coordinates and isotropic dp 's;

Cl_1, C_1, C_3, Oc1_1, Oc2_1, Oc3_1, Oc1_3, Oc2_3 and Oc3_3 restrained to share the same isotropic dp 's;

see section 3 for further details

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Table 4. Selected angles ($^{\circ}$), distances (\AA) and volumes (\AA^3) from the refined structure models of tetragonal scapolite at different pressures.

Experiment	P (GPa)	O1-O4-O3	8mR _[001] O4-O4 short	8mR _[001] O4-O4 long	8mR _[001] ϵ^{**}	4mR-I O1-O1	4mR-II O3-O3	<T1-O>	V(T1)	<T2-O>	V(T2)	V(Ca) ^{***}
Air ESD-MI	0.0001	93.60(6)	3.144(3)	9.318(3)	0.3374(4)	3.776(4)	3.858(3)	1.625(3)	2.199(4)	1.670(3)	2.378(4)	19.1(2)
HP - mew	0.0001*	93.7(1)	3.130(7)	9.325(6)	0.3357(7)	3.763(7)	3.855(6)	1.628(7)	2.215(9)	1.670(5)	2.375(7)	19.1(11)
HP - mew	0.15(2)	93.57(9)	3.137(5)	9.318(4)	0.3367(7)	3.775(6)	3.856(4)	1.624(5)	2.197(8)	1.670(4)	2.379(6)	19.1(7)
HP - mew	0.67(2)	93.1(1)	3.101(7)	9.318(6)	0.3328(9)	3.755(7)	3.840(6)	1.619(7)	2.18(1)	1.668(5)	2.365(8)	19.0(10)
HP - mew	1.29(2)	92.6(1)	3.054(6)	9.319(6)	0.3277(7)	3.763(6)	3.851(6)	1.621(5)	2.186(8)	1.668(4)	2.366(7)	18.6(8)
HP - mew	1.83(2)	92.2(1)	3.026(5)	9.307(6)	0.3251(8)	3.760(6)	3.843(4)	1.621(5)	2.183(7)	1.665(4)	2.353(7)	18.4(8)
HP - mew	2.46(2)	91.7(1)	2.987(6)	9.321(6)	0.320(1)	3.763(7)	3.843(6)	1.620(6)	2.181(9)	1.663(5)	2.347(8)	18.2(9)
HP - mew	3.24(2)	91.4(1)	2.964(7)	9.308(6)	0.3184(8)	3.747(7)	3.835(6)	1.614(7)	2.16(1)	1.662(5)	2.340(8)	18.0(10)
HP - mew	3.80(2)	91.1(1)	2.938(6)	9.305(6)	0.3157(8)	3.749(7)	3.828(6)	1.614(6)	2.155(9)	1.659(4)	2.329(7)	17.9(9)
HP - mew	4.48(2)	90.9(1)	2.924(6)	9.288(6)	0.315(1)	3.743(6)	3.825(6)	1.608(6)	2.133(9)	1.659(4)	2.327(7)	17.7(9)
HP - mew	5.27(2)	90.6(1)	2.900(9)	9.279(7)	0.313(1)	3.730(9)	3.809(7)	1.604(8)	2.12(1)	1.656(6)	2.316(9)	17.5(11)
HP - mew	6.03(2)	90.3(1)	2.877(7)	9.265(6)	0.311(1)	3.746(7)	3.814(6)	1.602(7)	2.11(1)	1.655(5)	2.309(8)	17.4(10)
HP - mew	6.75(2)	89.9(1)	2.846(7)	9.262(6)	0.307(1)	3.734(7)	3.811(5)	1.600(7)	2.10(1)	1.651(5)	2.292(8)	17.2(10)
HP - mew	7.63(2)	89.7(1)	2.810(7)	9.245(7)	0.304(1)	3.727(7)	3.805(5)	1.607(7)	2.13(1)	1.648(5)	2.279(8)	17.0(10)
HP - mew	8.49(2)	89.6(1)	2.804(7)	9.239(7)	0.304(1)	3.709(7)	3.783(5)	1.594(7)	2.08(1)	1.646(5)	2.270(8)	17.0(10)
HP - mew	9.23(2)	89.5(1)	2.793(7)	9.207(7)	0.303(1)	3.700(7)	3.782(7)	1.587(7)	2.05(1)	1.640(6)	2.248(9)	16.9(10)
HP - He	0.20(2)	93.57(8)	3.117(6)	9.319(7)	0.3345(9)	3.763(7)	3.841(6)	1.624(6)	2.196(8)	1.667(4)	2.365(6)	19.1(8)
HP - He	1.09(2)	92.63(8)	3.067(6)	9.309(6)	0.3295(9)	3.771(7)	3.877(6)	1.624(5)	2.197(7)	1.668(4)	2.365(5)	18.7(8)
HP - He	2.02(2)	92.22(8)	3.022(6)	9.314(7)	0.3245(9)	3.769(7)	3.835(6)	1.618(6)	2.170(8)	1.665(4)	2.354(6)	18.4(7)
HP - He	3.06(2)	91.61(8)	2.969(6)	9.297(6)	0.3194(9)	3.758(7)	3.819(6)	1.616(5)	2.162(7)	1.659(4)	2.330(5)	18.1(8)
HP - He	3.97(2)	91.08(9)	2.926(6)	9.300(7)	0.3146(8)	3.766(7)	3.801(6)	1.614(6)	2.158(8)	1.656(4)	2.318(6)	18.0(7)
HP - He	5.09(2)	90.63(9)	2.900(6)	9.282(6)	0.3124(9)	3.758(7)	3.814(6)	1.610(5)	2.141(7)	1.656(4)	2.315(5)	17.6(8)
HP - He	6.12(2)	90.29(9)	2.871(6)	9.269(7)	0.310(1)	3.759(7)	3.794(7)	1.606(6)	2.123(8)	1.654(4)	2.306(5)	17.5(8)

HP - He	7.00(2)	89.93(9)	2.834(7)	9.260(7)	0.306(1)	3.760(7)	3.782(7)	1.605(6)	2.118(8)	1.649(5)	2.286(6)	17.4(8)
HP - He	8.17(2)	89.63(9)	2.812(7)	9.237(7)	0.304(1)	3.744(7)	3.779(7)	1.598(6)	2.090(8)	1.645(5)	2.271(6)	17.1(9)
HP - He	9.02(2)	89.49(9)	2.787(7)	9.223(9)	0.302(1)	3.721(9)	3.767(7)	1.595(7)	2.080(9)	1.642(6)	2.254(8)	17.0(9)

* Sample in the DAC without *P*-medium; ** $\varepsilon = O4-O4_{short}/O4-O4_{long}$;
 *** fictive volume defined as $\langle Ca-Of \rangle^3$, see section 5.2 for further details;











