

Revision_1**Crystal-chemistry and temperature behavior of the natural hydrous borate colemanite, a mineral commodity of boron**

Paolo Lotti^{1,2,*}, G. Diego Gatta^{1,3}, Nicola Demitri², Giorgio Guastella⁴, Silvia Rizzato⁵, Marco Aldo Ortenzi^{5,6}, Fabrizio Magrini¹, Davide Comboni¹, Alessandro Guastoni⁷, Maria Teresa Fernandez-Diaz⁸

¹ Dipartimento di Scienze della Terra, Università degli Studi di Milano, Via Botticelli 23, 20133 Milano, Italy

² Elettra Sincrotrone Trieste S.c.P.A., Strada Statale 14 km 163.5, 34149 Basovizza, Trieste, Italy

³ CNR-Istituto di Cristallografia, Sede di Bari, Via Amendola 122/O, 70126 Bari, Italy

⁴ Agenzia delle Dogane e dei Monopoli, Direzione Regionale per la Lombardia, Laboratorio e Servizi Chimici, Via Marco Bruto 14, 20138 Milano, Italy

⁵ Dipartimento di Chimica, Università degli Studi di Milano, Via Golgi 19, 20122 Milano, Italy

⁶ CRC Materiali Polimerici “LaMPo”, Dipartimento di Chimica, Università degli Studi di Milano, Via Golgi 19, 20122 Milano, Italy

⁷ Dipartimento di Geoscienze, Università degli Studi di Padova, Via Gradenigo 6, 35131 Padova, Italy

⁸ Institut Laue-Langevin, 71 Avenue des Martyrs, 38042 Grenoble-Cedex 9, France

* Corresponding Author: paolo.lotti@unimi.it; +390250315598 (Tel); +390250315597 (fax)

21 **Abstract**

22 Colemanite, $\text{CaB}_3\text{O}_4(\text{OH})_3 \cdot \text{H}_2\text{O}$, is the most common hydrous Ca-borate, as well as a major mineral
23 commodity of boron. In this study, we report a thorough chemical analysis and the low-temperature
24 behavior of a natural sample of colemanite, by means of a multi-methodological approach. From the
25 chemical point of view, the investigated sample resulted to be relatively pure, its composition being
26 very close to the ideal one, with only a minor substitution of Sr^{2+} for Ca^{2+} . At about 270.5 K a
27 displacive phase transition from the centrosymmetric $P2_1/a$ to the acentric $P2_1$ space group occurs.
28 On the basis of in situ single-crystal synchrotron X-ray (down to 104 K) and neutron diffraction (at
29 20 K) data, the hydrogen-bonding configuration of both the polymorphs and the structural
30 modifications at the atomic scale at varying temperatures are described. The asymmetric
31 distribution of ionic charges along the [010] axis, allowed by the loss of the inversion center, is
32 likely responsible for the reported ferroelectric behavior of colemanite below the phase transition
33 temperature.

34
35 **Keywords**

36 Colemanite, borates, low-temperature, phase transition, neutron diffraction, synchrotron,
37 ferroelectric behavior.

38 **1. Introduction**

39 Borates are nowadays important industrial minerals with main applications in the fields of glass and
40 ceramic industries (for improving chemical and thermal properties or as fluxing agents), fertilizers
41 and detergents production (Crangle 2015). During the last decade, the world borates production
42 substantially doubled from 4750 thousand metric tons in 2006 (U.S. Geological Survey 2007) to
43 9400 thousand metric tons in 2016 (excluding US production, U.S. Geological Survey 2017), with
44 Turkey being the leading producer sharing more than 50% of the world production. Despite more
45 than 250 boron-containing mineralogical species exist, only four of them are presently of major
46 economic importance as mineral commodities: borax, colemanite, ulexite and kernite (Crangle
47 2015).

48 Colemanite, $\text{CaB}_3\text{O}_4(\text{OH})_3 \cdot \text{H}_2\text{O}$, is the most important Ca-borate and is currently extracted mainly
49 from the Emet and Bigadiç deposits (Turkey), as a commodity for B_2O_3 and for the production of
50 Na-free fiberglass (Helvacı 2015). Economically exploitable colemanite deposits usually occur for
51 chemical precipitation of this mineral from relatively diluted waters of lacustrine basins, hosted in
52 continental semi-arid to arid environments and fed by B-rich hydrothermal springs related to a local
53 volcanic activity (Helvacı 1995, 2015; Garret 1998; Helvacı and Alonso 2000). In the last years, the
54 large availability of colemanite as an economic raw material triggered several researches aimed to
55 explore the potential applications of this mineral in different technological processes, a short list of
56 which can be found, e.g., in Lotti et al. (2017).

57 The crystal structure of colemanite was first solved by Christ et al. (1954) and later refined by
58 Christ et al. (1958) and Clark et al. (1964) by means of single-crystal X-ray diffraction data. It is
59 characterized by infinite chains of B-coordination polyhedra running along the [100] direction.
60 These chains are built by the repetition of corner-sharing rings, each made by three polyhedra: one
61 BO_3 triangle and two $\text{B}\phi_4$ ($\phi = \text{O}, \text{OH}$) tetrahedra (Figure 1). Along the [001] axis, the chains of B-

62 polyhedra are connected through chains of corner-sharing Ca-coordination polyhedra (Figure 1),
63 giving rise to hetero-polyhedral sheets perpendicular to [010]. The connection among adjacent
64 sheets along [010] is granted by two Ca-O(H)-B bonds per unit cell and by an extensive network of
65 H-bonds (Figure 1), which is responsible for the perfect (010) cleavage observed in colemanite
66 crystals. A model for the hydrogen positions was first proposed by Christ et al. (1954) and Clark et
67 al. (1964), based on interatomic oxygen-oxygen distances, and was later refined by Hainsworth and
68 Petch (1966) and Burns and Hawthorne (1993), on the basis of single-crystal neutron and X-ray
69 diffraction data, respectively. A discussion on the structure model of colemanite including the
70 hydrogen atoms is given in section 1.2.

71 A second-order phase transition from the paraelectric colemanite, stable at ambient conditions, to a
72 ferroelectric, pyroelectric and piezoelectric polymorph is long-time known to occur in the T -range
73 between 273 and 261 K (Chynoweth 1957; Wieder 1959; Wieder et al. 1962; Fenzl and Shuppler
74 1994; Slabkaya et al. 2004; Gavrilova et al. 2006). The displacive phase transition from the
75 centrosymmetric $P2_1/a$ space group to the acentric $P2_1$ was suggested by Perloff and Block (1960),
76 based on the analysis of systematic extinctions in single-crystal X-ray diffraction patterns collected
77 before and after the transition, and later confirmed by Hainsworth and Petch (1966), by means of
78 neutron diffraction data collected at ambient T and 253 K, respectively. Wieder et al. (1962) found
79 that for a pure synthetic colemanite the phase transition occurred at 233 K (vs. 261 K for a natural
80 sample investigated by the same authors) and suggested that small chemical impurities (namely, the
81 substitution of Sr^{2+} for Ca^{2+}) are responsible for the different experimentally determined phase-
82 transition temperatures. In particular, the higher the deviation from the ideal $\text{CaB}_3\text{O}_4(\text{OH})_3 \cdot \text{H}_2\text{O}$
83 composition, the higher the temperature of the phase transition (and the larger the stability field of
84 the ferroelectric $P2_1$ -colemanite).

85 Despite the early structural studies on colemanite date back to half a century ago and the recent
86 technological interest triggered by the economic importance as a bulk commodity, several open

87 questions persist about the crystal structure of this mineral and its behavior at non-ambient
88 conditions. In this light, our group has recently published a study on the high-pressure behavior of
89 colemanite, by means of in situ single-crystal synchrotron X-ray diffraction experiments using a
90 diamond anvil cell (Lotti et al. 2017), showing that this natural hydrous borate undergoes a
91 reconstructive phase transition at ca. 14.5 GPa, with an increase of the average coordination number
92 of both the B and Ca sites. In particular, a fraction of the boron cations increases its coordination
93 from triangular to tetrahedral, by making new bonds with H₂O-oxygen atoms (Lotti et al. 2017). In
94 this study, using in situ single-crystal synchrotron X-ray diffraction and differential scanning
95 calorimetry techniques, we inspect the low-temperature behavior of colemanite and the paraelectric-
96 to-ferroelectric phase transition, reporting, to the best of our knowledge for the first time, the *T*-
97 induced structural evolution down to 104 K. In addition, a single-crystal neutron diffraction
98 experiment at 20 K was performed to resolve the uncertainties concerning the hydrogen positions
99 below the transition temperature (see section 1.2). Recently, the potential role of colemanite as a
100 host for pollutants (e.g., arsenic, Lin et al. 2011) or metals of economic relevance (e.g., REE,
101 Helvaci et al. 2017) has been studied. In this light, and taking into account the potential influence of
102 chemical impurities on the phase stability field of the ferroelectric polymorph (Wieder et al. 1962),
103 we have conducted a thorough chemical characterization of the studied natural sample of
104 colemanite. In particular, adopting a multi-methodological approach, the presence and abundance of
105 more than 50 chemical species have been investigated, to carefully determine the chemical
106 composition of our sample.

107 This work belongs to a larger study of the phase stability and of the elastic and structural behavior
108 of borate compounds, both natural and synthetic, at non-ambient conditions (e.g., Gatta et al. 2010a,
109 2010b, 2011, 2013, 2017).

110

111 1.1. The crystal structure of colemanite: the hydrogen positions

112 The crystal-structure models of the paraelectric (space group $P2_1/a$) and ferroelectric (space group
113 $P2_1$) polymorphs of colemanite have been reported and discussed by Hainsworth and Petch (1966),
114 based on structure refinements from neutron diffraction data collected at ambient temperature and
115 253 K, respectively. From the ambient data of the $P2_1/a$ colemanite, the authors report the presence
116 of diffuse residues in the difference-Fourier syntheses of nuclear densities close to the position of
117 the H99 (H5 in this work) and H54 (H2 in this work) atoms, which are interpreted as due to the split
118 of these two hydrogens in two different positions [from this point, we will make use only of the
119 notation of Burns and Hawthorne (1993) to refer to atomic positions: O9, H96, H99, O5, H54 in
120 Hainsworth and Petch (1966) are, respectively, Ow8, H4, H5(A,B), O2 and H2 in this work]. In
121 fact, in the colemanite structure two H₂O molecules are symmetry-related through the inversion
122 center (Figure 2). However, due to steric hindrance, only the hydrogen (in position “A”, H5A) of
123 one molecule may act as a bridge between the two oxygen atoms, the hydrogen of the second
124 molecule being forced to occupy a position “B”, where it can form H-bonds to different framework
125 oxygens. According to Hainsworth and Petch (1966), the position of the hydrogen in A or B slightly
126 affects also the position of the closer Ca cation, which is attracted to or rejected from the Ow8 site
127 depending on whether it is shielded or not by the positive charge of H5B. In turn, according to the
128 authors, the position adopted by Ca induces the H2 atom in one of two mutually exclusive
129 configurations (labelled “C” and “D”). In the $P2_1/a$ structure, the presence of the inversion center
130 implies that both the adjacent water molecules statistically donate the H5 atom in bridging position
131 A. This condition can be accomplished by a dynamical disorder of the H5 and H2 atoms, which
132 continuously flip among the two alternative and mutually exclusive configurations. The $P2_1/a$ -to-
133 $P2_1$ phase transition, with the loss of the inversion center, changes such a condition. As a
134 consequence, based on neutron diffraction data collected at 253 K, Hainsworth and Petch (1966)
135 reported the ordering of the hydrogens in one of the two possible configurations, so that, e.g., if an
136 H5 atom freezes in the A position, the adjacent H₂O molecule will display H5 in B configuration.
137 Through the influence on the Ca positions, the ordering of H5 will also imply the ordering of the H2

138 atoms all over the crystal. The shift from a dynamical disorder to a static ordering of the hydrogen
139 atoms at the phase transition was also suggested by Holuj and Petch (1960), based on proton
140 resonance analysis, from which the freezing of some proton motions was inferred.

141 It is worth to report that a different model was proposed by Burns and Hawthorne (1993) for the
142 hydrogen positions of colemanite at ambient conditions, by means of single-crystal X-ray
143 diffraction data. According to these authors, both the H₂O molecules contribute to the H-bonding in
144 a four-bond “donor-acceptor-donor-acceptor (…O-H…O-H…)” ring configuration.

145

146 **2. Materials and experimental methods**

147 **2.1 Colemanite sample and mineralogy**

148 This study was performed on a gem-quality sample of natural colemanite from the borate deposits
149 of the Bigadiç Mine (Balıkesir Province, Marmara Region, Turkey), provided by the Museum of
150 Mineralogy of the University of Padua (catalogue number MMP M14738). The colemanite and
151 ulexite deposits of the Bigadiç area were formed under evaporitic conditions in arid climate for the
152 precipitation of the borates in Neogene saline lakes, fed by both hydrothermal fluids related to an
153 underlying volcanism and streams weathering the neighboring volcanic rocks (Helvacı 1995).

154 Colemanite is reported by Helvacı (1995) to be of primary genesis, precipitating from the brine both
155 within unconsolidated sediments and, later, in veins and vugs.

156

157 **2.2 Chemical analysis**

158 The pure monomineralic nature and the relative abundance of the colemanite samples used for this
159 study, validated by optical analysis, allowed a thorough chemical investigation using a multi-
160 methodological approach, with a comprehensive survey of more than 50 chemical species. Boron

161 and calcium contents have been determined by adopting titrimetric methods. Thermal
162 decomposition and infrared absorption have been adopted to determine the amount of carbon and
163 hydrogen. Fluorine has been measured by ion selective electrode technique, whereas chloride,
164 bromide and iodide by ion chromatography. Inductive coupled plasma atomic emission
165 spectroscopy (ICP-AES) has been used to determine the weight fractions of minor elements. The
166 H₂O content has been determined by weight loss upon heating. A detailed description of the
167 combined experimental techniques adopted for the chemical analysis is given in Appendix I. The
168 full results are reported in Tables S1-S7 (supplementary materials). The chemical composition of
169 the studied colemanite, referred to the major elements, is reported in Table 1.

170

171 **2.3 Differential scanning calorimetry**

172 DSC analyses were conducted using a Mettler Toledo DSC1 apparatus with the samples sealed in
173 aluminum crucibles (6.31 mg mass). The thermal transition was studied in detail by performing the
174 following temperature cycles:

- 175 1. Heating from 233 to 423 K at 10 K/min;
- 176 2. 5 minutes isotherm at 423 K;
- 177 3. Cooling from 423 to 233 K at 10 K/min;
- 178 4. 5 minutes isotherm at 233 K;
- 179 5. Heating from 233 to 423 K at 10 K/min;

180 The initial heating to 423 K and the subsequent isothermal stage, i.e. cycles 1 and 2, were carried
181 out to *remove* adsorbed surface water or moisture that could give a small endothermic peak in the
182 temperature range of interest.

183 Since irreversible phase changes and/or transitions do not occur in both heating and cooling cycles,
184 a subsequent heating cycle, i.e. cycle 5, was performed to assess the reversible nature of the thermal
185 phenomena observed during the first heating.

186

187 **2.4 Low-temperature X-ray diffraction**

188 The low-temperature X-ray diffraction experiments were performed at the X-ray Diffraction
189 beamline (XRD1, Lausi et al. 2015) of the Elettra synchrotron source at Trieste, Italy. A colorless
190 platy crystal was dipped in NHV oil (Jena Bioscience GmbH) and mounted on the goniometer head
191 with a nylon loop. Complete datasets were collected at different temperatures (Table 2), through the
192 rotating crystal method, using a nitrogen stream from an Oxford Cryostream 700 series cryostat.
193 Data were acquired using a monochromatic wavelength of 0.700 Å on a Pilatus 2M hybrid-pixel
194 area detector. The diffraction data were indexed and integrated using the XDS software (Kabsch
195 2010). The structure refinements were performed using the JANA2006 software (Petříček et al.
196 2014) starting from the model of Burns and Hawthorne (1993), excluding the hydrogen atoms,
197 which were located by difference-Fourier syntheses. All the refinements were performed using
198 anisotropic displacements parameters (dp 's), except for the H atoms, which were restrained to share
199 the same isotropic dp . A soft restriction on the O-H distances (0.85 ± 0.02 Å) was applied. The
200 structure of the low- T polymorph of colemanite in the $P2_1$ space group has been derived according
201 to the group-subgroup relationship. The same restrictions reported for the $P2_1/a$ polymorph were
202 applied to the least-squares refinement of $P2_1$ -colemanite, except for the following: due to unstable
203 refinements, the displacement parameters of all the boron and of the O51 and O52 sites (also O11
204 and O12 for the refinement based on the data collected at 260 K) were restrained to be isotropic.
205 Statistical data of the structure refinements and selected structural parameters are reported in Tables
206 2 and 3, respectively. The refined structure models at 300 and 104 K are reported in Table 4. The
207 fully refined structure models are deposited as supplementary materials.

208 **2.5 Neutron diffraction experiment at 20 K**

209 A prismatic crystal of colemanite ($1.8 \times 3.8 \times 5.4 \text{ mm}^3$), free of defects under the polarised optical
210 microscope, was selected for the neutron diffraction experiment. Neutron-diffraction data were
211 measured at 20 K on the four-circle diffractometer D9, at the high-flux research reactor of the
212 Institut Laue-Langevin (ILL) in Grenoble, France, with a neutron beam of wavelength $0.8390(2) \text{ \AA}$,
213 obtained by reflection from a Cu(220) monochromator. The D9 diffractometer is equipped with a
214 small two-dimensional area detector (Lehmann et al. 1989), which allowed optimum resolution of
215 the peaks from the background. Diffraction data were collected up θ_{max} of 31° (h, k, l ranges are
216 listed in Table 2). For all data, background corrections following Wilkinson et al. (1988) and
217 Lorentz corrections were applied. Absorption corrections were made by Gaussian integration
218 (Coppens et al. 1965), using the calculated attenuation coefficient with account taken for the
219 wavelength dependence of the absorption for the hydrogen content (Howard et al. 1987). Initial
220 structure refinements showed that extinction affected only a few reflections, and could be well
221 accounted for by the simple isotropic extinction model in JANA2006 (Petriček et al. 2014). The low
222 degree of extinction meant that the data could be averaged over symmetry-equivalent reflections.
223 The 2724 reflections scanned gave 1923 unique reflections with an internal discrepancy index of
224 0.0507 (averaging in the $2/m$ Laue class). Since the three-dimensional count distribution around
225 each reflection was observed, the centroids of all scanned reflections could be found. Least-squares
226 matching of the observed and calculated centroids of a few hundreds of the strongest reflections
227 gave the lattice constants listed in Table 2. The reflection conditions suggested the space group $P2_1$.
228 Other details pertaining to the neutron data collections are listed in Table 2.

229 The structure refinement was performed based on the model of $P2_1$ -colemanite refined at 104 K
230 from X-ray diffraction data, except for the hydrogen positions, which were independently located
231 by difference-Fourier syntheses. The Ca, O (except Ow), H₂O-oxygens and H atoms were
232 constrained to share the same isotropic displacement parameter, respectively. Statistical data on the

233 structure refinement and selected structural parameters are reported in Tables 2, 4 and 5,
234 respectively.

235

236 **3. Results and discussion**

237 **3.1 Chemical composition**

238 The chemical composition of the sample of colemanite of this study has been thoroughly
239 investigated: the presence and relative abundance of 57 chemical species, including major and trace
240 elements, have been described by means of a multi-methodological approach (see section 2.2 and
241 Appendix I). The full results of the chemical analyses are reported in Tables S1-S7 (supplementary
242 material), whereas the composition of the most relevant chemical constituents is reported in Table
243 1. The relative purity of the colemanite sample, confirmed by the results of the ICP-AES analysis,
244 allowed the use of simple titrimetric methods for the determination of the B₂O₃ and CaO contents.
245 In particular, in the absence of cations such as Fe and Al, the acid-base titration with mannitol
246 provides the exact amount of boron entirely present as H₃BO₃ in acid environment. For the
247 determination of calcium it was not necessary to add any masking agent or precipitant before the
248 titration. The results show that, except for a minor substitution of Ca²⁺ by Sr²⁺ (Table 1), any other
249 trace element is below the detection limit ranging between 100 and 500 ppm. Within the scope of
250 this study, i.e. the characterization of the crystal chemistry of colemanite at ambient and non-
251 ambient conditions, we can conclude that the selected natural sample is virtually ideal, being the
252 composition very close to the nominal one: Ca_{0.99}Sr_{0.01}B_{3.00}O₄(OH)_{3.00}·0.99H₂O. The minimum
253 content of SiO₂, measured from ICP-AES analysis (Tables 1 and S5), may be attributed either to a
254 substitution of tetrahedral B by Si, or to a minor amount of silicate-mineral impurities within the
255 massive sample.

256

257 **3.2 Crystal structure of the $P2_1/a$ -colemanite at ambient conditions**

258 The structure refinement performed on the basis of the X-ray diffraction data collected at 300 K
259 substantially confirms the model proposed by Hainsworth and Petch (1966). Despite the
260 intrinsically weak X-ray scattering factor of hydrogen (Wilson and Prince 1999), the difference-
261 Fourier syntheses of electron density, based on H-free structure refinements, allowed the location of
262 the hydrogen positions. As expected, three peaks were found close to the H₂O oxygen atom: the
263 most intense corresponding to the H4 site and the remaining to two mutually exclusive
264 configurations of H5 (see section 1.2) (Figure 2; Table 4). A diffuse residue was found at the
265 expected position for the H2 atom. Any attempt to refine two split and mutually exclusive sites,
266 according to the model of Hainsworth and Petch (1966), failed. Therefore, the refined H2
267 coordinates (Table 4) must be interpreted as the barycentric position of a dynamically disordered
268 atom. The hydrogen bonding network of colemanite is reported in Table 5. As previously
269 mentioned by Hainsworth and Petch (1966), the hydrogen atoms in position H2 and H5B are
270 generically oriented towards a region where they can make alternative bonds with the framework
271 oxygens (Figure 2; Table 5).

272

273 **3.3 The paraelectric to ferroelectric phase transition.**

274 The phase transition from the (high-temperature) paraelectric $P2_1/a$ -colemanite to the (low-
275 temperature) ferroelectric $P2_1$ -polymorph has been investigated by means of differential-scanning
276 calorimetry and in situ low-temperature single-crystal X-ray diffraction.

277 The differential scanning calorimetry analysis (Figures 3 and 1S, supplementary material) confirms
278 that a reversible transition takes place and this is consistent with the structural modifications,
279 corresponding to an enantiotropic phase transition, observed by X-ray diffraction (Giron 1995;
280 Kawakami 2007). In the first heating cycle the thermogram exhibits a weak endothermic peak

281 centered at about 270.5 K (-2.5 °C) with an onset temperature of about 263 K (-10°C) and an endset
282 temperature around 275 K (2°C) (Figure 3). In the successive cooling step, an exothermal transition
283 is observed over the same temperature range while in the final heating cycle an endothermic event
284 analogous to that observed in the first cycle is reproduced (Figure 3). No hysteresis phenomena are
285 detected as clearly shown in Figure 3. The heat involved in the transition is clearly very low (less
286 than 0.4 J/g) but it cannot be determined with high accuracy given the relatively unstable baseline in
287 proximity of the transition itself. An estimation is provided in Figure 3.

288 The single-crystal X-ray diffraction datasets, collected at low temperature, have been investigated
289 following the intensities of the classes of reflections systematically absent in the $P2_1/a$ space group,
290 i.e.:

- 291 • $h00$, for $h = 2n + 1$
- 292 • $0k0$, for $k = 2n + 1$
- 293 • $h0l$, for $h = 2n + 1$.

294 The $P2_1/a$ -to- $P2_1$ phase transition can be identified since in the latter space group no reflection
295 conditions apply to $h00$ and $h0l$, in contrast to the $0k0$ peaks, which keep the extinction conditions
296 for $k = 2n + 1$. Table 6 shows the average intensities of these classes of reflections at varying
297 temperatures, as well as the number of peaks violating the extinction conditions according to three
298 different cut-off criteria: $I_{hkl}/\sigma(I_{hkl}) \geq 1, \geq 3$ and ≥ 6 , respectively. A reconstruction of the $h0l^*$
299 reciprocal lattice planes, based on the data collected at 300 and 104 K, respectively, is reported in
300 Figure 4. The results reported in Table 6 show a discontinuity between 265 and 260 K, which is
301 followed by an increasing number of violating reflections with decreasing temperature, as can be
302 detected in Figure 4.

303 These results confirm that the phase transition is displacive in character, from the centrosymmetric
304 $P2_1/a$ space group to the acentric $P2_1$ subgroup, and does not induce the occurrence of any

305 spontaneous strain (Figure 5). The differential scanning calorimetry results show that this phase
306 transition occurs in the range between 263 and 275 K. The slightly lower temperature range derived
307 from the X-ray diffraction data can be attributed to the difficulties in recognizing the phase
308 transition temperature relying only on the systematic extinctions.

309 The loss of the glide plane and of the related inversion center provides the structural basis for the
310 ferro-, pyro- and piezo-electric behavior of colemanite at low temperatures, as already reported by
311 Perloff and Block (1960) and Hainsworth and Petch (1966). In the following sections, we report, to
312 the best of our knowledge for the first time, the elastic and structural evolution of the ferroelectric
313 polymorph of colemanite at varying temperatures down to 104 K.

314

315 **3.4 Low-temperature elastic behavior**

316 The evolution of the unit-cell volume and linear parameters of colemanite as a function of
317 temperature, based on X-ray diffraction data, are reported in Figure 5 and Table 2. Apparently, the
318 elastic behavior of colemanite is unaffected by the occurrence of the phase transition. In this light,
319 the experimental volume data were fitted with a Berman T - V equation of state within the entire T -
320 range investigated using the *EoSFit7-GUI* software (Gonzalez-Platas et al. 2016). The following
321 parameters were refined adopting a reference temperature of 298 K: $V_0 = 560.3(1) \text{ \AA}^3$, $\alpha_0 =$
322 $4.4(6) \cdot 10^{-5} \text{ K}^{-1}$ and $\alpha_1 = 8(7) \cdot 10^{-8} \text{ K}^{-2}$, for which the thermal expansion coefficients predicted at 298
323 and 104 K, respectively, are: $\alpha_{V298K} = \alpha_0$ and $\alpha_{V104K} = 2.8(7) \cdot 10^{-5} \text{ K}^{-1}$.

324 The unit-cell linear parameters, reported in Table 2 and Figure 5, show that the volume reduction
325 with decreasing temperature is accommodated along the b and c axes, being the a axis unmodified
326 within the experimental uncertainties. It is worth to note that [100], which corresponds to the axial
327 direction of the borate chains (Figure 1), was also found to be the less compressible axis at high
328 pressure conditions (Lotti et al. 2017).

329 3.5 Crystal-structure modifications with decreasing temperature

330 The main effect of the $P2_1/a$ -to- $P2_1$ phase transition in colemanite is the loss of the glide plane a ,
331 and of the related inversion center, which allows the transition to the ferroelectric state. The loss of
332 the glide plane gives rise to a change of the symmetry constraints among the neighboring H₂O
333 molecules, which are symmetry-independent in the $P2_1$ polymorph (Figure 2). According to
334 Hainsworth and Petch (1966), this leads to a static ordering of the H5 and H2 hydrogen atoms all
335 over the crystal volume: i.e., with H51 ordered in the A configuration (bridging H-bond between the
336 H₂O molecules) and H52 ordered in the B configuration, or *vice versa*. In order to check the validity
337 of this model, we calculated the difference-Fourier maps of the electron density, based on the X-ray
338 diffraction data collected between 260 and 104 K, and the difference-Fourier maps of the nuclear
339 density, based on neutron diffraction data collected at 20 K (Figure 6). In any calculated map, the
340 residual peaks of the electron and nuclear densities (based on H-free structure refinements)
341 suggested the persistence of the A and B configurations for both the symmetry-independent H51
342 and H52 sites (Figure 6). These results can be in agreement with the model proposed by Hainsworth
343 and Petch (1966) if we assume the distribution over the crystal volume of two different domains,
344 each of them showing an opposite internal order.

345 The structure refinements based on the X-ray diffraction data collected at different temperatures
346 allow a comparative analysis of the T -induced structural modifications. The in situ high-pressure
347 study (Lotti et al. 2017) showed that the hydrostatic compression in colemanite is mainly
348 accommodated by tilting of the cations polyhedra around the shared oxygen atoms and by the
349 compression of the Ca-polyhedron. Following the same protocol adopted by Lotti et al. (2017), the
350 volumes of the B and Ca coordination polyhedra have been calculated using the tools implemented
351 in the software *Vesta* (Momma and Izumi 2011). The calculated values are reported in Table 3 and
352 show that no significant changes occur to the B tetrahedra at decreasing temperature and only a
353 minor shrinkage affects the Ca-polyhedra. Therefore, in contrast to the high- P behavior, the

354 (moderate) volume contraction induced by the T -decrease is mainly accommodated by a tilting
355 mechanism of the structural units, as this mechanism is energetically more favorable than distortion
356 or compression (Gatta 2010). It is worth to note that the unit-cell volume shrinking at 104 K (0.9
357 %), according to the isothermal equation of state reported by Lotti et al. (2017), is equivalent (in
358 magnitude) to the bulk compression observed at 0.66 GPa.

359 The loss of the glide plane due to the phase transition to the $P2_1$ space group induces the split of
360 every atomic site in two independent positions. The loss of the symmetry constraints allows the
361 displacement, from the previous centrosymmetric configuration, of any couple of atoms with a
362 common parent site. This displacement allows an asymmetrical distribution of charged ions along
363 the b axis, which was proposed to be the source for the ferro-, pyro- and piezo-electric behavior of
364 colemanite below the transition temperature (Hainsworth and Petch 1966). This displacement has
365 been modeled for any couple of atoms as the virtual interatomic distance (along [010]) in the $P2_1/a$
366 space group (Figure 5 and Table S8). Figure 5 shows that, for the heavier Ca, B and O couples of
367 atoms, the average displacement from the centrosymmetric configuration increases in the range
368 between 260 and 180 K and is substantially constant in the range between 180 and 104 K. A similar
369 behavior was reported for the spontaneous polarization of colemanite below the transition
370 temperature (Wieder 1959; Wieder et al. 1962).

371

372 4. Conclusions

- 373 • The crystal chemistry and the low-temperature behavior of natural colemanite, a hydrous
374 Ca-borate of high economic relevance, were investigated by means of a multi-
375 methodological approach.
- 376 • The composition of the major and of more than fifty potential trace elements has been, to the
377 best of our knowledge for the first time, thoroughly investigated adopting different

378 analytical techniques, representing a unique experimental approach in the crystal chemistry
379 of borate minerals.

- 380 • The displacive phase transition from the $P2_1/a$ space group to the ferroelectric $P2_1$ subgroup
381 was found to occur between 261 and 275 K with a peak at 270.5 K.
- 382 • The structure refinements of the $P2_1$ -colemanite, based on in situ low- T X-ray and neutron
383 diffraction data, suggest that the distribution of the proton sites (belonging to H₂O
384 molecules) is still disordered.
- 385 • The comparative elastic and structural analyses at varying temperature showed that the
386 borate chains direction (i.e., the a axis) is almost unaffected by the temperature variation and
387 that the asymmetric distribution of ionic charges along the b crystallographic axis, following
388 the phase transition, is likely responsible for the reported ferro-, pyro- and piezo-electric
389 behavior of the $P2_1$ -colemanite.

390

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395

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- 484

485 **Appendix I.**

486 A thorough chemical analysis of the studied colemanite sample has been performed by adopting a
487 multi-methodological approach. In the following, a detailed description of the experimental
488 techniques, reported in section 2.2, is given.

489

490 **I.a Titrimetric determination of boron**

491 120-200 mg of the sample of colemanite were placed in a 50 ml plastic test tube. 5 ml of water and
492 3 ml of HCl 1M were added. The plastic test tube was then covered and transferred in an ultrasound
493 bath for 1-2 hours. The resulting clear solution was transferred in a 200-300 ml beaker with water
494 up to about 100 ml of total solution.

495 A combined glass electrode (InLab® Routine Pro – Mettler Toledo) was immersed in the solution
496 and the pH was adjusted to 5.5-6.5, by the addition of HCl 0.1-1M and NaOH 0.1-1M. 5-6 grams of
497 mannitol were added and stirred until complete dissolution. The resulting solution was titrated with
498 NaOH 0.1M up to pH = 8.3-8.7.

499 Due to the absence in the sample of hydrolyzing elements, as well as of elements able to influence
500 the acidity of the solution, it can be inferred that the titrated acid content is entirely due to the
501 presence of boric acid in solution. The results are reported in Table S1 (supplementary materials).

502

503 **I.b EDTA (Ethylenediaminetetraacetic acid) titrimetric method of Calcium**

504 40-80 mg of colemanite were placed in a 50 ml plastic test tube along with 5 ml of water and 1 ml
505 of HCl 1M. The plastic tube was subsequently covered with lid and transferred in an ultrasound
506 bath for 1-2 hours.

507 The resulting clear solution was transferred in a 300-400 ml beaker and diluted to 200 ml with
508 water. 10 ml of buffer solution (pH = 10 mixture of ammonium chloride/ammonia) and 3-4 drops of
509 Eriochrome black T solution (2gr/l in ethanol) were added. The solution was titrated with a standard
510 solution of EDTA 0.01 M [solution of EDTA with $5 \cdot 10^{-4}$ mol/l of magnesium chloride
511 exahydrate($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$)], until its purple color was altered to blue. The total volume of EDTA
512 added to the solution is proportional to the average content of Ca and Sr in the colemanite sample
513 (Table S2, supplementary material).

514

515 **I.c Determination of carbon and hydrogen by thermal decomposition and detection by**
516 **Infrared absorption (C,H).**

517 100-300 mg of the natural sample of colemanite were decomposed at 950°C in an elementary
518 analyzer LECO Truspec CHN, in excess of oxygen for 90 seconds. The products of decomposition
519 were passed through a second furnace (Afterburner) at 850°C for a further oxidation and particulate
520 removal. The gases, collected and homogenized in a container of 4.5 liters at 50°C , were sent to the
521 detectors for infrared absorption for the measurement of CO_2 and H_2O (i.e., carbon is measured in
522 the form of CO_2 and hydrogen in the form of H_2O).

523 EDTA, sodium tetraborate decahydrate (borax, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$), boric acid (H_3BO_3), calcium
524 carbonate (CaCO_3), sodium nitrate (NaNO_3) and oxalic acid (dehydrated) ($\text{HO}_2\text{CCO}_2\text{H} \cdot 2\text{H}_2\text{O}$) were
525 used as calibration standards. The results are reported in Table S3 (supplementary material).

526

527 **I.d Determination of fluorine by Ion selective electrode**

528 5-20 mg of the colemanite sample were placed in a 50 ml plastic test tube along with 5 ml of water
529 and 3 ml of hydrochloric acid 1M. The plastic test tube was covered and transferred in an
530 ultrasound bath for 1-2 hours. Later, 2-3 ml of Total Ionic Strength Adjustment Buffer (Commercial

531 solution TISAB III) were added to the solution and diluted to 20 ml with water. The content of
532 fluorine was determined using a *perfectION™ Combination Fluoride Ion Selective Electrode* (from
533 Mettler Toledo) adopting the standard addition method of certified reference material solution of F
534 from 0.1 to 2 mg/l (Table S4, supplementary material).

535

536 **I.e Determination of minor elements by ICP-AES**

537 All the measurements were performed in radial view mode with an ICP/AES Perkin Elmer Optima
538 7000DV spectrometer. For the rare earth elements, 5-20 mg of colemanite sample were placed in a
539 50 ml plastic test tube along with 5 ml of water and 3 ml of hydrochloric acid 1M. The plastic test
540 tube was covered and transferred in an ultrasound bath for 1-2 hours. The solution was transferred
541 and diluted with water in a 25 ml volumetric flask. A blank solution and series solution for
542 calibrations were prepared carrying out the same procedure without the sample. A certified
543 reference material (CRM) multi-elemental standard mix for ICP (50mg/l) of each element was used
544 for preparing the solution series for calibration (5 solutions from 0,05 mg/l to 1 mg/l for each
545 element).

546 For the analysis of the other elements investigated by ICP-AES (Table S5, supplementary material),
547 the decomposition of the colemanite sample was obtained by alkaline fusion of 5-20 mg in a
548 platinum crucible with 100 mg of Na₂CO₃ or K₂CO₃ in a muffle furnace at 1000°C for 5 minutes,
549 followed by dissolution in 10 ml of water and 1 ml of H₂SO₄ 1M or 1 ml of HCl 1M. The resulting
550 clear solution was transferred and diluted with water in a 25 ml volumetric flask containing 2.5 ml
551 of Sc solution (100 mg/l) as internal standard.

552

553 **I.f Determination of chloride, bromide, iodide by ion-chromatography**

554 25 mg of the colemanite sample were placed in a 50 ml plastic test tube along with 20 ml of water
555 and one drop of nitric acid. The plastic test tube was covered and transferred in an ultrasound bath
556 for 1-2 hours. The solution was transferred and diluted with water in a 25 ml volumetric flask. A
557 blank solution and series solutions for calibrations were made carrying out the same procedure
558 without the sample. CRM containing 100 mg/l of each element was used for preparing the solution
559 series for calibration (5 solutions from 0,1 mg/l to 2 mg/l for each element). The analysis was
560 performed using a *Dionex ICS-1600 Standard Integrated IC* system equipped with *Columns ION*
561 *PACK AG23 Guard 4x50 mm + AS23 4x250mm*. A solution of KOH 10mM was used as eluent. The
562 results are reported in Table S6 (supplementary material).

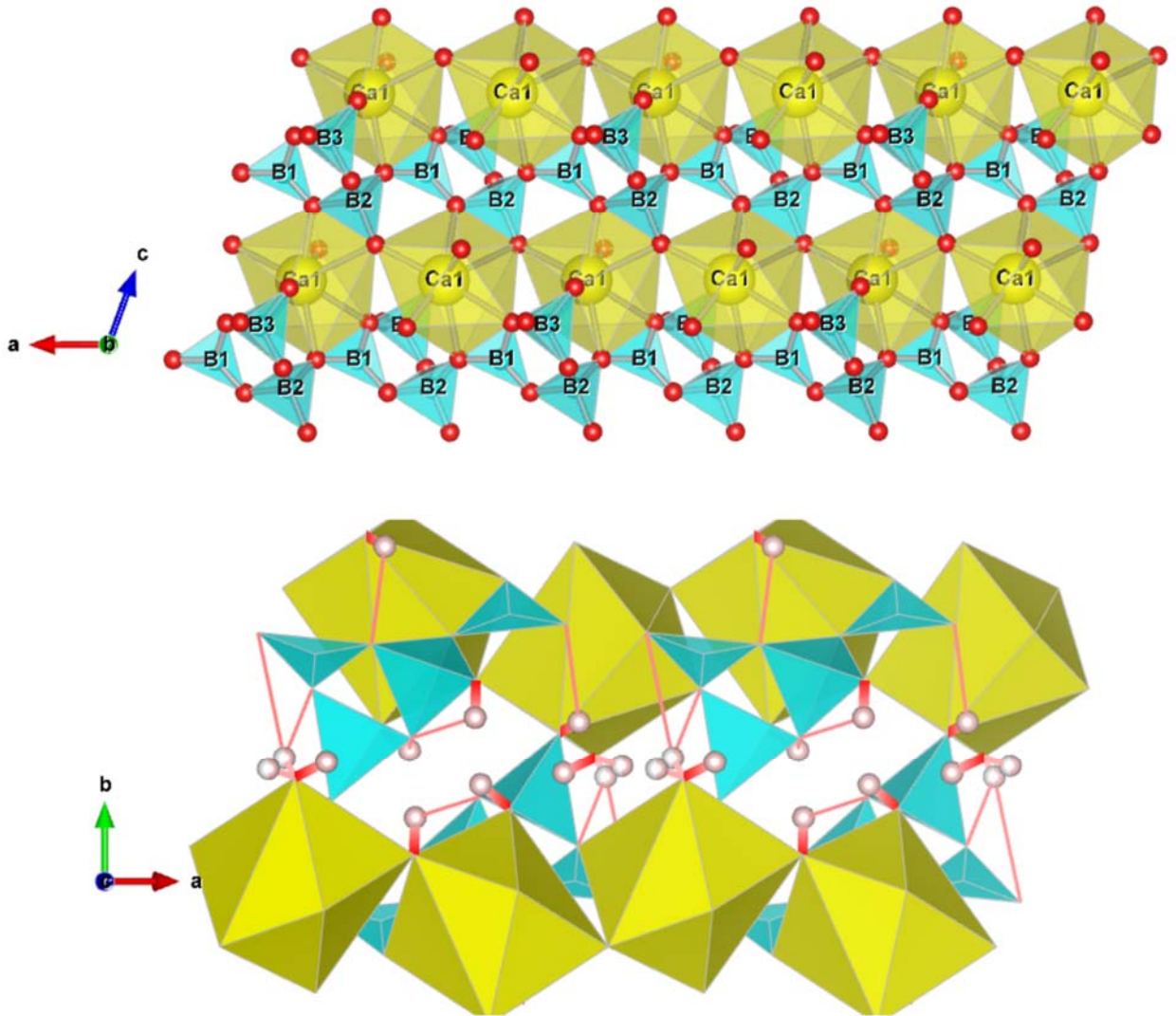
563

564 **I.g Determination of water content by heating**

565 500-600 mg of the colemanite sample were placed in a quartz crucible with lid and gradually heated
566 in a muffle furnace from ambient temperature up to 800°C. Between 300 and 400°C, the sample
567 was partially lost during heating, the weight loss being due to H₂O and partially to inorganic matter.
568 B, Ca and Sr were analyzed in the residual sample in order to provide suitable corrections. The
569 results are reported in Table S7 (supplementary material).

570

571 **Figure 1.** (Top) The structure of colemanite viewed down the [010] axis. The heteropolyhedral
572 sheet made by the B- and Ca-polyhedra chains is shown. (Bottom) The structure of colemanite
573 viewed down the [001] axis, showing the complex H-bonding network.



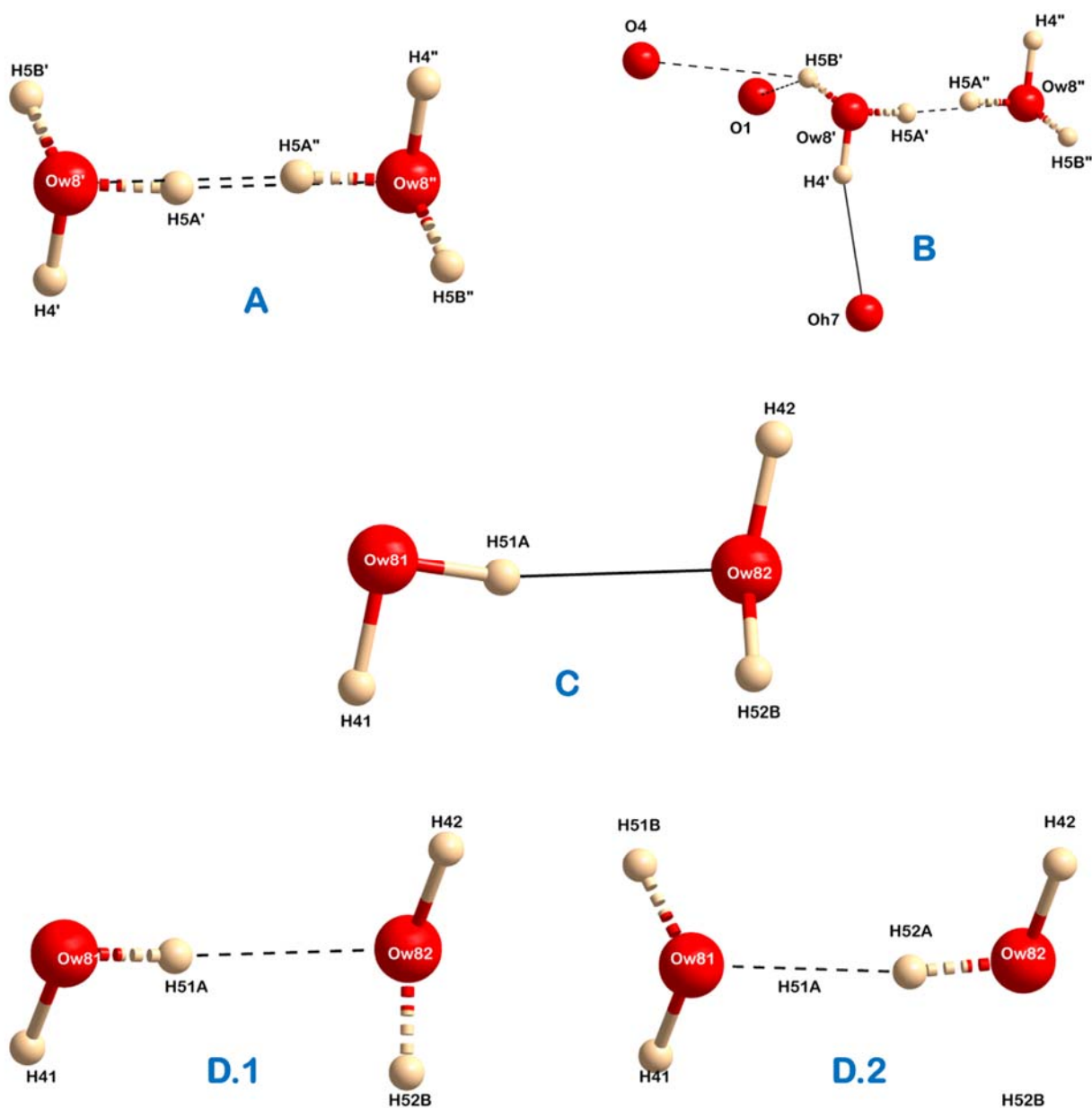
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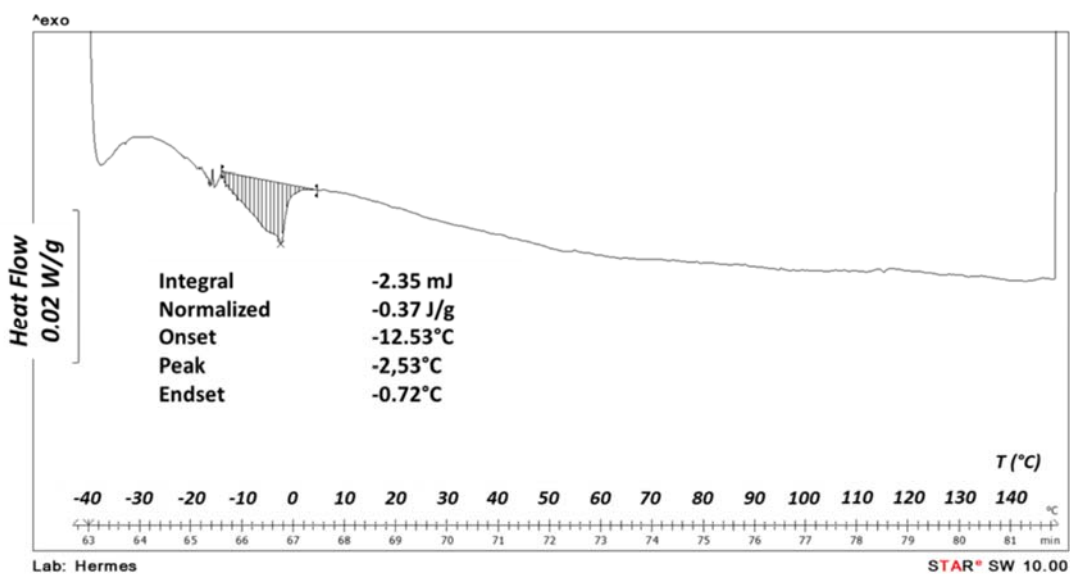
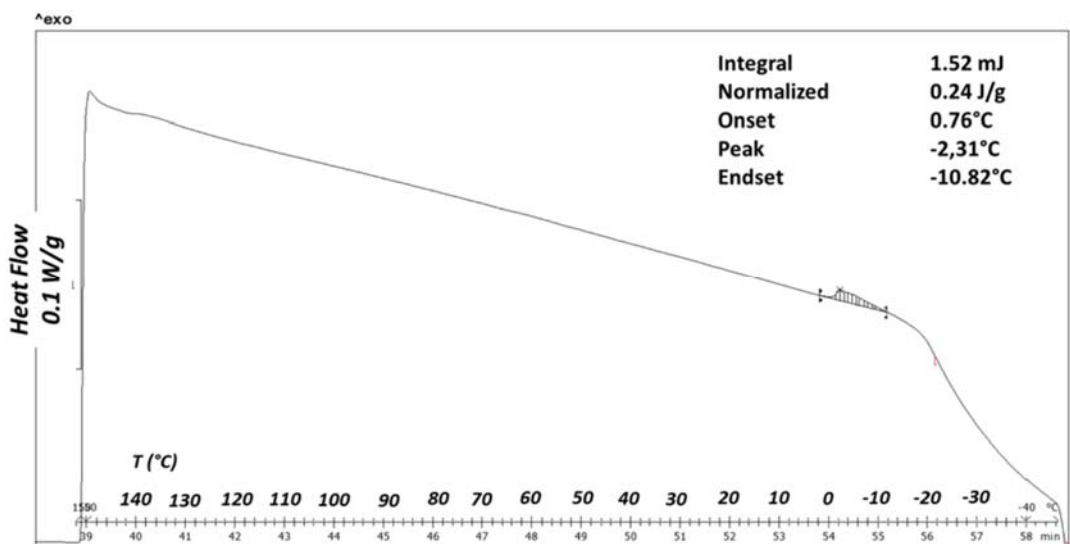
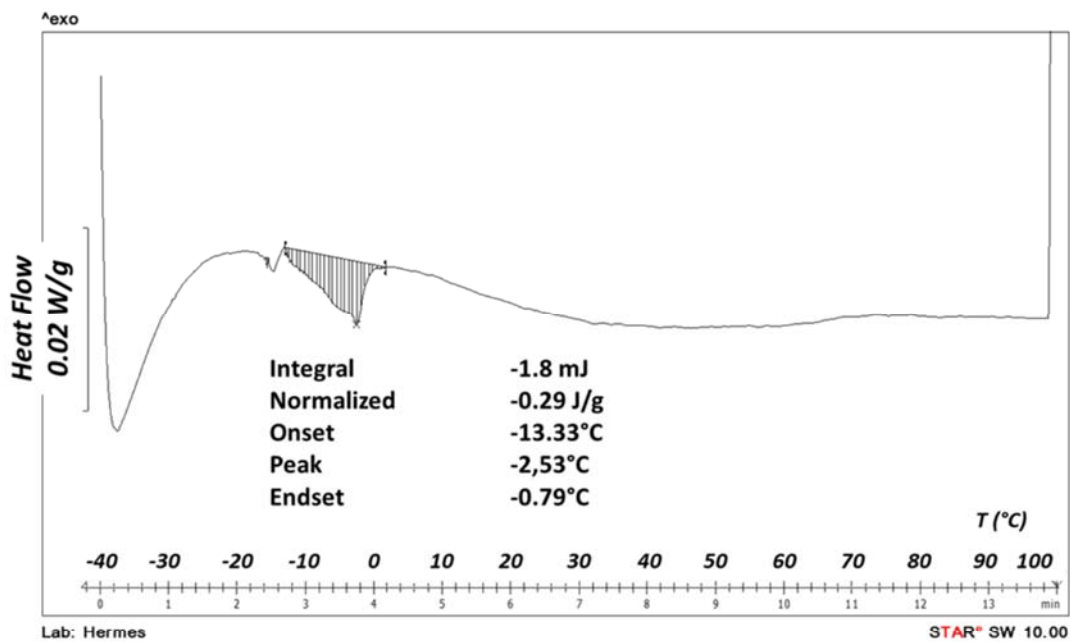
577

578 **Figure 2.** Bonding configuration of the H₂O molecules of: (A and B) *P*2₁/*a*-colemanite; (C) *P*2₁-
 579 colemanite, according to the model proposed by Hainsworth and Petch (1966); (D.1 and D.2)
 580 *P*2₁-colemanite, according to the structure refinement of this study, based on neutron diffraction
 581 data collected at 20 K. Thick and thin lines represent ionic- and hydrogen-bonds, respectively.
 582 Dashed lines represent mutually exclusive bonds. D.1 and D.2 represent two mutually exclusive
 583 configurations.

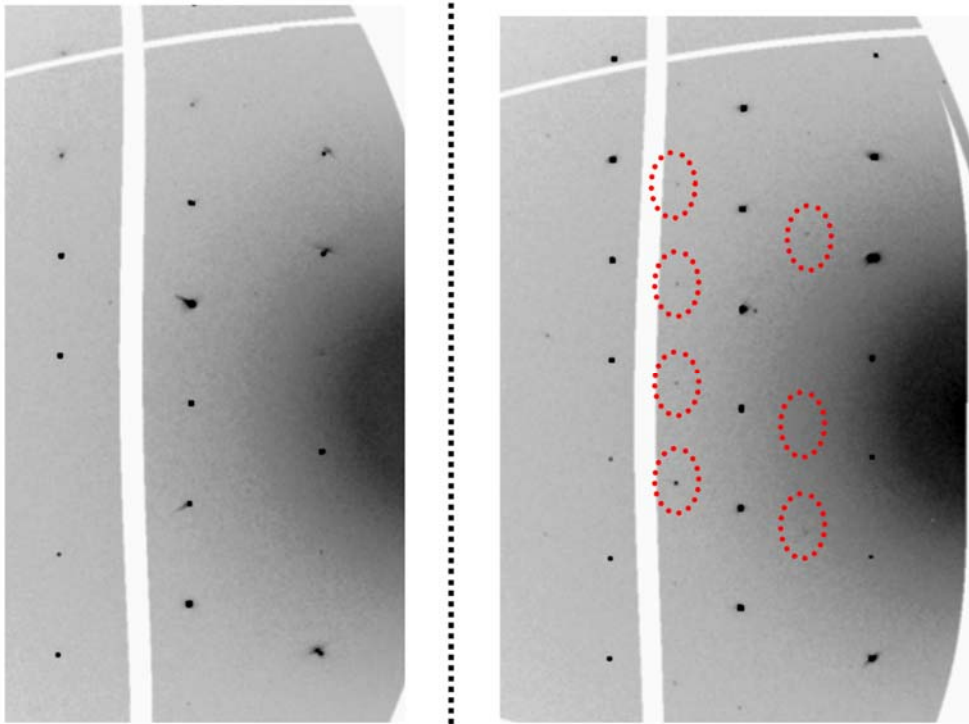


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 585

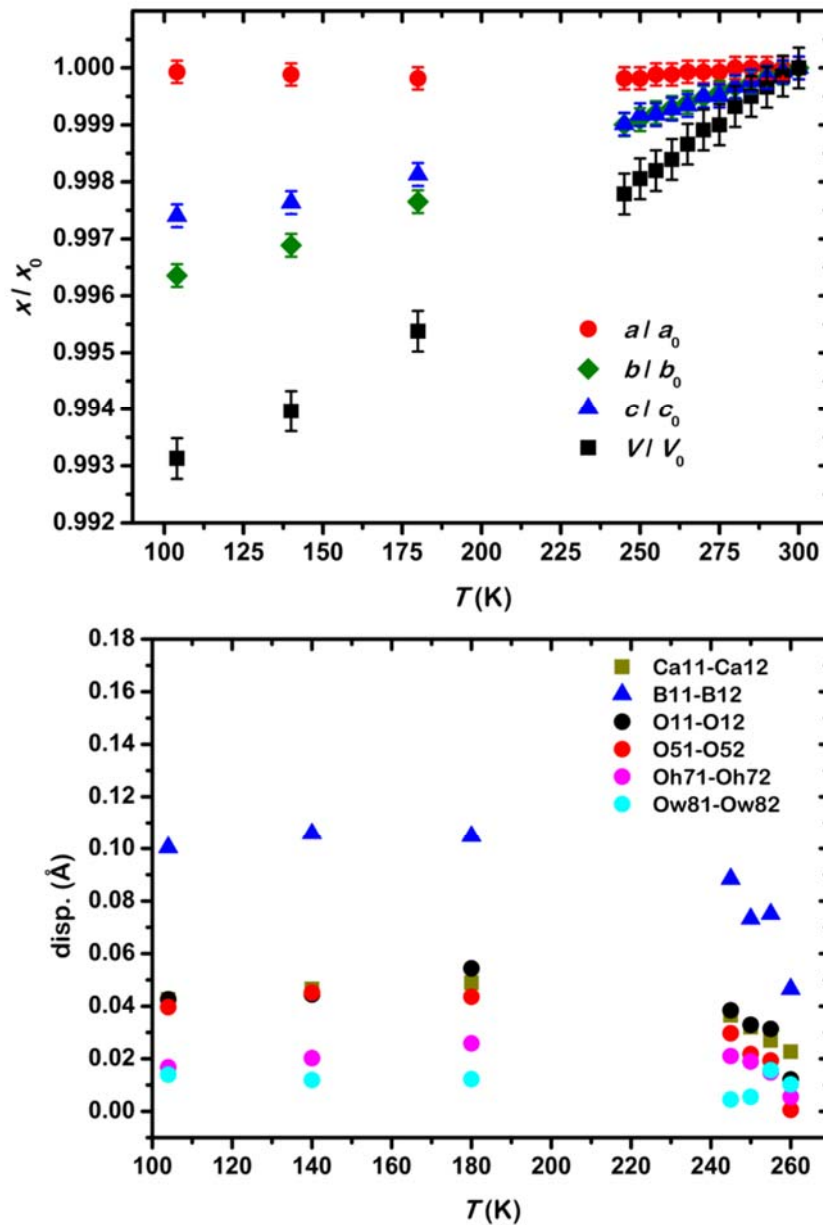
586 **Figure 3.** Excerpts from the differential scanning calorimetry (DSC) curve of the colemanite
587 sample showing: A) the endothermic peak observed in the first heating cycle; B) the exothermic
588 peak observed in the cooling cycle and C) the endothermic peak observed in the second heating
589 cycle. No hysteresis phenomena can be detected. An estimate of the calorimetric enthalpy
590 obtained by integration of the transition peaks is reported. The full spectrum of the experimental
591 DSC curve is reported in Figure 1S (supplementary materials).



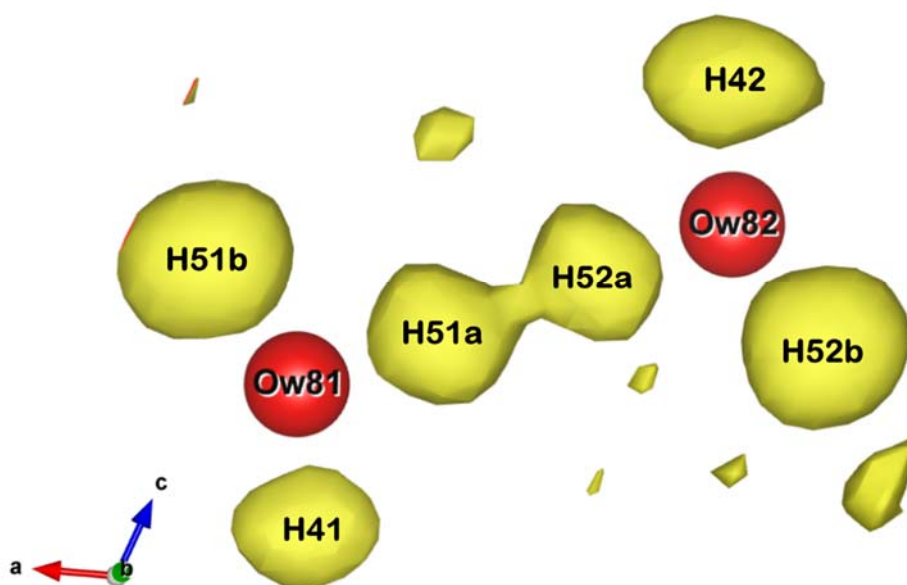
594 **Figure 4.** Reconstruction of the $h0l^*$ reciprocal lattice planes, based on the X-ray diffraction data
595 collected at 300 K (*left*) and 104 K (*right*), respectively. The diffraction peaks violating the
596 extinction condition for $h = 2n + 1$ are encircled.



598 **Figure 5.** (Top). Evolution of the unit-cell parameters of colemanite with T , normalized to their
 599 values at 300 K. (Bottom). Calculated displacement along the \mathbf{b} -axis, with respect to the
 600 centrosymmetric configuration, of selected couples of atoms of $P2_1$ -colemanite, sharing a
 601 common parent site in the $P2_1/a$ space group (see section 3.5 for further details).



604 **Figure 6.** Difference-Fourier map of the nuclear density in the proximity of the H₂O molecules,
605 based on H-free neutron structure refinements at 20 K. The negative residues related to the H
606 positions are shown. The yellow surfaces represent the isosurface at $-1.5 \text{ fm}/\text{\AA}^3$. For a sake of
607 clarity, the positive residues are not shown. The red spheres represent the H₂O-oxygen sites.
608



609 **Table 1.** The mass fractions of the main chemical components of the sample of colemanite here
610 investigated, measured by means of a multi-methodological approach. Further details are in the text
611 (sections 2.2, 3.1 and Appendix I) and in Tables S1-S7 (supplementary materials).

612

	wt%
B ₂ O ₃	50.8(4)
CaO	27.2(2)
SrO	0.30(5)
SiO ₂	0.03(1)
H ₂ O	21.8(4)

613 **Table 2.** Unit-cell parameters of colemanite and details of the structure refinements at different temperatures.

<i>T</i> (K)	300	295	290	285	280	275	270	265	260	255	250
Space group	<i>P</i> ₂₁ / <i>a</i>	<i>P</i> ₂₁ / <i>a</i>	<i>P</i> ₂₁ / <i>a</i>	<i>P</i> ₂₁ / <i>a</i>	<i>P</i> ₂₁ / <i>a</i>	<i>P</i> ₂₁ / <i>a</i>	<i>P</i> ₂₁ / <i>a</i>	<i>P</i> ₂₁ / <i>a</i>	<i>P</i> ₂₁	<i>P</i> ₂₁	<i>P</i> ₂₁
<i>a</i> (Å)	8.714(2)	8.714(2)	8.714(2)	8.714(2)	8.714(2)	8.713(2)	8.713(2)	8.713(2)	8.713(2)	8.713(2)	8.712(2)
<i>b</i> (Å)	11.244(2)	11.243(2)	11.242(2)	11.241(2)	11.240(2)	11.239(2)	11.238(2)	11.237(2)	11.236(2)	11.235(2)	11.234(2)
<i>c</i> (Å)	6.0904(10)	6.0900(10)	6.0894(10)	6.0894(10)	6.0884(10)	6.0874(10)	6.0874(10)	6.0864(10)	6.0860(10)	6.0854(10)	6.0854(10)
β (°)	110.12(3)	110.12(3)	110.12(3)	110.12(3)	110.12(3)	110.12(3)	110.12(3)	110.12(3)	110.13(3)	110.13(3)	110.13(3)
<i>V</i> (Å ³)	560.3(2)	560.2(2)	560.1(2)	560.0(2)	559.9(2)	559.8(2)	559.7(2)	559.6(2)	559.4(2)	559.3(2)	559.2(2)
$\min \leq h, k, l \leq \max$	$0 \leq h \leq 12$ $-16 \leq k \leq 0$ $-8 \leq l \leq 8$	$0 \leq h \leq 12$ $-16 \leq k \leq 0$ $-8 \leq l \leq 8$	$0 \leq h \leq 12$ $-16 \leq k \leq 0$ $-8 \leq l \leq 8$	$0 \leq h \leq 12$ $-16 \leq k \leq 0$ $-8 \leq l \leq 8$	$0 \leq h \leq 12$ $-16 \leq k \leq 0$ $-8 \leq l \leq 8$	$0 \leq h \leq 12$ $-16 \leq k \leq 0$ $-8 \leq l \leq 8$	$0 \leq h \leq 12$ $-16 \leq k \leq 0$ $-8 \leq l \leq 8$	$0 \leq h \leq 12$ $-16 \leq k \leq 0$ $-8 \leq l \leq 8$	$0 \leq h \leq 12$ $-16 \leq k \leq 0$ $-8 \leq l \leq 8$	$0 \leq h \leq 12$ $-16 \leq k \leq 0$ $-8 \leq l \leq 8$	$0 \leq h \leq 12$ $-16 \leq k \leq 0$ $-8 \leq l \leq 8$
Unique peaks	1695	1700	1693	1691	1706	1696	1695	1708	1785	1787	1784
Observed peaks $F_o^2/\sigma(F_o^2) > 3$	1675	1679	1670	1667	1686	1675	1678	1686	1718	1739	1740
<i>R</i> _{int} (obs)	0.0361	0.0355	0.0355	0.0357	0.0379	0.0352	0.0369	0.0376	0.0383	0.0384	0.0402
<i>R</i> _{int} (all)	0.0361	0.0355	0.0355	0.0357	0.0379	0.0352	0.0369	0.0376	0.0383	0.0384	0.0402
Refined param.	129	129	129	129	129	129	129	129	205*	215	215
<i>R</i> ₁ (obs)	0.0242	0.0236	0.0224	0.0236	0.0257	0.0251	0.0228	0.0266	0.0307	0.0277	0.0268
<i>R</i> ₁ (all)	0.0243	0.0237	0.0225	0.0238	0.0258	0.0252	0.0229	0.0267	0.0318	0.0282	0.0273
<i>wR</i> ₁ (obs)	0.0418	0.0405	0.0400	0.0417	0.0425	0.0424	0.0418	0.0433	0.0489	0.0442	0.0407
Residuals (<i>e</i> /Å ³)	+0.45 -0.45	+0.48 -0.53	+0.41 -0.44	+0.39 -0.45	+0.56 -0.70	+0.63 -0.65	+0.41 -0.57	+0.74 -0.69	+0.63 -0.66	+0.40 -0.72	+0.47 -0.73

* O11 and O12 displacement parameters refined as isotropic for the data collected at 260 K, see section 2.4 for further details

<i>T</i> (K)	245	180	140	104	20*
Space group	<i>P</i> ₂₁	<i>P</i> ₂₁	<i>P</i> ₂₁	<i>P</i> ₂₁	<i>P</i> ₂₁
<i>a</i> (Å)	8.712(2)	8.712(2)	8.713(2)	8.713(2)	8.711(5)
<i>b</i> (Å)	11.233(2)	11.218(2)	11.209(2)	11.203(2)	11.189(8)

c (Å)	6.0844(10)	6.0790(10)	6.0760(10)	6.0746(10)	6.071(4)
β (°)	110.13(3)	110.16(3)	110.19(3)	110.21(3)	110.3(2)
V (Å ³)	559.1(2)	557.7(2)	556.9(2)	556.5(2)	555(2)
min $\leq h,k,l \leq$ max	$0 \leq h \leq 12$	$0 \leq h \leq 12$	$0 \leq h \leq 12$	$0 \leq h \leq 12$	$-12 \leq h \leq 7$
	$-16 \leq k \leq 0$	$-16 \leq k \leq 0$	$-16 \leq k \leq 0$	$-16 \leq k \leq 0$	$-15 \leq k \leq 13$
	$-8 \leq l \leq 8$	$-8 \leq l \leq 8$	$-8 \leq l \leq 8$	$-8 \leq l \leq 8$	$-7 \leq l \leq 8$
Unique peaks	1764	1776	1779	1784	1923
Observed peaks $F_o^2/\sigma(F_o^2) > 3$	1724	1747	1744	1755	1777
R_{int} (obs)	0.0344	0.0389	0.0330	0.0323	0.0501
R_{int} (all)	0.0344	0.0389	0.0330	0.0323	0.0507
Refined param.	215	215	215	215	117
R_1 (obs)	0.0218	0.0220	0.0214	0.0211	0.0905
R_1 (all)	0.0222	0.0223	0.0219	0.0214	0.0988
wR_1 (obs)	0.0367	0.0360	0.0396	0.0404	0.0987
Residuals (e/Å ³ ; fm/Å ³)	+0.38 -0.33	+0.36 -0.35	+0.38 -0.34	+0.39 -0.35	+4.60 -3.66

*neutron diffraction data

$$R_{\text{int}} = \frac{\sum |F_{\text{obs}}^2 - F_{\text{obs}(\text{mean})}^2|}{\sum (F_{\text{obs}}^2)}; R_1 = \frac{\sum (|F_{\text{obs}} - F_{\text{calc}}|)}{\sum |F_{\text{obs}}|};$$

$$wR_1 = \frac{(\sum (w(F_{\text{obs}}^2 - F_{\text{calc}}^2)^2))^{0.5}}{\sum (w(F_{\text{obs}}^2)^{0.5})}, w = 1/(\sigma^2(F_{\text{obs}}^2))$$

Table 3. Average bond lengths (\AA , triangularly coordinated boron) and volumes (\AA^3) of the cations coordination polyhedra at different temperatures, based on the X-ray structure refinements.

T (K)	<B1-O> <B11-O>	<B12-O>	V(B2) V(B21)	V(B22)	V(B3) V(B31)	V(B32)	V(Ca) V(Ca11)	V(Ca12)	Residual voids*
300	1.3678(9)		1.638(1)		1.640(1)		26.142(8)		442.6(3)
295	1.3677(9)		1.639(1)		1.639(1)		26.140(7)		442.6(2)
290	1.3678(9)		1.639(1)		1.639(1)		26.135(7)		442.5(2)
285	1.3678(9)		1.639(1)		1.639(1)		26.133(8)		442.4(3)
280	1.3679(9)		1.639(1)		1.639(1)		26.129(8)		442.3(3)
275	1.3678(9)		1.638(1)		1.639(1)		26.123(8)		442.2(3)
270	1.3682(9)		1.638(1)		1.639(1)		26.121(7)		442.1(2)
265	1.368(1)		1.638(1)		1.639(1)		26.118(8)		442.0(3)
260	1.368(3)	1.369(3)	1.641(3)	1.643(4)	1.638(3)	1.654(3)	26.10(2)	26.11(2)	441.9(3)
255	1.366(3)	1.369(3)	1.636(3)	1.641(3)	1.634(3)	1.644(3)	26.07(2)	26.16(2)	441.7(3)
250	1.366(3)	1.368(3)	1.637(2)	1.644(2)	1.632(2)	1.645(2)	26.06(2)	26.16(2)	441.7(3)
245	1.368(3)	1.367(3)	1.640(2)	1.640(3)	1.636(2)	1.642(2)	26.07(2)	26.15(2)	441.5(3)
180	1.369(3)	1.368(3)	1.638(2)	1.641(2)	1.639(2)	1.642(3)	25.99(2)	26.12(2)	440.4(3)
140	1.369(3)	1.368(3)	1.645(2)	1.635(2)	1.637(2)	1.643(3)	25.92(2)	26.14(2)	439.7(3)
104	1.369(3)	1.368(3)	1.643(2)	1.637(2)	1.634(2)	1.647(2)	25.8888	26.15(2)	439.3(3)

* defined as $R.V. = V_{\text{unit-cell}} - \sum_{\text{unit cell}} [V(\text{B}) + V(\text{Ca})]$

Table 4. Atomic coordinates, site occupancy factors (fixed) and isotropic/equivalent displacement parameters (\AA^2) from the structure refinements based on the X-ray diffraction data collected at 300 K (space group $P2_1/a$) and 104 K (space group $P2_1$), respectively, and on the neutron diffraction data collected at 20 K (space group $P2_1$).

<i>P2₁/a</i> -colemanite at 300 K					
Site	s.o.f.	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso/eq}
Ca	1	0.63476(2)	0.21111(1)	0.73665(2)	0.0082(1)
B1	1	0.3344(1)	0.21262(6)	0.3139(1)	0.0057(2)
B2	1	0.03969(9)	0.17114(6)	0.1622(1)	0.0049(2)
B3	1	0.2206(1)	0.05222(7)	0.4962(1)	0.0053(2)
O1	1	-0.01827(6)	0.24681(5)	0.31544(9)	0.0074(2)
O2	1	0.18867(6)	0.23154(5)	0.13902(9)	0.0066(2)
Oh3	1	-0.08002(6)	0.16395(5)	-0.07283(9)	0.0083(2)
O4	1	0.34211(7)	0.14801(5)	0.50994(9)	0.0093(2)
O5	1	0.08715(6)	0.05573(4)	0.27086(8)	0.0058(2)
Oh6	1	0.29469(8)	-0.06590(5)	0.5144(1)	0.0114(2)
Oh7	1	0.16693(7)	0.07702(5)	0.69755(9)	0.0087(2)
Ow8	1	0.61366(8)	0.01897(6)	0.9010(1)	0.0164(2)
H1	1	-0.077(2)	0.094(1)	-0.128(3)	0.030(2)
H2	1	0.091(2)	0.033(1)	0.701(3)	0.030(2)
H3	1	0.345(2)	-0.086(1)	0.638(2)	0.030(2)
H4	1	0.695(2)	-0.010(1)	1.010(2)	0.030(2)
H5a	0.5	0.586(4)	-0.018(3)	0.770(3)	0.030(2)
H5b	0.5	0.544(4)	0.003(3)	0.972(6)	0.030(2)
<i>P2₁</i> -colemanite at 104 K					
Ca11	1	0.88407(4)	0.21247(3)	0.73771(5)	0.0036(1)
Ca12	1	-0.38444(4)	-0.20863(4)	-0.73580(5)	0.0033(1)
B11	1	0.5843(2)	0.2082(2)	0.3135(3)	0.0026(3)
B12	1	-0.0839(2)	-0.2172(2)	-0.3160(3)	0.0038(3)
B21	1	0.2895(2)	0.1693(2)	0.1623(3)	0.0023(3)
B22	1	0.2186(2)	-0.1725(2)	-0.1625(3)	0.0032(3)
B31	1	0.4709(2)	0.0500(2)	0.4998(3)	0.0015(3)

B32	1	0.0211(3)	-0.0530(2)	-0.4958(3)	0.0036(3)
O11	1	0.2394(1)	0.2445(1)	0.3158(2)	0.0037(3)
O12	1	0.2676(1)	-0.2484(1)	-0.3175(2)	0.0037(3)
O21	1	0.4384(1)	0.2309(1)	0.1399(2)	0.0032(3)
O22	1	0.0678(1)	-0.2327(1)	-0.1383(2)	0.0035(3)
Oh31	1	0.1617(2)	0.1626(1)	-0.0729(2)	0.0045(3)
Oh32	1	0.3306(2)	-0.1648(1)	0.0725(2)	0.0036(4)
O41	1	0.5931(2)	0.1449(1)	0.5104(2)	0.0043(3)
O42	1	-0.0916(2)	-0.1504(1)	-0.5124(2)	0.0045(3)
O51	1	0.3381(1)	0.0533(1)	0.2707(2)	0.0024(2)
O52	1	0.1665(1)	-0.0566(1)	-0.2732(2)	0.0033(2)
Oh61	1	0.5445(2)	-0.0684(1)	0.5224(2)	0.0054(4)
Oh62	1	-0.0466(2)	0.0650(1)	-0.5101(2)	0.0060(4)
Oh71	1	0.4150(2)	0.0773(1)	0.6969(2)	0.0038(3)
Oh72	1	0.0888(2)	-0.0760(1)	-0.7025(2)	0.0054(4)
Ow81	1	0.8588(2)	0.0181(1)	0.9004(2)	0.0081(4)
Ow82	1	-0.3664(2)	-0.0170(1)	-0.8999(2)	0.0085(4)
H11	1	0.188(4)	0.091(2)	-0.121(6)	0.027(2)
H12	1	0.327(4)	-0.097(2)	0.131(6)	0.027(2)
H21	1	-0.060(4)	0.110(3)	-0.622(4)	0.027(2)
H22	1	0.615(3)	-0.085(3)	0.652(3)	0.027(2)
H31	1	0.337(3)	0.035(3)	0.697(5)	0.027(2)
H32	1	0.157(3)	-0.031(3)	-0.715(5)	0.027(2)
H41	1	0.930(3)	-0.018(4)	1.002(6)	0.027(2)
H42	1	-0.455(3)	0.008(5)	-1.008(5)	0.027(2)
H51a	0.5	0.773(5)	0.007(8)	0.94(1)	0.027(2)
H51b	0.5	0.844(5)	-0.026(4)	0.783(5)	0.027(2)
H52a	0.5	-0.302(6)	-0.005(8)	-0.978(8)	0.027(2)
H52b	0.5	-0.300(5)	0.026(4)	-0.779(6)	0.027(2)

*P*₂₁-colemanite at 20 K

Ca11	1	0.8821(9)	0.2081(6)	0.734(1)	0.0031(5)
Ca12	1	-0.3857(9)	-0.2131(6)	-0.741(1)	0.0031(5)

B11	1	0.5809(8)	0.2140(5)	0.314(1)	0.0023(3)
B12	1	-0.0878(8)	-0.2114(5)	-0.316(1)	0.0023(3)
B21	1	0.2901(7)	0.1679(5)	0.165(1)	0.0023(3)
B22	1	0.2191(7)	-0.1739(5)	-0.161(1)	0.0023(3)
B31	1	0.4725(7)	0.0522(6)	0.496(1)	0.0023(3)
B32	1	0.0399(7)	-0.0521(6)	-0.501(1)	0.0023(3)
O11	1	0.2394(7)	0.2460(5)	0.315(1)	0.0040(3)
O12	1	0.2675(7)	-0.2467(5)	-0.318(1)	0.0040(3)
O21	1	0.4363(7)	0.2314(5)	0.141(1)	0.0040(3)
O22	1	0.0696(8)	-0.2327(5)	-0.139(1)	0.0040(3)
Oh31	1	0.1602(7)	0.1572(4)	-0.077(1)	0.0040(3)
Oh32	1	0.3315(7)	-0.1691(4)	0.069(1)	0.0040(3)
O41	1	0.5926(7)	0.1504(5)	0.515(1)	0.0040(3)
O42	1	-0.0926(7)	-0.1460(5)	-0.509(1)	0.0040(3)
O51	1	0.3405(7)	0.0537(5)	0.273(1)	0.0040(3)
O52	1	0.1635(7)	-0.0561(5)	-0.272(1)	0.0040(3)
Oh61	1	0.5440(7)	-0.0669(5)	0.5077(9)	0.0040(3)
Oh62	1	-0.0469(8)	0.0668(6)	-0.5278(9)	0.0040(3)
Oh71	1	0.4199(7)	0.0718(5)	0.7063(9)	0.0040(3)
Oh72	1	0.0820(7)	-0.0805(5)	-0.6930(9)	0.0040(3)
Ow81	1	0.8637(7)	0.0138(6)	0.901(1)	0.0040(3)
Ow82	1	-0.3628(7)	-0.0188(5)	-0.901(1)	0.0040(3)
H11	1	0.179(1)	0.0777(7)	-0.142(2)	0.0185(5)
H12	1	0.335(1)	-0.0974(8)	0.125(2)	0.0185(5)
H21	1	-0.069(1)	0.0999(8)	-0.673(2)	0.0185(5)
H22	1	0.628(1)	-0.0812(8)	0.651(2)	0.0185(5)
H31	1	0.332(1)	0.021(1)	0.706(2)	0.0185(5)
H32	1	0.190(1)	-0.030(1)	-0.692(2)	0.0185(5)
H41	1	0.955(2)	-0.021(2)	1.020(3)	0.0185(5)
H42	1	-0.450(2)	0.021(1)	-1.016(3)	0.0185(5)
H51a	0.5	0.770(2)	0.0046(19)	0.955(3)	0.0185(5)
H51b	0.5	0.7859(15)	-0.0133(11)	0.762(2)	0.0185(5)

H52a	0.5	0.706(2)	0.0050(19)	1.024(3)	0.0185(5)
H52b	0.5	-0.3352(15)	0.0283(10)	-0.767(2)	0.0185(5)

Table 5. Hydrogen-bonding network as determined from the structure refinements based on the X-ray diffraction data collected at 300 and 104 K, respectively, and on the neutron diffraction data collected at 20 K.

T (K)	O _{donor}	H	O _{acceptor}	O _d -H (Å)	H...O _a (Å)	O _d -H-O _a (°)
300	Oh3	H1	O5	0.86(1)	1.89(1)	175(1)
104	Oh31	H11	O52	0.88(3)	1.87(2)	167(3)
	Oh32	H12	O51	0.85(3)	1.87(3)	175(3)
20	Oh31	H11	O52	0.97(1)	1.69(1)	176.1(8)
	Oh32	H12	O51	0.869(5)	1.905(6)	175.0(5)
300	* Oh6	H2	O1	0.76(1)	2.37(2)	119(1)
	* Oh6	H2	O2	0.76(1)	2.53(2)	130(1)
104	° Oh61	H21	O11	0.83(2)	2.31(3)	119(3)
	° Oh61	H21	O21	0.83(2)	2.54(3)	117(3)
	# Oh62	H22	O12	0.81(3)	2.28(3)	121(3)
	# Oh62	H22	O22	0.81(3)	2.30(3)	162(3)
20	° Oh61	H21	O11	0.94(1)	2.26(1)	117.2(8)
	° Oh61	H21	O21	0.94(1)	2.61(1)	110.9(8)
	# Oh62	H22	O12	0.92(1)	2.43(1)	102.2(9)
	# Oh62	H22	O22	0.92(1)	2.21(1)	143.9(9)
300	Oh7	H3	O5	0.83(2)	1.91(2)	174(2)
104	Oh71	H31	O52	0.83(3)	1.88(3)	174(3)
	Oh72	H32	O51	0.82(3)	1.90(3)	172(3)
20	Oh71	H31	O52	0.95(1)	1.73(1)	172(1)
	Oh72	H32	O51	0.98(1)	1.75(1)	172(1)
300	Ow8	H4	Oh7	0.85(1)	1.93(1)	164(2)
104	Ow81	H41	Oh72	0.86(3)	1.90(3)	160(4)
	Ow82	H42	Oh71	0.87(3)	1.92(3)	156(3)
20	Ow81	H41	Oh72	0.95(2)	1.85(2)	161(2)
	Ow82	H42	Oh71	0.95(2)	1.77(2)	160(2)
300	* Ow8	H5a	Ow8	0.87(4)	1.81(4)	174(3)
	* Ow8	H5b	O1	0.86(2)	2.72(3)	129(2)
	* Ow8	H5b	O4	0.86(2)	2.48(3)	150(3)

104	°	Ow81	H51a	W82	0.87(5)	1.82(6)	165(5)
	°	Ow81	H51b	O11	0.84(4)	2.67(4)	135(3)
	°	Ow81	H51b	O42	0.84(4)	2.48(4)	135(3)
	#	Ow82	H52a	Ow81	0.86(6)	1.81(6)	171(4)
	#	Ow82	H52b	O12	0.87(3)	2.59(4)	137(3)
	#	Ow82	H52b	O41	0.87(3)	2.57(4)	130(3)
20	°	Ow81	H51a	W82	0.91(2)	1.77(2)	172(2)
	°	Ow81	H51b	O11	0.93(1)	2.73(1)	117.1(9)
	°	Ow81	H51b	O42	0.93(1)	2.69(2)	115(1)
	#	Ow82	H52a	Ow81	0.91(2)	1.78(2)	165(2)
	#	Ow82	H52b	O12	0.93(1)	2.60(1)	134(1)
	#	Ow82	H52b	O41	0.93(1)	2.43(2)	152(1)

* , ° , #: mutually exclusive configurations

Table 6. Experimental X-ray diffraction peaks violating the extinction conditions expected for the $P2_1/a$ space group, at selected temperatures.

T (K)	Classes of reflections	$\langle I_{hkl}/\sigma(I_{hkl}) \rangle$	$I_{hkl}/\sigma(I_{hkl}) > 1.0$ *	$I_{hkl}/\sigma(I_{hkl}) > 3.0$ *	$I_{hkl}/\sigma(I_{hkl}) > 6.0$ *
300	$h00, h = 2n+1$	0.2	0	0	0
	$0k0, k = 2n+1$	0.2	1	0	0
	$h0l, h = 2n+1$	0.2	8	0	0
275	$h00, h = 2n+1$	0.2	0	0	0
	$0k0, k = 2n+1$	0.2	1	0	0
	$h0l, h = 2n+1$	0.3	10	0	0
270	$h00, h = 2n+1$	0.1	0	0	0
	$0k0, k = 2n+1$	0.2	0	0	0
	$h0l, h = 2n+1$	0.3	12	0	0
265	$h00, h = 2n+1$	0.3	0	0	0
	$0k0, k = 2n+1$	0.2	1	0	0
	$h0l, h = 2n+1$	0.3	20	0	0
260	$h00, h = 2n+1$	0.4	1	0	0
	$0k0, k = 2n+1$	0.2	0	0	0
	$h0l, h = 2n+1$	0.6	48	5	0
255	$h00, h = 2n+1$	0.7	4	1	0
	$0k0, k = 2n+1$	0.3	2	1	0
	$h0l, h = 2n+1$	1.5	139	38	18
250	$h00, h = 2n+1$	1.5	7	2	1
	$0k0, k = 2n+1$	0.2	1	0	0
	$h0l, h = 2n+1$	2.5	188	97	32
245	$h00, h = 2n+1$	1.1	8	1	0
	$0k0, k = 2n+1$	0.3	3	1	0
	$h0l, h = 2n+1$	2.4	197	94	30
104	$h00, h = 2n+1$	2.3	7	5	4
	$0k0, k = 2n+1$	0.2	0	0	0
	$h0l, h = 2n+1$	3.9	241	151	72

* Number of peaks violating the reported cut-off criterion