

1 **Thermal stability and high-temperature behavior of the natural**
2 **borate colemanite:**
3 **an aggregate in radiation-shielding concretes.**
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21

22 **Abstract**

23 Colemanite is a natural borate that can be used as an aggregate in neutron-radiation shielding
24 concretes. In this study, we report its thermal behavior, up to 500°C, by describing: 1) its
25 dehydration mechanisms and 2) its thermo-elastic parameters. The thermal expansion of
26 colemanite is significantly anisotropic. The refined volume thermal expansion coefficient at
27 ambient conditions is: $\alpha_{v0} = 4.50(10) \cdot 10^{-5} \text{ K}^{-1}$. The loss of structural H₂O occurs at least from ~
28 240 °C and at $T > 325 \text{ °C}$, an irreversible amorphization occurs, followed by a complete
29 dehydration. The potential implications on the use of colemanite as concrete-aggregate are
30 discussed.

31

32 **Keywords**

33

34 Colemanite, boron, neutron radiation shielding concretes, high temperature, dehydration,
35 amorphization, thermal expansion coefficient, synchrotron X-ray diffraction

36

37 1. Introduction

38

39 The need to protect workers and public exposed to radiation emitted, for example, by nuclear
40 reactors for energy production or by neutron facilities for scientific research or medical
41 applications requires the development and the production of suitable materials able to shield
42 from harmful radiations. In this light, ^{10}B (which accounts for approximately the 20% of natural
43 boron [1]) emerges as an interesting isotope for its elevated ability to absorb thermal neutrons
44 due to its high cross section for $^{10}\text{B}(n,\alpha)^7\text{Li}$ reaction (3840 barns [2,3]). Consequently, neutrons
45 reaction with ^{10}B suppresses escaping radiations and generates alpha particles (easily absorbable
46 by few μm of material) and ^7Li , a stable isotope. It follows that boron compounds are target
47 materials to be added as aggregates for the production of radiation-shielding concretes. Synthetic
48 B_4C , for example, can be successfully used for this scope [4], but due to its high costs it is often
49 replaced by cheaper natural borates [5]. Among them, colemanite, ideal formula
50 $\text{CaB}_3\text{O}_4(\text{OH})_3\cdot\text{H}_2\text{O}$, is one of the major candidates, due to its large availability in nature and the
51 resulting abundance of waste colemanite ore at the mining site, which recycling may result in an
52 economic profit [6-8]. Colemanite is also largely utilized as a raw material for the production of
53 boric acid [9]. For these reasons, the use of colemanite as an aggregate has been the subject of a
54 series of investigations [10-14]. In the nuclear field, colemanite has been widely applied for the
55 production of radiation-shielding concretes prototypes [5,15], which showed that its addition is
56 efficient in reducing the transmission of radiation [5,10,12] and lowering the concrete activation
57 for radiation emission in the low and medium term [11,15,16]. In fact, concrete containing
58 colemanite or boron ores, in association with high-density aggregates, proved to possess low
59 radioactive permeability and effectively prevent both neutrons and gamma radiation transmission
60 [17-21]. These materials have been successfully employed not only as heavyweight concrete
61 biological shield of nuclear reactors and research laboratories, but also of neutron therapy
62 centers, such as radiation oncology and radiology departments [17]. Furthermore, the high
63 radiation shielding property has been successfully applied to improve shielding from Am-Be
64 sources, since they emit neutrons along with gamma radiations. The use of colemanite concrete
65 proved to be an easier and more effective solution than distributing gamma shields (e.g. lead
66 blocks) within neutron absorbing materials, such as paraffin [22-23]. In presence of high-energy
67 gamma- and X-ray sources, the lower atomic number of elements constituting colemanite
68 concrete represents a further advantage with respect to lead shields, in particular in the pair
69 production and Compton scattering regions [17,24]. Moreover, with a view to ensure safe
70 shipment of nuclear material, boron enriched cementitious containers have been proficiently
71 proposed. In this perspective, the optimization of the neutron shielding effect requires a
72 homogeneous distribution of boron within the cement matrix [25].

73 For its large availability and low costs, colemanite has also been investigated to be added in
74 ordinary cements and mortars, lightweight concretes and bricks, and geopolymers [7,8,26-32].
75 By way of example, colemanite could be added to pumice lightweight concrete to improve its
76 radiation shielding, thus extending the applicability of this low density and low cost, high
77 thermal insulation and high durability material to the nuclear field [32]. These applications drove

78 the interest in studying the effects induced by the addition of colemanite on the physico-chemical
79 properties of cements and concretes, from which it emerged that the major drawbacks are a delay
80 in the cement setting and a lowering of the concrete compressive strength [14,17,26-29,32-34],
81 even though they resulted to be less pronounced than those induced by two other common
82 natural borates as ulexite and borax [34].

83 It is of the utmost importance to investigate the intrinsic properties at non-ambient conditions of
84 the individual compounds making the cement and the aggregates, in order to understand and
85 forecast the behavior of the concretes at the same conditions. In the case of a hydrous mineral
86 like colemanite, for example, it is necessary to determine its high-temperature phase stability
87 field, its thermal-elastic behavior (*i.e.*, bulk volume expansion and axial anisotropic scheme),
88 how and when the temperature-induced release of structural H₂O occurs (taking into account that
89 colemanite contains molecular H₂O and hydroxyl groups). Surprisingly, despite the interest
90 driven by the applications of colemanite, only a few experiments have been focused to study its
91 intrinsic thermal behavior [35-38]. The effect of mechanical treatment on colemanite thermal
92 properties was studied, taking into consideration thermal stability and other thermodynamic
93 parameters related to phase transition, such as structural relaxation and crystallization [39]. The
94 modification of some colemanite physical properties, such as porosity, density and surface area,
95 has been investigated as a function of temperature, up to 600 °C [30]. To the best of our
96 knowledge, neither a structure refinement based on *in situ* high-*T* data, nor the *T*-induced
97 evolution of the bulk volume and unit-cell parameters of colemanite has so far been reported
98 and, therefore, its thermal behavior is not completely known.

99 In this light, the scope of this study is to provide, by means of *in situ* differential scanning
100 calorimetry, thermogravimetric and synchrotron X-ray diffraction analyses, a clearer picture of
101 the behavior of colemanite at high temperature by: 1) providing a thorough characterization of
102 the dehydration process and of its influence on the structural stability and 2) quantifying the
103 volume thermal expansion coefficient at ambient conditions and at varying temperature. This
104 study is part of a long-term project devoted to the characterization of the behavior of B-
105 containing compounds at non-ambient conditions [40-46], which included: 1) the study of the
106 high-pressure behavior of colemanite, reporting a *P*-induced reconstructive phase transition,
107 characterized by the increased coordination of a fraction of B atoms from triangular to
108 tetrahedral [45], and 2) the study of the low-*T* behavior of colemanite, with the transition to its
109 ferroelectric polymorph [46].

110

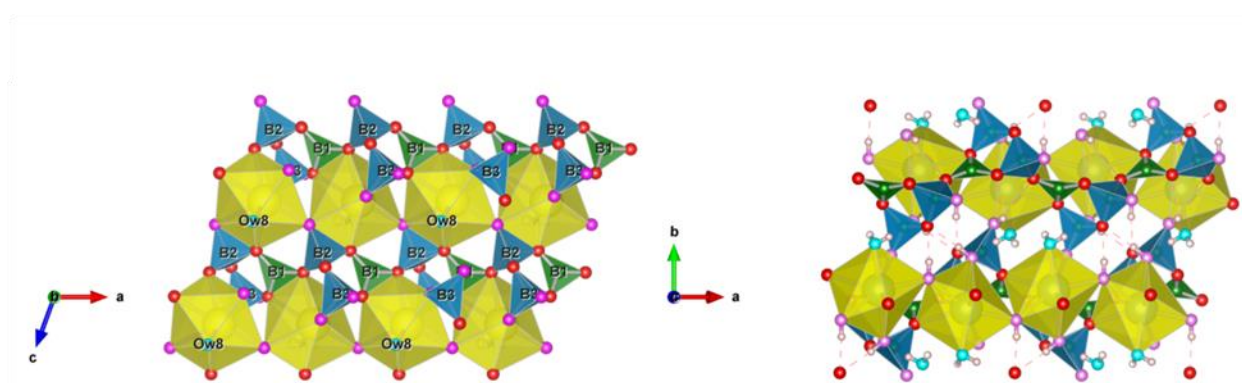
111 2. Crystal structure of colemanite

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113 At ambient conditions, colemanite is monoclinic, space group $P2_1/a$, unit-cell parameters: $a \sim$
114 8.74 , $b \sim 11.26$, $c \sim 6.10$ Å and $\beta \sim 110.12^\circ$. Its crystal structure has been first solved by Christ et
115 al. [47] and later refined by Christ et al. [48] and Clark et al. [49]. It is characterized by infinite
116 chains of B-coordination polyhedra running along the **a** crystallographic axis (Figure 1). These
117 chains are built by the repetition of the same corner-sharing building unit, made by one B atom
118 in triangular coordination with oxygens, and two B atoms in tetrahedral coordination with both

119 oxygens and hydroxyl groups. The borate chains are linked along the **c** crystallographic direction
120 by chains of corner-sharing Ca-coordination polyhedra (coordination number: 8, Figure 1),
121 building up heteropolyhedral layers perpendicular to the **b** axis. Along that direction, the layers
122 are interconnected by few Ca-O(H)-B bonds and an extensive network of H-bonds made by both
123 the hydroxyl groups and the H₂O molecules [46], resulting in weaker connections along the **b**
124 axis that are responsible for the perfect (010) cleavage plane observed in colemanite crystals. On
125 cooling, at temperatures between 0 and -12°C, depending on the amount of chemical impurities
126 [50], colemanite undergoes a phase transition toward a ferroelectric polymorph, still monoclinic,
127 but with space group $P2_1$ and a slightly displaced atomic arrangement [46,51].

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129

130

131 **Figure 1.** (Left) The crystal structure of colemanite viewed down the **b** crystallographic axis,
132 showing the heteropolyhedral layers made by alternating borate and Ca-polyhedra chains. Every
133 borate chain is made by the repetition of three-membered rings, formed by one boron site in
134 triangular coordination and two boron sites in tetrahedral coordination. (Right). The colemanite
135 structure viewed down the **c** axis: the heteropolyhedral layers are weakly interconnected by few
136 Ca-O(H)-B bonds and by a network of H-bonds. These pictures have been created using the
137 software VESTA [61].

138

139 3. Materials and experimental methods

140

141 The same natural sample of massive and transparent colemanite, already investigated and
142 described by [45,46], has been used for this study. The sample, provided by the Museum of
143 Mineralogy of the University of Padua (Italy), comes from the borate deposits of the Bigadiç
144 Mine (Balıkesir Province, Marmara Region, Turkey [52]). In order to perform the analyses
145 described in the following section, the massive sample was ground in an agate mortar into a
146 homogeneous powder.

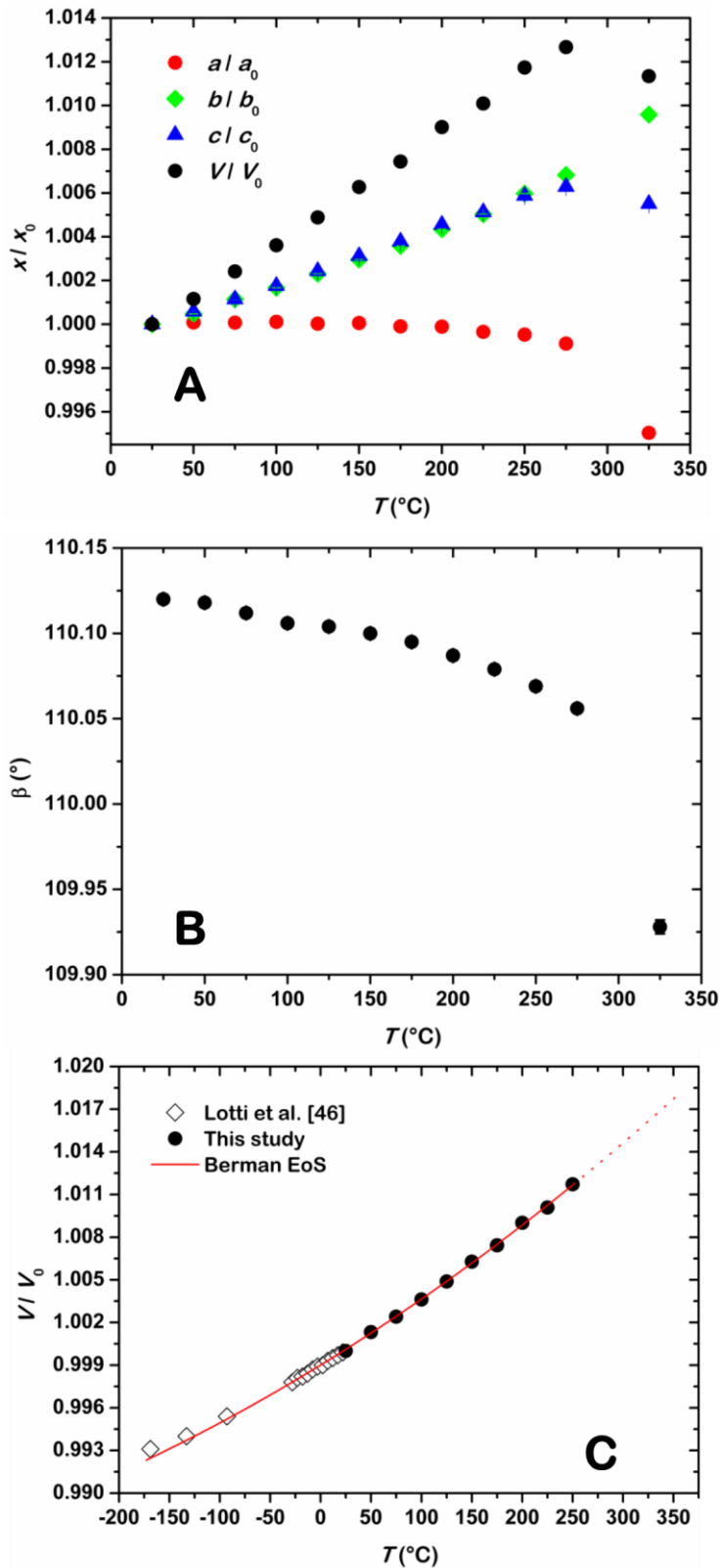
147 The chemical analysis has been performed by means of a multi-methodological approach, which
148 surveyed more than 50 chemical species. The analytical protocol is described in [46], whereas
149 the chemical composition, summarizing the major components, is reported in Table 1.

150 Differential scanning calorimetry (DSC) and thermogravimetric (TG) analyses have been
151 performed in the temperature range 30-500 °C with a scanning rate of 2 °C/min under 50mL/min
152 flux of air using the Mettler Toledo TGA/DSC 3+ instrument.

153 *In situ* high-temperature synchrotron powder X-ray diffraction (SR-XRPD) experiments have
154 been carried out at the MCX beamline of the Elettra facility (Trieste, Italy), which experimental
155 setup is described in [53]. The polycrystalline sample of colemanite was loaded in a quartz
156 capillary (300- μm in diameter), which was kept spinning during the data collection. For all the
157 point analyses, a monochromatic incident beam ($\lambda = 0.827 \text{ \AA}$) was used and the diffraction
158 patterns were collected using the high-resolution scintillator detector mounted on the four-circle
159 diffractometer available at the beamline. The following data collection strategy was adopted: 2θ
160 range between 5 and 50°, step-width = 0.008°, exposure time 1 s. High- T conditions were
161 obtained using a hot gas blower directing a hot air flux on the spinning quartz-capillary, whereas
162 temperature was measured by a thermocouple and previously calibrated using the thermal
163 expansion and phase transition of quartz. A first temperature ramp was performed from ambient
164 conditions (25 °C) up to 375°C, with data collections every 50°C. A second ramp was later
165 performed using the same batch sample at the same experimental conditions of the first ramp
166 from 50 to 250°C, with data collections every 50 °C. Overall, a total of thirteen XRD patterns
167 have been collected at the temperature conditions reported in Table 2.

168 Full-profile fits were performed by the Rietveld method, using the GSAS [54] and EXPGUI [55]
169 packages. The atomic coordinates reported in [46], for the same colemanite sample, were used as
170 starting model. The background curve was modeled by a Chebyshev polynomial with 19 variable
171 parameters, whereas the peak profiles were modelled using the pseudo-Voigt function of
172 Thomson et al. [56]. The unit-cell and structural parameters of colemanite were also refined
173 adopting the following restraints: 1) displacement parameters were modeled as isotropic (U_{iso})
174 and the B and O atoms were restrained to share the same U_{iso} group-value, respectively; 2) $\text{B}^{\text{III}}\text{-O}$
175 and $\text{B}^{\text{IV}}\text{-O}$ (where B^{III} and B^{IV} are boron atoms in triangular and tetrahedral coordination,
176 respectively) bond distances were restrained to 1.36 ± 0.05 and $1.46 \pm 0.05 \text{ \AA}$, respectively. In
177 addition, the refinement of the fractional occupancy of the H_2O -oxygen atom (Ow) was always
178 tried if the refined value deviated from the full site occupancy ($\pm 1\sigma$). In the final cycles of
179 refinement, the following parameters were simultaneously refined: scale factor, background and
180 peak profiles parameters, unit-cell parameters, atomic coordinates and displacement parameters.
181 The zero-shift correction was also refined for the dataset collected at 25 °C and kept constant to
182 this refined value in the Rietveld refinements based on the diffraction patterns collected at higher
183 temperatures. The unit-cell parameters of colemanite at varying temperature are reported in
184 Figure 2 and Table 2. The calculated diffraction patterns, based on the Rietveld refinements at 25
185 and 225 °C, respectively, are reported in Figure S1 (deposited as supplementary materials). The
186 refined structure models (cif files) are deposited as supplementary materials.

187



188
 189 **Figure 2.** (A). High-temperature evolution of the unit-cell parameters of colemantite, normalized
 190 to their ambient-conditions values. (B). High- T evolution of the unit-cell monoclinic β angle of
 191 colemantite. (C). Unit-cell volume as a function of temperature (normalized to ambient-
 192 conditions value) of the same natural sample of colemantite, from this study and from the low- T
 193 study of Lotti et al. [46]. The refined Berman-type thermal equation of state (EoS) is plotted.

194

195 **4. Results**

196

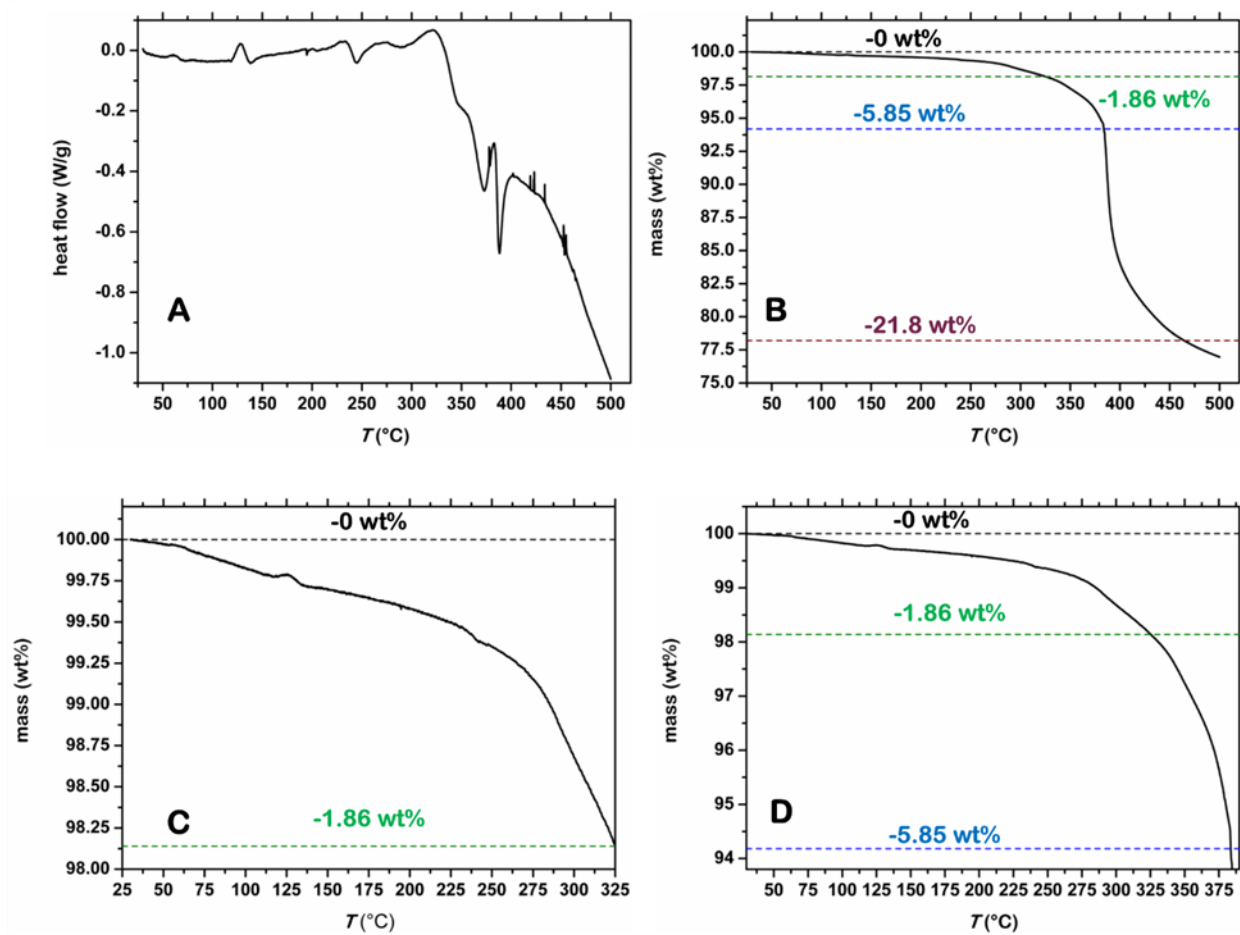
197 **4.1. DSC and TG analyses**

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199 The differential scanning calorimetry and thermogravimetric data of colemanite are plotted in
200 Figure 3. The main features of the DSC pattern are the following: 1) an endothermic peak at
201 247°C; 2) a broad exothermic region between 280 and 310°C; 3) two marked endothermic peaks,
202 centered at 372 and 388°C, can be observed, preceded by an inflection point at 345°C and
203 followed by a broad endothermic region up to the highest temperature investigated of 500°C.
204 These endothermic peaks correspond to those already reported in the literature at close
205 temperatures by several authors, e.g. [35,36,38].

206 The TG pattern shows that the mass loss begins already at $T > 50^\circ\text{C}$. Around 240°C, a minor
207 increase in mass loss is observed, whereas at $T > 275^\circ\text{C}$ a sudden increase in the rate of mass
208 loss occurs. Up to 275°C, the total mass loss is around 1 wt%, whereas it is around 2 wt% at
209 325°C, where a further increase in the rate of mass loss occurs. At 372 °C (endothermic peak in
210 the DSC plot), the mass loss is 4.05 wt% and at $T > 388^\circ\text{C}$ (endothermic peak in the DSC plot) a
211 dramatic increase in the mass loss rate is observed with a final weight at 500°C that is 23.03%
212 lower than the initial value.

213



214
 215 **Figure 3.** (A). The heat flow rate as a function of temperature, from the full T -range investigated
 216 by differential scanning calorimetry. (B). The weight loss (in wt%) as a function of temperature,
 217 from the full T -range investigated by TG analysis. TG data in the T -ranges up to 325 and 375 °C
 218 are reported in graphs (C) and (D), respectively. For an ease of clarity, the weight losses at -1.86
 219 wt% (corresponding to 325 °C, *i.e.* the highest T where crystalline colemanite occurs by XRD
 220 data), at -5.85 wt% (corresponding to the contribution of H₂O molecules of colemanite) and at -
 221 21.8 wt% (corresponding to the contribution of H₂O molecules and hydroxyl groups) are plotted
 222 as reference lines.

223
 224 **4.2. High-temperature behavior of unit-cell parameters and crystal structure**

225
 226 The X-ray diffraction patterns reveal the persistence of a crystalline sample of colemanite up to
 227 325°C (Figure S2, deposited). On the contrary, at 375°C the collected diffraction pattern is
 228 typical of an amorphous substance (Figure S3, deposited). The Rietveld refinements reached
 229 convergence with good statistical parameters up to 275°C (Table 2), whereas for the pattern
 230 collected at 325°C only the unit-cell parameters could be satisfactorily refined.

231 The refined unit-cell parameters at different temperatures are reported in Table 2 and plotted in
 232 Figure 2. The unit-cell a edge undergoes a minor expansion up to 175 °C, where a slight
 233 contraction rate takes place. At the same temperature, a change in the experimental β - T trend can

234 also be observed. At 275°C, a further deviation from the previous T -trends can be observed along
235 the unit-cell c axis and for the volume. At 325°C, a significant volume reduction can be
236 observed, governed by the contraction along the a and c axial edges, whereas the b axis shows an
237 opposite behavior with a boosted expansion with respect to the previous T -trend.

238 The refinement of the occupancy of the Ow site was always tried, but the refined value was 1
239 (within the e.s.d.) up to 250 °C. At 275°C, the Ow refined occupancy was found, for the first
240 time, lower than 1 ($sof = 0.96 \pm 0.02$). Despite the Rietveld refinement of the structural
241 parameters did not converge at 325°C, at least a qualitative analysis of the refined model can be
242 attempted: at this temperature, the site occupancy factor of Ow was ~ 0.77 .

243 The amorphization observed at $T > 325$ °C was found to be irreversible when ambient conditions
244 were recovered.

245

246 **5. Discussion**

247

248 **5.1. Dehydration mechanism of colemanite**

249

250 Despite the dehydration mechanism of colemanite has already been investigated by several
251 authors, a clear picture was still not available: Hartung and Heide [35] reported TG and DTA
252 patterns, describing two endothermic peaks coupled with amorphization at $\sim 400^\circ\text{C}$, two
253 exothermic peaks coupled with recrystallization at $\sim 800^\circ\text{C}$ and an endothermic peak coupled
254 with melting at $\sim 1000^\circ\text{C}$. Waclawska et al. [36] also reported TG, DTG and DTA data of
255 colemanite, and described the occurrence of two endothermic peaks at 369 and 386°C,
256 respectively. Based on IR spectra, they assigned the first peak to the loss of hydroxyl groups,
257 which would be kept as “*intracrystalline water*” up to the T of the second peak, assigned to the
258 explosive release of water and amorphization. Frost et al. [37], based on TG and IR data,
259 reported that the dehydration occurs in a single step at 400.8 °C. Very recently, Rusen [38]
260 reported the first *in situ* high-temperature X-ray diffraction experiment on a commercial sample
261 of colemanite, with minor fractions of quartz and calcite, coupled with TG and DTA analyses.
262 The occurrence of two endothermic peaks at 384 and 399°C, associated to the dehydration of
263 colemanite between 350 and 650°C (and a consequent amorphization) was reported. At 754°C,
264 Rusen [38] reports the crystallization of CaB_2O_4 and $\text{Ca}_2\text{B}_2\text{O}_5$.

265 A comparative analysis of the DSC and TG patterns of this study, coupled with the Rietveld
266 refinements based on the collected XRD data, allows a thorough description of the dehydration
267 mechanism of colemanite. The TG data show that the dehydration already begins at $T \geq 50^\circ\text{C}$
268 (Figure 3). The endothermic peak at 247°C can be coupled with the corresponding minor
269 increase in the rate of mass loss and with the deviations in the a - T and β - T trends observed at $T \geq$
270 175°C (Figures 2 and 3, Table 2). At 275°C, the mass loss is around 1 wt% and, for the first
271 time, the refined occupancy of the H₂O-oxygen Ow site is lower than 1.0. Therefore, if up to \sim
272 240°C the mass loss may also be attributed to moisture or superficial water, the results from
273 DSC, TG and XRD suggest that above this temperature the loss of structural H₂O

274 unambiguously occurs. At $T > 275^{\circ}\text{C}$, an increase in the rate of mass loss is observed (Figure 3)
275 and at 325°C the dehydration clearly affects the unit-cell volume of colemanite, which undergoes
276 a significant contraction governed by the shortening along the **a** and **c** axes, whereas an
277 expansion along **b** is observed (Figure 2 and Table 2). Despite still crystalline, the structural
278 parameters could not be satisfactorily refined at this temperature, suggesting that the mechanism
279 of structural collapse is triggered and is likely acting along the preferential cleavage plane, *i.e.*
280 (010), where the weaker interactions occur between the adjacent layers made by Ca-polyhedra
281 and borate chains (Figure 1). If we consider, from the chemical composition of colemanite
282 (Table 1), that the total H_2O content is 21.8(4) wt% (of which 15.98 wt% can be attributed to the
283 hydroxyls groups and 5.85 wt% to the H_2O molecules), and that at 325°C the mass loss
284 measured from the TG data is 1.86 wt% (Figure 3), we can conclude that the structural collapse
285 of colemanite is induced in the very early stages of dehydration. Between 325 and 375°C , the
286 amorphization process is completed and a mass loss of 5.85 wt% (corresponding to the weight
287 fraction of structural H_2O molecules) is reached at $\sim 382^{\circ}\text{C}$ (Figure 3), whereas at $T > 388^{\circ}\text{C}$
288 (endothermic peak in the DSC pattern, Figure 3) a significant weight loss is shown by the TG
289 data (Figure 3).

290 The colemanite dehydration pattern can, therefore, be summarized as in the following:

- 291 - At $T > 240^{\circ}\text{C}$, the weight loss is unambiguously attributed to the release of structural H_2O ,
292 which is more pronounced at $T \geq 275^{\circ}\text{C}$, triggering the structural collapse that is completed
293 before the H_2O molecules are fully released at $T \sim 375\text{-}385^{\circ}\text{C}$;
- 294 - The endothermic peak at 388°C may be assigned to the dehydroxylation process;
- 295 - At 500°C , the mass loss is 23.03 wt% (Figure 3), that is quite close to the total measured H_2O
296 content of colemanite (*i.e.*, 21.8 wt%), from which it can be concluded that the high-temperature
297 amorphous phase is fully anhydrous, being consistent with the recrystallization of anhydrous Ca-
298 borates reported in [38].

299

300 **5.2. Thermo-elastic behavior of colemanite**

301

302 The intrinsic anisotropy and bulk thermal expansion of the compounds used as aggregates concur
303 in controlling the high-temperature behavior of a concrete. For this reason, one of the scope of
304 this work was to characterize the thermo-elastic behavior of colemanite, by determining the bulk
305 thermal expansion coefficient at ambient conditions and as a function of temperature.

306 The T -induced evolution of the unit-cell parameters, reported in Figure 2 and Table 2, reveals
307 that the thermal expansion of colemanite is significantly anisotropic, being substantially
308 accommodated only along the **b** and **c** crystallographic axes, whereas the **a** axis, which
309 corresponds to the direction of the borate chains (Figure 1), experiences only a minor expansion
310 up to 175°C , where a slight contraction takes place (Figure 2 and Table 2). These results are
311 consistent with those reported in [46] for the range 104-300 K (*i.e.*, from -169 to 27°C) and an
312 analogy can also be found with the high-pressure data [45], where the **a** direction is reported to
313 be the less compressible crystallographic axis.

314 We merged in a single dataset the unit-cell volume data of this study (excluding the points at 275
 315 and 325°C) and those reported in [46] for the same sample in the range $-169 \leq T$ (°C) ≤ 27 ,
 316 normalizing the data to the respective ambient- T values. The experimental (V/V_0) vs. T data
 317 (Figure 2) have been fitted by a Berman T - V equation of state [57] using the EOSFIT7-GUI
 318 software [58], yielding the following refined parameters: $V_{25^\circ\text{C}} = 563.93(3) \text{ \AA}^3$, $a_0 = \alpha_{V25^\circ\text{C}} =$
 319 $4.50(10) \cdot 10^{-5} \text{ K}^{-1}$ and $a_1 = 5.7(8) \cdot 10^{-8} \text{ K}^{-2}$, where $\alpha_V = 1/V \cdot (\partial V / \partial T)_P$. The Berman equation of
 320 state is expressed as:

$$321 \quad V(T) = V(T_0) \cdot [1 + a_0(T - T_0) + 0.5a_1(T - T_0)^2],$$

$$322 \quad \text{and } \alpha_V [\text{K}^{-1}] \approx a_0 + a_1(T - T_0) = 4.50(10) \cdot 10^{-5} + 5.7(8) \cdot 10^{-8}[T(^\circ\text{C}) - 25].$$

323 In order to quantify the anisotropy of the bulk thermal expansion of colemanite, the l vs. T
 324 datasets of this study ($l = a, b, c$) have been fitted by linear Berman-type thermal equations of
 325 state using the EOSFIT7-GUI software [58], excluding the points at 275 and 325 °C as for the
 326 volume. The refined linear thermo-elastic parameters are reported in the following: $a_{25^\circ\text{C}} =$
 327 $8.7342(3) \text{ \AA}$, $a_{0(a)} = \alpha_{a25^\circ\text{C}} = 0.28(8) \cdot 10^{-5} \text{ K}^{-1}$ and $a_{1(a)} = -4.4(7) \cdot 10^{-8} \text{ K}^{-2}$; $b_{25^\circ\text{C}} = 11.26318(4) \text{ \AA}$,
 328 $a_{0(b)} = \alpha_{b25^\circ\text{C}} = 2.1(2) \cdot 10^{-5} \text{ K}^{-1}$ and $a_{1(b)} = 4(2) \cdot 10^{-8} \text{ K}^{-2}$; $c_{25^\circ\text{C}} = 6.1034(2) \text{ \AA}$, $a_{0(c)} = \alpha_{c25^\circ\text{C}} =$
 329 $2.30(9) \cdot 10^{-5} \text{ K}^{-1}$ and $a_{1(c)} = 3.2(9) \cdot 10^{-8} \text{ K}^{-2}$. We can, therefore, conclude that the thermal
 330 anisotropy at ambient conditions can be expressed as $\alpha_{a25^\circ\text{C}} : \alpha_{b25^\circ\text{C}} : \alpha_{c25^\circ\text{C}} = 1 : 7.5 : 8.2$.

331

332 **6. Conclusions**

333

334 The thermal bulk volume (isotropic or anisotropic) expansion and the dehydration mechanism of
 335 a given hydrated compound used as an aggregate are important parameters that allow to
 336 understand and forecast the behavior of a concrete under heating or cooling. In this study, by
 337 means of in situ DSC, TG and XRD data, we have characterized the dehydration mechanism of
 338 colemanite, a hydrous Ca-borate mineral used as an aggregate in radiation-shielding concretes,
 339 and determined its bulk thermal expansion coefficient along with its expansion anisotropic
 340 scheme.

341 The TG data show that the dehydration already begins at $T \geq 50^\circ\text{C}$, whereas the release of
 342 structural H_2O unambiguously occurs at least from $\sim 240^\circ\text{C}$. A minor fraction of released H_2O (\sim
 343 2 wt%) is sufficient to trigger the structural collapse, which likely acts along the preferential
 344 cleavage plane, *i.e.* (010), with a boosted expansion of the **b** crystallographic axis. At $T > 388^\circ\text{C}$
 345 all the structural H_2O (*i.e.*, H_2O molecules + OH groups) are released and colemanite is
 346 irreversibly converted into an anhydrous amorphous phase.

347 The experimental findings of this study should be carefully considered for the utilization of
 348 colemanite as aggregate (expected to preserve its crystalline form) for concretes, as its T -induced
 349 structural transformations may impact on the stability of the manufactures, at least at $T \geq 250^\circ\text{C}$.
 350 This is certainly compatible with colemanite employment in radiation shields of radiotherapy
 351 centers and should not represent an issue for most of actual nuclear reactors. By way of example,
 352 the temperature of concrete biological shield of the widely prevalent Light Water Reactors

353 (LWR) is well below 100°C [59]. In the case of High Temperature Gas Reactors (HTGR), where
354 fuel elements can exceed 1000°C, suitable cooling panels are usually installed on the inner
355 concrete wall, in order to maintain the concrete temperature below 50-65°C [60].

356 Based on the refined thermo-elastic parameters of this study and on the high-pressure elastic
357 parameters reported in [45] for the same sample, it is possible to define the equation of state of
358 colemanite that, at a first approximation, is valid in the ranges $-169 \leq T$ (°C) ≤ 250 and $0.0001 \leq$
359 P (GPa) ≤ 13.59 :

360 $V(T,P) \approx V(T_0,P_0) + \alpha_{VT_0}(T - T_0) - \beta_{VT_0}(P - P_0) = 563.93(3) + 4.50(10) \cdot 10^{-5}(T - T_0) - 0.0149(9)(P$
361 $- P_0)$, where $T_0 = 25^\circ\text{C}$ and $P_0 = 0.0001\text{GPa}$.

362

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364

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370

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372

373 **Black and white should be used for any figures in print**

374

375

376 **8. References**

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- 532

533

534 **Figure captions**

535 **Figure 1.** (*Left*) The crystal structure of colemanite viewed down the **b** crystallographic axis,
536 showing the heteropolyhedral layers made by alternating borate and Ca-polyhedra chains. Every
537 borate chain is made by the repetition of three-membered rings, formed by one boron site in
538 triangular coordination and two boron sites in tetrahedral coordination. (*Right*). The colemanite
539 structure viewed down the **c** axis: the heteropolyhedral layers are weakly interconnected by few
540 Ca-O(H)-B bonds and by a network of H-bonds. These pictures have been created using the
541 software VESTA [61].

542 **Figure 2.** (A). High-temperature evolution of the unit-cell parameters of colemanite, normalized
543 to their ambient-conditions values. (B). High-*T* evolution of the unit-cell monoclinic β angle of
544 colemanite. (C). Unit-cell volume as a function of temperature (normalized to ambient-
545 conditions value) of the same natural sample of colemanite, from this study and from the low-*T*
546 study of Lotti et al. [46]. The refined Berman-type thermal equation of state (EoS) is plotted.

547 **Figure 3.** (A). The heat flow rate as a function of temperature, from the full *T*-range investigated
548 by differential scanning calorimetry. (B). The weight loss (in wt%) as a function of temperature,
549 from the full *T*-range investigated by TG analysis. TG data in the *T*-ranges up to 325 and 375 °C
550 are reported in graphs (C) and (D), respectively. For an ease of clarity, the weight losses at -1.86
551 wt% (corresponding to 325 °C, *i.e.* the highest *T* where crystalline colemanite occurs by XRD
552 data), at -5.85 wt% (corresponding to the contribution of H₂O molecules of colemanite) and at -
553 21.8 wt% (corresponding to the contribution of H₂O molecules and hydroxyl groups) are plotted
554 as reference lines.

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559 **Table 1.** (*Left*). The mass fractions (in oxides wt%) of the main chemical components of the
 560 investigated natural sample of colemanite, as obtained by a multi-methodological approach
 561 described in [46]. (*Right*). Selected physical properties of colemanite.

	wt%				
B ₂ O ₃	50.8(4)	Density	[g/cm ³]	2.423(5)	[62]
CaO	27.2(2)	Hardness	[Mohs scale]	4.5	[62]
SrO	0.30(5)	α_{v0}	[K ⁻¹]	4.50(10)·10 ⁻⁵	This study
SiO ₂	0.03(1)	β_{v0}	[GPa ⁻¹]	0.0149(9)	[45]
H ₂ O	21.8(4)	The low- <i>T</i> polymorph of colemanite (space group <i>P2</i> ₁ [46]) is pyroelectric and piezoelectric [50].			

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Table 2. Unit-cell parameters of colemanite and details pertaining to the structure refinements performed at different temperatures

Ramp 1							
<i>T</i> (°C)	25	75	125	175	225	275	325***
Space group	<i>P2₁/a</i>	<i>P2₁/a</i>	<i>P2₁/a</i>	<i>P2₁/a</i>	<i>P2₁/a</i>	<i>P2₁/a</i>	<i>P2₁/a</i>
<i>a</i> (Å)	8.7342(2)	8.7348(2)	8.7344(2)	8.7333(2)	8.7312(2)	8.7268(2)	8.6863(9)
<i>b</i> (Å)	11.2646(2)	11.2774(2)	11.2906(2)	11.3049(2)	11.3212(2)	11.3413(2)	11.3745(8)
<i>c</i> (Å)	6.10352(9)	6.11049(8)	6.11840(8)	6.12661(8)	6.1348(1)	6.1418(2)	6.1348(6)
β (°)	110.120(1)	110.112(1)	110.104(1)	110.095(1)	110.080(1)	110.056(2)	109.913(8)
<i>V</i> (Å ³)	563.86(1)	565.219(8)	566.612(8)	568.053(8)	569.547(9)	571.01(2)	569.89(6)
Observed peaks [<i>F_o</i> ² / σ (<i>F_o</i> ²)>3]	662	662	663	666	667	670	686
Refined param.	67*	66	66	66	66	67**	67**
<i>R</i> (<i>F</i> ²) (obs)	0.0848	0.0907	0.0921	0.1035	0.1157	0.1675	0.1415
<i>R</i> _{peaks} (fitted)	0.0885	0.0897	0.0903	0.0925	0.0993	0.1167	0.1279
<i>wR</i> _{peaks} (fitted)	0.1118	0.1137	0.1143	0.1178	0.1264	0.1522	0.1737
Residuals	+0.94	+1.03	+1.00	+1.22	+1.32	+1.66	+2.09
(<i>e</i> /Å ³)	-0.56	-0.60	-0.54	-0.62	-0.69	-0.95	-0.73
<i>s.o.f.</i> (Ow)	1.0	1.0	1.0	1.0	1.0	0.96(2)	0.77(3)
Ramp 2							
<i>T</i> (°C)	50	100	150	200	250		
Space group	<i>P2₁/a</i>	<i>P2₁/a</i>	<i>P2₁/a</i>	<i>P2₁/a</i>	<i>P2₁/a</i>		
<i>a</i> (Å)	8.7349(2)	8.7351(2)	8.7346(2)	8.7332(2)	8.7301(2)		
<i>b</i> (Å)	11.2699(2)	11.2834(2)	11.2979(2)	11.3135(2)	11.3318(2)		
<i>c</i> (Å)	6.10707(9)	6.11423(8)	6.12257(8)	6.13128(9)	6.1394(2)		
β (°)	110.118(1)	110.109(1)	110.100(1)	110.088(1)	110.069(2)		
<i>V</i> (Å ³)	564.509(9)	565.895(8)	567.396(9)	568.939(9)	570.47(1)		

Observed peaks [$F_o^2/\sigma(F_o^2)>3$]	662	660	660	667	669
Refined param.	66	66	66	66	66
$R(F^2)$ (obs)	0.1301	0.1047	0.1246	0.1386	0.1524
R_{peaks} (fitted)	0.1037	0.0978	0.1023	0.1041	0.1130
wR_{peaks} (fitted)	0.1468	0.1255	0.1302	0.1325	0.1442
Residuals ($e^-/\text{\AA}^3$; fm/ \AA^3)	+1.66 -0.97	+1.62 -0.62	+1.64 -0.63	+1.64 -0.78	+1.95 -0.99
s.o.f. (Ow)	1.0	1.0	1.0	1.0	1.0

* Zero shift refined. The value refined for the 25°C data has been kept constant during the Rietveld refinements based on the experimental data collected at higher temperatures.

** Ow site occupancy factor refined

*** Rietveld refinement at 325°C did not reach convergence
