

High-pressure behavior and *P*-induced phase transition of $\text{CaB}_3\text{O}_4(\text{OH})_3 \cdot \text{H}_2\text{O}$ (colemanite)

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Abstract

Colemanite (ideally $\text{CaB}_3\text{O}_4(\text{OH})_3 \cdot \text{H}_2\text{O}$, space group $P2_1/a$, unit-cell parameters: $a \sim 8.74$, $b \sim 11.26$, $c \sim 6.10$ Å, $\beta \sim 110.1^\circ$) is one of the principal mineralogical components of borate deposits and the most important mineral commodity of boron. Its high-pressure behavior is here described, for the first time, by means of in situ single-crystal synchrotron X-ray diffraction with a diamond anvil cell up to 24 GPa (and 293 K). Colemanite is stable, in its ambient-conditions polymorph, up to 13.95 GPa. Between 13.95 and 14.91 GPa, an isosymmetric first-order single-crystal to single-crystal phase transition (reconstructive in character) toward a denser polymorph (colemanite-II) occurs, with: $\mathbf{a}_{\text{COL-II}} = 3 \cdot \mathbf{a}_{\text{COL}}$, $\mathbf{b}_{\text{COL-II}} = \mathbf{b}_{\text{COL}}$ and $\mathbf{c}_{\text{COL-II}} = 2 \cdot \mathbf{c}_{\text{COL}}$. Up to 13.95 GPa, the bulk compression of colemanite is accommodated by the Ca-coordination and the tilting of the rigid three-membered rings of boron polyhedra. The phase transition leads to an increase of the average coordination number of both the B and Ca sites. A detailed description of the crystal structure of the high- P polymorph, compared to the ambient-conditions colemanite, is given. The elastic behaviors of colemanite and of its high- P polymorph are described by means of III- and II-order Birch-Murnaghan equations of state, respectively, yielding the following refined parameters: $K_{V0} = 67(4)$ GPa and $K_V' = 5.5(7)$ [$\beta_{V0} = 0.0149(9)$ GPa $^{-1}$] for colemanite; $K_{V0} = 50(8)$ GPa [$\beta_{V0} = 0.020(3)$ GPa $^{-1}$] for its high- P polymorph.

Keywords

Colemanite, borates, high pressure, phase transition, compressibility

1. Introduction

Colemanite, a calcium hydrous borate (ideal chemical formula: $\text{CaB}_3\text{O}_4(\text{OH})_3 \cdot \text{H}_2\text{O}$), is a main mineralogical component in natural borate deposits and likely the most important mineral commodity for boron worldwide, e.g.¹⁻³.

Colemanite can also be considered a material of technological and industrial relevance. Several studies have been focused on its use as an additive in concretes⁴⁻⁷ or epoxy-resins⁸, in order to improve the shielding efficiency of these materials for neutron radiations, as already suggested for other B-bearing materials, e.g.⁹⁻¹². Other studies were addressed to investigate the feasibility and the effects induced by the addition of colemanite-rich wastes in the production of lightweight concretes¹³⁻¹⁵, heavy clay ceramics¹⁶ or to improve the mechanical performances of epoxy-resins¹⁷. Similar studies were also performed in the fields of ceramics- and glass-production. Yildiz¹⁸ and Yildiz et al.¹⁹ report that calcined colemanite can be used as a starting material in the production process of CaB_6 , whereas the use of colemanite as source of boron in the production of borosilicate glasses and heatproof ceramics was reported by Pavlyukevich et al.²⁰ and Kichkailo and Levitskii²¹, respectively. This interest in the use of colemanite in different production processes is triggered by the presence of large volumes of colemanite-rich tailings at the mining extraction sites^{15,16}, which is the source for a low-cost material.

In this light, and in view of the reported drawbacks following the use of colemanite as an additive in concretes⁴ and in ceramics production processes¹⁹, a detailed characterization of the structure-property relationships of this borate is advisable.

Colemanite is monoclinic (space group $P2_1/a$) at ambient conditions, unit-cell parameters: $a = 8.743$, $b = 11.264$, $c = 6.102 \text{ \AA}$, $\beta = 110.116^\circ$ and $V = 564.27 \text{ \AA}^3$. Its crystal structure has long been known²²⁻²⁶ and is characterized by the presence of infinite chains of corner-sharing B-

coordination polyhedra running along the **a** crystallographic axis (Figure 1). These chains are built through the repetition of a ring made by three B-polyhedra: one BO₃ triangle and two Bφ₄ tetrahedra (φ = O or OH, following the notation of Burns and Hawthorne²⁵, Figure 1). Neighboring rings are linked through an oxygen hinge shared between a B-triangle and a B-tetrahedron (Figure 1). The borate chains are connected along the crystallographic **c** axis through chains of Ca-coordination polyhedra, with coordination number (CN) 8, which share an oxygen corner (Figure 1). As a result, heteropolyhedral layers are formed parallel to the (010) plane (Figure 1). The neighboring layers are staggered, so that a borate chain is followed in the previous and next layers by Ca-chains. These layers are bonded along the **b** axis only by few Ca-Oh-B links and by the network of H-bonds, which involves the OH groups and the H₂O molecules^{24,25}. This configuration gives rise to weak interlayer bonds, responsible for the perfect (010) cleavage. The H-bonding network has been described on the basis of neutron²⁴ and X-ray²⁵ diffraction data. However, the reported models show partially contrasting results.

Despite the interest shown on the industrial and technological applications of colemanite, we have only a surprisingly incomplete knowledge on the behavior of this compound at non-ambient conditions. In particular, very little is known on the structural modifications at the atomic scale. A second-order phase transition to a ferroelectric phase is long time known to occur at a temperature between 0 and -7 °C^{24,27-29}, which was suggested to be related to a *P*_{21/a}-to-*P*₂₁ symmetry transition³⁰. Several thermogravimetric analyses of colemanite report its dehydration in a range of temperatures between 330 and 400 °C^{18,20,31,32}. However, a model of the structural modifications induced by temperature is still missing and, to the best of our knowledge, nothing is known about the high-pressure behavior of this compound.

In this light, we planned to investigate the behavior of this important borate mineral at non-ambient temperature and pressure conditions. In this paper, we report the high-*P* behavior of

colemanite, on the basis of in situ synchrotron single-crystal X-ray diffraction data collected up to ca. 30 GPa. We will provide the refined elastic parameters, to be included in the thermodynamic databases, and we will describe the structural modifications induced by pressure at the atomic scale. In addition, a phase transition towards a high-pressure polymorph (hereafter colemanite-II) is reported and discussed. The study of the low- and high- T behavior of colemanite is in progress and will be discussed in a forthcoming paper along with the results of a single-crystal neutron-diffraction investigation.

2. Materials and experimental procedure

A natural gem-quality sample of colemanite from the borate deposits of the Bigadiç Mine (Balıkesir Province, Marmara Region, Turkey), provided by the Museum of Mineralogy of the University of Padua (catalogue number MMP M14738), was selected for this study. The chemical formula was determined by a combination of titrimetric, CHN, Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES), and Thermogravimetric (TG) analyses. Further details about the occurrence and the mineralogical description of the colemanite sample used in this study, along with the experimental protocol used for the chemical analyses, are given as *supplementary material*.

The quality of a few single crystals of colemanite was initially checked by X-ray diffraction at the Earth Sciences Dept. of the University of Milan, using a four-circle Xcalibur diffractometer equipped with a point-detector and a CCD, and with the $\text{MoK}\alpha$ -radiation. The high-pressure experiment (at 293 K) was performed at the P02.2 “Extreme Conditions Beamline” at the Petra III synchrotron source at DESY, Hamburg (Germany), for which a description is given in Liermann et al.³³, using a membrane-driven diamond anvil cell (DAC) and Ne as P -transmitting medium. Pressure was measured on the basis of the shift of neon diffraction

peaks³⁴ and of the ruby fluorescence line R_1 ³⁵. An in-house software script³⁶ was used to convert data in order to be processed by the *Crysalis*³⁷ software. More details pertaining to the X-ray diffraction experiment and to the data reduction are reported in the *supplementary material*.

The refinement of the (H-free) colemanite structure, at the different experimental pressures, was performed using the *JANA2006* software³⁸, starting from the model reported by Burns and Hawthorne²⁵. In order to overcome the limited accessibility to reciprocal space (*i.e.* the reduced number of experimental diffraction data with respect to an ambient-conditions collection), which is due to the shadowing of the DAC metal components³⁹, the number of refined variables was kept as low as possible by refining an isotropic displacement parameter (U_{iso}) for each atomic site. In addition, soft restraints to the B-O interatomic distances were applied to target values of 1.36 ± 0.02 and 1.46 ± 0.02 Å for ^[III]B and ^[IV]B, respectively. All refinements converged without any significant correlation among the refined parameters and any significant residual peak in the difference-Fourier maps of the electron density. Statistical details of the structure refinements and a selection of relevant structural parameters are reported in Tables 2 and 3, respectively. The refined site coordinates and displacement parameters of selected datasets are reported in Table S1 (supplementary materials). The full refined structure models (cif files) are deposited.

3. Results and discussion

3.1. High-pressure behavior of colemanite

Colemanite was found to be stable in its ambient-conditions polymorph at least up to 13.95 GPa. Between 13.95 and 14.91 GPa, a single-crystal to single-crystal phase transition occurs, towards a new high- P polymorph (Figure 2, Table 2).

In order to describe the (isothermal) compressional behavior of colemanite, the unit-cell volume vs. pressure data were fitted to a Birch-Murnaghan equation of state truncated to the third order (hereafter III-BM EoS). The BM-EoS, which belongs to the group of the empirical equations of state formulated to describe the V - P relationship of a solid at a fixed temperature, relies on the assumption that the strain energy of a solid under compression can be expressed as a Taylor series in the finite strain. Further details on this EoS and on its widespread use for minerals can be found in Birch⁴⁰, Duffy and Wang⁴¹ and Angel⁴². The unit-cell parameters refined at 13.95 GPa (P_{10}) show a slight deviation, with respect to the general trend defined by the previous points (especially concerning the **b** and the **c** axes, Figure 2 and Table 2), likely in response to the impending phase transition. For this reason, only the data in the P_1 - P_9 range (Table 2) were used for the III-BM EoS fit, using the *EoSFit7.0-GUI* software⁴³, yielding the following refined parameters: $V_0 = 556(1) \text{ \AA}^3$, $K_{V0} = 67(4) \text{ GPa}$ and $K_V' = 5.5(7)$, where K_{V0} is the isothermal bulk modulus at ambient conditions (defined as the inverse of the volume compressibility, $K_{V0} = \beta_V^{-1}$) and K_V' is its P -derivative ($K_V' = \partial K_V / \partial P$). In order to describe the anisotropy of the elastic behavior of colemanite, the components of the compressibility tensor were calculated between 3.54 (P_1) and 13.59 GPa (P_9) using the *Win_Strain* software⁴⁴ and are reported in Table S2. These values show that the structure compressibility is higher along the **c** and the **b** crystallographic axes, whereas is significantly lower along **a**, which corresponds to the direction of the borate and Ca-polyhedra chains (Figure 1).

A comparative analysis of the refined colemanite structure models up to 13.95 GPa was performed to describe the mechanisms of structure deformation. The volumes of the

coordination polyhedra of the B and Ca cations were calculated using the tools implemented in the *Vesta* software⁴⁵ and are reported in Table 3. The values show the different behavior between the **more rigid** B-tetrahedra and the higher compressibility of the Ca-polyhedron, for which a fit with a II-BM EoS yields a $K_{V0} = 81(6)$ GPa. At a first approximation, we can assume that the unit-cell volume not occupied by the coordination polyhedra is made by “structural voids” (note that this rough approximation does not take into account the H atoms and the related H-bonding). These “structural voids” can, therefore, be calculated as $V_{sv} = V_{cell} - [(4 \cdot V_{B2}) + (4 \cdot V_{B3}) + (4 \cdot V_{Ca})]$. Their values are reported in Table 3: the bulk modulus refined from a II-BM EoS fit is $K_{V0} = 74(3)$ GPa. These elastic parameters, which resemble those refined for the bulk material, suggest that the accommodation of the *P*-induced strain in colemanite is almost equally shared by the compression of the Ca-polyhedron and by the tilting of the structural units. Unlike the Ca-polyhedron, the average $\langle B-O \rangle$ bond lengths, as well as the volumes of the B2 and B3 tetrahedra, show only a minor decreasing trend with pressure (Table 3). In addition, not only the single B-polyhedra, but the 3-membered ring is internally undeformed with increasing pressure, and, hence, it also behaves as a quasi-rigid unit. Table 3 reports the high-pressure evolution of the B1-O2-B2 angle (Figure 1), which shows a monotonic closing trend. This behavior suggests that the strain of the borate chain along the **a**-axis (*i.e.* the less compressible direction among the three crystallographic axes) is accommodated by the tilting of the 3-membered rings around the shared O2 hinges. This is a common mechanism of strain accommodation adopted by different classes of materials, as for example the open-framework silicates⁴⁶⁻⁴⁸.

3.2. Phase transition

A single-crystal to single-crystal first-order phase transition occurs between 13.95 and 14.91 GPa, towards a new polymorph which retains the $P2_1/a$ symmetry, but shows the tripling of the **a**-axis length and the doubling of the **c**-axis length (Table 2). At 14.91 GPa, the unit-cell parameters of the new high-pressure polymorph (*i.e.* colemanite-II) are: $a = 25.27(3)$, $b = 10.2064(14)$, $c = 11.726(11)$ Å, $\beta = 112.45(10)^\circ$ and $V = 2795(5)$ Å³. As a result, colemanite-II shows a unit-cell six times larger than that of colemanite, and every independent atomic site in colemanite generates six new independent sites in colemanite-II: 6 calcium sites, 18 boron sites and 48 oxygen sites (24 O, 18 OH and 6 H₂O).

The crystal structure of colemanite-II was solved *ab initio*, based on the integrated intensities of the diffraction peaks, using initially the *Superflip* software⁴⁹ implemented in *JANA2006*³⁸ and, subsequently, by several cycles of Fourier-syntheses and least-squares refinement to locate the missing atomic positions. The final cycles of structure refinement were conducted using the same restrictions used for the ambient-conditions polymorph reported in section 2 and, in addition, all the B and all the O sites were restrained to share the same isotropic displacement parameter (U_{iso}), respectively. The refined structure model is reported in Table S3. In the colemanite structure, the alternation of the borate chains and Ca-polyhedra occurs along the **c**-axis (Figure 1). The doubling of this unit-cell parameter in colemanite-II is reflected by the doubling of these structural components: *i.e.*, (borate chain)'-(Ca-polyhedra)'-(borate chain)''-(Ca-polyhedra)'', as shown in Figure 3. In colemanite, the borate chain is built by the repetition, along the **a**-axis, of the same ring unit made by one B in triangular coordination and two B sites in tetrahedral coordination, whereas the Ca chain shows the repetition of the same Ca-polyhedron. In colemanite-II, every borate chain, or sequence of Ca-polyhedra, is made by the repetition of three independent units: *i.e.* three 3-membered rings of B-polyhedra and three independent Ca sites, respectively (Figures 4 and 5). The principal structural change in response to the phase transition is based on the average

coordination number of the B atoms. In colemanite, two of the three independent B sites show a tetrahedral coordination (66.6%), whereas in colemanite-II fifteen of the eighteen independent B sites are tetrahedrally coordinated (83.3%): *i.e.* among the six new boron sites in colemanite-II, which are generated by the B1 site of colemanite, only three keep the triangular coordination, while the remaining three increase their coordination number to four (Figure 4). A detailed description of the independent borate chains and sequences of Ca-polyhedra, of the two polymorphs, is given below.

- (Borate chain)': In colemanite-II, this chain is topologically identical to the borate chain of colemanite, with the tripling of the independent 3-membered rings along the **a**-axis. Each of the three independent rings is made by a B in triangular coordination (B4, B12 and B17, respectively) and two B-tetrahedra (Figure 4, Table S3). The rings are connected through oxygen hinges shared between a ^[III]B of a ring and a ^[IV]B of the next ring, as in colemanite.
- (Ca-polyhedra)': The configuration of the first sequence of Ca-polyhedra in colemanite-II is similar to that in colemanite. The polyhedra build a chain running along the **a**-direction, where the tripling of the unit-cell edge is reflected by the tripling of the independent Ca sites: Ca4, Ca5 and Ca6 (Figure 5). All of these Ca are coordinated to nine O atoms, showing, therefore, an increase of the coordination number (from 8 to 9) with respect to the Ca site in colemanite.
- (Borate-chain)'': The second borate chain in colemanite-II is also made by the repetition of three independent 3-membered rings of B-polyhedra, but, in this case, all the B sites show a tetrahedral coordination (Figure 4). Namely, the three B sites generated from the parent B1 in colemanite all form an additional bond to an oxygen and the coordination number increases from three to four. Deducing the mechanisms that lead to the formation of the new B-O bonds is not straightforward. However, if we

assume that no break of the intra-chain B-O-B links occurs, this can be accomplished by the migration of a hydroxyl group from the sites generated from the parent B3 (i.e. B2, B9 and B15) to the sites generated from the triangular B1, giving rise to the new bonds: B6-Oh21, B8-Oh7 and B14-Oh23 (Figure 4). According to this hypothesis, the sites B2, B9 and B15 keep their tetrahedral coordination by forming a bond to a H₂O-oxygen site: in fact, three Ow sites generated from the Ow8 site of colemanite (i.e., Ow43, Ow44 and Ow45, respectively) act, in colemanite-II, as the vertices of the previously reported B-tetrahedra (Figure 4). In contrast, the remaining three H₂O-oxygen sites (Ow46, Ow47 and Ow48), excluding the H-network, are only bonded to Ca4, Ca6 and Ca5, respectively (Figure 5), with the same configuration of Ow8 in colemanite. The potential H-bonding network of Ow43, Ow44 and Ow45 is reported in Table S4. The suggested mechanism of structural rearrangement as a consequence of the phase transition, although not unambiguous, would imply that the internal B-O-B links of the borate chains stay intact (i.e. no break on the chain itself) and relatively small spatial displacements are responsible, which fits well the single-crystal to single-crystal nature of the phase transition. It is worth to note that the OH-groups and H₂O sites distribution in the structural model of colemanite-II reported here is also supported by bond valence calculation.

- (Ca-polyhedra)'': In this structural unit, three independent Ca-polyhedra (Ca1, Ca2 and Ca3, respectively) are linked along the **a**-axis, but the link among subsequent Ca-triplets is missing, therefore breaking the chain (Figure 5). However, every triplet is linked to the neighboring triplets along **b** according to the $2_1/a$ symmetry, giving rise to a corrugated two-dimensional layer of Ca-polyhedra, where Ca1 and Ca2 are characterized by a coordination number (CN) equal to 8, while Ca3 has CN= 9 (Figure 5).

The structure of colemanite-II confirms that the first-order phase transition between 13.95 and 14.91 GPa is reconstructive in character.

3.3. High-pressure behavior of colemanite-II

The diffraction patterns collected up to 30.43 GPa show that the high- P polymorph colemanite-II retains crystallinity up to the highest pressure investigated. However, due to a continuous decrease in the intensity of the diffraction spots, the refinement of the crystal structure of colemanite-II was possible only up to 23.29 GPa (P_{18}). In addition, the unit-cell parameters refined at higher pressures showed a strong scattering. Therefore, for both the elastic and the structural analyses only the data collected up to 23.29 GPa (P_{18}) were considered and reported.

The fit of the V - P data to a III-BM EoS was first used, but unsuccessfully, due to an unstable refinement. Therefore, a II-BM EoS (for which K_V' is fixed to 4, e.g.⁴¹) was fitted to the experimental data, leading to the following elastic parameters of colemanite-II: $V_0 = 3413(87)$ Å³ and $K_{V0} = 50(8)$ GPa. The components of the compressibility tensor, based on the unit-cell parameters at 14.91 (P_{11}) and at 23.29 GPa (P_{18}), were calculated using *Win_Strain*⁴⁴ and are reported in Table S2. The elastic data show that the phase transition involves an increase in compressibility, as can be observed in Figure 2, being e.g the calculated bulk moduli at 13.95 and 14.91 GPa: $K_{V-13.95(\text{COL})} = 137(4)$ GPa and $K_{V-14.91(\text{COL-II})} = 104(8)$ GPa, respectively. The calculated components of the compressibility tensor (Table S2) reveal that, even though any significant difference can be observed for the linear compressibility along **b**, a drastic change affects the elastic behavior on the (010) plane. On this basis, it can be concluded that the phase transition influences not only the bulk compressibility of colemanite, but also its elastic anisotropy.

The comparative structural analysis, based on the structure refinements performed up to 23.29 GPa, is affected by moderately large uncertainties and scattering of the refined variables, due to the combined effect of the intrinsic structural complexity of colemanite-II and of the decreasing intensity of the diffraction peaks at high pressure, with a consequent reduction of the number of observed reflections (Table 2). Although a moderate scattering occurs, II-BM EoS fits of the $V_{Ca}-P$ (where V_{Ca} are the volumes of Ca coordination polyhedra) data were performed, leading to the refined ambient-conditions bulk moduli reported in Table 4. These data, though affected by large uncertainties, provide, at least at a first approximation, a qualitative description of the role played by the Ca-polyhedra at increasing pressure. The higher refined bulk moduli of Ca4, Ca5 and Ca6 suggest that the Ca-chain (the first component described in section 3.2, Figures 3 and 5) is apparently less compressible than the Ca-polyhedra layer (Figure 5), which appears to be the most compressible unit able to accommodate the bulk strain. A II-BM EoS fit of the “structural voids” (see section 3.1) led to refined $K_{V0} = 46(10)$ GPa. From these values, it can be concluded that the P -induced compression in colemanite-II is likely accommodated by both the compression of the Ca-polyhedra and by the re-arrangement of the structural units possibly governed by a tilting mechanism, even though the quality of the structure refinements, as discussed at the beginning of this section, prevents a more detailed description of the mechanisms of structure deformation.

The diffraction data collected in decompression at 8.24 GPa show that the colemanite-to-colemanite-II phase transition is completely reversible.

4. Summary

- The polyborate colemanite is stable, in its ambient-conditions polymorph, up to 13.95 GPa. It shows an anisotropic elastic behavior, where the less compressible direction is parallel to the borate and Ca-polyhedra chains axes (Figure 1, Table S2). The refined bulk compressibility ($\beta_V = 0.0149(9) \text{ GPa}^{-1}$) is comparable to that shown by, for example, common framework rock-forming minerals as K- and Na-feldspars⁵⁰. The *P*-induced strain is accommodated by both the compression of the Ca-polyhedra and the tilting of the structural units, whereas the B-polyhedra and the rings, building up the borate chain, show a more rigid behavior. The borate-chain deformation is mainly accommodated by the tilt of the rings around the shared O hinges.
- Between 13.95 and 14.91 GPa, a first-order phase transition (reconstructive in character) occurs towards a new polymorph, colemanite-II, with the same *P2₁/a* symmetry, but a six times larger unit-cell volume.
- The colemanite-to-colemanite-II phase transition leads not only to an increase of the average coordination number of the Ca sites, but also of the B sites. In particular, three of the six independent B sites (generated from the B1 site of the low-*P* polymorph) gain a bond with an additional oxygen, increasing their coordination from triangular to tetrahedral. A mechanism, based on the migration of hydroxyl groups among three different couples of B-coordination polyhedra and their replacement by H₂O molecules, is suggested.
- The high-pressure polymorph colemanite-II is characterized by a higher compressibility and by a different elastic anisotropic pattern with respect to the low-*P* polymorph. A similar behavior, though not so common, was already observed in other classes of minerals, in particular in open-framework silicates^{10,51–53}. Although the quality of the experimental data prevents a detailed comparative structural analysis,

we can, at a first approximation, infer that the *P*-induced strain in colemanite-II is accommodated by the same general structural mechanisms observed in colemanite.

5. Acknowledgements

Petra III at DESY is acknowledged for the allocation of beamtime. Two anonymous reviewers, the associate editor and the editor in chief, Dr. J. Halloran, are thanked for the fruitful comments and suggestions.

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Figure Captions

Figure 1. A) The crystal structure of colemanite viewed along the **b**-axis. The (010)-layers of alternated borate and Ca-polyhedra chains are shown. B) The borate chain is built by the repetition, *via* corner-sharing, of a 3-membered ring made by one BO_3 triangle and two $\text{B}\phi_4$ tetrahedra ($\phi = \text{O}, \text{OH}$). C) The Ca-chain is built by the repetition, along the **a**-axis, of one symmetry-independent polyhedron (coordination number = 8). Ow_8 represents the only H_2O -molecule oxygen site.

Figure 2. The P -induced evolution of the unit-cell parameters of colemanite, and of its high- P polymorph (colemanite-II), are shown. The Birch-Murnaghan equations of state, fitted to the experimental V - P data, are also reported, along with the refined elastic parameters. For a comparative analysis, the unit-cell parameters of colemanite-II have been normalized to the colemanite unit cell (i.e., $V_n = 1/6 \cdot V$; $a_n = 1/3 \cdot a$; $c_n = 1/2 \cdot c$, see section 3.2 for further details).

Figure 3. The crystal structure of the high-pressure polymorph colemanite-II viewed down the **b**-axis. The alternation of two symmetry-independent borate chains and two independent sequences of Ca-polyhedra is shown.

Figure 4. (*Top*). The first borate chain in colemanite-II is made by the repetition of three independent 3-membered rings, each made of one BO_3 triangle and two $\text{B}\phi_4$ tetrahedra ($\phi = \text{O}, \text{OH}$). (*Bottom*). The second borate chain is made by the repetition of three independent 3-membered rings, all made by three $\text{B}\phi_4$ tetrahedra ($\phi = \text{O}, \text{OH}, \text{H}_2\text{O}$).

Figure 5. (A). The first sequence of Ca-polyhedra in colemanite-II is a chain made by the repetition, *via* edge-sharing, of three independent Ca-polyhedra (Ca_4 , Ca_5 and Ca_6 , all with coordination number = 9). B). The second sequence of Ca-polyhedra is based on the triplet made by the coordination polyhedra of Ca_1 , Ca_2 (both with CN = 8) and Ca_3 (CN = 9), linked *via* corner- and edge-sharing. C) Every triplet is linked to the neighboring triplets along

the **b**-axis (see section 3.2 for further details), giving rise to an irregular and corrugated (001)-layer.

Table 1. Chemical composition (determined by a combination of titrimetric, CHN, chromatographic, ICP-AES, and TG analyses) of the natural sample of colemanite used in this study.

	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)
<hr/>	
Total	100.13

Table 2. Unit-cell parameters and details of the structure refinements of colemanite, and of the high-*P* polymorph colemanite-II, at different pressures

<i>P</i> (GPa)	<i>P</i> ₁ 3.54(5)	<i>P</i> ₂ 4.99(5)	<i>P</i> ₃ 6.57(5)	<i>P</i> ₄ 6.87(5)	<i>P</i> ₅ 8.50(5)	<i>P</i> ₆ 9.65(5)	<i>P</i> ₇ 12.17(5)	<i>P</i> ₈ 12.93(5)	<i>P</i> ₉ 13.59(5)	<i>P</i> ₁₀ 13.95(5)	<i>P</i> _{dec} 8.24(5)
<i>a</i> (Å)	8.6249(10)	8.6195(10)	8.5818(10)	8.5788(12)	8.5494(12)	8.5297(12)	8.4834(12)	8.4750(12)	8.4627(14)	8.4556(11)	8.5776(14)
<i>b</i> (Å)	10.9643(12)	10.9097(13)	10.8331(13)	10.8252(12)	10.7639(13)	10.7248(13)	10.6593(12)	10.6381(12)	10.6204(12)	10.6352(13)	10.8217(18)
<i>c</i> (Å)	5.968(8)	5.917(8)	5.873(8)	5.872(9)	5.831(8)	5.801(8)	5.740(6)	5.731(7)	5.719(7)	5.689(9)	5.882(7)
β (°)	109.94(2)	109.93(3)	109.85(3)	109.85(3)	109.76(3)	109.71(3)	109.53(2)	109.53(2)	109.46(3)	109.49(3)	109.88(3)
<i>V</i> (Å ³)	530.5(7)	523.1(7)	513.6(7)	512.9(7)	504.9(6)	499.5(7)	489.2(5)	486.9(6)	484.7(6)	482.3(8)	513.4(5)
Unique refls.	800	640	624	767	665	672	652	707	670	657	506
Observed refls. <i>F</i> _o ² /σ(<i>F</i> _o ²)>3	595	513	499	642	528	532	498	474	520	475	383
<i>R</i> _{int} (obs)	0.0247	0.0287	0.0264	0.0241	0.0241	0.0279	0.0309	0.0273	0.0261	0.0434	0.0501
<i>R</i> _{int} (all)	0.0258	0.0297	0.0276	0.0251	0.0251	0.0291	0.0332	0.0308	0.0274	0.0458	0.0531
Refined param.	49	49	49	49	49	49	49	49	49	49	49
<i>R</i> ₁ (obs)	0.0496	0.0733	0.0799	0.0619	0.0796	0.0824	0.0885	0.0762	0.0899	0.0957	0.1111
<i>R</i> ₁ (all)	0.0643	0.0879	0.0976	0.0707	0.0942	0.0984	0.1094	0.1011	0.1077	0.1192	0.1389
w <i>R</i> ₁ (obs)	0.0513	0.0777	0.0807	0.0682	0.0800	0.0806	0.0848	0.0729	0.0868	0.0897	0.1036
Residuals (<i>e</i> /Å ³)	+ 0.44 - 0.49	+ 0.51 - 0.51	+ 0.59 - 0.52	+ 0.88 - 0.87	+ 0.75 - 0.70	+ 0.94 - 0.86	+ 0.96 - 0.91	+ 1.06 - 1.16	+ 1.23 - 1.12	+ 0.92 - 0.89	+ 0.39 - 0.54
<i>P</i> (GPa)	<i>P</i> ₁₁ 14.91(5)	<i>P</i> ₁₂ 15.79(5)	<i>P</i> ₁₃ 17.14(5)	<i>P</i> ₁₄ 18.05(5)	<i>P</i> ₁₅ 19.23(5)	<i>P</i> ₁₆ 20.57(5)	<i>P</i> ₁₇ 21.97(5)	<i>P</i> ₁₈ 23.29(5)			
<i>a</i> (Å)	25.27(3)	25.10(3)	25.06(3)	24.99(3)	24.85(2)	24.85(4)	24.81(4)	24.74(3)			
<i>b</i> (Å)	10.2064(14)	10.1862(13)	10.1410(14)	10.1068(14)	10.0822(12)	10.0383(14)	9.9893(12)	9.9393(13)			
<i>c</i> (Å)	11.726(11)	11.663(12)	11.692(10)	11.664(11)	11.579(12)	11.578(14)	11.595(11)	11.547(10)			
β (°)	112.45(10)	112.64(10)	112.44(10)	112.81(11)	113.18(10)	113.24(14)	113.33(11)	113.50(10)			
<i>V</i> (Å ³)	2795(5)	2752(5)	2746(5)	2716(5)	2667(4)	2654(6)	2639(5)	2604(4)			
Unique refls.	1814	1799	1771	1753	1736	1651	1645	1613			

Observed refs. $F_o^2/\sigma(F_o^2)>3$	972	930	959	934	909	817	733	612
R_{int} (obs)	0.0438	0.0457	0.0480	0.0488	0.0993	0.0731	0.0972	0.1038
R_{int} (all)	0.0508	0.0532	0.0558	0.0571	0.1086	0.0892	0.1202	0.1322
Refined param.	225	225	225	225	225	225	225	225
R_1 (obs)	0.0806	0.0711	0.0713	0.0699	0.0962	0.0918	0.1050	0.1274
R_1 (all)	0.1256	0.1171	0.1154	0.1199	0.1511	0.1579	0.1880	0.2431
wR_1 (obs)	0.0758	0.0650	0.0665	0.0645	0.0864	0.0778	0.0859	0.1017
Residuals ($e/\text{\AA}^3$)	+ 1.30 - 0.75	+ 1.09 - 0.66	+ 0.85 - 0.69	+ 0.65 - 0.56	+ 0.80 - 0.74	+ 0.78 - 0.66	+ 0.93 - 0.73	+ 0.98 - 1.02

$$R_{int} = \frac{\sum |F_{obs}^2 - F_{obs}^2(\text{mean})|}{\sum (F_{obs}^2)}; R_1 = \frac{\sum (|F_{obs} - F_{calc}|)}{\sum |F_{obs}|}; wR_1 = \frac{(\sum (w(F_{obs}^2 - F_{calc}^2)^2))^{0.5}}{\sum (w(F_{obs}^2)^{0.5})}, w = 1/(\sigma^2(F_{obs}^2))$$

Table 3. High-pressure evolution of selected structural parameters of colemanite.

	P (GPa)	$\langle \text{Ca-O} \rangle$ (Å)	V_{Ca} (Å ³)	$\langle \text{B1-O} \rangle$ (Å)	$\langle \text{-B2-O} \rangle$ (Å)	V_{B2} (Å ³)	$\langle \text{B3-O} \rangle$ (Å)	V_{B3} (Å ³)	V_{sv} (Å ³)	B1-O1-B2 (°)	* $V_{\text{poly}}/V_{\text{cell}}$
P_1	3.54(5)	2.468(8)	25.11(8)	1.361(9)	1.459(8)	1.588(9)	1.471(8)	1.626(9)	417.2(11)	135.9(5)	0.212
P_2	4.99(5)	2.447(4)	24.30(4)	1.366(10)	1.464(8)	1.605(9)	1.466(8)	1.608(9)	413.1(9)	135.3(5)	0.210
P_3	6.57(5)	2.431(6)	24.04(6)	1.361(10)	1.461(9)	1.596(10)	1.461(8)	1.592(9)	404.7(10)	135.1(5)	0.210
P_4	6.87(5)	2.432(5)	24.08(5)	1.357(10)	1.459(8)	1.588(9)	1.461(8)	1.592(9)	403.9(10)	135.1(5)	0.211
P_5	8.50(5)	2.422(6)	23.79(6)	1.354(10)	1.454(9)	1.571(10)	1.459(8)	1.585(9)	397.1(9)	135.1(5)	0.212
P_6	9.65(5)	2.411(6)	23.47(6)	1.353(10)	1.454(9)	1.570(10)	1.457(8)	1.580(9)	393.0(10)	133.7(6)	0.212
P_7	12.17(5)	2.395(7)	23.04(7)	1.347(12)	1.448(9)	1.550(10)	1.451(9)	1.558(10)	384.6(9)	134.1(6)	0.214
P_8	12.93(5)	2.392(7)	22.98(7)	1.345(12)	1.449(10)	1.555(11)	1.454(9)	1.570(10)	382.5(10)	133.3(6)	0.214
P_9	13.59(5)	2.384(7)	22.69(7)	1.349(12)	1.447(10)	1.545(10)	1.453(9)	1.562(10)	381.5(10)	133.9(6)	0.212
P_{10}	13.95(5)	2.378(8)	22.61(8)	1.355(13)	1.449(12)	1.552(13)	1.456(11)	1.577(12)	379.4(12)	132.2(6)	0.213
P_{dec}	8.24(5)	2.436(6)	24.18(6)	1.358(9)	1.456(9)	1.578(9)	1.455(9)	1.571(9)	405.4(9)	136.2(5)	0.213
** K_{V0} (GPa)			81(6)			282(63)		219(61)	74(3)		

* Fraction of unit-cell volume occupied by Ca- and B-coordination polyhedra

** Isothermal bulk moduli refined from II-BM EoS fits using the *EoSFit7.0-GUI* software⁴², see section 3.1 for further details

Table 4. Selected structural parameters of colemanite-II at different pressures.

	P (GPa)	V_{Ca1} (\AA^3)	V_{Ca2} (\AA^3)	V_{Ca3} (\AA^3)	V_{Ca4} (\AA^3)	V_{Ca5} (\AA^3)	V_{Ca6} (\AA^3)	V_{sv} (\AA^3)	$*V_{poly}/V_{cell}$
P_{11}	14.91(5)	23.7(2)	22.8(2)	27.0(2)	26.0(2)	27.5(3)	27.1(2)	2086(12)	0.254
P_{12}	15.79(5)	23.07(17)	22.27(17)	26.63(18)	26.2(2)	26.9(2)	26.8(2)	2052(11)	0.254
P_{13}	17.14(5)	23.01(18)	22.45(19)	26.40(19)	26.2(2)	27.1(2)	26.2(2)	2048(11)	0.254
P_{14}	18.05(5)	22.45(19)	22.08(17)	26.28(19)	25.6(2)	26.6(2)	26.3(2)	2026(10)	0.254
P_{15}	19.23(5)	21.9(2)	21.68(2)	26.0(3)	25.6(3)	26.3(3)	25.6(3)	1987(13)	0.255
P_{16}	20.57(5)	21.9(2)	21.3(2)	25.6(3)	25.0(3)	26.0(3)	25.8(2)	1981(14)	0.254
P_{17}	21.97(5)	22.3(3)	21.2(3)	24.7(3)	25.1(3)	26.1(3)	25.3(3)	1968(14)	0.254
P_{18}	23.29(5)	21.6(3)	20.7(3)	25.5(4)	24.6(3)	26.7(4)	25.4(3)	1934(15)	0.257
** K_{V0} (GPa)		18(12)	25(9)	34(13)	49(20)	50(32)	42(14)	46(10)	

* Fraction of unit-cell volume occupied by Ca- and B-coordination polyhedra

** Isothermal bulk moduli refined from II-BM EoS fits using the *EoSFit7.0-GUI* software⁴², see section 3.3 for further details and for a discussion on these values and their large uncertainties