High-pressure behaviour and phase stability of $Ca_2B_6O_6(OH)_{10}\cdot2(H_2O)$ (meyerhofferite)

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Abstract

The high-pressure behaviour of meyerhofferite [ideally $Ca_2B_6O_6(OH)_{10}\cdot2(H_2O)$, with a ~6.63 Å, b ~8.34 Å, c ~6.47 Å, $\alpha = 90.8°$, $\beta = 102°$, $\gamma=86.8°$, Sp. Gr. $P\bar{1}$], a B-bearing raw material (with $B_2O_3 \approx 46$ wt%) and a potential B-rich aggregate, has been studied by single-crystal synchrotron X-ray diffraction up to 9 GPa, under hydrostatic conditions. Meyerhofferite undergoes a first-order phase transition to meyerhofferite-II, likely iso-symmetric, bracketed between 3.05 and 3.48 GPa, with a spectacular unit-cell volume discontinuity (*i.e.*, $\Delta V\sim 30$ Å^3). The isothermal bulk modulus ($K_{V0}= \beta^{-1}_{P0,T0}$, where $\beta_{P0,T0}$ is the volume compressibility coefficient) of meyerhofferite was found to be $K_{V0} =31.6(5)$ GPa, and a marked anisotropic compressional pattern, with $K(a)_0 : K(b)_0 : K(c)_0$ ~1.5:1:3, was observed. The bulk modulus of meyerhofferite-II increases to 55(2) GPa and, differently to the majority of the borates studied at high pressure so far, the anisotropic compressional pattern of meyerhofferite decreases markedly in the high-pressure form. The *P*-induced deformation mechanisms controlling, at the atomic scale, the bulk compression of meyerhofferite are here described. Considerations about the use of meyerhofferite as a potential B-based aggregate in concretes, mortars or resins, are provided.

Keywords: meyerhofferite; borates; B-rich aggregates; high-pressure; phase-transition.

1. Introduction

Natural borates are the most important source of boron, which is an important geochemical marker (in particular in pegmatitic and granitic systems) for petrogenetic processes and a strategic element in a series of technological processes. Boron, although is a trace element in the lithosphere (average concentration <10 wt ppm), is widely used in a number of different applications. According to the US Geological Survey (2019), more than 75% of the world consumption is due to the production of ceramics, detergents (in particular boric acid), fertilizers, and glasses. Nowadays, Turkey is the largest borates provider, with estimated reserves of more than 1.1 billion tons (USGS 2020). Borates with a high content of B_2O_3 (*e.g.*, kernite, colemanite, kurnakovite, ulexite, etc.) can be employed in the production of radiation-shielding materials, for the ability of ^{10}B (*ca.* 20% of the natural boron) to absorb thermal neutrons, due to its high cross section, for the $^{10}B(n,\alpha)^{7}Li$ reaction (~3840 barns) (Carter et al. 1953; Palmer and Swihart 1996). For these reasons, in the last two decades, several studies investigated the shielding and mechanical properties of borate-based aggregates in concretes, mortars and epoxy resins, in order to enhance the shielding efficiency towards neutron radiations (*e.g.*, Kaplan 1989; Okuno 2005; Gencel et al. 2012; Oto and Gür 2013; Binici et al. 2014; Aksołan et al. 2016; Guzel et al. 2016; Piotrowski et al. 2019; Yildiz Yorgun et al. 2019). Meyerhofferite, ideally $Ca_2B_6O_6(OH)_{10} \cdot 2(H_2O)$, with unit-cell parameters a ~6.63 Å, b ~8.34 Å, c ~6.47 Å, $\alpha = 90.8°$, $\beta = 102°$, $\gamma = 86.8°$, Sp. Gr. $P\bar{1}$, was first reported in 1914 in the Death Valley, California, US, and named after Wilhelm Meyerhoffer (Schaller 1916; Foshag 1924). Meyerhofferite usually occurs in white complex acicular aggregates or as single large crystals with length up to several cm. It is also found in the form of fibrous, divergent, radiating aggregates or reticulated in sedimentary or lake-bed borate deposits (Frost et al. 2013). Meyerhofferite has been found in some Neogene borate occurrences (*i.e.*, in the playa deposits of Kirka and Emet, western Turkey and in the Kramer deposit, California, US), as alteration product of inyoite $(CaB_3O_3(OH)_5 \cdot 4(H_2O))$ or other borates. Meyerhofferite is not one of the most common hydrous borates, but it is associated with the most common ones as ulexite, kernite, borax or colemanite (Palmer and Helvaci 1997; García-Veigas and Helvaci 2013), which account for about 90% of the borates mined worldwide (Birsoy and Özbaş 2012; Helvacı and Palmer 2017; USGS 2019). The first X-ray diffraction data on meyerhofferite were reported by Palache (1938), and its structure was later solved and refined by Christ and Clark (1956). Because of its structural complexity, the first structure model of meyerhofferite was refined as H-free, until Burns and Hawthorne (1993) located the proton sites and described its complex hydrogen-bond network. The crystal structure of meyerhofferite consists of corner-sharing BO_3 and BO_4 units, linked together to form $[B_3O_3(OH)_5]^{2-}$ rings (Fig.1). Ca is coordinated by eight oxygen atoms to form distorted polyhedra, which are edge-sharing connected to give continuous chains along

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the [001] crystallographic direction. The Ca-polyhedral chains are corner- and edge-sharing connected to the $[B_3O_3(OH)_5]^{2-}$ rings (Burns and Hawthorne 1993). The lateral connection between the heteropolyhedral chains is provided by a series of hydrogen bonds (Burns and Hawthorne 1993) (Fig. 1). The complex hydrogen bonding network is critical to the structure stability of meyerhofferite, and it is not excluded that can play an important role in the structure deformation at non-ambient pressures, similarly to what observed by previous studies on other hydrous compounds (*e.g.*, Comboni et al. 2019, 2020). Recently, the high-temperature behaviour of meyerhofferite was studied by Frost et al. (2017), by thermogravimetric analysis, infrared spectroscopy and X-ray powder diffraction. Results show a decomposition starting at about 453 K, governed by the dehydration phenomena that leads to the amorphization of the mineral. Thermogravimetric data show a total mass loss of 28.1% upon heating up to 1000° C (Frost et al. 2017). Because of its low density (2.12 g/cm^3), meyerhofferite could be utilised for the production of lightweight concretes and, contrarily to other B-bearing minerals (*e.g.*, kernite), meyerhofferite does not contain Na, at a significant level. High Na content is known to be deleterious for the stability of Portland cement-based concretes, because promoting undesired reactions undermining the durability of cements (*e.g.*, "alkali-silica reactions" – ASR). Furthermore, meyerhofferite could be added to Sorel cements (*i.e.*, magnesium oxychloride cements) which are commonly used to make floor tiles and panels for fire protection. In this light, B-additivated Sorel cements could be efficiently used for the production of radiation-shielding tiles or panels. To the best of our knowledge, no *in-situ* X-ray diffraction experiments were devoted to unveil the high-pressure behaviour mechanisms that govern the structure deformation at the atomic scale of meyerhofferite. Our research group investigated the behaviour of a series of natural anhydrous and hydrous borates at non-ambient conditions, with the aim to provide accurately determined thermo-elastic parameters, description of the deformation mechanisms at the atomic scale and of their *P-T* phase stability ranges (*e.g.*, Gatta et al. 2010, 2011, 2013, 2017, 2020; Lotti et al. 2017, 2018, 2019, Comboni et al. 2020, Pagliaro et al. 2020). Overall, we bracketed phase transitions occurring at relatively low pressure in kernite, colemanite and kurnakovite, which have some structural similarities with meyerhoferrite. Furthermore, the compressional parameters of meyerhofferite are still unknown, and an exhaustive description of its thermodynamic parameters is advisable if meyerhofferite will be employed in radiation-shielding tiles (*e.g.,* impact resistance) or as an aggregate in radiation shield concretes. For these reasons, we investigated the high-pressure behaviour of meyerhofferite by *in-situ* single-crystal X-ray diffraction up to 9 GPa under hydrostatic conditions, in order to obtain the compressional-elastic parameters and the *P*-stability fields of this borate.

2. Experimental procedures

A sample of meyerhofferite, made by cm-sized transparent crystals from the Beğendikler borates deposit (Bigadiç District, Balikesir Province, Marmara Region, Turkey), was used for this study. Electron microprobe analysis in energy-dispersive mode showed the presence, at a significant level, only of the chemical elements expected by the ideal formula, as observed even for other borates (*e.g.*, colemanite by Lotti et al. 2019, kurnakovite by Gatta et al. 2019, kernite by Gatta et al. 2020). A crystal with size ~ 40 × 30 × 20 μm^3 was selected for the X-ray diffraction experiment. An *in-situ* high-pressure single-crystal synchrotron X-ray diffraction experiment was performed at the ID15-b beamline, at the ESRF, Grenoble (France). A parallel monochromatic beam (*E*~30 keV, λ~0.414 Å) was used for the diffraction experiment. The diffraction patterns were collected by a MAR555 flat-panel detector, positioned at about 280 mm from the sample position. Sample-to-detector distance was calibrated using a Si powder standard and an enstatite (MgSiO$_3$) crystal. Further details on the beamline setup are reported in Merlini and Hanfland (2013). The crystal was loaded in the pressure-chamber of a membrane-driven DAC, with 600 μm culet Boehler-Almax design anvils, along with a few ruby spheres for *P*-determination (pressure uncertainty ± 0.05 GPa (Mao et al. 1986)). A stainless-steel foil (with thickness~250 μm) was pre-indented to 80 μm and then drilled by spark-erosion, leading to a *P*-chamber of ~300 μm in diameter. As previous pilot experiments did not show any relevant interaction between meyerhofferite and alcohol-rich fluids, the methanol:ethanol=4:1 mixture was used as hydrostatic *P*-transmitting fluid (Angel et al. 2007). The data collection strategy consisted in a pure ω-scan (−32°≤ω≤+32°), with 0.5° step width and 1 s exposure time per step. Indexing of the diffraction peaks and integration of their intensities (corrected for Lorentz-polarization effects) was performed using the CrysAlis package (Rigaku Oxford Diffraction 2018). Corrections for absorption (caused by the DAC components) were applied using the semi-empirical *ABSPACK* routine implemented in CrysAlis (Rigaku Oxford Diffraction 2018).

As the mineral experiences a *P*-induced phase transition between 3.0 and 3.5 GPa, described in the next sections, two independent high-*P* experiments were performed in order to better bracket the transition pressure. To assess the reversibility of the phase transition and its hysteresis, a few data-points were collected in decompression. Selected diffraction patterns are shown in Fig. 2. The unit-cell parameters at high pressure are listed in Table 1a, b and their evolution with *P* is shown in Fig. 3.

3. Structure refinement protocol and elasticity analysis

All the structure refinements were performed using the package JANA2006 (Petrícek et al. 2014), in the space group $P\bar{1}$, using the atomic coordinates from Burns and Hawthorne (1993) as

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starting model. No H-sites were located and refined, due to the poor X-ray scattering of H that hinders a reliable evaluation of position and displacement parameters of the protons based on high-P data. In order to increase the quality of the structure refinements, the displacement parameters (D.P.) of the Ca site were refined as anisotropic. No restraints on bond distances or angles were used. Atomic coordinates, site occupancy factors and D.P. of the structure refinements are given in Tables S1(SM) and S2(SM) (SM Supplementary Material). The principal statistical parameters of the refinements are listed in Table S3(SM). Interatomic distances pertaining to the BO_x groups are given in Table S4(SM). CIFs (crystallographic information files) are deposited as Supplementary materials.

Between 3.0 and 3.5 GPa, meyerhofferite experienced a first-order phase transition to the meyerhofferite-II polymorph, which is metrically triclinic. Meyerhofferite-II is stable up to the maximum pressure achieved in these experiments (9 GPa). Unfortunately, an abrupt drop in intensity and number of observed (*i.e.* with $F_o^2 > 3\sigma(F_o^2)$) reflections hindered and ultimately prevented the structure solution of the meyerhofferite-II polymorph.

The (isothermal) compressional behaviour of both the polymorphs was described using the Birch-Murnaghan Equation of State (BM-EoS; Birch 1947). The *fe-F*e plot (where $fe = [(V_0/V)^{2/3} - 1]/2$ is the Eulerian finite strain and Fe is the normalised pressure, defined as $Fe=P/3fe(1+2fe)^{5/2}$, Birch 1947; Angel et al. 2014) for both the polymorphs led to the conclusion that the truncation to the second-order (in energy) of the BM-EoS provides the best figure of merit for both of them. This EoS allows to refine the bulk modulus (K_{V0} or $K_{P0,T0}$, defined as $-V_0(\partial P/\partial V)_{T0} = \beta^{-1}_{P0,T0}$, where $\beta_{P0,T0}$ is the volume compressibility coefficient at room conditions) and its P-derivatives ($K'=\partial K_{P0,T0}/\partial P$ and $K''=\partial^2 K_{P0,T0}/\partial P^2$). Truncated to the second order in energy, *i.e.* with $K'=\partial K_{P0,T0}/\partial P = 4$, the EoS transforms to: $P(fe) = 3K_{P0,T0} fe (1 + 2fe)^{5/2}$. The BM-EoS parameters (listed in Table 2), were refined minimizing the differences between the EoS curves and the experimental data (weighted by their uncertainties in P and V), using the EOS-FIT7-GUI software (Angel et al. 2014). Data were fitted taking into account an estimated uncertainty of ± 0.05 GPa for pressure (Mao et al. 1986).

4. Results and discussion

The evolution of the unit-cell parameters of meyerhofferite with pressure (shown in Fig. 3 and listed in Table 1) appears to be monotonic up to about 3 GPa. At higher pressure, a phase transition (meyerhofferite-to-meyerhofferite-II) occurs.

Comparing the unit-cell volume of the low-P polymorph at 3.05(5) GPa and that of meyerhofferite-II at 3.48(5) GPa, a difference of about 10% is observed (*i.e.*, $\Delta V \sim 30$ Å^3). This is a rather abrupt decrease of volume and the phase transition is, therefore, a first-order transformation. Meyerhofferite-II is metrically triclinic, as observed by the inspection of the single-crystal diffraction

patterns (Fig. 2), and the meyerhofferite-to-meyerhofferite-II phase transition would preserve the space group of the structure, *i.e.*, $P\bar{1}$. In response to the phase transition, the unit-cell edges parallel to *a* and *b* decrease by about 5.7 and 6.2 %, respectively, whereas that along *c* increases by almost 6.2%. Interestingly enough, at pressure slightly higher than the meyerhofferite-to-meyerhofferite-II transition, the length of the unit cells edges along *a* and *c* first increase and then decrease again, following a new monotonic trend within the stability field of the H*P*-polymorph (Fig. 3). This kind of transient behaviour was already observed in other borates experiencing *P*-induced phase transitions with a relevant change in volume (*e.g.,* kernite, Comboni et al. 2020). In the low-*P* polymorph, the α angle decreases from ~90.8° at ambient pressure to ~89.9° at 3.05(5) GPa, whereas *β* increases from ~101.9° to ~103.3° in the same *P*-range. Minor changes on *γ* angle occurs (Fig. 3, Tables 1a, b). In response to the phase transition, *α* and *γ* angles abruptly decrease from ~89.9° to ~82.3° and from ~86.9° to ~79.7°, respectively, whereas *β* increases from ~103.3° to ~107.3° (Fig. 3, Tables 1a, b).

The elastic parameters refined with the EOS-FIT7-GUI software (Gonzalez-Platas et al. 2016) revealed that meyerhofferite is a relatively soft mineral, with a bulk modulus of 31.6(5) GPa. Similar values were obtained for other borates (*e.g.*, kernite and kurnakovite, Comboni et al. 2020; Pagliaro et al. 2020).

In meyerhofferite-II, the bulk modulus increases to 55(2) GPa. Similar decrease in the bulk compressibility was observed also in other borates after a first-order phase transition (*e.g.*, kernite, Comboni et al. 2020). However, the low-pressure polymorph of meyerhofferite displays a marked anisotropic pattern, being $K(a)_0 : K(b)_0 : K(c)_0 \sim 1{:}3{:}1.5$, but, after the phase transition, the anisotropic pattern in meyerhofferite-II transforms to almost isotropic, being $K(a)_0{:}K(b)_0{:}K(c)_0 \sim 1.1{:}1{:}1.1$ (Table 2).

Meyerhofferite is a triclinic mineral, and the unit-cell angles *α, β, γ* are free to vary with pressure. Therefore, the linear bulk moduli along the principal crystallographic directions are not sufficient for a full description of the compressional behavior. Nevertheless, such abrupt decrease in the anisotropic scheme is rather impressive. Eulerian finite strain analyses were, therefore, performed with the *Win_Strain* software (Angel 2011), in order to describe magnitude and orientation of the unit-strain ellipsoids for both the polymorphs, and the results are reported in Table S5(SM). The geometrical relationships between the strain ellipsoid and the crystallographic axes of meyerhofferite and meyerhofferite-II can be described by the following matrixes (with $\varepsilon_1 > \varepsilon_2 > \varepsilon_3$):

$$\begin{pmatrix} \varepsilon_1 \\ \varepsilon_2 \\ \varepsilon_3 \end{pmatrix} = \begin{pmatrix} 57(2)° & 124(2)° & 63.6(3)° \\ 128(1)° & 143(2)° & 93(1)° \\ 55.4(6)° & 103.2(2)° & 153.3(5)° \end{pmatrix} \cdot \begin{pmatrix} a \\ b \\ c \end{pmatrix}$$

for meyerhofferite between 0.0001 and 2.74(5) GPa and with $\varepsilon_1{:}\varepsilon_2{:}\varepsilon_3 = 5.78{:}4.71{:}1$,

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$$\begin{pmatrix} \varepsilon_1 \\ \varepsilon_2 \\ \varepsilon_3 \end{pmatrix} = \begin{pmatrix} 65(7)° & 106(7)° & 54(2)° \\ 120(4)° & 159(7)° & 97(6)° \\ 40(4)° & 103(3)° & 143(3)° \end{pmatrix} \cdot \begin{pmatrix} a \\ b \\ c \end{pmatrix}$$

202 for meyerhofferite-II between 4.34(5) and 9.10(5) GPa and with $\varepsilon_1{:}\varepsilon_2{:}\varepsilon_3 = 2.33{:}1.90{:}1$.

203 The results (Table S5(SM)) show that there are not significant changes on the orientation of the three
204 principal directions of compression. However, there is a drastic change in the magnitude along the
205 first and second principal direction of compression that decrease notably, governing the decrease
206 observed in the bulk compressibility.

207 Data collected in decompression show a significant hysteresis loop, as meyerhofferite-II
208 survives at least down to 1.2 GPa. This is a common behaviour in minerals subjected to *P*-induced
209 first-order phase transitions (*e.g.* kurnakovite, Pagliaro et al. 2020). Any attempt to further decrease
210 the pressure was unsuccessful, due to the plastic deformation of the gasket, making impossible the
211 estimation of the hysteresis ΔP.

212 In order to describe the structure deformation mechanisms occurring in meyerhofferite, stable
213 between 0 and 3 GPa, the volumes of the Ca-polyhedra and B-tetrahedra with increasing *P* were
214 calculated with the software VESTA (Momma and Izumi 2011), and reported in Table 3. The
215 evolution with *P* of the Ca-polyhedra volume was modelled with a second-order Birch-Murnaghan
216 Equation of State (Birch 1947). Notably, the obtained bulk modulus (55(5) GPa) is higher than the
217 bulk modulus of meyerhofferite (Table 2). As the B-tetrahedra are substantially uncompressible
218 (Tables 3 and S4), this leads to the conclusion that the deformations in response to the applied pressure
219 in meyerhofferite structure are mainly accommodated through the tilting of the Ca-polyhedra and B-
220 tetrahedra around the oxygen hinges (Table 4), or by compression of the H-bonds. The Ca-O3-B1
221 and B2-O5-B3 angles decrease with pressure from 127.4(5)° to 124.6(6)° and from 125.1(8)° to
222 122.2(10)° between 0-3 GPa, respectively, whereas the Ca-O5-B3 angle increases from 135.6(3)° to
223 138.0(5)°. These three tilting angles show the maximum variation with *P*, producing only a modest
224 corrugation of the heteropolyhedral chain along [001] (Fig. 1). Coupled with the aforementioned
225 polyhedral tilting, the lateral connections between the heteropolyhedral chains, based on a complex
226 H-bond network, experience a significant change. The chains are connected *via* hydrogen bonds
227 almost parallel to [100] and along [010] (listed in Table 5; see also Fig. 1); additional H-bonds occur
228 between intra-chains *donors* and *acceptors* (Burns and Hawthorne 1993). All the aforementioned
229 extra-chains H-bonds, lying on (001), experience a significant shortening between 0 and 3 GPa (with
230 variations in *donor-acceptor* distances ranging between 0.06-0.15 Å, Table 5). On the whole:

231 i)   Along [001], the heteropolyhedral chains behave like "pillars". Ca- and B-polyhedra are
232   almost rigid units within the considered *P*-range, and the modest polyhedral tilting is the

233		energetically less-costly mechanism to accommodate the effect of pressure with a
234		moderate compression along the *c* axis.
235	ii)	Inter-chains H-bonding network acts mainly on (001). H sites cannot be located in the
236		structure refinements at high pressure, but the shortening of the *donor-acceptor* distances
237		(Table 5) shows why the structure of meyerhofferite is pronouncedly compressible on the
238		(001) plane (Table 2).

239 These two considerations can explain the compressional anisotropy of meyerhofferite.

240 The lack of the structure model of meyerhofferite-II does not allow any discussion on the deformation

241 mechanisms at the atomic scale of the H*P*-polymorph, on which is based the drastic change of the

242 compressional anisotropy if compared to the low-*P* polymorph. However, we can make some

243 speculations based on the high-pressure behaviour of others borates with structural homologies (*e.g.*,

244 kernite, colemanite and kurnakovite) and in particular on the pressure value at which the phase

245 transitions occur. In the colemanite-I-to-colemanite-II phase transition (bracketed between 14 and 15

246 GPa, Lotti et al. 2017), part of the trigonal-planar B become [IV]B and the CN of the Ca site increases

247 (CN=8 in colemanite-I, CN=9 in colemanite-II). In the kernite-I-to-kernite-II phase transition

248 (bracketed between 1.6 and 2 GPa), the related volume decrease reflects only the increase of the CN

249 of the Na site (CN from 6 to 7) (Comboni et al. 2020). In the kurnakovite-I-to-kurnakovite-II phase

250 transition (bracketed between 9 and 11 GPa), a fraction of the B sites increases its coordination

251 configuration from trigonal-planar to tetrahedral (Pagliaro et al. 2020). Therefore, we could presume

252 that the abrupt change in the unit-cell volume of meyerhofferite, in response to the *P*-induced phase

253 transition, is likely ascribable to a change in the coordination environments of the B sites (*i.e.*, CN

254 from 3 to 4) or of the Ca site (from CN 8 to 9) or both. Such changes presumably imply even a

255 reconfiguration of the H-bonding network. However, the *P*-induced increase in the coordination

256 number of a fraction of B sites from 3 to 4 has been observed to occur in colemanite and kurnakovite

257 at relatively high pressures (*i.e.,* above 9 GPa). As the *P*-induced phase transition of meyerhofferite

258 takes place at lower pressure, we are inclined to believe that the meyerhofferite-to-meyerhofferite-II

259 transformation is more likely governed by a change in the coordination sphere of the Ca site and does

260 not involve the B sites.

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5. Concluding remarks

In this study, we have investigated, for the first time, the high-pressure behaviour of meyerhofferite by *in-situ* single crystal X-ray diffraction up to 9 GPa. Data collected at high pressure show that:

1. Meyerhofferite is stable, in its ambient-conditions polymorph, up to 3.05(5) GPa, a pressure higher than the working conditions of any aggregate in concretes or in other materials. At high-temperature, meyerhofferite is unstable at $T > 468$ K (Frost et al. 2017). This mineral can, therefore, be considered as a potential candidate in radiation-shielding concretes, mortars and epoxy resins, taking into account that most operating conditions do not reach temperatures higher than ~373 K (Lotti et al. 2019 and references therein).

2. Between 3.05(5) and 3.48(5) GPa, meyerhofferite undergoes a first-order phase transition to a denser polymorph (mayerhofferite-II, still triclinic), characterized by an abrupt volume decrease (~10%).

3. Contrarily to other borate structures, the elastic anisotropy pattern of meyerhofferite decreases after the phase transition, as observed either along the principal crystallographic axes or along the principal (and mutually orthogonal) directions of the unit-strain ellipsoid.

A decrease of 10% of the unit-cell volume, in response to the meyerhofferite-to-meyerhofferite-II phase transition, probably reflects the increase of coordination of the Ca sites, or even of the boron sites B1 and B4 (from CN 3 to 4). Similar evidences were observed in other hydrous borates (*e.g*, kernite, colemanite, kurnakovite) (Lotti et al. 2017; Comboni et al. 2020; Pagliaro et al. 2020). The *P*-induced phase transition likely leads also to a densification of the H-bonds network, which may play a key role on the bulk compressibility (*e.g.*, Comboni et al. 2019; Gatta et al. 2020).

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Table 1a: Unit-cell parameters of meyerhofferite with pressure (* data collected in decompression); first experiment.

P(GPa)	V(Å^3)	a(Å)	b(Å)	c(Å)	α(°)	β(°)	γ(°)
0.04(5)	351.1(2)	6.640(3)	8.3533(2)	6.4807(2)	90.778(2)	101.921(1)	86.720(9)
0.11(5)	350.3(2)	6.634(3)	8.3445(2)	6.4777(2)	90.757(2)	101.965(1)	86.731(9)
0.20(5)	348.8(2)	6.623(3)	8.3313(2)	6.4741(2)	90.726(2)	102.036(1)	86.73(1)
0.33(5)	347.5(2)	6.617(3)	8.3157(2)	6.4694(2)	90.689(2)	102.099(1)	86.73(1)
0.52(5)	345.6(2)	6.607(3)	8.2932(2)	6.4626(2)	90.615(2)	102.193(1)	86.733(9)
0.97(5)	340.8(2)	6.575(3)	8.2435(2)	6.4475(2)	90.481(2)	102.426(1)	86.750(9)
1.52(5)	335.8(2)	6.547(3)	8.1896(1)	6.4303(2)	90.328(2)	102.679(1)	86.769(9)
2.10(5)	330.6(2)	6.509(3)	8.1395(2)	6.4139(2)	90.169(2)	102.95(1)	86.790(9)
2.74(5)	325.6(2)	6.472(3)	8.0907(2)	6.3981(2)	90.017(2)	103.24(1)	86.81(1)
4.34(5)	290.4(1)	6.124(2)	7.585(1)	6.792(1)	82.447(2)	107.35(2)	79.62(2)
4.71(5)	289.1(2)	6.119(3)	7.570(1)	6.782(2)	82.409(2)	107.37(4)	79.59(3)
5.47(5)	286.8(3)	6.104(5)	7.550(3)	6.766(4)	82.440(4)	107.37(6)	79.52(5)
6.33(5)	283.1(1)	6.077(2)	7.5252(5)	6.742(1)	82.352(9)	107.68(2)	79.66(2)
7.10(5)	280.7(1)	6.061(2)	7.5024(8)	6.724(1)	82.35(1)	107.72(2)	79.69(2)
7.54(5)	279.0(1)	6.048(2)	7.4882(8)	6.716(1)	82.33(1)	107.82(2)	79.72(2)
8.11(5)	277.6(2)	6.043(3)	7.4720(6)	6.692(1)	82.31(1)	107.83(3)	79.73(2)
8.47(5)	276.8(2)	6.041(3)	7.464(1)	6.692(2)	82.30(2)	107.90(4)	79.79(2)
9.10(5)	275.6(4)	6.035(6)	7.443(4)	6.692(6)	82.22(6)	107.96(8)	79.79(2)
4.60(5)*	289.4(4)	6.115(5)	7.579(5)	6.784(6)	82.54(7)	107.51(8)	79.76(7)
2.94(5)*	296.4(3)	6.164(5)	7.634(2)	6.837(3)	82.48(3)	107.17(6)	79.53(4)
1.205(5)*	306(2)	6.24(3)	7.67(2)	6.91(2)	82.5(2)	107.3(4)	80.3(3)

Table 1b: Unit-cell parameters of meyerhofferite with pressure; second experiment.

P (GPa)	V(Å^3)	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)
0.06(5)	350.3(1)	6.637(2)	8.342(1)	6.4771(2)	90.765(6)	101.92(1)	86.76(2)
0.55(5)	344.9(2)	6.606(2)	8.283(2)	6.4593(2)	90.609(7)	102.20(1)	86.69(2)
1.05(5)	339.6(2)	6.578(4)	8.231(1)	6.4439(1)	90.49(1)	102.84(4)	86.84(2)
1.70(5)	334.6(2)	6.524(2)	8.192(2)	6.426(2)	90.20(2)	102.62(3)	86.72(2)
2.87(5)	325.2(2)	6.476(2)	8.078(2)	6.3938(8)	89.93(2)	103.17(2)	86.81(3)
3.05(5)	323.7(1)	6.463(2)	8.062(2)	6.3929(8)	89.905(2)	103.29(2)	86.87(2)
3.48(5)	292.2(1)	6.09(1)	7.64(2)	6.811(8)	82.2(1)	106.7(2)	79.48(2)
3.80(5)	291.1(3)	6.115(5)	7.592(6)	6.814(2)	82.31(4)	107.33(4)	79.71(7)

Table 2: Refined elastic parameters pertaining to the two polymorphs of meyerhofferite, based on the isothermal II-BM Equation of State fits (*fixed parameter).

Meyerhofferite	V_0, x_0 ($Å^3$, Å)	$K_{V0, x0}$ (GPa)	K'	$\beta_{V0, x0}$ (GPa^{-1})
V	351.1(2)	31.6(5)	4*	0.0316(5)
a	6.640(2)	32.3(7)	4*	0.0103(4)
b	8.355(3)	23.0(4)	4*	0.0145(3)
c	6.480(1)	66(2)	4*	0.0051(2)
				II-BM EoS, P< 3.05(5) GPa
Meyerhofferite-II	V_0, x_0 ($Å^3$, Å)	$K_{V0, x0}$ (GPa)	K'	$\beta_{V0, x0}$ (GPa^{-1})
V	311.5(6)	55(2)	4*	0.0182(6)
a	6.245(7)	67(3)	4*	0.0050(3)
b	7.745(3)	61(1)	4*	0.0055(1)
c	6.925(4)	67(2)	4*	0.0050(2)
				II-BM EoS, P>3.48(5) GPa

Table 3: Evolution of the polyhedral volumes with pressure in meyerhofferite. Average uncertainties on the Ca-polyhedra and BO_4 tetrahedra are estimated to be ~0.3 $Å^3$ and ~0.01 $Å^3$, respectively.

P(GPa)	Ca-polyhedra ($Å^3$)	B2 tetrahedra ($Å^3$)	B3 tetrahedra ($Å^3$)
0.04(5)	25.2	1.63	1.65
0.11(5)	25.2	1.63	1.63
0.20(5)	25.1	1.63	1.63
0.33(5)	25.1	1.62	1.67
0.52(5)	25.0	1.64	1.64
0.97(5)	24.8	1.65	1.63
1.52(5)	24.7	1.66	1.64
2.10(5)	24.5	1.64	1.63
2.74(5)	24.0	1.66	1.60

Table 4: Evolution, with pressure, of selected angles in meyerhofferite structure.

P(GPa)	Ca-O5-B3 (º)	Ca-O3-B1(º)	B2-O5-B3(º)
0.04(5)	135.6(3)	127.4(5)	125.1(8)
0.11(5)	135.6(3)	127.0(5)	125.5(8)
0.20(5)	135.8(3)	127.0(5)	125.2(8)
0.33(5)	135.5(3)	127.4(5)	125.2(8)
0.52(5)	136.6(3)	126.4(5)	123.7(7)
0.97(5)	136.2(3)	126.1(5)	124.6(8)
1.52(5)	136.3(6)	126.6(1)	124.0(10)
2.10(5)	136.5(3)	125.4(5)	124.2(8)
2.74(5)	138.0(5)	124.6(6)	122.2(10)

Table 5: Evolution, with pressure, of the *donor-acceptor* distances (Å) involved in hydrogen bonds.

P(GPa)	O2···O7 //[100]	O4···O9 //[100]	O6···O1 //[100]	O7···O8 //[010]	O8···O2 //[010]	O7···O8' //[001]	O9···O2 //[001]
0.04(5)	2.74(2)	2.82(2)	2.85(2)	2.86(1)	2.90(1)	2.690(7)	2.920(9)
0.11(5)	2.74(2)	2.81(2)	2.86(2)	2.85(1)	2.90(1)	2.690(7)	2.909(9)
0.20(5)	2.73(2)	2.81(1)	2.85(2)	2.85(1)	2.88(1)	2.688(8)	2.909(9)
0.33(5)	2.71(2)	2.82(2)	2.82(2)	2.84(1)	2.88(1)	2.687(7)	2.907(9)
0.52(5)	2.71(2)	2.81(1)	2.81(2)	2.83(1)	2.86(1)	2.682(6)	2.892(8)
0.97(5)	2.69(2)	2.78(1)	2.79(2)	2.81(1)	2.83(1)	2.672(7)	2.878(8)
1.52(5)	2.67(4)	2.76(3)	2.75(3)	2.81(3)	2.79(3)	2.66(1)	2.84(2)
2.10(5)	2.65(2)	2.75(1)	2.74(2)	2.78(1)	2.77(1)	2.646(7)	2.84(9)
2.74(5)	2.59(2)	2.77(2)	2.73(2)	2.80(2)	2.75(2)	2.63(1)	2.84(1)

Figure captions

Fig. 1: Crystal structure of meyerhofferite at ambient P-T conditions, BO_x polyhedra in green, Ca polyhedra in blue.

Fig. 2: Reconstruction, based on the experimental data, of the $h0l^*$ reciprocal lattice plane of meyerhofferite (*left side*) and meyerhofferite-II (*right side*).

Fig. 3: Evolution of the unit-cell volume with pressure. First experiment data in *blue circles* (compression) and *green downward triangles* (decompression), second experiment data in *red diamonds*.