

1 **High-pressure behaviour and phase stability of  $\text{Ca}_2\text{B}_6\text{O}_6(\text{OH})_{10}\cdot 2(\text{H}_2\text{O})$**   
2 **(meyerhofferite)**  
3

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15  
16 **Abstract**

17 The high-pressure behaviour of meyerhofferite [ideally  $\text{Ca}_2\text{B}_6\text{O}_6(\text{OH})_{10}\cdot 2(\text{H}_2\text{O})$ , with  $a \sim 6.63 \text{ \AA}$ ,  $b$   
18  $\sim 8.34 \text{ \AA}$ ,  $c \sim 6.47 \text{ \AA}$ ,  $\alpha = 90.8^\circ$ ,  $\beta = 102^\circ$ ,  $\gamma = 86.8^\circ$ , Sp. Gr.  $P\bar{1}$ ], a B-bearing raw material (with  $\text{B}_2\text{O}_3$   
19  $\approx 46 \text{ wt\%}$ ) and a potential B-rich aggregate, has been studied by single-crystal synchrotron X-ray  
20 diffraction up to 9 GPa, under hydrostatic conditions. Meyerhofferite undergoes a first-order phase  
21 transition to meyerhofferite-II, likely iso-symmetric, bracketed between 3.05 and 3.48 GPa, with a  
22 spectacular unit-cell volume discontinuity (*i.e.*,  $\Delta V \sim 30 \text{ \AA}^3$ ). The isothermal bulk modulus ( $K_{V0} = \beta^{-1}$   
23  $_{P0,T0}$ , where  $\beta_{P0,T0}$  is the volume compressibility coefficient) of meyerhofferite was found to be  $K_{V0}$   
24  $= 31.6(5) \text{ GPa}$ , and a marked anisotropic compressional pattern, with  $K(a)_0 : K(b)_0 : K(c)_0 \sim 1.5:1:3$ ,  
25 was observed. The bulk modulus of meyerhofferite-II increases to  $55(2) \text{ GPa}$  and, differently to the  
26 majority of the borates studied at high pressure so far, the anisotropic compressional pattern of  
27 meyerhofferite decreases markedly in the high-pressure form. The  $P$ -induced deformation  
28 mechanisms controlling, at the atomic scale, the bulk compression of meyerhofferite are here  
29 described. Considerations about the use of meyerhofferite as a potential B-based aggregate in  
30 concretes, mortars or resins, are provided.

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

33 **1. Introduction**

34 Natural borates are the most important source of boron, which is an important geochemical  
35 marker (in particular in pegmatitic and granitic systems) for petrogenetic processes and a strategic  
36 element in a series of technological processes. Boron, although is a trace element in the lithosphere  
37 (average concentration <10 wt ppm), is widely used in a number of different applications. According  
38 to the US Geological Survey (2019), more than 75% of the world consumption is due to the  
39 production of ceramics, detergents (in particular boric acid), fertilizers, and glasses. Nowadays,  
40 Turkey is the largest borates provider, with estimated reserves of more than 1.1 billion tons (USGS  
41 2020). Borates with a high content of B<sub>2</sub>O<sub>3</sub> (e.g., kernite, colemanite, kurnakovite, ulexite, etc.) can  
42 be employed in the production of radiation-shielding materials, for the ability of <sup>10</sup>B (ca. 20% of the  
43 natural boron) to absorb thermal neutrons, due to its high cross section, for the <sup>10</sup>B(n,α)<sup>7</sup>Li reaction  
44 (~3840 barns) (Carter et al. 1953; Palmer and Swihart 1996). For these reasons, in the last two  
45 decades, several studies investigated the shielding and mechanical properties of borate-based  
46 aggregates in concretes, mortars and epoxy resins, in order to enhance the shielding efficiency  
47 towards neutron radiations (e.g., Kaplan 1989; Okuno 2005; Gencel et al. 2012; Oto and Gür 2013;  
48 Binici et al. 2014; Aksoğan et al. 2016; Guzel et al. 2016; Piotrowski et al. 2019; Yildiz Yorgun et al.  
49 2019). Meyerhofferite, ideally Ca<sub>2</sub>B<sub>6</sub>O<sub>6</sub>(OH)<sub>10</sub>·2(H<sub>2</sub>O), with unit-cell parameters *a* ~6.63 Å, *b* ~8.34  
50 Å, *c* ~6.47 Å, α = 90.8°, β = 102°, γ = 86.8°, Sp. Gr. *P* $\bar{1}$ , was first reported in 1914 in the Death Valley,  
51 California, US, and named after Wilhelm Meyerhoffer (Schaller 1916; Foshag 1924). Meyerhofferite  
52 usually occurs in white complex acicular aggregates or as single large crystals with length up to  
53 several cm. It is also found in the form of fibrous, divergent, radiating aggregates or reticulated in  
54 sedimentary or lake-bed borate deposits (Frost et al. 2013). Meyerhofferite has been found in some  
55 Neogene borate occurrences (i.e., in the playa deposits of Kirka and Emet, western Turkey and in the  
56 Kramer deposit, California, US), as alteration product of inyoite (CaB<sub>3</sub>O<sub>3</sub>(OH)<sub>5</sub>·4(H<sub>2</sub>O)) or other  
57 borates. Meyerhofferite is not one of the most common hydrous borates, but it is associated with the  
58 most common ones as ulexite, kernite, borax or colemanite (Palmer and Helvacı 1997; García-Veigas  
59 and Helvacı 2013), which account for about 90% of the borates mined worldwide (Birsoy and Özbaş  
60 2012; Helvacı and Palmer 2017; USGS 2019). The first X-ray diffraction data on meyerhofferite  
61 were reported by Palache (1938), and its structure was later solved and refined by Christ and Clark  
62 (1956). Because of its structural complexity, the first structure model of meyerhofferite was refined  
63 as H-free, until Burns and Hawthorne (1993) located the proton sites and described its complex  
64 hydrogen-bond network. The crystal structure of meyerhofferite consists of corner-sharing BO<sub>3</sub> and  
65 BO<sub>4</sub> units, linked together to form [B<sub>3</sub>O<sub>3</sub>(OH)<sub>5</sub>]<sup>2-</sup> rings (Fig.1). Ca is coordinated by eight oxygen  
66 atoms to form distorted polyhedra, which are edge-sharing connected to give continuous chains along  
67 the [001] crystallographic direction. The Ca-polyhedral chains are corner- and edge-sharing

68 connected to the  $[\text{B}_3\text{O}_3(\text{OH})_5]^{2-}$  rings (Burns and Hawthorne 1993). The lateral connection between  
69 the heteropolyhedral chains is provided by a series of hydrogen bonds (Burns and Hawthorne 1993)  
70 (Fig. 1). The complex hydrogen bonding network is critical to the structure stability of meyerhofferite,  
71 and it is not excluded that can play an important role in the structure deformation at non-ambient  
72 pressures, similarly to what observed by previous studies on other hydrous compounds (*e.g.*, Comboni  
73 et al. 2019, 2020). Recently, the high-temperature behaviour of meyerhofferite was studied by Frost  
74 et al. (2017), by thermogravimetric analysis, infrared spectroscopy and X-ray powder diffraction.  
75 Results show a decomposition starting at about 453 K, governed by the dehydration phenomena that  
76 leads to the amorphization of the mineral. Thermogravimetric data show a total mass loss of 28.1%  
77 upon heating up to 1000° C (Frost et al. 2017). Because of its low density (2.12 g/cm<sup>3</sup>), meyerhofferite  
78 could be utilised for the production of lightweight concretes and, contrarily to other B-bearing  
79 minerals (*e.g.*, kernite), meyerhofferite does not contain Na, at a significant level. High Na content is  
80 known to be deleterious for the stability of Portland cement-based concretes, because promoting  
81 undesired reactions undermining the durability of cements (*e.g.*, “alkali-silica reactions” – ASR).  
82 Furthermore, meyerhofferite could be added to Sorel cements (*i.e.*, magnesium oxychloride cements)  
83 which are commonly used to make floor tiles and panels for fire protection. In this light, B-additivated  
84 Sorel cements could be efficiently used for the production of radiation-shielding tiles or panels. To the  
85 best of our knowledge, no *in-situ* X-ray diffraction experiments were devoted to unveil the high-  
86 pressure behaviour mechanisms that govern the structure deformation at the atomic scale of  
87 meyerhofferite. Our research group investigated the behaviour of a series of natural anhydrous and  
88 hydrous borates at non-ambient conditions, with the aim to provide accurately determined thermo-  
89 elastic parameters, description of the deformation mechanisms at the atomic scale and of their *P-T*  
90 phase stability ranges (*e.g.*, Gatta et al. 2010, 2011, 2013, 2017, 2020; Lotti et al. 2017, 2018, 2019,  
91 Comboni et al. 2020, Pagliaro et al. 2020). Overall, we bracketed phase transitions occurring at  
92 relatively low pressure in kernite, colemanite and kurnakovite, which have some structural  
93 similarities with meyerhoferrite. Furthermore, the compressional parameters of meyerhofferite are  
94 still unknown, and an exhaustive description of its thermodynamic parameters is advisable if  
95 meyerhofferite will be employed in radiation-shielding tiles (*e.g.*, impact resistance) or as an aggregate  
96 in radiation shield concretes. For these reasons, we investigated the high-pressure behaviour of  
97 meyerhofferite by *in-situ* single-crystal X-ray diffraction up to 9 GPa under hydrostatic conditions,  
98 in order to obtain the compressional-elastic parameters and the *P*-stability fields of this borate.

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## 2. Experimental procedures

A sample of meyerhofferite, made by cm-sized transparent crystals from the Beğendikler borates deposit (Bigadiç District, Balıkesir 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  $\sim 40 \times 30 \times 20 \mu\text{m}^3$  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 ( $E \sim 30 \text{ keV}$ ,  $\lambda \sim 0.414 \text{ \AA}$ ) 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 ( $\text{MgSiO}_3$ ) 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  $\mu\text{m}$  culet Boehler-Almax design anvils, along with a few ruby spheres for  $P$ -determination (pressure uncertainty  $\pm 0.05 \text{ GPa}$  (Mao et al. 1986)). A stainless-steel foil (with thickness  $\sim 250 \mu\text{m}$ ) was pre-indented to 80  $\mu\text{m}$  and then drilled by spark-erosion, leading to a  $P$ -chamber of  $\sim 300 \mu\text{m}$  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  $\omega$ -scan ( $-32^\circ \leq \omega \leq +32^\circ$ ), with  $0.5^\circ$  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 (Petřicek et al. 2014), in the space group  $P\bar{1}$ , using the atomic coordinates from Burns and Hawthorne (1993) as

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

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

147 The (isothermal) compressional behaviour of both the polymorphs was described using the  
148 Birch-Murnaghan Equation of State (BM-EoS; Birch 1947). The  $fe$ - $Fe$  plot (where  $fe = [(V_0/V)^{2/3} -$   
149  $1]/2$  is the Eulerian finite strain and  $Fe$  is the normalised pressure, defined as  $Fe = P/3fe(1+2fe)^{5/2}$ ,  
150 Birch 1947; Angel et al. 2014) for both the polymorphs led to the conclusion that the truncation to  
151 the second-order (in energy) of the BM-EoS provides the best figure of merit for both of them. This  
152 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  $\beta_{P0,T0}$   
153 is the volume compressibility coefficient at room conditions) and its  $P$ -derivatives ( $K' = \partial K_{P0,T0}/\partial P$   
154 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  
155 transforms to:  $P(fe) = 3K_{P0,T0} fe (1 + 2fe)^{5/2}$ . The BM-EoS parameters (listed in Table 2), were refined  
156 minimizing the differences between the EoS curves and the experimental data (weighted by their  
157 uncertainties in  $P$  and  $V$ ), using the EOS-FIT7-GUI software (Angel et al. 2014). Data were fitted  
158 taking into account an estimated uncertainty of  $\pm 0.05$  GPa for pressure (Mao et al. 1986).

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#### 160 **4. Results and discussion**

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

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

168 patterns (Fig. 2), and the meyerhofferite-to-meyerhofferite-II phase transition would preserve the  
 169 space group of the structure, *i.e.*,  $P\bar{1}$ . In response to the phase transition, the unit-cell edges parallel  
 170 to  $a$  and  $b$  decrease by about 5.7 and 6.2 %, respectively, whereas that along  $c$  increases by almost  
 171 6.2%. Interestingly enough, at pressure slightly higher than the meyerhofferite-to-meyerhofferite-II  
 172 transition, the length of the unit cells edges along  $a$  and  $c$  first increase and then decrease again,  
 173 following a new monotonic trend within the stability field of the HP-polymorph (Fig. 3). This kind  
 174 of transient behaviour was already observed in other borates experiencing  $P$ -induced phase transitions  
 175 with a relevant change in volume (*e.g.*, kernite, Comboni et al. 2020). In the low- $P$  polymorph, the  $\alpha$   
 176 angle decreases from  $\sim 90.8^\circ$  at ambient pressure to  $\sim 89.9^\circ$  at 3.05(5) GPa, whereas  $\beta$  increases from  
 177  $\sim 101.9^\circ$  to  $\sim 103.3^\circ$  in the same  $P$ -range. Minor changes on  $\gamma$  angle occurs (Fig. 3, Tables 1a, b). In  
 178 response to the phase transition,  $\alpha$  and  $\gamma$  angles abruptly decrease from  $\sim 89.9^\circ$  to  $\sim 82.3^\circ$  and from  
 179  $\sim 86.9^\circ$  to  $\sim 79.7^\circ$ , respectively, whereas  $\beta$  increases from  $\sim 103.3^\circ$  to  $\sim 107.3^\circ$  (Fig. 3, Tables 1a, b).

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

184 In meyerhofferite-II, the bulk modulus increases to 55(2) GPa. Similar decrease in the bulk  
 185 compressibility was observed also in other borates after a first-order phase transition (*e.g.*, kernite,  
 186 Comboni et al. 2020). However, the low-pressure polymorph of meyerhofferite displays a marked  
 187 anisotropic pattern, being  $K(a)_0 : K(b)_0 : K(c)_0 \sim 1:3:1.5$ , but, after the phase transition, the anisotropic  
 188 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  
 189 2).

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

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$$199 \begin{pmatrix} \varepsilon_1 \\ \varepsilon_2 \\ \varepsilon_3 \end{pmatrix} = \begin{pmatrix} 57(2)^\circ & 124(2)^\circ & 63.6(3)^\circ \\ 128(1)^\circ & 143(2)^\circ & 93(1)^\circ \\ 55.4(6)^\circ & 103.2(2)^\circ & 153.3(5)^\circ \end{pmatrix} \cdot \begin{pmatrix} a \\ b \\ c \end{pmatrix}$$

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

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

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

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

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

In order to describe the structure deformation mechanisms occurring in meyerhofferite, stable between 0 and 3 GPa, the volumes of the Ca-polyhedra and B-tetrahedra with increasing  $P$  were calculated with the software VESTA (Momma and Izumi 2011), and reported in Table 3. The evolution with  $P$  of the Ca-polyhedra volume was modelled with a second-order Birch-Murnaghan Equation of State (Birch 1947). Notably, the obtained bulk modulus (55(5) GPa) is higher than the bulk modulus of meyerhofferite (Table 2). As the B-tetrahedra are substantially incompressible (Tables S3 and S4), this leads to the conclusion that the deformations in response to the applied pressure in meyerhofferite structure are mainly accommodated through the tilting of the Ca-polyhedra and B-tetrahedra around the oxygen hinges (Table 4), or by compression of the H-bonds. The Ca-O3-B1 and B2-O5-B3 angles decrease with pressure from 127.4(5) $^\circ$  to 124.6(6) $^\circ$  and from 125.1(8) $^\circ$  to 122.2(10) $^\circ$  between 0-3 GPa, respectively, whereas the Ca-O5-B3 angle increases from 135.6(3) $^\circ$  to 138.0(5) $^\circ$ . These three tilting angles show the maximum variation with  $P$ , producing only a modest corrugation of the heteropolyhedral chain along [001] (Fig. 1). Coupled with the aforementioned polyhedral tilting, the lateral connections between the heteropolyhedral chains, based on a complex H-bond network, experience a significant change. The chains are connected *via* hydrogen bonds almost parallel to [100] and along [010] (listed in Table 5; see also Fig. 1); additional H-bonds occur between intra-chains *donors* and *acceptors* (Burns and Hawthorne 1993). All the aforementioned extra-chains H-bonds, lying on (001), experience a significant shortening between 0 and 3 GPa (with variations in *donor-acceptor* distances ranging between 0.06-0.15 Å, Table 5). On the whole:

- i) Along [001], the heteropolyhedral chains behave like “pillars”. Ca- and B-polyhedra are 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 HP-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 <sup>[IV]</sup>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  $\sim 373$  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 (meyerhofferite-II, still triclinic), characterized by an abrupt volume decrease ( $\sim 10\%$ ).
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.

$P(\text{GPa})$	$V(\text{\AA}^3)$	$a(\text{\AA})$	$b(\text{\AA})$	$c(\text{\AA})$	$\alpha(^{\circ})$	$\beta(^{\circ})$	$\gamma(^{\circ})$
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)	$V(\text{\AA}^3)$	$a$ (\AA)	$b$ (\AA)	$c$ (\AA)	$\alpha$ ( $^\circ$ )	$\beta$ ( $^\circ$ )	$\gamma$ ( $^\circ$ )
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	$V_0, x_0$ ( $\text{\AA}^3, \text{\AA}$ )	$K_{V_0, x_0}$ (GPa)	$K'$	$\beta_{V_0, x_0}$ ( $\text{GPa}^{-1}$ )
$V$	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)
<i>II-BM EoS, <math>P &lt; 3.05(5)</math> GPa</i>				
Meyerhofferite-II	$V_0, x_0$ ( $\text{\AA}^3, \text{\AA}$ )	$K_{V_0, x_0}$ (GPa)	$K'$	$\beta_{V_0, x_0}$ ( $\text{GPa}^{-1}$ )
$V$	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)
<i>II-BM EoS, <math>P &gt; 3.48(5)</math> GPa</i>				

**Table 3:** Evolution of the polyhedral volumes with pressure in meyerhofferite. Average uncertainties on the Ca-polyhedra and  $\text{BO}_4$  tetrahedra are estimated to be  $\sim 0.3 \text{\AA}^3$  and  $\sim 0.01 \text{\AA}^3$ , respectively.

$P$ (GPa)	Ca-polyhedra ( $\text{\AA}^3$ )	B2 tetrahedra ( $\text{\AA}^3$ )	B3 tetrahedra ( $\text{\AA}^3$ )
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.

$P(\text{GPa})$	Ca-O5-B3 ( $^\circ$ )	Ca-O3-B1( $^\circ$ )	B2-O5-B3( $^\circ$ )
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 ( $\text{\AA}$ ) involved in hydrogen bonds.

$P(\text{GPa})$	O2 $\cdots$ O7 //[100]	O4 $\cdots$ O9 //[100]	O6 $\cdots$ O1 //[100]	O7 $\cdots$ O8 //[010]	O8 $\cdots$ O2 //[010]	O7 $\cdots$ O8' //[001]	O9 $\cdots$ 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,  $\text{BO}_x$  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*.