



On the crystal-chemistry of inderite, $\text{Mg}[\text{B}_3\text{O}_3(\text{OH})_5](\text{H}_2\text{O})_4 \cdot \text{H}_2\text{O}$

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Abstract

The crystal chemistry of inderite, a hydrous borate with known ideal formula $\text{MgB}_3\text{O}_3(\text{OH})_5 \cdot 5\text{H}_2\text{O}$ from the Kramer deposit, was re-investigated by electron probe micro-analysis in wavelength dispersive mode, laser ablation-(multi collector)-inductively coupled plasma-mass spectrometry and single-crystal neutron diffraction. The chemical data prove that the real composition of the investigated inderite is substantially identical to the ideal one, with insignificant content of potential isomorphic substituents, so that, excluding B, inderite does not contain any other industrially-relevant element (e.g., Li concentration is lower than 2.5 wt ppm, Be or REE lower than 0.1 wt ppm). The average $\delta^{11}\text{B}_{\text{NIST951}}$ value of *ca.* -7‰ lies within the range of values in which the source of boron is ascribable to terrestrial reservoirs (e.g., hydrothermal brines), rather than to marine ones. Neutron structure refinements, at both 280 and 10 K, confirm that the building units of the structure of inderite consist of: two $\text{BO}_2(\text{OH})_2$ tetrahedra (B-ion in sp^3 electronic configuration) and one $\text{BO}_2(\text{OH})$ triangle (B-ion in sp^2 electronic configuration), linked by corner-sharing to form a (soroborate) $\text{B}_3\text{O}_3(\text{OH})_5$ ring, and a Mg-octahedron $\text{Mg}(\text{OH})_2(\text{OH}_2)_4$. The $\text{B}_3\text{O}_3(\text{OH})_5$ ring and the Mg-octahedron are connected, by corner-sharing, to form an isolated $\text{Mg}(\text{H}_2\text{O})_4\text{B}_3\text{O}_3(\text{OH})_5$ (molecular) cluster. The tri-dimensional edifice of inderite is therefore built by heteropolyhedral $\text{Mg}(\text{H}_2\text{O})_4\text{B}_3\text{O}_3(\text{OH})_5$ clusters mutually connected by H-bonds, mediated by the zeolitic (“interstitial”) H_2O molecules lying between the clusters, so that the correct form of the chemical formula of inderite is $\text{Mg}[\text{B}_3\text{O}_3(\text{OH})_5](\text{H}_2\text{O})_4 \cdot \text{H}_2\text{O}$, rather than $\text{MgB}_3\text{O}_3(\text{OH})_5 \cdot 5\text{H}_2\text{O}$. All the thirteen independent oxygen sites of the structure are involved in H-bonding, as donors or as acceptors. This confirms the pervasive nature and the important role played by the H-bonding network on the structural stability of inderite. The differences between the crystal structure of the two dimorphs inderite and kurnakovite are discussed.

Keywords Inderite · Borates · Crystal chemistry · Single-crystal neutron diffraction · Hydrogen bonding

Introduction

Borates and borosilicates represent the main source for boron in the Earth’s Crust. Besides the average low concentration of B in the Crust (~ 11 wt ppm, Rudnick and Gao 2014), its distribution in various lithic reservoirs is highly anisotropic, leading to massive mineral deposits often governed by the high solubility in moderate-to-high temperature (> 270 K) aqueous fluids. Therefore, B can behave as a “fugitive” element, with a consequent redistribution under

conditions in which aqueous fluids are present, as commonly seen in hydrothermal or evaporitic-lacustrine deposits (Anovitz and Grew 1996; Smith and Medrano 1996). Hydrous borates are the dominant B-bearing minerals in hydrothermal or lacustrine deposits. It is worth to mention the rapid increase of the B demand over the last decades, which doubled in the last twenty years reaching at present about 10 Mtons/y (source: U.S.G.S. 2000–2021). Such a demand reflects the long series of technological processes and utilizations of boron, among those in, e.g., glass technology, ceramics, metallurgy, cosmetics, fertilizers and chemicals. More recently, natural borates are also being used for the fabrication of radiation-shielding concretes, used in nuclear energy plants and nuclear medicine applications, due to the elevated ability of ^{10}B to absorb thermal neutrons (Carter et al. 1953; Yazar and Bayülken 1994; Palmer and Swihart 1996; Kinno et al. 2002; Rauch and Waschkowski 2002;

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Okuno et al. 2009, 2013; Gatta et al. 2010, 2013, 2023; Korkut et al. 2010; Uysal et al. 2018).

Inderite, a hydrous borate named after the type locality (Inder Lake, Atyrau Region, Kazakhstan), occurs as colourless or white long prismatic crystals (even up to 20–30 cm), dominated by {110}, {120}, and {001}, or as aggregates of minute needles, or even as reniform nodules. Its ideal chemical formula is usually reported as $\text{MgB}_3\text{O}_3(\text{OH})_5 \cdot 5\text{H}_2\text{O}$ (or even $\text{Mg}_2\text{B}_6\text{O}_{11} \cdot 15\text{H}_2\text{O}$ in old literature; Boldyreva 1937). Inderite was firstly discovered by Boldyreva (1937) from Inder, Kazakhstan. However, Frondel and Morgan (1956) and Frondel et al. (1956) found the same mineral species in California, giving it the new name “lesserite”. An additional source of confusion was the discovery of the triclinic polymorph “kurnakovite”, found in the same Inder district by Godlevsky (1940). Only several years later, Schaller and Mrose (1960) proved that inderite and kurnakovite were actually dimorphs, and that “lesserite” corresponded to inderite firstly discovered by Boldyreva (1937), with a final discreditation of the mineral name “lesserite”.

The first H-free structural model of inderite was provided by Ashirov et al. (1962) and then improved by Rumanova and Ashirov (1963), based on single-crystal X-ray diffraction data collected with a Weissenberg camera and applying the direct methods to the intensity data. The structure was solved in the space group $P2_1/a$ with the following unit-cell geometry: $a \sim 12.02$, $b \sim 13.12$, $c \sim 6.84$ Å, $\beta \sim 104^\circ 40'$. Later, a structural re-investigation of inderite was performed by Corazza (1976), by single-crystal X-ray intensity data collected with a four-circle diffractometer equipped with a point-detector, and described in the space group $P2_1/c$ with $a = 6.8221(3)$, $b = 13.1145(13)$, $c = 12.0350(9)$ Å, and $\beta = 104.552(8)^\circ$, with the location also of 15 independent H sites. The structural model of Corazza (1976) is, to the best of our knowledge, the last one based on experimental data and reported in the literature. More recently, a model based on density functional theory (DFT) calculations was reported by Zhou et al. (2012). It is worth to note that the materials used by Rumanova and Ashirov (1963) and Corazza (1976) were not chemically analysed: their composition was assumed. Surprisingly, there is no data in the literature, based on modern standards, on the chemical composition of inderite, especially for minor and trace elements, so that the nature of potential substituents for Mg, B and OH-group is completely unknown.

In the framework of a long-term project on the high-pressure and high-temperature crystal-chemistry of hydrous borates, especially to select new B-bearing aggregates as potential radiation-shielding materials (Lotti et al. 2019; Comboni et al. 2020a,b, 2021, 2022), we have reinvestigated the crystal structure and the chemical composition (including the B isotopic signature) of inderite by single-crystal neutron diffraction, electron microprobe analysis

in wavelength-dispersive mode (EPMA-WDS), and laser ablation—inductively coupled plasma—mass spectrometry (LA-ICP-MS) and LA- multi collectors (MC-)ICP-MS, in order to provide: (1) a structural model with the unambiguous location of all the H sites and their vibrational regime, along with the description of the complex H-bonding scheme expected in inderite structure, (2) the chemical composition of this hydrous borate mineral, in terms of major, minor and trace elements, and its B isotopic signature. The occurrence of millimetric gem-quality crystals of inderite from the Kramer Borate Deposit, California (USA), along with its high B and H content (ideally: B_2O_3 37.3 wt% and H_2O 48.3 wt%), make this mineral as a good candidate for a neutron diffraction investigation. The results of this study are pivotal to describe the thermal and compressional behaviour of inderite, on which *in-situ* experiments are in progress, and the first experimental findings on the compressional behaviour of inderite have been published in Comboni et al. (2023).

Materials and experimental methods

Mineralogical description and chemical characterisation

The sample of inderite here investigated was kindly provided by the late Dr. Renato Pagano (Italy). The specimen consists of few colourless, prismatic, millimetric crystals from the “Boron Open Pit”, Kramer Borate Deposit, Boron, Kern County, California, USA, in which inderite coexists with other borates (e.g., borax, colemanite, inyoite, kernite, kurnakovite, meyerhofferite, probertite, sassolite, tinalconite, ulexite), carbonates (e.g., calcite, rhodochrosite), silicates (mainly clay minerals and zeolites) and some sulphides (e.g., pyrrhotite, realgar, smythite, stibnite). The geological studies of the area indicate that borates were deposited (probably within the Middle Miocene) in a small basin, fed from volcanic springs rich in boron (Gale 1946; Christ and Garrels 1959; Barnard and Kistler 1961).

The chemical composition of two millimetric crystals of inderite from the Kramer deposit, in terms of major and minor elements, was first investigated by EPMA-WDS using a JEOL 8200 Super Probe system, at the University of Milan. The following operating conditions were used: 15 kV and 5 nA, 10 µm beam diameter, 30 s of counting times on the peaks and 10 s on the backgrounds. A set of minerals was employed as standards: omphacite (Na), K-feldspar (K), sanbornite (Ba), celestine (Sr), forsterite-154 (Mg), fayalite-143 (Fe), grossular (Al, Si, Ca), apatite (F). Despite the large beam diameters, a modest degeneration of the crystals was observed under the electron beam, as previously observed for other hydrous borates (Gatta et al.

2022a, 2023). The raw data were corrected for matrix effects using the ZAF routine implemented in the JEOL suite of programs. The two crystals of inderite under investigation were found to be homogeneous. Only Mg and Ca concentrations were measured at a significant level. The measured weight fractions of Mg was virtually identical to the ideal one within the *e.s.d.*. The paucity of sample did not allow any thermal analysis of the mineral. The unit formula calculated on the basis of 3O + 5OH *apfu* and assuming 3B *apfu*, according to the experimental findings of the neutron structural refinement (as discussed later), is: $(\text{Mg}_{1.016}\text{Ca}_{0.008})\text{B}_3\text{O}_3(\text{OH})_5 \cdot 5\text{H}_2\text{O}$ or, at a first approximation, $(\text{Mg}_{1.02}\text{Ca}_{0.01})\text{B}_3\text{O}_3(\text{OH})_5 \cdot 5\text{H}_2\text{O}$. As it will be shown later, the correct form should be $(\text{Mg}_{1.02}\text{Ca}_{0.01})[\text{B}_3\text{O}_3(\text{OH})_5](\text{H}_2\text{O})_4 \cdot \text{H}_2\text{O}$.

The in-situ trace element concentrations were determined at the Geochemistry, Geochronology, and Isotope Geology laboratory (University of Milan) using a laser ablation system (Analyte Excite ArF excimer 193 nm, Teledyne Photon Machines) connected to a single collector quadrupole inductively coupled plasma mass spectrometer (ICP-MS, iCAP RQ from Thermo Fisher Scientific). The laser microprobe is equipped with a double volume chamber (HelEx II) and He was used as carrier gas of the ablated materials with fluxes of ~0.5 and ~0.2 l/min in the ablation cell and in the HelEx II cup, respectively. The laser spot size was set to 65 μm and a laser fluence of 2.0 J/cm², with a repetition rate of 7 Hz, was used. Each spot was analyzed for a total of 120 s, including 40 s of gas blank acquisition (comprising 10 s of laser warm up), 60 s of laser ablation measuring isotope peak intensity followed by 20 s of wash time. The NIST SRM 610 synthetic glass (Jochum et al. 2011) and ⁴³Ca (from EPMA) were used as external and internal standards, respectively. Quality control was achieved analyzing the USGS reference basaltic glass GSD-2 g (Wilson 2018), the NIST SRM 612 synthetic glass (Jochum et al. 2011), and the IAEA-B6 obsidian (Tonarini et al. 2003) together with the unknown. Precision and accuracy are better than 5% and 10%, respectively, for most of the elements. Data reduction was carried out using the Glitter software package (Griffin et al. 2008). Data are reported in Table 1.

The in-situ B isotope composition of the Kramer inderite was measured coupling the same laser microprobe system used for the determination of trace element to a double focusing multi collector (MC-)ICP-MS (Neptune XT, Thermo Fisher Scientific) hosted at the at the Geochemistry, Geochronology, and Isotope Geology laboratory of the University of Milan. Instrumental setup and analytical conditions were the same as reported in Gatta et al. (2023). The results are reported in the common delta(δ)-notation as permil (‰) and expressed relative to the isotopic ratio of the NIST SRM 951 boric acid (¹¹B/¹⁰B = 4.04362 ± 0.00137, 2σ; Catanzaro et al. 1970). The IAEA-B4 tourmaline (schorl, Tonarini et al. 2003) was employed as primary bracketing

Table 1 Trace element concentrations (given in wt ppm, 1σ) and B isotope composition (in ‰, 2σ) of the inderite of this study, based on the LA-ICP-MS and LA-MC-ICP-MS data

Analyzed isotope	Analyte symbol	Average (N = 4)	1σ
7	Li	2.23	1.22
9	Be	0.074	0.074
45	Sc	< 0.250	
49	Ti	< 0.740	
51	V	0.710	0.138
53	Cr	1.29	0.95
55	Mn	115	15
59	Co	< 0.190	
60	Ni	< 0.840	
65	Cu	< 1.03	
66	Zn	1.04	0.46
75	As	0.640	0.198
85	Rb	< 0.093	
88	Sr	0.022	0.005
89	Y	0.006	0.003
90	Zr	0.011	0.001
93	Nb	< 0.005	
111	Cd	< 0.106	
121	Sb	< 0.051	
133	Cs	< 0.030	
137	Ba	0.101	0.038
139	La	0.004	0.003
140	Ce	0.003	0.001
141	Pr	0.001	0.001
146	Nd	< 0.015	
149	Sm	< 0.018	
151	Eu	< 0.003	
157	Gd	< 0.018	
159	Tb	< 0.002	
163	Dy	< 0.009	
165	Ho	< 0.001	
167	Er	< 0.010	
169	Tm	< 0.003	
173	Yb	< 0.013	
175	Lu	< 0.002	
177	Hf	< 0.010	
181	Ta	< 0.001	
182	W	< 0.006	
208	Pb	< 0.023	
232	Th	< 0.001	
238	U	< 0.001	
		Weighted mean (N = 4)	2σ
$\delta^{11}\text{B}$		− 7.70	1.85

standard to correct instrumental isotope fractionation. Assessment of accuracy was achieved by analyzing two dravitic tourmalines (Marschall et al. 2006) and the B-rich synthetic andesitic glass ARM-2 (10,500 wt. ppm of B, Wu et al. 2021) in the same analytical run with the Kramer inderite. The measured $\delta^{11}\text{B}$ are accurate within uncertainties with published values (see Gatta et al. 2023 for further details). The B isotopic composition of the Kramer inderite is reported in Table 1.

Single-crystal neutron diffraction and structure refinement

Neutron diffraction data on an inderite crystals of size $1.1 \times 2.8 \times 4.2$ mm were collected at 10 and 280 K on the single-crystal diffractometer SXD (Keen et al. 2006) at the ISIS spallation neutron source (UK), which is equipped with an array of eleven 2D position-sensitive detectors statically placed around the sample position. At each temperature, a series of 7 orientations of the sample around the vertical axis of the instrument were used, with a counting time of ~6 h each. Data at 280 K were initially indexed with the unit cell available from the X-ray measurement. Integrated intensities were extracted for both datasets using the 3D-profile fitting method implemented in the SXD2001 software (Gutmann 2017) and corrected for the Lorentz effect. An absorption correction was applied to all the data with an in-house software package that reconstructs the three-dimensional shape of the crystal via image-processing of a 360° panoramic, and calculates the exact path-length of neutrons through the crystal for characteristic diffraction shape nodes (de Meulenaer and Tompa 1965). The transmission factor is, then, calculated via analytic solution of the integral of diffraction centers across the whole crystal volume, according to diffraction angles and neutron wavelengths (Leonardi and Capelli 2022, in preparation). Final unit cell parameters were refined against the fitted positions of the Bragg peaks after the 3D profile integration.

The structural refinement of inderite, based on the data collected at 280 K, was performed starting from the (H-free) X-ray model reported by Corazza (1976). The refinement was conducted by full matrix least squares on F^2 , using the SHELXL-2018/3 software (Sheldrick 2008, 2014). The secondary isotropic extinction effect was corrected adopting the Larson's formalism (Larson 1967). The neutron scattering lengths of Mg, B, O and H were taken from Sear (1986). The first cycles of refinement were conducted with isotropic displacement parameters for all the atomic site. When convergence was achieved, a series of minima in the Fourier-difference maps of the nuclear density function were observed, all assigned to H sites for the H's negative neutron scattering length. The newly assigned 15 independent H sites were located near O sites, with bond distances all compatible

with O–H groups (of hydroxyls or H_2O molecules). Convergence was then rapidly achieved and, in the last cycles of refinement, all atomic sites occupied by Mg, O and H were modelled anisotropically, with a significant improving of the figures of merit (Table 2). At the end of the refinement, no significant correlations among the refined variables were found in the variance–covariance matrix, with all the principal mean-square atomic displacement parameters positive, H included (Tables 2, 3 and 4). However, a careful inspection of the difference-Fourier maps of the nuclear density showed evidence of a positional disorder of the $\text{O}9_{\text{w}}$ site. An additional test refinement was then performed assuming a split configuration of this oxygen site in two subsites (labelled as $\text{O}9_{\text{w}}$ and $\text{O}9'_{\text{w}}$, Tables 2 and 3), only ~0.4 Å apart, with partial site occupancies and, therefore, mutually exclusive (Table 3). The final model obtained with the split $\text{O}9_{\text{w}}\text{--O}9'_{\text{w}}$ sites was found to be consistent, in terms of bond distances and angles, being $\text{O}9_{\text{w}}$ and $\text{O}9'_{\text{w}}$ oxygen sites of a H_2O molecule (Fig. 1, Tables 2, 3 and 5).

A second refinement was conducted with the intensity data collected at low temperature (10 K), starting with the structure model obtained at 280 K. The best figures of merit were obtained with a model in which all the fifteen H sites were refined anisotropically, while the other sites (i.e., Mg, B and O sites) were left isotropic (Table 4). At this temperature, no evidence of the $\text{O}9_{\text{w}}\text{--O}9'_{\text{w}}$ split sites was found, with only one unique site position (Table 3).

Further details pertaining to the structural refinements at both 280 and 10 K are given in Table 2. Atomic coordinates and displacement parameters are listed in Tables 3 and 4, whereas a series of selected interatomic distances and angles are given in Table 5. CIF is available as supplementary electronic material.

Results and discussion

The experimental findings obtained in this study confirm the ideal formula of inderite previously reported in the literature: $\text{MgB}_3\text{O}_3(\text{OH})_5 \cdot 5\text{H}_2\text{O}$ (or $\text{Mg}[\text{B}_3\text{O}_3(\text{OH})_5](\text{H}_2\text{O})_4 \cdot \text{H}_2\text{O}$). The only potential substituents of Mg is Ca, though for less than 0.01 apfu, whereas no substituents for B are found at a significant level (Table 1). Potential substituents of the hydroxyl group (e.g., F or Cl) are not measured at a significant level. Excluding B, inderite does not contain any other industrially-relevant element (e.g., Li concentration is lower than 2.5 wt ppm, Be or REE lower than 0.1 wt ppm). Among the trace elements measured by LA-ICP-MS, only Mn emerges with a concentration of 115(15) wt ppm; all the others are lower than 2.5 wt ppm. Overall, the EPMA-WDS and LA-ICP-MS data show that the chemical composition of inderite from the Kramer deposit is virtually identical to the ideal one. This finding is consistent with our previous

Table 2 Details of the neutron data collection and refinement of inderite

<i>T</i> (K)	280	10
Crystal shape	Prism	Prism
Crystal volume (mm)	1.1 × 2.8 × 4.2	1.1 × 2.8 × 4.2
Crystal colour	White, pale green	White, pale green
Unit-cell parameters	<i>a</i> = 6.8509(2) Å <i>b</i> = 13.0846(2) Å <i>c</i> = 12.0747(2) Å β = 104.445(3)° <i>V</i> = 1048.17(4) Å ³	<i>a</i> = 6.8437(2) Å <i>b</i> = 13.0456(2) Å <i>c</i> = 11.9560(2) Å β = 104.273(3)° <i>V</i> = 1034.48(4) Å ³
Chemical formula	Mg[B ₃ O ₃ (OH) ₅](H ₂ O) ₄ ·H ₂ O	Mg[B ₃ O ₃ (OH) ₅](H ₂ O) ₄ ·H ₂ O
Space Group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>Z</i>	4	4
Radiation type, Wavelength (Å)	Neutron, ToF	Neutron, ToF
Diffraction/Beamline	SXD, ISIS	SXD, ISIS
<i>d</i> _{min}	0.502	0.504
	− 15 ≤ <i>h</i> ≤ + 14 − 20 ≤ <i>k</i> ≤ + 39 − 27 ≤ <i>l</i> ≤ + 23	− 19 ≤ <i>h</i> ≤ + 19 − 29 ≤ <i>k</i> ≤ + 32 − 31 ≤ <i>l</i> ≤ + 29
Measured unique refl	4897	3922
Unique reflections with <i>F</i> _o > 4σ(<i>F</i> _o)	4897	3921
Refined parameters	278	206
<i>R</i> _σ	0.0692	0.1127
<i>R</i> _{<i>I</i>} (<i>F</i>) with <i>F</i> _o > 4σ(<i>F</i> _o)	0.1248	0.1005
<i>R</i> _{<i>I</i>} (<i>F</i>) for all reflections	0.1248	0.1005
<i>wR</i> ₂ (<i>F</i> ²)	0.2126	0.2271
GooF	1.356	1.765
Residuals (fm/Å ³)	− 3.04/+ 5.27	− 3.61/+ 4.29
Refinement with the split <i>O</i> 9 _w site		
Refined parameters	283	
<i>R</i> _{<i>I</i>} (<i>F</i>) with <i>F</i> _o > 4σ(<i>F</i> _o)	0.1223	
<i>R</i> _{<i>I</i>} (<i>F</i>) for all reflections	0.1223	
<i>wR</i> ₂ (<i>F</i> ²)	0.2083	
GooF	1.328	
Residuals (fm/Å ³)	− 3.1/+ 3.3	

Statistical parameters according to the Shelxl-2018 definition; $R_{\sigma} = \Sigma[\sigma(F_o^2)]/\Sigma[F_o^2]$, $R_I(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2(F^2) = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$

results obtained on a series of hydrous borates: colemanite (ideally CaB₃O₄(OH)₃·H₂O; Lotti et al. 2017a,b), kurnakovite (ideally MgB₃O₃(OH)₅·5H₂O, Gatta et al. 2019), kernite (ideally Na₂B₄O₆(OH)₂·3H₂O, Gatta et al. 2020), probertite (ideally CaNa[B₅O₇(OH)₄]₂·3H₂O, Gatta et al. 2022a), meyerhofferite (ideally CaB₃O₃(OH)₅·H₂O, Gatta et al. 2022b) and inderborite (ideally CaMg[B₃O₃(OH)₅]₂(H₂O)₄·2H₂O, Gatta et al. 2023). For all of those, no significant content of isomorphic substituents was measured. It is worth nothing that the aforementioned hydrous borates share a similar crystallization environment, represented by lacustrine basins fed by thermal springs, but they come from different deposits dislocated even in different continents. This led to discussion whether the unusual purity of the hydrous borates is the

effect of the absence of potential substituents, in the growing environment, or if it is governed by crystallochemical reasons. Even in the case of the inderite from the Kramer deposit, with its complex mineral assemblages described in one of the previous sections, it is unlikely a scenario with the absence of potential substituents, especially for Mg. However, this common feature of all the borates formed in lacustrine deposits under hydrothermal activity led Gatta et al. (2019, 2020, 2022a,b) to consider that, in this peculiar geological environment, crystal nucleation and growth could promote purification by iterated dissolution and recrystallization. Furthermore, even crystallochemical reasons can be invoked to explain the compositional purity: the bonding configuration of the slightly distorted Mg-octahedron

Table 3 Refined fractional atomic coordinates and equivalent/isotropic displacement factors ($\text{\AA}^2$), based on the neutron structure refinement

	$T = 280\text{ K}$				$T = 10\text{ K}$			
	x/a	y/b	z/c	U_{iso}/U_{eq}	x/a	y/b	z/c	U_{iso}/U_{eq}
<i>Mg1</i>	0.2560(9)	0.2163(5)	0.1175(5)	0.0063(9)	0.2498(5)	0.2165(3)	0.1191(3)	0.00103(16)
<i>O1</i>	0.6885(8)	0.1447(5)	0.4348(5)	0.0079(9)	0.6833(5)	0.1451(3)	0.4370(3)	0.0026(4)
<i>O2</i>	0.5003(8)	0.2095(5)	0.2556(5)	0.0068(7)	0.5004(5)	0.2090(3)	0.2537(3)	0.0021(3)
<i>O3</i>	0.7662(8)	0.0855(4)	0.2583(5)	0.0069(9)	0.7677(5)	0.0843(3)	0.2609(3)	0.0016(3)
<i>O4</i>	0.4547(7)	0.0348(4)	0.3041(4)	0.0040(8)	0.4537(5)	0.0340(3)	0.3050(3)	0.0012(3)
<i>O5</i>	0.2779(8)	− 0.1105(5)	0.2029(5)	0.0086(10)	0.2774(5)	− 0.1122(3)	0.2019(3)	0.0022(3)
<i>O6</i>	0.5459(8)	− 0.0363(5)	0.1389(5)	0.0068(9)	0.5448(5)	− 0.0368(3)	0.1379(3)	0.0019(3)
<i>O7</i>	0.8640(9)	− 0.0069(5)	0.1095(5)	0.0132(11)	0.8670(5)	− 0.0101(3)	0.1110(3)	0.0032(4)
<i>O8</i>	0.2355(8)	0.0592(4)	0.1156(4)	0.0046(8)	0.2345(5)	0.0585(3)	0.1158(3)	0.0016(3)
<i>O9_w</i>	0.4218(12)	0.2063(7)	− 0.0092(7)	0.0221(14)	0.4009(6)	0.2107(4)	− 0.0167(3)	0.0047(4)
<i>O10_w</i>	− 0.0120(11)	0.2170(6)	− 0.0128(6)	0.0187(13)	− 0.0244(6)	0.2149(4)	− 0.0058(3)	0.0057(4)
<i>O11_w</i>	0.2771(10)	0.3707(5)	0.1054(5)	0.0133(11)	0.2699(6)	0.3720(3)	0.1070(3)	0.0039(4)
<i>O12_w</i>	0.0716(11)	0.2319(6)	0.2380(6)	0.0184(13)	0.0735(6)	0.2317(3)	0.2446(3)	0.0049(4)
<i>O13_w</i>	0.1532(10)	0.0204(6)	0.4094(6)	0.0152(12)	0.1536(5)	0.0197(3)	0.4105(3)	0.0045(4)
<i>B1</i>	0.6003(8)	0.1186(4)	0.3143(5)	0.0033(9)	0.5982(5)	0.1179(3)	0.3151(3)	0.00103(16)
<i>B2</i>	0.3797(8)	− 0.0129(4)	0.1927(5)	0.0023(8)	0.3796(5)	− 0.0136(3)	0.1922(3)	0.00103(16)
<i>B3</i>	0.7223(9)	0.0165(5)	0.1707(5)	0.0043(9)	0.7244(5)	0.0146(3)	0.1715(3)	0.00103(16)
<i>H1</i>	0.9899(19)	0.0281(11)	0.1263(11)	0.025(2)	0.9930(14)	0.0263(9)	0.1282(10)	0.0158(15)
<i>H2</i>	0.2112(17)	0.0362(10)	0.0364(9)	0.020(2)	0.2102(15)	0.0366(9)	0.0337(8)	0.0145(12)
<i>H3</i>	0.2593(17)	0.0348(10)	0.3686(10)	0.022(2)	0.2566(14)	0.0337(9)	0.3683(9)	0.0149(13)
<i>H4</i>	0.5841(17)	0.2712(9)	0.2707(10)	0.019(2)	0.5849(15)	0.2701(9)	0.2702(9)	0.0152(13)
<i>H5</i>	0.443(2)	0.1482(11)	− 0.0521(11)	0.027(3)	0.4314(19)	0.1501(9)	− 0.0560(10)	0.0192(17)
<i>H6</i>	0.2166(19)	0.4032(10)	0.0319(11)	0.023(2)	0.2110(16)	0.4062(10)	0.0336(9)	0.0177(16)
<i>H7</i>	− 0.115(2)	0.2706(11)	− 0.0269(11)	0.027(3)	− 0.1281(15)	0.2695(8)	− 0.0215(9)	0.0153(13)
<i>H8</i>	0.1917(19)	− 0.1073(11)	0.2529(11)	0.027(3)	0.1887(17)	− 0.1097(11)	0.2523(10)	0.0190(16)
<i>H9</i>	0.024(2)	0.0371(12)	0.3616(11)	0.028(3)	0.0214(17)	0.0386(12)	0.3613(11)	0.0212(18)
<i>H10</i>	− 0.043(2)	0.1897(12)	0.2408(12)	0.030(3)	− 0.0370(16)	0.1872(10)	0.2500(9)	0.0168(14)
<i>H11</i>	0.7332(19)	0.0859(10)	0.4827(11)	0.024(2)	0.7321(16)	0.0878(9)	0.4864(9)	0.0156(13)
<i>H12</i>	0.382(2)	0.4145(12)	0.1434(12)	0.032(3)	0.3826(18)	0.4166(11)	0.1439(11)	0.0209(18)
<i>H13</i>	− 0.066(2)	0.1654(12)	− 0.0670(12)	0.030(3)	− 0.0792(17)	0.1621(11)	− 0.0640(11)	0.0194(17)
<i>H14</i>	0.511(2)	0.2595(11)	− 0.0219(12)	0.029(3)	0.4968(15)	0.2634(9)	− 0.0271(9)	0.0163(14)
<i>H15</i>	0.137(3)	0.2469(14)	0.3138(14)	0.040(3)	0.1496(19)	0.2467(14)	0.3239(10)	0.024(2)
<i>T = 280 K Model with split O9_w site</i>								
	x/a	y/b	z/c	U_{iso}/U_{eq}				
<i>Mg1</i>	0.2559(9)	0.2162(5)	0.1176(5)	0.0062(9)				
<i>O1</i>	0.6885(8)	0.1448(5)	0.4347(5)	0.0080(9)				
<i>O2</i>	0.5001(8)	0.2095(5)	0.2556(5)	0.0067(7)				
<i>O3</i>	0.7663(8)	0.0854(4)	0.2584(5)	0.0071(9)				
<i>O4</i>	0.4547(7)	0.0349(4)	0.3041(4)	0.0039(8)				
<i>O5</i>	0.2778(8)	− 0.1104(5)	0.2030(5)	0.0083(10)				
<i>O6</i>	0.5459(8)	− 0.0363(4)	0.1389(5)	0.0068(9)				
<i>O7</i>	0.8637(9)	− 0.0069(5)	0.1094(5)	0.0132(11)				
<i>O8</i>	0.2354(8)	0.0592(4)	0.1156(4)	0.0046(8)				
<i>O9_w</i>	0.403(4)	0.2096(12)	− 0.018(2)	0.010(4)	<i>s.o.f.</i> 0.60(10)			
<i>O9_w'</i>	0.452(5)	0.2992(17)	0.505(3)	0.008(5)	<i>s.o.f.</i> 0.40(10)			
<i>O10_w</i>	− 0.0121(11)	0.2170(6)	− 0.0128(6)	0.0188(13)				
<i>O11_w</i>	0.2770(9)	0.3707(5)	0.1054(5)	0.0132(11)				

Table 3 (continued)

	$T = 280\text{ K}$	<i>Model with split $O9_w$ site</i>		
	x/a	y/b	z/c	U_{iso}/U_{eq}
$O12_w$	0.0711(11)	0.2318(6)	0.2378(6)	0.0182(13)
$O13_w$	0.1532(10)	0.0203(6)	0.4094(6)	0.0153(12)
$B1$	0.6001(8)	0.1186(4)	0.3142(5)	0.0032(9)
$B2$	0.3798(8)	− 0.0129(4)	0.1927(4)	0.0025(8)
$B3$	0.7225(8)	0.0165(5)	0.1708(5)	0.0045(9)
$H1$	0.9904(18)	0.0280(11)	0.1266(11)	0.024(2)
$H2$	0.2112(17)	0.0364(9)	0.0363(9)	0.020(2)
$H3$	0.2594(17)	0.0348(10)	0.3686(10)	0.022(2)
$H4$	0.5839(17)	0.2712(9)	0.2706(10)	0.020(2)
$H5$	0.443(2)	0.1477(11)	− 0.0522(11)	0.027(3)
$H6$	0.2164(18)	0.4031(10)	0.0315(10)	0.023(2)
$H7$	− 0.115(2)	0.2707(11)	− 0.0269(10)	0.027(3)
$H8$	0.192(2)	− 0.1073(12)	0.2529(11)	0.028(3)
$H9$	0.023(2)	0.0371(11)	0.3613(11)	0.028(3)
$H10$	− 0.043(2)	0.1898(12)	0.2408(12)	0.030(3)
$H11$	0.7331(19)	0.0860(10)	0.4825(10)	0.024(2)
$H12$	0.382(2)	0.4149(11)	0.1435(12)	0.032(3)
$H13$	− 0.066(2)	0.1653(11)	− 0.0668(12)	0.029(3)
$H14$	0.512(2)	0.2600(11)	− 0.0220(12)	0.029(3)
$H15$	0.138(3)	0.2467(14)	0.3140(14)	0.040(3)

U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor. All the sites show *s.o.fs* of 100% (if not specified otherwise)

hinders a substitution of the other environmentally available fluid-mobile cations (both during formation and later diagenesis), *e.g.*, Na, K, Ca, Sr; any potential substitution would require a significant local distortion of the structure, with a consequent chemical strain. The same consideration can be extended also to B, likely with higher barriers: despite Al, Si or S could replace B at least in tetrahedral coordination, though with a strong chemical strain into the structure, only C could be considered for the planar-triangular configuration. In this light, the high purity of inderite can be reasonably ascribed even to crystallochemical reasons, in the form of a high elemental selectivity required by the crystal structure.

The LA-MC-ICP-MS data shows that the B isotopic composition of the Kramer inderite is relatively homogeneous. Single spot analyses along a rim-core-rim profile, parallel to the *b*-axis of the investigated crystal, report fairly similar B isotope composition within error (from -6.97 ± 1.83 to -9.52 ± 1.23 ‰), with a weighted mean $\delta^{11}\text{B}$ of -7.70 ± 1.85 ‰ (2σ , $N=4$) (Table 1). This average $\delta^{11}\text{B}$ value lies within the range of values in which the source of boron is ascribable to terrestrial reservoirs (*e.g.*, hydrothermal brines), rather than to marine ones (*e.g.*, Swihart and Moore 1986; Hussain et al. 2021, and references therein). This negative B isotopic signature is consistent with what we recently reported on the hydrous borate probertite from the

Kramer deposit (Gatta et al. 2022a) and with previous isotopic data from other borates from the same deposit reported by Swihart et al. (1996), ranging from -9 to $+2$ ‰. These findings corroborate what was previously inferred on the basis of geological evidence about the genesis of the deposit (Gale 1946; Christ and Garrels 1959; Barnard and Kistler 1961).

The neutron structure model here obtained is consistent, in first approximation, with that previously reported by Corazza (1976) based on single-crystal X-ray intensity data. The building units of the structure of inderite consist of: two $\text{BO}_2(\text{OH})_2$ tetrahedra (B-ion in sp^3 electronic configuration) and one $\text{BO}_2(\text{OH})$ triangle (B-ion in sp^2 electronic configuration), linked by corner-sharing to form a (soroborate) $\text{B}_3\text{O}_3(\text{OH})_5$ ring, and a Mg-octahedron $\text{Mg}(\text{OH})_2(\text{OH}_2)_4$ (Fig. 1, Tables 3 and 5). The $\text{B}_3\text{O}_3(\text{OH})_5$ ring and the Mg-octahedron are connected, by corner-sharing, to form an isolated $\text{Mg}(\text{H}_2\text{O})_4\text{B}_3\text{O}_3(\text{OH})_5$ (molecular) cluster (Fig. 1). The tri-dimensional edifice of inderite is therefore built by heteropolyhedral $\text{Mg}(\text{H}_2\text{O})_4\text{B}_3\text{O}_3(\text{OH})_5$ clusters mutually connected by H-bonds, even mediated by the zeolitic (“interstitial”) $H3\text{-}O13_w\text{-}H9$ molecules lying between the clusters (Figs. 1 and 2, Table 5). The corner-sharing $\text{B}_3\text{O}_3(\text{OH})_5$ ring is a combined building unit that occurs in the crystal structure of a series of hydrous borates, among those: kurnakovite, meyerhofferite, inderborite, or inyoite

Table 4 Refined displacement parameters ($\text{\AA}^2$) in the expression: $-2\pi^2[(ha^*)^2U_{11} + \dots + 2hka^*b^*U_{12} + \dots + 2klb^*c^*U_{23}]$, based on the neutron structure refinements

$T=280\text{ K}$	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
<i>Mg1</i>	0.0067 (15)	0.0050 (16)	0.0063 (14)	0.0000 (12)	0.0003 (12)	0.0000 (12)
<i>O1</i>	0.0095 (15)	0.0068 (16)	0.0065 (14)	− 0.0007 (11)	0.0002 (12)	− 0.0006 (12)
<i>O2</i>	0.006 (1)	0.0058 (14)	0.0073 (13)	0.0009 (10)	− 0.0012 (10)	0.0005 (10)
<i>O3</i>	0.0076 (13)	0.0062 (14)	0.0067 (13)	− 0.0015 (10)	0.0015 (10)	− 0.0006 (11)
<i>O4</i>	0.0049 (12)	0.0029 (13)	0.0039 (12)	− 0.0006 (10)	0.0006 (10)	− 0.0007 (10)
<i>O5</i>	0.0098 (15)	0.0056 (16)	0.0099 (15)	− 0.0007 (12)	0.0013 (12)	− 0.0013 (12)
<i>O6</i>	0.0067 (14)	0.0065 (16)	0.0070 (14)	− 0.0028 (11)	0.0015 (12)	− 0.0012 (12)
<i>O7</i>	0.0127 (16)	0.0156 (18)	0.0127 (16)	− 0.0044 (13)	0.0058 (13)	− 0.0006 (13)
<i>O8</i>	0.0059 (14)	0.0031 (15)	0.0041 (14)	− 0.0010 (11)	0.0001 (11)	0.0004 (11)
<i>O9_w</i>	0.0241 (19)	0.022 (2)	0.0223 (19)	− 0.0015 (14)	0.0104 (14)	− 0.0026 (14)
<i>O10_w</i>	0.0184 (18)	0.0164 (19)	0.0189 (18)	− 0.0021 (14)	0.0001 (13)	0.0018 (14)
<i>O11_w</i>	0.0151 (16)	0.0100 (17)	0.0128 (16)	− 0.0002 (13)	− 0.0002 (13)	− 0.0002 (13)
<i>O12_w</i>	0.0191 (18)	0.0193 (19)	0.0185 (18)	− 0.0018 (14)	0.0079 (14)	0.0000 (14)
<i>O13_w</i>	0.0159 (17)	0.0157 (18)	0.0140 (17)	0.0006 (13)	0.0040 (13)	− 0.0003 (13)
<i>H1</i>	0.023 (5)	0.028 (6)	0.024 (5)	− 0.008 (4)	0.008 (4)	− 0.005 (4)
<i>H2</i>	0.024 (4)	0.020 (5)	0.015 (4)	0.001 (3)	0.003 (3)	0.002 (4)
<i>H3</i>	0.021 (4)	0.023 (5)	0.021 (4)	0.002 (4)	0.004 (4)	0.000 (4)
<i>H4</i>	0.019 (2)	0.018 (2)	0.020 (2)	0.003 (1)	0.0031 (15)	− 0.0005 (15)
<i>H5</i>	0.034 (5)	0.022 (6)	0.027 (5)	− 0.002 (4)	0.014 (4)	− 0.005 (4)
<i>H6</i>	0.026 (5)	0.018 (5)	0.021 (5)	0.000 (4)	− 0.002 (4)	0.002 (4)
<i>H7</i>	0.030 (5)	0.028 (6)	0.022 (5)	0.003 (4)	0.001 (4)	0.008 (4)
<i>H8</i>	0.027 (3)	0.028 (3)	0.028 (3)	0.0007 (16)	0.0091 (17)	− 0.0008 (16)
<i>H9</i>	0.027 (5)	0.031 (6)	0.023 (5)	− 0.003 (4)	0.002 (4)	0.001 (4)
<i>H10</i>	0.029 (5)	0.033 (6)	0.030 (5)	− 0.001 (4)	0.013 (4)	− 0.001 (4)
<i>H11</i>	0.028 (5)	0.021 (5)	0.021 (5)	0.003 (4)	0.005 (4)	0.000 (4)
<i>H12</i>	0.036 (6)	0.027 (6)	0.027 (5)	− 0.004 (4)	− 0.003 (4)	− 0.006 (5)
<i>H13</i>	0.034 (5)	0.023 (5)	0.027 (5)	− 0.001 (4)	− 0.002 (4)	− 0.005 (4)
<i>H14</i>	0.036 (6)	0.023 (6)	0.030 (5)	0.000 (4)	0.012 (4)	− 0.006 (5)
<i>H15</i>	0.048 (6)	0.039 (6)	0.034 (6)	− 0.002 (5)	0.014 (5)	− 0.009 (5)
$T=280\text{ K}$	Model with split <i>O9_w</i> site					
<i>Mg1</i>	0.0066 (14)	0.0050 (16)	0.0063 (14)	0.0001 (12)	0.0001 (11)	0.0001 (12)
<i>O1</i>	0.0096 (15)	0.0069 (16)	0.0065 (14)	− 0.0010 (11)	0.0001 (12)	− 0.0008 (12)
<i>O2</i>	0.006 (1)	0.0057 (13)	0.0072 (12)	0.0009 (10)	− 0.0013 (9)	0.0004 (10)
<i>O3</i>	0.0078 (13)	0.0065 (14)	0.0068 (13)	− 0.0016 (10)	0.0015 (10)	− 0.0008 (11)
<i>O4</i>	0.0048 (12)	0.0028 (13)	0.0038 (12)	− 0.0005 (10)	0.0005 (10)	− 0.0008 (10)
<i>O5</i>	0.0094 (15)	0.0053 (16)	0.0095 (15)	− 0.0008 (11)	0.0010 (12)	− 0.0014 (12)
<i>O6</i>	0.0069 (14)	0.0066 (16)	0.0070 (14)	− 0.0027 (11)	0.0016 (11)	− 0.0010 (12)
<i>O7</i>	0.0127 (16)	0.0157 (18)	0.0126 (16)	− 0.0044 (13)	0.0058 (13)	− 0.0007 (13)
<i>O8</i>	0.0060 (14)	0.0028 (15)	0.0042 (13)	− 0.0009 (11)	− 0.0001 (11)	0.0002 (11)
<i>O9_w</i>	0.012 (6)	0.009 (5)	0.010 (5)	0.001 (3)	0.004 (4)	− 0.002 (3)
<i>O10_w</i>	0.0184 (18)	0.0166 (19)	0.0190 (18)	− 0.0019 (14)	0.0001 (13)	0.0019 (14)
<i>O11_w</i>	0.0149 (16)	0.0100 (17)	0.0128 (16)	− 0.0003 (13)	− 0.0003 (13)	− 0.0002 (13)
<i>O12_w</i>	0.0190 (18)	0.0191 (19)	0.0182 (18)	− 0.0017 (13)	0.0078 (14)	− 0.0001 (14)
<i>O13_w</i>	0.0161 (17)	0.0160 (18)	0.0140 (17)	0.0005 (13)	0.0042 (13)	− 0.0004 (13)
<i>H1</i>	0.023 (5)	0.027 (5)	0.024 (5)	− 0.007 (4)	0.008 (4)	− 0.005 (4)
<i>H2</i>	0.024 (4)	0.020 (5)	0.014 (4)	0.001 (3)	0.002 (3)	0.001 (4)
<i>H3</i>	0.021 (4)	0.023 (5)	0.022 (4)	0.002 (4)	0.005 (4)	0.000 (4)
<i>H4</i>	0.020 (2)	0.018 (2)	0.020 (2)	0.003 (1)	0.0031 (15)	− 0.0005 (15)

Table 4 (continued)

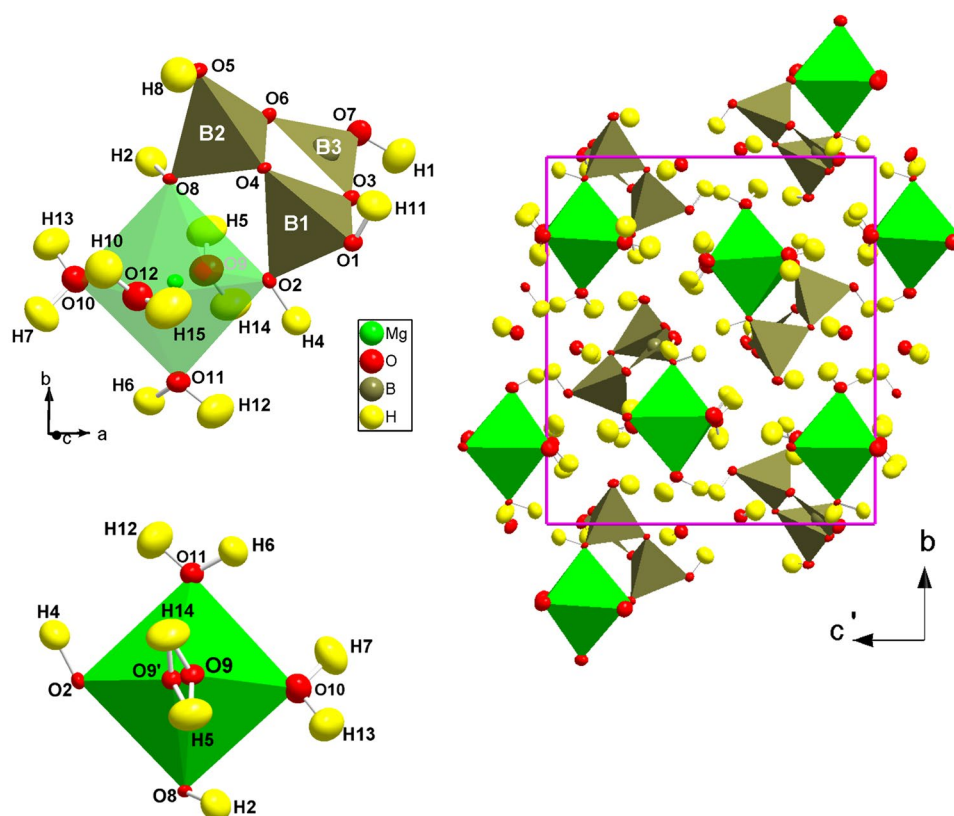
$T=280\text{ K}$	Model with split OH_w site					
H5	0.035 (5)	0.021 (5)	0.028 (5)	− 0.005 (4)	0.014 (4)	− 0.003 (4)
H6	0.026 (5)	0.017 (5)	0.020 (4)	− 0.001 (3)	− 0.003 (4)	0.002 (4)
H7	0.029 (5)	0.027 (6)	0.022 (5)	0.003 (4)	0.001 (4)	0.007 (4)
H8	0.028 (3)	0.029 (3)	0.029 (3)	0.0006 (16)	0.0095 (17)	− 0.0007 (16)
H9	0.028 (5)	0.031 (6)	0.022 (5)	− 0.003 (4)	0.002 (4)	0.001 (4)
H10	0.029 (5)	0.034 (6)	0.031 (5)	− 0.001 (4)	0.013 (4)	− 0.001 (4)
H11	0.029 (5)	0.020 (5)	0.022 (5)	0.004 (4)	0.005 (4)	0.000 (4)
H12	0.036 (5)	0.028 (6)	0.027 (5)	− 0.005 (4)	− 0.003 (4)	− 0.007 (5)
H13	0.033 (5)	0.023 (5)	0.027 (5)	− 0.001 (4)	− 0.002 (4)	− 0.005 (4)
H14	0.035 (5)	0.023 (5)	0.030 (5)	0.000 (4)	0.012 (4)	− 0.008 (4)
H15	0.049 (6)	0.040 (7)	0.034 (6)	− 0.003 (5)	0.014 (5)	− 0.009 (5)
$T=10\text{ K}$						
H1	0.011 (2)	0.015 (4)	0.022 (3)	0.000 (2)	0.006 (2)	− 0.001 (2)
H2	0.019 (3)	0.014 (3)	0.011 (2)	− 0.002 (2)	0.003 (2)	0.002 (3)
H3	0.013 (2)	0.017 (3)	0.016 (3)	− 0.001 (2)	0.006 (2)	0.000 (2)
H4	0.0153 (15)	0.0143 (16)	0.0155 (15)	0.003	0.0029 (10)	− 0.0002 (10)
H5	0.027 (4)	0.014 (4)	0.019 (3)	− 0.004 (3)	0.011 (3)	0.004 (3)
H6	0.017 (3)	0.020 (4)	0.015 (3)	0.005 (3)	0.001 (2)	− 0.001 (3)
H7	0.017 (3)	0.012 (3)	0.017 (3)	0.001 (2)	0.006 (2)	0.004 (2)
H8	0.0188 (18)	0.0196 (19)	0.0194 (18)	0.0000 (10)	0.0061 (10)	− 0.0004 (10)
H9	0.016 (3)	0.027 (4)	0.019 (3)	− 0.001 (3)	0.002 (3)	0.000 (3)
H10	0.0168 (16)	0.0171 (17)	0.0169 (16)	0.0005 (10)	0.0051 (10)	− 0.0005 (10)
H11	0.0164 (16)	0.0149 (16)	0.0153 (16)	0.0013 (10)	0.0033 (10)	0.0006 (10)
H12	0.020 (3)	0.020 (4)	0.021 (4)	− 0.005 (3)	0.002 (3)	− 0.007 (3)
H13	0.0197 (19)	0.0192 (19)	0.0191 (18)	− 0.0010 (10)	0.0045 (10)	− 0.0003 (10)
H14	0.0164 (16)	0.0163 (17)	0.0168 (16)	0.0003 (10)	0.0052 (10)	− 0.0005 (10)
H15	0.026 (4)	0.031 (5)	0.013 (3)	− 0.004 (3)	0.005 (3)	− 0.003 (4)

(Hawthorne et al. 1996). The weak interconnections between $Mg(H_2O)_4B_3O_3(OH)_5$ molecular clusters govern the perfect cleavage {010}, observed in the crystals of inderite, along with its low hardness (Mohs 3).

The neutron structure refinements of this study prove that:

1. The planar-triangular $BO_2(OH)$ unit shows a fairly regular geometrical configuration, with $\Delta(B3-O)_{\max} \sim 0.03\text{ \AA}$ (i.e., here defined as the difference between the longest and the shortest bond length; structural model at 280 K without the OH_w split), average $O-B3-O \sim 120^\circ$ (with $O-B3-O$ angles ranging between $\sim 115^\circ$ and $\sim 124^\circ$), and aplanarity $< 1.4^\circ$ (here defined as the average angle described by the plane on which the 3-oxygen sites lie and each of the three independent $B3-O_n$ vectors) (Table 5). The two independent tetrahedral $BO_2(OH)_2$ units show a modest distortion, in response to the common feature with one bond length systematically longer than the other three, with $\Delta(B1-O)_{\max} \sim 0.06\text{ \AA}$ and $\Delta(B2-O)_{\max} \sim 0.05\text{ \AA}$, and an average $O-B-O$ angle for both the tetrahedra of $\sim 109.5^\circ$ (Table 5). The
2. The neutron structure refinement at 280 K shows evidence of a static disorder pertaining to the OH_w site, which is better modelled with two mutually exclusive subsites (OH_w and OH'_w , Table 3) only $\sim 0.4\text{ \AA}$ apart. This local disorder disappears at low temperature: the refinement based on the intensity data collected at 10 K does not show any robust evidence of the two split subsites. Static disorder pertaining to the hydroxyl groups or H_2O molecules is not unusual in this class of material, as previously observed in colemanite (Lotti et al. 2017a,b) or in kernite (Gatta et al. 2020). However, the reason of the structural disorder in inderite remains unclear. The only significant difference between the $H5-OH_w-H14$ molecule and the other three independent H_2O molecules pertains to their H-bond geometry: whereas the $O6...OH_w...$

Fig. 1 (Top left) The principal building unit of the structure of inderite, i.e., $\text{Mg}(\text{OH})_4\text{B}_3\text{O}_3(\text{OH})_5$, and (right) a view of the structure down to $[100]$, based on the model derived by the neutron structure refinement of this study at 280 K. (Bottom left) Detail of the structure model with the split (and mutually exclusive) $\text{O}9_{\text{w}}\text{-O}9_{\text{w}}'$ sites. Displacement ellipsoid probability factor: 80%



$\text{O}1$ angle is $\sim 105.5^\circ$, the other configurations show acute angles (i.e., $\text{O}5\ldots\text{O}10_{\text{w}}\ldots\text{O}1 \sim 81.1^\circ$, $\text{O}3\ldots\text{O}12_{\text{w}}\ldots\text{O}10_{\text{w}} \sim 76.2^\circ$ and $\text{O}4\ldots\text{O}11_{\text{w}}\ldots\text{O}13_{\text{w}} \sim 88.3^\circ$). However, the split configuration does not change significantly the scenario: the $\text{O}6\ldots\text{O}9_{\text{w}}\ldots\text{O}1$ angle is $\sim 104.7^\circ$ and $\text{O}1\ldots\text{O}9_{\text{w}}'\ldots\text{O}6$ is $\sim 105.8^\circ$. In addition, at low temperature, the unique $\text{O}6\ldots\text{O}9_{\text{w}}\ldots\text{O}1$ angle is only slightly lower if compared to the one at 280 K (unsplit model): $\sim 104.8^\circ$. Furthermore, the libration regime of some O and H sites is significantly anisotropic, as shown by the U_{ij} tensors at 280 and even at 10 K (Fig. 2, Table 4). This could partially be the effect of an ineffective absorption correction due to high B content of inderite ($\text{B}_2\text{O}_3 \sim 37.3$ wt%).

3. All the thirteen independent oxygen sites of the structure are involved in H-bonding, as *donors* ($\text{O}1$, $\text{O}2$, $\text{O}5$, $\text{O}7$, $\text{O}8$, $\text{O}9_{\text{w}}$, $\text{O}10_{\text{w}}$, $\text{O}11_{\text{w}}$, $\text{O}12_{\text{w}}$, $\text{O}13_{\text{w}}$) or as *acceptors* ($\text{O}1$, $\text{O}3$, $\text{O}4$, $\text{O}5$, $\text{O}6$, $\text{O}7$, $\text{O}8$, $\text{O}9_{\text{w}}$, $\text{O}10_{\text{w}}$, $\text{O}12_{\text{w}}$, $\text{O}13_{\text{w}}$) (Table 5). This confirms the pervasive nature and the important role played by the H-bonding network on the structural stability.
4. The four independent H_2O molecule bonded to Mg (i.e., $\text{H}5\text{-O}9_{\text{w}}\text{-H}14$, $\text{H}7\text{-O}10_{\text{w}}\text{-H}13$, $\text{H}6\text{-O}11_{\text{w}}\text{-H}12$, $\text{H}10\text{-O}12_{\text{w}}\text{-H}15$; Table 5) shows an almost regular geometry, with the $\text{H-O}_{\text{w}}\text{-H}$ angles ranging between 104.5° and 107.7° at 280 K, and between 103.8° and

106.0° at 10 K (Table 5). Differently, the zeolitic $\text{H}3\text{-O}13_{\text{w}}\text{-H}9$ molecule shows a stretched configuration with the $\text{H}3\text{-O}13_{\text{w}}\text{-H}9$ angle of 110.0° at 280 K and 108.6° at 10 K. This configuration likely reflects the H-bonding scheme in which the molecule is involved: the $\text{O}3\ldots\text{H}9\text{-O}13_{\text{w}}\text{-H}3\ldots\text{O}4$ angle is 111.5° at 280 K and 112.0° at 10 K, so that the opening of the $\text{H-O}_{\text{w}}\text{-H}$ angle is an adaptive effect driven by the bonding geometry. All the O-H distances of the H_2O molecules, corrected for “riding motion effect” (following Busing and Levy 1964), range between 0.962 and 1.001 Å at 280 K and between 0.983 and 1.004 at 10 K (Table 5). Excluding the $\text{H}10\text{-O}12_{\text{w}}\text{-H}15$ molecule, all the others belonging to the coordination environment of Mg show a H-bonding scheme with one *donor* (O_{D}) and one *acceptor* (O_{A}) site, with $\text{O}_{\text{D}}\text{-H}\ldots\text{O}_{\text{A}}$ angle ranging between 152.3° and 172.9° (at 280 K, but without any significant variation at 10 K), $\text{O}_{\text{D}}\ldots\text{O}_{\text{A}}$ distance between 2.69 and 2.91 Å and $\text{H}\ldots\text{O}_{\text{A}}$ between 1.72 and 1.94 Å at 280 K (1.68–1.97 Å at 10 K) (Table 5), with an energetically favourable configuration (i.e., Steiner 1998; Gatta et al. 2021). The $\text{H}10\text{-O}12_{\text{w}}\text{-H}15$ molecule shows a more complex configuration: $\text{H}10$ is H-bonded to $\text{O}3$ (with $\text{H}10\ldots\text{O}3 \sim 1.94$ Å, $\text{O}12_{\text{w}}\text{-H}10_{\text{w}}\ldots\text{O}3 \sim 169.0^\circ$ at 280 K, Table 5) and $\text{H}15$ shows a bifurcate bonding scheme

Table 5 Relevant bond distances (Å) and angles (°) based on the neutron structure refinements (*distances corrected for riding motion effect, according to Busing and Levy 1964; < > indicates the average bond distances of a given polyhedron)

T = 280 K

<i>Mg1-O11_w</i>	2.033 (10)		<i>O11_w-Mg1-O2</i>	92.5 (4)	<i>O2-B1-O4</i>	109.9 (5)
<i>Mg1-O2</i>	2.049 (8)		<i>O11_w-Mg1-O8</i>	175.2 (4)	<i>O2-B1-O1</i>	108.5 (5)
<i>Mg1-O8</i>	2.061 (9)		<i>O2-Mg1-O8</i>	90.3 (3)	<i>O4-B1-O1</i>	111.1 (5)
<i>Mg1-O10_w</i>	2.099 (9)		<i>O11_w-Mg1-O10_w</i>	90.4 (4)	<i>O2-B1-O3</i>	109.1 (5)
<i>Mg1-O9_w</i>	2.125 (10)		<i>O2-Mg1-O10_w</i>	174.0 (4)	<i>O4-B1-O3</i>	108.5 (5)
<i>Mg1-O12_w</i>	2.161 (9)		<i>O8-Mg1-O10_w</i>	87.2 (4)	<i>O1-B1-O3</i>	109.7 (5)
< <i>Mg1-O</i> >	2.088		<i>O11_w-Mg1-O9_w</i>	87.1 (4)	< <i>O-B1-O</i> >	109.5
<i>B1-O1</i>	1.470 (8)		<i>O2-Mg1-O9_w</i>	96.2 (4)	<i>O4-B2-O5</i>	111.1 (5)
<i>B1-O2</i>	1.464 (8)		<i>O8-Mg1-O9_w</i>	88.7 (4)	<i>O4-B2-O6</i>	111.2 (4)
<i>B1-O3</i>	1.523 (7)		<i>O10_w-Mg1-O9_w</i>	89.2 (4)	<i>O5-B2-O6</i>	106.8 (5)
<i>B1-O4</i>	1.466 (8)		<i>O11_w-Mg1-O12_w</i>	91.1 (3)	<i>O4-B2-O8</i>	109.2 (5)
< <i>B1-O</i> >	1.481		<i>O2-Mg1-O12_w</i>	87.3 (3)	<i>O5-B2-O8</i>	110.0 (5)
<i>B2-O4</i>	1.455 (7)		<i>O8-Mg1-O12_w</i>	93.0 (3)	<i>O6-B2-O8</i>	108.5 (4)
<i>B2-O5</i>	1.475 (8)		<i>O10_w-Mg1-O12_w</i>	87.4 (4)	< <i>O-B2-O</i> >	109.5
<i>B2-O6</i>	1.477 (7)		<i>O9_w-Mg1-O12_w</i>	176.1 (4)	<i>O6-B3-O3</i>	124.2 (5)
<i>B2-O8</i>	1.508 (8)				<i>O6-B3-O7</i>	115.2 (5)
< <i>B2-O</i> >	1.479				<i>O3-B3-O7</i>	120.5 (5)
<i>B3-O3</i>	1.366 (8)				< <i>O-B3-O</i> >	120.0
<i>B3-O6</i>	1.361 (8)					
<i>B3-O7</i>	1.392 (8)					
< <i>B3-O</i> >	1.373					
<i>O1-H11</i>	0.966 (15)	0.984*	<i>O1-H11_w...O13_w</i>	172.8 (12)		
			<i>O1...O13_w</i>	2.893 (9)		
			<i>H11...O13_w</i>	1.932 (14)		
<i>O2-H4</i>	0.982 (14)	0.995*	<i>O2-H4...O5</i>	176.1 (12)		
			<i>O2...O5</i>	2.780 (8)		
			<i>H4...O5</i>	1.800 (13)		
<i>O5-H8</i>	0.944 (14)	0.966*	<i>O5-H8...O13_w</i>	133.6 (11)	<i>O5-H8...O12_w</i>	120.4 (11)
			<i>O5...O13_w</i>	3.308 (10)	<i>O5...O12_w</i>	3.369 (10)
			<i>H8...O13_w</i>	2.585 (16)	<i>H8...O12_w</i>	2.792 (17)
<i>O7-H1</i>	0.953 (14)	0.967*	<i>O7-H1...O8</i>	157.4 (13)		
			<i>O7...O8</i>	2.672 (9)		
			<i>H1...O8</i>	1.767 (14)		
<i>O8-H2</i>	0.977 (13)	0.994*	<i>O8-H2...O7</i>	171.5 (11)		
			<i>O8...O7</i>	2.720 (8)		
			<i>H2...O7</i>	1.750 (13)		
<i>O9_w-H5</i>	0.951 (17)	0.957*	<i>O9_w-H5...O6</i>	174.0 (14)		
			<i>O9_w...O6</i>	2.761 (11)		
			<i>H5...O6</i>	1.814 (16)		
<i>O9_w-H14</i>	0.962 (17)	0.972*	<i>O9_w-H14...O1</i>	172.3 (14)		
			<i>O9_w...O1</i>	2.866 (11)		
			<i>H14...O1</i>	1.910 (17)		
<i>H5-O9_w-H14</i>	107.7 (14)					
<i>O10_w-H7</i>	0.978 (16)	0.989*	<i>O10_w-H7...O1</i>	172.9 (14)		
			<i>O10_w...O1</i>	2.689 (10)		
			<i>H7...O1</i>	1.716 (15)		
<i>O10_w-H13</i>	0.949 (17)	0.963*	<i>O10_w-H13...O5</i>	152.3 (14)		
			<i>O10_w...O5</i>	2.906 (9)		
			<i>H13...O5</i>	2.032 (14)		

Table 5 (continued)*T* = 280 K

<i>H7-O10_w-H13</i>	104.5(14)				
<i>O11_w-H6</i>	0.977 (14)	0.989*	<i>O11_w-H6...O13_w</i>	167.4 (12)	
			<i>O11_w...O13_w</i>	2.711 (9)	
			<i>H6...O13_w</i>	1.749 (14)	
<i>O11_w-H12</i>	0.945 (16)	0.970*	<i>O11_w-H12_w...O4</i>	163.0 (14)	
			<i>O11_w...O4</i>	2.859 (8)	
			<i>H12...O4</i>	1.942 (16)	
<i>H6-O11_w-H12</i>	106.0 (13)				
<i>O12_w-H10_w</i>	0.967 (16)	0.980*	<i>O12_w-H10...O3</i>	168.9 (14)	
			<i>O12_w...O3</i>	2.892 (10)	
			<i>H10...O3</i>	1.937 (17)	
<i>O12_w-H15</i>	0.93 (2)	0.960*	<i>O12_w-H15...O10_w</i>	129.7 (14)	<i>O12_w-H15...O9_w</i> 160.2 (15)
			<i>O12_w...O10_w</i>	3.270 (11)	<i>O12_w...O9_w</i> 3.475 (10)
			<i>H15...O10_w</i>	2.593 (21)	<i>H15...O9_w</i> 2.582 (17)
<i>H10-O12_w-H15</i>	106.4 (16)				
<i>O13_w-H3</i>	0.992 (13)	0.998*	<i>O13_w-H3...O4</i>	168.6 (12)	
			<i>O13_w...O4</i>	2.689 (10)	
			<i>H3...O4</i>	1.709 (15)	
<i>O13_w-H9</i>	0.955 (16)	0.970*	<i>O13_w-H9...O3</i>	174.1 (13)	
			<i>O13_w...O3</i>	2.944 (8)	
			<i>H9...O3</i>	1.993 (13)	
<i>H3-O13_w-H9</i>	110.0 (13)				
<i>T</i> = 280 K	Model with split <i>O9_w</i> site				
<i>Mg1-O11_w</i>	2.035 (9)		<i>O11_w-Mg1-O2</i>	92.5 (4)	<i>O2-B1-O4</i> 109.9 (5)
<i>Mg1-O2</i>	2.048 (8)		<i>O11_w-Mg1-O8</i>	175.1 (4)	<i>O2-B1-O1</i> 108.4 (5)
<i>Mg1-O8</i>	2.059 (8)		<i>O2-Mg1-O8</i>	90.3 (3)	<i>O4-B1-O1</i> 111.2 (5)
<i>Mg1-O10_w</i>	2.100 (9)		<i>O11_w-Mg1-O10_w</i>	90.3 (4)	<i>O2-B1-O3</i> 109.2 (4)
<i>Mg1-O9_w</i>	2.122 (12)		<i>O2-Mg1-O10_w</i>	174.1 (4)	<i>O4-B1-O3</i> 108.5 (4)
<i>Mg1-O12_w</i>	2.160 (9)		<i>O8-Mg1-O10_w</i>	87.3 (3)	<i>O1-B1-O3</i> 109.6 (5)
<i>Mg1-O9_w</i>	2.15 (2)		<i>O11_w-Mg1-O9_w</i>	85.9 (5)	< <i>O-B1-O</i> > 109.5
< <i>Mg1-O</i> >	2.096		<i>O2-Mg1-O9_w</i>	100.1 (9)	<i>O4-B2-O5</i> 111.1 (4)
<i>B1-O1</i>	1.470 (8)		<i>O8-Mg1-O9_w</i>	89.7 (5)	<i>O4-B2-O6</i> 111.3 (4)
<i>B1-O2</i>	1.464 (8)		<i>O10_w-Mg1-O9_w</i>	85.3 (9)	<i>O5-B2-O6</i> 106.9 (5)
<i>B1-O3</i>	1.524 (7)		<i>O11_w-Mg1-O12_w</i>	91.1 (3)	<i>O4-B2-O8</i> 109.2 (5)
<i>B1-O4</i>	1.465 (8)		<i>O2-Mg1-O12_w</i>	87.4 (3)	<i>O5-B2-O8</i> 110.0 (4)
< <i>B1-O</i> >	1.481		<i>O8-Mg1-O12_w</i>	93.0 (3)	<i>O6-B2-O8</i> 108.5 (4)
<i>B2-O4</i>	1.455 (7)		<i>O10_w-Mg1-O12_w</i>	87.3 (4)	< <i>O-B2-O</i> > 109.5
<i>B2-O5</i>	1.475 (8)		<i>O9_w-Mg1-O12_w</i>	172.0 (10)	<i>O6-B3-O3</i> 124.2 (5)
<i>B2-O6</i>	1.477 (7)		<i>O11_w-Mg1-O9_w'</i>	88.9 (6)	<i>O6-B3-O7</i> 115.1 (5)
<i>B2-O8</i>	1.508 (8)		<i>O2-Mg1-O9_w'</i>	89.8 (11)	<i>O3-B3-O7</i> 120.7 (5)
< <i>B2-O</i> >	1.479		<i>O8-Mg1-O9_w'</i>	87.2 (6)	< <i>O-B3-O</i> > 120.0
<i>B3-O3</i>	1.365 (8)		<i>O10_w-Mg1-O9_w'</i>	95.5 (11)	
<i>B3-O6</i>	1.363 (8)		<i>O12_w-Mg1-O9_w'</i>	177.2 (11)	
<i>B3-O7</i>	1.392 (8)				
< <i>B3-O</i> >	1.373		<i>O9_w-O9_w'</i>	0.40 (2)	
<i>O1-H11</i>	0.964 (14)	0.984*	<i>O1-H11...O13_w</i>	172.7 (12)	
			<i>O1...O13_w</i>	2.893 (9)	
			<i>H11...O13_w</i>	1.934 (14)	
<i>O2-H4</i>	0.981 (13)	0.995*	<i>O2-H4...O5</i>	176.1 (11)	

Table 5 (continued)

<i>T</i> = 280 K		Model with split <i>O</i> _w site				
			<i>O2-O5</i>	2.782 (8)		
			<i>H4...O5</i>	1.802 (13)		
<i>O5-H8</i>	0.944 (16)	0.968*	<i>O5-H8...O13_w</i>	133.5 (11)	<i>O5-H8...O12_w</i>	120.4 (11)
			<i>O5...O13_w</i>	3.305 (10)	<i>O5...O12_w</i>	3.368 (10)
			<i>H8...O13_w</i>	2.583 (16)	<i>H8...O12_w</i>	2.790 (17)
<i>O7-H1</i>	0.956 (14)	0.967*	<i>O7-H1...O8</i>	157.4 (13)		
			<i>O7...O8</i>	2.672 (8)		
			<i>H1...O8</i>	1.764 (14)		
<i>O8-H2</i>	0.977 (12)	0.994*	<i>O8-H2...O7</i>	171.6 (11)		
			<i>O8...O7</i>	2.719 (8)		
			<i>H2...O7</i>	1.749 (12)		
<i>O9_w-H5</i>	0.952 (25)	1.003*	<i>O9_w-H5...O6</i>	165.9 (16)	<i>O9_w'-H5...O6</i>	169.9 (18)
<i>O9_w'-H5</i>	0.969 (24)	1.012*	<i>O9_w...O6</i>	2.769 (21)	<i>O9_w'...O6</i>	2.771 (25)
			<i>H5...O6</i>	1.807 (15)		
<i>O9_w-H14</i>	1.006 (29)	1.028*	<i>O9_w-H14...O1</i>	167.4 (17)	<i>O9_w'-H14...O1</i>	165.3 (21)
<i>O9_w'-H14</i>	0.973 (28)	1.016*	<i>O9_w...O1</i>	2.889 (26)	<i>O9_w'...O1</i>	2.847 (28)
			<i>H14...O1</i>	1.899 (16)		
<i>H5-O9_w-H14</i>	103.3 (17)					
<i>H5-O9_w'-H14</i>	106.8 (18)					
<i>O10_w-H7</i>	0.977 (16)	0.987*	<i>O10_w-H7...O1</i>	172.7 (14)		
			<i>O10_w...O1</i>	2.689 (9)		
			<i>H7...O1</i>	1.717 (15)		
<i>O10_w-H13</i>	0.948 (16)	0.962*	<i>O10_w-H13...O5</i>	152.1 (13)		
			<i>O10_w...O5</i>	2.906 (9)		
			<i>H13...O5</i>	2.035 (14)		
<i>H7-O10_w-H13</i>	104.8 (14)					
<i>O11_w-H6</i>	0.981 (13)	0.992*	<i>O11_w-H6...O13_w</i>	167.3 (12)		
			<i>O11_w...O13_w</i>	2.711 (9)		
			<i>H6...O13_w</i>	1.746 (14)		
<i>O11_w-H12</i>	0.946 (15)	0.972*	<i>O11_w-H12...O4</i>	163.5 (14)		
			<i>O11_w...O4</i>	2.861 (8)		
			<i>H12...O4</i>	1.941 (15)		
<i>H6-O11_w-H12</i>	106.0 (13)					
<i>O12_w-H10</i>	0.964 (17)	0.980*	<i>O12_w-H10...O3</i>	169.0 (14)		
			<i>O12_w...O3</i>	2.890 (10)		
			<i>H10...O3</i>	1.938 (17)		
<i>O12_w-H15</i>	0.940 (17)	0.966*	<i>O12_w-H15...O10_w</i>	129.4 (14)	<i>O12_w-H15...O9_w</i>	161.0 (16)
			<i>O12_w...O10_w</i>	3.272 (11)	<i>O12_w...O9_w</i>	3.337 (23)
			<i>H15...O10_w</i>	2.593 (21)	<i>H15...O9_w</i>	2.434 (27)
<i>H10-O12_w-H15</i>	106.3 (16)					
<i>O13_w-H3</i>	0.993 (15)	1.001*	<i>O13_w-H3...O4</i>	168.6 (12)		
			<i>O13_w...O4</i>	2.688 (10)		
			<i>H3...O4</i>	1.708 (14)		
<i>O13_w-H9</i>	0.960 (15)	0.975*	<i>O13_w-H9...O3</i>	174.1 (13)		
			<i>O13_w...O3</i>	2.944 (8)		
			<i>H9...O3</i>	1.987 (13)		
<i>H3-O13_w-H9</i>	110.0 (13)					
<i>T</i> = 10 K						
<i>Mg1-O11_w</i>	2.041 (6)		<i>O11_w-Mg1-O2</i>	92.6 (2)	<i>O2-B1-O4</i>	110.5 (3)

Table 5 (continued) $T = 10$ K

$Mg1-O2$	2.044 (5)		$O11_w-Mg1-O8$	174.5 (2)	$O2-B1-O1$	108.6 (3)
$Mg1-O8$	2.063 (5)		$O2-Mg1-O8$	89.8 (2)	$O4-B1-O1$	110.9 (3)
$Mg1-O10_w$	2.090 (5)		$O11_w-Mg1-O10_w$	91.3 (2)	$O2-B1-O3$	108.7 (3)
$Mg1-O9_w$	2.130 (5)		$O2-Mg1-O10_w$	173.2 (2)	$O4-B1-O3$	108.7 (3)
$Mg1-O12_w$	2.153 (5)		$O8-Mg1-O10_w$	86.8 (2)	$O1-B1-O3$	109.4 (3)
$\langle Mg1-O \rangle$	2.087		$O11_w-Mg1-O9_w$	85.8 (2)	$\langle O-B1-O \rangle$	109.5
$B1-O1$	1.474 (5)		$O2-Mg1-O9_w$	97.3 (2)	$O4-B2-O5$	111.1 (3)
$B1-O2$	1.469 (5)		$O8-Mg1-O9_w$	89.0 (2)	$O4-B2-O6$	111.5 (3)
$B1-O3$	1.526 (5)		$O10_w-Mg1-O9_w$	88.5 (2)	$O5-B2-O6$	106.6 (3)
$B1-O4$	1.460 (5)		$O11_w-Mg1-O12_w$	91.0 (2)	$O4-B2-O8$	108.8 (3)
$\langle B1-O \rangle$	1.482		$O2-Mg1-O12_w$	87.8 (3)	$O5-B2-O8$	109.7 (3)
$B2-O4$	1.458 (5)		$O8-Mg1-O12_w$	94.1 (2)	$O6-B2-O8$	109.0 (3)
$B2-O5$	1.481 (5)		$O10_w-Mg1-O12_w$	86.6 (2)	$\langle O-B2-O \rangle$	109.5
$B2-O6$	1.467 (5)		$O9_w-Mg1-O12_w$	174.1 (2)	$O6-B3-O3$	123.7 (3)
$B2-O8$	1.502 (5)				$O6-B3-O7$	115.4 (3)
$\langle B2-O \rangle$	1.477				$O3-B3-O7$	120.8 (3)
$B3-O3$	1.378 (5)				$\langle O-B3-O \rangle$	120.0
$B3-O6$	1.371 (5)					
$B3-O7$	1.388 (5)					
$\langle B3-O \rangle$	1.379					
$O1-H11$	0.961 (12)	0.976*	$O1-H11...O13_w$	175.6 (10)		
			$O1...O13_w$	2.862 (5)		
			$H11...O13_w$	1.903 (12)		
$O2-H4$	0.976 (11)	0.999*	$O2-H4...O5$	175.6 (10)		
			$O2-O5$	2.764 (5)		
			$H4...O5$	1.790 (11)		
$O5-H8$	0.955 (14)	0.970*	$O5-H8...O13_w$	133.1 (9)	$O5-H8...O12_w$	120.1 (9)
			$O5...O13_w$	3.307 (6)	$O5...O12_w$	3.329 (6)
			$H8...O13_w$	2.589 (14)	$H8...O12_w$	2.746 (14)
$O7-H1$	0.961 (10)	0.976*	$O7-H1...O8$	156.7 (9)		
			$O7...O8$	2.656 (5)		
			$H1...O8$	1.747 (11)		
$O8-H2$	0.997 (10)	1.009*	$O8-H2...O7$	170.7 (8)		
			$O8...O7$	2.704 (5)		
			$H2...O7$	1.715 (10)		
$O9_w-H5$	0.968 (13)	0.982*	$O9-H5...O6$	172.9 (11)		
			$O9...O6$	2.767 (6)		
			$H5...O6$	1.803 (13)		
$O9_w-H14$	0.980 (12)	0.995*	$O9_w-H14...O1$	172.9 (10)		
			$O9_w...O1$	2.846 (6)		
			$H14...O1$	1.872 (12)		
$H5-O9_w-H14$	106.3 (11)					
$O10_w-H7$	0.990 (11)	1.004*	$O10_w-H7...O1$	173.2 (10)		
			$O10_w...O1$	2.670 (6)		
			$H7...O1$	1.684 (11)		
$O10_w-H13$	0.985 (13)	0.999*	$O10_w-H13...O5$	152.4 (11)		
			$O10_w...O5$	2.879 (5)		
			$H13...O5$	1.970 (12)		
$H7-O10_w-H13$	103.8 (11)					
$O11_w-H6$	0.979 (11)	0.994*	$O11_w-H6...O13_w$	168.1 (10)		

Table 5 (continued) $T = 10$ K

			$O11_w \dots O13_w$	2.689 (5)		
			$H6 \dots O13_w$	1.724 (12)		
$O11_w-H12$	0.980 (13)	0.995*	$O11_w-H12 \dots O4$	163.0 (12)		
			$O11_w \dots O4$	2.858 (5)		
			$H12 \dots O4$	1.907 (14)		
$H6-O11_w-H12$	103.8 (11)		$O12_w-H10 \dots O3$	172.5 (11)		
$O12_w-H10$	0.968 (13)	0.983*	$O12_w \dots O3$	2.884 (5)		
			$H10 \dots O3$	1.922 (13)		
$O12_w-H15$	0.983 (12)	0.998*	$O12_w-H15 \dots O10_w$	123.2 (9)	$O12_w-H15 \dots O9_w$	163.5 (10)
			$O12_w \dots O10_w$	3.291 (6)	$O12_w \dots O9_w$	3.253 (5)
			$H15 \dots O10_w$	2.647 (14)	$H15 \dots O9_w$	2.298 (12)
$H10-O12_w-H15$	106.9 (11)		$O13_w-H3 \dots O4$	168.3 (9)		
$O13_w-H3$	0.980 (12)	0.995*	$O13_w \dots O4$	2.668 (5)		
			$H3 \dots O4$	1.701 (11)		
$O13_w-H9$	0.981 (12)	0.996*	$O13_w-H9 \dots O3$	176.2 (11)		
			$O13_w \dots O3$	2.925 (5)		
			$H9 \dots O3$	1.945 (12)		
$H3-O13_w-H9$	108.6 (11)					

with $O10_w$ and $O9_w$ as acceptors ($H15 \dots O10_w \sim 2.59$ Å and $O12_w-H15 \dots O10_w \sim 129.4^\circ$, $H15 \dots O9_w \sim 2.43$ Å and $O12_w-H15 \dots O9_w \sim 161.0^\circ$ at 280 K).

All the O–H distances of the hydroxyl groups (i.e., $O1-H11$, $O2-H4$, $O5-H8$, $O7-H1$, $O8-H2$, Table 5), corrected for “riding motion effect”, range between 0.967 and 0.995 Å at 280 K (and between 0.970 and 1.009 Å at 10 K) (Table 5). All the OH groups, excluding $O5-H8$, are involved in H-bonds

with one acceptor site, with $O_D \dots O_A$ distances between 2.67 and 2.89 Å, $H \dots O_A$ between 1.75–1.93 Å and $O_D-H \dots O_A$ between 157.4 and 176.1° at 280 K (Table 5). The $O5-H8$ group shows a bifurcated H-bonding scheme, with $O12_w$ and $O13_w$ as acceptors (with $O5 \dots O_A$ between 3.30 and 3.37 Å, $H8 \dots O_A$ 2.58–2.79 Å, $O5-H8 \dots O_A$ 120.4 – 133.5° , at 280 K, Table 5). There is no significant variation of the bonding scenario of the OH-group at 10 K (Table 5), if compared to that at 280 K.

On the whole, all the H-bonds, in which OH_2 molecules or OH-groups are involved, are relatively strong, excluding the $H10-O12_w-H15$ molecule and the $O5-H8$ group that show relatively weak H-bonds. Interestingly, there is no evidence of *intra* $Mg(H_2O)_4B_3O_3(OH)_5$ cluster H-bonding: all the H-bonds here observed are *inter* $Mg(H_2O)_4B_3O_3(OH)_5$ clusters.

A careful analysis of the structural data obtained in this study reveals a substantial consistency with the previous structural model obtained by DFT calculations by Zhou et al. (2012). More specifically, the *ab initio* DFT calculations were performed using Full Potential Linear Augmented Plane Wave (FP LAPW) with the WIEN2k software package, in combination with high-resolution solid-state ^{11}B and ^{25}Mg MAS NMR spectroscopy, permitting the location even of the hydrogen positions at their 15 crystallographically-independent sites. The atomic coordinates of all the independent crystallographic sites have been provided by Zhou et al. (2012), but not all the O–H bond distances. However,

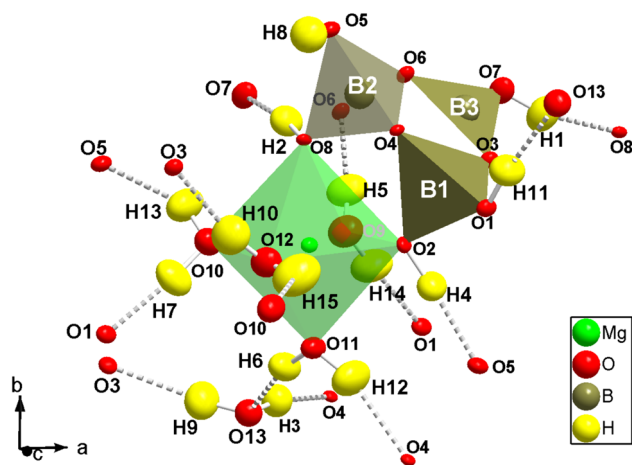


Fig. 2 The complex and pervasive H-bonding network in inderite structure, based on the neutron structure refinement of this study (at 280 K). Displacement ellipsoid probability factor: 80%

a general comparative analysis can be done, and the most important results are given in Table 6, in which the average bond distances of coordination polyhedra and $O-H$ distances are listed, based on the DFT modelling and on the experimental data obtained in this study. It is worth noting that the difference between DFT and experimental data (*e.g.*, ND at 280 K, Table 6), pertaining to the average bond distances of the Mg-octahedron, B1- and B2-tetrahedra and B3-planar unit, are all ≤ 0.01 Å. The scenario is only slightly worse if we consider that $O-H$ distances: the maximum difference between the theoretical vs. experimental $O-H$ distances pertaining to the hydroxyl groups is ≤ 0.08 Å, to the H_2O molecules (including even the zeolitic $H3-O13_w-H9$ molecule) is ≤ 0.07 Å (Table 6). Overall, the theoretical structural model appears to be highly consistent with the experimental one.

The crystal structure of inderite and its dimorph kurnakovite are significantly different. In kurnakovite, the same building units observed in inderite structure (*i.e.*, $B_3O_3(OH)_5$ ring + Mg-octahedron $Mg(OH)_2(OH)_4$) form $Mg(H_2O)_4B_3O_3(OH)_5$ clusters, but with a different bonding topology: clusters are connected to give (neutral) $\cdots[Mg(H_2O)_4B_3O_3(OH)_5]\cdots$ chains parallel to [001]. Such chains are mutually bonded to give the tri-dimensional structure only via H-bonds, even mediated by the extra-chains zeolitic H_2O molecules (as also observed in inderite). In response

to the different bonding topology, in kurnakovite structure there are even *intra* $\cdots[Mg(H_2O)_4B_3O_3(OH)_5]\cdots$ chain H-bonds; in contrast, as already reported above, in inderite only *inter* $Mg(H_2O)_4B_3O_3(OH)_5$ clusters H-bonds occur.

The H-bonding scheme obtained in this study can be considered as consistent with the IR and Raman spectra of inderite reported by Li et al. (1995), Klopogge and Frost (1999), Frost et al. (2013), and Chukanov (2014), in particular referred to the $O-H$ stretching region. Frost et al. (2013) reported a series of distinct Raman bands at 3052, 3233, 3330, and 3392 cm^{-1} , attributed to $H-O_w-H$ stretching vibrations, and at 3459, 3530 and 3562 cm^{-1} , assigned to hydroxyl $O-H$ stretching vibrations. However, some broader bands likely reflect the convolution of more independent active modes. Even the IR spectra show a series of signals ascribable to the $O-H$ stretching region of $H-O_w-H$ and $O-H$ groups (at least at 3625, 3580, 3470, 3435, 3360, 3260, 3060, 2940 cm^{-1}), with systematic convolutions. Such complex Raman and IR spectra reflects the occurrence of a series of independent $O-H$ stretching bonds, ascribable to hydroxyl groups or H_2O molecules, consistently with the complex and pervasive H-bonding network observed on the basis on the neutron structure refinements of this study. The almost superimposed Raman or IR signals are the effect of similar geometric configurations of a series of independent H-bonds, as observed in this study in terms of $O_D\cdots O_A$ and $H\cdots O_A$ distances (Table 5).

We have recently investigated the high-pressure behavior of inderite by *in-situ* single-crystal synchrotron X-ray diffraction up to 17 GPa (Comboni et al. 2023), to explore its stability field at high-pressure, the anisotropy of its compressional pattern and the deformation mechanisms at the atomic scale. We observed that inderite experiences a first-order phase transition (from $P2_1/c$ to $P2_1/n$, with $a = 13.4308(7)$, $b = 11.9970(5)$, $c = 10.4466(8)$ Å, and $\beta = 100.030(6)^\circ$), between 6.45(5) and 6.94(5) GPa. Such a pressure-mediated transition is reconstructive in character, and perfectly elastic. The structure of the high-pressure polymorph (called “inderite-II”) was successfully solved and refined. In response to the phase transition, the *B*-site with a triangular coordination changes its coordination configuration from planar-triangular to tetrahedral, bonding the zeolitic H_2O . As a consequence, if the crystal structure of inderite can be described as a repetition of isolated $Mg(H_2O)_4B_3O_3(OH)_5$ clusters, in inderite-II the newly formed *B*-tetrahedra connect two of these clusters, thus forming complex cluster units made by 2 *Mg*-octahedra and 6 *B*-tetrahedra, with $Mg_2(H_2O)_8B_6O_6(OH)_{10}(H_2O)$ stoichiometry. The $Mg_2(H_2O)_8B_6O_6(OH)_{10}(H_2O)$ units are mutually connected by a complex net of H-bonds to form the crystalline edifice of the high-pressure polymorph. The effects of low temperature observed in this study, in terms of structural deformation at the atomic scale, are almost incomparable with those

Table 6 Comparison of the bond distances (Å) obtained by DFT calculations (Zhou et al. 2012) and in this study (ND: neutron diffraction, Table 5) (*distances corrected for riding motion effect; $\langle \rangle$ indicates the average bond distances of a given polyhedron; n.p.: not provided)

	DFT	ND (280 K)		ND (10 K)	
$\langle Mg1-O \rangle$	2.0864	2.088		2.087	
$\langle B1-O \rangle$	1.4787	1.481		1.482	
$\langle B2-O \rangle$	1.4706	1.479		1.477	
$\langle B3-O \rangle$	1.3722	1.373		1.379	
$O1-H11$	0.9003	0.966 (15)	0.984*	0.961 (12)	0.976*
$O2-H4$	0.9160	0.982 (14)	0.995*	0.976 (11)	0.999*
$O5-H8$	0.8962	0.944 (14)	0.966*	0.955 (14)	0.970*
$O7-H1$	0.9074	0.953 (14)	0.967*	0.961 (10)	0.976*
$O8-H2$	n.p.	0.977 (13)	0.994*	0.997 (10)	1.009*
$O9_w-H5$	n.p.	0.951 (17)	0.957*	0.968 (13)	0.982*
$O9_w-H14$	0.9016	0.962 (17)	0.972*	0.980 (12)	0.995*
$O10_w-H7$	0.9157	0.978 (16)	0.989*	0.990 (11)	1.004*
$O10_w-H13$	0.9556	0.949 (17)	0.963*	0.985 (13)	0.999*
$O11_w-H6$	n.p.	0.977 (14)	0.989*	0.979 (11)	0.994*
$O11_w-H12$	n.p.	0.945 (16)	0.970*	0.980 (13)	0.995*
$O12_w-H10$	n.p.	0.967 (16)	0.980*	0.968 (13)	0.983*
$O12_w-H15$	0.9045	0.93 (2)	0.960*	0.983 (12)	0.998*
$O13_w-H3$	0.9277	0.992 (13)	0.998*	0.980 (12)	0.995*
$O13_w-H9$	0.9146	0.955 (16)	0.970*	0.981 (12)	0.996*

observed at high pressure, as the unit-cell volume at 10 K corresponds to that estimated at 0.1–0.2 GPa, and the first structural refinement at high pressure was performed on the basis of the data collected at 0.46(5) GPa.

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Declarations

Competing interests The authors declare no competing interests.

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