

A multi-methodological study of kernite, a mineral commodity of boron

G. DIEGO GATTA^{1,*}, ALESSANDRO GUASTONI², PAOLO LOTTI¹, GIORGIO GUASTELLA³, OSCAR FABELO⁴,
AND MARIA TERESA FERNANDEZ-DIAZ⁴

¹Dipartimento di Scienze della Terra, Università degli Studi di Milano, Via Botticelli 23, I-20133 Milano, Italy

²Dipartimento di Geoscienze, Università degli Studi di Padova, Via G. Gradenigo 6, I-35131, Padova, Italy

³Agenzia delle Dogane e dei Monopoli, Direzione Regionale per la Lombardia, Ufficio Antifrode-Sezione Laboratorio, Via Marco Bruto 14, I-20138 Milan, Italy

⁴Institut Laue-Langevin, 71 Avenue des Martyrs, F-38000 Grenoble, France

ABSTRACT

Kernite, ideally $\text{Na}_2\text{B}_4\text{O}_6(\text{OH})_2 \cdot 3\text{H}_2\text{O}$, is a major constituent of borate deposits and one of the most important mineral commodities of B. The chemical composition and crystal structure of kernite from the Kramer Deposit (Kern County, California) were investigated by a suite of analytical techniques (i.e., titrimetric determination of B content, gravimetric method for Na, ion selective electrode for F, high- T mass loss for H_2O content, inductively coupled plasma atomic emission spectroscopy for REE and other minor elements, elemental analysis for C, N, and H contents) and single-crystal X-ray (at 293 K) and neutron (at 20 K) diffraction. The concentrations of more than 50 elements were measured. The general experimental formula of the kernite sample used in this study is $\text{Na}_{1.99}\text{B}_{3.99}\text{O}_6(\text{OH})_2 \cdot 3.01\text{H}_2\text{O}$. The fraction of other elements is, overall, insignificant: excluding B, kernite from the Kramer Deposit does not act as geochemical trap of other technologically relevant elements (e.g., Li, Be, or REE). The X-ray and neutron structure model obtained in this study confirms that the structure of kernite is built up by: two (crystallographically independent) triangular BO_2OH groups and two tetrahedral BO_4 groups, which share corner-bridging O atoms to form threefold rings, giving chains running along $[010]$, and $\text{NaO}_4(\text{OH})(\text{OH}_2)$ and $\text{NaO}_2(\text{OH})(\text{OH}_2)_3$ polyhedra. Positional disorder of two H sites of H_2O molecules was observed by the neutron structure refinement and corroborated by the maximum-entropy method calculation, which consistently provided a model based on a static disorder, rather than a dynamic one. The H-bonding network in the structure of kernite is complex, pervasive, and plays a primary role on its structural stability: the majority of the oxygen sites are involved in H-bonding, as *donors* or as *acceptors*. The potential utilizations of kernite, as a source of B ($\text{B}_2\text{O}_3 \sim 50$ wt%), are discussed, on the basis of the experimental findings of this study.

Keywords: Kernite, borates, mineral commodity, X-ray diffraction, neutron diffraction, crystal chemistry, hydrogen bonding

INTRODUCTION

Kernite is a hydrous borate with ideal chemical formula $\text{Na}_2\text{B}_4\text{O}_6(\text{OH})_2 \cdot 3\text{H}_2\text{O}$. It is a constituent of sedimentary borate deposits of which the more common minerals are borax (ideally $\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 8\text{H}_2\text{O}$), ulexite (ideally $\text{NaCa}[\text{B}_3\text{O}_6(\text{OH})_6] \cdot 5\text{H}_2\text{O}$), colemanite (ideally $\text{Ca}[\text{B}_3\text{O}_4(\text{OH})_3] \cdot \text{H}_2\text{O}$), kernite, and tincalconite (ideally $\text{Na}_6[\text{B}_4\text{O}_5(\text{OH})_4]_3 \cdot 8\text{H}_2\text{O}$). Ulexite, colemanite, kernite, and tincalconite account for more than 90% of the borate minerals used by industry worldwide (USGS 2019).

There is a rising interest in light elements, in particular Li, B, and Be, as they are technologically and industrially relevant, and are considered as “critical elements” (or “critical raw materials,” according to the European Commission 2017), on the basis of their high economic importance and high supply risk. Natural borates represent the most important source of boron. In 1998, the world production on borates accounted for about 3.1 millions of tons;

in 2009 the production increased to 4.5 Mtons and in 2017 to 9.8 Mtons (USGS 2018, and previous reports). Only a few mineral commodities (and among those is Li) experienced such a trend of production and consumption over the last decades. The principal reason of this raise is ascribed to the fact that boron is a strategic element for a series of technologically relevant processes and products, e.g., heat-resistant glasses and ceramics, boron-treated low-alloy steels (in which B is used to influence the hardenability and the behavior of the alloys at high temperature), radiation-shielding materials (due to the elevated ability of ^{10}B to absorb thermal neutrons), as a critical micronutrient to the growth and health of plants or as an insecticide, and as an effective photothermocatalyst for the conversion of carbon dioxide. Among the aforementioned utilizations, one is referred to radiation emitted by nuclear reactors for energy production, scientific research activities or medical applications (i.e., boron neutron capture therapy = BNCT), and it is the only one in which the isotopic signature of B plays an important role: ^{10}B shows a high capacity to absorb thermal neutrons due to its high cross section for the $^{10}\text{B}(\text{n},\alpha)^7\text{Li}$ reaction (~ 3840 barns;

* E-mail: diego.gatta@unimi.it. ORCID 0000-0001-8348-7181.

Carter et al. 1953; Sears 1986; Palmer and Swihart 1996; Rauch and Waschkowski 2002), whereas that of ^{11}B is almost irrelevant (~ 0.006 barns). About 20% of natural boron occurs as ^{10}B .

In the framework of a long-term project to identify potential B-bearing aggregates, we have recently investigated the crystal chemistry and phase stability of colemanite (Lotti et al. 2017, 2018, 2019) and kurnakovite (ideally $\text{Mg}[\text{B}_3\text{O}_3(\text{OH})_3] \cdot 5\text{H}_2\text{O}$, Gatta et al. 2019a) at non-ambient conditions (high and low temperature, high pressure) using a multi-methodological approach. We now extend our crystal-chemical investigation to kernite, considering its availability in nature and the high B_2O_3 content (~ 48 wt%); this study is accompanied by experiments on its P - T behavior and chemical stability (Comboni et al. 2020).

Only a few studies were dedicated to kernite. The first important description of this mineral is ascribed to Schaller (1927), who provided optical parameters and a chemical wet analysis. Its crystal structure was first reported by Amoros (1945) using X-ray diffraction techniques, and later reinvestigated by Giese (1966), Cialdi et al. (1967), and Cooper et al. (1973). The X-ray structure refinement of Cooper et al. (1973) is the last one reported in the open literature. Kernite crystallizes in the monoclinic $P2_1/c$ space group, with $a \cong 7.02$ Å, $b \cong 9.15$ Å, $c \cong 15.68$ Å, and $\beta \cong 108.9^\circ$ ($Z = 4$). As observed in other borates (e.g., colemanite, kurnakovite), even kernite contains both triangular planar BO_2OH - and tetrahedral BO_4 -groups (Fig. 1). Two independent Na sites are sixfold-coordinated by O atoms, OH-groups and H_2O molecules. One triangular BO_2OH group and two tetrahedral BO_4 groups share corner-bridging O atoms to form threefold rings ($3\text{B}:\Delta+2\text{T}$ or $3\text{B}:\langle\Delta 2\Box\rangle$, according to the Heller 1986 and Grice et al. 1999 notation), giving chains running along $[010]$ and held together by hydrogen bonding (Fig. 1). FTIR and Raman spectra of kernite were reported and interpreted by Jun et al. (1995) and Klopogge and Frost (1999), and its high-pressure behavior was later described by Silva et al. (2018) on the basis of in situ IR and Raman spectra evolution collected in a diamond-anvil cell. Even the T -induced dehydration behavior (under vacuum and in air) of a natural kernite was reported by Sennova et al. (2005), on the basis of thermo-gravimetric analysis and X-ray powder diffraction data. However, no structural data (at room or non-ambient conditions) were reported in the studies of Jun et al. (1995), Klopogge and Frost (1999), Sennova et al. (2005), and Silva et al. (2018).

Despite the general structure model reported by Cooper et al. (1973) appears to be consistent with other studies (in terms of bond distances and angles), their structure refinement provides only a partial view of the H-bonding configuration, due to the limitation of the X-ray diffraction at that time. For example, some of the H sites were described with isotropic displacement parameters up to six times larger (in Å²) than others, which could reflect a positional (static or dynamic) disorder. The occurrence of hydroxyl groups and cation-coordinated H_2O , which account for a total H_2O content of about 26 wt%, generates the need for a structure model with an accurate location of the H-sites. In addition, the very few chemical analyses of kernite available in the literature reported only the major constituents, and are based on analytical protocols of the last century (Schaller 1927; Cipriani 1958; Hurlbut et al. 1973).

The aim of the present study is a reinvestigation of the crystal chemistry of kernite from the Kramer Deposit (California), by single-crystal X-ray (at room temperature) and neutron diffraction

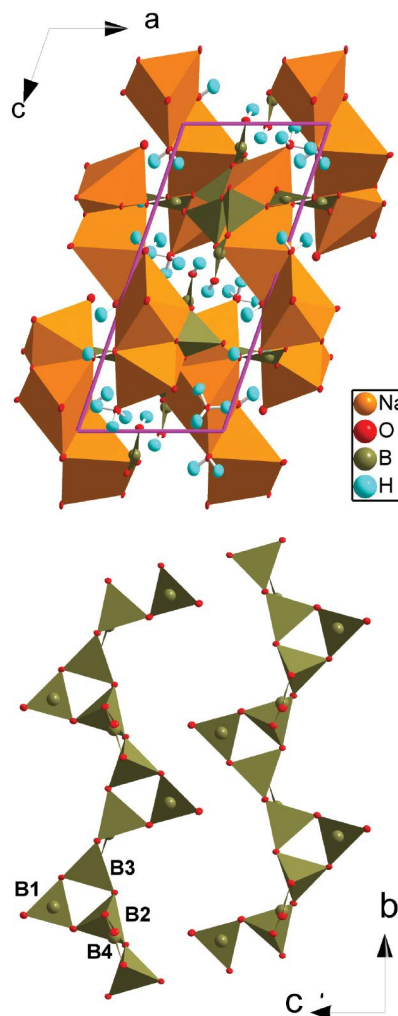


FIGURE 1. The crystal structure of kernite viewed down $[010]$ (**top**), along with the infinite chains of threefold rings ($3\text{B}:\Delta+2\text{T}$ units) running along $[010]$ (**bottom**), based on the neutron structure refinement (data collected at 20 K). Displacement ellipsoid probability factor is 70%. (Color online.)

(at 20 K) along with a series of other analytical techniques aimed to fully characterize the chemical composition of the sample [i.e., titrimetric determination of B content, gravimetric method for Na, ion selective electrode for F, high- T mass loss for H_2O content, inductively coupled plasma atomic emission spectroscopy (ICP-AES) for REE and other minor elements, elemental analysis for C, N, and H content]. With this multi-methodological approach, we provided: a description of the chemical composition of kernite in terms of major and minor components, with a particular attention to the potential B- and Na-substituents; an unambiguous location of all the proton sites and their vibrational regime, along with a picture of the complex H-bonding network; a description of B-coordination environment [e.g., aplanarity of the triangular $\text{BO}_2(\text{OH})$ -group, polyhedral distortion of the tetrahedral $\text{BO}_2(\text{OH})_2$ -groups].

The experimental findings of this study will be pivotal to fully understand if kernite can act as a carrier of other technologically relevant elements (e.g., Li, Be, REE), its conditions of formation and occurrence, its behavior at non-ambient P - T conditions and

the chemical reactivity, as its structural stability appears to be substantially governed by the H-bonding network.

SAMPLE DESCRIPTION AND OCCURRENCE

The kernite sample used in this study belongs to the collection of the Museum of Mineralogy of the University of Padova, Italy. The hand specimen is a colorless to white, glassy fragment of a large centimetric crystal elongated parallel to the *c* axis and bounded by alternating cleavage faces, nearly perfect, of the basal pinacoid *c* {001} and the prism *a* {100}.

The specimen was collected at the Kramer Deposit, Mohave desert, Kern County, California. Over 80 minerals were reported occurring in this deposit including several borates: borax, colemanite, greigite, hydroboracite, indierite, inyoite, kernite, kurnakovite, meyerhofferite, probertite, searlesite, tincalconite, tunellite, and ulexite (Noble 1926; Schaller 1930; Morgan and Erd 1969; Puffer 1975).

The Kramer deposit consists of a lenticular mass of kernite and borax with lower fractions of colemanite and ulexite, measuring 1.6 km long, 0.8 km wide, and up to 100 m thick. The borate minerals, several hundred feet underground, occur in a complex clay series, underlain by igneous rocks composed of basaltic lavas, upper Miocene in age and overlain by a stratigraphic series of continental arkosic sands (Obert and Long 1962; Siefke 1991). For tens of meter deep, kernite is the only borate observed in the deposit and is the dominant mineral, while the clay matrix is almost negligible in amount (Schaller 1930). The mode of occurrence shows the deposit was originally composed only of borax at the floor of a saline lake. The kernite abundance increases with depth, indicating that dehydration of borax increases as a result of depth and pressure. Borax dehydration to kernite occurs under natural conditions. When borax is exposed to open air, it alters to tincalconite, while kernite alteration to tincalconite occurs only partially and very slowly. The abundance of kernite in the lower part of the Kramer deposit suggests the temperature-pressure (depth) conditions from the borax-to-kernite reaction are in the range 50–60 °C and about 750 m deep (Christ and Garrels 1959).

EXPERIMENTAL METHODS AND RESULTS

Titrimetric determination of the boron content

80–100 mg of the kernite sample were placed in a 50 mL plastic test tube, along with 5 mL of water and 3 mL of 1 M hydrochloric acid. The tube was covered and transferred to an ultrasound bath for 1–2 h. The resulted clear solution was transferred to a 300 mL beaker, with water up to about 100 mL of the total solution. A combined glass electrode (produced by InLab Routine Pro, Mettler Toledo) was immersed in the solution, and the pH was adjusted to 5.5–6.5 with solutions of 0.1–1 M HCl and 0.1–1 M NaOH. Then, 5–6 g of mannitol was added and stirred, until its complete dissolution. The solution was then titrated with 0.1 M NaOH up to 8.3–8.7 pH. The content of acid titrated was completely due to the presence of boric acid in solution, as the sample does not contain elements capable to hydrolyze the medium, or in general influence its acidity. The measured fraction of B₂O₃ was 50.9(2) wt%.

Gravimetric determination of the sodium content

500–600 mg of the kernite sample were placed in a weighed platinum crucible (m₁), acidified with 20 mL of hydrochloric acid 1:1 and evaporated to dryness. Residue was treated with 25 mL of methyl alcohol and 10 mL of concentrated hydrochloric acid, and evaporated to dryness. The latter operation was repeated 4–5 times. Residue, in absence of other elements at a significant level (see other analyses) is pure NaCl. Platinum crucible was dried in an oven at 110–130 °C for 1–2 h, cooled in a desiccator and weighed (m₂). The different of weigh (m₂ – m₁) is the Na content in the mineral, expressed as NaCl. The measured fraction of Na₂O was 22.6(2) wt%.

Determination of fluorine content

20 mg of the kernite sample were placed in a 50 mL plastic test tube, along with 5 mL of water and 3 mL of 1 M hydrochloric acid. The tube was covered and transferred to an ultrasound bath for 1–2 h. A volume of 2–3 mL of Total Ionic Strength Adjustment Buffer (Commercial solution TISAB III) was added to the clear solution and diluted to 20 mL with water. The F content was then determined using the perfectION Combination Fluoride Ion Selective Electrode (Mettler Toledo), adopting the conventional method of standard addition. Solutions of fluorine from 0.1 to 5.0 mg/L were prepared by Certified Reference Material (CRM) 1000 mg/L of fluorine. The resulting F fraction was 0.01 wt% (uncertainty not determined).

Determination of H₂O content

500–600 mg of the kernite sample were placed in a quartz crucible with lid, gradually heated in a muffle furnace from 20 to 800 °C with a constant rate of 4–5 °C min⁻¹, and then kept for 60 min at 800 °C. Assuming that the mass loss represents the total amount of H₂O, the estimated H₂O fraction of the sample was 26.4(2) wt%.

Determination of minor elements by inductively coupled plasma atomic emission spectroscopy (ICP-AES)

All measurements were performed in axial view mode for REE, and radial view mode for other minor elements, with a Perkin Elmer Optima 7000DV ICP-AES spectrometer.

Determination of REE concentrations by ICP-AES. We placed 50 mg of the kernite sample in a 50 mL plastic test tube, along with 5 mL of water and 3 mL of 1 M hydrochloric acid. The tube was covered and transferred to an ultrasound bath for 1–2 h. The resulting clear solution was then transferred to a 50 mL volumetric flask and diluted with water. A calibration protocol was performed with a blank solution and a series of solutions prepared with: similar fractions of sodium and boron as those of the sample under investigation and REE concentrations from 0.001 to 0.050 mg/L for each element (using CRM multi elemental standard mix for ICP). Results and instrumental parameters are listed in Table 1.

Determination of other minor element concentrations by ICP-AES. The determination of the non-REE minor elements was performed using two different protocols:

(1) 10–20 mg of the kernite sample were placed in a 50 mL plastic test tube, along with 5 mL of water and 3 mL of 1 M hydrochloric acid. The tube was covered and transferred to an ultrasound bath for 1–2 h. The resulted clear solution was then transferred and diluted with water in a 25 mL volumetric flask, containing 2.5 mL of scandium solution (100 mg/L) as the internal standard. A calibration protocol was adopted with a blank solution and 5 solutions with concentrations between 0.05 and 1.0 mg/L for each element (using CRM multi elemental standard mix for ICP).

(2) Decomposition by alkaline fusion of 10–20 mg of the kernite sample was achieved in a platinum crucible with 100 mg of sodium or potassium carbonate in a muffle furnace at 1000 °C for 5 min, followed by dissolution in 10 mL of water and 1 mL of 1 M sulfuric acid or 1 mL of 1 M hydrochloric acid. The clear solution was then transferred and diluted with water in a 25 mL volumetric flask containing 2.5 mL of scandium solution (100 mg/L) as the internal standard. A calibration protocol was adopted with a blank solution and 5 solutions with concentrations between 0.05 and 1.0 mg/L for each element (using CRM multi elemental standard mix for ICP). Results and instrumental parameters are given in Table 2.

TABLE 1. REE concentration by ICP-AES (see text for details)

	%m/m	ICP-AES (nm)	LOD	LOQ
Ce ₂ O ₃	<LOD	413.764	0.003	0.01
Dy ₂ O ₃	<LOD	353.170	0.0001	0.0003
Er ₂ O ₃	<LOD	369.265	0.002	0.007
Eu ₂ O ₃	<LOD	381.967	0.0001	0.0003
Gd ₂ O ₃	<LOD	342.247	0.0003	0.001
Ho ₂ O ₃	<LOD	345.600	0.0001	0.0003
La ₂ O ₃	<LOD	398.852	0.0001	0.0003
Lu ₂ O ₃	<LOD	261.542	0.0002	0.0006
Nd ₂ O ₃	<LOD	406.109	0.0002	0.0006
Pr ₂ O ₃	<LOD	390.844	0.0002	0.0006
Sm ₂ O ₃	<LOD	359.260	0.0005	0.002
Sc ₂ O ₃	<LOD	361.383	0.0005	0.002
Tb ₂ O ₃	<LOD	350.917	0.0005	0.002
Tm ₂ O ₃	<LOD	313.126	0.004	0.015
Yb ₂ O ₃	<LOD	328.937	0.0001	0.0003
Y ₂ O ₃	<LOD	371.029	0.0001	0.0003
ThO ₂	<LOD	283.730	0.001	0.004
UO ₂	<LOD	385.958	0.01	0.04

Note: LOD = Limit of detection (3σ); LOQ = Limit of quantification (10σ).

Determination of C, N, and H contents

200–300 mg of the kernite sample were decomposed at 950 °C in an elementary analyzer LECO Truspec CHN, in excess of oxygen for 90 s. The decomposition products were transferred to a second furnace (Afterburner) at 850 °C for further oxidation and particulate removal. After collection and homogenization of the gases in a container of 4.5 L at 50 °C, Infrared absorption detectors were used to measure the CO₂ and H₂O concentrations (as the C concentration was measured in the form of CO₂ and the H one in the form of H₂O). A different portion of the decomposition products was instead transferred in a stream of helium through a copper catalyst to convert NO_x to N₂ and to remove oxygen, carbon dioxide and water. A thermal conductivity detector was used to determine the N₂ content. EDTA, sodium tetra-borate deca-hydrate, boric acid, calcium carbonate, sodium nitrate, and acid oxalic di-hydrate were employed as the calibration standards. The measured fractions were: C < 0.02 wt% (uncertainty not determined), N < 0.02 wt% (uncertainty not determined), and H = 3.0(2) wt%.

A representative chemical composition of kernite from the Kramer deposit is given in Table 3, and its chemical formula is virtually identical to the ideal one: Na₂B₄O₆(OH)₂·3H₂O.

Single-crystal X-ray and neutron diffraction

X-ray and neutron data collection and analysis. Single-crystal X-ray diffraction data were collected at room temperature with a Rigaku XtaLABSynergy-i diffractometer, equipped with a PhotonJet-i MoK α microfocus source and a HyPix-6000HE Hybrid Photon Counting (HPC) detector, at the Earth Science Department, University of Milan. To maximize the reciprocal space coverage and the quality of the intensity data, a series of collection runs were optimized using the ad hoc routine of the CrysAlisPro suite (Rigaku, Oxford Diffraction 2019), with the ω scan strategy, step size of 0.5°, and an exposure time per frame of 2 s. A total number of 13 010 reflections up to 2 $\theta_{\max}$ of 60° was collected (with $-9 \leq h \leq +8$, $-12 \leq k \leq +12$, and $-19 \leq l \leq +20$), out of which 2296 were unique ($R_{\text{int}} = 0.0361$, Laue class 2/m) and 1908 with $F_o > 4\sigma(F_o)$, giving a metrically monoclinic unit cell with $a = 6.9983(3)$, $b = 9.1375(3)$, $c = 15.6389(7)$ Å, $\beta = 108.832(5)^\circ$, and $V = 946.53(7)$ Å³ (Supplemental¹ Table S1). Corrections for Lorentz-polarization effects and (semi-empirical) X-ray absorption were applied using the ABSPACK routine, implemented in the CrysAlisPro package (Rigaku, Oxford Diffraction 2019). The systematic extinctions were consistent with the space group $P2_1/c$. X-ray intensity data were then processed with the E-STATISTICS program, implemented in the WinGX package (Farrugia 1999): the statistics of distributions of the normalized structure factors showed that the structure is centrosymmetric at ~93% likelihood (the Sheldrick's $|E^2 - 1|$ criterion is 0.969).

Single-crystal neutron diffraction data were collected at low temperature from a crystal of kernite (approx. $3 \times 2 \times 2$ mm³) on the four-circle diffractometer D9 at the Institut Laue-Langevin (ILL), Grenoble (Gatta et al. 2019b). The crystal was glued on a vanadium pin and placed on a close-circuit displacer device operated at 20.0(5) K (Archer and Lehmann 1986). The wavelength of 0.8347 Å, obtained from a Cu(220) monochromator, and a small two-dimensional area detector were used. The measurement strategy consisted of a series of ω -scans and ω -2 θ scans for low and high-Q reflections, respectively. The Bragg reflections were collected with varying the ω -range as a function of the instrument resolution curve. A total number of 3434 reflections were collected (with $-10 \leq h \leq +10$, $0 \leq k \leq +18$, and $-23 \leq l \leq +24$), out of which 3161 were unique ($R_{\text{int}} = 0.0488$, Laue class 2/m) and 2656 with $F_o > 4\sigma(F_o)$, with $d_{\text{min}} = 0.59$ Å (Supplemental¹ Table S1). Intensity integration, background, and

Lorentz factor correction of the scans were done with the Racer program (written by Clive Wilkinson and Garry McIntyre, ILL integration program suite, <https://forge.ill.fr/projects/xtalsoft/repository/show/racer>). The unit cell was found to be metrically monoclinic (Supplemental¹ Table S1), and consistent with the X-ray results reported above. Absorption correction was applied, based on composition and shape of the crystal using the ILL program Datap (the current version of this program is available online on <https://forge.ill.fr/>). The reflection conditions were found to be consistent with the space group $P2_1/c$. The Wilson plot and the statistics of distributions of the normalized structure factors showed that the structure is centrosymmetric at ~91% likelihood (the Sheldrick's $|E^2 - 1|$ criterion is 0.958).

Further details pertaining to the X-ray and neutron data collection strategies are listed in Supplemental¹ Table S1.

X-ray and neutron structure refinements. Anisotropic crystal-structure refinements, based on the X-ray and neutron intensity data, collected at room and low T , respectively, were conducted in the space group $P2_1/c$ using the SHELXL-97 software (Sheldrick 1997, 2008), and starting from the structure model of Cooper et al. (1973), without any H atom. Neutral X-ray scattering factors of Na, B, O, and H were taken from the *International Tables for X-ray Crystallography* (vol. C) and used for the X-ray refinement, whereas neutron scattering lengths of Na, B, O, and H were taken from Sears (1986). Secondary isotropic extinction effect was corrected according to the formalism of Larson (1967).

For both refinements (i.e., X-ray at 293 K and neutron at 20 K), convergence was rapidly achieved after the first cycles, with a series of residual peaks in the final difference-Fourier map of the electron or nuclear density (positive for the X-ray refinement, negative for the neutron refinement). The complex configuration of the H population was first modeled on the basis of the neutron data, and then implemented in the X-ray refinement. The negative residual peaks found in the difference-Fourier map of the nuclear density were assigned to the H sites in the next cycles (i.e., H has a negative neutron scattering length). Shape and magnitude of the minima in the difference-Fourier maps showed no evidence of positional or dynamic disorder for six of the H sites (i.e., H1-H6, Supplemental¹ Table S2). However, evidence of disorder was observed for the H population bonded to the (opposite) O8 and O11 sites, which are vertices of the Na1 and Na2 polyhedra, respectively (Fig. 2, Supplemental¹ Table S2). After a series of tests, the best figures of merit were obtained with three H sites bonded to O8 [i.e., H6, H72, and H82, with site occupancy factor $s.o.f.(H6) = 1$ and $s.o.f.(H72) + s.o.f.(H82) = 1$] and three bonded to O11 [i.e., H1, H71, and H81, with $s.o.f.(H1) = 1$ and $s.o.f.(H71) + s.o.f.(H81) = 1$], with the following mutually exclusive configurations: (H6-O8-H82 + H1-O11-H71) and (H6-O8-H72 + H1-O11-H81) (Fig. 2, Supplemental¹ Table S2). With such a structure model, convergence was achieved and the variance-covariance matrix showed no significant correlation among the refined variables; all the principal mean-square atomic displacement parameters were positive (including those for the H sites, Supplemental¹ Table S3) and the final $R_1(F) = 0.0723$, for 2656obs./226par. (Supplemental¹ Table S1).

Implementing the structure model from the neutron refinement, convergence of

TABLE 2. Concentration of other minor elements by ICP-AES (see text for details)

	%m/m	ICP-AES (nm)		%m/m	ICP-AES (nm)
Li ₂ O	<0.01	670.784	NiO	<0.01	231.604
MgO	0.01	285.213	CuO	<0.01	327.393
K ₂ O	0.02	766.490	Ag ₂ O	<0.01	328.068
Rb ₂ O	<0.02	780.023	ZnO	<0.01	206.200
Cs ₂ O	<0.02	455.531	CdO	<0.01	228.802
BeO	<0.01	313.107	Al ₂ O ₃	0.01	396.153
CaO	<0.01	317.933	Ti ₂ O	<0.02	190.801
BaO	<0.02	233.527	PbO	<0.05	220.353
TiO ₂	<0.01	334.940	P ₂ O ₅	<0.02	213.617
ZrO ₂	<0.01	343.823	As ₂ O ₃	<0.02	193.696
V ₂ O ₅	<0.02	292.464	Sb ₂ O ₃	<0.02	206.836
Cr ₂ O ₃	<0.01	267.716	Bi ₂ O ₃	<0.02	223.061
MoO ₃	<0.02	202.031	SiO ₂	0.01	251.611
MnO	<0.01	257.610	SrO	<0.01	407.771
Fe ₂ O ₃	<0.01	238.204	B ₂ O ₃	^a	249.677
CoO	<0.01	228.616	Na ₂ O	^a	589.592

^a Data were not reproducible and therefore discarded.

TABLE 3. Representative chemical composition of kernite from Kramer Deposit (Kern County, California), and empirical formula recalculated on the basis of 11 anions

Oxides	wt%	e.s.d.
B ₂ O ₃	50.90	± 0.20
Na ₂ O	22.55	± 0.20
SiO ₂	0.01	± n.d.
Al ₂ O ₃	0.01	± n.d.
MgO	0.01	± n.d.
K ₂ O	0.02	± n.d.
F	0.01	± n.d.
H ₂ O	26.40	± 0.20
Total	99.91	
Elements	apfu	
B ³⁺	3.99	
Na ⁺	1.99	
Si ⁴⁺	<0.01	
Al ³⁺	<0.01	
Mg ²⁺	<0.01	
K ⁺	<0.01	
F ⁻	<0.01	
H ⁺	8.02	
Empirical formula:		
Na _{1.99} B _{3.99} O ₆ (OH) ₂ ·3.01H ₂ O		
Ideal formula:		
Na ₂ B ₄ O ₆ (OH) ₂ ·3H ₂ O		

the X-ray refinement was rapidly achieved, with no significant correlation among the refined variables. The final $R_1(F) = 0.0324$, for 1908obs./193par. (Supplemental Table S1).

Additional details of the structure refinements are given in Supplemental Table S1. Atomic coordinates and displacement parameters are listed in Supplemental Table S2 and S3, selected interatomic distances and angles are given in Table 4.

To corroborate (or deny) the structure model based on the neutron least-square refinement, with its disordered H-sites configuration, nuclear density distribution was also analyzed by the maximum-entropy method (MEM), using the program DYSNOMIA (Momma et al. 2013) and the graphical representation of nuclear density maps by VESTA (Momma and Izumi 2011). The nuclear density maps were obtained from the single-crystal neutron data collected at 20 K. 2435 unique reflections with $I/\sigma(I) > 3$ were used in the MEM calculation giving rise a final $R(F)$ and $wR(F)$ of 3.7 and 3.5%, respectively. A grid of $256 \times 256 \times 256$ voxels were used to obtain a detailed density map. Figure 3 shows a section of the nuclear density function corresponding to the (0.1, 0.5, 0.6) plane. This plane was selected as O8, O11, and symmetry-related H₂O molecules lay on it.

DISCUSSION AND IMPLICATIONS

Chemical and structural analyses of the kernite sample under investigation confirm the general formula previously reported in the literature: $\text{Na}_2\text{B}_4\text{O}_6(\text{OH})_2 \cdot 3\text{H}_2\text{O}$. The only potential substituents of Na⁺ here detected, distributed over the two independent Na1 and Na2 sites and giving distorted coordination polyhedra with CN = 6, are represented by Mg²⁺ and K⁺, but their sum is less than 0.01 apfu (Table 3). Similarly, the only potential substituents of B³⁺ (in tetrahedral coordination) are Si⁴⁺ and Al³⁺, but for less than 0.01 apfu (Tables 2 and 3). Even the F⁻ fraction, as potential OH-group substituent, is not significant (i.e., <0.01 apfu, Tables 2 and 3). The concentrations of other minor elements and of the REE are mostly minor (Tables 1 and 2). Overall, kernite does not show any significant isomorphic substitution, and thus cannot act as geochemical trap of technologically relevant elements (e.g., Li or REE). This finding can be compared with the results that we recently obtained on other borates: even in colemanite ($\text{Ca}[\text{B}_3\text{O}_4(\text{OH})_3] \cdot \text{H}_2\text{O}$, from the Bigadiç Mine, Balıkesir Province, Marmara Region, Turkey; Lotti et al. 2018, 2019) and in kurnakovite ($\text{Mg}[\text{B}_3\text{O}_3(\text{OH})_5] \cdot 5\text{H}_2\text{O}$, from

the Kramer Deposit, Mohave desert, Kern County, California; Gatta et al. 2019a) no significant isomorphic substituents were found, i.e., the experimentally determined formulas were virtually identical to the ideal ones. In this light, the surprising chemical purity observed for kernite in this study, and previously in colemanite and kurnakovite (for which a similar chemical analytical protocol was used; Gatta et al. 2019a; Lotti et al. 2018, 2019), appears not to be a peculiarity of the single species or of a given deposit, but it is a common feature of the hydrous borates that share the same geological environment: lacustrine deposits with hydrothermal activity. The reasons for such a high purity are still obscure: whereas it is more difficult to find a substituent of B (in CN 3 or 4), which generates a low chemical strain into the structure, Na could be efficiently replaced by alkaline or even earth-alkaline cations, if we consider the bonding configuration of the (distorted) Na-polyhedra in the kernite structure (Table 4). The same considerations, though referred to different cations, were previously done on colemanite and kurnakovite by Gatta et al. (2019a). However, the chemical composition of a given hydrothermal mineral is dictated by not only its crystal structure, but also the composition of the solution. In this light, a possible explanation is that crystal nucleation and growth could promote purification by iterated dissolution and recrystallization.

The structure model of kernite obtained in this study, based on X-ray and neutron diffraction data, is (partially) consistent with that previously reported by Cooper et al. (1973). The structure is built by two crystallographically independent triangular BO_2OH groups (with the B-ions in sp^2 electronic configuration) and two tetrahedral BO_4 groups (with the B-ions in sp^3 electronic configuration), which share corner-bridging O atoms to form threefold rings ($3\text{B}:\Delta+2\text{T}$ units), giving chains running along [010] and held together by hydrogen bonding (Fig. 1). Two independent Na sites are sixfold-coordinated by O atoms, OH-groups and H₂O molecules, though the bonding configuration of the strongly distorted Na2-polyhedron would suggest a CN = 5+1, as five Na2-O distances are shorter than 2.5 Å and one is about 3.1 Å (Table 4, room-*T* X-ray refinement).

The X-ray (data collected at 293 K) and neutron (data collected at 20 K) structure refinements consistently show the following.

(1) The triangular $[\text{BO}_2(\text{OH})]$ -groups have an almost ideal configuration, with $\Delta(\text{B1-O})_{\text{max}} \sim \Delta(\text{B4-O})_{\text{max}} \sim 0.02\text{--}0.03$ Å (i.e., the difference between the longest and the shortest bond distances), average O-B-O angles of 120° (ranging between $118.5\text{--}122.8^\circ$ for B1- and $115.3\text{--}124.4^\circ$ for B4-triangular groups), and aplanarity $<1^\circ$ (here defined as the average angle described by the plane on which the 3-oxygen sites lie and each of the three independent B-O_n vectors); the tetrahedral $[\text{BO}_4]$ -groups are only slightly distorted, with $\Delta(\text{B2-O})_{\text{max}} \sim \Delta(\text{B3-O})_{\text{max}} \sim 0.06$ Å; the $\text{Na1O}_4(\text{OH})(\text{OH}_2)$ polyhedron has $\Delta(\text{Na1-O})_{\text{max}} \sim 0.22$ Å and is less distorted than the $\text{Na2O}_2(\text{OH})(\text{OH}_2)_2$ one with $\Delta(\text{Na2-O})_{\text{max}} \sim 0.7$ Å. The B-O and Na-O distances are slightly different as a function of bonding configuration of the oxygen sites (i.e., oxygen of a OH- or OH₂-group or as a bridging site between polyhedra).

(2) Three crystallographically independent H₂O molecules occur in the structure of kernite (i.e., H3-O10-H5, H6-O8-H72 or H6-O8-H82, H1-O11-H71 or H1-O11-H81, Table 4). Among those, two are affected by positional disorder of the H sites, so that two mutually exclusive configurations occur, here modeled as: (H6-O8-H82 + H1-O11-H71) or (H6-O8-H72 + H1-O11-H81)

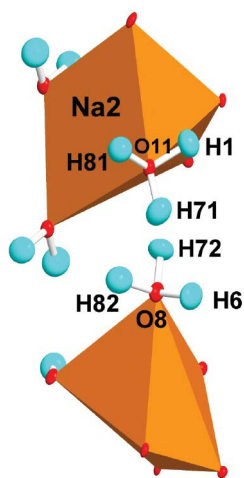


FIGURE 2. Positional disorder of H in the structure of kernite, based on the neutron structure refinement (data collected at 20 K). The mutually exclusive configurations are: (H6-O8-H82 + H1-O11-H71) and (H6-O8-H72 + H1-O11-H81). $s.o.f.(\text{H6}) = 1$, $s.o.f.(\text{H1}) = 1$, $[s.o.f.(\text{H72}) + s.o.f.(\text{H82})] = 1$, $[s.o.f.(\text{H71}) + s.o.f.(\text{H81})] = 1$. Displacement ellipsoid probability factor is 70%. (Color online.)

TABLE 4. Relevant bond distances (Å) and angles (°) based on the X-ray structure refinement at 293 K and neutron refinement at 20 K

X-ray $T = 293\text{ K}$						Neutron $T = 20\text{ K}$					
Na1-O8	2.2835(18)	O11-H1	0.94(2)	O8-H72	0.93(4)	Na1-O8	2.294(5)	O11-H1	0.988(4)	O8-H72	1.000(8)
Na1-O6	2.3879(17)	O11-H1 ^a	0.97	O8-H72 ^a	0.96	Na1-O6	2.377(2)	O11-H1 ^a	1.003	O8-H72 ^a	1.014
Na1-O4	2.3918(14)	O11...O2	2.669(2)	O8...O11	2.787(3)	Na1-O4	2.395(4)	O11...O2	2.663(3)	O8...O11	2.769(3)
Na1-O9	2.4095(15)	H1...O2	1.74(2)	H72...O11	1.93(4)	Na1-O9	2.393(2)	H1...O2	1.680(84)	H72...O11	1.800(9)
Na1-O2	2.4226(14)	O11-H1...O2	170(2)	O8-H72...O11	152(3)	Na1-O2	2.422(4)	O11-H1...O2	173.0(4)	O8-H72...O11	162.2(7)
Na1-O3	2.5058(15)					Na1-O3	2.493(3)				
		O11-H71	0.94(7)	O8-H82	0.94(4)			O11-H71	0.995(17)	O8-H82	1.038(13)
Na2-O11	2.2790(17)	O11-H71 ^a	0.97	O8-H82 ^a	0.97	Na2-O11	2.291(3)	O11-H71 ^a	1.012	O8-H82 ^a	1.051
Na2-O4	2.3880(15)	O11...O8	2.787(3)	O8...O11	2.814(3)	Na2-O4	2.382(3)	O11...O8	2.769(3)	O8...O11	2.796(3)
Na2-O10	2.4274(18)	H71...O8	1.86(6)	H82...O11	1.90(5)	Na2-O10	2.411(3)	H71...O8	1.792(17)	H82...O11	1.773(14)
Na2-O10'	2.4287(19)	O11-H71...O8	169(5)	O8-H82...O11	163(4)	Na2-O10'	2.411(4)	O11-H71...O8	167(1)	O8-H82...O11	168(1)
Na2-O1	2.4791(16)					Na2-O1	2.453(3)				
Na2-O6	3.099(4)	O11-H81	0.92(4)	H6-O8-H72	102(3)	Na2-O6	3.134(21)	O11-H81	0.966(7)	H6-O8-H72	105.8(5)
		O11-H81 ^a	0.95	H6-O8-H82	100(4)			O11-H81 ^a	0.981	H6-O8-H82	102.7(7)
B1-O1	1.363(2)	O11...O8	2.814(3)			B1-O1	1.3685(17)	O11...O8	2.796(3)		
B1-O7	1.370(2)	H81...O8	1.91(4)			B1-O7	1.375(3)	H81...O8	1.835(7)		
B1-O9	1.346(2)	O11-H81...O8	168(3)			B1-O9	1.350(3)	O11-H81...O8	173.1(6)		
B2-O2	1.443(2)	H1-O11-H71	108(5)			B2-O2	1.4457(16)	H1-O11-H71	108.4(7)		
B2-O4	1.434(2)	H1-O11-H81	106(3)			B2-O4	1.4353(18)	H1-O11-H81	108.3(5)		
B2-O9	1.493(2)					B2-O9	1.501(3)				
B2-O3	1.520(2)	O6-H2	0.93(2)			B2-O3	1.523(3)	O6-H2	0.960(4)		
		O6-H2 ^a	0.96					O6-H2 ^a	0.978		
B3-O1	1.497(2)	O6...O5	3.292(2)			B3-O1	1.496(3)	O6...O5	3.273(2)		
B3-O2	1.450(2)	H2...O5	2.36(2)			B3-O2	1.454(3)	H2...O5	2.316(4)		
B3-O4	1.438(2)	O6-H2...O5	177(1)			B3-O4	1.445(2)	O6-H2...O5	174.9(3)		
B3-O5	1.493(2)					B3-O5	1.494(3)				
		O10-H3	0.91(3)					O10-H3	0.974(4)		
B4-O3	1.352(2)	O10-H3 ^a	0.94			B4-O3	1.363(3)	O10-H3 ^a	0.988		
B4-O5	1.353(2)	O10...O3	2.790(2)			B4-O5	1.3577(17)	O10...O3	2.772(2)		
B4-O6	1.384(3)	H3...O3	1.91(3)			B4-O6	1.385(3)	H3...O3	1.818(4)		
		O10-H3...O3	164(3)					O10-H3...O3	165.7(4)		
O1-B1-O9	122.8(2)	O7-H4	0.94(3)			O1-B1-O9	122.5(2)	O7-H4	0.977(4)		
O7-B1-O9	118.7(2)	O7-H4 ^a	0.97			O7-B1-O9	118.97(13)	O7-H4 ^a	0.990		
O1-B1-O7	118.5(2)	O7...O1	2.773(2)			O1-B1-O7	118.56(18)	O7...O1	2.759(3)		
		H4...O1	1.84(3)					H4...O1	1.787(4)		
O4-B2-O2	111.24(14)	O7-H4...O1	169(2)			O4-B2-O2	110.93(11)	O7-H4...O1	172.4(3)		
O4-B2-O9	109.61(14)					O4-B2-O9	109.47(14)				
O2-B2-O9	110.91(14)	O10-H5	0.92(4)			O2-B2-O9	110.90(18)	O10-H5	0.974(6)		
O4-B2-O3	109.58(14)	O10-H5 ^a	0.95			O4-B2-O3	109.79(18)	O10-H5 ^a	0.994		
O2-B2-O3	107.95(14)	O10...O5	2.869(2)			O2-B2-O3	107.92(13)	O10...O5	2.840(3)		
O9-B2-O3	107.46(14)	H5...O5	1.96(4)			O9-B2-O3	107.76(12)	H5...O5	1.885(6)		
		O10-H5...O5	168(3)					O10-H5...O5	165.8(5)		
O4-B3-O2	113.89(15)					O4-B3-O2	113.7(2)				
O4-B3-O5	111.57(14)	H3-O10-H5	101(3)			O4-B3-O5	111.38(11)	H3-O10-H5	102.9(5)		
O2-B3-O5	108.45(15)					O2-B3-O5	108.49(11)				
O4-B3-O1	105.85(14)	O8-H6	0.93(3)			O4-B3-O1	105.57(11)	O8-H6	0.974(4)		
O2-B3-O1	110.79(14)	O8-H6 ^a	0.96			O2-B3-O1	111.29(11)	O8-H6 ^a	0.988		
O5-B3-O1	106.00(14)	O8...O7	2.736(2)			O5-B3-O1	106.2(2)	O8...O7	2.737(2)		
		H6...O7	1.81(3)					H6...O7	1.766(4)		
O3-B4-O5	124.41(17)	O8-H6...O7	176(3)			O3-B4-O5	123.67(19)	O8-H6...O7	175.0(4)		
O3-B4-O6	120.31(17)					O3-B4-O6	116.01(17)				
O5-B4-O6	115.28(17)					O5-B4-O6	120.32(12)				

^a Bond distance corrected for "riding motion" effect, following Busing and Levy (1964).

(Figs. 2 and 4). The results obtained by the structure refinements are consistent with a model based on a static disorder of the H sites, rather than a dynamic one.

The nuclear density distribution around pairs of the oxygen atoms O8 and O11 obtained by MEM confirms a double well potential, which gives rise to a splitting of the H sites (Fig. 3). The nuclear density maps indicate that the H71/H72 and H81/H82, and those related by symmetry, could be modeled using a statically disordered configuration with hydrogen atoms filling two well-defined sites. The unbalanced nuclear density between each hydrogen position suggests a non-equivalent occupancy of each site, in agreement with the refined structural model (Supplemental¹ Table S2). However, other scenarios could also explain the observed H network. Two different hydrogen networks are derived from the current model: one configuration if H71 and H82 are present

and the other for the case of H72 and H81. The H71 and H72 sites could be seen as a splitting of the hydrogen atom located between two opposite oxygen sites (in this case: O8 and O11). A similar scenario was reported for ice phases, where the jump between both configurations was ascribed to "proton tunneling" (Bove et al. 2009; Yen and Gao 2015). The tunneling occurs at low temperature when a proton has the same probability to be located on each minimum of a double well potential. Therefore, this effect involves, in most of the cases, symmetric potentials. In this case, the nuclear density maps obtained from the MEM clearly show that the two sites do not have the same density, and therefore a different energy barrier occurs in each well of potential. Although a proton tunneling could not be completely discarded, based on the current results this scenario is unlikely.

It is worth noting that a similar kind of disorder of the H₂O hy-

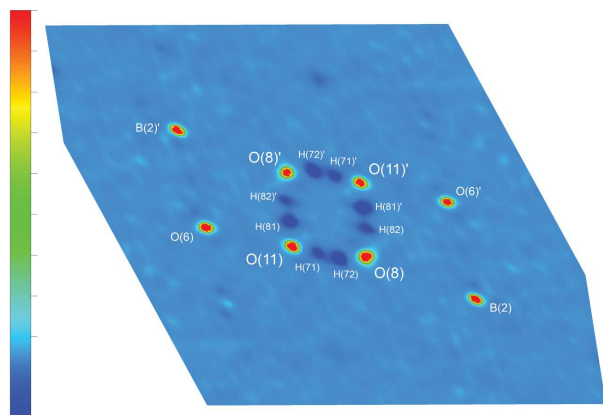


FIGURE 3. Section of the nuclear density function, corresponding to the (0.1, 0.5, 0.6) plane (which contains O8, O11, and symmetry-related H₂O molecules), calculated using the maximum-entropy method applied to the neutron data collected at 20 K. A grid of $256 \times 256 \times 256$ voxels was used to obtain a detailed density map. Further details are given in the text. Graphical representation was generated by VESTA. Color bar: maxima at the top, minima at the bottom of the nuclear density. Atom labels with a prime denote the atoms generated by application of a symmetry operator. (Color online.)

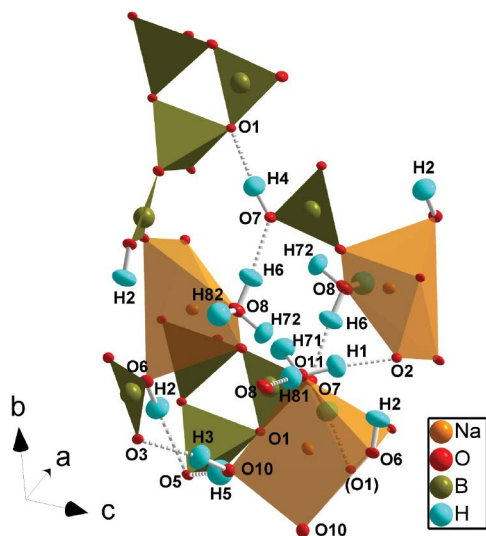


FIGURE 4. The complex H-bonding network in the structure of kernite obtained from neutron structure refinement (data collected at 20 K). Details are given in Table 4. Displacement ellipsoid probability factor is 70%. (Color online.)

drogen atoms also occurs in colemanite (Lotti et al. 2018), leading to two possible (and mutually exclusive) H-bonding configurations.

(3) Geometrically, the three crystallographically independent H₂O molecules show: (a) H-O-H angles ranging between 102° and 108° (neutron data), consistent with the observed H-O-H angles in solid-state materials (e.g., Steiner 1998, and references therein; Gatta et al. 2008, 2012, 2019a; Lotti et al. 2018). (b) O-H distances (corrected for “riding motion effect” following Busing and Levy 1964) ranging between 0.98 and 1.05 Å (neutron data). (c) O-H···O angles $\geq 162^\circ$ (Table 4), approaching a configuration

energetically favorable (i.e., toward linearity), and O_{donor}···O_{acceptor} distances of about 2.7–2.8 Å (Table 4, neutron data). The two independent hydroxyl groups (i.e., O6-H2 and O7-H4, Table 4) show O-H distances (corrected for “riding motion effect”) ranging between 0.98–0.99 Å, O_{donor}···O_{acceptor} distances between 2.8–3.3 Å, and O-H···O $> 172^\circ$ (Table 4, neutron data).

(4) If we exclude O4 and O9, all the other oxygen sites in the structure of kernite are involved in H-bonding, as *donors* or as *acceptors* (Fig. 4, Table 4).

(5) The X-ray and neutron refinements, based on the intensity data collected at 293 and 20 K, respectively, show that this borate does not experience any *T*-induced phase transition, within the *T*-range investigated. The two structure models are virtually identical. As expected, there is a drastic reduction of the magnitude of the atomic displacement ellipsoids at low *T*, as shown by the U_{eq} values (calculated as one third of the trace of the orthogonalized U_{ij} tensor, Supplemental¹ Tables S2 and S3). Some of the atomic displacement ellipsoids are significantly anisotropic at 20 K (Supplemental¹ Table S3, Figs. 1, 2, and 4), though still realistic. We are inclined to believe that this is a twofold effect generated by: (a) an inefficient correction for the extinction effect with the isotropic model of Larson (1967) and (b) the static disorder of the H-sites associated with the H₂O molecules of the NaI- and Na2-polyhedra, which affect all the sites of the Na-coordination shells.

The structure model obtained in this study is consistent with the FTIR and Raman spectra of kernite reported by Jun et al. (1995), Klopogge and Frost (1999), and Silva et al. (2018). Our results confirm that in kernite, as in other hydrous borates (Gatta et al. 2019a), the H-bonding network is complex, pervasive, and plays a primary role in the crystalline edifice. This could also explain the almost insignificant F[−] (or even Cl[−]) vs. OH[−] substitution (Table 3). The first implication on potential utilizations of kernite is that any environmental variable affecting the H-bonding network (i.e., under chemical, thermal, or compressional stress conditions) can generate a structure instability. This can be deduced, for example, by the thermal behavior of kernite reported by Sennova et al. (2005; without structure refinement) or by the static compressional behavior reported by Silva et al. (2018; without structure refinement), along with the reported solubility in water (Mineral Data Publishing, <http://ruff.info/doclib/hom/kernite.pdf>). However, the mechanisms, at the atomic scale, that govern the thermal and compressional behavior of kernite are still obscure and are the aim of our further experiments, based on in situ X-ray diffraction investigations (Comboni et al. 2020).

The solubility of kernite in water (or in other polar solvents) could be considered a positive feature for a mineral commodity of B, which contains up to 15 wt% of elemental B (B₂O₃ ~50 wt%). However, the potential utilization of kernite as B-rich aggregate in Portland cement concretes (used as radiation-shielding materials for the elevated ability of ¹⁰B to absorb thermal neutrons) is hindered by its high Na content (16 wt% of elemental Na; Na₂O 21.3 wt%), which could promote deleterious reactions for the durability of cements (e.g., the so-called “alkali-silica reactions,” ASR). The national standards are not identical in different countries but, in general, the alkali content in ordinary Portland cements (calculated by Na₂O + 0.658 K₂O, the so-called “Na₂O_{equivalent}”) should not exceed 0.60 wt%, to avoid or minimize the risk of ASR. However, it is still unclear regarding the role of Na and B in Sorel cements

(i.e., magnesium oxychloride cements). Sorel cements are not used as reinforced concretes, as they are incompatible with steel reinforcement due to the presence of chloride, but are commonly used to make floor tiles and panels for fire protection. Whether B-additive Sorel cements can be efficiently used for the production of radiation-shielding tiles or panels requires further studies.

ACKNOWLEDGMENTS

The Associate Editor and an anonymous reviewer are thanked for their suggestions aimed to improve the quality of the manuscript.

FUNDING

The authors thank the Institut Laue-Langevin (Grenoble, France) for the allocation of the neutron beamtime; further information is available under the identifier DOI:10.5291/ILL-DATA.DIR-179. G.D.G. and P.L. acknowledge the support of the Italian Ministry of Education (MIUR) through the projects “Dipartimenti di Eccellenza 2018–2022” and “PRIN2017—Mineral reactivity, a key to understand large-scale processes”. P.L. acknowledges the support of the University of Milan through the project “PSR2018—Georisorse e Geomateriali”.

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MANUSCRIPT RECEIVED JANUARY 8, 2020

MANUSCRIPT ACCEPTED FEBRUARY 22, 2020

MANUSCRIPT HANDLED BY OLIVER TSCHAUNER

Endnote:

¹Deposit item AM-20-97433, Supplemental Tables. Deposit items are free to all readers and found on the MSA website, via the specific issue's Table of Contents (go to http://www.minsocam.org/MSA/AmMin/TOC/2020/Sep2020_data/Sep2020_data.html).