

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

G. Diego Gatta, Alessandro Guastoni, Paolo Lotti, Giorgio Guastella,
Oscar Fabelo and Maria Teresa Fernandez-Diaz

Running title: Crystal chemistry of kernite

Abstract, Keywords

Introduction

Sample description and occurrence

Experimental methods and Results

- 1) **Titrimetric determination of the boron content**
- 2) **Gravimetric method to determine the sodium content**
- 3) **Determination of fluorine content**
- 4) **Determination of H₂O content by heating**
- 5) **Determination of minor elements by inductively coupled plasma atomic emission spectroscopy (ICP-AES)**
 - 5.1) *Determination of REE concentration by ICP-AES*
 - 5.2) *Determination of other minor elements concentration by ICP-AES*
- 6) **Determination of C, N, and H**
- 7) **Single-crystal X-ray and neutron diffraction**
 - 7.1) *X-ray and neutron data collections and treatments*
 - 7.2) *X-ray and neutron structure refinements*

Discussion and Implications

Acknowledgements

References

Figures/Tables

Corresponding author: G. Diego GATTA

Dipartimento di Scienze della Terra, Università degli Studi di Milano

Via Botticelli 23, I-20133 Milano, Italy

Tel. +39 02 503 15607, Fax +39 02 503 15597, E-Mail: diego.gatta@unimi.it

Manuscript submitted to American Mineralogist

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

G. Diego Gatta¹, 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 one of the major constituent of the borate deposits and one of the most important mineral commodity of B. The chemical composition and the crystal structure of kernite from the Kramer Deposit (Kern County, California) were investigated by a series 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 content) and by single-crystal X-ray (at 293 K) and neutron (at 20 K) diffraction. The concentration of more than 50 elements was 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 confirm 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 3-fold 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 play 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 source of B ($\text{B}_2\text{O}_3 \sim 50\text{wt}\%$), are discussed, on the basis of the experimental findings of this study.

76

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

79

80 **Introduction**

81 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
82 of sedimentary borate deposits, of which the more common minerals are borax (ideally
83 $\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 8\text{H}_2\text{O}$), ulexite (ideally $\text{NaCa}[\text{B}_5\text{O}_6(\text{OH})_6] \cdot 5\text{H}_2\text{O}$), colemanite (ideally
84 $\text{Ca}[\text{B}_3\text{O}_4(\text{OH})_3] \cdot \text{H}_2\text{O}$), 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,
85 kernite, and tincalconite account for more than 90% of the borate minerals used by industry worldwide
86 (USGS 2019).

87 There is a raising interest to the light elements, in particular Li, B and Be, as technologically and
88 industrially relevant: they are currently considered as “critical elements” (or “critical raw materials”,
89 according to the European Commission 2017), on the basis of their high economic importance and high
90 supply risk. Natural borates represent the most important source of boron. In 1998, the world production
91 on borates accounted for about 3.1 millions of tons; in 2009 the production increased to 4.5 Mtons and
92 in 2017 to 9.8 Mtons (USGS 2018, and previous reports). Only a few mineral commodities (and among
93 those Li) experienced such a trend of production and consumption over the last decades. The principal
94 reason of this raise is ascribed to the fact that boron is a strategic element for a series of technologically
95 relevant processes and products: *e.g.*, to produce heat-resistant glasses and ceramics, for the production
96 of boron-treated low-alloy steels (in which B is used to influence the hardenability and the behaviour of
97 the alloys at high temperature), for the production of radiation-shielding materials (due by the elevated
98 ability of ^{10}B to absorb thermal neutrons), as a critical micronutrient to the growth and health of plants
99 or as insecticide, as an effective photothermocatalyst for the conversion of carbon dioxide. Among the
100 aforementioned utilizations, one is referred to radiation emitted by nuclear reactors for energy
101 production, scientific research activities or medical applications (*i.e.*, boron neutron capture therapy -
102 BNCT), and it is the only one in which the isotopic signature of B plays an important role: ^{10}B shows a
103 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
104 barns; Carter et al. 1953, Sears 1986, Palmer and Swihart 1996, Rauch and Waschkowski 2002), whereas
105 that of ^{11}B is almost irrelevant (~ 0.006 barns). About 20% of natural boron occurs as ^{10}B .

106 In the framework of a long-term project to select potential B-bearing aggregates, we have recently
107 investigated the crystal chemistry and the stability at non-ambient conditions (at high and low
108 temperature, high pressure) of colemanite (Lotti et al. 2017, 2018, 2019) and kurnakovite (ideally

109 Mg[B₃O₃(OH)₅]·5H₂O, Gatta et al. 2019a) using a multi-methodological approach. We now extend our
110 crystal-chemical investigation to kernite, considering its availability in nature and the high B₂O₃ content
111 (~48wt%); this study will be followed by experiments on its *P-T* behaviour and chemical stability.

112 Only a few studies were so far dedicated to kernite. The first important description of this mineral is
113 ascribed to Schaller (1927), who provided optical parameters and a chemical wet analysis. Its crystal
114 structure was first reported by Amoros (1945) using X-ray diffraction techniques, and later reinvestigated
115 by Giese (1966), Cialdi et al. (1967), and Cooper et al. (1973). The X-ray structure refinement of Cooper
116 et al. (1973) is the last one reported in the open literature. Kernite crystallizes in the monoclinic *P*2₁/*c*
117 space group, with *a* ≅ 7.02 Å, *b* ≅ 9.15 Å, *c* ≅ 15.68 Å, and β ≅ 108.9° (*Z* = 4). As observed in other
118 borates (*e.g.*, colemanite, kurnakovite), even kernite contains both triangular planar BO₂OH- and
119 tetrahedral BO₄-groups (Fig. 1). Two independent Na sites are sixfold-coordinated by O atoms, OH-
120 groups and H₂O molecules. One triangular BO₂OH group and two tetrahedral BO₄ groups share corner-
121 bridging O atoms to form 3-fold rings (3B:Δ + 2T or 3B:<Δ2[>], according to the Heller 1996 and Grice
122 et al. 1999 notation), giving chains running along [010] and held together by hydrogen bonding (Fig. 1).
123 FT-IR and Raman spectra of kernite were reported and interpreted by Jun et al. (1995) and Klopogge
124 and Frost (1999), and its high-pressure behaviour was later described by Silva et al. (2018) on the
125 basis of *in situ* IR and Raman spectra evolution collected in a diamond-anvil cell. Even the *T*-induced
126 dehydration behaviour (in vacuum and in air) of a natural kernite was reported by Sennova et al.
127 (2005), on the basis of thermo-gravimetric analysis and X-ray powder diffraction data. However, no
128 structural data (at room or at non-ambient conditions) are reported in the manuscripts of Jun et al.
129 (1995), Klopogge and Frost (1999), Sennova et al. (2005) and Silva et al. (2018).

130 Despite the general structure model reported by Cooper et al. (1973) appears to be consistent (in terms
131 of bond distances and angles), their structure refinement provides only a partial view of the H-bonding
132 configuration, due to the limitation of the X-ray diffraction at that time. For example, some of the H sites
133 were described with isotropic displacement parameters up to six times larger (in Å²) than others, which
134 could reflect a positional (static or dynamic) disorder. The occurrence of hydroxyl groups and cation-
135 coordinated H₂O, which account for a total H₂O content of about 26 wt%, generates the need for a
136 structure model with an accurate location of the H-sites. In addition, the very few chemical analyses of
137 kernite available in the open literature reported only the major constituents, and are based on analytical
138 protocols of the last century (Schaller 1927, Cipriani 1958, Hurlbut et al. 1973).

139 In this light, the aim of the present study is a reinvestigation of the crystal chemistry of kernite from
140 the Kramer Deposit (California), by single-crystal X-ray (at room conditions) and neutron diffraction
141 (at low temperature: 20 K) along with a series of other analytical techniques aimed to fully characterise

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 H₂O 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 can provide: 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 BO₂(OH)-group, polyhedral distortion of the tetrahedral BO₂(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 behaviour at non-ambient *P-T* conditions and the chemical reactivity, as its structure stability appears to be substantially governed by the H-bonding network.

155

156 **Sample description and occurrence**

The sample of kernite 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 a number of borates: borax, colemanite, greigite, hydroboracite, inderite, inyoite, kernite, kurnakovite, meyerhofferite, probertite, searlesite, tinalconite, tunellite and ulexite (Noble 1926, Schaller 1930, Morgan and Erd, 1969, Puffer 1975).

The Kramer deposit consists of a lenticular mass of kernite, borax and lower fraction 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 rock composed by 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 it is the dominant mineral, so that 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. Kernite increases abundance 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 tinalconite, whilst kernite alteration to

175 tincalconite occurs only partially and very slowly. The abundance of kernite in the lower part of the
176 Kramer deposit suggests the temperature-pressure conditions from the borax-to-kernite reaction
177 occurs in the range 50-60 °C and about 750 meters deep (Christ and Garrels 1959).

178

179

180 **Experimental methods and Results**

181

182 **1) Titrimetric determination of the boron content**

183 A mass of 80-100 mg of kernite was placed in a 50 ml plastic test tube, along with 5 ml of
184 water and 3 ml of hydrochloric acid 1M. The plastic test tube was covered and transferred in an
185 ultrasound bath for 1-2 hours. The resulting clear solution was transferred in a 300 ml beaker, with
186 water up to about 100 ml of the total solution. A combined glass electrode (produced by InLab®
187 Routine Pro – Mettler Toledo) was immersed in the solution, and the pH was adjusted to 5.5-6.5 with
188 solutions of HCl 0.1-1M and NaOH 0.1-1M. A mass of 5-6 grams of mannitol was added and stirred,
189 until the complete dissolution of the solid phase. The solution was then titrated with NaOH 0.1M up
190 to pH 8.3-8.7. The content of acid titrated was completely due to the presence of boric acid in solution,
191 as the sample does not contain elements capable to hydrolyze the medium, or in general able to
192 influence its acidity. The measured fraction of B₂O₃ was 50.9(2) wt%.

193

194 **2) Gravimetric method to determine the sodium content**

195 A mass of 500-600 mg of kernite was placed in a weighed platinum crucible (m_1), acidified
196 with 20 ml of hydrochloric acid 1:1 and evaporated to dryness. Residue was treated with 25 ml of
197 methyl alcohol and 10 ml of concentrated hydrochloric acid, and evaporated to dryness. The latter
198 operation was repeated 4-5 times. Residue, in absence of other elements at a significant level (see
199 other analyses) is pure NaCl. Platinum crucible was dried in an oven at 110-130°C for 1-2 h, cooled
200 in a desiccator and weighed (m_2). The different of weigh ($m_2 - m_1$) is the Na content in the mineral,
201 expressed as NaCl. The measured fraction of Na₂O was 22.6(2) wt%.

202

203 **3) Determination of fluorine content**

204 A mineral sample of 20 mg in mass was placed in a 50 ml plastic test tube, along with 5 ml of
205 water and 3 ml of hydrochloric acid 1M. The plastic test tube was covered and transferred in an
206 ultrasound bath for 1-2 hours. A volume of 2-3 ml of Total Ionic Strength Adjustment Buffer
207 (Commercial solution TISAB III) was added to the clear solution and diluted to 20 ml with water.

208 The F content ~~then~~ was then determined using the perfectION™ Combination Fluoride Ion Selective
209 Electrode (Mettler Toledo), adopting the conventional method of standard addition. Solutions of
210 fluorine from 0.1 to 5.0 mg/l were prepared by Certified Reference Material - CRM 1000 mg/l of
211 fluorine. The resulting F fraction was 0.01 wt% (uncertainty not determined).

212

213 **4) Determination of H₂O content by heating**

214 A mass of 500-600 mg of sample was placed in a quartz crucible with lid, and gradually heated
215 in a muffle furnace from 20°C up to 800°C. Assuming that the mass loss represents the total amount
216 of H₂O, the estimated H₂O fraction of the kernite sample was 26.4(2) wt%.

217

218 **5) Determination of minor elements by inductively coupled plasma atomic emission** 219 **spectroscopy (ICP-AES)**

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

222

223 **5.1) *Determination of REE concentration by ICP-AES***

224 A mass of 50 mg of kernite sample was placed in a 50 ml plastic test tube, along with 5 ml of
225 water and 3 ml of hydrochloric acid 1M. The plastic test tube was covered and transferred in an
226 ultrasound bath for 1-2 hours. The resulting clear solution was then transferred in a 50 ml volumetric
227 flask and diluted with water. A calibration protocol was performed with a blank solution and a series
228 of solutions prepared with: similar fractions of sodium and boron as those of the sample under
229 investigation and REE concentration from 0.001 to 0.050 mg/l for each element (using CRM multi
230 elemental standard mix for ICP). Results and instrumental parameters are listed in Table 1.

231

232 **5.2) *Determination of other minor elements concentration by ICP-AES***

233 The determination of the non-REE minor elements was performed using two different
234 protocols, described below:

- 235 i) A mass of 10-20 mg of kernite sample was placed in a 50 ml plastic test tube, along
236 with 5 ml of water and 3 ml of hydrochloric acid 1M. The plastic test tube was covered
237 and transferred in an ultrasound bath for 1-2 hours. The resulting clear solution was
238 then transferred and diluted with water in a 25 ml volumetric flask, containing 2.5 ml
239 of scandium solution (100 mg/l) as internal standard. A calibration protocol was
240 adopted with a blank solution and a series of 5 solutions prepared with concentration

between 0.05 and 1.0 mg/l for each element (using CRM multi elemental standard mix for ICP).

- ii) Decomposition by alkaline fusion of 10-20 mg of kernite sample in platinum crucible with 100 mg of sodium or potassium carbonate in a muffle furnace at 1000°C for 5 minutes, followed by dissolution in 10 ml of water and 1 ml of sulphuric acid 1M or 1 ml of hydrochloric acid 1M. 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 internal standard. A calibration protocol was adopted with a blank solution and a series of 5 solutions prepared with concentration ranging 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.

6) Determination of C, N, and H

200-300 mg of mineral sample were decomposed at 950°C in an elementary analyzer LECO Truspec CHN, in excess of oxygen for 90 seconds. The decomposition products were transferred to a second furnace (Afterburner) at 850°C for a further oxidation and particulate removal. After collection and homogenization of the gases in a container of 4.5 liters at 50°C, Infrared absorption detectors were used to measure the CO₂ and H₂O concentration (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 in order 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 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 experimental chemical formula is virtually identical to the ideal one: Na₂B₄O₆(OH)₂·3H₂O.

7) Single-crystal X-ray and neutron diffraction

7.1) X-ray and neutron data collections and treatments

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 Dept. Univ. Milan. To maximize the reciprocal space coverage and the quality of the intensity data, a series of collection runs were optimised using the *ad hoc* routine of the CrysAlisProTM suite (Rigaku – Oxford Diffraction 2019), with ω scan strategy, step size of 0.5° and an exposure time per frame of 2 s. A total number of 13010 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 (Table 4). Corrections for Lorentz-polarization effects and (semi-empirical) X-ray absorption were applied using the *ABSPACK* routine, implemented in the CrysAlisProTM 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 x 2 x 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 or ω - 2θ scans for low and high-Q reflections, respectively. The Bragg reflections were collected 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 $d_{\min} = 0.59$ Å (Table 4). 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/sxtalsoft/repository/show/racer>). The lattice was found to be metrically monoclinic (Table 4), and consistent with the X-ray experimental findings reported above. Absorption correction was applied, based on composition and shape of the crystal using the ILL

305 program Datap (the current version of this program is available online on <https://forge.ill.fr/>). The
306 reflection conditions were found to be consistent with the space group $P2_1/c$. The Wilson plot and the
307 statistics of distributions of the normalized structure factors showed that the structure is
308 centrosymmetric at ~91% likelihood (the Sheldrick's $|E^2-1|$ criterion is 0.958).

309 Further details pertaining to the X-ray and neutron data collection strategies are listed in Table
310 4 (*deposited*).

311

312 7.2) *X-ray and neutron structure refinements*

313 Anisotropic crystal-structure refinements, based on the X-ray and neutron intensity data,
314 collected at room and at low T , respectively, were conducted in the space group $P2_1/c$ using the
315 SHELXL-97 software (Sheldrick 1997, 2008), and starting from the structure model of Cooper et al.
316 (1973), without any H atom. Neutral X-ray scattering factors of Na, B, O and H were taken from the
317 *International Tables for X-ray Crystallography (Vol. C)* and used for the X-ray refinement, whereas
318 neutron scattering lengths of Na, B, O and H were taken from Sears (1986). Secondary isotropic
319 extinction effect was corrected according to the formalism of Larson (1967).

320 For both the refinements (*i.e.*, X-ray at 293 K and neutron at 20 K), convergence was rapidly
321 achieved after the first cycles, with a series of residual peaks in the final difference-Fourier map of
322 the electron or nuclear density (positive for the X-ray refinement, negative for the neutron
323 refinement). The complex configuration of the H population was first modelled on the basis of the
324 neutron data, and then implemented in the X-ray refinement. The negative residual peaks found in
325 the difference-Fourier map of the nuclear density were assigned to the H sites in the next cycles (*i.e.*,
326 H has a negative neutron scattering length). Shape and magnitude of the minima in the difference-
327 Fourier maps showed no evidence of positional or dynamic disorder for six of the H sites (*i.e.*, H1-
328 H6, Table 5). However, evidence of disorder was observed for the H population bonded to the
329 (opposite) O8 and O11 sites, which are vertices of the Na1 and Na2 polyhedra, respectively (Fig. 2,
330 Table 5). After a series of tests, the best figures of merit was obtained with three H sites bonded to
331 O8 [*i.e.*, H6, H72 and H82, with site occupancy factor $s.o.f.(H6) = 1$ and $s.o.f.(H72)+s.o.f.(H82) = 1$]
332 and three bonded to O11 [*i.e.*, H1, H71 and H81, with $s.o.f.(H1) = 1$ and $s.o.f.(H71)+s.o.f.(H81) = 1$],
333 with the following mutually exclusive configurations: (H6-O8-H82 + H1-O11-H71) and (H6-O8-
334 H72 + H1-O11-H81) (Fig. 2, Table 5). With such a structure model, convergence was achieved and
335 the variance-covariance matrix showed no significant correlation among the refined variables; all the
336 principal mean-square atomic displacement parameters were positive (including those for the H sites,
337 Table 6) and the final $R_1(F) = 0.0723$, for 2656obs./226par. (Table 4 - *deposited*).

338 Implementing the structure model based on the neutron refinement, even convergence of the
339 X-ray refinement was rapidly achieved, with no significant correlation among the refined variables.
340 The final $R_1(F) = 0.0324$, for 1908obs./193par. (Table 4 - *deposited*).

341 Additional details pertaining to structure refinements are given in Table 4 (*deposited*). Atomic
342 coordinates and displacement parameters are listed in Tables 5 (*deposited*) and 6 (*deposited*); selected
343 interatomic distances and angles are given in Table 7.

344 In order to corroborate (or deny) the structure model based on the neutron least-square
345 refinement, with its disordered H-sites configuration, nuclear density distribution was also analysed
346 by the maximum-entropy method (MEM), using the program DYSNOMIA (Momma et al. 2013) and
347 the graphical representation of nuclear density maps by VESTA (Momma and Izumi 2011). The
348 nuclear density maps were obtained from the single-crystal neutron data collected at 20 K. 2435
349 unique reflections with $I/\sigma(I) > 3$ where used in the MEM calculation giving rise a final $R(F)$ and
350 $wR(F)$ of 3.7 and 3.5 %, respectively. A grid of 256 x 256 x 256 voxels were used to obtain a detailed
351 density map. Fig. 3 shows a section of the nuclear density function corresponding to the (0.1, 0.5,
352 0.6) plane. This plane was selected as O8, O11 and symmetry-related H₂O molecules lay on it.

353

354 Discussion and Implications

355 Chemical and structural analysis of the kernite sample under investigation confirm the general
356 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
357 Na^+ here detected, distributed in the two independent Na1 and Na2 sites and giving distorted
358 coordination polyhedra with CN = 6, are represented by Mg^{2+} and K^+ , but their sum is less than 0.01
359 *a.p.f.u.* (Table 3). Similarly, the only potential substituents of B^{3+} (in tetrahedral coordination) are
360 Si^{4+} and Al^{3+} , but for less than 0.01 *a.p.f.u.* (Tables 2 and 3). Even the F^- fraction, as potential OH-
361 group substituent, is not significant (*i.e.*, < 0.01 *a.p.f.u.*, Tables 2 and 3). The concentration of other
362 minor elements and of the REE is substantially irrelevant, as shown in Tables 1 and 2. Overall, kernite
363 does not show any significant isomorphic substitution, and thus cannot act as geochemical trap of
364 technologically-relevant elements (*e.g.*, Li or REE). This finding can be compared with the results
365 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
366 Mine, Balıkesir Province, Marmara Region, Turkey; Lotti et al. 2018, 2019) and in kurnakovite
367 ($\text{Mg}[\text{B}_3\text{O}_3(\text{OH})_5] \cdot 5\text{H}_2\text{O}$, from the Kramer Deposit, Mohave desert, Kern County, California; Gatta et
368 al. 2019a) no significant isomorphic substituents were found, so that the experimental formulae were
369 virtually identical to the ideal ones. In this light, the surprising chemical purity observed for kernite
370 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 rather a common feature of the hydrous borates which 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 7). 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 it is not only dictated by its crystal structure, but even by 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 3-fold 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 H_2O molecules, though the bonding configuration of the strongly distorted Na_2 -polyhedron would suggest a $\text{CN} = 5+1$, as five Na2-O distances are shorter than 2.5 Å and one is about 3.1 Å (Table 7, room- T X-ray refinement).

The X-ray (data collected at 293 K) and neutron (data collected at 20 K) structure refinements consistently show that:

- 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 $118.5^\circ\text{-}122.8^\circ$ for B1- and $115.3^\circ\text{-}124.4^\circ$ 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 $\text{Na2O}_2(\text{OH})(\text{OH}_2)_3$ 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 OH_2 -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 7). Among those, two are affected by positional disorder of the H sites, so that two mutually exclusive configurations occur, here modelled as: (H6-O8-H82 + H1-O11-H71) or (H6-O8-H72 + H1-O11-H81) (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 confirm 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 modelled 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 (Table 5). 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 a second 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 tunnelling” (Bove et al. 2009, Yen and Gao 2015). The tunnelling 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 our case, the nuclear density maps obtained from the MEM clearly show that both sites have not the same density, and therefore a different energy barrier occurs in each well of potential. Although a proton tunnelling could not completely discarded, based on the current results this scenario is unlikely.
- It is worth noting that a similar kind of disorder of the H₂O hydrogen 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 7), approaching a configuration energetically favourable (*i.e.*, toward linearity), and O_{donor}...O_{acceptor} distances of about 2.7-2.8 Å (Table 7, neutron data). The two independent hydroxyl groups (*i.e.*, O6-H2 and O7-H4, Table 7) 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 7, 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 7).
- 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 orthogonalised U_{ij} tensor, Tables 5 and 6 - *deposited*). Some of the atomic displacement ellipsoids are significantly anisotropic at 20 K (Table 6 - *deposited*, Figs. 1, 2 and 4), though still realistic. We are inclined to believe that this is the twofold effect generated by: *a*) a not efficient correction for the extinction effect with the isotropic model of Larson (1967) and *b*) the static disorder of the H-sites belonging the H₂O molecules of the Na1- and Na2-polyhedra, which affect all the sites of the Na-coordination shells.

The structure model obtained in this study is consistent with the FT-IR and Raman spectra of kernite reported and interpreted by Jun et al. (1995), Klopprogge and Frost (1999) and Silva et al. (2018). The experimental findings of this study confirm that also in kernite, as for other hydrous borates (Gatta et al. 2019a), the H-bonding network is complex, pervasive and play a primary role into 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 able to affect 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 behaviour of kernite reported by Sennova et al. (2005; without structure refinement) or by the static compressional behaviour reported by Silva et al. (2018; without structure refinement), along with the reported solubility in water (Mineral Data Publishing, <http://rruff.info/doclib/hom/kernite.pdf>). However, the mechanisms, at the atomic scale, that govern the thermal and compressional behaviour of kernite are still obscure, and will be the aim of our future experiments, based on *in situ* X-ray diffraction investigations.

468 The solubility of kernite in water (or in other polar solvents) could be considered a positive feature
469 for a mineral commodity of B, which contains up to 15 wt% of elemental B ($B_2O_3 \sim 50$ wt%). However,
470 the potential utilization of kernite as B-rich aggregate in Portland cement concretes (used as radiation-
471 shielding materials for the elevated ability of ^{10}B to absorb thermal neutrons) is hindered by its high
472 Na content (16 wt% of elemental Na; Na_2O 21.3 wt%), which could promote deleterious reactions
473 for the durability of cements (*e.g.*, the so-called “alkali-silica reactions” – ASR). The national
474 standards are not identical in the different countries but, in general, the alkali content in ordinary
475 Portland cements (calculated by $Na_2O + 0.658 K_2O$, the so-called “ $Na_2O_{equivalent}$ ”) should not exceed
476 0.60 wt%, in order to avoid or minimize the risk of ASR. However, it is still obscure the role of Na
477 and B in Sorel cements (*i.e.*, magnesium oxychloride cements), leaving room for experiments in this
478 direction. Sorel cements are not used as reinforced concretes, as basically incompatible with steel
479 reinforcement because the presence of chloride, but are commonly used to make floor tiles and panels
480 for fire protection. Could B-additivated Sorel cements be efficiently used for the production of
481 radiation-shielding tiles or panels?

482

483

484 **Acknowledgements**

485 The authors thank the Institut Laue-Langevin (Grenoble, France) for the allocation of the beamtime,
486 further information could be consulted under the identifier DOI:10.5291/ILL-DATA.DIR-179. GDG
487 and PL acknowledge the support of the Italian Ministry of Education (MIUR) through the projects
488 'Dipartimenti di Eccellenza 2018-2022' and 'PRIN2017 - Mineral reactivity, a key to understand large-
489 scale processes'. PL acknowledge the support of the University of Milan through the project 'PSR2018
490 – Georisorse e Geomateriali'. The Associate Editor and an anonymous reviewer are thanked for their
491 suggestions aimed to improve the quality of the manuscript.

492

493

494

References

Amoros, J.L.P. (1945) La estructura de la kernita. *Euclides*, 57-58, 599-608.

Archer, J. and Lehmann, M.S. (1986) A simple adjustable mount for a two-stage cryorefrigerator on an Eulerian cradle. *Journal of Applied Crystallography*, 19, 456-459.

Bove, L.E., Klotz, S., Paciaroni, A., and Sacchetti, F. (2009) Anomalous Proton Dynamics in Ice at Low Temperatures. *Physical Review Letter*, 103, 165901-4.

Busing, W.R. and Levy, H.A. (1964) The effect of thermal motion on the estimation of bond lengths from diffraction measurements. *Acta Crystallographica*, 17, 142-146.

Carter, R.S., Palevsky, H., Myers, V.W., and Hughes, D.J. (1953) Thermal neutron absorption cross sections of boron and gold. *Physical Review*, 96, 716-721.

Christ, C.L. and Garrels, R.M. (1959) Relations among sodium borate hydrates at the Kramer deposit, Born, California. *American Journal of Science*, 257, 516-528.

Cialdi, G., Corazza, E., and Sabelli, C. (1967) La struttura cristallina della kernite, $\text{Na}_2\text{B}_4\text{O}_6(\text{OH})_2 \cdot 3\text{H}_2\text{O}$. *Rendiconti dell'Accademia Nazionale dei Lincei, Ser. VIII*, 42, 236-251.

Cipriani, C. (1958) Ricerche sulla disidratazione di alcuni borati naturali. *Atti della Società Toscana di Scienze Naturali*, 65A, 284-322.

Cooper, W.F., Larsen, F.K., and Coppens, P. (1973) Electron population analysis of accurate diffraction data. V. Structure and one-center charge refinement of the light-atom mineral kernite, $\text{Na}_2\text{B}_4\text{O}_6(\text{OH})_2 \cdot 3\text{H}_2\text{O}$. *American Mineralogist*, 58, 21-31.

European Commission (2017) Critical Raw Materials for the EU. Document 52017DC0490, https://ec.europa.eu/growth/sectors/raw-materials/specific-interest/critical_en.

Farrugia, L.J. (1999) WinGX suite for small-molecule single-crystal crystallography. *Journal of Applied Crystallography*, 32, 837-838.

Gatta, G.D., Rotiroti, N., McIntyre, G.J., Guastoni, A., and Nestola, F. (2008) New insights into the crystal chemistry of epididymite and eudidymite from Malosa, Malawi: a single-crystal neutron diffraction study. *American Mineralogist*, 93, 1158-1165.

Gatta, G.D., McIntyre, G.J., Swanson, G.J., and Jacobsen, S.D. (2012) Minerals in cement chemistry: a single-crystal neutron diffraction and Raman spectroscopic study of thaumasite, $\text{Ca}_3\text{Si}(\text{OH})_6(\text{CO}_3)(\text{SO}_4) \cdot 12\text{H}_2\text{O}$. *American Mineralogist*, 197, 1060-1069.

Gatta G.D., Guastoni A., Lotti P., Guastella G., Fabelo O., Fernandez-Diaz. M.T. (2019) A multi-methodological study of kurnakovite: A potential B-rich aggregate. *American Mineralogist*, 104, 1315-1322.

527 Gatta, G.D., Fabelo-Rosa O.R., and Fernandez-Diaz M.T. (2019b) Crystal chemistry of kernite
 528 mineral $[\text{Na}_2\text{B}_4\text{O}_6(\text{OH})_2 \cdot 3\text{H}_2\text{O}]$: a sustainable approach for boron-based cements. Experimental
 529 Report, Institut Laue-Langevin (ILL), doi:10.5291/ILL-DATA.DIR-179.

530 Giese, R. F. Jr. (1966) Crystal structure of kernite, $\text{Na}_2\text{B}_4\text{O}_6(\text{OH})_2 \cdot 3\text{H}_2\text{O}$. Science, 154, 1453-
 531 1454.

532 Grice, J.D., Burns, P.C., and Hawthorne, F.C. (1999) Borate minerals. II. A hierarchy of
 533 structures based upon the borate fundamental building block. Canadian Mineralogist, 37, 731-762.

534 Heller, G. (1986) A survey of structural types of borates and polyborates. Topics in Current
 535 Chemistry, 131, 39-98.

536 Hurlbut, C. S. Jr., Aristarain, L.F., and Erd, R.C. (1973) Kernite from Tincalayu, Salta,
 537 Argentina. American Mineralogist, 58, 308-313.

538 Jun, L., Shuping, X., and Shiyang, G. (1995) FT-IR and Raman spectroscopic study of hydrated
 539 borates. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 51, 519-532.

540 Klopogge, J.T. and Frost, R.L. (1999) Raman microscopic study of some borate minerals:
 541 Ulexite, kernite, and inderite. Applied spectroscopy, 53, 356–364.

542 Larson, A.C. (1967) Inclusion of secondary extinction in least-squares calculations. Acta
 543 Crystallographica, 23, 664-665.

544 Lotti, P., Gatta, G.D., Comboni, D., Guastella, G., Merlini, M., Guastoni, A., and Liermann, H.P.
 545 (2017) High-pressure behavior and *P*-induced phase transition of $\text{CaB}_3\text{O}_4(\text{OH})_3 \cdot \text{H}_2\text{O}$ (colemanite).
 546 Journal of American Ceramic Society, 100, 2209-2220.

547 Lotti, P., Gatta, G.D., Demitri, N., Guastella, G., Rizzato, S., Ortenzi, M.A., Magrini, F.,
 548 Comboni, D., Guastoni, A., and Fernandez-Diaz, M.T. (2018) Crystal-chemistry and temperature
 549 behavior of the natural hydrous borate colemanite, a mineral commodity of boron. Physics and
 550 Chemistry of Minerals, 45, 405-422.

551 Lotti, P., Comboni, D., Gigli, L., Carlucci, L., Mossini, E., Macerata, E., Mariani, M., and Gatta,
 552 G.D. (2019) Thermal stability and high-temperature behavior of the natural borate colemanite: An
 553 aggregate in radiation-shielding concretes. Construction and Building Materials, 203, 679–686.

554 Momma, K., and Izumi, F. (2011) Vesta 3 for three-dimensional visualization of crystal,
 555 volumetric and morphology data. Journal of Applied Crystallography, 44, 1272-1276.

556 Momma, K., Ikeda, T., Belik, A.A., and Izumi, F. (2013) Dynomia, a computer program for
 557 maximum-entropy method (MEM) analysis and its performance in the MEM-based pattern fitting.
 558 Powder Diffraction, 28, 184-193.

559 Morgan, V. and Erd, R.C. (1969) Minerals of the Kramer borate district, California. California
 560 Division of Mines and Geology Mineral Information Service, 22, pp. 143-153 and 165-172.

561 Noble, L.F. (1926) Borate deposits in the Kramer district, Kern County, California. U.S.
 562 Geological Survey Bulletin, 785, 45-61.

563 Obert, L. and Long, A.E. (1962) Underground borate mining, Kern County, California. U.S.
 564 Bureau of Mines Report of Investigation, 6110, 1-12.

565 Palmer M.R. and Swihart, G.H. (1996) Boron Isotope Geochemistry: An Overview. In L.M.
 566 Anovitz, E.S. Grew (Eds.), Boron: Mineralogy, Petrology, and Geochemistry, Review in Mineralogy
 567 33, Mineralogical Society of America, Chantilly, pp. 709-744.

568 Puffer, J.H. (1975) The Kramer borate mineral assemblage. Mineralogical Record, 6, 84-91.

569 Rauch, H., and Waschkowski, W. (2002) Neutron Scattering Lengths. In A.J. Dianoux, G.
 570 Lander (Eds.), Neutron Data Booklet, first ed., Institut Laue Langevin, Grenoble, pp. 1-18.

571 Schaller, W. T. (1927) Kernite, a new sodium borate. American Mineralogist, 12, 24-25.

572 Schaller, W. T. (1930) Borate minerals from the Kramer district, Mohave Desert, California.
 573 U.S. Geological Survey Professional Paper, 158, 137-170.

574 Sears, V.F. (1986) Neutron Scattering Lengths and Cross-Sections. In K. Sköld and D.L.
 575 Price, Eds., Neutron Scattering, Methods of Experimental Physics, Vol. 23A, Academic Press, New
 576 York, pp. 521-550.

577 Sennova, N.A., Bubnova, R.S., Filatov, S.K., Paufler, P., Meyer, D.C., Levin, A.A., and
 578 Polyakova, I.G. (2005) Room, low, and high temperature dehydration and phase transition of kernite
 579 in vacuum and in air. Crystal Research and Technology, 40, 563–572.

580 Sheldrick, G.M. (1997) SHELXL-97. Programs for crystal structure determination and
 581 refinement. University of Göttingen, Germany.

582 Sheldrick, G.M. (2008) A short history of SHELX. Acta Crystallographica, A64, 112-122.

583 Siefke, J.W. (1991) The Boron open Pit Mine at the Kramer Borate Deposit. The Diversity of
 584 Mineral and Energy Resources of Southern California. In M.A. McKibben, Ed., Society of Economic
 585 Geologist Guidebook Series, 12, 4-15.

586 Silva, M., O'Bannon, E.F., and Williams, Q. (2018) A vibrational spectroscopic study of
 587 kernite to 25 GPa: Implications for the high-pressure stability of borate polyhedra. American
 588 Mineralogist, 103, 1306–1318.

589 Steiner, T. (1998) Opening and narrowing of the water H-O-H angle by hydrogen-bonding
 590 effects: Re-inspection of neutron diffraction data. Acta Crystallographica, B54, 464-470.

591 U.S.G.S. (2018) Mineral commodity summaries 2018. U.S. Geological Survey, 200 p., Reston,
592 Virginia, U.S.A.

593 U.S.G.S. (2019) Mineral commodity summaries 2019. U.S. Geological Survey, 200 p., Reston,
594 Virginia, U.S.A.

595 Yen, F. and Gao, T. (2015) Dielectric Anomaly in Ice near 20 K: Evidence of Macroscopic
596 Quantum Phenomena. *Journal of Physical Chemistry Letter*, 6, 2822–2825.

597

598

599

600

601

602

603

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

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

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

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

	%m/m	ICP-AES (nm)		%m/m	ICP-AES (nm)
619	Li ₂ O	< 0.01	670.784	NiO	< 0.01
620	MgO	0.01	285.213	CuO	< 0.01
	K ₂ O	0.02	766.490	Ag ₂ O	< 0.01
621	Rb ₂ O	< 0.02	780.023	ZnO	< 0.01
	Cs ₂ O	< 0.02	455.531	CdO	< 0.01
622	BeO	< 0.01	313.107	Al ₂ O ₃	0.01
	CaO	< 0.01	317.933	Tl ₂ O	< 0.02
623	BaO	< 0.02	233.527	PbO	< 0.05
	TiO ₂	< 0.01	334.940	P ₂ O ₅	< 0.02
624	ZrO ₂	< 0.01	343.823	As ₂ O ₃	< 0.02
	V ₂ O ₅	< 0.02	292.464	Sb ₂ O ₃	< 0.02
625	Cr ₂ O ₃	< 0.01	267.716	Bi ₂ O ₃	< 0.02
626	MoO ₃	< 0.02	202.031	SiO ₂	0.01
	MnO	< 0.01	257.610	SrO	< 0.01
	Fe ₂ O ₃	< 0.01	238.204	B ₂ O ₃	*
	CoO	< 0.01	228.616	Na ₂ O	*

* data were not reproducible and therefore discarded

627 Table 3. Representative chemical composition of kernite from Kramer Deposit (Kern County,
 628 California), and empirical formula recalculated on the basis of eleven anions.
 629
 630
 631
 632
 633
 634

<i>Oxides</i>	<i>Wt%</i>	<i>e.s.d.</i>
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	
<i>Elements</i>	<i>a.p.f.u.</i>	
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		

645
 646
 647
 648
 649
 650
 651
 652
 653
 654
 655
 656
 657
 658
 659
 660
 661
 662
 663
 664
 665
 666
 667
 668
 669
 670
 671
 672
 673
 674
 675
 676
 677
 678

679
680
681
682
683
684
685
686
687
688
689
690
691
692
693
694
695
696
697
698
699
700
701
702
703

Table 4 (*deposited*). Details of neutron and X-ray data collections and refinements of kernite.

T (K)	20	293
Crystal shape	Prism	Prism
Crystal volume (mm)	3 x 2 x 2	0.22 x 0.12 x 0.11
Crystal colour	White	White
Unit-cell parameters	$a = 6.996(1) \text{ \AA}$ $b = 9.128(3) \text{ \AA}$ $c = 15.608(3) \text{ \AA}$ $\beta = 109.06(3)^\circ$ $V = 942.0(4) \text{ \AA}^3$	$a = 6.9983(3) \text{ \AA}$ $b = 9.1375(3) \text{ \AA}$ $c = 15.6389(7) \text{ \AA}$ $\beta = 108.832(5)^\circ$ $V = 946.53(7) \text{ \AA}^3$
Chemical formula	$\text{Na}_2\text{B}_4\text{O}_6(\text{OH})_2 \cdot 3\text{H}_2\text{O}$	$\text{Na}_2\text{B}_4\text{O}_6(\text{OH})_2 \cdot 3\text{H}_2\text{O}$
Space Group	$P 2_1/c$	$P 2_1/c$
Z	4	4
Radiation type, λ (Å)	Neutron CW, 0.8347	X-ray, MoK α
Diffractometer	D9 four-circle - ILL	Rigaku XtaLABSynergy-i
Data-collection method	ω -scans, ω -2 θ scans	ω -scans
$d_{\min.}$ (Å)	0.59	0.71
	$-10 \leq h \leq +10$	$-9 \leq h \leq +8$
	$0 \leq k \leq +18$	$-12 \leq k \leq +12$
	$-23 \leq l \leq +24$	$-19 \leq l \leq +20$
Measured reflections	3434	13010
Unique reflections	3161	2296
Unique reflections with $F_o > 4\sigma(F_o)$	2656	1908
Refined parameters	226	193
Extinction coeff.	0.014(2)	0.001(1)
R_{Int}	0.0488	0.0361
R_σ	0.0557	0.0259
$R_I(F)$ with $F_o > 4\sigma(F_o)$	0.0723	0.0324
$R_I(F)$ for all reflections	0.0884	0.0412
$wR_2(F^2)$	0.1491	0.0655
GooF	1.636	1.519
Residuals (fm/Å ³ , e ⁻ /Å ³)	-1.9/+2.5	-0.3/+0.5

Note: Statistical parameters according to the Shelxl-97 definition (Sheldrick 1997, 2008).

704 Table 5 (*deposited*). Refined fractional atomic coordinates and equivalent/isotropic displacement
705 factors (\AA^2) of kernite, based on the X-ray structure refinement at 293 K and neutron refinement at
706 20 K. U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.
707
708

Site	X-ray 293 K					Neutron 20 K				
	<i>s.o.f.</i>	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	U_{eq}	<i>s.o.f.</i>	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	U_{eq}/U_{iso}
Na1	1	0.31944(12)	0.46480(8)	0.31093(6)	0.0245(2)	1	0.3190(4)	0.4638(2)	0.3102(2)	0.0067(7)
Na2	1	0.18563(14)	0.36644(9)	0.07250(6)	0.0353(2)	1	0.1869(4)	0.3681(2)	0.0703(2)	0.0073(8)
O1	1	0.4874(2)	0.52527(13)	0.10281(8)	0.0182(3)	1	0.4865(2)	0.52517(13)	0.10184(13)	0.0050(4)
O2	1	0.55971(19)	0.59894(13)	0.25905(8)	0.0157(3)	1	0.5610(2)	0.59800(12)	0.25950(12)	0.0038(4)
O3	1	0.23252(19)	0.70586(14)	0.23145(9)	0.0192(3)	1	0.2321(2)	0.70429(13)	0.23132(13)	0.0046(4)
O4	1	0.46514(18)	0.35087(12)	0.20889(8)	0.0138(3)	1	0.4642(2)	0.34976(12)	0.20771(12)	0.0038(4)
O5	1	0.79157(19)	0.44857(14)	0.21541(9)	0.0200(3)	1	0.7920(2)	0.44738(13)	0.21481(13)	0.0046(4)
O6	1	0.0623(2)	0.29066(16)	0.24061(11)	0.0293(4)	1	0.0648(2)	0.28819(15)	0.24073(14)	0.0062(4)
O7	1	0.4154(2)	0.70621(16)	-0.00985(10)	0.0301(4)	1	0.4169(3)	0.70779(14)	-0.01111(14)	0.0074(5)
O8	1	0.2249(3)	0.53337(18)	0.43187(11)	0.0338(4)	1	0.2223(3)	0.53220(17)	0.43146(15)	0.0105(5)
O9	1	0.5654(2)	0.27258(13)	0.36300(9)	0.0188(3)	1	0.5643(2)	0.27324(13)	0.36308(13)	0.0050(4)
O10	1	-0.0389(2)	0.56220(18)	0.08468(11)	0.0311(4)	1	-0.0380(3)	0.55883(16)	0.08588(15)	0.0080(5)
O11	1	0.1674(2)	0.11763(17)	0.07646(11)	0.0294(4)	1	0.1662(3)	0.11800(15)	0.07555(14)	0.0074(5)
B1	1	0.4469(3)	0.6680(2)	0.07836(14)	0.0173(4)	1	0.4480(2)	0.66898(13)	0.07755(14)	0.00330(18)
B2	1	0.5532(3)	0.2325(2)	0.26885(13)	0.0137(4)	1	0.5530(2)	0.23179(13)	0.26849(13)	0.00260(18)
B3	1	0.5736(3)	0.4804(2)	0.19976(14)	0.0141(4)	1	0.5738(2)	0.48006(13)	0.19901(13)	0.00272(17)
B4	1	0.1323(3)	0.8137(2)	0.25825(15)	0.0184(4)	1	0.1300(2)	0.81241(13)	0.25821(13)	0.00304(18)
H1	1	0.264(4)	0.100(4)	0.1327(16)	0.072(10)	1	0.2679(5)	0.1025(4)	0.1359(3)	0.0207(10)
H2	1	0.106(4)	0.1942(16)	0.2510(19)	0.056(9)	1	0.1110(6)	0.1887(4)	0.2510(3)	0.0202(8)
H3	1	0.048(4)	0.622(3)	0.1249(19)	0.067(10)	1	0.0591(5)	0.6211(4)	0.1296(3)	0.0195(9)
H4	1	0.431(5)	0.626(2)	-0.0447(19)	0.072(10)	1	0.4388(6)	0.6245(4)	-0.0462(3)	0.0195(9)
H5	1	-0.109(4)	0.523(3)	0.120(2)	0.071(10)	1	-0.1151(7)	0.5161(5)	0.1215(3)	0.0247(10)
H6	1	0.293(5)	0.620(3)	0.454(2)	0.088(12)	1	0.2962(6)	0.6219(4)	0.4549(3)	0.0214(8)
H71	0.40(3)	0.197(10)	0.058(6)	0.033(4)	0.046(8)	0.361(14)	0.2060(18)	0.0590(12)	0.0305(11)	0.023(3)
H72	0.60(3)	0.252(7)	0.478(4)	0.485(2)	0.046(8)	0.639(14)	0.2305(10)	0.4714(6)	0.4858(6)	0.0192(17)
H81	0.60(3)	0.048(5)	0.082(5)	0.081(3)	0.046(8)	0.639(14)	0.0370(9)	0.0838(7)	0.0774(5)	0.0208(14)
H82	0.40(3)	0.092(5)	0.568(7)	0.418(5)	0.046(8)	0.361(14)	0.0729(19)	0.5631(12)	0.4193(9)	0.024(2)

709
710
711
712
713
714
715

716
717
718
719
720
721
722
723
724
725
726
727
728
729
730
731
732
733
734
735
736
737
738
739
740
741
742
743
744

Table 6 (*deposited*). Refined displacement parameters (\AA^2) of kernite in the expression: $-2\pi^2[(ha^*)^2U_{11} + \dots + 2hka^*b^*U_{12} + \dots + 2klb^*c^*U_{23}]$, based on the X-ray refinement at 293 and neutron structure refinement at 20 K.

<i>T</i> = 293 K	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Na1	0.0299(5)	0.0193(4)	0.0302(5)	0.0008(3)	0.0177(4)	0.0011(3)
Na2	0.0352(5)	0.0245(5)	0.0360(5)	0.0007(4)	-0.0027(4)	-0.0016(4)
O1	0.0291(7)	0.0128(6)	0.0134(6)	0.0002(5)	0.0078(5)	0.0018(5)
O2	0.0222(7)	0.0105(6)	0.0136(6)	-0.0005(5)	0.0048(5)	0.0020(5)
O3	0.0171(7)	0.0162(6)	0.0249(7)	-0.0048(5)	0.0078(5)	-0.0035(5)
O4	0.0146(6)	0.0103(6)	0.0165(6)	0.0013(5)	0.0052(5)	0.0007(4)
O5	0.0174(6)	0.0165(6)	0.0288(7)	0.0020(5)	0.0112(5)	-0.0001(5)
O6	0.0191(7)	0.0249(8)	0.0462(9)	0.0009(6)	0.0138(6)	0.0025(6)
O7	0.0527(8)	0.0212(7)	0.0172(6)	0.0021(5)	0.0126(6)	0.0074(6)
O8	0.0398(8)	0.0335(8)	0.0306(7)	-0.0049(6)	0.0150(6)	-0.0050(6)
O9	0.0286(7)	0.0131(6)	0.0148(6)	-0.0013(5)	0.0073(5)	-0.0028(5)
O10	0.0331(8)	0.0358(8)	0.0249(8)	-0.0046(7)	0.0103(7)	-0.0087(7)
O11	0.0310(7)	0.0292(7)	0.0248(7)	-0.0015(6)	0.0048(6)	-0.0006(6)
B1	0.0216(11)	0.0154(10)	0.0152(10)	0.0008(8)	0.0064(8)	0.0006(8)
B2	0.0167(10)	0.0112(9)	0.0133(10)	0.0007(7)	0.0051(8)	0.0002(7)
B3	0.0177(10)	0.0113(9)	0.0148(10)	0.0002(7)	0.0073(8)	0.0005(7)
B4	0.0181(10)	0.0190(10)	0.0191(10)	0.0016(8)	0.0071(8)	-0.0004(8)
<i>Note:</i> All the H sites were modelled isotropically in the X-ray structure refinement at 293 K						

745
746
747
748

<i>T</i> = 20 K	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₂₃	<i>U</i> ₁₃	<i>U</i> ₁₂
Na1	0.0050(9)	0.0059(6)	0.0090(15)	0.0005(7)	0.0019(10)	0.0004(6)
Na2	0.0055(9)	0.0066(6)	0.0084(15)	0.0009(7)	0.0005(10)	-0.0010(6)
O1	0.0054(5)	0.0035(3)	0.0052(8)	-0.0004(4)	0.0003(6)	0.0009(4)
O2	0.0026(5)	0.0038(3)	0.0049(7)	-0.0002(4)	0.0013(5)	0.0005(3)
O3	0.0019(4)	0.0047(3)	0.0069(7)	-0.0010(4)	0.0012(5)	-0.0006(3)
O4	0.0016(5)	0.0037(3)	0.0055(7)	0.0008(3)	0.0002(5)	-0.0003(3)
O5	0.0023(4)	0.0049(3)	0.0065(7)	0.0005(4)	0.0014(5)	0.0005(3)
O6	0.0028(5)	0.0069(4)	0.0094(7)	0.0000(4)	0.0026(5)	0.0011(4)
O7	0.0098(6)	0.0056(4)	0.0065(9)	0.0006(4)	0.0021(6)	0.0017(4)
O8	0.0084(7)	0.0106(5)	0.0123(11)	-0.0035(6)	0.0030(7)	-0.0029(5)
O9	0.0040(5)	0.0044(3)	0.0062(9)	-0.0007(4)	0.0011(6)	-0.0007(4)
O10	0.0053(6)	0.0083(4)	0.0093(10)	-0.0009(5)	0.0008(7)	-0.0006(4)
O11	0.0043(6)	0.0075(4)	0.0094(10)	0.0000(5)	0.0009(6)	-0.0002(4)
H1	0.0159(14)	0.0222(12)	0.020(2)	0.0008(12)	0.0010(13)	-0.0002(11)
H2	0.0178(12)	0.0159(9)	0.0264(16)	0.0027(10)	0.0063(11)	0.0062(9)
H3	0.0150(12)	0.0202(11)	0.0232(18)	-0.0044(11)	0.0059(12)	-0.0085(10)
H4	0.0224(15)	0.0163(10)	0.020(2)	-0.0008(11)	0.0068(14)	-0.0002(11)
H5	0.0213(16)	0.0244(14)	0.029(2)	0.0010(15)	0.0095(16)	-0.0038(14)
H6	0.0214(13)	0.0185(10)	0.0235(16)	-0.0045(11)	0.0064(11)	-0.0083(10)
H71	0.018(4)	0.022(3)	0.029(7)	-0.005(4)	0.008(4)	0.000(3)
H72	0.021(2)	0.0195(17)	0.016(3)	0.0053(18)	0.005(2)	0.0008(17)
H81	0.0170(19)	0.0234(16)	0.022(2)	-0.0018(15)	0.0058(14)	-0.0013(13)
H82	0.023(3)	0.024(2)	0.024(3)	0.0001(10)	0.0078(11)	-0.0002(10)
<i>Note:</i> B1, B2, B3, and B4 sites were modelled isotropically in the neutron structure refinement at 20 K						

749
750

751 Table 7. Relevant bond distances (Å) and angles (°) based on the X-ray refinement at 293 K and
752 neutron structure refinement at 20 K.
753

754

755

756

757

758

759

760

761

762

763

764

765

766

767

768

769

770

771

772

773

774

775

776

777

778

779

780

781

782

783

784

785

786

787

788

789

790

791

792

793

794

<i>X-ray</i> <i>T = 293 K</i>					
Na1-O8	2.2835(18)	O11-H1	0.94(2)	O8-H72	0.93(4)
Na1-O6	2.3879(17)	O11-H1*	0.97	O8-H72*	0.96
Na1-O4	2.3918(14)	O11...O2	2.669(2)	O8...O11	2.787(3)
Na1-O9	2.4095(15)	H1...O2	1.74(2)	H72...O11	1.93(4)
Na1-O2	2.4226(14)	O11-H1...O2	170(2)	O8-H72...O11	152(3)
Na1-O3	2.5058(15)				
		O11-H71	0.94(7)	O8-H82	0.94(4)
Na2-O11	2.2790(17)	O11-H71*	0.97	O8-H82*	0.97
Na2-O4	2.3880(15)	O11...O8	2.787(3)	O8...O11	2.814(3)
Na2-O10	2.4274(18)	H71...O8	1.86(6)	H82...O11	1.90(5)
Na2-O10'	2.4287(19)	O11-H71...O8	169(5)	O8-H82...O11	163(4)
Na2-O1	2.4791(16)				
Na2-O6	3.099(4)	O11-H81	0.92(4)	H6-O8-H72	102(3)
		O11-H81*	0.95	H6-O8-H82	100(4)
B1-O1	1.363(2)	O11...O8	2.814(3)		
B1-O7	1.370(2)	H81...O8	1.91(4)		
B1-O9	1.346(2)	O11-H81...O8	168(3)		
B2-O2	1.443(2)	H1-O11-H71	108(5)		
B2-O4	1.434(2)	H1-O11-H81	106(3)		
B2-O9	1.493(2)				
B2-O3	1.520(2)	O6-H2	0.93(2)		
		O6-H2*	0.96		
B3-O1	1.497(2)	O6...O5	3.292(2)		
B3-O2	1.450(2)	H2...O5	2.36(2)		
B3-O4	1.438(2)	O6-H2...O5	177(1)		
B3-O5	1.493(2)				
		O10-H3	0.91(3)		
B4-O3	1.352(2)	O10-H3*	0.94		
B4-O5	1.353(2)	O10...O3	2.790(2)		
B4-O6	1.384(3)	H3...O3	1.91(3)		
		O10-H3...O3	164(3)		
O1-B1-O9	122.8(2)	O7-H4	0.94(3)		
O7-B1-O9	118.7(2)	O7-H4*	0.97		
O1-B1-O7	118.5(2)	O7...O1	2.773(2)		
		H4...O1	1.84(3)		
O4-B2-O2	111.24(14)	O7-H4...O1	169(2)		
O4-B2-O9	109.61(14)				
O2-B2-O9	110.91(14)	O10-H5	0.92(4)		
O4-B2-O3	109.58(14)	O10-H5*	0.95		
O2-B2-O3	107.95(14)	O10...O5	2.869(2)		
O9-B2-O3	107.46(14)	H5...O5	1.96(4)		
		O10-H5...O5	168(3)		
O4-B3-O2	113.89(15)				
O4-B3-O5	111.57(14)	H3-O10-H5	101(3)		
O2-B3-O5	108.45(15)				
O4-B3-O1	105.85(14)	O8-H6	0.93(3)		
O2-B3-O1	110.79(14)	O8-H6*	0.96		
O5-B3-O1	106.00(14)	O8...O7	2.736(2)		
		H6...O7	1.81(3)		
O3-B4-O5	124.41(17)	O8-H6...O7	176(3)		
O3-B4-O6	120.31(17)				
O5-B4-O6	115.28(17)				

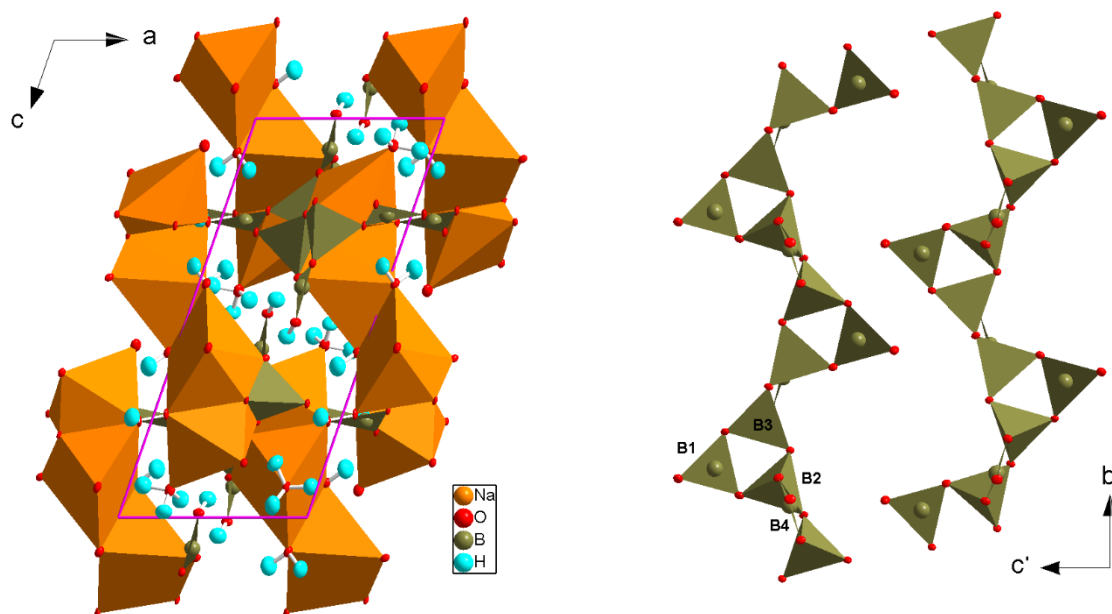
* Bond distance corrected for "riding motion" effect, following Busing and Levy (1964)

795
796
797
798
799
800
801
802
803
804
805
806
807
808
809
810
811
812
813
814
815
816
817
818
819
820
821
822
823
824
825
826
827
828
829
830
831
832
833
834
835
836
837
838
839

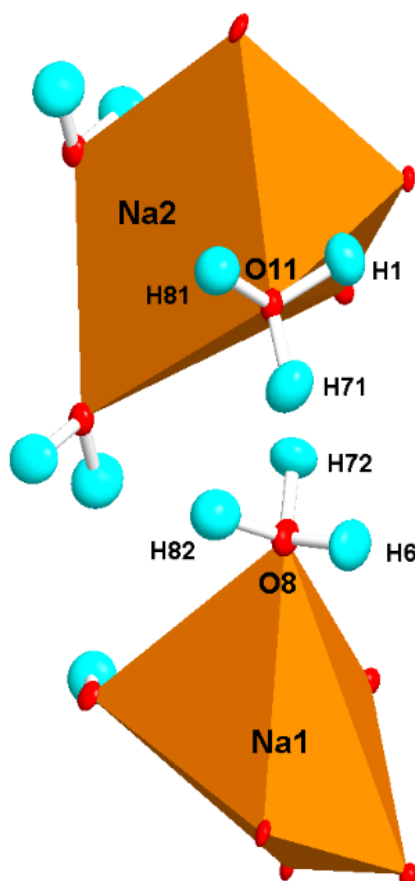
<i>Neutron</i> <i>T = 20 K</i>					
Na1-O8	2.294(5)	O11-H1	0.988(4)	O8-H72	1.000(8)
Na1-O6	2.377(2)	O11-H1*	1.003	O8-H72*	1.014
Na1-O4	2.395(4)	O11...O2	2.663(3)	O8...O11	2.769(3)
Na1-O9	2.393(2)	H1...O2	1.680(4)	H72...O11	1.800(9)
Na1-O2	2.422(4)	O11-H1...O2	173.0(4)	O8-H72...O11	162.2(7)
Na1-O3	2.493(3)				
		O11-H71	0.995(17)	O8-H82	1.038(13)
Na2-O11	2.291(3)	O11-H71*	1.012	O8-H82*	1.051
Na2-O4	2.382(3)	O11...O8	2.769(3)	O8...O11	2.796(3)
Na2-O10	2.411(3)	H71...O8	1.792(17)	H82...O11	1.773(14)
Na2-O10'	2.411(4)	O11-H71...O8	167(1)	O8-H82...O11	168(1)
Na2-O1	2.453(3)				
Na2-O6	3.134(21)	O11-H81	0.966(7)	H6-O8-H72	105.8(5)
		O11-H81*	0.981	H6-O8-H82	102.7(7)
B1-O1	1.3685(17)	O11...O8	2.796(3)		
B1-O7	1.375(3)	H81...O8	1.835(7)		
B1-O9	1.350(3)	O11-H81...O8	173.1(6)		
B2-O2	1.4457(16)	H1-O11-H71	108.4(7)		
B2-O4	1.4353(18)	H1-O11-H81	108.3(5)		
B2-O9	1.501(3)				
B2-O3	1.523(3)	O6-H2	0.960(4)		
		O6-H2*	0.978		
B3-O1	1.496(3)	O6...O5	3.273(2)		
B3-O2	1.454(3)	H2...O5	2.316(4)		
B3-O4	1.445(2)	O6-H2...O5	174.9(3)		
B3-O5	1.494(3)				
		O10-H3	0.974(4)		
B4-O3	1.363(3)	O10-H3*	0.988		
B4-O5	1.3577(17)	O10...O3	2.772(2)		
B4-O6	1.385(3)	H3...O3	1.818(4)		
		O10-H3...O3	165.7(4)		
O1-B1-O9	122.5(2)	O7-H4	0.977(4)		
O7-B1-O9	118.97(13)	O7-H4*	0.990		
O1-B1-O7	118.56(18)	O7...O1	2.759(3)		
		H4...O1	1.787(4)		
O4-B2-O2	110.93(11)	O7-H4...O1	172.4(3)		
O4-B2-O9	109.47(14)				
O2-B2-O9	110.90(18)	O10-H5	0.974(6)		
O4-B2-O3	109.79(18)	O10-H5*	0.994		
O2-B2-O3	107.92(13)	O10...O5	2.840(3)		
O9-B2-O3	107.76(12)	H5...O5	1.885(6)		
		O10-H5...O5	165.8(5)		
O4-B3-O2	113.7(2)				
O4-B3-O5	111.38(11)	H3-O10-H5	102.9(5)		
O2-B3-O5	108.49(11)				
O4-B3-O1	105.57(11)	O8-H6	0.974(4)		
O2-B3-O1	111.29(11)	O8-H6*	0.988		
O5-B3-O1	106.2(2)	O8...O7	2.737(2)		
		H6...O7	1.766(4)		
		O8-H6...O7	175.0(4)		
O3-B4-O5	123.67(19)				
O3-B4-O6	116.01(17)				
O5-B4-O6	120.32(12)				

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

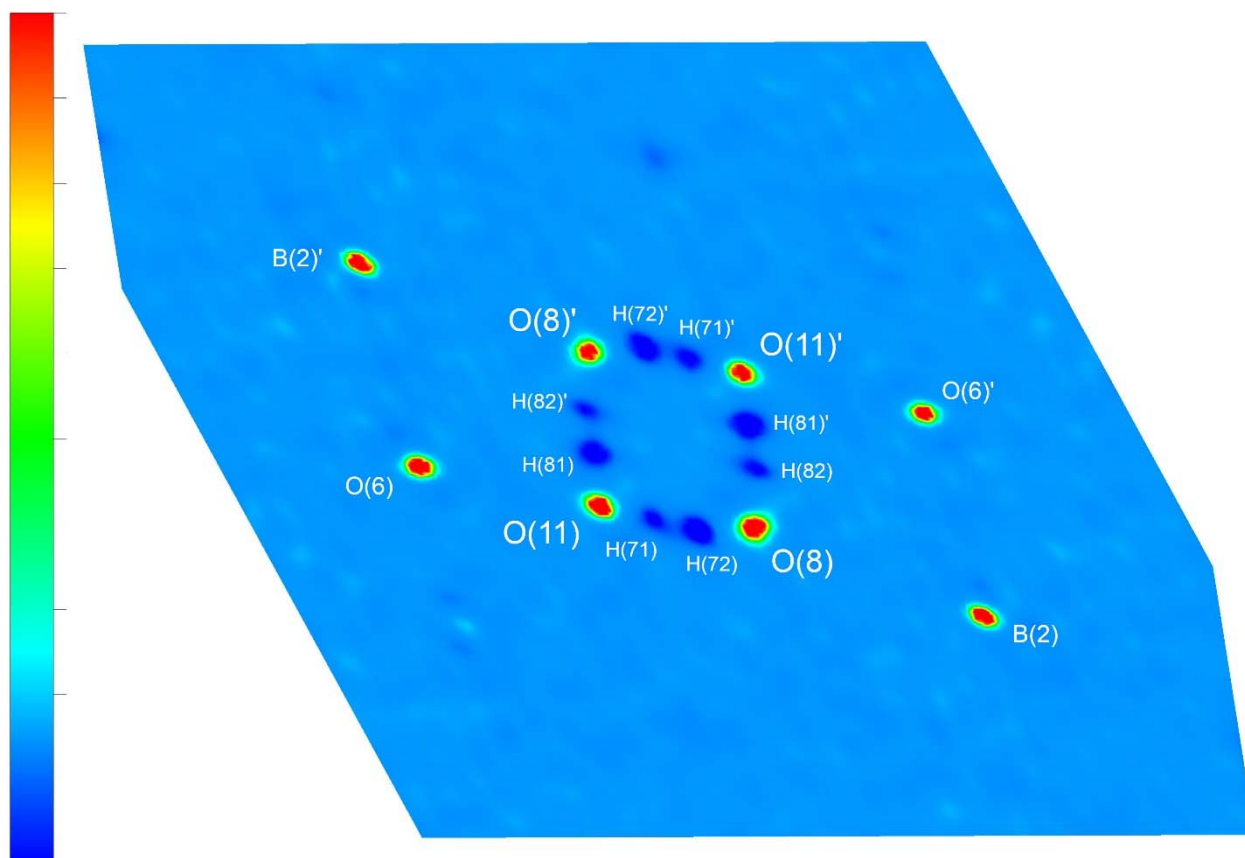
840 Figure 1. The crystal structure of kernite viewed down [010] (*left side*), along with the infinite chains
841 of 3-fold rings ($3\text{B}:\Delta + 2\text{T}$ units) running along [010] (*right side*), based on the neutron structure
842 refinement of this study (intensity data collected at 20 K). Displacement ellipsoid probability factor:
843 70%.



856 Figure 2. Positional disorder of the H sites in the structure of kernite, based on the neutron structure
 857 refinement of this study (intensity data collected at 20 K). The mutually exclusive configurations are:
 858 (H6-O8-H82 + H1-O11-H71) and (H6-O8-H72 + H1-O11-H81); $s.o.f.(H6) = 1$, $s.o.f.(H1) = 1$,
 859 $[s.o.f.(H72)+s.o.f.(H82)] = 1$, $[s.o.f.(H71)+s.o.f.(H81)] = 1$. Displacement ellipsoid probability factor:
 860 70%.



910 Figure 3. Section of the nuclear density function, corresponding to the (0.1, 0.5, 0.6) plane (which
 911 contains O8, O11 and symmetry-related H₂O molecules), calculated using the maximum-entropy
 912 method applied to the neutron intensity data collected at 20 K. A grid of 256 x 256 x 256 voxels was
 913 used to obtain a detailed density map. Further details are given in the text. Graphical representation
 914 by VESTA. Colour bar: maxima at the top, minima at the bottom of the nuclear density. Atom labels
 915 showing a prime involve that those atoms are generated by application of a symmetry operator.
 916
 917



918
 919
 920
 921
 922
 923
 924
 925
 926
 927
 928

929
930
931
932
933
934
935
936
937
938
939
940
941
942
943
944
945
946
947

Figure 4. The complex H-bonding network into the crystal structure of kernite, based on the neutron structure refinement (data collected at 20 K). Details in Table 7. Displacement ellipsoid probability factor: 70%.

