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

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## 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  $\text{H}_2\text{O}$  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  $\text{BO}_2\text{OH}$  groups and two tetrahedral  $\text{BO}_4$  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  $\text{H}_2\text{O}$  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  $^{10}\text{B}$  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:  $^{10}\text{B}$  shows a  
103 high capacity to absorb thermal neutrons due to its high cross section for the  $^{10}\text{B}(n,\alpha)^7\text{Li}$  reaction ( $\sim 3840$   
104 barns; Carter et al. 1953, Sears 1986, Palmer and Swihart 1996, Rauch and Waschkowski 2002), whereas  
105 that of  $^{11}\text{B}$  is almost irrelevant ( $\sim 0.006$  barns). About 20% of natural boron occurs as  $^{10}\text{B}$ .

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[B<sub>3</sub>O<sub>3</sub>(OH)<sub>5</sub>]·5H<sub>2</sub>O, 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 B<sub>2</sub>O<sub>3</sub> 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*2<sub>1</sub>/*c*  
117 space group, with  $a \cong 7.02 \text{ \AA}$ ,  $b \cong 9.15 \text{ \AA}$ ,  $c \cong 15.68 \text{ \AA}$ , and  $\beta \cong 108.9^\circ$  ( $Z = 4$ ). As observed in other  
118 borates (*e.g.*, colemanite, kurnakovite), even kernite contains both triangular planar BO<sub>2</sub>OH- and  
119 tetrahedral BO<sub>4</sub>-groups (Fig. 1). Two independent Na sites are sixfold-coordinated by O atoms, OH-  
120 groups and H<sub>2</sub>O molecules. One triangular BO<sub>2</sub>OH group and two tetrahedral BO<sub>4</sub> 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 Kloprogge  
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), Kloprogge 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 Å<sup>2</sup>) than others, which  
134 could reflect a positional (static or dynamic) disorder. The occurrence of hydroxyl groups and cation-  
135 coordinated H<sub>2</sub>O, which account for a total H<sub>2</sub>O 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

142 the chemical composition of the sample (*i.e.*, titrimetric determination of B content, gravimetric method  
143 for Na, ion selective electrode for F, high-*T* mass loss for H<sub>2</sub>O content, inductively coupled plasma  
144 atomic emission spectroscopy - ICP-AES - for REE and other minor elements, elemental analysis for  
145 C, N and H content). With this multi-methodological approach, we can provide: a description of the  
146 chemical composition of kernite in terms of major and minor components, with a particular attention to  
147 the potential B- and Na-substituents; an unambiguous location of all the proton sites and their vibrational  
148 regime, along with a picture of the complex H-bonding network; a description of B-coordination  
149 environment (*e.g.*, aplanarity of the triangular BO<sub>2</sub>(OH)-group, polyhedral distortion of the tetrahedral  
150 BO<sub>2</sub>(OH)<sub>2</sub>-groups).

151 The experimental findings of this study will be pivotal to fully understand if kernite can act as a carrier  
152 of other technologically-relevant elements (*e.g.*, Li, Be, REE), its conditions of formation and  
153 occurrence, its behaviour at non-ambient *P-T* conditions and the chemical reactivity, as its structure  
154 stability appears to be substantially governed by the H-bonding network.

155

### 156 **Sample description and occurrence**

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

161 The specimen was collected at the Kramer Deposit, Mohave desert, Kern County, California. Over  
162 80 minerals were reported occurring in this deposit including a number of borates: borax, colemanite,  
163 greigite, hydroboracite, inderite, inyoite, kernite, kurnakovite, meyerhofferite, probertite, searlesite,  
164 tinalconite, tunellite and ulexite (Noble 1926, Schaller 1930, Morgan and Erd, 1969, Puffer 1975).

165 The Kramer deposit consists of a lenticular mass of kernite, borax and lower fraction of colemanite  
166 and ulexite, measuring 1.6 km long, 0.8 km wide and up to 100 m thick. The borate minerals, several  
167 hundred feet underground, occur in a complex clay series, underlain by igneous rock composed by  
168 basaltic lavas, upper Miocenic in age and overlain by a stratigraphic series of continental arkosic  
169 sands (Obert and Long 1962, Siefke 1991). For tens of meter deep, kernite is the only borate observed  
170 in the deposit and it is the dominant mineral, so that the clay matrix is almost negligible in amount  
171 (Schaller 1930). The mode of occurrence shows the deposit was originally composed only of borax  
172 at the floor of a saline lake. Kernite increases abundance with depth, indicating that dehydration of  
173 borax increases as a result of depth and pressure. Borax dehydration to kernite occurs under natural  
174 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 B<sub>2</sub>O<sub>3</sub> 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 Na<sub>2</sub>O 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 H<sub>2</sub>O 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 H<sub>2</sub>O, the estimated H<sub>2</sub>O 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

241 between 0.05 and 1.0 mg/l for each element (using CRM multi elemental standard mix  
242 for ICP).  
243 ii) Decomposition by alkaline fusion of 10-20 mg of kernite sample in platinum crucible  
244 with 100 mg of sodium or potassium carbonate in a muffle furnace at 1000°C for 5  
245 minutes, followed by dissolution in 10 ml of water and 1 ml of sulphuric acid 1M or 1  
246 ml of hydrochloric acid 1M. The clear solution was then transferred and diluted with  
247 water in a 25 ml volumetric flask containing 2.5 ml of scandium solution (100 mg/l)  
248 as internal standard. A calibration protocol was adopted with a blank solution and a  
249 series of 5 solutions prepared with concentration ranging between 0.05 and 1.0 mg/l  
250 for each element (using CRM multi elemental standard mix for ICP).  
251 Results and instrumental parameters are given in Table 2.

252  
253

#### 254 **6) Determination of C, N, and H**

255 200-300 mg of mineral sample were decomposed at 950°C in an elementary analyzer LECO  
256 Truspec CHN, in excess of oxygen for 90 seconds. The decomposition products were transferred to  
257 a second furnace (Afterburner) at 850°C for a further oxidation and particulate removal. After  
258 collection and homogenization of the gases in a container of 4.5 liters at 50°C, Infrared absorption  
259 detectors were used to measure the CO<sub>2</sub> and H<sub>2</sub>O concentration (as the C concentration was measured  
260 in the form of CO<sub>2</sub> and the H one in the form of H<sub>2</sub>O). A different portion of the decomposition  
261 products was instead transferred in a stream of helium through a copper catalyst in order to convert  
262 NO<sub>x</sub> to N<sub>2</sub> and to remove oxygen, carbon dioxide and water. A thermal conductivity detector was  
263 used to determine the N<sub>2</sub> content. EDTA, sodium tetra-borate deca-hydrate, boric acid, calcium  
264 carbonate, sodium nitrate and acid oxalic di-hydrate were employed as calibration standards. The  
265 measured fractions were: C < 0.02 wt% (uncertainty not determined), N < 0.02 wt% (uncertainty not  
266 determined), and H = 3.0(2) wt%.

267

268 A representative chemical composition of kernite from the Kramer deposit is given in Table 3, and  
269 its experimental chemical formula is virtually identical to the ideal one: Na<sub>2</sub>B<sub>4</sub>O<sub>6</sub>(OH)<sub>2</sub>·3H<sub>2</sub>O.

270

271



## 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 $\alpha$  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 CrysAlisPro<sup>TM</sup> suite (Rigaku – Oxford Diffraction 2019), with  $\omega$  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  $V = 946.53(7)$  Å<sup>3</sup> (Table 4). Corrections for Lorentz-polarization effects and (semi-empirical) X-ray absorption were applied using the *ABSPACK* routine, implemented in the CrysAlisPro<sup>TM</sup> 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 mm<sup>3</sup>) 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  $\omega$ -scans or  $\omega$ - $2\theta$  scans for low and high-Q reflections, respectively. The Bragg reflections were collected varying the  $\omega$ -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 H<sub>2</sub>O 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  $\text{Na}^+$  here detected, distributed in the two independent Na1 and Na2 sites and giving distorted  
358 coordination polyhedra with CN = 6, are represented by  $\text{Mg}^{2+}$  and  $\text{K}^+$ , but their sum is less than 0.01  
359 *a.p.f.u.* (Table 3). Similarly, the only potential substituents of  $\text{B}^{3+}$  (in tetrahedral coordination) are  
360  $\text{Si}^{4+}$  and  $\text{Al}^{3+}$ , but for less than 0.01 *a.p.f.u.* (Tables 2 and 3). Even the  $\text{F}^-$  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

371 protocol was used; Gatta et al. 2019a; Lotti et al. 2018, 2019), appears not to be a peculiarity of the  
372 single species or of a given deposit, but it is rather a common feature of the hydrous borates which  
373 share the same geological environment: lacustrine deposits with hydrothermal activity. The reasons  
374 for such a high purity are still obscure: whereas it is more difficult to find a substituent of B (in CN 3  
375 or 4), which generates a low chemical strain into the structure, Na could be efficiently replaced by  
376 alkaline or even earth-alkaline cations, if we consider the bonding configuration of the (distorted) Na-  
377 polyhedra in the kernite structure (Table 7). The same considerations, though referred to different  
378 cations, were previously done on colemanite and kurnakovite by Gatta et al. (2019a). However, the  
379 chemical composition of a given hydrothermal mineral it is not only dictated by its crystal structure,  
380 but even by the composition of the solution. In this light, a possible explanation is that crystal  
381 nucleation and growth could promote purification by iterated dissolution and recrystallization.

382 The structure model of kernite obtained in this study, based on X-ray and neutron diffraction  
383 data, is (partially) consistent with that previously reported by Cooper et al. (1973). The structure is  
384 built by two crystallographically independent triangular  $\text{BO}_2\text{OH}$  groups (with the B-ions in  $sp^2$   
385 electronic configuration) and two tetrahedral  $\text{BO}_4$  groups (with the B-ions in  $sp^3$  electronic  
386 configuration), which share corner-bridging O atoms to form 3-fold rings ( $3\text{B}:\Delta + 2\text{T}$  units), giving  
387 chains running along  $[010]$  and held together by hydrogen bonding (Fig. 1). Two independent Na sites  
388 are sixfold-coordinated by O atoms, OH-groups and  $\text{H}_2\text{O}$  molecules, though the bonding configuration  
389 of the strongly distorted Na2-polyhedron would suggest a CN = 5+1, as five Na2-O distances are shorter  
390 than 2.5 Å and one is about 3.1 Å (Table 7, room- $T$  X-ray refinement).

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

393 1) The triangular  $[\text{BO}_2(\text{OH})]$ -groups have an almost ideal configuration, with  $\Delta(\text{B1-O})_{\text{max}} \sim$   
394  $\Delta(\text{B4-O})_{\text{max}} \sim 0.02\text{-}0.03$  Å (*i.e.*, the difference between the longest and the shortest bond  
395 distances), average O-B-O angles of  $120^\circ$  (ranging between  $118.5^\circ\text{-}122.8^\circ$  for B1- and  
396  $115.3^\circ\text{-}124.4^\circ$  for B4-triangular groups), and aplanarity  $< 1^\circ$  (here defined as the average  
397 angle described by the plane on which the 3-oxygen sites lie and each of the three  
398 independent B- $\text{O}_n$  vectors); the tetrahedral  $[\text{BO}_4]$ -groups are only slightly distorted, with  
399  $\Delta(\text{B2-O})_{\text{max}} \sim \Delta(\text{B3-O})_{\text{max}} \sim 0.06$  Å; the  $\text{Na1O}_4(\text{OH})(\text{OH}_2)$  polyhedron has  $\Delta(\text{Na1-O})_{\text{max}} \sim$   
400  $0.22$  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  
401 B-O and Na-O distances are slightly different as a function of bonding configuration of the  
402 oxygen sites (*i.e.*, oxygen of a OH- or  $\text{OH}_2$ -group or as a bridging site between polyhedra).

403 2) Three crystallographically independent H<sub>2</sub>O molecules occur in the structure of kernite (*i.e.*,  
404 H3-O10-H5, H6-O8-H72 or H6-O8-H82, H1-O11-H71 or H1-O11-H81, Table 7). Among  
405 those, two are affected by positional disorder of the H sites, so that two mutually exclusive  
406 configurations occur, here modelled as: (H6-O8-H82 + H1-O11-H71) or (H6-O8-H72 +  
407 H1-O11-H81) (Figs. 2 and 4). The results obtained by the structure refinements are  
408 consistent with a model based on a static disorder of the H sites, rather than a dynamic one.  
409 The nuclear density distribution around pairs of the oxygen atoms O8 and O11 obtained by  
410 MEM confirm a double well potential, which gives rise to a splitting of the H sites (Fig. 3).  
411 The nuclear density maps indicate that the H71/H72 and H81/H82, and those related by  
412 symmetry, could be modelled using a statically disordered configuration with hydrogen  
413 atoms filling two well defined sites. The unbalanced nuclear density between each hydrogen  
414 position suggests a non-equivalent occupancy of each site, in agreement with the refined  
415 structural model (Table 5). However, other scenarios could also explain the observed H  
416 network. Two different hydrogen networks are derived from the current model, one  
417 configuration if H71 and H82 are present and a second for the case of H72 and H81. The  
418 H71 and H72 sites could be seen as a splitting of the hydrogen atom located between two  
419 opposite oxygen sites (in this case: O8 and O11). A similar scenario was reported for ice  
420 phases, where the jump between both configurations was ascribed to “proton tunnelling”  
421 (Bove et al. 2009, Yen and Gao 2015). The tunnelling occurs at low temperature when a  
422 proton has the same probability to be located on each minimum of a double well potential.  
423 Therefore, this effect involves, in most of the cases, symmetric potentials. In our case, the  
424 nuclear density maps obtained from the MEM clearly show that both sites have not the same  
425 density, and therefore a different energy barrier occurs in each well of potential. Although  
426 a proton tunnelling could not completely discarded, based on the current results this scenario  
427 is unlikely.

428 It is worth noting that a similar kind of disorder of the H<sub>2</sub>O hydrogen atoms also occurs in  
429 colemanite (Lotti et al. 2018), leading to two possible (and mutually exclusive) H-bonding  
430 configurations.

431 3) Geometrically, the three crystallographically independent H<sub>2</sub>O molecules show: *a*) H-O-H  
432 angles ranging between 102° and 108° (neutron data), consistent with the observed H-O-H  
433 angles in solid-state materials (*e.g.*, Steiner 1998, and references therein; Gatta et al. 2008,  
434 2012, 2019a; Lotti et al. 2018); *b*) O-H distances (corrected for “riding motion effect”  
435 following Busing and Levy 1964) ranging between 0.98 and 1.05 Å (neutron data); *c*) O–

436 H...O angles  $\geq 162^\circ$  (Table 7), approaching a configuration energetically favourable (*i.e.*,  
437 toward linearity), and  $O_{donor}...O_{acceptor}$  distances of about 2.7-2.8 Å (Table 7, neutron data).  
438 The two independent hydroxyl groups (*i.e.*, O6-H2 and O7-H4, Table 7) show O-H  
439 distances (corrected for “riding motion effect”) ranging between 0.98-0.99 Å,  
440  $O_{donor}...O_{acceptor}$  distances between 2.8-3.3 Å, and O-H...O  $>172^\circ$  (Table 7, neutron data).  
441 4) If we exclude O4 and O9, all the other oxygen sites in the structure of kernite are involved  
442 in H-bonding, as *donors* or as *acceptors* (Fig. 4, Table 7).  
443 5) The X-ray and neutron refinements, based on the intensity data collected at 293 and 20 K  
444 respectively, show that this borate does not experience any *T*-induced phase transition,  
445 within the *T*-range investigated. The two structure models are virtually identical. As  
446 expected, there is a drastic reduction of the magnitude of the atomic displacement ellipsoids  
447 at low *T*, as shown by the  $U_{eq}$  values (calculated as one third of the trace of the  
448 orthogonalised  $U_{ij}$  tensor, Tables 5 and 6 - *deposited*). Some of the atomic displacement  
449 ellipsoids are significantly anisotropic at 20 K (Table 6 - *deposited*, Figs. 1, 2 and 4), though  
450 still realistic. We are inclined to believe that this is the twofold effect generated by: *a*) a not  
451 efficient correction for the extinction effect with the isotropic model of Larson (1967) and  
452 *b*) the static disorder of the H-sites belonging the H<sub>2</sub>O molecules of the Na1- and Na2-  
453 polyhedra, which affect all the sites of the Na-coordination shells.

454 The structure model obtained in this study is consistent with the FT-IR and Raman spectra of kernite  
455 reported and interpreted by Jun et al. (1995), Klopogge and Frost (1999) and Silva et al. (2018). The  
456 experimental findings of this study confirm that also in kernite, as for other hydrous borates (Gatta et  
457 al. 2019a), the H-bonding network is complex, pervasive and play a primary role into the crystalline  
458 edifice. This could also explain the almost insignificant F<sup>-</sup> (or even Cl<sup>-</sup>) *vs.* OH<sup>-</sup> substitution (Table  
459 3). The first implication on potential utilizations of kernite is that any environmental variable able to  
460 affect the H-bonding network (*i.e.*, under chemical, thermal or compressional stress conditions) can  
461 generate a structure instability. This can be deduced, for example, by the thermal behaviour of kernite  
462 reported by Sennova et al. (2005; without structure refinement) or by the static compressional  
463 behaviour reported by Silva et al. (2018; without structure refinement), along with the reported  
464 solubility in water (Mineral Data Publishing, <http://rruff.info/doclib/hom/kernite.pdf>). However, the  
465 mechanisms, at the atomic scale, that govern the thermal and compressional behaviour of kernite are  
466 still obscure, and will be the aim of our future experiments, based on *in situ* X-ray diffraction  
467 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 ( $B_2O_3$ ~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  $Na_2O + 0.658K_2O$ , 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

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

605

|     | %m/m                           | ICP-AES (nm) | LOD     | LOQ    |        |
|-----|--------------------------------|--------------|---------|--------|--------|
| 606 | Ce <sub>2</sub> O <sub>3</sub> | < LOD        | 413.764 | 0.003  | 0.01   |
|     | Dy <sub>2</sub> O <sub>3</sub> | < LOD        | 353.170 | 0.0001 | 0.0003 |
| 607 | Er <sub>2</sub> O <sub>3</sub> | < LOD        | 369.265 | 0.002  | 0.007  |
|     | Eu <sub>2</sub> O <sub>3</sub> | < LOD        | 381.967 | 0.0001 | 0.0003 |
| 608 | Gd <sub>2</sub> O <sub>3</sub> | < LOD        | 342.247 | 0.0003 | 0.001  |
|     | Ho <sub>2</sub> O <sub>3</sub> | < LOD        | 345.600 | 0.0001 | 0.0003 |
| 609 | La <sub>2</sub> O <sub>3</sub> | < LOD        | 398.852 | 0.0001 | 0.0003 |
|     | Lu <sub>2</sub> O <sub>3</sub> | < LOD        | 261.542 | 0.0002 | 0.0006 |
| 610 | Nd <sub>2</sub> O <sub>3</sub> | < LOD        | 406.109 | 0.0002 | 0.0006 |
|     | Pr <sub>2</sub> O <sub>3</sub> | < LOD        | 390.844 | 0.0002 | 0.0006 |
| 611 | Sm <sub>2</sub> O <sub>3</sub> | < LOD        | 359.260 | 0.0005 | 0.002  |
|     | Sc <sub>2</sub> O <sub>3</sub> | < LOD        | 361.383 | 0.0005 | 0.002  |
| 612 | Tb <sub>2</sub> O <sub>3</sub> | < LOD        | 350.917 | 0.0005 | 0.002  |
|     | Tm <sub>2</sub> O <sub>3</sub> | < LOD        | 313.126 | 0.004  | 0.015  |
| 613 | Yb <sub>2</sub> O <sub>3</sub> | < LOD        | 328.937 | 0.0001 | 0.0003 |
|     | Y <sub>2</sub> O <sub>3</sub>  | < LOD        | 371.029 | 0.0001 | 0.0003 |
| 614 | ThO <sub>2</sub>               | < LOD        | 283.730 | 0.001  | 0.004  |
| 615 | UO <sub>2</sub>                | < LOD        | 385.958 | 0.01   | 0.04   |

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

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

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|     | %m/m                           | ICP-AES (nm) |         | %m/m                           | ICP-AES (nm) |         |
|-----|--------------------------------|--------------|---------|--------------------------------|--------------|---------|
| 620 | Li <sub>2</sub> O              | < 0.01       | 670.784 | NiO                            | < 0.01       | 231.604 |
|     | MgO                            | 0.01         | 285.213 | CuO                            | < 0.01       | 327.393 |
| 621 | K <sub>2</sub> O               | 0.02         | 766.490 | Ag <sub>2</sub> O              | < 0.01       | 328.068 |
|     | Rb <sub>2</sub> O              | < 0.02       | 780.023 | ZnO                            | < 0.01       | 206.200 |
| 622 | Cs <sub>2</sub> O              | < 0.02       | 455.531 | CdO                            | < 0.01       | 228.802 |
|     | BeO                            | < 0.01       | 313.107 | Al <sub>2</sub> O <sub>3</sub> | 0.01         | 396.153 |
| 623 | CaO                            | < 0.01       | 317.933 | Tl <sub>2</sub> O              | < 0.02       | 190.801 |
|     | BaO                            | < 0.02       | 233.527 | PbO                            | < 0.05       | 220.353 |
| 624 | TiO <sub>2</sub>               | < 0.01       | 334.940 | P <sub>2</sub> O <sub>5</sub>  | < 0.02       | 213.617 |
|     | ZrO <sub>2</sub>               | < 0.01       | 343.823 | As <sub>2</sub> O <sub>3</sub> | < 0.02       | 193.696 |
| 625 | V <sub>2</sub> O <sub>5</sub>  | < 0.02       | 292.464 | Sb <sub>2</sub> O <sub>3</sub> | < 0.02       | 206.836 |
|     | Cr <sub>2</sub> O <sub>3</sub> | < 0.01       | 267.716 | Bi <sub>2</sub> O <sub>3</sub> | < 0.02       | 223.061 |
| 626 | MoO <sub>3</sub>               | < 0.02       | 202.031 | SiO <sub>2</sub>               | 0.01         | 251.611 |
|     | MnO                            | < 0.01       | 257.610 | SrO                            | < 0.01       | 407.771 |
|     | Fe <sub>2</sub> O <sub>3</sub> | < 0.01       | 238.204 | B <sub>2</sub> O <sub>3</sub>  | *            | 249.677 |
|     | CoO                            | < 0.01       | 228.616 | Na <sub>2</sub> O              | *            | 589.592 |

\* 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.  
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| <i>Oxides</i>   | <i>Wt%</i>      | <i>e.s.d.</i> |
|---|-----------------|---------------|
| B <sub>2</sub> O <sub>3</sub>   | 50.90           | ± 0.20        |
| Na <sub>2</sub> O   | 22.55           | ± 0.20        |
| SiO <sub>2</sub>  | 0.01            | ± n.d         |
| Al <sub>2</sub> O <sub>3</sub>  | 0.01            | ± n.d         |
| MgO   | 0.01            | ± n.d         |
| K <sub>2</sub> O  | 0.02            | ± n.d         |
| F <sup>-</sup>  | 0.01            | ± n.d         |
| H <sub>2</sub> O  | 26.40           | ± 0.20        |
| TOTAL   | 99.91           |               |
| <i>Elements</i>   |                 |               |
| B <sup>3+</sup>   | <i>a.p.f.u.</i> |               |
| Na <sup>+</sup>   | 3.99            |               |
| Si <sup>4+</sup>  | 1.99            |               |
| Al <sup>3+</sup>  | <0.01           |               |
| Mg <sup>2+</sup>  | <0.01           |               |
| K <sup>+</sup>  | <0.01           |               |
| F <sup>-</sup>  | <0.01           |               |
| H <sup>+</sup>  | 8.02            |               |
| Empirical formula:<br>Na <sub>1.99</sub> B <sub>3.99</sub> O <sub>6</sub> (OH) <sub>2</sub> ·3.01H <sub>2</sub> O<br>Ideal formula:<br>Na <sub>2</sub> B <sub>4</sub> O <sub>6</sub> (OH) <sub>2</sub> ·3H <sub>2</sub> O |                 |               |

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

|   |  |   |
|---|--|---|
| <i>T</i> (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  | <i>a</i> = 6.996(1) Å<br><i>b</i> = 9.128(3) Å<br><i>c</i> = 15.608(3) Å<br>$\beta$ = 109.06(3)°<br><i>V</i> = 942.0(4) Å <sup>3</sup> | <i>a</i> = 6.9983(3) Å<br><i>b</i> = 9.1375(3) Å<br><i>c</i> = 15.6389(7) Å<br>$\beta$ = 108.832(5)°<br><i>V</i> = 946.53(7) Å <sup>3</sup> |
| Chemical formula  | Na <sub>2</sub> B <sub>4</sub> O <sub>6</sub> (OH) <sub>2</sub> ·3H <sub>2</sub> O   | Na <sub>2</sub> B <sub>4</sub> O <sub>6</sub> (OH) <sub>2</sub> ·3H <sub>2</sub> O  |
| Space Group   | <i>P</i> 2 <sub>1</sub> / <i>c</i>   | <i>P</i> 2 <sub>1</sub> / <i>c</i>  |
| <i>Z</i>  | 4  | 4   |
| Radiation type, $\lambda$ (Å)   | Neutron CW, 0.8347   | X-ray, MoK $\alpha$   |
| Diffractometer  | D9 four-circle - ILL   | Rigaku XtaLABSynergy-i  |
| Data-collection method  | $\omega$ -scans, $\omega$ -2 $\theta$ scans  | $\omega$ -scans   |
| <i>d</i> <sub>min.</sub> (Å)  | 0.59   | 0.71  |
|   | -10 ≤ <i>h</i> ≤ +10   | -9 ≤ <i>h</i> ≤ +8  |
|   | 0 ≤ <i>k</i> ≤ +18   | -12 ≤ <i>k</i> ≤ +12  |
|   | -23 ≤ <i>l</i> ≤ +24   | -19 ≤ <i>l</i> ≤ +20  |
| Measured reflections  | 3434   | 13010   |
| Unique reflections  | 3161   | 2296  |
| Unique reflections with <i>F</i> <sub>o</sub> > 4σ( <i>F</i> <sub>o</sub> )                 | 2656   | 1908  |
| Refined parameters  | 226  | 193   |
| Extinction coeff.   | 0.014(2)   | 0.001(1)  |
| <i>R</i> <sub>int</sub>   | 0.0488   | 0.0361  |
| <i>R</i> <sub>σ</sub>   | 0.0557   | 0.0259  |
| <i>R</i> <sub>1</sub> ( <i>F</i> ) with <i>F</i> <sub>o</sub> > 4σ( <i>F</i> <sub>o</sub> ) | 0.0723   | 0.0324  |
| <i>R</i> <sub>1</sub> ( <i>F</i> ) for all reflections                                      | 0.0884   | 0.0412  |
| <i>wR</i> <sub>2</sub> ( <i>F</i> <sup>2</sup> )  | 0.1491   | 0.0655  |
| GooF  | 1.636  | 1.519   |
| Residuals (fm/Å <sup>3</sup> , e <sup>-</sup> /Å <sup>3</sup> )                             | -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 ( $\text{\AA}^2$ ) 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.  
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| Site | X-ray 293 K |             |             |              |           | Neutron 20 K |            |             |              |                  |
|------|-------------|-------------|-------------|--------------|-----------|--------------|------------|-------------|--------------|------------------|
|      | s.o.f.      | x/a         | y/b         | z/c          | $U_{eq}$  | s.o.f.       | x/a        | y/b         | z/c          | $U_{eq}/U_{iso}$ |
| 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)         |

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717 Table 6 (*deposited*). Refined displacement parameters ( $\text{\AA}^2$ ) of kernite in the expression: -  
 718  $2\pi^2[(ha^*)^2U_{11} + \dots + 2hka^*b^*U_{12} + \dots + 2klb^*c^*U_{23}]$ , based on the X-ray refinement at 293 and neutron  
 719 structure refinement at 20 K.  
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| <b><i>T</i> = 293 K</b> | $U_{11}$   | $U_{22}$   | $U_{33}$   | $U_{23}$   | $U_{13}$   | $U_{12}$   |
|-------------------------|------------|------------|------------|------------|------------|------------|
| 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) |

*Note:* All the H sites were modelled isotropically in the X-ray structure refinement at 293 K

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| <b><i>T = 20 K</i></b> | $U_{11}$   | $U_{22}$   | $U_{33}$   | $U_{23}$    | $U_{13}$   | $U_{12}$    |
|------------------------|------------|------------|------------|-------------|------------|-------------|
| 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) |

*Note:* B1, B2, B3, and B4 sites were modelled isotropically in the neutron structure refinement at 20 K

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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.  
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| <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)

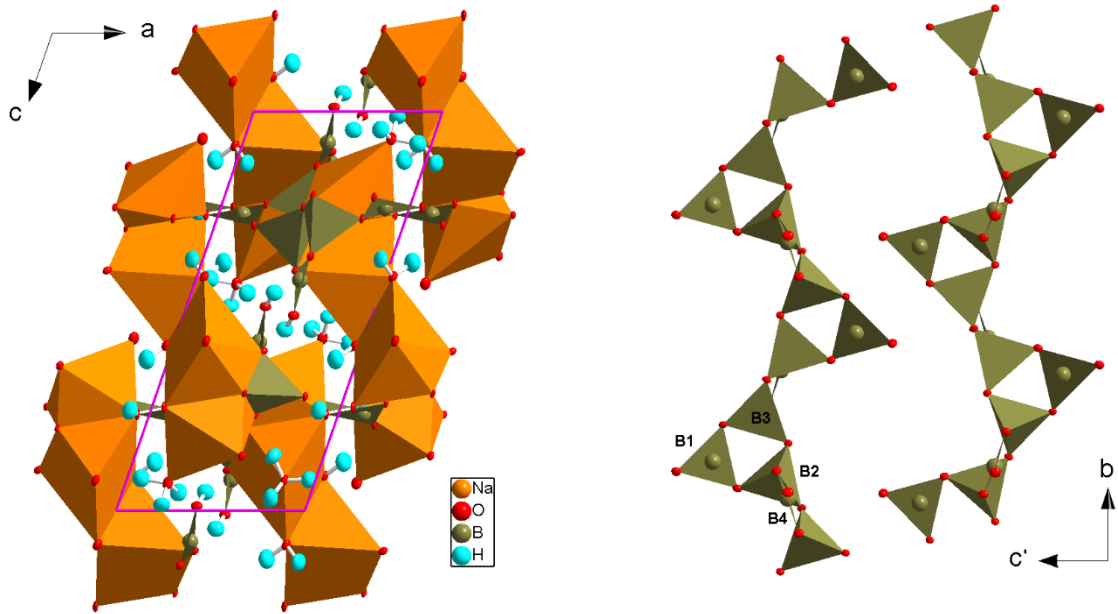
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| <i>Neutron</i>  |            |              |           |              |           |
|-----------------|------------|--------------|-----------|--------------|-----------|
| <i>T = 20 K</i> |            |              |           |              |           |
| 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      | 1.68084   | 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) |              |           |              |           |

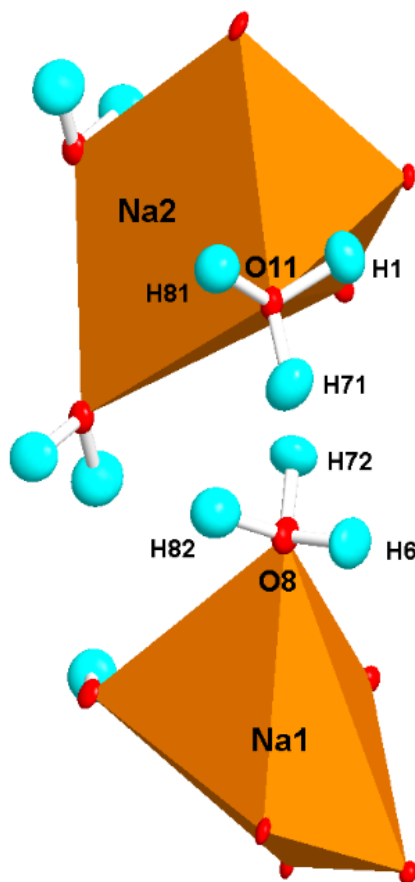
\* Bond distance corrected for "riding motion" effect, following Busing and Levy (1964)

840 Figure 1. The crystal structure of kernite viewed down [010] (*left side*), along with the infinite chains  
841 of 3-fold rings (3B: $\Delta$  + 2T 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%.

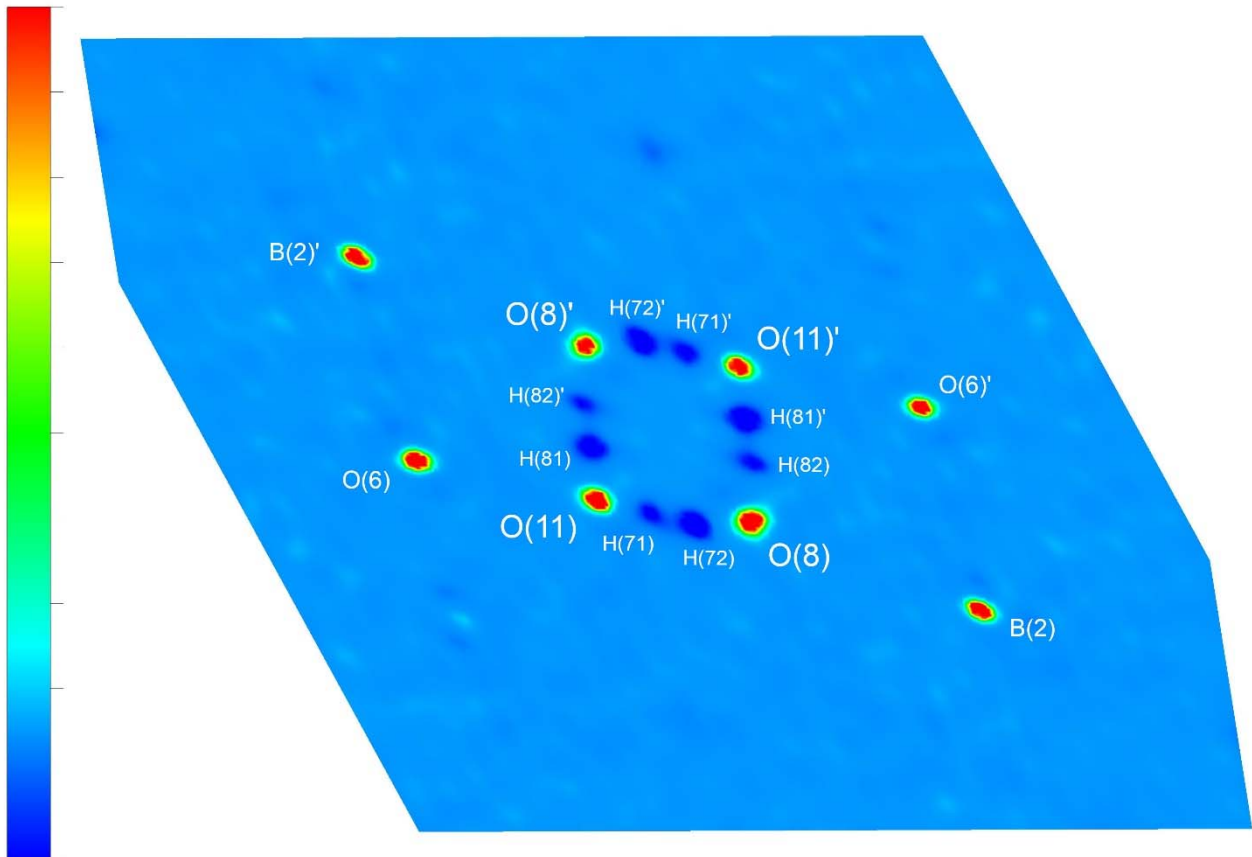
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856 Figure 2. Positional disorder of the H sites in the structure of kernite, based on the neutron structure  
857 refinement of this study (intensity data collected at 20 K). The mutually exclusive configurations are:  
858 (H6-O8-H82 + H1-O11-H71) 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 H<sub>2</sub>O 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.  
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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%.

