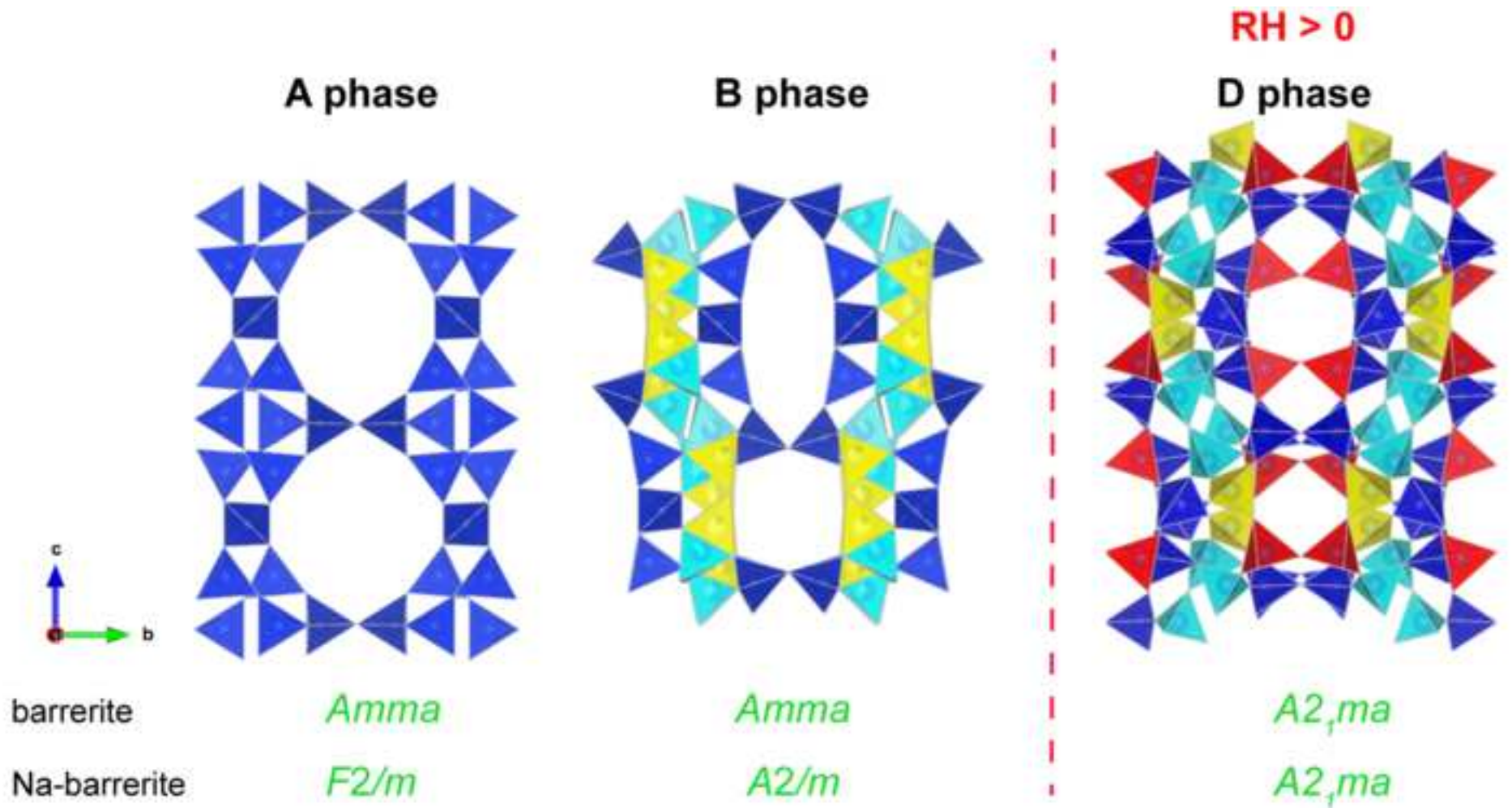


- Na-exchanged barrerite was found to be monoclinic ($F2/m$) similarly to stilbite
- D phase did not occur under dry (RH = 0) experimental conditions
- D phase of Na-exchanged barrerite was determined by *ex-situ* experiment
- A precursor model from B to D phase is suggested



1 Thermal Stability of Barrerite and Na-exchanged Barrerite: an *in situ* Single Crystal X- 2 ray Diffraction Study Under Dry Conditions

3 Georgia Cametti^{a*}, Thomas Armbruster^a, Mariko Nagashima^b

4 ^a*Mineralogical Crystallography, Institute of Geological Sciences, University of Bern Baltzerstr. 1+3, 3012 Bern,*
5 *Switzerland*

6 ^b*Graduate School of Science and Engineering, Yamaguchi University, Yamaguchi 753-8512, Japan*

7 **Abstract**

8 The thermal stability of barrerite ($\text{Na}_{8.2}\text{K}_{3.0}\text{Ca}_{2.2}\text{Mg}_{0.2}\text{Al}_{17}\text{Si}_{55}\text{O}_{144}\cdot 50\text{H}_2\text{O}$) from Kuiu Island,
9 Alaska, was investigated from 25°C to 500°C by *in situ* single-crystal X-ray diffraction under dry
10 conditions. Corresponding experiments were performed on Na-exchanged barrerite
11 $\text{Na}_{17}\text{Al}_{17}\text{Si}_{55}\text{O}_{144}\cdot 45\text{H}_2\text{O}$ from the same locality. The natural sample showed a gradual
12 transformation of the A phase with dehydration to the B phase associated with rupture of T-O-T
13 links and formation of new connections. Though, the high temperature modification (phase D) was
14 not observed in the studied temperature range. In contrast to natural barrerite (space group *Amma*),
15 Na-exchanged barrerite was found to be monoclinic *F2/m* at room temperature and transformed to
16 *A2/m* (same cell setting) with beginning dehydration at 50°C. Its dehydration trend, monitored by
17 unit-cell volume, corresponded to structural modifications observed for natural barrerite. The D
18 phase of this sample was produced by *ex situ* experiments at 525°C under ambient conditions. A
19 new model for transformation from the disordered B phase to the ordered highly condensed D
20 phase (space group *A2₁ma*) is presented. In addition, the new *in situ* equilibrated single-crystal
21 experiments are compared with dynamic X-ray powder diffraction studies.

22
23 **Keywords:** barrerite, dehydration, Na-exchanged barrerite, **STI** framework-type, zeolite

24 *corresponding author: georgia.cametti@krist.unibe.ch

25 **1. Introduction**

26 Barrerite with idealized chemical formula $\text{Na}_{16}\text{Al}_{16}\text{Si}_{56}\text{O}_{144}\cdot 52\text{H}_2\text{O}$ ($a = 13.2$, $b = 18.6$, $c =$
27 17.8 Å, space group *Amma*) is a natural zeolite [1] of stilbite framework-type (**STI**) [2]. Its structure is
28 built by $4^2 5^4$ secondary building units (SBUs) and consists of 10-membered ring channels along the **a**-
29 axis and 8-membered ring channels along the **c**-axis. Na ions and H₂O molecules are the most
30 abundant extraframework (EF) occupants that are disorderly distributed at partially occupied sites [3,
31 4]. Barrerite shares the same framework topology with other two zeolite minerals, stellerite
32 $\text{Ca}_8\text{Al}_{16}\text{Si}_{56}\text{O}_{144}\cdot 58\text{H}_2\text{O}$ and stilbite $\text{Na}_2\text{Ca}_8\text{Al}_{18}\text{Si}_{54}\text{O}_{144}\cdot 60\text{H}_2\text{O}$. The different symmetry of these three
33 minerals is controlled by the EF cations and their distribution within the zeolitic channels. Thus,
34 stellerite adopts the highest symmetry (*Fmmm*) [5, 6, 7], stilbite the lowest (*F2/m*) [8, 9, 10, 11] and
35 barrerite is orthorhombic *Amma* [3, 4]. The distinct space groups observed in barrerite, stilbite, and
36 stellerite are explained in terms of electrostatic repulsive forces between the extraframework cations
37 [3, 5, 12].

38 According to ²⁹Si and ²⁷Al MAS-NMR studies the natural **STI** type zeolites show a disordered
39 Si/Al distribution [13, 14, 15]. Based on ¹⁷O triplequantum magic-angle spinning nuclear magnetic
40 resonance (3QMAS NMR) natural stilbite contains even significant concentrations of Al-O-Al

41 linkages [16]. However, local Si/Al order was proposed for stilbite to explain small deviations from
42 monoclinic symmetry [17]. Several stilbite crystals (from different localities) exhibit optical symmetry
43 lower than that determined by X-ray diffraction [17]. This is explained by growth sectors of different
44 symmetry. The relation between the orthorhombic and monoclinic sectors was interpreted by variable
45 rotational order-disorder of framework tetrahedra occurring during crystal growth [17].

46 The exchange properties of stilbite, stellerite, and barrerite were investigated by Passaglia
47 (1980) [18] and the role of the exchangeable cations on the heating behavior was explored. Crystal
48 chemical and structural studies [19, 3, 5] demonstrated that repulsive action of the Na ions is
49 responsible for the reduction of symmetry. Stellerite and barrerite show almost the same Si/Al ratio,
50 therefore stellerite (*Fmmm*) crystals that were exchanged with Na ions should transform to space
51 group *Amma* (the space group of barrerite). However, this assumption was not confirmed by the
52 structural analysis of a completely Na-exchanged stellerite sample, which maintained the original
53 *Fmmm* symmetry [20]. ND₄⁻ and NH₄⁺-exchanged forms of barrerite adopt the same symmetry of
54 stellerite, *Fmmm* [21, 22]. Similarly, when barrerite crystals are completely exchanged with Ca, the
55 topological *Fmmm* symmetry resulted [23].

56 The dehydration behavior of barrerite was investigated by X-ray diffraction techniques and
57 mainly described as a two-step process: transformation from phase A to phase B at ca. 250°C and
58 additional structural change to phase D at ca. 450-500°C [24, 25, 26]. The modifications, which
59 barrerite undergoes upon heating, involve the statistical breaking of one T-O-T bridge that gives rise to
60 two half-occupied face-sharing tetrahedra in phase B [24]. Interrupted T-O-T connection may be
61 partially compensated by terminating T-OH groups [27]. The D phase is characterized by an additional
62 volume contraction (ca. 20% compared to the RT value), by lower space group symmetry *A2₁ma*, and
63 a new type of framework topology [25]. Stilbite and stellerite show similar trends upon heating [6, 11]
64 but in contrast to barrerite the high temperature D phase does not form. With increase of temperature
65 these structures collapse and turn X-ray amorphous [7].

66 In this study we investigated the dehydration process of a natural sample of barrerite by *in-situ*
67 single crystal X-ray diffraction under dry conditions. In addition, a crystal belonging to the same
68 sample was exchanged with NaCl solution in order to obtain a pure Na endmember of barrerite (Na-
69 barrerite), on which another set of X-ray experiments was performed from RT to 450°C. Our aim is to
70 compare these new results with those obtained by in situ synchrotron X-ray powder diffraction
71 (XRPD) [26] and to determine whether differences occur in dehydration behavior of endmember Na-
72 barrerite.

73

74 **2. Experimental methods**

75 *2.1 Chemical analyses*

76 The sample of barrerite used in the present study is from Rocky Pass, Kuiu Island, Alaska
77 (sample number 43186 of Natural History Museum of Bern) [28]. The chemical composition was
78 determined by electron-microprobe analyses (EMPA) by using a JEOL JXA-8230 instrument
79 (installed at the Yamaguchi University) with the following analytical conditions: excitation voltage 15
80 KV, beam current 2 nA, beam diameter 10 μm. The standards were: wollastonite (Si *Kα* and Ca *Kα*),
81 corundum (Al *Kα*), albite (Na *Kα*), rutile (Ti *Kα*), eskolaite (Cr *Kα*), Ca₃(VO₄)₂ (V *Kα*), hematite (Fe
82 *Kα*), manganosite (Mn *Kα*), periclase (Mg *Kα*), K-feldspar (K *Kα*), SrBaNb₄O₁₂ (Sr *Lα* and Ba *Lα*),
83 NiO (Ni *Kα*), KTiOPO₄ (P *Kα*), fluorite (F *Kα*), halite (Cl *Kα*). The ZAF (atomic number -absorption
84 - fluorescence) correction-method [29] was used for all elements.

85

86 *2.2 Cation exchange*

87 In order to obtain a pure Na endmember of barrerite additional crystals of barrerite with
88 dimension ranging from 0.10 to 0.50 mm were placed in a Teflon lined autoclave filled with 2 M NaCl
89 solution for 2 weeks at 100(5)°C. The NaCl solution was renewed every three days. The Na-
90 exchanged barrerite was qualitatively analyzed by a scanning electron microscope (SEM).

91 92 2.3 Single crystal X-ray diffraction

93 The crystal structure of barrerite was investigated by single-crystal X-ray diffraction
94 (SCXRD) using a BRUKER APEXII diffractometer with a MoK α radiation ($\lambda = 0.71073 \text{ \AA}$) and a
95 CCD area detector. The selected crystal (size ca. 0.35 x 0.40 x 0.25 mm) was glued on the tip of a
96 glass fiber mounted on a goniometer head. The dehydration process was investigated from RT to
97 500°C using a self-constructed temperature controlled N₂-blower. The temperature was increased in
98 steps of 25°C and before starting the data collection the sample was let equilibrated for ca. 40 minutes.
99 Under these experimental conditions the crystal was continuously exposed to a dry N₂ atmosphere
100 (RH = 0). Each data collection lasted ca. 8 hours. The data were integrated and an empirical absorption
101 correction was applied using the Apex 2v. 2011.4-1 software package. Structures were solved using
102 Shelxtl-2008 [30].

103 Structural refinements were carried out by SHELXL-2014 [31], using neutral atomic scattering
104 factors.

105 The structure of barrerite at room temperature (phase A) was solved in space group *Cmcm*,
106 transformed in *Amma* according to Galli and Alberti [3]. Atomic coordinates and labels of the
107 framework were those adopted from Sacerdoti et al. [4]. The extra-framework occupants, both cations
108 and H₂O molecules, were located by exploring difference-Fourier maps. The positions were assigned
109 on the basis of the cation to oxygen framework distances and taking into account the chemical
110 composition. Nevertheless, discrepancy between calculated and refined chemical composition occurs
111 due to partial occupancy and closely spaced disordered sites.

112 *Amma* space group was maintained in the whole temperature range. Labels of atomic
113 coordinates of the framework from 150°C to 500°C were those used by Ori et al. [26]. Extra-
114 framework occupants were renamed because no correspondence was found with reference data [26].
115 In all data sets, framework sites were refined anisotropically whereas, in general, atomic displacement
116 parameters of EF cations and H₂O sites were kept isotropic (exceptions are indicated in Tables). At
117 250°C the O3 site showed positional disorder and was split in two subsites, O3 and O3A, 0.58(3) Å
118 apart.

119 A second set of X-ray diffraction experiments were performed on a Na-exchanged single
120 crystal of barrerite with dimension of approximately 0.35 x 0.20 x 0.20 mm. The dehydration behavior
121 of this sample was investigated from RT to 450°C applying the same experimental set-up used before.
122 Structure solution at room temperature indicated monoclinic symmetry *C2/m*, transformed to the non-
123 standard setting *F2/m* [32] to allow a direct comparison of cell dimension of **STI** type structures.
124 Atomic coordinates and labels of framework sites were those of stilbite reported in [32]. For easy
125 comparison with the RT data set structural data obtained from 50°C to 450°C were transformed to
126 *A2/m* setting with corresponding axial orientations as for space group *F2/m* (Table 2).
127 Pseudomerohedral twinning (matrix: [100 010 00-1], twin fraction ca. 0.12/0.88) was observed for all
128 data sets. Additional refinement details are summarized in the supplementary material (SM1).

129 Another Na-exchanged crystal (size ca. 0.20 x 0.10 x 0.15 mm) of barrerite was heated *ex situ*
130 at 525°C in order to investigate a possible transformation to the D phase reported for natural barrerite.
131 Under this experimental conditions the sample was not exposed to dry conditions but heated in air.
132 The crystal was gradually heated (65°C/h) up to 525°C. This temperature was kept for ca. 4 h and then
133 the crystal was let cool down for ca. 2 h before starting the data collection. The structure was solved in
134 space group *A2₁ma* [25] and atomic coordinates and labels by Sacerdoti [25] were used. Crystal data
135 and refinement parameters are reported in Table 1a,b.

136

137 **3. Results**

138 The crystal-chemical formula of natural barrerite calculated according to chemical analyses is
139 $\text{Na}_{8.24}\text{K}_{3.04}\text{Ca}_{2.24}\text{Mg}_{0.24}\text{Al}_{16.8}\text{Si}_{54.96}\text{O}_{144}\cdot 50\text{H}_2\text{O}$ (Table 3). Coordinates of this barrerite structure at room
140 temperature and corresponding bond-length distances are reported in Tables S1 and S2, respectively.
141 Structural data for natural barrerite at 150 and 275°C are shown in Table S3 and S4. Table 4 displays
142 structure parameters of Na-exchanged barrerite at room temperature. Results of structure refinements
143 of the B-phase at 150°C and at 350°C are summarized in Tables S5 and S6, respectively, and those of
144 the *ex-situ* D-phase (produced at 525°C) in Table S8. Table S7 summarizes the relation between labels
145 of tetrahedral sites in different barrerite structures. CIF files have been submitted as supplementary
146 material.

147

148 *3.1 Natural barrerite*

149 The structure at room temperature of natural barrerite was found to be in agreement with
150 previously reported results [3, 4]. The main difference is related to the location of the EF cations that
151 in our study are distributed over 9 partially occupied crystallographic sites (Table S1, S2). Sacerdoti et
152 al. [4] refined a sample from the same locality with 5 independent sites. H₂O molecules were located
153 on 21 partially occupied sites in contrast to 14 sites found by Sacerdoti et al. [4].

154 The dehydration process started at 50°C and proceeded up to 275°C. In this temperature range
155 the transition from the A to the B phase was observed and the unit-cell volume decreased from
156 4409.8(3) Å³ at 25°C to 3738.66(15) Å³ at 275°C (Fig.1). This reduction of volume was accompanied
157 by the total loss of the original water content (55.6 H₂O) at 275°C. The structural transformations
158 affecting barrerite in this first dehydration step mainly involved the rotation of the SBUs leading to a
159 more elliptical shape of the channel cross-sections (Fig. 2). At 150°C new electron-density peaks
160 appeared in difference Fourier maps close to oxygen-framework atoms of the triangular basis of the
161 SiO₄ tetrahedra (Table S3). These peaks corresponded to low-occupied new tetrahedral Si, Al sites
162 occurring as a consequence of the T-O-T breaking. At 200°C, in addition to the new T centers, a new
163 oxygen site (OD) was found representing the alternate tetrahedral apex linking the new T1D and T4D
164 tetrahedra. The occupancy of these new sites progressively increased with temperature while the
165 occupancy of the original sites decreased until at 275°C both were half occupied and the B phase
166 reported by Alberti and Vezzalini [24] was obtained (Table S4). This process has to be regarded as a
167 gradual transition from the *Amma* room temperature structure to the *Amma* contracted B phase at
168 275°C, during which Si, Al atoms migrated toward the new positions in a disordered fashion.

169 At 300°C the so called face-sharing tetrahedra remained half occupied by Si, Al. Upon further
170 heating up to 500°C the structure did not undergo additional significant modification preserving space
171 group *Amma*. Transformation to the D phase was not observed.

172

173 *3.2 Na-barrerite*

174 Complete Na-exchange was confirmed (absence of Ca and K) by qualitative energy dispersive
175 analysis using a scanning electron microscope (SEM). The crystal structure of the Na-barrerite sample
176 at room temperature was solved and successfully refined in the monoclinic space group *F2/m* (Table
177 4), similar to the structure of the stilbite. The monoclinic angle, $\beta = 90.429(1)^\circ$, is close to that
178 reported for natural stilbite [8, 9]. The **STI** type framework-topology is maintained but the symmetry
179 lowered to monoclinic (Fig. 3). The investigated sample showed a strong orthorhombic pseudo-
180 symmetry *Cmcm* (*Amma*). However, we tested different crystals and all the data sets exhibited an
181 angle $\beta = 90.2-90.5^\circ$. The data were collected with high redundancy (8 for orthorhombic and 4 for
182 monoclinic) and in orthorhombic symmetry the final R_{int} (0.0796) value was larger than R_σ (0.0531),

183 whereas in monoclinic R_{int} (0.0501) was similar to R_{σ} (0.0569). This discrepancy became enhanced at
184 higher temperatures.

185 Moreover, choice of *Amma* symmetry (for test purposes) at elevated temperature indicated few
186 significant systematic absence violations (*a* glide) and more important an extended list of inconsistent
187 equivalent F_{obs} values. Corresponding discrepancies were not seen in monoclinic refinements.

188 The dehydration behavior proceeded via a similar trend as observed for the natural sample. As
189 shown in Figure 1 the decrease of the unit-cell volume (from $V = 4407.12(14) \text{ \AA}^3$ at RT to $V =$
190 $3742.42(17) \text{ \AA}^3$ at 450°C) upon heating and the associated release of water was very similar for both
191 barrerite samples. Nevertheless, as soon as the dehydration started at 50°C the structure of the Na-
192 barrerite changed Bravais centering from $F2/m$ to $A2/m$ with corresponding cell setting and volume.
193 The $A2/m$ space group was preserved up to 450°C . The gradual transformation to the B phase
194 accompanied by formation of disordered “face-sharing” tetrahedra started at 150°C at which the
195 monoclinic B phase is characterized by rupture of two T-O-T connections, T1M-O3-T4M and T4-O5-
196 T2, though related by pseudo-symmetry (Table S5). Surprisingly, the occupancies of the new T sites
197 (T1MD, T4MD connected by OD2 and T4D, T2D connected by OD1) converged at 350°C to $1/3$ and
198 $2/3$, respectively (Table S6) and not to $1/2$ each, determined for natural barrerite. This uneven ratio
199 remained unchanged up to the maximum temperature of 450°C . The new connections T1MD-OD2-
200 T4MD and T4D-OD1-T2D in the B phase of Na-barrerite ($A2/m$) correspond topologically to T1D-
201 OD-T4D in the B phase of natural barrerite in space group *Amma* (S7). Thus, averaged over the Na-
202 barrerite ($A2/m$) B phase structure the number of new T-O-T connections is the same as in natural
203 barrerite. The uneven ratio of new T-O-T connections in Na-barrerite is also the reason that with
204 increasing temperature the difference to orthorhombic diffraction symmetry becomes more
205 pronounced.

206 207 3.2.1 Na-barrerite phase D

209 Our *ex situ* experiment demonstrated that the monoclinic Na-barrerite transforms to a highly-
210 condensed orthorhombic ordered D phase (space group $A2_1ma$, $a = 12.955(4)$, $b = 16.850(5)$, $c =$
211 $16.236(5) \text{ \AA}$, $V = 3544.3(18) \text{ \AA}^3$) without microporous character in contrast to the B phase (Fig. 4).
212 The structure (Table S8) corresponds to that reported by Sacerdoti [25] for a natural sample of
213 barrerite. The total decrease of the unit-cell volume is 20% with respect to the fully hydrated sample
214 measured at room temperature.

215 216 4. Discussion

217 4.1 Comparison with synchrotron XRPD

218 In general, the structural transformations of natural barrerite found in our experiments correspond to
219 those previously reported [24, 25, 26]. However, comparing our results with the dynamic *in situ*
220 dehydration study performed by Ori *et al.* [26] differences are observed. In the powder diffraction
221 experiments the authors reported that the percentage of broken T-O-T bridges begins at 250°C and
222 remains unchanged with temperature. In our study, the change from A to B phase of barrerite is
223 described by a gradual transition due to progressive rupture of the T-O-T bridges. The percentage of
224 broken T-O-T bridges increases as a function of temperature from 150°C to 275°C until it reaches
225 50%. Only after this value is achieved the occupancy of T sites remains unvaried up to 500°C .

226 The different kinetics, due to experimental set-up, resulted in our data a shift of the structural
227 transformations toward lower temperatures compared to XRPD experiments (Fig. 1). This is a well-
228 known effect [33, 34] that non-equilibrium experiments (XRPD) show a larger unit cell associated to
229 the dehydration steps compared to equilibrated experiments (SCXRD). Surprisingly, the trend is
230 inverted above 300°C . The volume change observed in our experiments reaches a plateau above

231 275°C and it does not vary significantly afterward. At 500°C the B phase is still preserved and
232 barrerite does not transform to the D phase. In contrast to our single-crystal results, the XRPD
233 experiments show in the range from ca. 340 to 470°C, at which only the B phase is analyzed, a gradual
234 decrease of the unit-cell volume. Then the volume rapidly decreases because of the strong contraction
235 characteristic of the D phase.

236 The different volume trend observed in our experiments and the fact that heating effects are
237 shifted to lower temperatures with the exception of formation of the D phase, may be interpreted in
238 terms of the dynamic nature of the XRPD experiments and the different EF cation content of our
239 sample compared to the one used in Ori et al. [26], typical of natural samples. The transformation from
240 A to B phase is mainly related to the strain induced on the O framework by the EF cations to achieve
241 more energetically balanced coordination after the release of water. In contrast, the subsequent phase
242 transition from B to D is not related to loss of H₂O (barrerite above 275°C is in our experiments
243 anhydrous). The D phase, as discussed below, involves a severe readjustment of the framework
244 tetrahedra that may be influenced by locally ordered Si/Al distribution [17]. Another factor that at this
245 stage becomes important, is the small size of grains in powder material compared to our single crystal
246 (ca. 0.3 mm). A faster reaction is expected as a consequence of the short diffusion-path in powder
247 compared to single crystal. A more convincing interpretation of the constant volume observed in our
248 experiments between 275 and 500°C is suggested by considering the following section.

249

250 4.2 The role of $RH = 0$ and T-OH termination on the formation of D phase

251

252 Alberti et al. [27] provided convincing evidence by *near infrared* (NIR) diffuse reflectance
253 spectra that the B, C (rehydrated B phase), and the D phase display absorptions at ca. 2200 nm (4550
254 cm⁻¹) interpreted as ν_{OH} and δ_{SiOH} combination bands due to OH groups. These absorptions did not
255 occur in phase A barrerite and are characteristic of zeolite structures with broken T-O-T connections
256 investigated under ambient conditions [35, 36]. In test refinements we controlled the occupancies of
257 the new occurring and original T sites without any constraints. Our results did not indicate significant
258 deviations of equal occupancies of pairs for T sites involved in formation of new T-O-T connections.
259 This result is also corroborated by the independently refined atomic displacement parameters of these
260 sites, which converged to very similar values. The same test (refinement without constraints) was
261 performed on the oxygen site of the new tetrahedral apex (OD). The refined occupancy and values of
262 atomic displacement parameters confirmed that the OD site is always shared by the two tetrahedral
263 sites (T1D and T4D), excluding significant T-OH groups in our B phase. Thus, the dry conditions in
264 our experiments may even have prevented formation of terminating T-OH groups.

265 An interesting conclusion can be drawn concerning this point. If OH groups do not form under
266 our experimental conditions, the B phase that we observed is actually different form that analyzed
267 under ambient conditions (mainly relative humidity higher than 0) in previous studies [24, 27].
268 Assuming that the D phase arises only as a consequence of the function and subsequent loss of OH
269 groups from B phase [24], our dry conditions also explain why we did not observe the D phase up to
270 500°C in the *in situ* experiments. The idea that our B phase is not hydroxylated is also supported by
271 the constant volume observed from 275 to 500°C (Fig. 1). Curing of T-OH terminations to T-O-T
272 connections would lead to increasing condensation associated with a decrease of volume.

273 The D phase [25] does not contain OH groups or at least, if it does, only in very low
274 concentration below the resolution of the single-crystal experiment. The OH-bearing barrerite D phase
275 in Alberti et al. [27] was obtained after heating the crystal at 398°C and it may correspond to a T-OH
276 containing precursor of the real phase D.

277 Finally, the percentage of T-OH terminations reported in Alberti et al. [27] is probably
278 overestimated; Ori et al. [26] did not report (and even mention) evidence of significant OH
279 terminations that are probably under the detection limit of the XRPD technique (SFig. 1).

280 Interestingly, powder data on stilbite phase B also indicated a small percentage of T-OH terminations
281 [11], whereas the structure of stellerite B is even characterized by dominating T-OH with less new T-
282 O-T connections leading to an interrupted framework [7]. The framework structure of stellerite B [6]
283 is topologically equivalent to that of barrerite, whereas the one of stilbite B [11] is different because
284 different T-O-T connections are broken.

285

286 4.3 Formation of the D phase: a hypothetical precursor phase

287

288 The reinvestigation of the D phase suggested a different idealized B phase, as a precursor
289 model, compared to that previously reported [25]. In the latter model, complete migration from
290 original to new tetrahedral sites is assumed whereas in our model 50% of each new (T1D and T4D)
291 and original (T1 and T4) T sites are arranged in an ordered fashion. Thus, the transformation from the
292 B phase to the precursor structure of the D phase represents a disorder-order transition. In the observed
293 condensed D phase, strain release causes additional rupture of T-O-T bonds (T1-O1-T4) associated
294 with new T-O-T (T1D-OD-T4D) connections.

295 The D phase arises from the rearrangement of the B phase framework through two main
296 processes. In the B phase, T atoms are randomly distributed at the original tetrahedral sites
297 (corresponding to those fully occupied in the A phase) and at new ones formed as a consequence of
298 the T-O-T rupture. In addition, T-OH terminations are statistically replacing T-O-T connections in the
299 B structure [27]. Partial curing of such terminated T-OH units in favor of new T-O-T links may be the
300 cause of the initial volume decrease observed between 340 and 470°C in XRPD data [26]. The first
301 step requires a transition from the disordered tetrahedral framework of the B phase to an ordered
302 orthorhombic precursor structure of the D phase. This ordering process is catalyzed by OH groups.
303 The resulting precursor phase is assumed to have 50% of the new tetrahedra and 50% of the original
304 tetrahedra fully occupied in an ordered fashion (Fig. 5a,b). In a second step, this precursor phase
305 transforms to the D phase when additional tetrahedra flip inside the 8-ring channels forming new
306 linkages. Thus the channels become occluded and the new condensed structure (Fig. 5c) loses
307 microporous properties. If the T-OH terminations [27] either not form or are very scarce under dry
308 conditions (our experiments), the ordering process of the disordered B phase to the ordered precursor
309 phase is hampered and the D phase does not form in the investigated temperature range.

310 For Na-barrerite, formation of the D phase was only observed *ex situ* at 525°C under ambient
311 humidity conditions in the furnace. The observation that in the Na-barrerite B phase, produced under
312 dry conditions, unequal numbers of new T-O-T connections are formed and not ½ as required for the
313 D phase is additional support that formation of the D phase under dry conditions is hampered.

314

315 4.4 Considerations on the memory effect of the STI framework type

316 Our results demonstrate the sensitivity of the **STI** framework-type to the content of EF
317 cations. If the symmetry of a **STI** framework-type mineral is only governed by the EF cations and the
318 associated H₂O molecules, Na-exchanged end-members of stellerite, stilbite, and barrerite should be
319 symmetrically identical. Otherwise a memory effect (e.g. by slightly different Si, Al distributions) of
320 the framework must be considered as origin of different symmetry of Na-exchanged members.

321 Passaglia and Sacerdoti [20] investigated a completely Na-exchanged stellerite, demonstrating
322 that the framework preserved the space group *Fm $\bar{3}$ m* of the original stellerite crystal and did not adopt
323 *Amma* symmetry assumed for barrerite. At the first glance this finding would support existence of a
324 framework memory-effect. However, our new results showing *F2/m* symmetry for Na-exchanged
325 barrerite offer a different interpretation. Due to the topological *Fm $\bar{3}$ m* symmetry of the **STI**
326 framework type, differences between *Fm $\bar{3}$ m* and *F2/m* are difficult to resolve if the β angle is very
327 close to 90°. In our study, the difference between *Fm $\bar{3}$ m* and *F2/m* symmetry became mainly apparent

328 after collecting intensity data with high redundancy. Based on the internal agreement factors of
329 symmetry equivalent reflections, the intensity distribution is in agreement with $F2/m$ but not with
330 $Fmmm$ symmetry. Passaglia and Sacerdoti [20] essentially collected a unique data set for F -centered
331 orthorhombic setting as customary for diffractometers equipped with a point counter about 35 years
332 ago. We suppose that with the limited data they could not detect the lower symmetry. In addition, their
333 main intention was to demonstrate that the F -centered lattice was in contrast to A -centering expected
334 by them. This also confirmed by our structure refinements on Na-barrerite at RT.

335 Na-exchanged stilbite [37] showed an X-ray diffraction powder-pattern similar to stilbite
336 ($F2/m$) but the symmetry was not thoroughly investigated. Synthetic barrerite [38] produced an X-ray
337 powder pattern, which was only qualitatively evaluated to be in agreement with natural barrerite
338 ($Amma$). Thus none of the previous reports could provide a convincing answer on the true symmetry
339 of the fully hydrated Na-endmember with **STI** framework type. We currently produce Na-exchanged
340 stellerite crystals to test by new structure refinements whether assumption of the memory effect of the
341 **STI** framework-type can be maintained.

342

343 **Acknowledgements** We are thankful to Beda Hofmann of Natural History Museum of Bern who
344 kindly provided the barrerite sample and to Alfons Berger for assistance in SEM analyses. We also
345 thank two anonymous reviewers for their helpful comments.

346

347

348 **References**

349

- 350 [1] E. Passaglia, D. Pongiluppi, *Mineral. Mag.* 40 (1975) 208.
351 [2] Ch. Baerlocher, W.M. Meier, D. H. Olson, Atlas of zeolite framework types, Structure commission
352 of the IZA, Elsevier, 5th ed. 2001, 302p.
353 [3] E. Galli, A. Alberti, *Bull. Soc. Fr. Mineral. Cr.* 98 (1975) 331-340.
354 [4] M. Sacerdoti, A. Sani, G. Vezzalini, *Micropor. Mesopor. Mat.* 30 (1999) 103-109.
355 [5] E. Galli, A. Alberti, *Bull. Soc. Fr. Mineral. Cr.* 98 (1975a) 11-18.
356 [6] A. Alberti, R. Rinaldi, G. Vezzalini, *Phys. Chem. Miner.* 2 (1978) 365-375.
357 [7] R. Arletti, E. Mazzucato, G. Vezzalini, *Am. Mineral.* 91 (2006) 628-634.
358 [8] E. Galli, G. Gottardi, *Miner. Petrogr. Acta* 12 (1966) 1-10.
359 [9] M. Slaughter, *Am. Mineral.* 55 (1970) 387-397.
360 [10] W. J. Mortier, *Am. Mineral.* 68 (1983) 414-419.
361 [11] G. Cruciani, G. Artioli, A. Gualtieri, K. Ståhl, J. C. Hanson, *Am. Mineral.* 82 (1997) 729-739.
362 [12] E. Galli, *Acta Cryst.* B27 (1971) 833-841.
363 [13] E. Lippmaa, M. Mägi, A. Samoson, M. Tarmark, G. Engelhardt, *J. Am. Chem. Soc.* 103 (1981)
364 4992-4996.
365 [14] A. Sani, C. Marichal, C. Forte, *Plinius*, 22 (1999) 344-345.
366 [15] A. Sani, L. Del Motte, C. Marichal, Z. Gabelica, C. Forte, *Eur. J. Mineral.* 13 (2001) 101-111.
367 [16] J. F. Stebbins, P. Zhao, S. Keun Lee, X. Cheng, *Am. Mineral.* 84 (1999) 1680-1684.
368 [17] M. Akizuki, H. Konno, *Am. Mineral.* 70 (1985) 814-821.
369 [18] E. Passaglia, *Tscherm. Miner. Petrog. Mitt.* 27 (1980) 67-78.
370 [19] E. Passaglia, E. Galli, L. Leoni, G. Rossi, *Bull. Mineral.* 101 (1978) 368-375.
371 [20] E. Passaglia, M. Sacerdoti, *Bull. Mineral.* 105 (1982) 338-342.
372 [21] E. Meneghinello, A. Alberti, G. Cruciani, M. Sacerdoti, G. Mc Intyre, P. Ciambelli, M. T.
373 Rapacciuolo, *Eur. J. Mineral.* 12 (2000) 1123-1129.
374 [22] A. Martucci, A. Alberti, M. Sacerdoti, G. Vezzalini, P. Ciambelli, M. Rapacciuolo, in: C. Colella,
375 F. A. Mumpton (Eds.), *Natural Zeolites for the Third Millennium*, De Frede Editore, Napoli, 2000, p.
376 45.

- 377 [23] M. Sacerdoti, I. Gomedì, *Bull. Mineral.* 107 (1984) 799-804.
- 378 [24] A. Alberti, G. Vezzalini, in: L. B. Sand, J. Mumpton (Eds.), *Natural Zeolites. Occurrence,*
379 *Properties, Use*, Pergamon Press, New York, 1978, pp. 85-98.
- 380 [25] M. Sacerdoti, *Micropor. Mesopor. Mat.* 102 (2007) 299-303.
- 381 [26] S. Ori, E. Mazzucato, G. Vezzalini, *Am. Mineral.* 94 (2009) 64-73.
- 382 [27] A. Alberti, F. Cariati, L. Erre, P. Piu, G. Vezzalini, *Phys. Chem. Minerals*, 9 (1983) 189-191.
- 383 [28] F. Di Renzo, Z. Gabelica, *Can. Mineral.* 35 (1997) 691-698.
- 384 [29] J. L. Pouchou, F. Pichoir, in: *Microbeam Analysis 1988*, D. Newbury (Ed.), San Francisco Press,
385 319-324.
- 386 [30] G. M. Sheldrick, *Acta Cryst.* A64 (2008) 112-122
- 387 [31] G. M. Sheldrick, *Acta Cryst.* C71 (2015) 3-8.
- 388 [32] S. Quartieri, G. Vezzalini, *Zeolites* 7 (1987) 163-170.
- 389 [33] G. Cruciani, *J. Phys. Chem. Solids* 67 (2006) 1973-1994.
- 390 [34] A. Martucci, E. Rodeghero, G. Cruciani, *Eur. J. Mineral.* 28 (2016) 5-13.
- 391 [35] P. S. R. Prasad, K. S. Prasad, S. R. Murthy, *Am. Mineral.* 90 (2005) 1636-1640.
- 392 [36] D. L. Bish, R. Milliken, C. T. Johnston, in: R. S. Bowman, S. E. Delap (Eds), *Zeolite '06-7th*
393 *International Conference on the occurrence, Properties and Utilization of Natural Zeolites, Socorro,*
394 *New Mexico USA, 16-21 July 2006*, pp. 53-54.
- 395 [37] K. Harada, K. Tomita, *Am. Mineral.* 52 (1967) 1438-1450.
- 396 [38] H. Ghobarkar, O. Schäf, U. Guth, *J. Solid State Chem.* 142 (1999) 451-454.
- 397
- 398
- 399

Figure(s)
[Click here to download high resolution image](#)

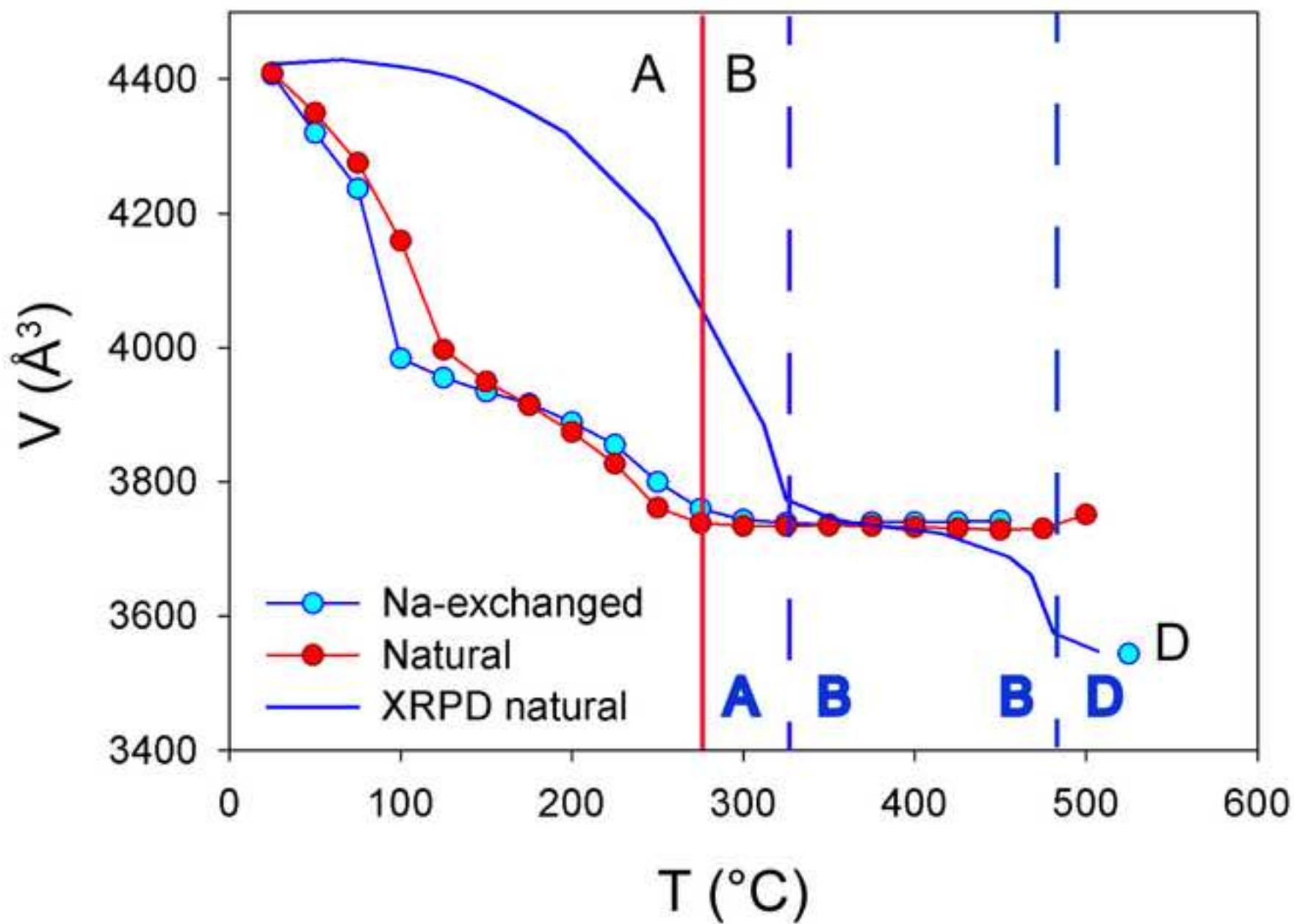


Figure 2
[Click here to download high resolution image](#)

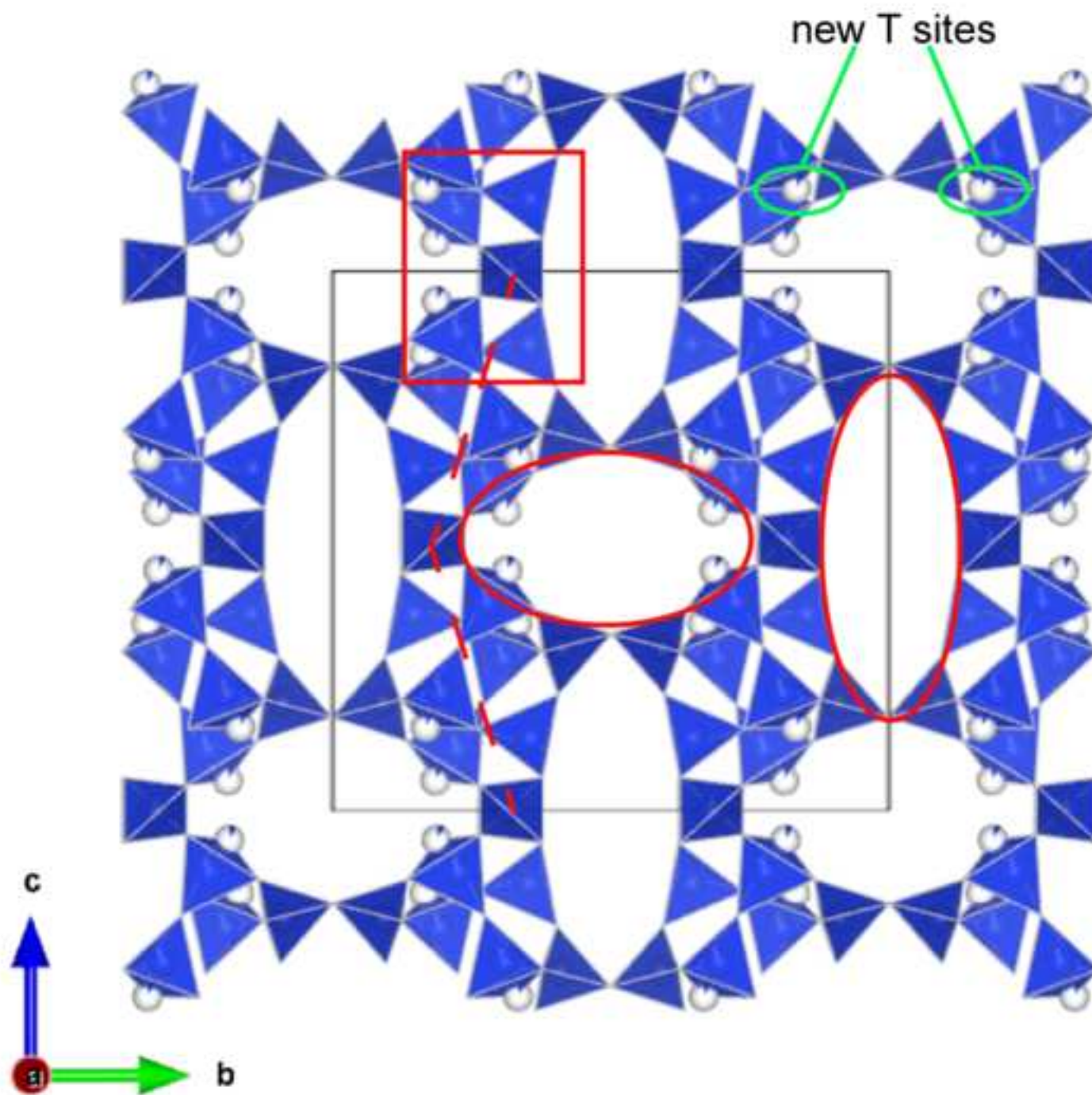


Figure 3
[Click here to download high resolution image](#)

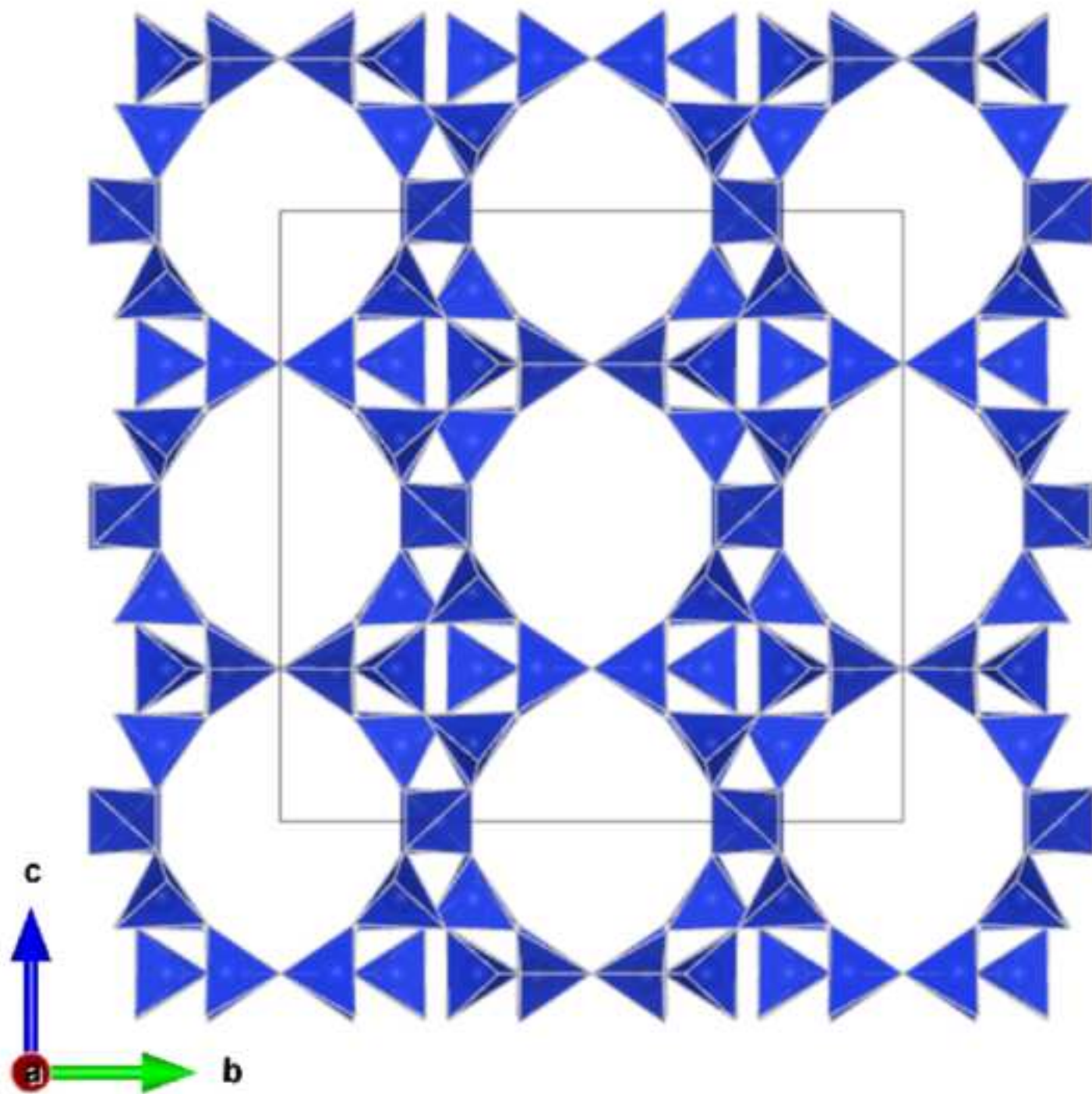
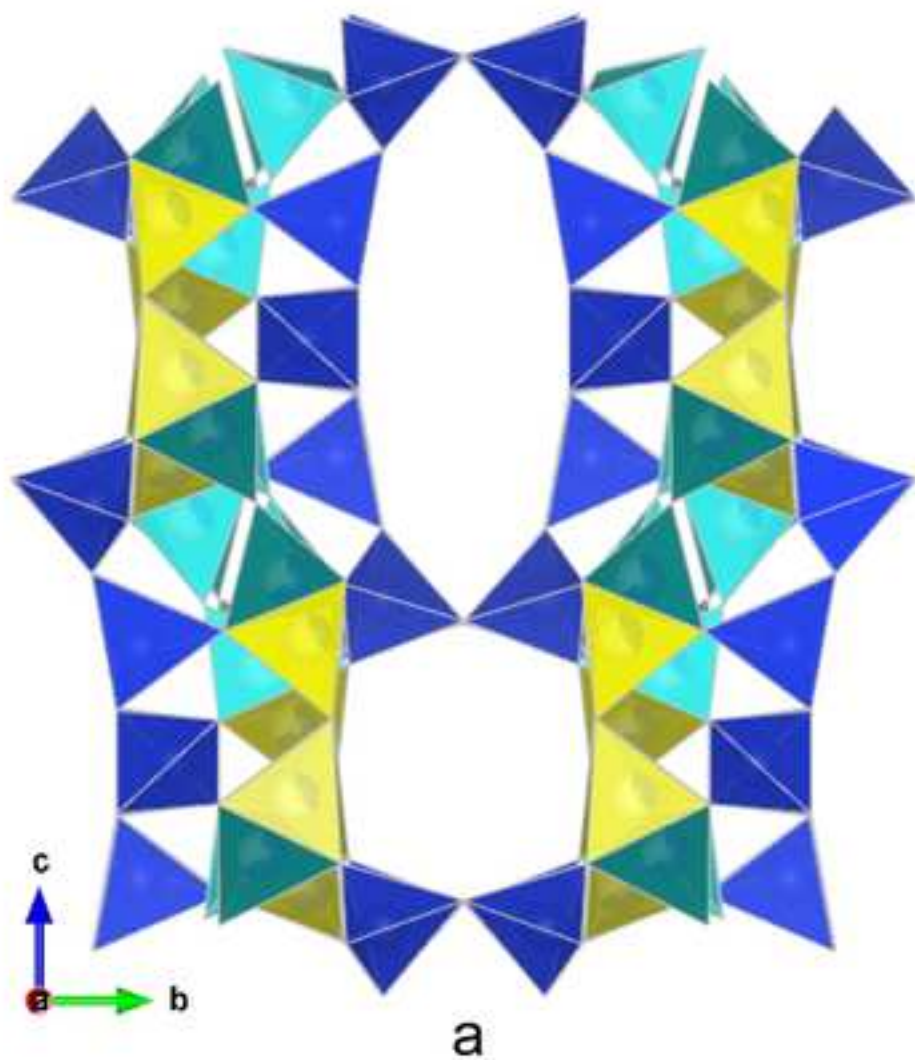


Figure 4
[Click here to download high resolution image](#)

B phase



D phase

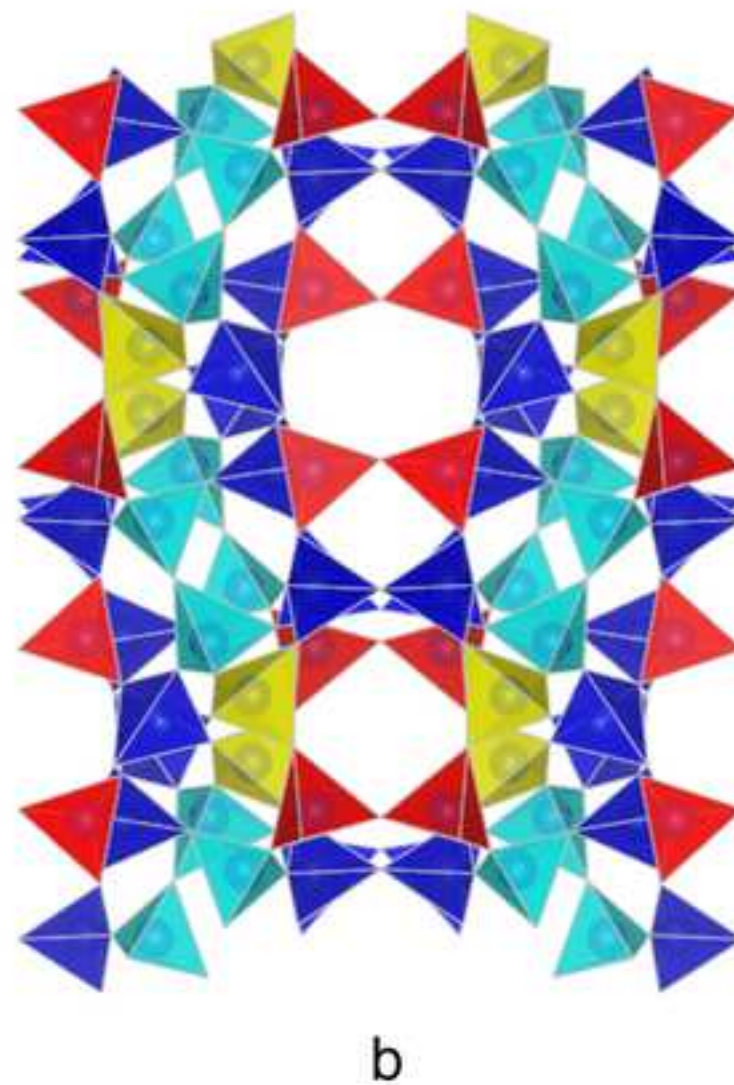
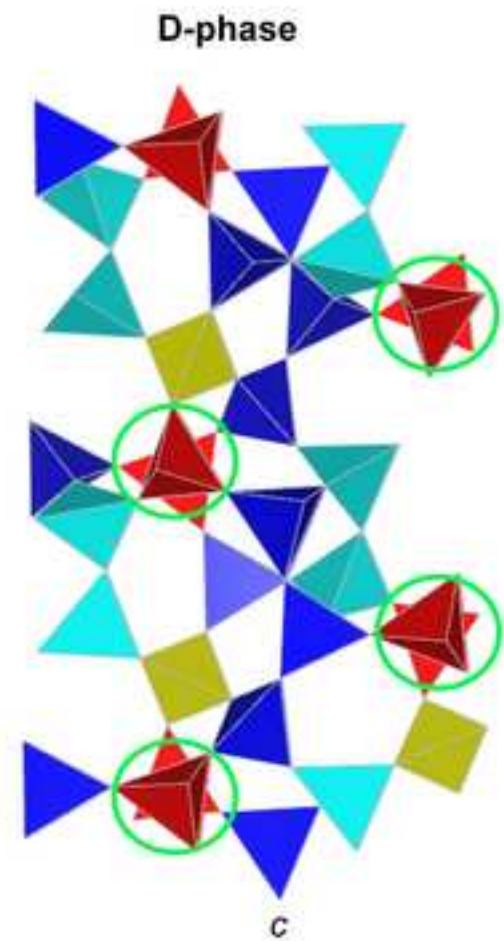
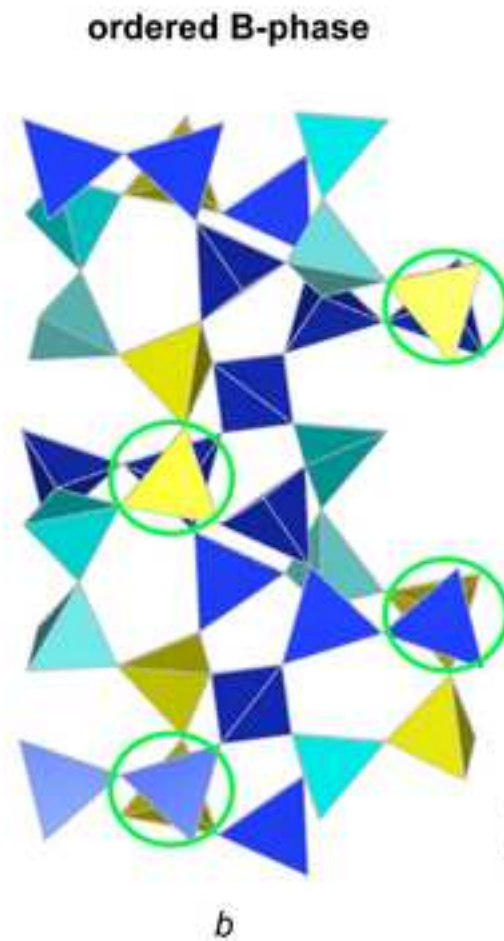


Figure 5
[Click here to download high resolution image](#)



Figures caption

Figure 1 Volume trend of natural (red dots) and Na-exchanged (light blue dots) barrerite as a function of temperature. Corresponding volume of Na-barrerite D phase (obtained *ex-situ* in air) is also shown. Synchrotron X-ray powder diffraction data (XRPD) are reported for comparison [25]. Vertical dotted blue lines at 325°C and 480°C represent the A-B and B-D transition as detected in XRPD reference data [25]. The vertical continuous red line at 275°C indicates the corresponding A-B transition in our dry experiments.

Figure 2 Tetrahedral framework of natural barrerite at 150°C. The deviation of subsequent $4^2 5^4$ secondary building units (SBUs) from the [001] direction is represented by the dotted line. Low-occupied new tetrahedral sites are shown as partially colored spheres. The elliptical shape of the channels is highlighted by red curves.

Figure 3 Framework of Na-exchanged barrerite at room temperature projected along [100] direction.

Figure 4 Phase B (a) and phase D (b) framework of Na-barrerite. Cyan (original T sites) and yellow (new T sites originated after the T-O-T rupture) polyhedra represent the statistically occupied face sharing tetrahedra associated with breaking of T-O-T bridges. The different occupancy ($\frac{2}{3}$ and $\frac{1}{3}$) of T sites in B phase is shown by dark and light colored (cyan and yellow) tetrahedra, respectively. Red tetrahedra correspond to those flipped inside the cages after the transformation to the condensed D phase.

Figure 5 Model of transformation from the disordered B phase to the orthorhombic ordered D phase. (a) Disordered B-phase at 350°C. Original (cyan) and new (yellow) tetrahedral sites are face-sharing and statistically occupied. (b) Hypothetic ordered B-phase; 50% of the original and 50% of the new T sites are fully occupied in an ordered-fashion. (c) condensed D-phase; apices of the red tetrahedra (in the circles) are reversed in viewing direction compared to (b) but the triangular basis is preserved.

Table 1a. Crystal data and refinement parameters for natural barrerite at room temperature (RT), 150°C (RH = 0), and 275°C (RH = 0).

Crystal data	Barrerite A RT	Barrerite A 150°C	Barrerite B 275°C
<i>a</i> -axis (Å)	13.6227(5)	13.6621(3)	13.6110(3)
<i>b</i> -axis (Å)	18.1780(7)	17.2677(4)	17.1485(4)
<i>c</i> -axis (Å)	17.8079(7)	16.7407(3)	16.0177(4)
Cell volume (Å ³)	4409.8(3)	3949.35(14)	3738.66(15)
Z	1	1	1
Space Group	<i>Amma</i>	<i>Amma</i>	<i>Amma</i>
Refined chemical formula	Na _{11.2} K _{1.16} Ca _{2.03} (Si,Al) ₇₂ O ₁₄₄ ·55.6H ₂ O	Na _{6.16} K _{1.30} Ca _{1.68} (Si,Al) ₇₂ O ₁₄₄ ·9H ₂ O	Na _{8.97} K _{1.30} Ca _{1.18} (Si,Al) ₇₂ O ₁₄₄
Intensity measurement			
Diffractometer		APEX II SMART	
X-ray radiation		MoKαλ=0.71073 Å	
X-ray power		50 kV, 30 mA	
Monochromator		Graphite	
Temperature (°C)	25	150	275
Time per frame	60	60	60
Max. 2θ	84.21°	87.44°	77.13°
Index ranges	-25 ≤ <i>h</i> ≤ 25 -34 ≤ <i>k</i> ≤ 34 -33 ≤ <i>l</i> ≤ 33	-26 ≤ <i>h</i> ≤ 26 -33 ≤ <i>k</i> ≤ 33 -31 ≤ <i>l</i> ≤ 32	-23 ≤ <i>h</i> ≤ 23 -30 ≤ <i>k</i> ≤ 30 -28 ≤ <i>l</i> ≤ 27
No. of measured reflections	69973	56782	48914
No. of unique reflections	8153	7911	5595
No. of observed reflections <i>I</i> > 2σ (<i>I</i>)	6038	5158	4141
Structure refinement			
No. of parameters used in the refinement	255	198	192
<i>R</i> (int)	0.0378	0.0438	0.0421
<i>R</i> (σ)	0.0250	0.0299	0.0239
GooF	1.065	1.057	1.089
<i>R</i> 1, <i>I</i> > 2σ (<i>I</i>)	0.0445	0.0535	0.0556
<i>R</i> 1, all data	0.0624	0.0823	0.0744
w <i>R</i> 2 (on <i>F</i> ²)	0.1490	0.1954	0.1862
Δρ _{min} (eÅ ⁻³) close to	-0.80 from W7	-1.56 C2	-0.67 C2
Δρ _{max} (eÅ ⁻³) close to	0.97 from W7	1.02 C5	1.22 CW4

Table 1b. Crystal data and refinement parameters for Na-exchanged barrerite at room temperature (RT), 150°C (RH = 0), 150°C (RH = 0), and produced at 525°C (measured at RT).

Crystal data	Na-Barrerite A RT	Na-Barrerite B 150°C	Na-Barrerite B 350°C	Na-Barrerite D 525°C
<i>a</i> -axis (Å)	13.6288(2)	13.6703(2)	13.6132(10)	12.955(4)
<i>b</i> -axis (Å)	18.1600(3)	17.2196(3)	17.1442(13)	16.850(5)
<i>c</i> -axis (Å)	17.8071(4)	16.7145(3)	16.0105(13)	16.236(5)
β (°)	90.4290(10)	90.2750(10)	90.229(5)	90
Cell volume (Å ³)	4407.12(14)	3934.50(11)	3736.6(5)	3544.3(18)
Z	2	2	2	2
Space Group	<i>F</i> 2/ <i>m</i>	<i>A</i> 2/ <i>m</i>	<i>A</i> 2/ <i>m</i>	<i>A</i> 21/ <i>ma</i>
Refined chemical formula	Na _{16.35} (Si,Al) ₇₂ O ₁₄₄ ·45.4H ₂ O	Na _{12.7} (Si, Al) ₇₂ O ₁₄₄ ·8.5H ₂ O	Na _{12.83} (Si, Al) ₇₂ O ₁₄₄	Na ₁₀ (Al,Si) ₇₂ O ₁₄₄
Intensity measurement				
Diffractionmeter		APEX II SMART		
X-ray radiation		MoKαλ=0.71073 Å		
X-ray power		50 kV, 30 mA		
Monochromator		Graphite		
Temperature (°C)	25	150	350	525
Time per frame	60	60	60	60
Max. 2θ	77.14°	64.45°	62.67°	34.60°
Index ranges	-23 ≤ <i>h</i> ≤ 23 -31 ≤ <i>k</i> ≤ 31 -31 ≤ <i>l</i> ≤ 30	-20 ≤ <i>h</i> ≤ 20 -25 ≤ <i>k</i> ≤ 25 -24 ≤ <i>l</i> ≤ 24	-19 ≤ <i>h</i> ≤ 19 -25 ≤ <i>k</i> ≤ 25 -23 ≤ <i>l</i> ≤ 22	-9 ≤ <i>h</i> ≤ 10 -13 ≤ <i>k</i> ≤ 14 -10 ≤ <i>l</i> ≤ 13
No. of measured reflections	27488	31207	23806	2310
No. of unique reflections	5092	6940	5862	932
No. of observed reflections <i>I</i> > 2σ (<i>I</i>)	3541	4995	4281	677
Structure refinement				
No. of parameters used in the refinement	207	357	342	133
<i>R</i> (int)	0.0501	0.0574	0.0524	0.1226
<i>R</i> (σ)	0.0569	0.0438	0.0423	0.1249
GooF	0.956	1.031	1.048	1.103
<i>R</i> 1, <i>I</i> > 2σ (<i>I</i>)	0.0506	0.0441	0.0588	0.1140
<i>R</i> 1, all data	0.0744	0.0672	0.0833	0.1400
w <i>R</i> 2 (on <i>F</i> ²)	0.1563	0.1327	0.1643	0.3006
Δρ _{min} (eÅ ⁻³) close to	-0.73 W10	-0.78 Na5	-0.67 Na5	-0.82 O7
Δρ _{max} (eÅ ⁻³) close to	0.70 W8	0.90 Na5	0.80 Na5	0.81 O11

Table 2. Space group setting of Na-barrerite at 25°C and at 50°C. Non-standard setting *A2/m* at 50°C was preferred to an easy comparison with RT data set.

space group setting	25°C		50°C	
	<i>C2/m</i>	<i>F2/m*</i>	<i>C2/m</i>	<i>A2/m</i>
<i>a</i> (Å)	13.6288(2)	13.6288(2)	17.6466(3)	13.6481(2)
<i>b</i> (Å)	18.1600(3)	18.1600(3)	17.9357(3)	17.9357(3)
<i>c</i> (Å)	11.1714(2)	17.8071(4)	13.6481(2)	17.6466(3)
β (°)	127.1580(10)	90.4290(10)	90.2730(10)	90.2730(10)
<i>V</i> (Å ³)	2203.56(7)	4407.12(14)	4319.63(12)	4319.63(12)

*transformation matrix from *C2/m* to *F2/m*: [100 0-10 -1 0-2]

Table 3. Results of quantitative chemical analyses of natural barrerite as obtained from EMPA.

Mean values from 16 analytical points			
	wt. %		<i>a.p.f.u.*</i>
SiO ₂	58.40(73)	Si	54.96(24)
TiO ₂	0.16(10)	Ti	0.08(8)
Al ₂ O ₃	15.17(19)	Al	16.80(24)
Cr ₂ O ₃	0.08(10)	Cr	0.08(8)
V ₂ O ₃	0.02(4)	V	0.00
Fe ₂ O ₃	0.05(7)	Fe	0.00
MnO	0.05(7)	Mn	0.00
MgO	0.17(10)	Mg	0.24(16)
CaO	2.20(7)	Ca	2.24(8)
SrO	0.02(5)	Sr	0.00
BaO	0.22(17)	Ba	0.08(8)
Na ₂ O	4.51(15)	Na	8.24(24)
K ₂ O	2.55(10)	K	3.04(8)
NiO	0	Ni	0.00
P ₂ O ₅	0.01(3)	P	0.00
F	0.14(19)	total	85.92
Cl	0.01(1)		
Total	83.77	F ⁻	0.20(56)
E%-value	2.77		

*atoms per formula unit calculated on the basis of 144 O

Table 4 Atomic coordinates, displacement parameters and occupancy of Na-barrerite structure under ambient conditions (T = 25°C, RH = 65%)

Framework					
Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U^{eq}</i> (Å ²)	<i>Occ.</i>
T1	0.36275(3)	0.30761(2)	0.12442(3)	0.01592(10)	1
T2	0.13440(3)	0.30857(2)	0.12780(3)	0.01465(10)	1
T3	-0.04995(3)	0.08891(2)	0.24713(3)	0.01565(10)	1
T4	-0.13912(3)	0.31597(2)	0.25047(3)	0.01339(9)	1
T5	½	0.24670(4)	0	0.01896(13)	1
O1	0.42803(13)	0.29989(11)	0.04649(12)	0.0359(4)	1

O2	0.06115(13)	0.30802(9)	0.05527(11)	0.0333(4)	1
O3	-0.12386(13)	0.26651(9)	0.17686(11)	0.0329(3)	1
O4	-0.10188(15)	0.11705(10)	0.16921(12)	0.0370(4)	1
O5	0.12251(12)	0.23129(9)	0.17321(10)	0.0306(3)	1
O6	0.10726(15)	0.37895(10)	0.17976(12)	0.0380(4)	1
O7	0.24616(11)	0.31801(9)	0.09743(9)	0.0287(3)	1
O8	0.06643(9)	0.11384(8)	0.24946(11)	0.0275(3)	1
O9	-0.05222(17)	0	0.25001(17)	0.0313(5)	1
O10	-1/4	0.35077(10)	1/4	0.0238(3)	1
Extraframework					
Na1	0.2497(8)	1/2	-0.0445(4)	0.050(3)	0.33(2)
Na1A	0.2938(13)	1/2	-0.0488(7)	0.059(4)	0.237(19)
Na2	-0.0852(19)	0	0.1026(15)	0.08*	0.175(11)
Na3	0.3383(12)	1/2	-0.2543(10)	0.063(5)	0.175(12)
Na4	-0.4447(15)	0.0824(9)	-0.0416(12)	0.08*	0.128(6)
Na5	-0.1787(17)	0	0.0804(10)	0.046(6)	0.126(16)
Na6	0.0766(14)	0.0785(8)	0.0496(11)	0.10*	0.196(8)
Na7	0.0225(15)	0.0745(7)	0.0266(10)	0.10*	0.353(11)
Na8	-0.1134(19)	0	0.0606(14)	0.10*	0.227(11)
Na9	0.042(3)	0	-0.074(2)	0.08*	0.116(10)
W1	0.3134(14)	1/2	-0.1729(12)	0.063(7)	0.28(3)
W2	0.2239(10)	0.3759(4)	-0.0556(5)	0.058(3)	0.46(3)
W3	0.136(2)	1/2	-0.1288(17)	0.087(11)	0.23(2)
W4	0.187(2)	1/2	-0.0432(15)	0.104(9)	0.36(3)
W5	0.346(2)	1/2	-0.1283(18)	0.120(11)	0.37(3)
W6	0.2638(11)	0.3754(4)	-0.0566(5)	0.064(3)	0.46(3)
W7	-0.2791(15)	0	0.0937(10)	0.076(6)	0.39(3)
W7A	-0.2242(16)	0	0.0864(8)	0.054(5)	0.34(3)
W8	0.0253(19)	0	0.0089(16)	0.080*	0.243(13)
W9	0.2362(17)	1/2	-0.1708(12)	0.120(8)	0.49(3)
W10	-0.3870(12)	0	0.0651(8)	0.08*	0.433(14)
*not refined					