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Occurrence and crystal structure.**

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3 **KIRCHERITE, A NEW MINERAL OF THE CANCRINITE - SODALITE GROUP WITH A**
4 **36-LAYER STACKING SEQUENCE: OCCURRENCE AND CRYSTAL STRUCTURE**

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ABSTRACT

27

28 This paper reports on the occurrence and the crystal structure of kircherite, a new
29 member of the cancrinite-sodalite group of minerals from Valle Biachella, Sacrofano
30 community (Rome, Latium, Italy). The mineral occurs in association with sodalite, biotite,
31 iron oxides, titanite, fluorite and a pyrochlore-group mineral. The groundmass of the
32 ejectum consists essentially of K-feldspar with subordinate plagioclase. Kircherite (3 mm
33 as largest size) is observed within miarolitic cavities of the rock and typically occurs as
34 parallel associations of hexagonal, thin, tabular colorless to light gray transparent crystals;
35 it is non-pleochroic and uniaxial negative, with $\omega = 1.510(2)$ and $\varepsilon = 1.502(2)$. D_{calc} is 2.457
36 g/cm^3 . Kircherite is trigonal with $a = 12.8770(7)$, $c = 95.244(6)$ Å, $V = 13677(1)$ Å³, $Z = 1$.
37 The structure has been refined in the trigonal space group $R\bar{3}2$, obtaining a R-value of
38 8.5% on 8131 reflections with $I/\sigma I > 2$. The strongest seven reflections in the X-ray powder
39 pattern are [d in Å (I %) (hkl): 3.717 (100) (3 0 0), 2.648 (100) (2 1 28; 0 0 36), 3.232 (65)
40 (2 1 19), 3.584 (60) (1 2 14), 3.604 (53) (1 0 25), 3.799 (52) (1 2 11), 3.220 (38) (2 2 0).
41 The single-crystal FTIR spectrum rules out OH groups and shows the presence of H₂O
42 and CO₂ molecules in the structural cages of the mineral. Chemical analysis gives (in
43 wt%): SiO₂ 32.05, Al₂O₃ 27.13, FeO 0.07, K₂O 4.38, CaO 8.75, Na₂O 13.62, MgO 0.01,
44 MnO 0.02, TiO₂ 0.01, SO₃ 12.87, Cl 0.35, F 0.05. The empirical formula calculated on the
45 basis of $\Sigma(\text{Si}+\text{Al}) = 216$ apfu is:

46 $(\text{Na}_{89.09}\text{Ca}_{31.63}\text{K}_{18.85}\text{Fe}_{0.20}\text{Mn}_{0.06}\text{Mg}_{0.05}\text{Ti}_{0.03})_{\Sigma=139.91}[(\text{Si}_{108.13}\text{Al}_{107.87})_{\Sigma=216.00}\text{O}_{430.00}](\text{SO}_4)_{32.58}$
47 $\text{Cl}_{2.00}\text{F}_{0.53}\cdot 6.86\text{H}_2\text{O}$, which corresponds to the ideal formula
48 $[\text{Na}_{90}\text{Ca}_{36}\text{K}_{18}]_{\Sigma=144}(\text{Si}_{108}\text{Al}_{108}\text{O}_{432})(\text{SO}_4)_{36}\cdot 6\text{H}_2\text{O}$.

49 The structure can be described as a stacking sequence of 36 layers of six-
50 membered rings of tetrahedra along the c axis. The stacking sequence is
51 ACABCABCABCACBCABCABCBCBABCABCABCAB..., where A, B and C represent
52 the positions of the rings within the layers. This sequence gives rise to cancrinite, sodalite

53 and losod cages, alternating along *c*. Sulfate groups occur within the sodalite and losod
54 cages associated by Na, K and Ca. H₂O groups occur within the cancrinite cages, bonded
55 to Ca and Na cations. Anion groups (SO₄²⁻) in sodalite cages show positional disorder, and
56 so do consequently the extraframework cation sites to them related.

57

58 **Keywords:** New minerals, kircherite, ordered interstratified sodalites-cancrinite,
59 crystal structure, IR spectroscopy, mechanical properties.

60

61

INTRODUCTION

62 The cancrinite group of feldspathoids includes several species structurally
63 characterized by layers of six-membered rings of [SiO₄] and [AlO₄] tetrahedra stacked
64 along the crystallographic *c* direction (hereafter 6mR ⊥ [00.1]). The different stacking
65 sequences give rise to different types of structural channels and cages (Bonaccorsi and
66 Merlino 2005). These pores may host several anions and molecular groups, such as H₂O,
67 Cl, (CO₃)²⁻, (SO₄)²⁻, (S₂)⁻, (S₃)⁻, (PO₄)³⁻, (C₂O₄)²⁻, CO₂ and extra-framework cations such as
68 Na, K and Ca. The stacking sequence can be simple like ...ABABAB... (where A and B
69 are the positions in successive layers, using the notation of the closest-packed structures)
70 as in cancrinite *sensu stricto*, or can be complex, leading to a variety of species for which
71 sequences of 4, 6, 8, 10, 12, 14, 16, 28, 30, and 33 layers for the *c* translation have been
72 described (for 4 to 16 see Table 2 in Bonaccorsi and Merlino 2005; 28 layers =
73 sacrofanite: Bonaccorsi et al. 2012; 30 layers = biachellaite: Chukanov et al. 2008,
74 Rastsvetaeva and Chukanov 2008; 33 layers = fantappièite: Cámara et al. 2010). Domains
75 with 18 and 24 layer sequences were also observed by transmission electron microscopy
76 (Rinaldi and Wenk 1979). An equal number of layers can also give rise to different
77 sequences, like in marinellite (Bonaccorsi and Orlandi 2003) vs tounkite (Rozenberg et al.
78 2004), both structures having 12 layers sequences, or to different anion-cation population

79 of the cages. An example of this latter case is represented by afghanite and alloriite which,
80 although having the same type of framework, differ in having Ca-Cl-Ca-Cl (Ballirano et al.
81 1997) or Na-H₂O-Na-H₂O (Chukanov et al. 2007; Rastsvetaeva et al. 2007)
82 extraframework contents, respectively. Recently, carbobystrite has been described as
83 having the same staking sequence of bystrite (ABAC) but having CO₃ and H₂O groups
84 instead of S²⁻ as in bystrite (Khomyakov et al. 2010).

85 Kircherite was found -- and donated to us by Mr. L. Mattei (1947 - 2012), a
86 distinguished amateur mineral collector -- within the miarolitic cavities of a holocrystalline
87 volcanic ejectum collected at Valle Biachella, Sacrofano community, in the Sabatini
88 volcanic complex, Latium (Italy). We succeeded to obtain a structural model for this
89 mineral, and a formal proposal was submitted the IMA-NMNC Commission, which
90 approved the species and the name (IMA 2009-086). The name kircherite is for
91 Athanasius Kircher (1602 – 1680), a German Jesuit scholar who published around 40
92 works, some of which dealt with magnetism, geology, mineralogy and volcanology.
93 Athanasius Kircher was in Rome from 1635 and was the founder of the museum of the
94 *Collegium Romanum* in 1651, hereafter named the *Museum Kircherianum*. It contained
95 collections of Roman, Etruscan, and Egyptian antiquities including mummies and large
96 collections of natural objects such as minerals and precious stones. The refined and
97 analyzed crystal is deposited at the Museum of Mineralogy of the "Sapienza" University of
98 Roma (code number MMUR 33035/1). This paper is dedicated to the memory of Luigi
99 Mattei.

100

101 **OCCURRENCE, PHYSICAL AND OPTICAL PROPERTIES**

102 The holocrystalline volcanic ejectum containing kircherite was collected at Valle
103 Biachella, Sacrofano community. Valle Biachella is a small valley on the inner side of the
104 Sacrofano caldera wall, in the eastern sector of the Sabatini volcanic complex which is

105 located in northern-central Latium about 20 km to the north of Rome. This complex,
106 together with the other Latian volcanic complexes, belongs to the so-called "Roman
107 Ultrapotassic Province." The Sabatini volcanic complex is characterized by an areal,
108 mainly explosive activity, with the emplacement of numerous eruptive centers, which
109 started about 0.6 Ma ago and ended about 0.08 Ma ago. This activity evolved throughout
110 several caldera collapses and the emission of large volumes of pyroclastic products having
111 the alkaline-potassic signature typical of the Roman Ultrapotassic Province. In Valle
112 Biachella outcrops essentially the "Sacrofano upper pyroclastic flow" unit linked to the
113 volcanic activity of the satellite center of Sacrofano (De Rita et al. 1983, 1993 and
114 references therein).

115 The ejectum, about 15 cm in size, is a granular but compact rock whitish-gray in
116 color. The groundmass consists of interlocking K-feldspar with minor sodalite, plagioclase,
117 brown mica and andraditic garnet. Fluorite, iron oxides, a pyrochlore-group mineral, and a
118 britholite-like phase are the accessory minerals (Fig. 1a and 1b). Kircherite, which occurs
119 within the interstices between the interlocking K-feldspar, occurs as parallel associations of
120 hexagonal thin tabular shaped crystals (Fig. 2a). The morphology of the kircherite crystals
121 results essentially from the combination of the {00.1} pinacoid with the $\{101; \bar{1}\}$
122 rhombohedron (Fig. 2b). The maximum size of the crystal groups does not exceed 2 or 3
123 mm in diameter and up to 1 mm in thickness; the single platelets have a thickness that
124 very rarely exceeds 0.5 mm.

125 Kircherite appears as transparent to translucent and even opaque in the most
126 altered parts of the material; the luster is greasy to silky and the streak is white. The
127 samples fluoresce light pink under long wave UV and deep red under short wave UV. It is
128 brittle with an uneven fracture and a good cleavage on {00.1}; parting is not observed. The
129 measured density, determined by flotation in a mixture of bromoform-ethanol, is $D_{\text{meas}} =$
130 2.42 g/cm^3 and the calculated density from the empirical formula is $D_{\text{calc}} = 2.457 \text{ g/cm}^3$.

131 Vickers hardness was measured at the Interdepartmental Laboratory of Electron
132 Microscopy (LIME), Università Roma Tre, by means of a Mitutoyo HM-124 microhardness
133 tester, with an applied load of 10 gf (0.1 N) (duration of force 10 s, other test parameters in
134 accordance with ASTM E384 Standard 2008). The average diagonal of the Vickers indent
135 was measured by a Digital Optical Microscope at a magnification of 1000x. Vickers
136 Hardness Number (VHN) was calculated by the following equation: $VHN=1.8544 * (P / d^2)$,
137 where the applied load P is in kgf, the average dimension d of the indentation marks is in
138 mm, with the resulting hardness number expressed in kgf/mm^2 . Results showed an
139 average Vickers hardness of 648.4 ± 107 (with a range of 208.9) HV 10 gf (corresponding
140 to about 5.5 in the Mohs scale). It is worth noting that the applied load of 10 gf was
141 selected in order to avoid cracking after indentation, and have a proper evaluation of the
142 actual hardness of the investigated material.

143 Kircherite is non-pleochroic, negative uniaxial with $\omega = 1.510(2)$ and $\varepsilon = 1.502(2)$.
144 The refractive indices were determined by the double variation method (see Su et al. 1987
145 and references therein) and the grain was oriented with the spindle stage so as to
146 measure the refractive indices (Gunter et al. 2005 and references therein).

147 According to the various studies done in the last decade on the rare minerals which
148 are typically observed in the cavities of the ejecta of Latium (e.g. Della Ventura et al.,
149 1992,1993, 1999, Bellatreccia et al., 2002) the mineral formed during late-stage
150 metasomatic processes related to the volcanic activity.

151

152 **CHEMICAL COMPOSITION**

153 The composition of kircherite was determined using a JEOL JXA 8200 WD-ED
154 electron microprobe at INGV, Rome. Operating conditions were 15 kV and 4.95 nA, with a
155 beam diameter of 5 μm ; counting time was 10 s on both peak and background. Standards,
156 spectral lines, and crystals used were: sodalite (AlK α , TAP; SiK α , PET; NaK α , TAP; ClK α ,

157 PET) augite (CaK α , PET; MgK α , TAP; FeK α , LIF), orthoclase (KK α , PET), anhydrite (SK α ,
158 PET), spessartine (MnK α , LIF), TiO (TiK α , LIF) and fluorite (FK α , TAPH). Data reduction
159 used the ZAF correction method. Analytical errors are 1% relative for major elements and
160 5% relative for minor elements. The crystal fragment used for single-crystal refinement
161 was found to be homogeneous within analytical error. The chemical composition and
162 empirical formula, calculated on the basis of 216 (Si+Al) atoms per formula unit, are given
163 in Table 1; site populations are based on the structure refinement. The simplified ideal
164 charge-balanced formula is: [Na₉₀Ca₃₆K₁₈] _{$\Sigma=144$} (Si₁₀₈Al₁₀₈O₄₃₂)(SO₄)₃₆·6H₂O, which can be
165 expressed as {[Na₅Ca₂K] _{$\Sigma=8$} (Si₆Al₆O₂₄)(SO₄)₂·0.33H₂O} × 18. This requires: K₂O 4.11,
166 Na₂O 13.51, CaO 9.78, Al₂O₃ 26.68, SiO₂ 31.44, SO₃ 13.96, H₂O 0.52, Total 100.00 wt.%.
167 The H₂O content was calculated and checked on the basis of the single-crystal refinement,
168 assuming that the 'cancrinite cages' host only H₂O, and that the (SO₄)²⁻ groups missing to
169 reach 36 per unit cell are substituted by (CO₃)²⁻ + (H₂O) + Cl⁻ + F⁻ in the 'losod' and
170 'sodalite cages' (see structure description); FTIR spectroscopy (see below) showed only
171 H₂O and a small but yet significant amount of CO₂; no OH was detected.

172

173 X-RAY DIFFRACTION AND DESCRIPTION OF THE STRUCTURE

174 The powder X-ray diffraction data of kircherite (Table 2) were collected at the
175 Dipartimento di Scienze Geologiche, Università Roma Tre, with a Scintag X1
176 diffractometer using: CuK α ($\lambda=1.5418$ Å) radiation, fixed divergence slits, and a Peltier-
177 cooled Si(Li) detector (resolution < 200eV). A divergent slit width of 2 mm and a scatter slit
178 width of 4 mm were employed for the beam source; a receiving slit width of 0.5 mm and
179 scatter slit width of 0.2 mm were used for the detector. Data were collected in step-scan
180 mode: 2-60° 2 θ range, step-size 0.02° 2 θ , counting time 3 s/step. Silicon powder SRM
181 640d was used as internal standard. The unit-cell parameters, determined using the least

182 squares refinement program LSUCRIPC (Garvey 1986), are (in Å): $a = 12.881(5)$, $c =$
183 $95.28(5)$, $V = 13,690(10) \text{ \AA}^3$.

184

185 **Structure determination and refinement**

186 A crystal of 0.73x0.40x0.27 mm was used for single crystal X-ray diffraction on a
187 Bruker AXS Smart Apex diffractometer, with $\text{MoK}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation and working
188 at 45 kV and 30 mA, at the Dipartimento di Scienze della Terra e dell'Ambiente, Università
189 di Pavia. The detector-to crystal working distance was 8 cm. L_p and empirical absorption
190 corrections (SADABS, Sheldrick 1998) were applied. The refined unit-cell parameters were
191 obtained from 9259 reflections with $I > 10\sigma(I)$ collected in the 2θ range $5\text{-}70^\circ$. Ten data
192 sets of 900 images were collected for 5 seconds performing 0.2° ω -scans at different ϕ
193 angles ($0, 90, 180$ and 270° with the detector at $\theta = 20^\circ$ and $0, 45, 90, 135, 180$ and 270°
194 with the detector at $\theta = 50^\circ$). Indexing of reflections in images was compatible with a
195 rhombohedral lattice [$a = 12.8767(7)$, $c = 95.244(6) \text{ \AA}$, in the hexagonal setting]. Integration
196 in the $2\text{-}30^\circ$ θ -range yielded 81225 reflections compatible with a maximum $3m1$ Laue
197 symmetry. The structure was tentatively solved in the space group $R3$ by direct methods
198 using SIR 2004 (Burla et al. 2005), which supplied an incomplete model with an R -value of
199 24.7 %, consisting mainly of framework cations and anions. The structure refinement was
200 completed by adding atoms to the model extracted from Fourier difference maps. This
201 allowed us to find extraframework cations and anionic groups $(\text{SO}_4)^{2-}$. We obtained a final
202 model with anisotropic displacement parameters yielding an agreement factor of $R = 0.125$
203 for 11517 reflections with $I > 2\sigma(I)$, and $R = 0.135$ for all 13437 unique reflections. There
204 were 12 four-fold coordinated cations composing the framework; and no Si-Al ordering
205 was found. The observed staking sequence in the hexagonal cell, following the Zhdanov
206 notation (Zhdanov, 1945; Patterson and Kasper, 1959), was:

207 - + + + + + + + + + - - + + + + + + + + + - - + + + + + + + + + -
 (A) C A B C A B C A B C A (C) B C A B C A B C A B C (B) A B C A B C A B C A B (A)
 0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 21 23 24 25 26 27 28 29 30 31 32 33 34 35 36

208

209 ..., where A, B and C represent the position of rings of tetrahedra within layers. The
 210 sequence for the rhombohedral cell is given below.

211 - + + + + + + + + + -
 (A) C A B C A B C A B C A [C]
 0 1 2 3 4 5 6 7 8 9 10 11 12

212

213 Therefore the sequence is expressed as an even period (12) and a different basic partition
 214 (i.e., $3 \times 12 [(10)(2)]$), and thus, following Patterson and Kasper (1959), should have a
 215 rhombohedral lattice. Both successions are centrosymmetric and both centers are in
 216 spheres. Therefore the space group should be $R3m$. However, so far all the cancrinite
 217 related minerals (but cancrsilite, where the Si:Al is not 1:1) have shown Si-Al ordering
 218 among the tetrahedral sites, and the $R3m$ space group would not allow for such ordering.
 219 Therefore we tried to lower the symmetry to that of space group $R3$. This model converged
 220 to a lower R -index (0.108). It had 24 four-fold sites this time showing ordering of Al and Si
 221 in 12 sites, respectively. Testing this model with PLATON/addsym (Spek 2008) yielded a
 222 higher symmetry model in $R32$ with 14 fourfold sites in the framework (7 Al + 7 Si sites).
 223 Refining for the presence of inversion center yielded 0.57(9) of merohedral twinning.
 224 Refinement of this model produced better <Al-O> and <Si-O> distances and maintained
 225 the Al and Si ordered. Although we cannot rule out a center of symmetry, the model with
 226 symmetry $R3$ showed no ordering; thus, we kept the highest symmetry allowing ordering of
 227 Al and Si. Refinement converged to $R = 0.084$ for 8131 reflections with $I > 2\sigma(I)$, and $R =$
 228 0.088 for all 8908 unique reflections [$R_{\text{int}} = 0.0308$, 69 restraints and 515 parameters,
 229 Goodness of fit on $F^2 = 1.056$]. The framework of tetrahedra builds up a series of cages,
 230 which are filled by cations and anions/anionic groups. The observed cage topologies are
 231 'cancrinite cages' (ϵ), $[4^36^5]$ in the IUPAC nomenclature (McCusker et al. 2001), $[4^66^8]$

232 'sodalite cages', and [4⁶11] 'losod cages'. The extraframework cation positions showed
233 strong static disorder and therefore we chose to refine those as split sites. Displacement
234 parameters of atoms in a split site were constrained to be equal. The model also has 6
235 anionic groups: 2 out of them (those located at the 'losod cages', see description of the
236 structure) are ordered; four are located in 'sodalite cages' in off-axis positions and were
237 refined with isotropic displacement parameters. Careful search for maxima in the Fourier-
238 difference maps allowed location of some of the oxygen atoms at the vertexes of the
239 (SO₄)²⁻ groups. These were added to the model and refined with a soft constraint on the
240 bond-length; in order to let the model to reach a minimum, displacement parameters were
241 constrained to be equal to those observed for the ordered (SO₄)²⁻ groups. Final atomic
242 coordinates and equivalent isotropic displacement parameters are given in Table 4,
243 selected distances for framework cations in Table 5a and selected distances for extra-
244 framework cations and anionic groups in Table 5b and 5c (the CIF has been deposited as
245 electronic supplemental material).

246

247

FTIR SPECTROSCOPY

248 The powder FTIR spectrum of kircherite was collected at the Dipartimento di
249 Scienze Geologiche, Università Roma Tre on a Nicolet Magna 760 FTIR spectrometer
250 equipped with a DTGS detector and a KBr beamsplitter; the nominal resolution was 4 cm⁻¹
251 and 64 scans were averaged for each sample and for the background. The spectrum was
252 collected on a KBr disk with about 1 mg of sample in 150 mg of KBr. Single-crystal FTIR
253 spectra were collected on crystal fragments ~ 30 μm thick using a NicPlan microscope
254 equipped with a liquid nitrogen-cooled MCT detector; the nominal resolution was 4 cm⁻¹
255 and 128 scans were averaged for each sample and for the background.

256 The infrared powder spectrum of kircherite (Fig. 3a) shows a broad absorption from
257 3740 cm⁻¹ to 3000 cm⁻¹ due to the stretching modes plus the bending overtone (ν_1 , ν_3 and

258 $2\nu_2$) of the H₂O molecule(s) and at 2338 cm⁻¹ a small but sharp absorption assigned to the
259 stretching mode (ν_3) of the CO₂ molecules (Della Ventura et al. 2005, 2007, 2008). This
260 value is in the range observed for CO₂ bearing cancrinite group minerals, where the
261 wavenumber of this band has been observed to vary from 2338 cm⁻¹ for fantappièite
262 (Cámara et al. 2010) up to 2352 cm⁻¹ for marinellite (Bellatreccia et al. 2007). In the
263 frequency region from 400 to 1750 cm⁻¹ (Fig. 3b) there is a broad band due to the bending
264 mode (ν_2) of the H₂O molecule at 1635 cm⁻¹ and a multi-component strong band at 1200-
265 1000 cm⁻¹, which can be assigned to the stretching modes of the (SO₄)²⁻ and TO₄ groups
266 (Moenke 1974; Ross 1974). A sharp but very weak absorption is observed at 1384 cm⁻¹
267 which can be assigned to (CO₃)²⁻ groups. A group of well-defined bands occur in the range
268 800-500 cm⁻¹; in particular, six absorptions at 698, 651, 609, 590, 546 and a shoulder at
269 737 cm⁻¹ are resolved. Finally, a very intense and convoluted absorption is observed at
270 around 446 cm⁻¹. As already discussed in previous papers (e.g., Ballirano et al. 1996a;
271 Cámara et al. 2005, 2010) this spectral region is characteristic of any cancrinite group
272 species and is useful for identification purposes. In this particular case, although being
273 typical of kircherite, it shows some similarities with the spectra of haüyne, franzinite and
274 fantappièite (Ballirano et al. 1996a; Cámara et al. 2005, 2010).

275 The single-crystal FTIR spectrum was collected in the 6000-650 cm⁻¹ range; the
276 4000 to 1500 cm⁻¹ region is displayed in Figure 5. It shows a very intense multi-component
277 band which can be resolved into three main components at 3527 cm⁻¹, 3412 cm⁻¹ and
278 3246 cm⁻¹ which can be assigned to the stretching modes (ν_1 and ν_3) and the first bending
279 overtone ($2\nu_2$) of the H₂O molecule(s), respectively. The spectrum also shows a very
280 sharp absorption at 2338 cm⁻¹ which confirm the presence of CO₂ molecules in the
281 structural pores of kircherite (Della Ventura et al. 2005, 2007, 2008). The broad absorption
282 at 2125 cm⁻¹ can be assigned to the first overtone or combination modes of the T-O bonds
283 and to the first overtone of the asymmetric stretching mode (ν_3) of the (SO₄)²⁻ group (Della

284 Ventura et al. 2008). The strong absorption at 1636 cm^{-1} is due to the H_2O bending mode
285 (ν_2) and the shoulder at 1687 cm^{-1} can be attributed to combination of T-O modes. Finally,
286 a broad absorption at around 5234 cm^{-1} (not shown) is assigned to the combination of the
287 stretching (ν_3) + bending (ν_3) modes of H_2O (lhinger et al. 1994). The absence of bands in
288 the $4300\text{-}4100\text{ cm}^{-1}$ range (inset in Fig. 5), due to the combination modes of the in OH
289 group (lhinger et al. 1994), rules out the presence of hydroxyl groups in kircherite.

290

291

DESCRIPTION OF THE CRYSTAL STRUCTURE

292 The structure has six 'cancrinite cages' (ϵ), [4^36^5] in the IUPAC nomenclature
293 (McCusker et al. 2001), 24 [4^66^8] 'sodalite cages' (S), and 6 [4^66^{11}] 'losod cages' (Lo)
294 within the unit cell. There is a unique sequence of cages, and adjacent sequences are
295 shifted $1/3$ along $[00.1]$. Different types of cages are ordered as $\epsilon\text{SSSLoSSLoSS}\epsilon$ (Fig.
296 6).

Cancrinite (ϵ) cages

298 Cancrinite cages contain (H_2O) groups, which coordinate Na atoms at Na1 site in
299 the $6\text{mR} \perp [00.1]$ window shared by two consecutive ϵ -cages and to Ca atoms at the other
300 $6\text{mR} \perp [00.1]$ windows with long and weak bonds (2.93 \AA). Refined site scattering is
301 compatible with almost full occupancy of H_2O in one on-axis position completing the
302 ditrigonal pyramid corresponding to the Na coordinating environment. There are 6 ϵ cages
303 per unit cell, which accounts for 6 H_2O p.f.u.

Losod cages

305 Six [4^66^{11}] cages (losod cages) are present p.f.u., which match with two sodalite
306 cages ($[4^66^8]$) along $[00.1]$. The losod cage occurs in many members of the group: bystrite
307 and carbobystrite, liottite (Ballirano et al. 1996b), franzinite, tounkite, biachellaite,
308 fantappiéite, sacrofanite, and obviously kircherite. In kircherite, each losod cage contains

309 two $(\text{SO}_4)^{2-}$ groups ordered with apexes pointing oppositely along $[00.1]$, which coordinate
310 3 K atoms off-axis in the plane between the bases of the two $(\text{SO}_4)^{2-}$ groups, Ca atoms at
311 the Ca3 site in one of the $6\text{mR} \perp [00.1]$ windows and Ca and minor Na atoms at the Ca7
312 site centered approximately at the other the $6\text{mR} \perp [00.1]$ window. Na and Ca at the Na2
313 and Na4 sites in the center of the six membered rings in the wall of the cage (hereafter
314 $6\text{mR} \parallel [00.1]$) also coordinates with the oxygen apexes of the $[(\text{S1})\text{O}_4]^{2-}$ and $[(\text{S2})\text{O}_4]^{2-}$
315 anionic groups, respectively. These two cation positions have different occupancy as a
316 function of the anion located at the center of the adjacent sodalite cages.

317 *Sodalite cages*

318 Sodalite cages ($[4^66^8]$) are the most frequent cages in kircherite (up to 24 sodalite
319 cages per unit cell). They mostly contain $(\text{SO}_4)^{2-}$ groups disordered so that it was not
320 possible to find the position of all oxygen atoms in the four symmetrically independent
321 sites. This disorder is common in all the minerals of the cancrinite group showing this type
322 of cage, usually containing sulfate groups in more than one orientation, as well as split
323 cation sites in the two $6\text{mR} \perp [00.1]$ and the six $6\text{mR} \parallel [00.1]$ windows that may host Na or
324 Ca cations. Sodalite cages also contain minor Cl (and F) that coordinates Ca and (H_2O)
325 which coordinates Na (up to complete 36 anion groups and anions per formula unit; see
326 Table 6). Therefore the composition of sodalite cages are mostly related to haüynic and to
327 a lesser degree sodalitic and noseanic. The white color of kircherite probably excludes the
328 presence of $(\text{S}_3)^-$ at the sodalitic cages, which usually results in the blue coloration of
329 these minerals (Ostroumov et al. 2002; Fleet et al. 2005). Overall, the number and type of
330 cages in the unit cell account for a maximum of 36 $(\text{SO}_4)^{2-}$ groups and 6 (H_2O) molecules
331 (or Cl^- anions).

332 *Site assignment*

333 Assigned site population on the basis of observed site scattering and site geometry
334 (i.e., bonding environment) is reported Table 6. There is a slight disagreement between

335 the Ca + K assignments based on the refinement as compared to that determined by
336 electron microprobe. However, considering the similar scattering power of both atomic
337 species, the observed disagreement might be ascribed to erroneous assignment of
338 elements to these sites, which is done on the basis of the mean bond lengths, as the
339 bonding environments put some restrictions to the occupying species on the basis of their
340 ionic radii. Considering the large cell, the complexity of the structure and the observed *R*-
341 factor, the disagreement should be ascribed to difficulties on refining the split positions
342 thus leading to local geometries incompatible for Ca population or excess observed site
343 scattering. Disagreement with the calculated site scattering for cation sites from EMP
344 analyses is 7.8%. This is the case in particular for the split sites K6B, K9B, K1G and K1L,
345 which account for 17.53 K apfu; their bonding environment is too large for Ca and Na.

346 Considering the extraframework composition obtained by EMP analyses and the
347 dominant anionic species or groups in the cages, the simplified ideal charge-balanced
348 formula is: $[\text{Na}_{90}\text{Ca}_{36}\text{K}_{18}]_{\Sigma=144}(\text{Si}_{108}\text{Al}_{108}\text{O}_{432})(\text{SO}_4)_{36}\cdot 6\text{H}_2\text{O}$, which can be expressed as
349 $\{[\text{Na}_5\text{Ca}_2\text{K}]_{\Sigma=8}(\text{Si}_6\text{Al}_6\text{O}_{24})(\text{SO}_4)_2\cdot 0.33\text{H}_2\text{O}\}^*18$. This requires: K₂O 4.11, Na₂O 13.51, CaO
350 9.78, Al₂O₃ 26.68, SiO₂ 31.44, SO₃ 13.96, H₂O 0.52, Total 100.00 wt.%.

351 The compatibility indices (Mandarino 1981) are: $(1 - K_P)/K_C = -0.022$ (i.e., excellent)
352 by using D_{calc} , and $(1 - K_P)/K_C = -0.038$ (i.e., excellent) by using D_{meas} , indicating excellent
353 agreement between physical and chemical data.

354

355

RELATION TO OTHER SPECIES

356 Kircherite is a new mineral of the cancrinite-sodalite group and is a member of the
357 subgroup with a complex sequence. Within this subgroup, kircherite, having 36 layers (in
358 the hexagonal setting; 12 in the rhombohedral), is the cancrinite with the longest complex
359 sequence described to date. Considering the rhombohedral setting, it is the third mineral of
360 the cancrinite-sodalite group showing 12 layers sequence, along with tounkite (Rozenberg

361 et al. 2004) and marinelite (Bonaccorsi and Orlandi 2003). The three structures have very
362 different layers sequences, Zhdanov symbol and number and type of cages:

363 Marinelite: ABCBCBACBCBC |1(4)1|1(4)1| 2 lio, 4 sod, 6 ϵ

364 Tounkite: ABABACACABAC (2)211(2)211 2 lio, 2 sod, 8 ϵ

365 Kircherite: ACABCABCABCA [(10)(2)] 2 los, 8 sod, 2 ϵ

366 being lio = 'liottite cages' [$4^6 6^{17}$]. The different topology in terms of cages constrain the
367 chemistry of the three different minerals. Nevertheless, a correct identification cannot be
368 done on the basis of only a chemical analysis, and requires a X-ray diffraction.

369 Careful inspection of the sequence (Fig. 6) reveals that the structure of kircherite
370 can be derived from that of sodalite by inserting a shifted layer every 11 layers, as for
371 fantappièite and franzinite. In the case of fantappièite the structure can be obtained from
372 sodalite by inserting a shifted layer every 10 layers [sequence (9)(2)], and from franzinite
373 by inserting a shifted layer every 9 layers [sequence (8)(2)]. Therefore, kircherite
374 represents the third member of a particular subgroup in which ordered interstratified
375 sodalite-cancrinite sequences are found to follow the scheme: (*nsod*)(*can*), for $n = 1, 2, 3,$
376 $4, \dots$ Expected sequences are (3)(2), (4)(2), (5)(2), (6)(2), (7)(2), (8)(2), (9)(2), (10)(2), \dots ,
377 of which the last three have been discovered. Two of these have hexagonal cells [i.e.,
378 (5)(2) and (8)(2)], while the remainder have rhombohedral cells and therefore sequences
379 of 15, 18, 24, 27, 33 and 36 layers in the hexagonal setting, corresponding to *c* axis
380 lengths of *ca* 39.7, 47.6, 63.5, 71.4, 87.3, and 95.2 Å.

381

382

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389

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513 **TABLE CAPTIONS**

514

515 **Table 1.** Chemical composition determined using electron microprobe (mean of 18
516 analyses) and empirical formula of kircherite calculated on the basis of $\Sigma(\text{Si}+\text{Al}) = 216$
517 apfu.

518

519 **Table 2.** Powder X-ray diffraction data for kircherite.

520

521 **Table 3.** Crystal data and structure refinement for kircherite.

522

523 **Table 4.** Atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for
524 framework cations and anions in kircherite.

525

526 **Table 4 ctd.** Atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for
527 extraframework cations and anions in kircherite.

528

529 **Table 5a.** Selected distances of framework cations for kircherite.

530

531 **Table 5b.** Selected distances of extra-framework cations sites for kircherite.

532

533 **Table 5c.** Selected distances of extra-framework anionic groups for kircherite.

534

535 **Table 6.** Cation site assignments on the basis of observed site scattering and geometries
536 of the sites reported in Table 5 for kircherite

537

538

539 **FIGURE CAPTIONS**

540

541 **Fig. 1.** Photomicrographs (crossed polars) of kircherite in thin section: a) kircherite (kir)
542 with k-feldspar (Kf) and biotite (bio); b) typically twinned crystals of kircherite.

543

544 **Fig. 2.** a) Photomicrographs and b) morphological sketch of kircherite (sample and photo
545 L. Mattei).

546

547 **Fig. 3.** FTIR powder spectrum of kircherite: a) H₂O (stretching) and CO₂ absorptions (* =
548 grease); b) low frequency region with the H₂O (bending), SO₄²⁻, trace of CO₃²⁻ and the
549 typical (Si,Al)O₄ absorptions (see text for explanations).

550

551 **Fig. 4.** The FTIR powder spectrum of kircherite compared to the spectra of haüyne,
552 franzinite, and fantappièite.

553

554 **Fig. 5.** The single-crystal unpolarized-light FTIR spectrum of kircherite; NIR region in the
555 inset.

556

557 **Fig. 6.** Projection of the kircherite structure along $[112; \bar{0}]$ showing the stacking sequence
558 of cages along $[00.1]$ at $(0,0,z)$. ε: 'cancrinite cage' (gray); s: 'sodalite cage' (light gray); los:
559 'losod cage' (dark gray). Si: dark gray spheres; Al: light gray spheres.

First revision 20/03/2012

Table 1. Chemical composition determined using electron microprobe (mean of 18 analyses) and empirical formula of kircherite calculated on the basis of $\Sigma(\text{Si}+\text{Al}) = 216$ apfu.

	Wt. %	Range		apfu
SiO ₂	32.05	31.17-33.31	Si	108.13
Al ₂ O ₃	27.13	26.66-27.62	Al	107.87
FeO	0.07	0.00-0.18	Σ	216.00
K ₂ O	4.38	4.15-4.62		
CaO	8.75	8.48-9.29	Ca	31.63
Na ₂ O	13.62	12.66-14.02	Fe ²⁺	0.20
MgO	0.01	0.00-0.05	K	18.85
MnO	0.02	0.00-0.08	Na	89.09
TiO ₂	0.01	0.00-0.05	Ti	0.03
SO ₃	12.87	12.61-13.46	Mg	0.05
Cl	0.35	0.28-0.42	Mn	0.06
F	0.05	0.00-0.20	Σ	139.91
H ₂ O [‡]	0.61	0.74-0.44		
	99.92	98.75-102.02	SO ₄ ²⁻	32.58
O=F,Cl	0.10	0.06-0.16	Cl ⁻	2.00
Total	99.82	98.65-101.86	F ⁻	0.53
			H ₂ O [‡]	6.86
			O	430.19

[‡] Calculated on the basis of the single-crystal refinement (see text).

First revision 20/03/2012

Table 2. Powder X-ray diffraction data for kircherite.

I/I_0 (%)	d_{meas} (Å)	d_{calc} (Å)	hkl	I/I_0 (%)	d_{meas} (Å)	d_{calc} (Å)	hkl
4	31.75	31.76	003	12	2.914	2.914	3,1,11
3	15.88	15.88	006	7	2.886	2.887	0,0,33
10	11.10	11.08	101	2	2.843	2.849	1,1,30; 1,3,13
5	10.85	10.86	012	5	2.817	2.817	3,1,14
15	10.04	10.10	104	4	2.783	2.784	042; 401
2	9.461	9.627	015	4	2.766	2.766	1,2,26; 045
3	6.868	6.842	0,1,11	3	2.751	2.751	2,2,18; 1, 3, 16
17	6.440	6.440	110	100	2.648	2.648	2,1,28; 0,0,36
11	5.809	5.810	0,1,14	3	2.603	2.606	4,0,13
4	5.576	5.568	021	7	2.577	2.581	0,4,14
2	5.460	5.431	024	3	2.549	2.545	324; 235
3	5.292	5.293	0,0,18	3	2.516	2.515	327; 1,0,37
3	5.248	5.253	1,0,16	2	2.499	2.501	2,2,24; 0,4,17
2	5.075	5.051	208	3	2.466	2.472	3,2,10
3	5.012	5.008	0,1,17	5	2.451	2.448	1,1,36; 2,0,35
6	4.792	4.814	0,2,10	5	2.434	2.434	410; 1,2,32
3	4.697	4.689	2,0,11	3	2.408	2.407	0,4,20; 416
3	4.572	4.574	1,0,19	3	2.401	2.402	1,3,25; 2,3,14
3	4.421	4.439	0,2,13	2	2.352	2.351	3,2,16
3	4.329	4.314	2,0,14	6	2.250	2.251	4,0,25; 3,1,29
7	4.215	4.212	211; 122	7	2.168	2.172	0,5,10; 1,0,43
3	4.157	4.152	214	17	2.156	2.157	4,0,28
7	4.107	4.117	125	21	2.147	2.145	3,1,32
7	4.090	4.089	1,1,18	12	2.141	2.140	1,1,42; 333
4	4.070	4.071	0,2,16	3	2.045	2.045	2,2,36; 3,1,35
6	4.037	4.037	1,0,22	3	2.040	2.042	3,0,39; 0,5,19
3	3.983	3.975	128	3	2.003	2.003	511; 152; 4,1,27
3	3.945	3.954	2,0,17	2	1.954	1.952	1,5,11; 0,4,35
52	3.799	3.791	1,2,11	4	1.926	1.926	1,2,44; 4,2,20; 0,5,25
100	3.717	3.718	300	18	1.916	1.916	1,0,49
3	3.657	3.655	2,1,13	3	1.878	1.878	0,1,50
53	3.604	3.607	1,0,25	3	1.873	1.868	0,0,51
60	3.584	3.584	1,2,14	3	1.865	1.866	0,5,28; 2,3,35
24	3.551	3.529	0,0,27	3	1.834	1.834	431; 3,3,27
5	3.466	3.482	0,1,26	3	1.830	1.831	609; 434
5	3.445	3.441	2,1,16	3	1.825	1.825	345; 5,1,22
8	3.370	3.369	1,2,17	2	1.818	1.817	437; 3,2,37
9	3.353	3.367	3,0,12	6	1.796	1.794	1,1,51; 3,4,11
19	3.313	3.326	2,0,23	7	1.793	1.792	2,4,28; 4,1,36
13	3.252	3.255	1,0,28	5	1.787	1.786	520; 5,0,32
65	3.232	3.227	2,1,19	3	1.646	1.646	1,3,49; 6,0,27
38	3.220	3.220	220	11	1.633	1.631	2,4,37; 5,1,34
11	3.152	3.152	0,1,29; 0,2,25	3	1.614	1.614	4,3,28; 1,5,35
9	3.050	3.043	3,0,18	8	1.610	1.610	440; 3,2,46
8	3.021	3.021	2,1,22	4	1.606	1.605	6,0,30; 2,1,55
6	2.994	2.995	318	2	1.573	1.572	0,5,43; 7,0,10
5	2.944	2.943	1,3,10	3	1.568	1.567	0,7,11; 1,5,38

First revision 20/03/2012

Table 3. Crystal data and structure refinement for kircherite.

Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Trigonal	
Space group	<i>R</i> 32	
Unit cell dimensions	a = 12.8770(7) Å	α = 90°
	b = 12.8770(7) Å	β = 90°
	c = 95.244(6) Å	γ = 120°
Volume	13677.2(13) Å ³	
Z	1	
Density (calculated)	2.383 Mg/m ³	
Crystal size	0.73 x 0.40 x 0.27 mm ³	
Theta range for data collection	1.28 to 30.03°.	
Index ranges	-18 ≤ h ≤ 17, -18 ≤ k ≤ 18, -133 ≤ l ≤ 133	
Reflections collected	81125	
Independent reflections	8900 [<i>R</i> _(int) = 0.0308]	
Completeness to theta = 30.03°	99.7 %	
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Data / restraints / parameters	8900 / 10 / 510	
Goodness-of-fit on <i>F</i> ²	1.038	
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0847, <i>wR</i> ² = 0.2304	
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0893, <i>wR</i> ² = 0.2370	
Absolute structure parameter	0.53(9)	
Largest diff. peak and hole	3.246 and -2.136 e.Å ⁻³	

First revision 20/03/2012

Table 4. Atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for framework cations and anions in kircherite.

Atom	Wyck.	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	U(eq)
Si1	9d	0.25209(13)	0	0	0.0153(4)
Si2	18f	0.92141(11)	0.58468(10)	0.028745(16)	0.0138(3)
Si3	18f	0.25017(11)	-0.00038(10)	0.056598(17)	0.0153(3)
Si4	18f	0.33285(11)	0.41471(13)	0.084480(16)	0.0165(3)
Si5	18f	0.41674(13)	0.08479(13)	0.112132(17)	0.0176(3)
Si6	18f	0.24895(14)	0.24891(14)	0.139370(16)	0.0180(3)
Si7	9e	1/3	0.91414(17)	1/6	0.0189(4)
Al1	9d	0	0.74422(14)	0	0.0150(4)
Al2	18f	0.40708(12)	0.08485(12)	0.028747(18)	0.0155(3)
Al3	18f	0.25229(13)	0.25532(13)	0.056187(18)	0.0151(3)
Al4	18f	0.33367(13)	0.91923(15)	0.084777(19)	0.0184(4)
Al5	18f	0.41672(15)	0.33299(12)	0.111910(18)	0.0179(4)
Al6	18f	0.24778(16)	-0.00033(13)	0.139511(19)	0.0206(4)
Al7	9e	0.58118(19)	0.91451(19)	1/6	0.0189(5)
O1	18f	0.1218(4)	0.8853(4)	0.00247(3)	0.0257(6)
O2	18f	0.3374(3)	0.0159(4)	0.01327(4)	0.0216(8)
O3	18f	0.9782(4)	0.6459(4)	0.01398(4)	0.0265(10)
O4	18f	0.7830(3)	0.5489(3)	0.03041(3)	0.0241(6)
O5	18f	0.5400(4)	0.0786(3)	0.02974(3)	0.0273(6)
O6	18f	0.0006(4)	0.6698(5)	0.04121(5)	0.0293(10)
O7	18f	0.3192(4)	-0.0016(4)	0.04249(5)	0.0270(9)
O8	18f	0.1132(4)	0.8975(4)	0.05576(3)	0.0284(6)
O9	18f	0.2539(3)	0.1258(4)	0.05938(3)	0.0286(6)
O10	18f	0.3256(5)	0.9846(4)	0.06921(5)	0.0336(11)
O11	18f	0.3276(5)	0.3547(5)	0.06976(6)	0.0379(11)
O12	18f	0.4495(4)	0.8905(3)	0.08400(4)	0.0354(7)
O13	18f	0.2192(4)	0.4260(4)	0.08817(4)	0.0368(8)
O14	18f	0.3496(6)	0.3371(5)	0.09634(6)	0.0413(12)
O15	18f	0.3505(6)	0.0155(7)	0.09803(7)	0.0561(18)
O16	18f	0.4517(5)	0.2220(5)	0.11056(5)	0.0530(11)
O17	18f	0.5372(6)	0.0802(5)	0.11528(5)	0.0554(12)
O18	18f	0.3335(8)	0.0189(7)	0.12516(8)	0.077(3)
O19	18f	0.3153(7)	0.3075(7)	0.12514(7)	0.0612(19)
O20	18f	0.1171(5)	0.2216(6)	0.13723(5)	0.0691(17)
O21	18f	0.2402(6)	0.1267(6)	0.14278(6)	0.0774(19)
O22	18f	0.6607(9)	0.9789(8)	0.15169(8)	0.086(3)
O23	18f	0.3132(7)	0.9767(7)	0.15362(8)	0.088(3)
O24	18f	0.4455(6)	0.8978(7)	0.16380(6)	0.093(2)

Table 4 ctd. Atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for extraframework cations and anions in kircherite.

Atom	Wyck.	Occ.	x	y	Z	U(eq)
K1	18f	1	0.21935(14)	0.78244(14)	0.026734(9)	0.0316(2)
Na1	3a	1	0	0	0	0.0620(19)
Na2A	9d	0.616(16)	0	0.49632(18)	0	0.0281(7)
Ca2B	9d	0.384(16)	0	0.49632(18)	0	0.0281(7)
Ca3	6c	1.009(8)	2/3	1/3	0.035016(17)	0.0283(5)
Na4A	18f	0.771(12)	0.4865(2)	0.97775(17)	0.055175(17)	0.0383(6)
Ca4B	18f	0.229(12)	0.4865(2)	0.97775(17)	0.055175(17)	0.0383(6)
Na5A	6c	0.720(14)	0	0	0.06575(15)	0.051(2)
Ca5B	6c	0.280(14)	0	0	0.05922(19)	0.051(2)
Na6A	18f	0.644(9)	0.3399(6)	0.1714(5)	0.08322(4)	0.0451(10)
K6B	18f	0.249(4)	0.4289(6)	0.2173(6)	0.07941(5)	0.0451(10)
Na6B	18f	0.193(8)	0.2762(19)	0.1439(16)	0.08739(14)	0.0451(10)
Na7A	6c	0.05(2)	1/3	2/3	0.08904(2)	0.0354(7)
Ca7B	6c	0.95(2)	1/3	2/3	0.08904(2)	0.0354(7)
Na8A	6c	0.452(15)	2/3	1/3	0.10234(13)	0.055(3)
Na8B	6c	0.08(2)	2/3	1/3	0.1135	0.055(3)
Na8C	6c	0.68(2)	2/3	1/3	0.12063(11)	0.055(3)
K9A	18f	0.236(5)	0.1242(10)	0.2467(9)	0.10791(7)	0.0544(14)
Na9A	18f	0.630(9)	0.1591(7)	0.3183(7)	0.11131(5)	0.0544(14)
Na9B	18f	0.203(7)	0.2035(18)	0.4025(18)	0.11546(13)	0.0544(14)
Na1C	6c	0.53(2)	0	0	0.13014(15)	0.065(4)
Na1D	6c	0.18(3)	0	0	0.1396	0.065(4)
Na1E	6c	0.50(2)	0	0	0.14781(19)	0.065(4)
Na1F	18f	0.23(3)	0.4939(10)	0.9927(7)	0.13870(8)	0.016(3)
K1G	18f	0.411(16)	0.4686(13)	0.930(2)	0.13597(9)	0.117(7)
Na1G	18f	0.367(13)	0.5223	1.0488(18)	0.1413	0.117(7)
Na1K	6c	0.516(17)	1/3	2/3	0.15719(9)	0.044(3)
K1L	18f	0.210(4)	0.2474(9)	0.1287(10)	0.17056(6)	0.0575(16)
Na1L	9d	0.580(7)	1/3	0.1667(9)	1/6	0.0575(16)
Ow25	6c	0.94(4)	0	0	0.02844(18)	0.148(10)
S1	6c	1	0.3333	0.6667	0.00351(2)	0.0270(3)
O1SA	6c	1	0.6667	0.3333	0.01182(7)	0.0530(18)
O1SB	18f	1	0.2093(3)	0.6027(5)	0.00861(5)	0.0464(9)
S2	6c	1	0.3333	0.6667	0.05032(2)	0.0313(4)
O2SA	6c	1	0.3333	0.6667	0.06586(9)	0.0553(8)
O2SB	18f	1	0.2101(4)	0.6033(6)	0.04503(5)	0.0553(8)
S3	18f	0.307(7)	0.6293(5)	0.2982(5)	0.06703(5)	0.0616(15)
O3SA	18f	0.158(11)	0.5436(13)	0.2755(19)	0.07575(14)	0.0553(8)
O3SB	18f	0.142(10)	0.6010(19)	0.2033(13)	0.05750(14)	0.0553(8)
S4	18f	0.300(6)	-0.005(2)	-0.0256(11)	0.09660(6)	0.088(3)
O4SA	18f	0.169(11)	0.0632	-0.0619	0.1048	0.0553(8)
O4SB	18f	0.135(10)	-0.0589	-0.1188	0.0872	0.0553(8)
S5	18f	0.229(7)	0.3110(8)	0.6776(9)	0.12342(4)	0.0473(17)
O5SA	18f	0.151(11)	0.394	0.7873	0.1326	0.0553(8)
O5SB	18f	0.119(11)	0.2726	0.7297	0.1137	0.0553(8)
S6	18f	0.94(4)	0.7000(8)	0.3668(8)	0.15261(7)	0.060(3)
O6SA	18f	0.307(7)	0.7945	0.3943	0.1438	0.0553(8)
O6SB	18f	0.158(11)	0.7271	0.4598	0.1613	0.0553(8)

Table 5a. Selected distances of framework cations for kircherite.

Si1—O1 ⁱ	1.604(4)	Al1—O1	1.722(5)
Si1—O1 ⁱⁱ	1.604(4)	Al1—O1 ^{xii}	1.722(5)
Si1—O1 ⁱⁱⁱ	1.619(4)	Al1—O3 ^{xiii}	1.761(4)
Si1—O1	1.619(4)	Al1—O3 ^{xiv}	1.761(4)
<Si1—O>	1.612	<Al1—O>	1.742
Si2—O4	1.611(4)	Al2—O7	1.725(4)
Si2—O3	1.599(4)	Al2—O5	1.756(5)
Si2—O5 ^v	1.590(5)	Al2—O4 ^v	1.717(4)
Si2—O6 ^{vi}	1.591(4)	Al2—O2	1.724(4)
<Si2—O>	1.598	<Al2—O>	1.731
Si3—O10 ^j	1.616(4)	Al3—O6 ^{xv}	1.706(5)
Si3—O9	1.623(5)	Al3—O8 ^{xv}	1.732(5)
Si3—O8 ⁱ	1.590(5)	Al3—O9	1.735(4)
Si3—O7	1.615(4)	Al3—O11	1.735(5)
<Si3—O>	1.611	<Al3—O>	1.727
Si4—O11	1.586(5)	Al4—O15 ^x	1.705(5)
Si4—O12 ^{viii}	1.601(6)	Al4—O13 ^{viii}	1.744(5)
Si4—O14	1.592(5)	Al4—O12	1.708(6)
Si4—O13	1.580(5)	Al4—O10	1.733(5)
<Si4—O>	1.590	<Al4—O>	1.723
Si5—O18	1.581(5)	Al5—O14	1.731(5)
Si5—O17	1.609(7)	Al5—O16	1.705(7)
Si5—O16	1.597(7)	Al5—O17 ^{xvi}	1.680(7)
Si5—O15	1.602(5)	Al5—O19	1.724(6)
<Si5—O>	1.597	<Al5—O>	1.710
Si6—O19	1.579(6)	Al6—O21	1.716(7)
Si6—O22 ^{viii}	1.577(6)	Al6—O20 ^{iv}	1.715(7)
Si6—O21	1.554(7)	Al6—O23 ⁱⁱⁱ	1.689(6)
Si6—O20	1.565(6)	Al6—O18	1.695(6)
<Si6—O>	1.569	<Al6—O>	1.704
Si7—O24	1.584(7)	Al7—O22	1.710(6)
Si7—O24 ^x	1.584(7)	Al7—O22 ^{xi}	1.710(6)
Si7—O23	1.571(5)	Al7—O24 ^{xi}	1.673(7)
Si7—O23 ^x	1.572(5)	Al7—O24	1.673(7)
<Si7—O>	1.578	<Al7—O>	1.692

Symmetry codes:

- (i) x-y, -y, -z; (ii) 1+x-y, 1-y, -z; (iii) x, -1+y, z; (iv) -x+y, -x, z;
(v) 1-y, x-y, z; (vi) 1+x, y, z; (vii) 2-y, 1+x-y, z; (viii) -x+y, 1-x, z;
(ix) 0.66667-x, 0.33333-x+y, 0.33333-z; (x) x, 1+y, z;
(xi) -0.33333+y, 0.33333+x, 0.33333-z; (xii) -x, -x+y, -z;
(xiii) 1-x, 1-x+y, -z; (xiv) -1+x, y, z; (xv) 1-y, 1+x-y, z; (xvi) 1-x+y, 1-x, z

Table 5b. Selected distances of extra-framework cations sites for kircherite.

K1-O1SB ^{viii}	2.788(6)	Na1-O1 ^{xviii}	2.648(3)	Na2A-O3XIV	2.471(5)	Ca3-O1SA	2.209(7)
K1-O2SB ^{viii}	2.800(7)	Na1-O1 ^{xv}	2.648(3)	Na2A-O3XIII	2.471(5)	Ca3-O4 ^{xvi}	2.447(3)
K1-O6	2.803(5)	Na1-O1 ⁱⁱ	2.648(3)	Na2A-O1SB	2.474(4)	Ca3-O4 ^v	2.447(3)
K1-O1SB	2.839(5)	Na1-O1 ^{xviii}	2.648(3)	Na2A-O1SBXII	2.474(4)	Ca3-O4	2.447(3)
K1-O7 ^x	2.840(5)	Na1-O1 ^{xix}	2.648(3)	Na2A-O2XX	2.498(4)	Ca3-O3SB ^v	2.586(14)
K1-O2SB	2.845(7)	Na1-O1 ⁱ	2.648(3)	Na2A-O2XXI	2.499(4)	Ca3-O3SB	2.586(14)
K1-O2 ^x	2.902(5)	Na1-Ow25 ^{xx}	2.709(17)	Na2A-O5XXI	2.965(3)	Ca3-O3SB ^{xvi}	2.586(14)
K1-O3 ^{xiv}	2.958(5)	Na1-Ow25	2.709(17)	Na2A-O5XX	2.965(3)	Ca3-O5	2.885(3)
K1-O1	3.216(3)	<Na1-O>	2.663	<Na2A-O>	2.602	Ca3-O5 ^v	2.885(3)
<K1-O>	2.888					Ca3-O5 ^{xvi}	2.885(3)
		Na5A-O4SB ^{xxi}	2.435(12)	Ca5B-O8 ^{xviii}	2.429(4)	<Ca3-O>	2.596
Na4A-O2SB ^{viii}	2.307(5)	Na5A-O4SB ^{iv}	2.435(12)	Ca5B-O8 ⁱ	2.429(4)		
Na4A-O11XV	2.498(7)	Na5A-O4SB	2.435(12)	Ca5B-O8 ^{xv}	2.429(4)	Na6A-O3SA	2.381(16)
Na4A-O10	2.504(6)	Na5A-O8X ^{vii}	2.587(6)	Ca5B-O9 ^{iv}	2.831(3)	Na6A-O14	2.422(8)
Na4A-O3SBX	2.525(15)	Na5A-O8I	2.587(6)	Ca5B-O9	2.831(3)	Na6A-O9	2.465(4)
Na4A-O6VIII	2.593(6)	Na5A-O8 ^{xv}	2.587(6)	Ca5B-O9 ^{xxi}	2.831(3)	Na6A-O4SB ^{xxi}	2.495(7)
Na4A-O7X	2.597(5)	Na5A-O9 ^{iv}	2.895(5)	Ca5B-Ow25	2.93(3)	Na6A-O15	2.512(9)
Na4A-O5X	2.672(3)	Na5A-O9	2.895(5)	Ca5B-O4S ^{bxxi}	2.976(16)	Na6A-O10 ^j	2.675(7)
Na4A-O12	2.914(4)	Na5A-O9 ^{xxi}	2.895(5)	Ca5B-O4SB ^{iv}	2.976(16)	Na6A-O11	2.759(8)
<Na4A-O>	2.576	<Na5A-O>	2.639	Ca5B-O4SB	2.976(16)	Na6A-O16	2.888(6)
		Na5A-Ca5B	0.622(15)	<Ca5B-O>	2.801	<Na6A-O>	2.575
Na6B-O14	2.336(17)			Na6A-Na6B	0.816(18)		
Na6B-O15	2.501(18)	K6B-O9	2.730(6)	Na6A-K6B	1.057(8)	Na7A-O2SA	2.207(9)
Na6B-O9	2.681(13)	K6B-O14	2.757(9)	K6B-Na6B	1.87(2)	Na7A-O12 ^{xv}	2.542(4)
Na6B-O16	2.952(14)	K6B-O10 ⁱ	2.776(8)			Na7A-O12	2.542(4)
Na6B-O11	2.972(18)	K6B-O11	2.826(9)	Na8C-O16V	2.583(7)	Na7A-O12 ^{viii}	2.542(4)
Na6B-O10 ^j	2.986(18)	K6B-O15	2.880(11)	Na8C-O16	2.583(7)	Na7A-O13 ^{viii}	2.686(4)
<Na6B-O>	2.738	K6B-O16	2.979(6)	Na8C-O16XVI	2.583(7)	Na7A-O13 ^{xv}	2.686(4)
		K6B-O3SB ^{xvi}	3.10(2)	Na8C-O6SA	2.628(9)	Na7A-O13	2.686(4)
Na8A-O16 ^v	2.523(6)	<K6B-O>	2.864	Na8C-O6SAXVI	2.628(9)	Na7A-O5SB	2.7255(17)
Na8A-O16 ^{xvi}	2.523(6)			Na8C-O6SAV	2.628(9)	Na7A-O5SB ^{viii}	2.7255(17)
Na8A-O16	2.523(6)	Na8B-O16 ^v	2.414(5)	Na8C-O17	2.868(6)	Na7A-O5SB ^{xv}	2.7255(17)
Na8A-O3SA	2.881(18)	Na8B-O16 ^{xvi}	2.414(5)	Na8C-O17V	2.868(6)	<Na7A-O>	2.607
Na8A-O3SA ^v	2.881(18)	Na8B-O16	2.414(6)	Na8C-O17XVI	2.868(6)		
Na8A-O3SA ^{xvi}	2.881(18)	Na8B-O17 ^v	2.828(6)	<Na8C-O>	2.693	Na8A-Na8B	1.063(12)
<Na8A-O>	2.702	Na8B-O17	2.828(6)			Na8A-Na8C	1.742(18)
		Na8B-O17 ^{xvi}	2.828(6)	Na9B-O19	2.49(2)	Na8B-Na8C	0.679(11)
Na9A-O4SA ^{xxi}	2.242(8)	<Na8B-O>	2.621	Na9B-O13	2.613(12)		
Na9A-O19	2.465(10)			Na9B-O18 ^{xxi}	2.66(2)	Na1K-Na1KXI	1.806(17)
Na9A-O13	2.511(5)	K9A-O19	2.727(13)	Na9B-O20	2.894(15)	Na1K-O24	2.654(7)
Na9A-O5SB ^{xv}	2.515(8)	K9A-O15 ^{xxi}	2.731(13)	<Na9B-O>	2.664	Na1K-O24XV	2.654(7)
Na9A-O18 ^{xxi}	2.624(12)	K9A-O13	2.745(8)	K9A-Na9A	0.861(9)	Na1K-O24VIII	2.654(7)
Na9A-O15 ^{xxi}	2.681(10)	K9A-O14	2.760(12)	K9A-Na9B	1.88(2)	Na1K-O5SA ^{xv}	2.701(7)
Na9A-O20	2.695(7)	K9A-O20	2.807(8)	Na9A-Na9B	1.019(18)	Na1K-O5SA	2.701(7)
Na9A-O14	2.741(9)	K9A-O18 ^{xxi}	2.909(15)			Na1K-O5SA ^{viii}	2.701(7)
<Na9A-O>	2.559	K9A-O4SB ^{xxi}	3.085(10)	Na1E-O20 ^{xxi}	2.670(10)	Na1K-O24XI	2.834(9)
		<K9A-O>	2.823	Na1E-O20 ^{iv}	2.670(10)	Na1K-O24 ^{xxv}	2.834(9)
Na1C-O20	2.563(7)			Na1E-O20	2.670(10)	Na1K-O24 ^{ix}	2.834(9)
Na1C-O20 ^{xxi}	2.563(7)	Na1D-O20 ^{xxi}	2.483(7)	Na1E-O6SB ^{xxiii}	2.703(15)	<Na1K-O>	2.730
Na1C-O20 ^{iv}	2.563(7)	Na1D-O20	2.483(7)	Na1E-O6SB ^{xxiv}	2.703(15)		
Na1C-O4SA ^{iv}	2.788(13)	Na1D-O20 ^{iv}	2.483(7)	Na1E-O6SB ^{ix}	2.703(15)	K1L-O21	2.647(9)
Na1C-O4SA	2.788(13)	Na1D-O21 ^{iv}	2.697(7)	Na1E-O21 ^{iv}	2.722(7)	K1L-O22XXV	2.735(14)
Na1C-O4SA ^{xxi}	2.788(13)	Na1D-O21	2.697(7)	Na1E-O21	2.722(7)	K1L-O21IX	2.760(11)
Na1C-O21 ^{iv}	2.938(10)	Na1D-O21 ^{xxi}	2.697(7)	Na1E-O21 ^{xxi}	2.722(7)	K1L-O23XVI	2.798(13)
Na1C-O21	2.938(10)	<Na1D-O>	2.590	<Na1E-O>	2.698	K1L-S6XXIV	2.967(15)
Na1C-O21 ^{xxi}	2.938(10)	Na1D-Na1E	0.782(18)			K1L-O23I	2.968(14)
<Na1C-O>	2.763	Na1C-Na1D	0.901(14)	Na1G-O17X	2.504(5)	K1L-O22VIII	2.991(15)
		Na1C-Na1E	1.68(3)	Na1G-O22	2.563(19)	K1L-O6SAXXIV	2.992(10)
Na1F-O5SA	2.363(8)			Na1G-O23	2.644(10)	<K1L-O>	2.857
Na1F-O6SA ^{xxii}	2.423(8)	K1G-O17 ^x	2.588(12)	Na1G-O24	2.724(15)		
Na1F-O17 ^x	2.435(9)	K1G-O24	2.676(9)	Na1G-O18X	2.737(12)	Na1L-O6SB ^v	2.3629(2)
Na1F-O22	2.561(15)	K1G-O22	2.684(17)	Na1G-O19XV	2.935(15)	Na1L-O6SB ^{xxiii}	2.3630(2)
Na1F-O18 ^x	2.597(15)	K1G-O18 ^x	2.718(13)	<Na1G-O>	2.685	Na1L-O21	2.502(7)
Na1F-O24	2.614(10)	K1G-O19 ^{xv}	2.738(12)			Na1L-O21 ^{ix}	2.503(7)
Na1F-O23	2.646(15)	K1G-O23	2.898(15)			Na1L-O23 ⁱ	2.638(14)
Na1F-O19 ^{xv}	2.784(15)	<K1G-O>	2.717			Na1L-O23 ^{xvi}	2.638(14)
<Na1F-O>	2.553	Na1F-Na1G	0.673(19)	K1L-Na1L	1.030(10)	Na1L-O22 ^{viii}	2.729(14)
		Na1F-K1G	0.75(2)	K1L-K1LIX	2.06(2)	Na1L-O22 ^{xxv}	2.729(14)
		K1G-Na1G	1.42(3)			<Na1L-O>	2.558

Symmetry transformations used to generate equivalent atoms:

- (I) x,y-1,z; (II) x-y+1,-y+1,-z; (III) x-y,-y,-z; (IV) -x+y,-x,z; (V) -y+1,x-y,z; (VI) x+1,y,z; (VII) -y+2,x-y+1,z; (VIII) -x+y,-x+1,z;
 (IX) -x+2/3,-x+y+1/3,-z+1/3; (X) x,y+1,z; (XI) y-1/3,x+1/3,-z+1/3; (XII) -x,-x+y,-z; (XIII) -x+1,-x+y+1,-z; (XIV) x-1,y,z;
 (XV) -y+1,x-y+1,z; (XVI) -x+y+1,-x+1,z; (XVII) -x,-x+y-1,-z; (XVIII) -x+y-1,-x,z; (XIX) y-1,x,-z; (XX) y,x,-z; (XXI) -y,x-y,z
 (XXII) -x+y+1,-x+2,z; (XXIII) y-1/3,x-2/3,-z+1/3; (XXIV) x-y-1/3,-y+1/3,-z+1/3; (XXV) x-y+2/3,-y+4/3,-z+1/3; (XXVI) -x+2/3,-x+y-2/3,-z+1/3; (XXVII) -x+2/3,-x+y+4/3,-z+1/3; (XXVIII) y+2/3,x+1/3,-z+1/3; (XXIX) x-y+2/3,-y+1/3,-z+1/3

Table 5c. Selected distances of extra-framework anionic groups for kircherite.

S1-O1SA ^{XX}	1.461(7)	S2-O2SB	1.464(5)	S3-O3SA	1.293(16)
S1-O1SB ^{VIII}	1.466(4)	S2-O2SB ^{VIII}	1.464(5)	S3-O3SB	1.416(16)
S1-O1SB	1.466(4)	S2-O2SB ^{XV}	1.464(5)	S3-O3SA ^V	1.679(16)
S1-O1SB ^{XV}	1.466(4)	S2-O2SA	1.481(8)	S3-O3SB ^{XVI}	1.755(16)
<S1-O>	1.465	<S2-O>	1.468	S3-S3 ^V	0.809(9)
S4-O4SB	1.375(11)	S5-O5SB	1.371(4)	S6-O6SB	1.351(9)
S4-O4SA	1.42(2)	S5-O5SA ^{XV}	1.430(9)	S6-O6SA	1.370(9)
S4-O4SA ^{IV}	1.58(2)	S5-O5SA	1.547(9)	S6-O6SB ^{XVI}	1.684(10)
S4-O4SB ^{XXI}	1.67(2)	S5-O5SB ^{XV}	1.798(8)	S6-O6SA ^V	1.698(10)
S4-S4 ^{XXI}	0.52(2)	S5-S5 ^{VIII}	0.657(8)	S6-S6 ^V	0.745(14)

Symmetry transformations used to generate equivalent atoms:

(IV) $-x+y, -x, z$; (V) $-y+1, x-y, z$; (VIII) $-x+y, -x+1, z$; (X) $x, y+1, z$; (XI) $y-1/3, x+1/3, -z+1/3$;
(XV) $-y+1, x-y+1, z$; (XVI) $-x+y+1, -x+1, z$; (XX) $y, x, -z$; (XXI) $-y, x-y, z$

First revision 20/03/2012

Table 6. Cation site assignments on the basis of observed site scattering and geometries of the sites reported in Table 5 for kircherite

atom	Site multiplicity	Site occupancy factor	Site scattering (eps)*	Cation population (apfu)**
K1	18f	1.000	19	18 K
Na1	3a	1.000	11.0	3 Na
Na2A	9d	0.616(16)	14.5	5.54 Na + 3.46 Ca
Ca2B	9d	0.384(16)		
Ca3	6c	1.009(8)	20.2	6 Ca
Na4A	18f	0.771(12)	13.1	13.88 Na + 4.12 Ca
Ca4B	18f	0.229(12)		
Na5A	6c	0.720(14)	13.5	4.32 Na + 1.68 Ca
Ca5B	6c	0.280(14)		
Na6A	18f	0.644(9)	13.9	11.60 Na + 4.48 K +1.91 Ca
K6B	18f	0.249(4)		
Na6B	18f	0.193(8)		
Na7A	6c	0.05(2)	19.6	5.70 Ca + 0.30 Na
Ca7B	6c	0.95(2)		
Na8A	6c	0.452(15)	13.3	4.46 Na + 1.55 Ca
Na8B	6c	0.08(2)		
Na8C	6c	0.68(2)		
K9A	18f	0.236(5)	13.6	12.24 Na + 4.25 K +1.52 Ca
Na9A	18f	0.630(9)		
Na9B	18f	0.203(7)		
Na1C	6c	0.53(2)	13.3	4.46 Na + 1.54 Ca
Na1D	6c	0.18(3)		
Na1E	6c	0.50(2)		
Na1F	18f	0.23(3)	14.4	10.71 Na + 5.02 K +2.28 Ca
K1G	18f	0.411(16)		
Na1G	18f	0.367(13)		
Na1K	6c	0.516(17)	5.7	2.88 Na+ 0.12 Ca
K1L	18f	0.210(4)	4.0	3.78 K
Na1L	9d	0.580(7)	6.4	5.22 Na
Total extra framework cations (XRD)				78.62 Na + 35.53 K + 29.86 Ca
Total extra framework cations (EMPA)				89.09 Na + 18.85 K + 31.63 Ca
Ow25	6c	0.94(4)	45.1	5.64 H ₂ O
S1	6c	1	96	6 S
S2	6c	1	96	6 S
S3	18f	0.333	96	5.04 S+0.84 Cl+0.02 F***
S4	18f	0.300(6)	88.4	4.80 S+0.40 Cl+0.46 H ₂ O+0.12 F
S5	18f	0.229(7)	86.4	4.71 S+0.34 Cl+0.45 H ₂ O+0.17 F
S6	18f	0.94(4)	66.0	3.51 S+0.35 Cl+0.35 H ₂ O+0.13 F

* eps = electrons per site, **apfu (atoms per formula unit); *** We opted to assign Cl, F and excess H₂O over the amount in Ow25 disordered over S3, S4,S5 and S6 because splitting off axis did not allowed to distinguish the different species. The sum < 6 apfu per site is to ascribe to the difficulty on modelling the disordering.

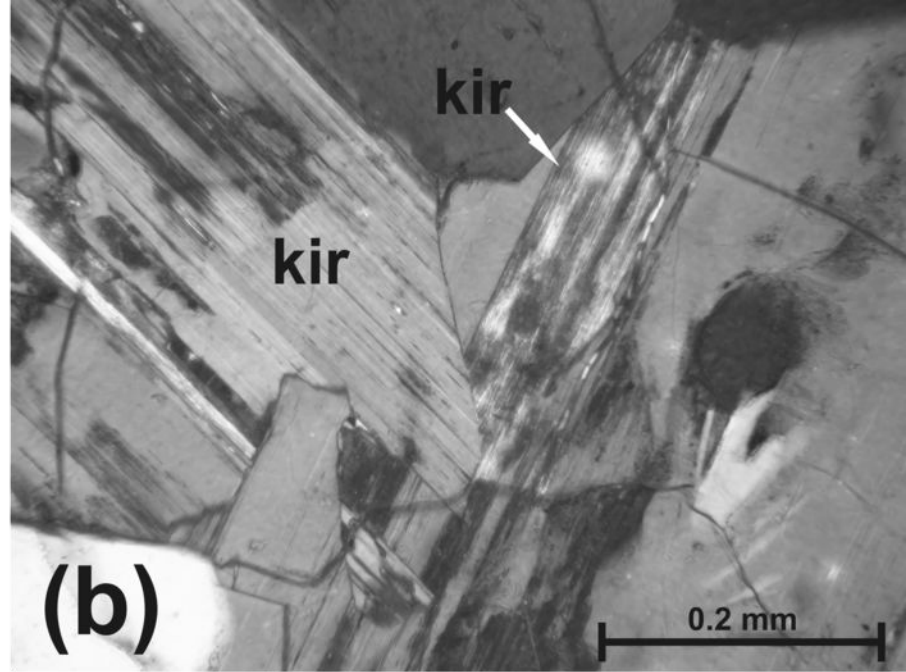
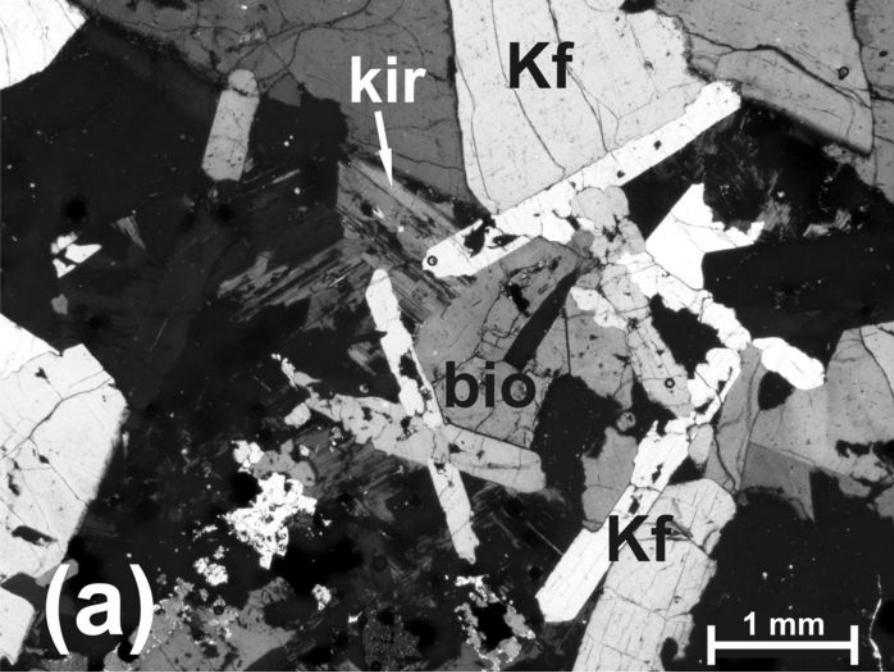


Figure 1

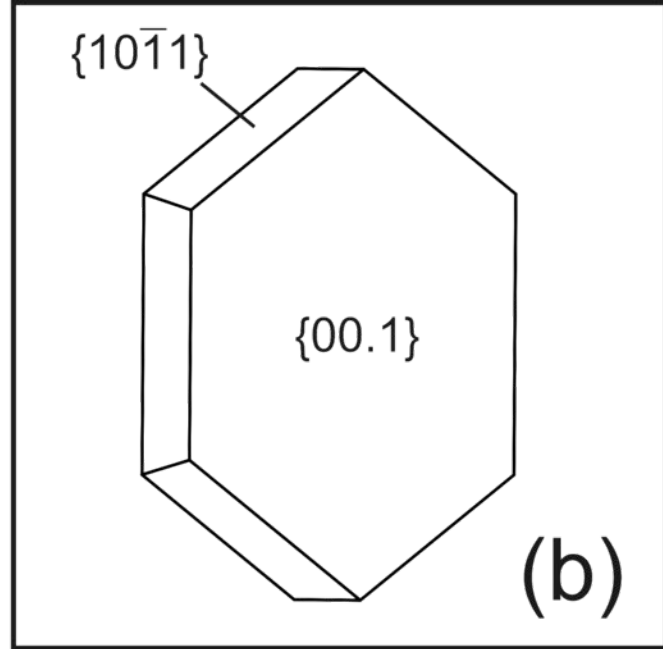
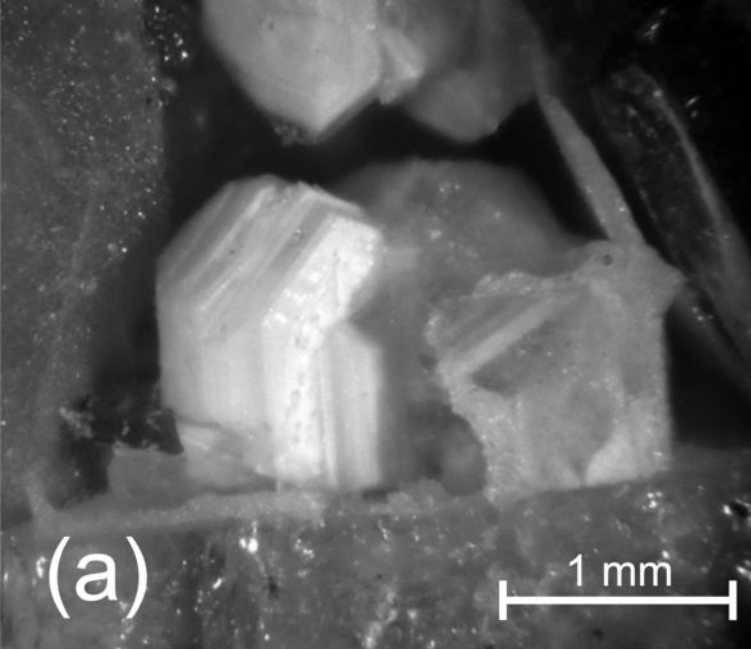


Figure 2 first revision

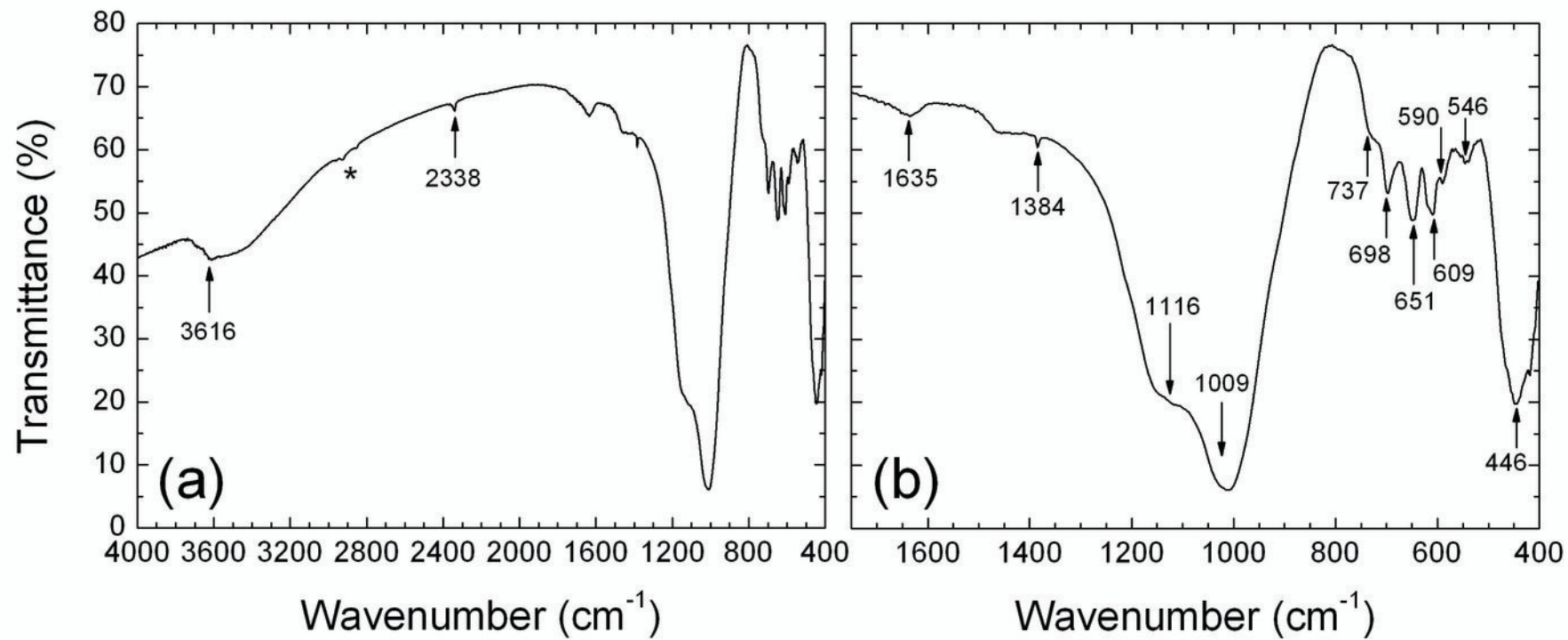


Figure 3

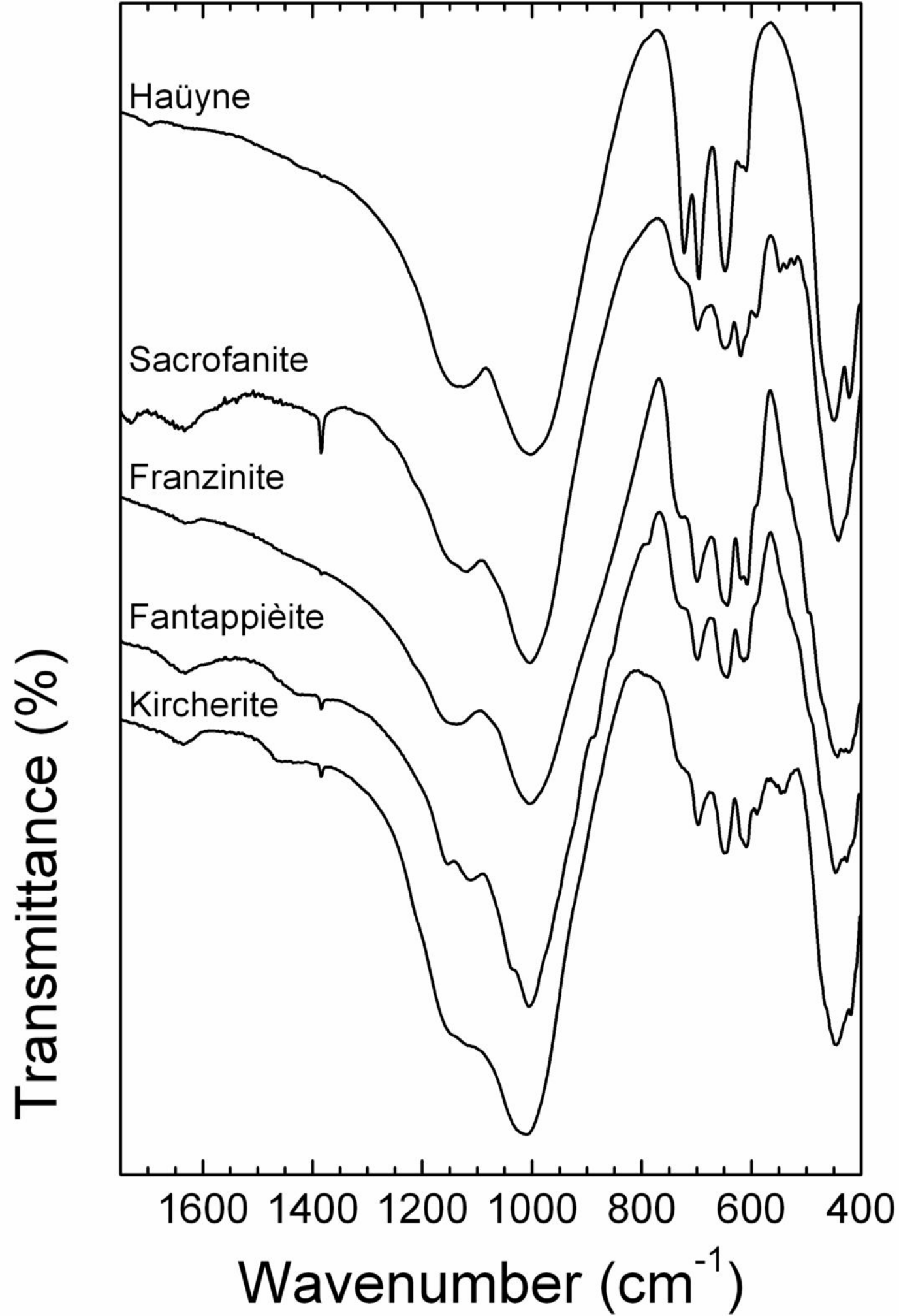


Figure 4

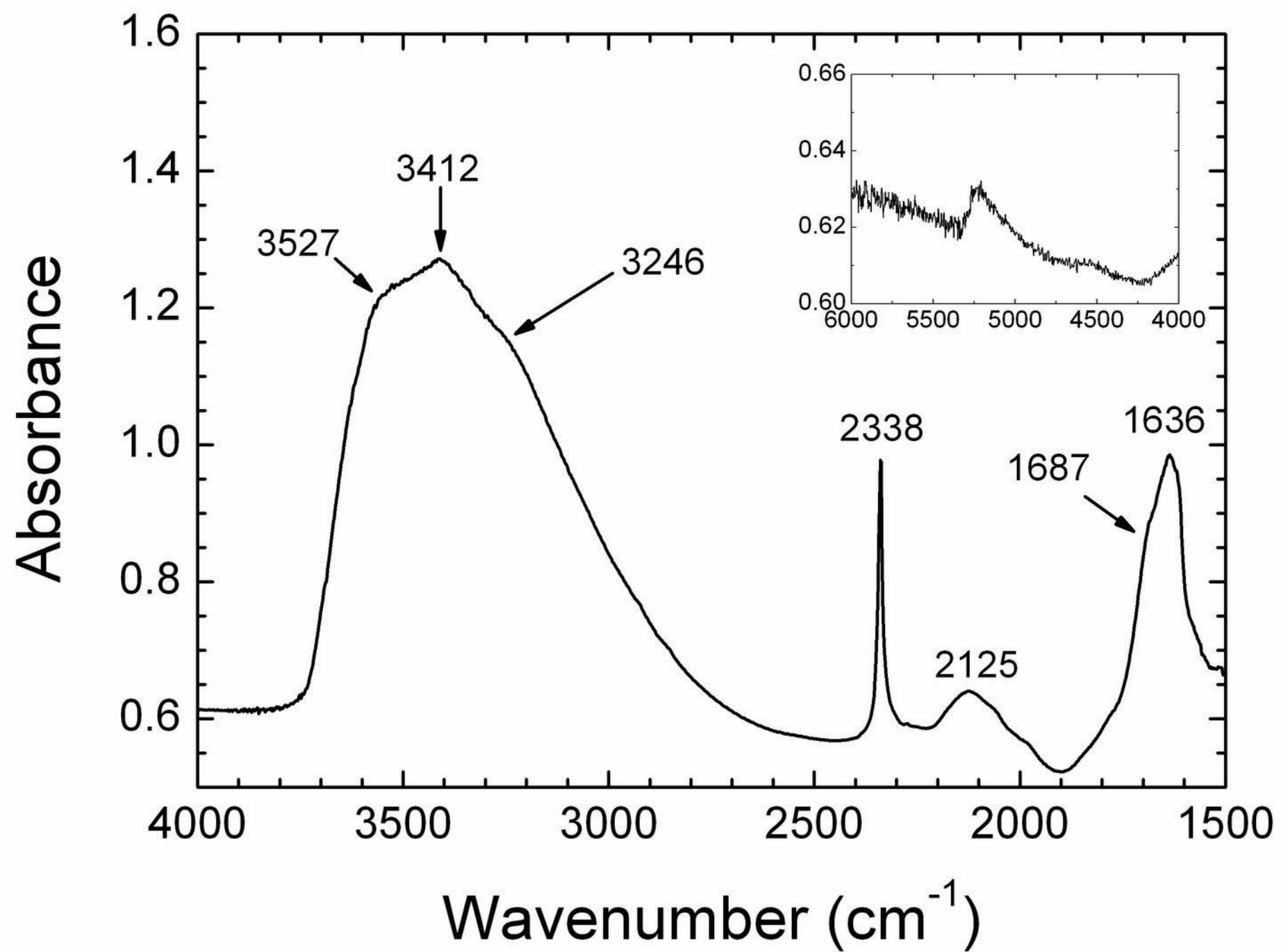


Figure 5

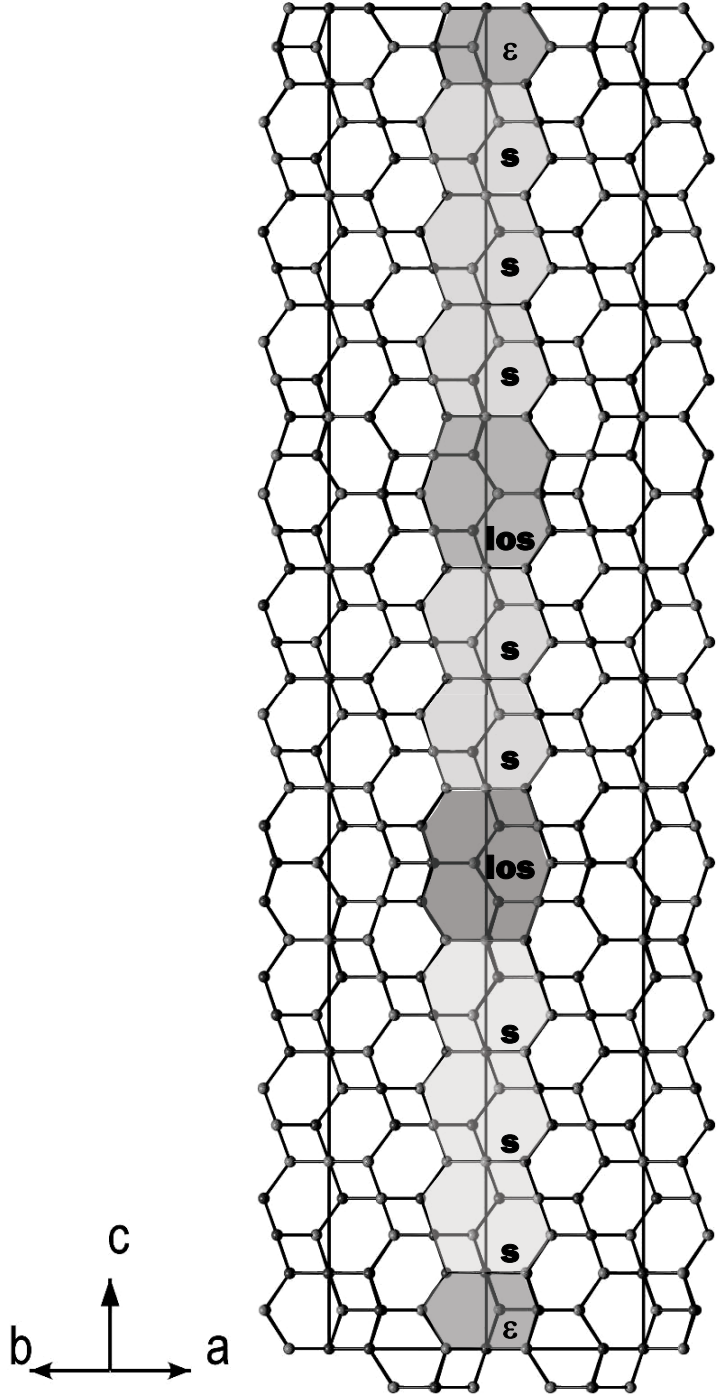


Figure 6