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**Lucabindiite, (K,NH₄)As₄O₆(Cl,Br), a new fumarole mineral from the “La Fossa” crater
at Vulcano, Aeolian Islands, Italy**

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Running title: lucabindiite, a new mineral from Vulcano

19 **ABSTRACT**

20 Lucabindiite, ideally $(\text{K},\text{NH}_4)\text{As}_4\text{O}_6(\text{Cl},\text{Br})$, is a new mineral found as a medium-
21 temperature fumarole encrustation ($T = 170^\circ\text{C}$) at “La Fossa” crater of Vulcano, Aeolian
22 Islands, Italy. The mineral deposited as aggregates of micrometer-sized hexagonal, and platy
23 crystals on the surface of the pyroclastic breccia in association with arsenolite, sal ammoniac,
24 sulfur and amorphous arsenic-rich sulfurite. The new mineral is colorless to white,
25 transparent, non-fluorescent, has a vitreous lustre and a white streak. The calculated density is
26 $3.68 \text{ g}\cdot\text{cm}^{-3}$. Lucabindiite is hexagonal, space group $P6/mmm$, with $a = 5.2386(7) \text{ \AA}$, $c =$
27 $9.014(2) \text{ \AA}$, $V = 214.23(7) \text{ \AA}^3$, $Z = 1$. The eight strongest reflections in the X-ray powder-
28 diffraction data [d in \AA (hkl)] are: 3.20 (100) (102), 2.62 (67) (110), 4.51 (52) (002), 4.54
29 (30) (100), 1.97 (28) (113), 1.49 (21) (115), 1.60 (21) (212), 2.26 (19) (112). Lucabindiite
30 average chemical composition is (wt%): K_2O 5.14, As_2O_3 84.71, Cl 3.63, Br 6.92, F 0.77,
31 $(\text{NH}_4)_2\text{O}$ 2.73, $\text{O} = \text{F}, \text{Cl}, \text{Br}$ -1.84, total 102.06. The empirical chemical formula, calculated
32 on the basis of 7 anions *pfu*, is $[\text{K}_{0.51}(\text{NH}_4)_{0.49}]_{\Sigma 1.00}\text{As}_{4.00}\text{O}_{5.93}(\text{Cl}_{0.48}\text{Br}_{0.40}\text{F}_{0.19})_{\Sigma 1.07}$. According
33 to chemical analyses and X-ray data, lucabindiite is the natural analogue of the synthetic
34 phases with general formula $M\text{As}_4\text{O}_6X$ where $M = \text{K}, \text{NH}_4$ and $X = \text{Cl}, \text{Br}, \text{I}$. The crystal
35 structure is characterized by neutral As_2O_3 sheets arranged parallel to (001). The As atoms of
36 two neighboring sheets point at each other and the sheets are separated by interlayer M (= K,
37 NH_4) and X (= Cl, Br, F) atoms. The name is in honour of Luca Bindi (1971), Professor of
38 Mineralogy and former Head of the Division of Mineralogy of the Natural History Museum
39 of the University of Florence. Both the mineral and the mineral name have been approved by
40 the IMA-CNMNC Commission (IMA 2011-010).

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42 keywords: lucabindiite, As-oxychlorides, new mineral, sublimates, fumaroles, crystal
43 structure, Vulcano, Aeolian Islands, Italy.

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46 **INTRODUCTION**

47 The history of the discovery of lucabindiite began at the beginning of the nineties,
48 during the years of the PhD studies of one of us (Garavelli 1994). At that time Vulcano was in
49 a thermal-increase period reflecting the increase in activity at the “La Fossa” crater (Garavelli
50 et al. 1997 and references therein). Temperature values grew up quickly and the maximum
51 temperature of the fumaroles reached the value of 700°C in October 1992. In order to
52 contribute to the understanding of the genesis and evolution both of fluids and depositional
53 environments of sublimates at Vulcano, with the aim also to give a contribution to volcanic
54 surveillance, the fumarolic products and encrustations at La Fossa crater have been studied
55 systematically from a mineralogical and geochemical point of view (Garavelli 1994; Garavelli
56 and Vurro 1994; Borodaev et al. 1998; Vurro et al. 1999; Cheynet et al. 2000; Borodaev et al.
57 2000, 2001, 2003; Garavelli et al. 2005; Pinto et al. 2006a, 2006b, 2006c, 2008; Mitolo et al.
58 2009, 2011; Pinto et al. 2011). Sublimates and encrustations were collected directly from the
59 ground, but also by means of quartz tubes inserted as deep as possible into the fumarolic vents
60 (Cheynet et al. 2000; Garavelli et al. 1997). Volcanic fluids vented freely through the tubes
61 and gradually deposited sublimates on the tube inner walls. In this way we could collect a
62 large variety of volcanic sublimates, some of which are known as minerals, others not; the
63 latter have been considered new potential minerals. Of particular interest was the finding, in
64 the sampling tubes, of an unidentified compound containing As, Cl and S in typical rose-like
65 aggregates of hexagonal crystals. We supposed that the lack of this phase among sublimates

66 from the ground was due to its metastability. In any case, we never stopped looking for this
67 phase among sublimates from the ground, with no success until the discovery of a similar
68 phase containing As and Cl, with no sulfur but with K, NH₄ and O: here it is the lucabindiite!

69 The mineral and its name were approved by the IMA Commission on New Minerals,
70 Nomenclature and Classification, CNMNC (2011-010). It was named “lucabindiite” in
71 honour of Luca Bindi (b. 1971), Professor of Mineralogy and former Head of the Division of
72 Mineralogy of the Natural History Museum of the University of Florence, in
73 acknowledgement of his major contribution to the study of the structural complexity in
74 minerals (*i.e.*, incommensurate structures, superstructures, twinned structures), integrating
75 together mineralogy and the most advanced fields of crystallography. In the last years he
76 covered the field of quasicrystals. In this context of investigations, his recent discovery of the
77 first natural quasicrystal, icosahedrite, (Bindi et al. 2009, 2011, 2012, Bindi and Steinhardt
78 2012) is remarkable.

79 The holotype of lucabindiite is deposited in the mineral collection of the Museum
80 “C.L. Garavelli”, Dipartimento di Scienze della Terra e Geoambientali, Università di Bari,
81 Italy, under the catalogue number 11/nm-V28.

82 OCCURRENCE AND PHYSICAL PROPERTIES

83 Lucabindiite was found as a fumarole encrustation collected in 1998, during a
84 sampling trip at the “La Fossa” crater (Vulcano island, Aeolian archipelago, Italy), from the
85 fumarole F1 ($T = 170\text{ }^{\circ}\text{C}$), sited on the crater rim of the volcano (Figure 1). The micrometer-
86 sized, hexagonal and platy crystals, were directly deposited on the surface of the pyroclastic
87 breccia of the “La Fossa” cone, and were covered by a vitreous reddish crust containing
88 mainly sulfur and arsenic. Associated minerals are sal ammoniac, sulfur and an amorphous
89 arsenic-rich sulfurite (Figure 2). Arsenolite (Figure 3), was found in the same sample in which
90 lucabindiite occurs, but no clear paragenetic relation between the two arsenic minerals could
91 be observed. Geological and metallogenic data for the “La Fossa” crater area are given in
92 previous papers (Garavelli et al. 1997; Campostrini et al. 2011 and references therein).
93 Individual single crystals of lucabindiite are very rare. Generally the mineral occurs as
94 aggregates of minute, hexagonal, and platy crystals (Figures 4 and 5) up to $70 \times 70 \times 3\text{ }\mu\text{m}$ in
95 size. The very small dimensions, as well as the softness and friability of the crystals, made it
96 difficult to handle the crystals of the new phase and to measure some of its physical
97 properties.

98 Lucabindiite is colorless to white in color, with a white streak and a vitreous luster.
99 Minute crystals are transparent to translucent. Unfortunately, the direct measure of refractive
100 index could not be done due to the minute size of the crystals available. The mean refractive
101 index was calculated using the method proposed by Korotkov and Atuchin (2008). Taking
102 into account the empirical chemical formula, the mean refractive index of lucabindiite should
103 be 1.88. This is in good agreement with the value of 1.92 obtained using the method proposed
104 by Mandarino (1981).

105 Density was not measured because of the scarcity of available material; the calculated
106 density is $3.68 \text{ g}\cdot\text{cm}^{-3}$.

107 Lucabindiite is brittle. No cleavage, parting or fracture could be observed. Mohs
108 hardness could not be directly measured because of the small crystal size.

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111 **CHEMICAL AND SPECTROSCOPIC STUDIES**

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113 The presence of ammonium in lucabindiite was first suspected, then proved combining
114 SEM-EDS chemical analysis, crystal structure solution and FTIR spectroscopy. At a first step,
115 the chemical analyses showed the presence of K, As, Cl, Br and F as the only significant
116 elements. The crystal structure study then indicated a formula close to stoichiometric
117 $\text{KA}_{5.4}\text{O}_6\text{Cl}$, but with a deficit on the occupancy of the K site (and thus a deficit of positive
118 charges), suggesting the additional presence of another monovalent cation. Ammonium was
119 considered as the most probable candidate. At Vulcano island the abundance of ammonium
120 minerals has been reported since the end of the last eruption in 1888-1890 (Panichi 1924 and
121 references therein), and in more recent years a notable quantity of ammonium minerals have
122 been investigated and/or identified (Garavelli and Vurro 1994; Coradossi et al. 1996; Demartin
123 et al. 2009a, 2009b; Campostrini et al. 2010; Demartin et al. 2010a, 2010b, in press; Mitolo et
124 al. 2012, submitted). So a FTIR study was performed on lucabindiite, and it confirmed
125 qualitatively the presence of NH_4^+ ions.

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128 **SEM-EDS Chemical analyses**

129 Quantitative chemical analyses were obtained by SEM-EDS methods. The instrument
130 used for this research was a S360 Cambridge Scanning Electron Microscope coupled with an
131 Oxford-Link Ge ISIS Energy Dispersive Spectrometer equipped with a Super Atmosphere
132 Thin Window ©, since this allows better detection of light elements. An ED spectrometer was
133 chosen for quantitative analyses of the small sized crystals instead of a WD detector. The
134 investigated sample consisted of a lucabindiite crystal aggregate, 100 µm in size (Figure 5),
135 sputtered with a 30-nm-thick carbon film. Operating conditions were: 15 kV accelerating
136 potential, 500 pA probe current, 2500 cps as average count rate on the whole spectrum,
137 typical counting time 100 s. X-ray intensities were converted to wt% by ZAF4/FLS
138 quantitative analysis software support of Oxford-Link Analytical (U.K.). This allows to match
139 the peaks (heights and areas) of the standards with the ones of the analyzed mineral, taking
140 into account the relative contribution of the matrix and also partial or complete overlaps
141 among peaks of different elements. The ED detector gives accurate analyses of small volumes
142 of investigated sample also with probe current lower than 1 nA. Moreover the ED detector
143 gives good results also when it collect X-ray from a non perfectly flat surface of the
144 specimen: this is due to its capability to give quantitative analytical data also with a “non-
145 critical” working distance (Ruste, 1979; Acquafredda and Paglionico, 2004). The standards
146 employed were: orthoclase (K), halite (Cl), synthetic InAs (As), synthetic KBr (Br) and
147 synthetic LiF (F). The analytical results (mean of 12 analyses) are represented in Table 1. The
148 empirical chemical formula, calculated on the basis of 7 anions per formula unit,
149 is $[(K_{0.51}(NH_4)_{0.49}]_{\Sigma 1.00}As_4.00O_{5.93}(Cl_{0.48}Br_{0.40}F_{0.19})_{\Sigma 1.07}$. The ammonium content was
150 deduced from the K content, taking into account the $(K,NH_4)As_4O_6(Cl,Br)$ stoichiometry
151 $(K+NH_4=1 \text{ apfu})$. The presence of ammonium was confirmed by FTIR spectroscopy and from
152 the structure refinement. The simplified formula of lucabindiite is $(K,NH_4)As_4O_6(Cl,Br)$

153 which requires: K₂O 4.89, (NH₄)₂O 2.70 As₂O₃ 82.10, Cl 3.68, Br 8.29 O = Cl, Br 1.66,
154 total 100.00 wt%.

155

156 **FTIR Spectroscopy**

157 The infrared spectrum of lucabindiite was collected in the range 4000-400 cm⁻¹ using a
158 Nicolet Avatar FTIR spectrometer with a nominal resolution of 4 cm⁻¹, equipped with a
159 Continuum microscope, a MCT nitrogen-cooled detector, and a KBr beamsplitter. The
160 measurement was performed on a single crystal mounted on glass capillary. The observed IR-
161 patterns resulted from the average of 400 scans. The single crystal FTIR spectra provided
162 evidence for the presence of ammonium in the lucabindiite structure (Farmer 1974). The
163 NH₄⁺ stretching regions (3350–2750 and 1550-1250 cm⁻¹) were modeled using the program
164 PeakFit (by Jandel Scientific), assuming Gaussian functions to describe a linear function to
165 approximate the background and the peaks shape as $y = A \exp[-0.5(x - P/W)^2]$ where A is the
166 amplitude, P is the peak centroid, and W is the full width at half maximum (FWHM).

167 Figure 6 illustrates the FTIR spectra of the lucabindiite crystal in the range of 4000–
168 800 cm⁻¹. Band position and FWHM were derived from the interactive optimization and least-
169 squares refinement of the digitized IR absorption spectra.

170 Band assignments for vibrational features are given in Table 2. In the 3350–1250 cm⁻¹
171 region, a group of well-defined bands at 3257, 3159, 3045, 2926, 2850 and 1417 cm⁻¹ were
172 assigned to ν NH₄⁺ vibrations (Figure 7, Table 2, Farmer 1974). The additional band at 3375
173 cm⁻¹ could be related to a minor OH⁻ incorporation.

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176 **X-RAY DIFFRACTION STUDIES**

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178 **X-ray powder diffraction**

179 Gandolfi powder-pattern for lucabindiite (Table 3) was obtained using a CCD-
180 equipped single crystal diffractometer (CuK α radiation). Calculated powder pattern and
181 Indexing of the reflections was done on the basis of $a = 5.2386(7)$ Å, $c = 9.014(2)$ Å, and
182 with the atomic coordinates and occupancies reported in Table 4. Intensities were calculated
183 using XPOW software version 2.0 (Downs et al. 1993).

184 The refined unit-cell parameters, based on 15 reflections between 4.54 and 1.310 Å,
185 are: $a = 5.2372(2)$ Å, $c = 9.0085(7)$ Å, $V = 213.98(2)$ Å³.

186

187 **Single-crystal X-ray diffraction**

188 Single-crystal X-ray diffraction data were collected from a selected crystal fragment
189 (110x150x50 μ m) using a Bruker AXS X8 APEX2 CCD automated diffractometer equipped
190 with a kappa-geometry goniometer and graphite monocromated MoK α radiation (50 kV and
191 30 mA operating conditions). The *Miracol* fiber optics capillary *collimator* (0.3 mm size) was
192 used to enhance the intensity of the Mo K α radiation and to reduce X-ray beam divergence.
193 Five sets of 19 frames were used for initial cell determination, whereas complete data
194 collection was accomplished by several φ and ω scans with 0.5° frame width, 120 s exposure
195 time per frame and a crystal-to-detector distance of 40 mm. The collection strategy was
196 optimized by the Apex suite program (Bruker 2003a). Details about data collection and
197 refinement are summarized in Table 5.

198 Data reduction, including intensity integration, correction for Lorentz, polarization,
199 background effects and scale variation, was done using the package SAINT-IRIX (Bruker

200 2003b). A semi-empirical absorption correction (Blessing 1995) was applied using the
201 SADABS program (Sheldrick 2008). The minimum and maximum X-ray transmission-factors
202 were 0.4136 and 0.7454, respectively.

203 The structure refinement was performed in the space group $P6/mmm$ using the SHELX
204 program (Sheldrick 2008), starting from the atomic coordinates of synthetic KAs_4O_6Cl
205 (Pertlik 1988). Indeed the synthetic compounds MAs_4O_6X ($M = K, NH_4$; $X = Cl, Br, I$)
206 described by Pertlik (1988) were ascribed to the acentric space group $P622$, although there
207 was no clear reason given as to why the crystal-structures of these compounds should be non-
208 centrosymmetric.

209 Taking into account the results of chemical data, the two substitutions $K^+ \leftrightarrow NH_4^+$ and
210 $Cl^- \leftrightarrow (Br^-, F^-)$ were considered during the structure refinement. The presence of NH_4^+
211 substituting for K^+ was confirmed by the refinement although it was not possible to locate the
212 H atoms of the NH_4^+ group. Refinement of the occupancy of the M site gave 0.52(4)K and
213 0.48(4) NH_4 , in good agreement with the chemical data. The occupancies for Cl, Br and F
214 were assigned in the anion site X on the basis of the results of the chemical analysis as the
215 simultaneous refinement of these three atoms in the same position is not expected to give any
216 reliable result.

217 The refinement converged to the agreement R value of 0.0384 for 136 reflections with
218 $F_o > 4\sigma(F_o)$ [$R = 0.0617$ for all the 174 unique reflections]. Scattering factors for neutral
219 atoms were taken from the *International Tables for X-ray Crystallography* (Ibers and
220 Hamilton 1974). In the final refinement anisotropic displacement factors were used for all the
221 atoms.

222 Fractional atomic coordinates, occupancies and anisotropic displacement parameters
223 are presented in Table 4, whereas selected interatomic distances are in Table 6.

224 The cif-file with structure data of lucabindiite can be download from the *Inorganic*
225 *Crystal Structure Database* at FIZ Karlsruhe, Germany (CSD number 424826).

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228 **DESCRIPTION OF THE STRUCTURE AND RELATION WITH SYNTHETIC**
229 **SPECIES**

230 The crystal structure of lucabindiite is topologically identical to that of the synthetic
231 compounds MAs_4O_6X ($M = K, NH_4$; $X = Cl, Br, I$) reported by Pertlik (1988). The structure
232 (Figure 8) is characterized by (001) layers consisting of neutral As_2O_3 sheets. Each As_2O_3
233 sheet is formed by AsO_3 pyramids connected by shared oxygen atoms. The As atoms of two
234 neighboring sheets point at each other and the sheets are connected by interlayer M (= K,
235 NH_4) and X (= Cl, Br, F) atoms. The M atoms are coordinated to twelve O atoms in the form
236 of a regular hexagonal prism, with M -O distances almost intermediate between K-O and NH_4 -
237 O distances (Table 6) in the synthetic phases described by Pertlik (1988). As the symmetry of
238 the M site is higher than the symmetry of an NH_4 molecule, Pertlik (1988) suggested that each
239 H atom is statistically distributed over at least three symmetry equivalent sites in the structure
240 framework of the $NH_4As_4O_6X$ ($X = Cl, Br, I$) compounds. This explains the impossibility to
241 locate the H atoms of the NH_4^+ group by the X-Ray Diffraction.

242 The apices of the As_2O_3 sheets, the As atoms, point towards the X atoms, and twelve
243 As atoms form the first coordination sphere around the X atoms (hexagonal prisms). The
244 coordination of As atoms is thus characterized by three typical short As-O distances
245 [1.796(5)] against three opposite long As-X contacts [3.536(1)]. According to Pertlik (1988)
246 the As-O and O-O first-neighbor distances in the MAs_4O_6X compounds (Table 6) are greatly

247 influenced by the site occupancy of *X*. As a matter of fact, Pertlik noticed that both the As-O
248 and O-O distances increase systematically from Cl through Br to I containing compounds,
249 whereas they are equal within limits of error for the compounds containing the same halogen
250 (the two Br resp. the two I compounds) and independent of the occupancy of the *M* site [note
251 that synthetic $\text{NH}_4\text{As}_4\text{O}_6\text{Cl}$ could not be synthesized by Pertlik (1988) and therefore no
252 structural data are known for it]. The above evidence suggests that the values of the As-O and
253 O-O distances observed in the structure of lucabindiite, which are practically equal with those
254 of the compound $\text{KAs}_4\text{O}_6\text{Cl}$ (Table 6), are related to the simultaneous occurrence of F and Br,
255 in addition to Cl, in the *X* site. The same is also true for the *X*-As bond-lengths (Table 6). As
256 expected, in the $\text{MAs}_4\text{O}_6\text{X}$ compounds the *X*-As distances increase systematically from Cl
257 through Br to I containing compounds and are not influenced by the occupancy of *M* (Pertlik
258 1988). The values of *X*-As distances in the structure of lucabindiite are very close to those of
259 the compound $\text{KAs}_4\text{O}_6\text{Cl}$.

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262 GENETIC FEATURES AND DISCUSSION

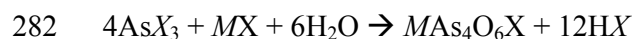
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264 Lucabindiite, ideally $(\text{K},\text{NH}_4)\text{As}_4\text{O}_6(\text{Cl},\text{Br})$, is an arsenic oxychloride which was
265 found as a sublimate phase at “La Fossa” crater, Vulcano islands, Aeolian archipelago, Italy.
266 It corresponds to the synthetic phase with general formula $\text{MAs}_4\text{O}_6\text{X}$ (Pertlik 1988), where *M*
267 = K, NH_4 and *X* = Cl, Br, I. In Table 7 chemical and crystallographic data of lucabindiite are
268 compared with those of the related synthetic phases (Pertlik 1988).

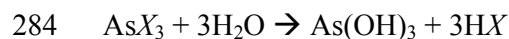
269 In laboratory, the synthetic analogues of lucabindiite were obtained by thermal
270 treatments of cubic As_2O_3 and potassium or ammonium halides in a saturated aqueous

271 solution of potassium acetate or ammonia (Pertlik 1988). Although both arsenolite and K and
272 NH₄ halides are present at Vulcano, it is not probable that lucabindiite formed by a similar
273 reaction, for which an earlier formation of arsenolite, As₂O₃, is required. As a matter of fact,
274 arsenolite was found in association with lucabindiite (Figure 3), but it was not in a clear
275 paragenetic sequence with the new mineral. On the contrary, their mode of appearance
276 suggests a simultaneous deposition of the two arsenic phases.

277 At Vulcano, the lucabindiite and arsenolite occurrence is most probably due to the
278 simultaneous presence in the steam of hydrogen halogenides and arsenic, whose transport as
279 AsCl₃ has been hypothesized to happen in the La Fossa crater fumaroles (Garavelli et al.
280 1997). In this context, possible reactions explaining their formation in the cooling of the
281 halogen-rich volcanic gases are:



283 or



286 with $M = K, NH_4$ and $X = Cl, Br, F$.

287 Arsenic minerals at Vulcano are relatively abundant. The occurrence of orpiment,
288 As₂S₃, and realgar, As₄S₄, has been reported for the area by a number of authors throughout
289 the nineteenth and the first 20 years of the twentieth century (Stromeyer 1824; Sainte-Claire
290 Deville 1856; Jervis 1873; Bellini 1918; Panichi 1924) but modern investigations
291 (Campostrini et al. 2011 and references therein) do not confirm their presence. On the
292 contrary, an amorphous arsenic-rich sulfurite, often containing selenium and/or tellurium, is
293 still today very abundant around medium temperature fumaroles and has been largely
294 described (Garavelli 1958; Garavelli 1994; Campostrini et al. 2011). Solid phases containing

295 As-S-Cl that look morphologically very similar to lucabindiite have been found as sublimates
296 collected in silica sampling tubes deeply inserted in high-temperature fumarole vents at
297 Vulcano (Garavelli 1994; Garavelli et al. 1997). It is not excluded that such phases could be
298 related to lucabindiite by a substitution S-O in the structure and the total substitution of NH₄
299 in place of K. This hypothesis is also supported by the our recent finding of a number of
300 “lucabindiites” from the ground around fumarole F5AT (sampling year 2009) containing As,
301 but no traces of K , I and Br substituting for Cl, and/or S partially substituting for O.
302 Investigations on these phases are still in progress. Around high-temperature fumaroles of
303 Vulcano, further minerals containing arsenic are represented by sulphosalts like kirkiite,
304 Pb₁₀(Bi,As)₆(S,Se)₁₉ (Borodaev et al. 1998) and vurroite Pb₂₀Sn₂(Bi,As)₂₂S₅₄C₁₆ (Garavelli et
305 al. 2005), whose occurrence is related both to the high fugacity of sulphur and to the high
306 activity of hydrogen halogenides in fumarolic fluids discharging from fumaroles (Borodaev et
307 al. 1998; Garavelli et al. 1997).

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446 **FIGURE CAPTIONS**

447 Figure 1. Location of fumarole F1 at Vulcano: the sampling site of lucabindiite.

448 Figure 2. SEM-BSD image of lucabindiite aggregates with well formed sulfur crystals on an
449 amorphous arsenic-rich sulfurite.

450 Figure 3. SEM-BSD image of arsenolite crystals, As_2O_3 , associated with rare plates of
451 lucabindiite on a base of amorphous arsenic-rich sulfurite.

452 Figure 4. Microscope-optical image of transparent- white aggregates of lucabindiite crystals
453 associated with a reddish arsenic-rich sulfurite.

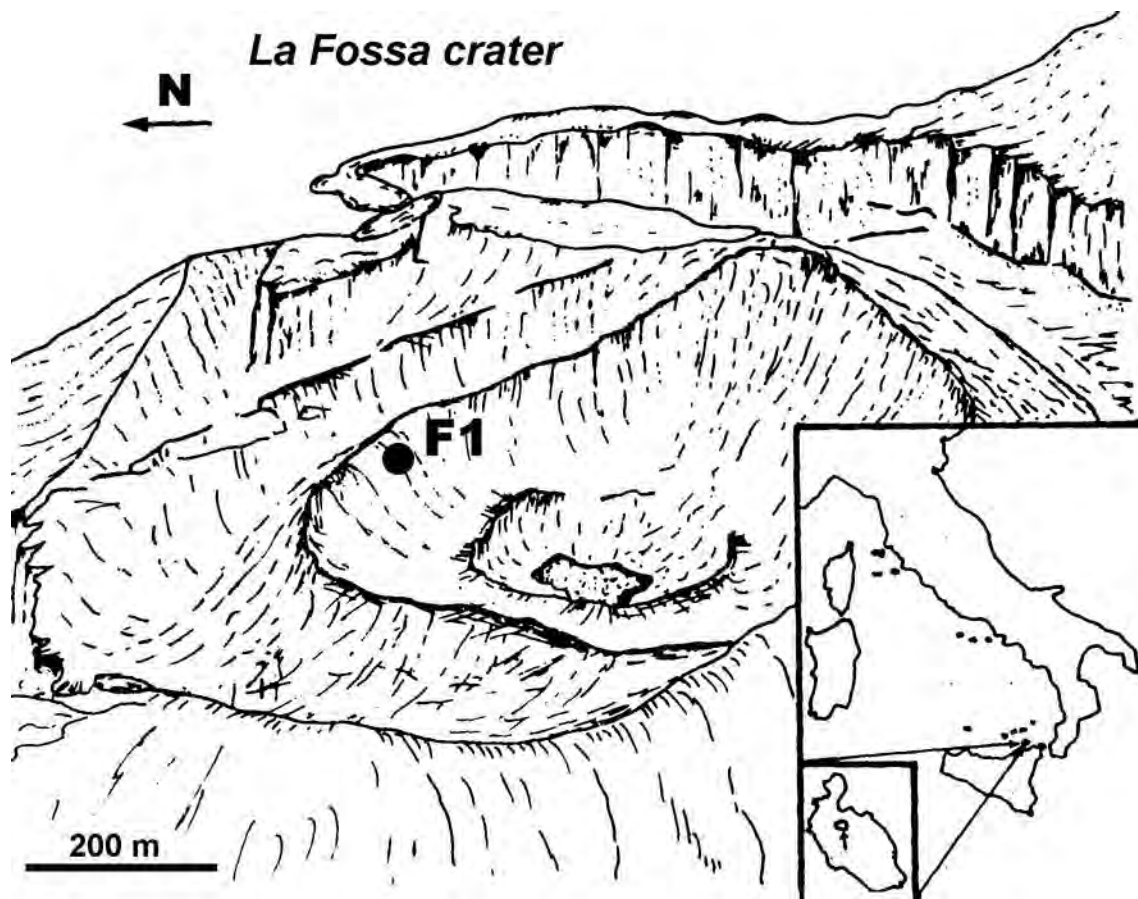
454 Figure 5. SEM-BSD image of an aggregate of lucabindiite crystals.

455 Figure 6. FTIR spectrum of lucabindiite in the range $4000\text{--}800\text{ cm}^{-1}$.

456 Figure 7. Detailed FTIR spectra of lucabindiite with absorption bands due to NH_4^+ .

457 Figure 8. The crystal structure of lucabindiite. Red: As atoms; dark: O atoms; light-blue: X
458 positions; orange: M positions. Dashed bonds indicate long As-(Cl,Br) contacts

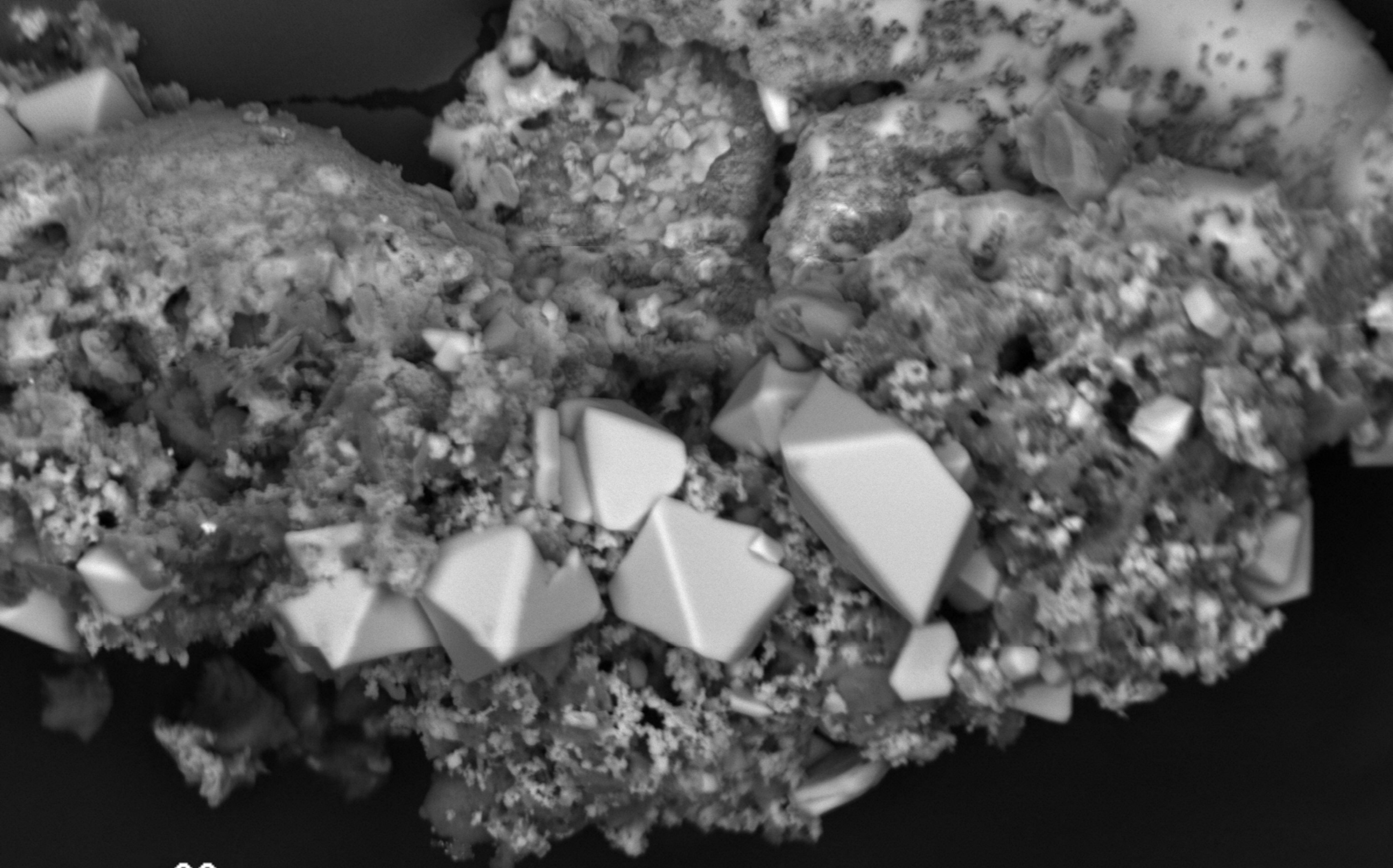
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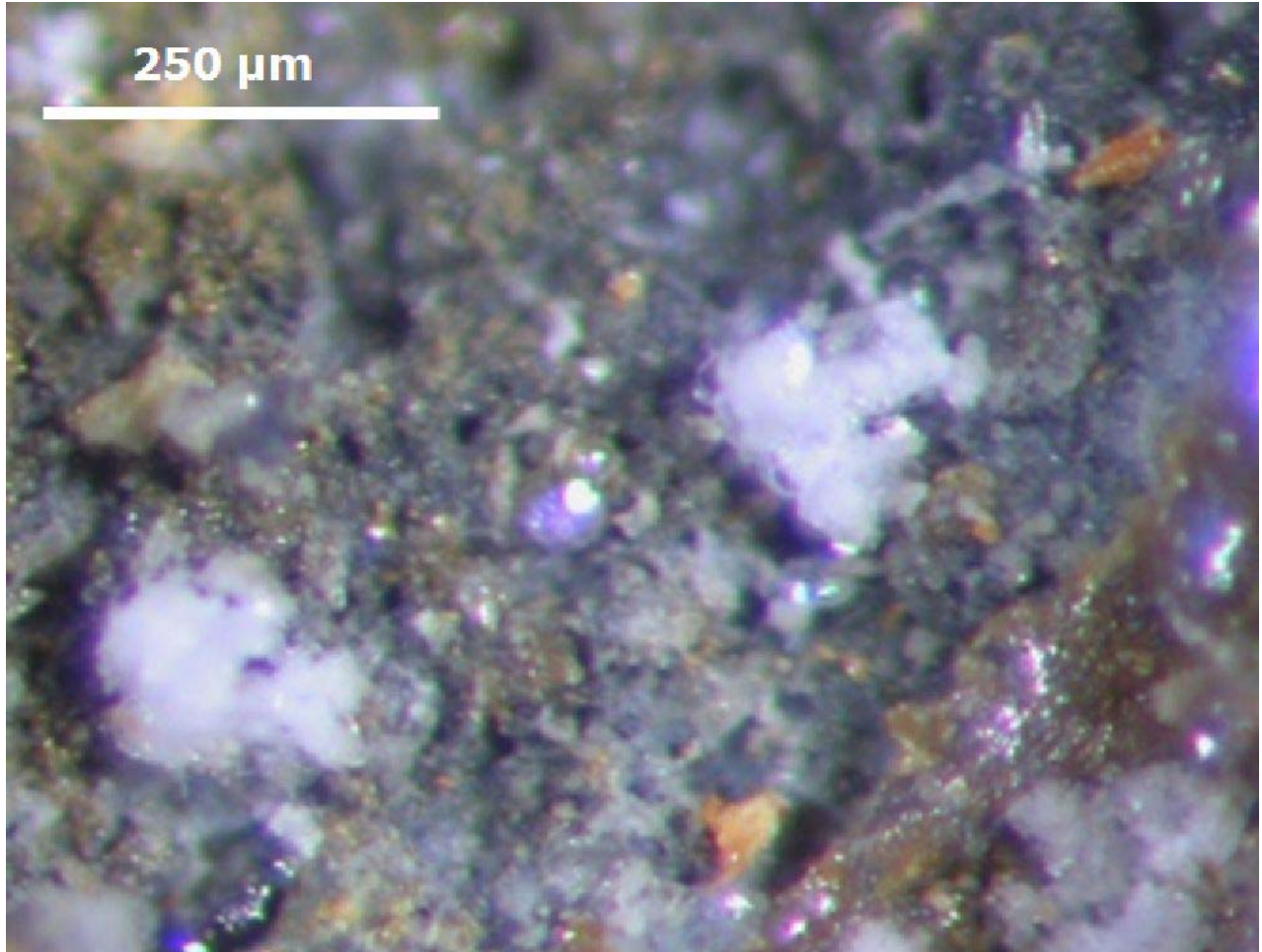


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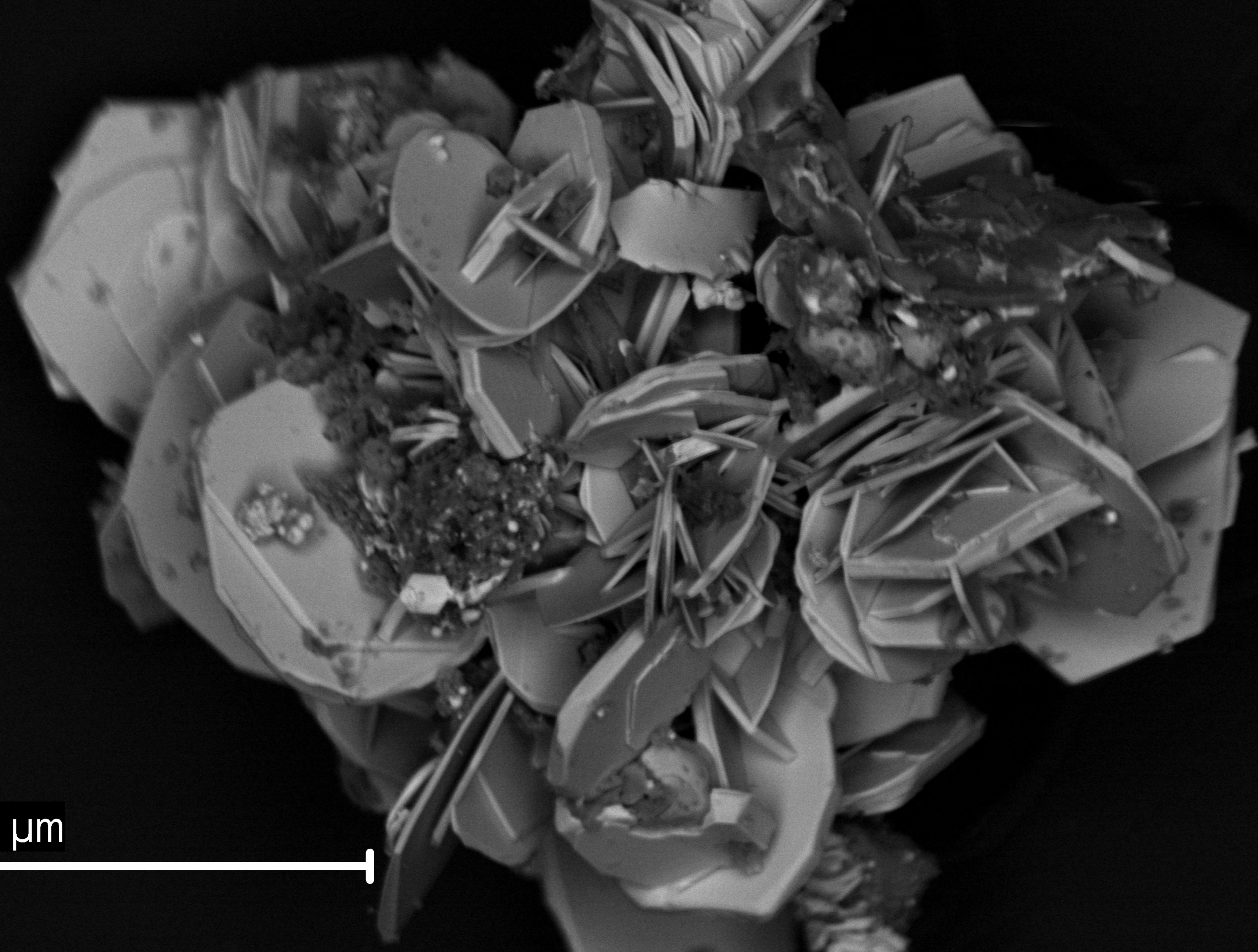


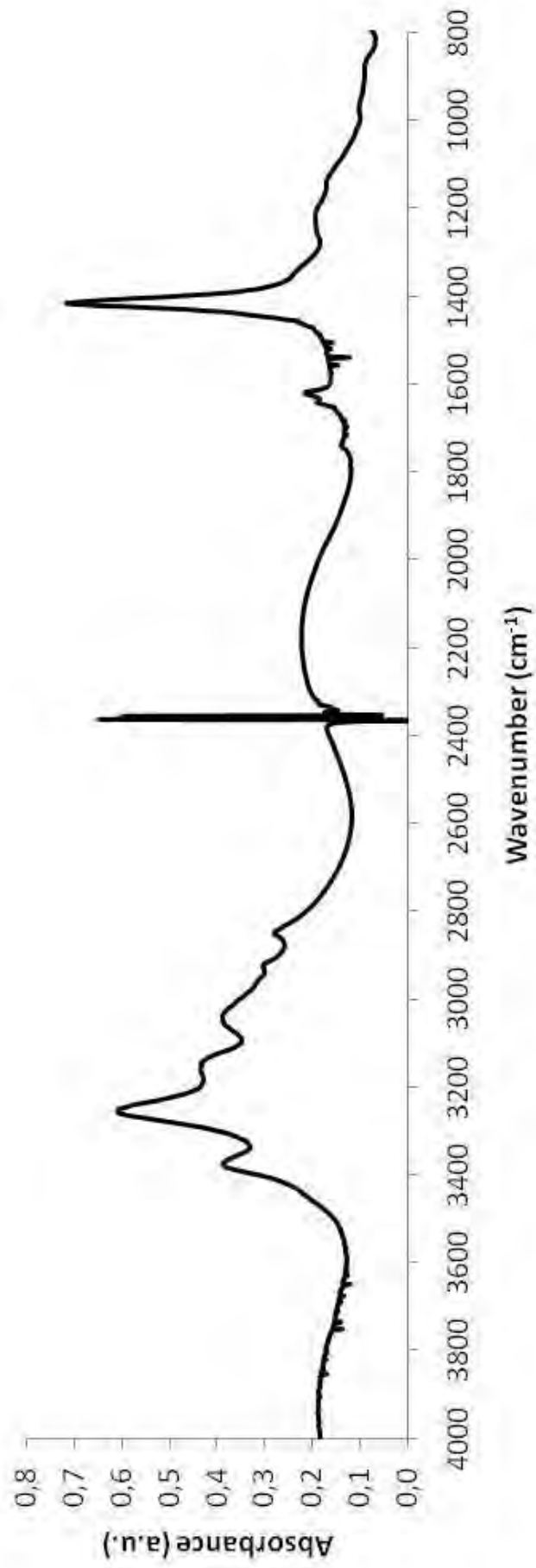


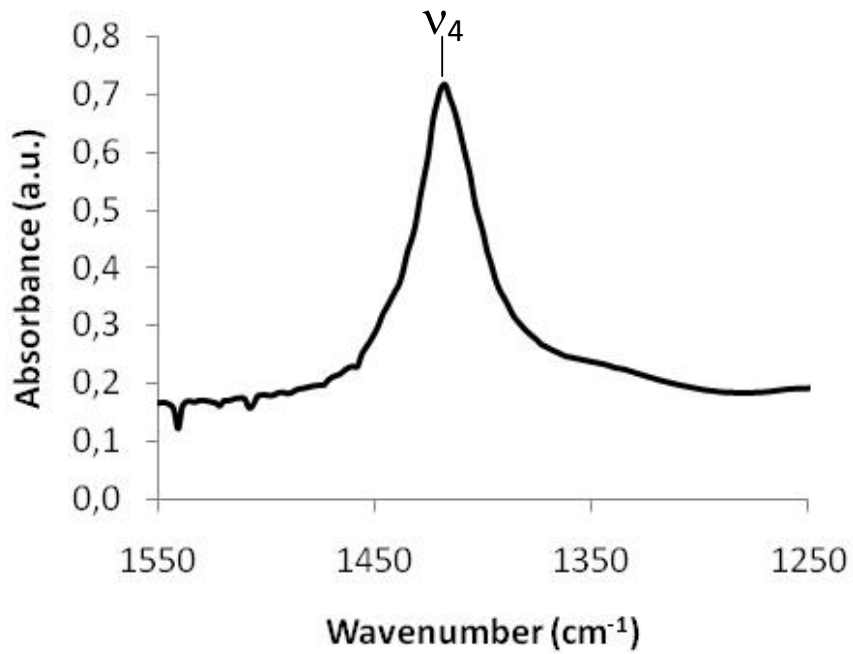
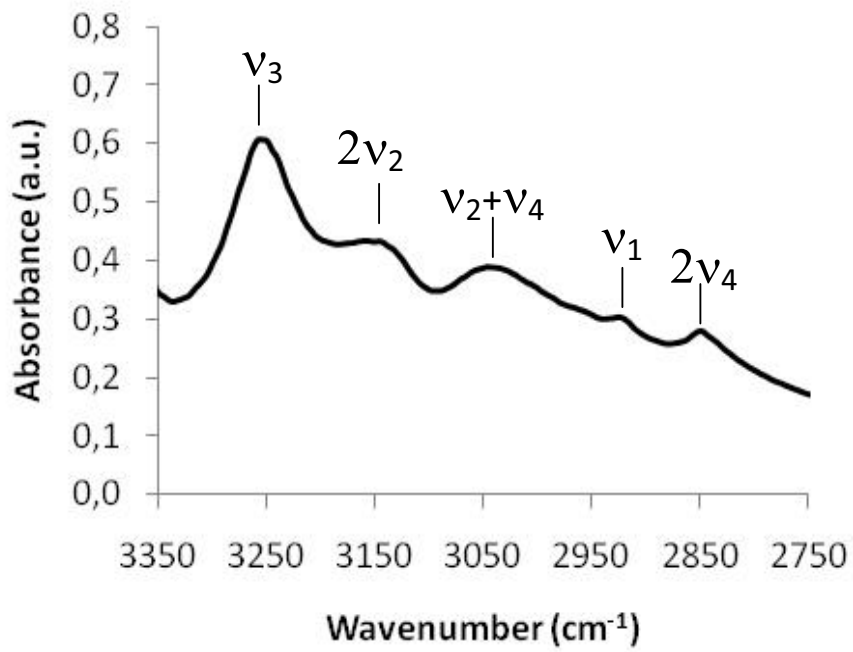
20 μm



100 μm







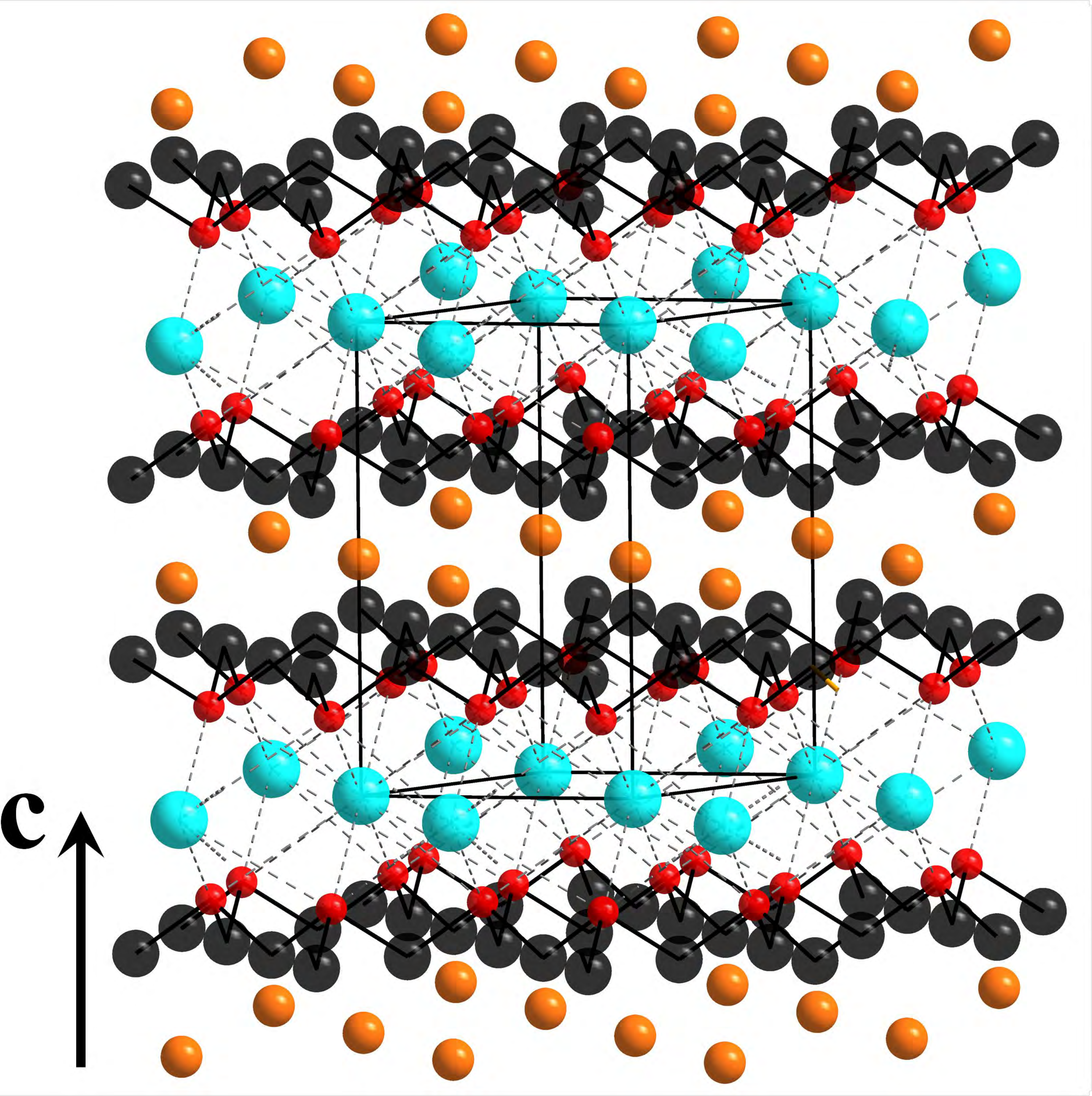


Table 1. SEM-EDS chemical data for lucabindiite (average of twelve point analyses).

CONSTITUENT	WT%	RANGE	SD
K ₂ O	5.14	3.67 – 6.70	0.70
As ₂ O ₃	84.71	80.52 – 88.84	2.90
Cl	3.63	1.90 – 5.81	1.41
Br	6.92	3.70 – 10.31	2.24
F	0.77	0.27 – 1.21	0.27
(NH ₄) ₂ O*	2.73	1.72 – 3.13	0.35
	103.90		
O = F, Cl, Br	-1.84		
Total	102.06		

*The ammonium content was deduced from the K content, taking into account the (K,NH₄)As₄O₆(Cl,Br) stoichiometry (K+NH₄=1 *apfu*).

Table 2. Band position and assignment for the bands in the FTIR spectrum of the lucabindiite single crystal.

POSITION (cm⁻¹)	ABSORBANCE (a.u.)	ASSIGNMENT NH₄⁺
3257	0,608	v ₃
3159	0,434	2v ₂
3045	0,389	v ₂ + v ₄
2926	0,303	v ₁
2850	0,280	2v ₄
1417	0,716	v ₄

Table 3. X-ray powder diffraction pattern for lucabindiite.

<i>hkl</i>	d_{calc} (Å)	I_{calc}	d_{obs} (Å)	I_{meas}
001	9.0140	16.30	-	-
100	4.5368	30.49	4.54	35
002	4.5070	51.64	4.50	50
102	3.1974	100.00	3.200	100
003	3.0047	4.33	-	-
110	2.6193	66.57	2.613	60
111	2.5153	14.14	2.516	10
103	2.5051	11.28	2.501	10
112	2.2646	18.89	2.262	20
004	2.2535	4.35	-	-
202	2.0262	8.78	2.021	5
113	1.9744	28.01	1.973	25
203	1.8104	15.97	1.809	15
005	1.8028	3.45	-	-
210	1.7147	3.81	-	-
114	1.7083	9.42	1.707	10
105	1.6754	3.13	-	-
212	1.6027	20.28	1.602	20
300	1.5123	11.04	1.513	10
213	1.4893	4.67	-	-
115	1.4850	20.99	1.486	20
302	1.4337	4.65	-	-
205	1.4114	5.78	-	-
303	1.3508	6.93	-	-
220	1.3096	10.34	1.310	10
222	1.2576	5.47	-	-
312	1.2119	6.81	-	-
305	1.1586	8.37	-	-
117	1.1556	4.69	-	-
225	1.0596	3.91	-	-
322	1.0141	3.89	-	-
410	0.9900	5.57	-	-
307	0.9804	3.05	-	-
218	0.9417	3.01	-	-
413	0.9403	4.77	-	-
415	0.8678	10.69	-	-
<u>1110</u>	0.8523	5.64	-	-
318	0.8394	3.39	-	-

Table 4. Fractional atomic coordinates, anisotropic displacement parameters and occupancies for lucabindiite.

Site	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{eq}
<i>M</i>	0	0	1/2	0.041(5)	0.041(5)	0.047(9)	0.020(3)	0.043(5)
<i>As</i>	1/3	2/3	0.7969(2)	0.0078(4)	0.0078(4)	0.0278(8)	0.0039(2)	0.0145(4)
<i>O</i>	1/2	0	0.6894(9)	0.0165(5)	0.007(3)	0.031(4)	0.003(1)	0.019(2)
<i>X</i>	0	0	0	0.0206(16)	0.0206(16)	0.069(5)	0.0103(8)	0.037(2)

Note: The anisotropic displacement parameters are defined as: $\exp [-2\pi^2 \Sigma_i^3 = {}_1\Sigma_j^3 = {}_1U_{ij} a_i^* a_j^* h_i h_j]$, U_{equiv} according to Fischer and Tillmanns (1988). U_{23} and U_{13} are equal to 0. Sites scattering: *M* = 0.52(4) K, 0.48(4) NH₄ (from the refinement); *X* = 0.5 Cl, 0.3 Br, 0.2 F (fixed on the basis of the chemical data).

Table 5. Summary of parameters describing data collection and refinement for lucabindiite.

Empirical structural formula	[K _{0.52} (NH ₄) _{0.48}]As ₄ O ₆ (Cl _{0.5} Br _{0.3} F _{0.2})
Crystal dimensions (mm)	0.05 x 0.11 x 0.15
Crystal system, space group	Hexagonal, <i>P6/mmm</i>
<i>a</i> (Å)	5.2886(7)
<i>c</i> (Å)	9.014(2)
<i>V</i> (Å ³)	214.23(7)
Z	1
Temperature (K)	293
D _x (Mg m ⁻¹)	3.645
X-ray conditions (kV, mA),	50, 30
Wavelength of radiation (Å)	0.71073
Detector to sample distance (mm)	40
Number of frames	1095
Rotation width per frame (°)	0.5
Measuring time (s)	120
Maximum covered 2θ (°)	61 (<i>d</i> = 0.70 Å)
Independent reflections	174
Reflections with <i>F</i> _o > 4σ(<i>F</i> _o)	136
<i>R</i> _{int}	0.0998
<i>R</i> _σ	0.0392
Ranges of <i>h</i> , <i>k</i> , <i>l</i>	-6 ≤ <i>h</i> ≤ 7 -7 ≤ <i>k</i> ≤ 5 -12 ≤ <i>l</i> ≤ 12
<i>R</i> [<i>F</i> _o > 4 σ (<i>F</i> _o)]	0.0384
<i>R</i> (all data)	0.0617
w <i>R</i> [<i>F</i> _o > 4 σ (<i>F</i> _o)]	0.0969
w <i>R</i> (all data)	0.1102
Goof	1.15
Refined parameters	13
Weighting scheme	w = 1/[σ ² (<i>F</i> _o ²) + (0.0608 <i>P</i>) ² + 1.0076 <i>P</i>] where <i>P</i> = [max(<i>F</i> _o) ² + 2(<i>F</i> _c) ²]/3
Dρ _{min} , Dρ _{max} (e/Å ³)	-1.58, 3.06

Table 6. Selected interatomic distances (Å) and angles (°) in lucabindiite.

	This study	Pertlik (1988)				
	lucabindiite	KAs ₄ O ₆ Cl	KAs ₄ O ₆ Br	KAs ₄ O ₆ I	NH ₄ As ₄ O ₆ Br	NH ₄ As ₄ O ₆ I
M – O (12 x)	3.127(5)	3.104(3)	3.097(2)	3.109(2)	3.158(1)	3.165(2)
As – O (3 x)	1.796(5)	1.795(2)	1.805(2)	1.807(2)	1.801(1)	1.806(2)
O – O (3 x)	2.619(1)	2.626(2)	2.629(2)	2.640(9)	2.632(1)	2.645(2)
X – As (12 x)	3.535(1)	3.538(3)	3.561(2)	3.631(2)	3.564(1)	3.632(2)
O – As – O (3 x)	93.6(3)	94.01(1)	93.45(9)	93.86(9)	93.87(9)	94.15(8)

Table 7. Crystal lattice parameters of lucabindiite and the strongest powder diffraction lines compared with those of the related synthetic phases.

	This study	Pertlik (1988)				
CHEMICAL FORMULA	$[\text{K}_{0.51}(\text{NH}_4)_{0.45}]_{\Sigma 0.96}\text{As}_{4.01}\text{O}_{5.95}(\text{Cl}_{0.48}, \text{Br}_{0.41}, \text{F}_{0.19})_{\Sigma 1.08}$	$\text{KAs}_4\text{O}_6\text{Cl}$	$\text{KAs}_4\text{O}_6\text{Br}$	$\text{KAs}_4\text{O}_6\text{I}$	$\text{NH}_4\text{As}_4\text{O}_6\text{Br}$	$\text{NH}_4\text{As}_4\text{O}_6\text{I}$
SPACE GROUP	<i>P6/mmm</i>	<i>P622</i>	<i>P622</i>	<i>P622</i>	<i>P622</i>	<i>P622</i>
UNIT-CELL PARAMETERS (Å)	$a = 5.2386(7)$ $c = 9.014(2)$	$a = 5.252(1)$ $c = 8.880(2)$	$a = 5.257(1)$ $c = 8.955(2)$	$a = 5.281(1)$ $c = 9.169(2)$	$a = 5.265(1)$ $c = 9.148(2)$	$a = 5.290(1)$ $c = 9.338(2)$
STRONGEST POWDER LINES	9.014/2 4.537/3 4.507/5 3.197/10	4.548/3 4.440/5 3.177/10	8.955/2 4.477/3 3.192/10	9.169/2 3.238/10 2.640/5	9.148/5 4.574/5 4.560/5	9.338/6 4.669/2 4.113/2
$d(\text{Å})/I$ (related to 10)	2.619/7 2.265/2 1.974/3 1.603/2 1.485/2	2.626/6 2.260/2 1.964/3	2.628/5 1.606/2	2.537/2 1.617/2	3.230/10 2.632/6 2.530/3 1.826/2	3.270/10 2.645/5 2.575/2 2.545/2