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The crystal structure of johnbaumite, $\text{Ca}_5(\text{AsO}_4)_3\text{OH}$, the arsenate analogue of hydroxylapatite

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CRISTIAN BIAGIONI^{1*}, MARCO PASERO¹

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33 ¹ *Dipartimento di Scienze della Terra, Università di Pisa, Via S. Maria 53, I-56126 Pisa, Italy*

34 *e-mail address: biagioni@dst.unipi.it

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ABSTRACT

38 The crystal structure of johnbaumite, ideally $\text{Ca}_5(\text{AsO}_4)_3\text{OH}$, was determined and refined
39 using crystals from the Harstigen mine, Värmland, Sweden, on the basis of X-ray diffraction data.
40 The structure was refined to $R_1 = 0.038$ in the $P6_3/m$ space group, with unit-cell parameters a
41 $9.7242(2)$, c $6.9657(9)$ Å, V $570.43(2)$ Å³. The chemical composition of the sample, determined by
42 electron-microprobe analysis, is $(\text{Ca}_{5.02}\text{Pb}_{0.03})_{\Sigma 5.05}[\text{As}_{2.91}\text{P}_{0.04}\text{Si}_{0.02}]_{\Sigma 2.97}\text{O}_{12}(\text{OH}_{0.97}\text{Cl}_{0.03})$.

43 Johnbaumite belongs to the calcium arsenate apatites, together with svabite, $\text{Ca}_5(\text{AsO}_4)_3\text{F}$,
44 and turneaureite, $\text{Ca}_5(\text{AsO}_4)_3\text{Cl}$. Johnbaumite is topologically similar to the other members of the
45 apatite supergroup: columns of face-sharing $M1$ polyhedra run along c and are connected through
46 TO_4 tetrahedra, giving rise to a zeolite-like microporous framework, with channels hosting $M2$
47 cations and X anions.

48 This is the first published single-crystal structure study of johnbaumite and the first report of
49 this calcium arsenate apatite from the Harstigen mine. Actually, johnbaumite was identified at this
50 locality at the end of the 19th Century but it was described as svabite.

51

52 *Key-words:* johnbaumite, calcium arsenate, apatite supergroup, crystal structure, Harstigen mine.

53

54 **Introduction**

55 Johnbaumite, $\text{Ca}_5(\text{AsO}_4)_3\text{OH}$, is a rare calcium arsenate belonging to the apatite supergroup. It
56 was described by Dunn et al. (1980) from the Franklin mine, New Jersey, USA. Together with
57 svabite, $\text{Ca}_5(\text{AsO}_4)_3\text{F}$ (Sjögren 1891, 1892), and turneaureite, $\text{Ca}_5(\text{AsO}_4)_3\text{Cl}$ (Dunn et al. 1985),
58 johnbaumite forms a series of three minerals which represent the arsenate analogues of the calcium
59 phosphates hydroxylapatite, fluorapatite, and chlorapatite, respectively (Pasero et al. 2010).

60 In recent years, the pollution of drinking water by arsenic in south-eastern Asia (*e.g.* Charlet
61 and Polyá 2006) has focused the attention of the researchers on these compounds, as possible
62 sequestrators of As from polluted waters. In the case of As^{5+} -containing waters, addition of lime has
63 been used to promote the precipitation of calcium arsenate phases. Consequently, structural studies
64 upon these compounds have been performed by different authors, *e.g.* Henderson et al. (2009) and
65 Lee et al. (2009). These papers present the results of Rietveld refinements of the crystal structure of
66 natural johnbaumite and synthetic $\text{Ca}_5(\text{AsO}_4)_3\text{OH}$. In contrast to fluorapatite, hydroxylapatite, and
67 chlorapatite, for which several high-quality single-crystal structural refinement have been published
68 (*e.g.*, Hughes and Rakovan 2002; White et al. 2005), the only available single-crystal refinement for
69 calcium arsenate apatites is that of synthetic $\text{Ca}_5(\text{AsO}_4)_3\text{Cl}$ (Wardojo and Hwu 1996). In a
70 conference abstract, the results of the X-ray single-crystal study for the three natural calcium
71 arsenate apatites were presented by Dai and Harlow (1991) but to our knowledge the details of their
72 work have not been published.

73 Johnbaumite has been assumed to crystallize in the $P6_3/m$ space group and we found no
74 evidence for lower symmetry in our study. Actually, in the apatite supergroup only 57% of the
75 chemical end-members adopt the space group $P6_3/m$, the others crystallizing in hexagonal
76 subgroups, or in monoclinic or triclinic space groups (White et al. 2005; Baikie et al. 2007).
77 Notably, the crystal structure of synthetic $\text{Ca}_5(\text{AsO}_4)_3\text{F}$ displays a triclinic symmetry, $P\bar{1}$ (Baikie et
78 al. 2007), whereas synthetic $\text{Ca}_5(\text{AsO}_4)_3\text{Cl}$ is hexagonal, $P6_3/m$ (Wardojo and Hwu, 1996).

79 For these reasons a structural study of johnbaumite performed through single-crystal
80 technique seems desirable, in order to provide a more robust basis for the structural characterization
81 of calcium arsenate apatites. This paper presents the results of the single-crystal X-ray diffraction
82 study performed on a specimen of johnbaumite from the Harstigen mine.

83

84 **Experimental**

85 A specimen labeled as “svabite” from the type locality was made available to us by the
86 mineral collector Ulf Nyberg (Marienham, Finland). Colorless, hexagonal prismatic crystals, deeply

87 striated along [0001], up to 1 mm in length, occur in association with andradite, calcite, and
88 caryopilite (Fig. 1). The studied specimen is kept in the mineralogical collection of the Museo di
89 Storia Naturale, University of Pisa, under catalogue number 19642.

90 Electron-microprobe analysis was carried on with a Cameca SX50 at the Electron-microprobe
91 laboratory of the CNR-Institute for Geosciences and Earth Resources of Padova, Italy, using the
92 following analytical conditions: accelerating voltage 20 kV, beam current 20 nA, beam size 1-2 μm .
93 Counting time for one spot analysis was 10 s per peak. Standards (element, emission line) are:
94 apatite ($\text{PK}\alpha$), diopside ($\text{SiK}\alpha$, $\text{CaK}\alpha$), vanadinite ($\text{ClK}\alpha$), GaAs ($\text{AsL}\alpha$), and PbS ($\text{PbM}\alpha$). F, Na,
95 Mg, Al, V, Cr, Mn, Fe, Sr, Y, La, Ce were sought but found below the detection limit.

96 Chemical data are reported in Table 1; the chemical formula, based on 13 anions, is
97 $(\text{Ca}_{5.02}\text{Pb}_{0.03})_{\Sigma 5.05}[\text{As}_{2.91}\text{P}_{0.04}\text{Si}_{0.02}]_{\Sigma 2.97}\text{O}_{12}(\text{OH}_{0.97}\text{Cl}_{0.03})$.

98 A crystal fragment ($100 \times 20 \times 20 \mu\text{m}^3$) was selected for the single-crystal X-ray diffraction
99 study. Intensities were collected using a Bruker Smart Breeze diffractometer (50 kV, 30 mA)
100 equipped with a CCD 4k low noise area detector. Graphite-monochromated Mo $K\alpha$ radiation was
101 used. 903 frames were collected in 0.5° slices; the exposure time was 60 s per frame. The data were
102 integrated and corrected for Lorentz and polarization, background effects, and absorption using the
103 package of softwares Apex2 (Bruker AXS Inc. 2004), resulting in a set of 749 independent
104 reflections. The refinement of unit-cell parameters gave a 9.7242(2), c 6.9657(9) Å, space group
105 $P6_3/m$.

106 The crystal structure was solved through direct methods using Shelxs-97 (Sheldrick, 2008).
107 After locating the positions of Ca and As, the structure was completed through successive
108 difference-Fourier maps and refined using Shelx-97 (Sheldrick, 2008). Then, the atom coordinates
109 were transformed in order to match those given by Henderson et al. (2009). Scattering curves from
110 neutral atoms were taken from the International Tables for X-ray Crystallography (1992).

111 The position of the X anion was initially located at $(0, 0, \frac{1}{4})$, showing a very elongated atomic
112 displacement parameter along the c axis, with $R_{\text{max}}/R_{\text{min}}$ of about 23.5; this ratio is lowered to ~ 8 if
113 the X anion is located in the position $(0, 0, z)$ with half-occupancy.

114 The $\langle T\text{-O} \rangle$ distance is slightly shorter than expected for an ideal As-O bond, thus suggesting
115 a possible substitution of minor P for As. The refinement of the site occupancy of the As site
116 confirmed the minor substitution of As by P, with a refined occupancy ($\text{As}_{0.93}\text{P}_{0.07}$). The refined
117 electron density, $31.7 e^-$, is in agreement with that obtained through electron-microprobe analysis,
118 *i.e.* $32.3 e^-$.

119 After ten cycles of anisotropic refinement, R_1 converged to 3.76%. Details of the data
120 collection and refinement are reported in Table 2.

121

122 **Crystal structure description**

123 Atomic coordinates, site occupancies, and displacement parameters are reported in Table 3
124 and 4, respectively; Table 5 reports selected bond distances, and Table 6 reports the bond-valence
125 calculations.

126 Johnbaumite is topologically similar to the other members of the apatite supergroup. Its
127 crystal structure (Fig. 2) can be described as formed by columns of face-sharing $M1$ -centered
128 polyhedra running along c ; those polyhedra can be described as triaugmented trigonal prisms.
129 Adjacent columns are connected by TO_4 tetrahedra through corner-sharing. This polyhedral
130 arrangement may be considered as a zeolite-like microporous framework, with channels hosting
131 seven-fold coordinated $M2$ cations and X anions (White et al. 2005).

132 Crystallographic data for johnbaumite from Harstigen are in agreement with those reported by
133 Henderson et al. (2009) for the specimen from Franklin and the synthetic $Ca_5(AsO_4)_3OH$ studied by
134 Lee et al. (2009).

135

136 **Discussion**

137 **Triclinic vs hexagonal symmetry in johnbaumite**

138 The prototype structure of the phases belonging to the apatite supergroup is hexagonal
139 ($P6_3/m$); however, ordering and/or distortions can reduce the symmetry. As stated above, Baikie et
140 al. (2007), combining diffraction data and *ab initio* calculations, obtained $P\bar{1}$ symmetry for the
141 synthetic $Ca_5(AsO_4)_3F$, the F-analogue of johnbaumite. According to these authors, the lowering
142 of symmetry is due to a distortion of the unit cell, required when the $M1_4(TO_4)_6$ framework is
143 expanded with respect to the $M2_6X_2$ channel contents. Therefore, the substitution of phosphorus by
144 arsenic, with the latter having a greater ionic radius, is the main cause of the triclinic symmetry of
145 synthetic $Ca_5(AsO_4)_3F$. On the contrary, Lee et al. (2009) investigated the solution series between
146 synthetic $Ca_5(PO_4)_3(OH)$ and $Ca_5(AsO_4)_3(OH)$, and did not find any evidence of a lowering of
147 symmetry due to the replacement of phosphorus by arsenic. The same results were obtained by
148 Henderson *et al.* (2009) studying a specimen of johnbaumite from the type locality.

149 To check for the true symmetry of johnbaumite, the crystal structure was solved and refined
150 in both the triclinic and hexagonal settings. The refined triclinic unit cell of johnbaumite is a
151 9.7199(10), b 9.7221(9), c 6.9651(7) Å, α 90.077(2), β 90.051(2), γ 119.944(2)°, as compared with
152 the unit cell of synthetic $Ca_5(AsO_4)_3F$ given by Baikie et al. (2007): a 9.6841(5), b 9.6906(5), c

153 6.9815(3) Å, α 90.623(3), β 88.869(3), γ 120.371(3)°. The deviation of the latter from the
154 hexagonal symmetry is definitely greater than that observed in johnbaumite.

155 In the triclinic setting, there are three independent *T* sites, three independent *M2* sites, and two
156 independent *M1* sites. In our triclinic refinement, the three *T* sites, with average bond lengths of
157 1.672(3), 1.673(3), and 1.666(3) Å respectively, are indistinguishable from one another; in addition,
158 the refinement of arsenic vs phosphorus shows that the three sites have the same electron density.
159 We conclude, in agreement with Lee et al. (2009), that no evidence of a lowering of symmetry can
160 be observed in johnbaumite. A possible explanation of the discrepancy between the data of Baikie
161 et al. (2007) and those obtained studying johnbaumite and synthetic Ca₅(AsO₄)₃OH (Henderson et
162 al., 2009; Lee et al., 2009; this work), can be related to the larger size of the hydroxyl group relative
163 to fluorine. If the lowering of symmetry of synthetic Ca₅(AsO₄)₃F is due to the distortion of the unit
164 cell related to the expansion of the framework, caused by the As⁵⁺ – P⁵⁺ substitution, the
165 introduction of (OH)⁻ in place of F⁻ in the channel could compensate for the distortion, reducing the
166 difference in size between the *M1*₄(*TO*₄)₆ framework and the *M2*₆*X*₂ channel contents.

167

168 **Nature of the *X* anion in the specimen from Harstigen**

169 In a first stage of our study (Biagioni and Pasero 2012), we identified the specimen from
170 Harstigen as svabite. In the crystal structure, every *X* anion is coordinated by three *M2* cations, in a
171 triangular configuration; the differences in the nature of the *X* anions result in different positions
172 with respect to the coordinating *M2* cations. In fact, when *X* = F⁻, the anion site is located at $z = \frac{1}{4}$
173 and $\frac{3}{4}$, whereas if *X* = OH⁻, the site is displaced off the special positions, in two half-occupied sites
174 at (0, 0, *z*), above and below the mirror plane (Hughes et al. 1989). The elongation of the
175 displacement ellipsoid of the *X* anion in the studied sample was consequently interpreted as due to a
176 mixed F/OH occupancy of the tunnels. After the introduction of a site at (0, 0, 0.19), corresponding
177 to the position of OH in hydroxylapatite, the refinement seemed to agree with such a mixed
178 occupancy, with a site occupancy of (F_{0.89}OH_{0.11}). Consequently, the specimen from Harstigen was
179 classified as svabite, with a limited substitution of fluorine by hydroxyl, on the basis of the
180 structural study only (Biagioni and Pasero 2012).

181 Subsequently, chemical analyses clearly indicated the absence of fluorine in the studied
182 crystal and a very limited content of chlorine, indicating that the preliminary identification reported
183 in Biagioni and Pasero (2012) was erroneous. Consequently, the crystal structure was refined
184 removing the maximum at (0, 0, $\frac{1}{4}$), and introducing an oxygen atoms, with half-occupancy, at (0,
185 0, 0.19). The refinement converged to the same *R*₁ value than the previous one, but the elongation
186 of the thermal ellipsoid along the *c* axis was reduced, with a ratio of ~ 8. Figure 3 compares the

187 anion position in johnbaumite (Fig. 3a), hydroxylapatite (Fig. 3b), and fluorapatite (Fig. 3c). In
188 addition, the $M2-X$ bond distance observed in johnbaumite, *i.e.* 2.396(2) Å, agrees with $Ca2-X$
189 bond length in hydroxylapatite, *i.e.* 2.3851(7) Å. The bond distance between Ca and F in
190 fluorapatite is significantly shorter, being 2.3108(7) Å (Hughes et al. 1989).

191

192 **Svabite vs johnbaumite at the Harstigen mine**

193 As reported by Dunn et al. (1980), johnbaumite was observed as early as 1944 at the Franklin
194 mine, but was not formally described until 1980. Actually, based on the original description of
195 svabite given by Sjögren (1891, 1892), johnbaumite may have been found about ninety years before
196 its formal description. In the paper published in 1891 Sjögren described the occurrence of svabite at
197 the Harstigen mine, whereas in the work of 1892 he reported the occurrence of svabite at Harstigen
198 and at the Jakobsberg mine. The chemical analyses of samples from these two localities are not
199 homogenous, showing different F/OH ratios: the sample from Harstigen is OH-dominant, whereas
200 that from Jakobsberg is F-dominant. It is important to stress that, at the end of the 19th Century,
201 little attention was paid to the nature of the monovalent X anion (whether fluorine, hydroxyl, or
202 chlorine) as the discriminant between three distinct species, among both calcium arsenates and
203 calcium phosphates, and the mineral svabite was merely considered as the arsenate analogue of
204 “apatite”, thus disregarding the dominant anion. As a matter of fact, even before the discovery of
205 johnbaumite and turneurite, svabite was assumed to be essentially a fluoride-arsenate of calcium
206 (Palache et al. 1951), with a variable F/OH ratio. However, it is worth noting that Sjögren (1891)
207 stated that the chemical formula of svabite corresponds to that of apatites, with P^{5+} replaced by As^{5+}
208 and F^- replaced by OH^- .

209 In agreement with the chemical analyses of Sjögren (1891, 1892), the mineral from Harstigen
210 was not svabite, but johnbaumite, whereas only the specimen from the Jakobsberg mine should be
211 confidently considered svabite. It is interesting to note that only two other chemical analyses are
212 available in literature for “svabite”, from Franklin, New Jersey, USA (Bauer and Berman 1930),
213 and from the Solongo boron deposit, Buryatia, Siberia, Russia (Malinko et al. 1966), but at both the
214 above occurrences the analysed sample has $(OH) > F$, and thus corresponds to johnbaumite (see
215 also Malinko and Chukanov 1998).

216

217 **Conclusion**

218 The crystal structure of johnbaumite displays the same features as the other members of the
219 apatite group, with $P6_3/m$ symmetry. No deviation from ideal hexagonal symmetry were detected. A

220 crystal structure study on svabite seems desirable in order to confirm the lowering of symmetry in
221 the F end-member of the calcium arsenate apatites.

222 The occurrence of johnbaumite at the Harstigen mine is in keeping with the original
223 description of Sjögren (1891, 1892) who did not distinguish between OH-dominant and F-dominant
224 calcium arsenate. Consequently, the validity of Harstigen as the type locality for svabite, should be
225 considered questionable, and the occurrence of the calcium arsenate fluoride at this locality needs to
226 be proven through the examination of further specimens.

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230 accessible literature. We are grateful to the mineral collector Ulf Nyberg (Marienham, Finland) for
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235

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293 **Table captions**

294 **Table 1** – Electron-microprobe data (mean of 5 spot analysis, in wt%) of johnbaumite and atoms
295 per formula unit (*apfu*), on the basis of 13 anions.

296 **Table 2** – Crystal data and summary of parameters describing data collection and refinement for
297 johnbaumite.

298 **Table 3** – Site occupancies, atom coordinates, and equivalent isotropic displacement parameters for
299 johnbaumite. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

300 **Table 4** – Anisotropic displacement parameters for johnbaumite.

301 **Table 5** – Selected bond distances (in Å) for johnbaumite.

302

303 **Figure captions**

304 **Fig. 1** – Johnbaumite, colorless prismatic crystals up to 1 mm with andradite and caryophyllite.

305 Harstigen mine, Värmland, Sweden. Specimen # 19642, Collection Museo di Storia Naturale e del
306 Territorio, University of Pisa.

307 **Fig. 2** – Crystal structure of svabite, as seen down *c*. Polyhedra: *M1* site, light grey; *T* site, dark
308 grey. Spheres: *M2* site, light grey; *X* site, dark grey.

309 **Fig. 3** – Comparison of anion columns in johnbaumite (a), hydroxylapatite (b), and fluorapatite (c),
310 with atoms drawn as displacement ellipsoids, as seen down [010]. Atomic coordinates and
311 anisotropic displacement parameters of fluorapatite and hydroxylapatite were taken from Hughes *et*
312 *al.* (1989).

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316 **Table 1** – Electron-microprobe data (mean of 5 spot analysis, in wt%) of johnbaumite and atoms
 317 per formula unit (*apfu*), on the basis of 13 anions.

Oxide	wt%	e.s.d.	apfu
As ₂ O ₅	51.71	1.01	2.91(3)
P ₂ O ₅	0.46	0.44	0.04(4)
SiO ₂	0.18	0.06	0.02(1)
CaO	43.49	1.45	5.02(6)
PbO	1.13	2.10	0.03(6)
Cl	0.18	0.15	0.03(3)
H ₂ O*	1.35		0.97
sum	98.50		
O = Cl	- 0.04		
total	98.46		

318 *recalculated in order to achieve 1 (OH+Cl) *pfu*.

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323 **Table 2** – Crystal data and summary of parameters describing data collection and refinement for
 324 johnbaumite.

325

Crystal data	
X-ray formula	Ca ₅ (As _{0.93} P _{0.07}) ₃ O ₁₂ (OH)
Crystal size (mm ³)	0.10 x 0.02 x 0.02
Cell setting, space group	Hexagonal, <i>P6₃/m</i>
<i>a</i> , <i>c</i> (Å)	9.7242(2), 6.9657(9)
<i>V</i> (Å ³)	570.43(2)
<i>Z</i>	2
Data collection and refinement	
Radiation, wavelength (Å)	MoKα, 0.71073
Temperature (K)	298
Detector-to-sample distance	50 mm
Number of frames	903
Rotation width per frame (°)	0.5
Maximum observed 2θ	65.20
Measured reflections	5501
Unique reflections	749
Reflections $F_o > 4\sigma(F_o)$	613
R_{int} after absorption correction	0.0627
	-14 ≤ <i>h</i> ≤ 14
Range of <i>h</i> , <i>k</i> , <i>l</i>	-14 ≤ <i>k</i> ≤ 13
	-10 ≤ <i>l</i> ≤ 10
$R_1 [F_o > 4 \sigma(F_o)]$	0.0376
R_4 (all data)	0.0523
wR_2 (on F_o^2)	0.0594
Goof	1.112
Number of l.s. parameters	43
Maximum and minimum residual	1.05 (at 0.84 Å from P1) -0.96 (at 1.68 Å from P1)

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328

329 **Table 3** – Site occupancies, atom coordinates, and equivalent isotropic displacement parameters
 330 for johnbaumite. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Site	Occupancy	x	y	z	U_{eq}
<i>T</i>	As _{0.93(1)} P _{0.07(1)}	0.3994(1)	0.3714(1)	¼	0.0078(1)
<i>M1</i>	Ca _{1.00}	1/3	2/3	0.0028(2)	0.0151(3)
<i>M2</i>	Ca _{1.00}	0.2448(1)	0.9993(1)	¼	0.0127(2)
<i>O1</i>	O _{1.00}	0.3254(4)	0.4929(4)	¼	0.0166(7)
<i>O2</i>	O _{1.00}	0.5992(4)	0.4706(4)	¼	0.0213(8)
<i>O3</i>	O _{1.00}	0.3410(4)	0.2512(3)	0.4407(4)	0.0270(6)
<i>X</i>	O _{0.50}	0	0	0.216(3)	0.019(5)

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333 **Table 4** – Anisotropic displacement parameters for johnbaumite.

Site	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
<i>T</i>	0.0077(2)	0.0062(2)	0.0090(2)	0	0	0.0031(2)
<i>M1</i>	0.0183(4)	0.0183(4)	0.0086(5)	0	0	0.0091(2)
<i>M2</i>	0.0117(4)	0.0140(4)	0.0115(4)	0	0	0.0056(4)
<i>O1</i>	0.0210(18)	0.0100(15)	0.0203(17)	0	0	0.0090(14)
<i>O2</i>	0.0097(16)	0.0140(17)	0.0379(22)	0	0	0.0043(14)
<i>O3</i>	0.0488(18)	0.0206(13)	0.0173(12)	0.0052(10)	0.0154(12)	0.0216(13)
<i>X</i>	0.0055(17)	0.0055(17)	0.046(15)	0	0	0.0028(8)

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335 **Table 5** – Selected bond distances (in Å) for johnbaumite.

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<i>M1</i>	O1 (× 3)	2.387(2)	<i>M2</i>	O3 (× 2)	2.335(3)	<i>T</i>	O1	1.662(3)
	O2 (× 3)	2.487(3)		X	2.396(2)		O3 (× 2)	1.670(2)
	O3 (× 3)	2.885(3)		O2	2.400(4)		O2	1.683(3)
				O3 (× 2)	2.520(3)			
				O1	2.857(4)			
	< <i>M1</i> -O>	2.586		< <i>M2</i> -O>	2.480		< <i>T</i> -O>	1.671

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339 **Table 6** – Bond-valence calculations for johnbaumite, in valence unit (*vu*), according to Brese &
 340 O’Keeffe (1991).

341

Site	O1	O2	O3	X	Σ cations
<i>M1</i>	^{3x} 0.32 ^{×2}	^{3x} 0.25 ^{×2}	^{3x} 0.08		1.95
<i>M2</i>	0.09	0.31	^{2x} 0.37 ^{2x} 0.22	0.31 ^{×3}	1.89
<i>T</i>	1.29	1.21	^{2x} 1.27		5.04
Σ anions	2.02	2.02	1.94	0.93	

Note: left and right superscripts indicates the number of bonds involving cations and anions, respectively.

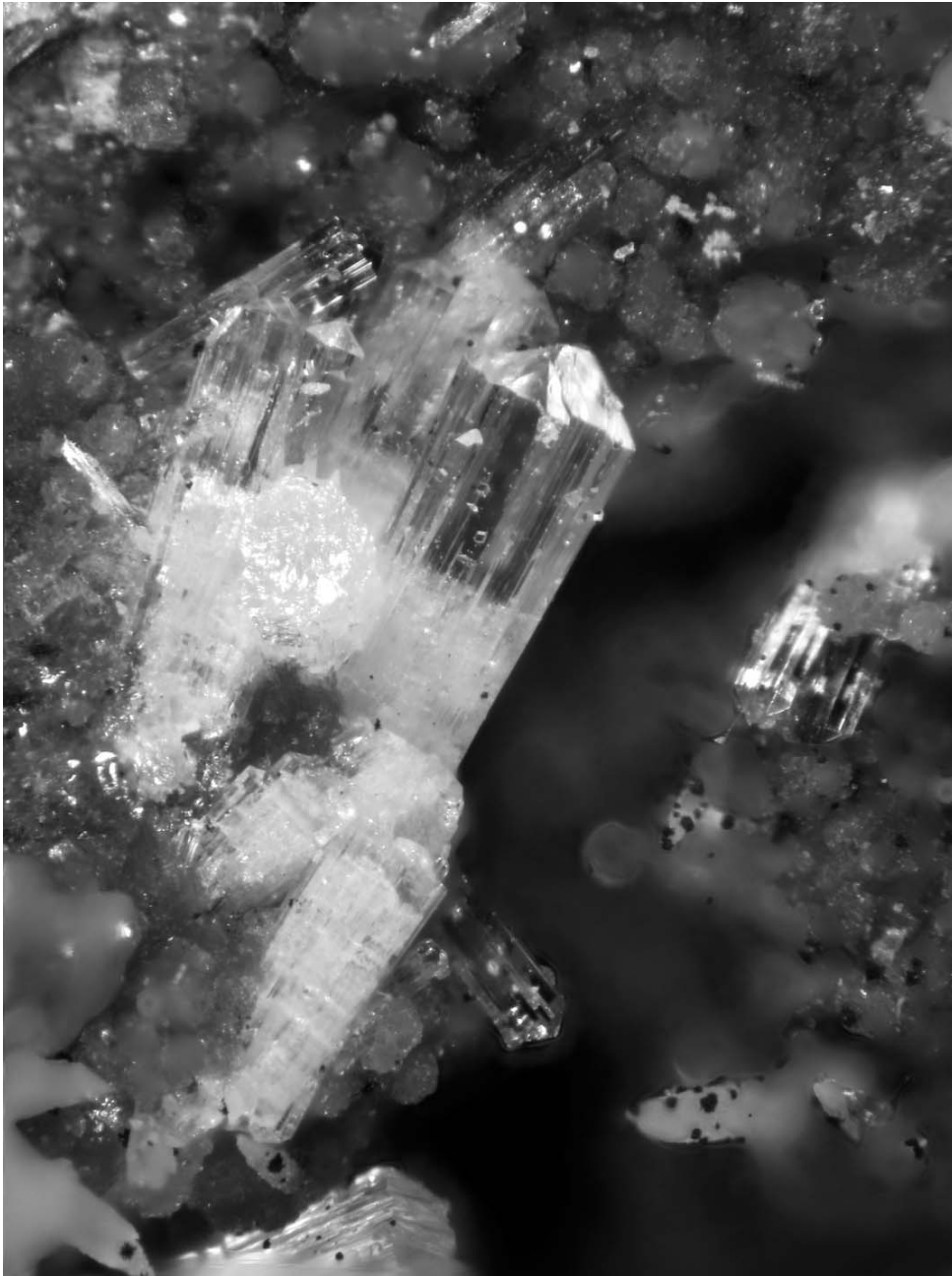
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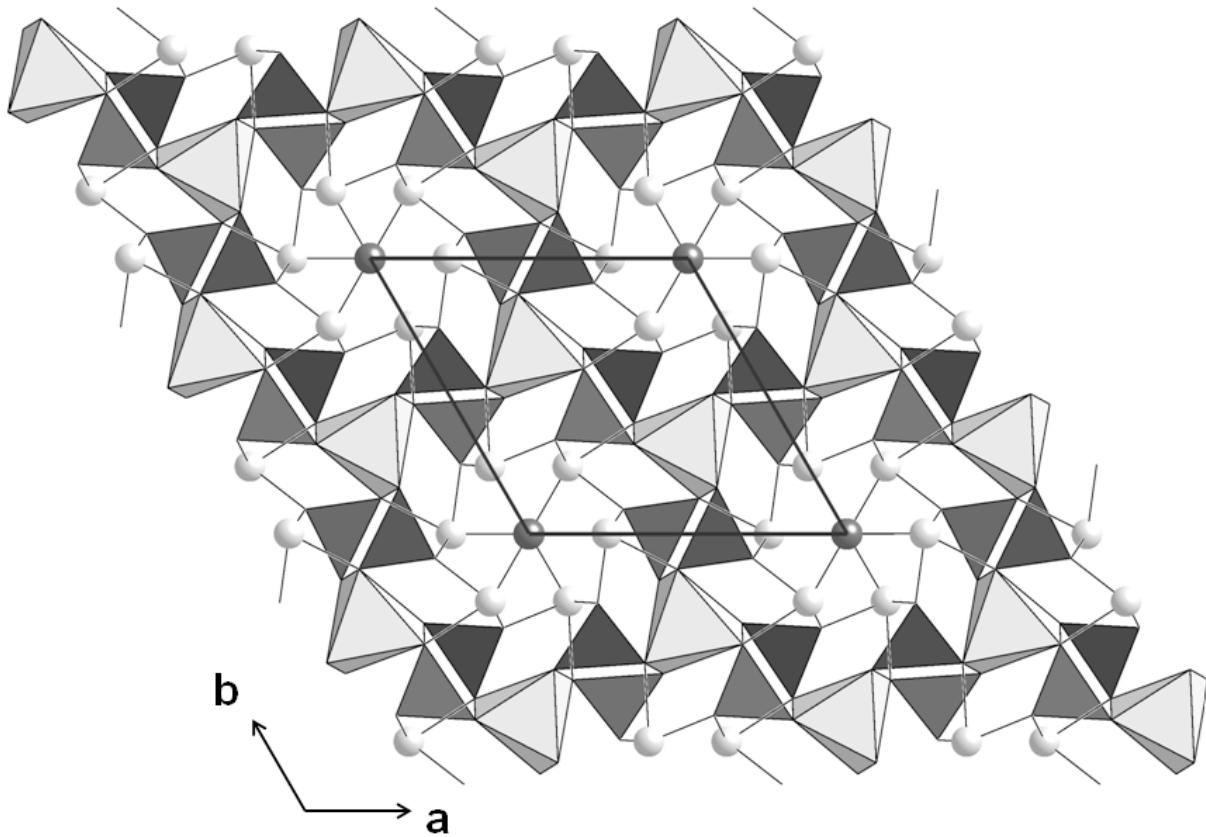
345 **Fig. 1** – Johnbaumite, colorless prismatic crystals up to 1 mm with andradite and caryophyllite.
346 Harstigen mine, Värmland, Sweden. Specimen # 19642, Collection Museo di Storia Naturale e del
347 Territorio, University of Pisa.

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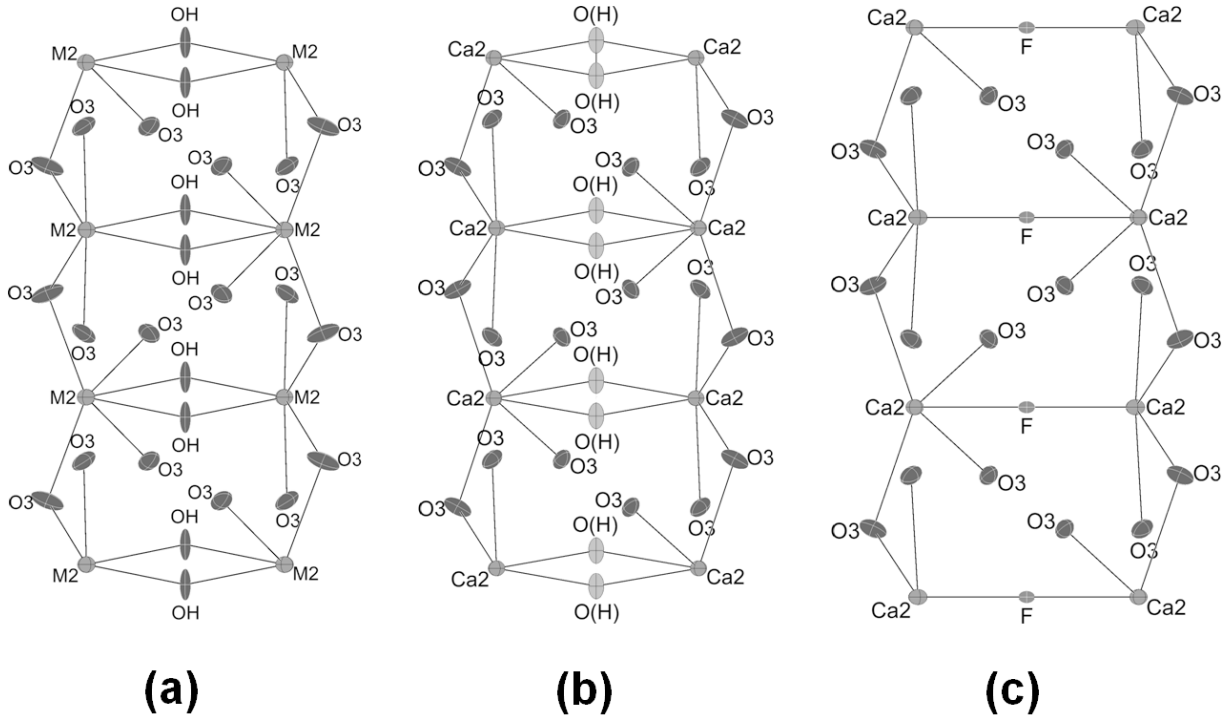
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356 **Fig. 2** – Crystal structure of johnbaumite, as seen down *c*. Polyhedra: *M1* site, light grey; *T* site,
357 dark grey. Spheres: *M2* site, light grey; *X* site, dark grey.

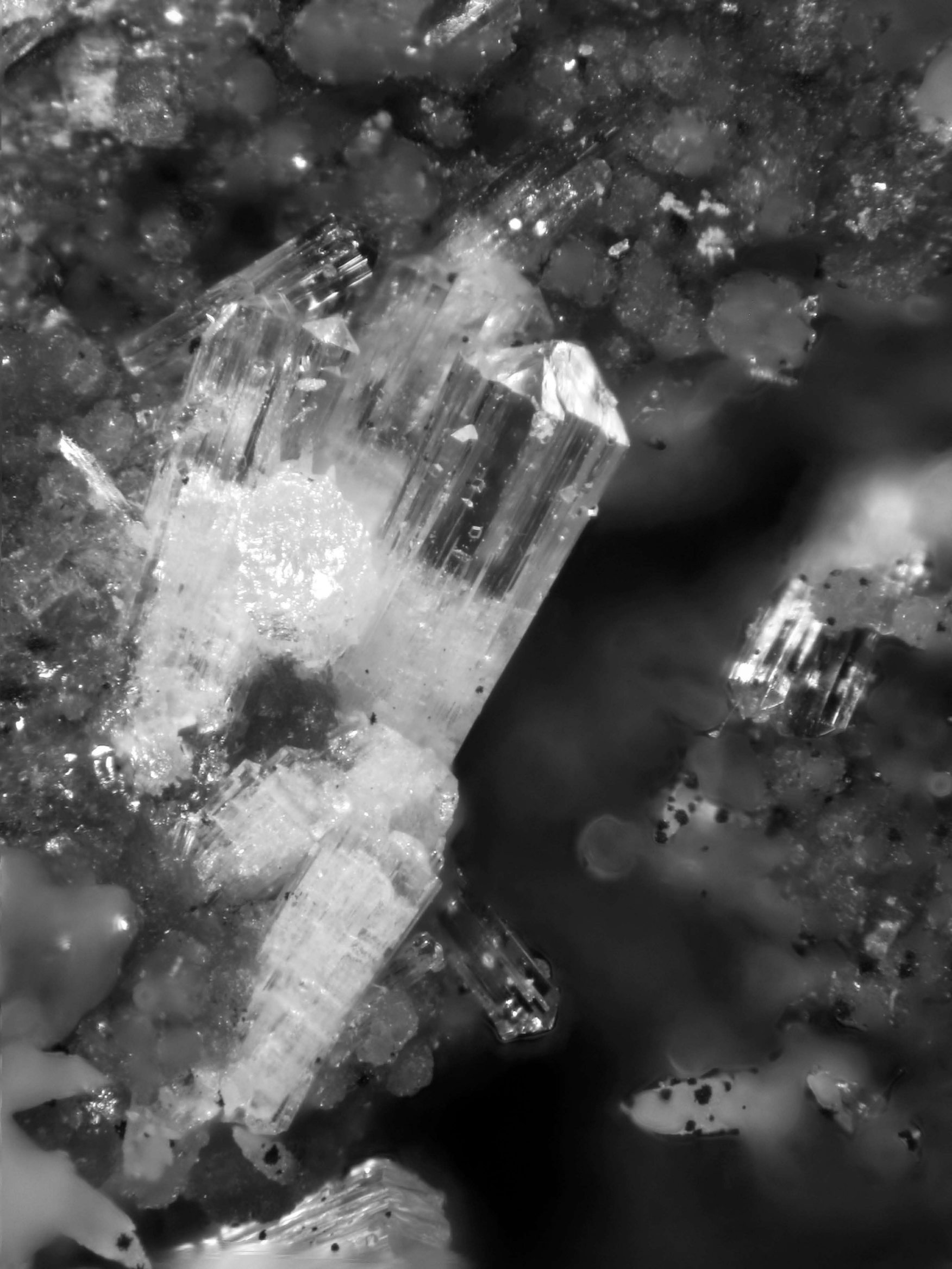


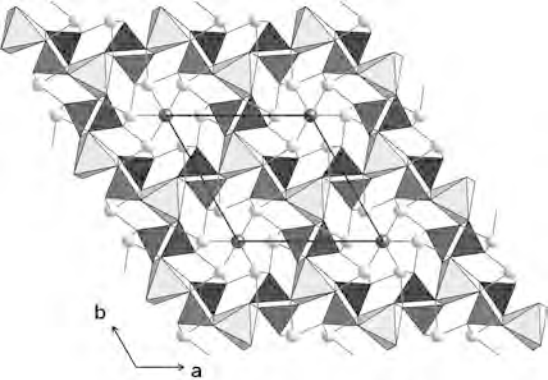
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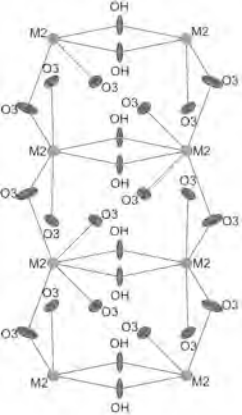
375 **Fig. 3** – Comparison of anion columns in johnbaumite (a), hydroxylapatite (b), and fluorapatite (c),
376 with atoms drawn as displacement ellipsoids, as seen down [010]. Atomic coordinates and
377 anisotropic displacement parameters of fluorapatite and hydroxylapatite were taken from Hughes *et*
378 *al.* (1989).



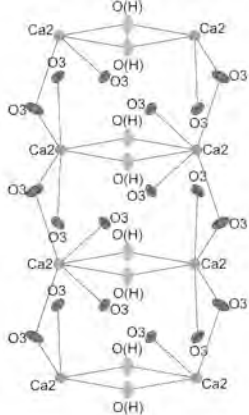
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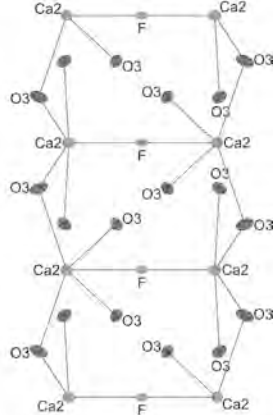




(a)



(b)



(c)