

Revision 1

The crystal structure of svabite, $\text{Ca}_5(\text{AsO}_4)_3\text{F}$, an arsenate member of the apatite supergroup

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ABSTRACT

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19 The crystal structure of svabite, ideally $\text{Ca}_5(\text{AsO}_4)_3\text{F}$, was studied using a specimen from the
 20 Jakobsberg mine, Värmland, Sweden, by means of single-crystal X-ray diffraction data. The
 21 structure was refined to $R_1 = 0.032$ on the basis of 928 unique reflections with $F_o > 4\sigma(F_o)$ in the
 22 $P6_3/m$ space group, with unit-cell parameters $a = 9.7268(5)$, $c = 6.9820(4)$ Å, $V = 572.07(5)$ Å³. The
 23 chemical composition of the sample, determined by electron-microprobe analysis, is (in wt% -
 24 average of 12 spot analyses): SO_3 0.49, P_2O_5 0.21, V_2O_5 0.04, As_2O_5 51.21, SiO_2 0.19, CaO 39.31,
 25 MnO 0.48, SrO 0.03, PbO 5.19, Na_2O 0.13, F 2.12, Cl 0.08, $\text{H}_2\text{O}_{\text{calc}}$ 0.33, O ($\equiv \text{F}+\text{Cl}$) -0.91, total
 26 98.90. On the basis of 13 anions per formula unit, the empirical formula corresponds to
 27 $(\text{Ca}_{4.66}\text{Pb}_{0.16}\text{Mn}_{0.04}\text{Na}_{0.03})_{\Sigma 4.89}(\text{As}_{2.96}\text{S}_{0.04}\text{Si}_{0.02}\text{P}_{0.02})_{\Sigma 3.04}\text{O}_{12}[\text{F}_{0.74}(\text{OH})_{0.24}\text{Cl}_{0.01}]$. Svabite is topologically
 28 similar to the other members of the apatite supergroup: columns of face-sharing $M1$ polyhedra
 29 running along c are connected through TO_4 tetrahedra with channels hosting $M2$ cations and X
 30 anions. The crystal structure of synthetic $\text{Ca}_5(\text{AsO}_4)_3\text{F}$ was previously reported as triclinic. On the
 31 contrary, the present refinement of the crystal structure of svabite shows no deviations from the
 32 hexagonal symmetry. An accurate knowledge of the atomic arrangement of this apatite-remediation
 33 mineral represents an improvement in our understanding of minerals able to sequester and stabilize
 34 heavy metals such as arsenic in polluted areas.

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36 *Key-words:* svabite, calcium arsenate, apatite supergroup, crystal structure, Jakobsberg mine,
 37 Sweden.

38

Introduction

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40 The general formula of the members of the apatite supergroup is ${}^{\text{IX}}M1_2{}^{\text{VII}}M2_3({}^{\text{IV}}\text{TO}_4)_3X$.
41 Svabite is a rare member of the supergroup with $M1 = M2 = \text{Ca}$, $T = \text{As}$, $X = \text{F}$ and ideal formula
42 $\text{Ca}_5(\text{AsO}_4)_3\text{F}$. Historically, svabite was described as the arsenate analogue of “apatite” (Sjögren
43 1891, 1892) at a time when little attention was paid to the nature of the X anion as a discriminant
44 between distinct species. As a consequence, the original description of svabite was based on
45 analyses of samples from two different localities (Harstigen mine, Persberg district, and Jakobsberg
46 mine, Nordmark district) in the Långban mining area, Värmland, Sweden.

47 The analyses were different: the sample from Harstigen was fluorine-free, the sample from
48 Jakobsberg had some 2 wt.% F. According to the current definition of mineral and to the specific
49 guidelines for the nomenclature of apatite supergroup minerals (Pasero et al. 2010), the sample from
50 Harstigen corresponds to johnbaumite, the sample from Jakobsberg to svabite. This
51 notwithstanding, it is Harstigen that has been designated as the type locality for svabite (e.g.,
52 Palache et al. 1951; Gaines et al. 1997), although svabite probably does not occur there.

53 Since then, svabite was reported from very few other localities worldwide. In two cases only
54 chemical analyses are given for the mineral: from Franklin, New Jersey, U.S.A. (Bauer and Berman
55 1930), and from the Solongo boron deposit, Buryatia, Siberia, Russia (Malinko et al. 1966). At both
56 these localities, OH is dominant and therefore the alleged svabite is actually johnbaumite. As a
57 consequence, the unique unequivocal occurrence of svabite is the Jakobsberg mine, based on a wet
58 chemical analysis dating back to the 19th Century and to an electron-microprobe analysis given by
59 Welin (1968). A crystal structure refinement of svabite was never carried out. The only available
60 structural data are for synthetic $\text{Ca}_5(\text{AsO}_4)_3\text{F}$ (Baikie et al. 2007).

61 As understanding the atomic arrangements of As-rich apatite minerals would help to better
62 refine their utility in environmental remediation (Rakovan and Pasteris 2015), we undertook a

63 chemical and crystallographic re-examination of material from the Jakobsberg mine, aiming to
64 confirm the occurrence of svabite at the type locality, and to refine its crystal structure.

65

66

Experimental

67 The studied specimen consists of a fine- to medium-grained mixed hausmannite and jacobsite
68 mineralization in which cm-sized areas of white to pale rose-colored assemblages of fine- to
69 medium-grained svabite and tilasite occur. Associated accessory and minor mineral phases are
70 baryte, dolomite, oxycalcioroméite, berzeliite, and adelite. This specimen was donated together with
71 his large mineral collection by Hjalmar Sjögren to the Swedish Museum of Natural History in 1902.
72 In the catalogue of this donation there exists two specimens from Jakobsberg labeled “svabite” that
73 were recorded as chemically analysed. It seems very likely that the analyses of svabite from
74 Jakobsberg reported by Sjögren in 1892 were obtained on these two samples. The presently studied
75 svabite comes from one of these two specimens (Swedish Museum of Natural History catalogue
76 #HS0255).

77 Electron microprobe analyses were obtained by wavelength dispersive spectroscopy (WDS
78 mode) with a Cameca SX50 instrument at the “Istituto di Geologia Ambientale e Geoingegneria,
79 CNR” of Rome, Italy, using the following analytical conditions: accelerating voltage 15 kV, beam
80 current 15 nA, nominal beam diameter 1 μm . Counting time for one spot analysis was 20 s per
81 peak. Standards (element, emission line) are: baryte ($\text{BaL}\alpha$, $\text{SK}\alpha$), YPO_4 ($\text{PK}\alpha$), GaAs ($\text{AsL}\alpha$),
82 wollastonite ($\text{CaK}\alpha$, $\text{SiK}\alpha$), vanadinite ($\text{VK}\alpha$), rhodonite ($\text{MnK}\alpha$), celestine ($\text{SrK}\alpha$), galena ($\text{PbM}\alpha$),
83 jadeite ($\text{NaK}\alpha$), phlogopite ($\text{FK}\alpha$), and sylvite ($\text{ClK}\alpha$). The PAP routine was applied (Pouchou and
84 Pichoir 1991) for correction of recorded raw data. Twelve spot analyses were performed on five
85 different grains that were found homogeneous. Chemical data are given in Table 1; the chemical
86 formula, based on 13 anions per formula unit, is
87 $(\text{Ca}_{4.66}\text{Pb}_{0.16}\text{Mn}_{0.04}\text{Na}_{0.03})_{\Sigma 4.89}(\text{As}_{2.96}\text{S}_{0.04}\text{Si}_{0.02}\text{P}_{0.02})_{\Sigma 3.04}\text{O}_{12}[\text{F}_{0.74}(\text{OH})_{0.24}\text{Cl}_{0.01}]$.

88 Polarised single-crystal infrared spectra of svabite and johnbaumite (catalogue #19642 of the
89 mineralogical collection of the Museo di Storia Naturale, University of Pisa) were recorded with a
90 Bruker Vertex 70 microscope spectrometer equipped with a halogen lamp source, a KBr beam-
91 splitter, a holographic ZnSe polarizer and a midband MCT detector. The crystals were oriented by
92 morphology and optical microscopy and doubly polished parallel to the **a-c** axis plane. The
93 thickness of the single crystal absorbers were in the range 17 to 46 μm . Polarized absorption spectra
94 were acquired parallel (E||E) and perpendicular (E||O) to the **c**-axis over the wavenumber range
95 600–5000 cm^{-1} with a resolution of 2 cm^{-1} during 32 cycles. In addition, unpolarised spectra of
96 powdered svabite (ca. 1 mg) in pressed KBr discs were recorded under identical conditions in order
97 to monitor the very intense IR-active AsO_4 -modes in the range 700–1000 cm^{-1} . The spectral region
98 of the O–H stretching bands of the recorded single-crystal spectra were fitted using the *PeakFit* 4.12
99 software (Jandel) assuming Gaussian peak shapes.

100 A crystal fragment ($230 \times 80 \times 50 \mu\text{m}^3$ in size) was selected for single-crystal X-ray
101 diffraction. Intensities were collected using a Bruker Smart Breeze diffractometer (50 kV, 30 mA)
102 equipped with a CCD 4k low-noise area detector. Graphite-monochromatized $\text{MoK}\alpha$ radiation was
103 used. The detector-to-crystal working distance was 50 mm. 3035 frames were collected in ω and ϕ
104 scan modes in 0.5° slices; the exposure time was 20 s per frame. The data were integrated and
105 corrected for Lorentz and polarization, background effects, and absorption using the package of
106 softwares *Apex2* (Bruker AXS Inc. 2004), resulting in a set of 1008 independent reflections. The
107 refinement of unit-cell parameters constrained to hexagonal symmetry gave $a = 9.7268(5)$, $c =$
108 $6.9820(4) \text{ \AA}$, $V = 572.07(5) \text{ \AA}^3$. The statistical tests on the distribution of $|E|$ values ($|E^2 - 1| =$
109 0.966) and the systematic absences suggested the space group $P6_3/m$.

110 The crystal structure was refined starting from the atomic coordinates of johnbaumite given
111 by Biagioni and Pasero (2013) using *Shelxl-97* (Sheldrick 2008). Scattering curves from neutral
112 atoms were taken from the International Tables for Crystallography (Wilson 1992). The

113 occupancies of the three cation and four anion sites were initially refined using the following
114 scattering curves: Ca at the *M1* and *M2* sites; As at the *T* site; O at the O1, O2, O3 sites; and F at the
115 *X* site. Owing to the different nature of the anion species at the latter site with respect to
116 johnbaumite, its position was found through difference-Fourier map and located at (0, 0, ¼). After a
117 few cycles of isotropic refinement R_1 converged to 0.071, confirming the correctness of the
118 structural model. The relatively low value of the displacement parameter at the *M2* site suggested
119 the partial replacement of Ca by a heavier element, i.e. Pb. Consequently, the site occupancy at the
120 *M2* site was refined, improving the refinement to $R_1 = 0.056$. After the introduction of the
121 anisotropic displacement parameters for cations, the R_1 converged to 0.049. Assuming an
122 anisotropic model also for the anions, the R_1 value converged to 0.032. However, the U^{33} value for
123 the column anion *X* was high [0.119(7) Å²], suggesting structural disorder and possibly masking the
124 positions of other column anion sites partially occupied. Consequently, the displacement parameter
125 of the *X* anion was refined isotropically; the refinement converged to $R_1 = 0.037$ and the highest
126 residual peak was at 0.47 Å from the *X* site, at (0, 0, 0.19). This new anion position, named *Xb*, was
127 added; the sum of the site occupation factors (s.o.f.) of *X* and *Xb* was constrained to 1 atom per
128 formula unit (apfu) and their displacement parameters were forced to be equal. Owing to the similar
129 scattering factors of oxygen and fluorine, these two elements were partitioned on the basis of the
130 refined scattering at *X* and *Xb*, assuming the F-to-OH ratio obtained through electron-microprobe
131 data, i.e. 0.75:0.25. The *X* position at (0, 0, ¼) was assigned to F, whereas the *Xb* position was
132 considered as a mixed (F,OH) site. The refinement converged to $R_1 = 0.0323$ for 928 unique
133 reflections with $F_o > 4 \sigma(F_o)$ (0.0364 for all 1008 reflections). The structural formula derived from
134 the structure refinement (SREF) of the studied crystal is (Ca_{4.84}Pb_{0.16})(AsO₄)₃(F_{0.75}OH_{0.25}), in fairly
135 good agreement with the chemical data. Details of data collection and refinement are given in Table
136 2.

137

Crystal structure description

138

139 **General features and cation coordination**

140 Atomic coordinates, site occupancies, and isotropic or equivalent isotropic displacement
141 parameters are reported in Table 3, and Table 4 gives anisotropic displacement parameters. Table 5
142 reports selected bond distances, and Table 6 shows the results of the bond-valence calculations. The
143 bond-parameters given by Krivovichev (2012) are used for the pair $\text{Pb}^{2+}\text{-O}$, whereas for the other
144 cation-anion pairs the bond-parameters are those proposed by Brese and O'Keeffe (1991).

145 The crystal structure of svabite is topologically similar to those of the other members of the
146 apatite supergroup. It is composed by columns of face-sharing *M1*-centered polyhedra running
147 along *c*; those polyhedra can be described as tricapped trigonal prisms. Adjacent columns are
148 connected by TO_4 tetrahedra through corner-sharing. Whereas the *M1* site is a virtually Ca pure site
149 (a very small substitution of Na may occur, in agreement with electron-microprobe data), the *M2*
150 site is a mixed (Ca,Pb) site, in agreement with the preference of Pb to be hosted at this position (e.g.
151 Lim et al. 2011). Average bond distances at these Ca-hosting sites are 2.586 and 2.485 Å for the *M1*
152 and *M2* sites, respectively. These data can be compared with analogous distances in the phosphate
153 analogue of svabite, fluorapatite, showing average distances at *M1* and *M2* of 2.554 and 2.463 Å
154 (Hughes et al. 1989), respectively. Similarly, one can compare these distances with those reported
155 in natural johnbaumite by Henderson et al. (2009), i.e. 2.62 and 2.45 Å, and by Biagioni and Pasero
156 (2013), i.e. 2.586 and 2.480 Å. The *T* site is occupied by As, with negligible substitutions of S^{6+} ,
157 Si^{4+} , and P^{5+} . The average $\langle T\text{-O} \rangle$ distance is 1.674 Å, similar to the bond distance observed in
158 johnbaumite from Harstigen (1.671 Å; Biagioni and Pasero 2013) and little shorter than that
159 reported for johnbaumite from Franklin (1.70 Å) studied by Henderson et al. (2009).

160 **The anion columns**

161 Neglecting the low Cl content, the studied specimen of svabite can be defined as a member in
162 the binary series between the endmember compositions of johnbaumite, ideally $\text{Ca}_5(\text{AsO}_4)_3\text{OH}$, and
163 svabite, $\text{Ca}_5(\text{AsO}_4)_3\text{F}$ containing about 25 mol% johnbaumite in solid solution.

164 As demonstrated by Hughes et al. (1989), the anion position in binary and ternary (F-OH-Cl)
165 apatites cannot be predicted from their positions in the endmembers. The crystal structure
166 refinement shows two anion sites in the [001] anion columns, one at $(0, 0, \frac{1}{4})$ and the other at $(0, 0,$
167 $0.19)$. The former is located in the $M2$ triangle within the mirror plane; it was assumed that this
168 position is occupied by fluorine. The latter is displaced 0.39 \AA above or below this plane, a position
169 similar to that of the hydroxyl group in hydroxylapatite (Hughes et al. 1989) and johnbaumite
170 (Biagioni and Pasero 2013); taking into account the electron microprobe data, a mixed (F,OH)
171 occupancy at this position is suggested. The occurrence of F sites displaced from the mirror plane in
172 anion columns has been reported by other authors, e.g. in synthetic F-Cl apatite (Hughes et al.
173 2014).

174 The split sites are actually inserted to model an electron density which is continuously
175 distributed around the mirror plane and that is constrained by the necessity of avoiding too short
176 anion–anion distances. Taking into account the refined anion positions, the only pair to be avoided
177 is the Xb_a and Xb_b , where the italic subscripts a and b correspond to *above* and *below* the mirror
178 plane; such a pair has a distance of only ca. 2.70 \AA . Other pairs have anion–anion distances ranging
179 from $3.10 (X-Xb_b)$ up to $3.88 \text{ \AA} (X-Xb_a)$. A third possible anion–anion distance is represented by
180 half of the c periodicity, 3.49 \AA .

181 Bond-valence sums (BVS, in valence units, v.u.) calculated for the X anions, reported in Table
182 6, show their underbonding. The sum of the BVS at the X and Xb positions is 0.78 v.u. ; this
183 underbonding is probably related to the disorder in the actual position of the column anions, and
184 agrees with the BVS calculated by Hughes et al. (1989) for F in pure fluorapatite (i.e. 0.84 v.u.).

185

Discussion

186

187 Triclinic vs hexagonal symmetry in svabite

188 The prototype structure of the phases belonging to the apatite supergroup is hexagonal
189 ($P6_3/m$); however, ordering and/or distortions can reduce the symmetry. As stated above, Baikie et
190 al. (2007), combining diffraction data and *ab initio* calculations, obtained the $P\bar{1}$ symmetry for
191 synthetic $\text{Ca}_5(\text{AsO}_4)_3\text{F}$. The lowering of symmetry could be due to a distortion of the unit cell
192 required when the $M1_4(\text{TO}_4)_6$ framework is expanded with respect to the $M2_6X_2$ column contents, as
193 a consequence of the As-to-P substitution.

194 Being aware of such a potential reduction of symmetry for svabite, a refinement in space
195 group $P\bar{1}$ starting from the atomic positions given by Baikie et al. (2007) was performed. The
196 refined triclinic unit-cell parameters of svabite are $a = 9.7277(5)$, $b = 9.7276(6)$, $c = 6.9814(4)$ Å, α
197 $= 90.184(3)$, $\beta = 89.931(3)$, $\gamma = 120.002(2)^\circ$, as compared to the unit cell of synthetic $\text{Ca}_5(\text{AsO}_4)_3\text{F}$
198 given by Baikie et al. (2007): $a = 9.6841(5)$, $b = 9.6906(5)$, $c = 6.9815(3)$ Å, $\alpha = 90.623(3)$, $\beta =$
199 $88.869(3)$, $\gamma = 120.371(3)^\circ$.

200 The refinement converged to $R_1 = 0.028$ for 11695 reflections with $F_o > 4 \sigma(F_o)$ (0.0374 for
201 all 14179 reflections). The structural formula derived from SREF is
202 $(\text{Ca}_{4.84}\text{Pb}_{0.16})(\text{AsO}_4)_3(\text{F}_{0.75}\text{OH}_{0.25})$. The $(\text{Ca}:\text{Pb})_{\text{at}}$ ratio is the same obtained for the hexagonal model.
203 The three independent T sites have the same average bond lengths, i.e. 1.672(2), 1.671(2), and
204 1.672(2) Å. The same occurs for the M sites showing indistinguishable average bond distances
205 within the experimental errors. In addition, the three mixed (Ca,Pb) sites have the same refined
206 $(\text{Ca}:\text{Pb})_{\text{at}}$ ratios. Consequently there is no convincing evidence for a lowering of symmetry in the
207 studied sample of svabite. Even if the final R_1 value is better than for the $P6_3/m$ structure (likely as a
208 consequence of the larger degree of freedom of the triclinic refinement), the crystal structure is

209 actually hexagonal; as a confirmation, the Hamilton test (Hamilton 1964, 1965) indicates that the
210 correctness of the hexagonal model can be assumed at a confidence level > 99.5%.

211 **The metaprism twist angle φ**

212 A parameter used for the assessment of the distortion of the apatite structure from an ideal
213 hexagonal close packing of oxygen is the metaprism twist angle φ , defined as the angle O1–M1–O2
214 projected on (001) (White and Dong 2003; Lim et al. 2011). The transition to lower symmetry is
215 promoted by larger twist angle values. The twist angle φ in svabite, calculated according to the
216 formula proposed by Henderson et al. (2009), is 21.5°, similar to that found in johnbaumite
217 (Biagioni and Pasero 2013), i.e. 21.1°. White and Dong (2003) and White et al. (2005) pointed out
218 that the twist angle tends to decrease like the unit-cell volume and in fact the studied crystal of
219 svabite has an unit-cell volume larger than that of johnbaumite studied by Biagioni and Pasero
220 (2013), i.e. 572.1 Å³ to be compared with 570.4 Å³, notwithstanding the slightly larger size of the
221 hydroxyl group (OH)⁻ with respect to F⁻. The svabite studied contains ca. 0.15 Pb apfu that could
222 explain the increase of the unit-cell volume. Taking into account the crystal structures of
223 fluorapatite and hydroxylapatite (Hughes et al. 1989), the corresponding twist angles are 23.2 and
224 23.1°, respectively. The values calculated for the corresponding calcium arsenate studied in this
225 work and by Biagioni and Pasero (2013) are smaller, in agreement with the substitution of P⁵⁺ by
226 the larger cation As⁵⁺. On the contrary, the twist angles obtained by Lee et al. (2009) for synthetic
227 Ca₅(AsO₄)₃(OH) and Henderson et al. (2009) for johnbaumite from Franklin are close to that of the
228 P-analogue, i.e. 23.5°. These authors did not find any evidence of deviation from an hexagonal
229 symmetry in their samples, even if in the Ca₅(P_{1-x}As_xO₄)₃(OH) series, the twist angle anomalously
230 decreased (Lee et al. 2009); according to Lim et al. (2011) this could suggest a change of symmetry
231 for the OH-endmember.

232 **Infrared spectroscopy of svabite and comparison with johnbaumite from Harstigen**

233 The recorded FTIR spectra of svabite and johnbaumite show large similarities (Fig. 1)
234 displaying strong absorption bands related to vibrational modes in AsO_4 -tetrahedra in the range
235 $750\text{--}950\text{ cm}^{-1}$ and distinct absorption related to O–H stretching modes in the range $3450\text{--}3600\text{ cm}^{-1}$.
236 In detail, however, the integrated intensity of the O–H stretching bands in the spectra of svabite is
237 merely 34% of that recorded in spectra of the johnbaumite reference crystals (Fig. 1). This
238 observation is in good agreement with the analytical data on the johnbaumite reference material
239 (Biagioni and Pasero 2013) and the present svabite indicating a $\text{OH}_{\text{svabite}}/\text{OH}_{\text{johnbaumite}}$ ratio of 0.25.
240 The positions of the OH-bands are almost identical in spectra of the two minerals: 3496, 3526 and
241 3560 cm^{-1} in svabite spectra and at 3498, 3528 and 3559 cm^{-1} in the johnbaumite spectra. Based on
242 the correlation between energies of O–H stretching bands and hydrogen bonds in minerals
243 (Libowitzky 1999) the O \cdots H distances in the two minerals are expected to be in the range 2.04–2.17
244 Å. Using the IR method for determining OH concentration in apatite (Wang et al. 2011), H_2O
245 contents in the present svabite and johnbaumite samples are calculated as 0.17 and 0.50 wt%,
246 respectively. These calculated H_2O concentrations are approximately one half that determined by
247 structure refinement. A likely cause for this difference may be that the molar absorption coefficients
248 ϵ for O–H stretching bands in spectra of the arsenates of the apatite supergroup are lower than for
249 corresponding bands in spectra of the phosphates belonging to this supergroup. Consequently,
250 application of calibration based on spectra of hydroxylapatite will result in underestimation of H_2O
251 concentrations in arsenate minerals, e.g. johnbaumite and svabite. Absorption bands related to
252 vibrational modes in AsO_4 occur at 838, 853 and 877 cm^{-1} in the svabite spectrum (Fig. 1).

253 **Svabite at the Jakobsberg mine**

254 Sjögren (1891) described the new mineral svabite from the Harstigen mine; one year later, the
255 same author reported the occurrence of this mineral both at Harstigen and at the Jakobsberg mine
256 (Sjögren 1892). As stressed by Biagioni and Pasero (2013), the chemical analyses of samples from
257 these two localities are not homogenous, showing different F/OH ratios. Indeed, the sample from

258 Harstigen is OH-dominant, corresponding to johnbaumite. Only the sample from Jakobsberg is F-
259 dominant and corresponds to svabite in its current definition (Pasero et al. 2010).

260 Wet chemical data given by Sjögren (1892), as well as electron-microprobe analysis reported
261 by Welin (1968), agree with the chemistry of svabite reported in the present study. Calcium is
262 partially replaced by Pb and by minor amounts of Mn and Na; arsenic is substituted by minor
263 amounts of S, Si, and P. The occurrence of Na^+ , S^{6+} , and Si^{4+} in the crystal structure of svabite can
264 be interpreted as the result of two possible substitutions, i.e. i) $\text{Ca}^{2+} + \text{As}^{5+} \leftrightarrow \text{Na}^+ + \text{S}^{6+}$, and ii)
265 $2\text{As}^{5+} \leftrightarrow \text{Si}^{4+} + \text{S}^{6+}$. The former substitution could be related to the occurrence of a cesanite
266 component in svabite whereas the latter could be related to the presence of an ellestadite
267 component.

268 The Jakobsberg mine represents an exceptional locality for the study of the crystal chemistry
269 of arsenate apatites. Indeed, five different species belonging to the apatite supergroup are reported
270 from this mine, i.e. hedyphane, johnbaumite, mimetite, morelandite, and svabite, the two latter
271 species having Jakobsberg as their type locality. As the occurrence of svabite at the Jakobsberg
272 mine is in keeping with the original description of Sjögren (1891, 1892) who did not distinguish
273 between OH-dominant and F-dominant calcium arsenate, we suggest that the type locality of
274 svabite should be considered Jakobsberg and not Harstigen.

275

276

Implications

277 Calcium arsenate apatites are actively studied owing to their potential role as sequestrators
278 and stabilizers of As from polluted waters, an environmental problem occurring in several areas,
279 e.g. in south-eastern Asia (e.g., Charlet and Polya 2006). Therefore, an accurate knowledge of the
280 crystal chemistry of these As-rich compounds is crucial for environment remediation (Rakovan and
281 Pasteris 2015). Whereas several high-quality single-crystal structure refinements have been reported
282 for calcium phosphate apatites (e.g. White et al. 2005), few data are available for the corresponding

283 As-analogues. Single-crystal X-ray diffraction studies have been performed by Wardojo and Hwu
284 (1996) on synthetic $\text{Ca}_5(\text{AsO}_4)_3\text{Cl}$ and Biagioni and Pasero (2013) on johnbaumite. The results of
285 the X-ray single-crystal study of the three natural calcium arsenate apatites were presented by Dai
286 and Harlow (1991) in a conference abstract, but to our knowledge the details of this work have not
287 been published.

288 The refinement of the crystal structure of svabite using single-crystal X-ray diffraction data
289 represents a new step in the knowledge of the crystal chemistry of calcium arsenate apatites. Svabite
290 displays the same features of the other members of the apatite group, with $P6_3/m$ symmetry. No
291 deviation from the ideal hexagonal symmetry was observed, in contrast to the findings of Baikie et
292 al. (2007).

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294

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298

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373

374 **Table captions**

375 **Table 1** – Electron-microprobe data (mean of 10 spot analysis, in wt%) of svabite and atoms per
376 formula unit (*apfu*), on the basis of 13 anions.

377 **Table 2** – Crystal data and summary of parameters describing data collection and refinement for
378 svabite.

379 **Table 3** – Site occupancies, atomic coordinates, and isotropic (*) or equivalent isotropic
380 displacement parameters (in \AA^2) for svabite. $U_{\text{eq/iso}}$ is defined as one third of the trace of the
381 orthogonalized U_{ij} tensor.

382 **Table 4** – Anisotropic displacement parameters (in \AA^2) for svabite.

383 **Table 5** – Selected bond distances (in \AA) for svabite.

384 **Table 6** – Bond-valence calculations for svabite, in valence unit (v.u.).

385

386 **Figure captions**

387 **Fig. 1** – Infrared spectra of svabite and johnbaumite from Harstigen. (a) Polarised single-crystal IR-
388 spectra of svabite and johnbaumite; (b) polarised single-crystal IR-spectra of svabite and
389 johnbaumite in the OH stretching region; (c) unpolarised IR-spectrum of powdered svabite in a
390 pressed KBr disc.

391 **Table 1** – Electron-microprobe data (mean of 10 spot analysis, in wt%) of svabite and atoms per
 392 formula unit (*apfu*), on the basis of 13 anions.

Oxide	wt%	range	e.s.d.
SO ₃	0.49	0.41 – 0.57	0.05
As ₂ O ₅	51.21	50.63 – 51.93	0.38
P ₂ O ₅	0.21	0.15 – 0.25	0.03
V ₂ O ₅	0.04	0.00 – 0.10	0.03
SiO ₂	0.19	0.10 – 0.25	0.04
CaO	39.31	38.79 – 39.87	0.28
MnO	0.48	0.43 – 0.55	0.04
SrO	0.03	0.00 – 0.07	0.02
BaO	0.01	0.00 – 0.04	0.01
PbO	5.19	4.90 – 5.36	0.15
Na ₂ O	0.13	0.09 – 0.16	0.02
F	2.12	1.72 – 2.49	0.22
Cl	0.08	0.06 – 0.13	0.02
H ₂ O*	0.33	0.15 – 0.52	0.11
O = (F+Cl)	-0.91		
Total	98.90	98.28 – 100.30	0.55
Element	apfu	range	e.s.d.
S ⁶⁺	0.041	0.035 – 0.048	0.004
As ⁵⁺	2.962	2.942 – 2.981	0.010
P ⁵⁺	0.019	0.014 – 0.023	0.003
V ⁵⁺	0.003	0.000 – 0.007	0.002
Si ⁴⁺	0.021	0.011 – 0.027	0.004
Ca ²⁺	4.660	4.631 – 4.697	0.024
Mn ²⁺	0.045	0.040 – 0.052	0.004
Sr ²⁺	0.002	0.000 – 0.005	0.002
Ba ²⁺	0.000	0.000 – 0.002	0.001
Pb ²⁺	0.155	0.146 – 0.160	0.004
Na ⁺	0.029	0.020 – 0.035	0.004
F ⁻	0.743	0.600 – 0.875	0.078
OH ⁻	0.243	0.110 – 0.383	0.079
Cl ⁻	0.014	0.010 – 0.025	0.004

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

394

395 **Table 2** – Crystal data and summary of parameters describing data collection and refinement for
 396 svabite.

397

Crystal data	
Structural formula	(Ca _{4.84} Pb _{0.16})(AsO ₄) ₃ [F _{0.75} (OH) _{0.25}]
Crystal size (mm)	0.23 x 0.08 x 0.05
Cell setting, space group	Hexagonal, <i>P6₃/m</i>
<i>a</i> , <i>c</i> (Å)	9.7268(5), 6.9820(4)
<i>V</i> (Å ³)	572.07(5)
<i>Z</i>	2
Data collection and refinement	
Radiation, wavelength (Å)	MoKα, 0.71073
Temperature (K)	298
Detector-to-sample distance (mm)	50
Number of frames	3035
Rotation width per frame (°)	0.5
Maximum observed 2θ (°)	73.70
Measured reflections	14160
Unique reflections	1008
Reflections $F_o > 4\sigma(F_o)$	928
R_{int} after absorption correction	0.0539
R_σ	0.0266
	-16 ≤ <i>h</i> ≤ 15
Range of <i>h</i> , <i>k</i> , <i>l</i>	-16 ≤ <i>k</i> ≤ 15
	-11 ≤ <i>l</i> ≤ 10
$R_1 [F_o > 4\sigma(F_o)]$	0.0323
R_1 (all data)	0.0364
wR_2 (on F^2_o)	0.0706
Goof	1.158
Number of l.s. parameters	40
Maximum and minimum residual	1.18 (at 0.74 Å from <i>T</i>) -1.03 (at 1.64 Å from O1)

398
 399

400 **Table 3** – Site occupancies, atomic coordinates, and isotropic (*) or equivalent isotropic
 401 displacement parameters (in Å²) for svabite. $U_{\text{eq/iso}}$ is defined as one third of the trace of the
 402 orthogonalized U_{ij} tensor.

Site	Occupancy	x/a	y/b	z/c	$U_{\text{eq/iso}}$
<i>T</i>	As _{1.00}	0.39945(5)	0.37179(5)	¼	0.0100(1)
<i>M1</i>	Ca _{1.00}	2/3	1/3	-0.0029(2)	0.0149(2)
<i>M2</i>	Ca _{0.95(1)} Pb _{0.05(1)}	0.2436(1)	0.9990(1)	¼	0.0139(2)
<i>O1</i>	O _{1.00}	0.3245(4)	0.4933(4)	¼	0.0178(6)
<i>O2</i>	O _{1.00}	0.5990(4)	0.4702(4)	¼	0.0212(7)
<i>O3</i>	O _{1.00}	0.3415(4)	0.2521(3)	0.4412(4)	0.0280(6)
<i>X</i>	F _{0.45}	0	0	¼	0.0207(14)*
<i>Xb</i>	F _{0.30} (OH) _{0.25}	0	0	0.195(2)	0.0207(14)*

403

404

405 **Table 4** – Anisotropic displacement parameters (in Å²) for svabite.

Site	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
<i>T</i>	0.0106(2)	0.0097(2)	0.0103(2)	0	0	0.0056(2)
<i>M1</i>	0.0183(2)	0.0183(2)	0.0082(4)	0	0	0.0092(1)
<i>M2</i>	0.0158(3)	0.0140(3)	0.0118(3)	0	0	0.0074(2)
<i>O1</i>	0.0258(15)	0.0161(13)	0.0172(14)	0	0	0.0148(12)
<i>O2</i>	0.0115(12)	0.0141(13)	0.0364(20)	0	0	0.0053(10)
<i>O3</i>	0.0504(16)	0.0263(12)	0.0173(11)	0.0094(10)	0.0164(11)	0.0268(12)

406

407 **Table 5** – Selected bond distances (in Å) for svabite.

408

<i>M1</i>	O1 (× 3)	2.384(2)	<i>M2</i>	O3 (× 2)	2.338(3)	<i>T</i>	O1	1.670(3)
	O2 (× 3)	2.490(2)		X	2.374(1)		O3 (× 2)	1.673(2)
	O3 (× 3)	2.883(3)		X _b	2.405(2)		O2	1.681(3)
				O2	2.415(3)			
				O3 (× 2)	2.531(3)			
				O1	2.853(4)			
	<M1-O>	2.586		<M2-O>	2.485		<T-O>	1.674

409

410

411 **Table 6** – Bond-valence calculations for svabite, in valence unit (v.u.).

Site	O1	O2	O3	X	Xb	Σ cations
<i>M1</i>	^{3x} 0.32 ^{x2}	^{3x} 0.24 ^{x2}	^{3x} 0.08			1.92
<i>M2</i>	0.09	0.30	^{2x} 0.37 ^{2x} 0.22	0.11 ^{x3}	0.15 ^{x3}	1.83
<i>T</i>	1.30	1.26	^{2x} 1.29			5.14
Σ anions	2.03	2.04	1.96	0.33	0.45	

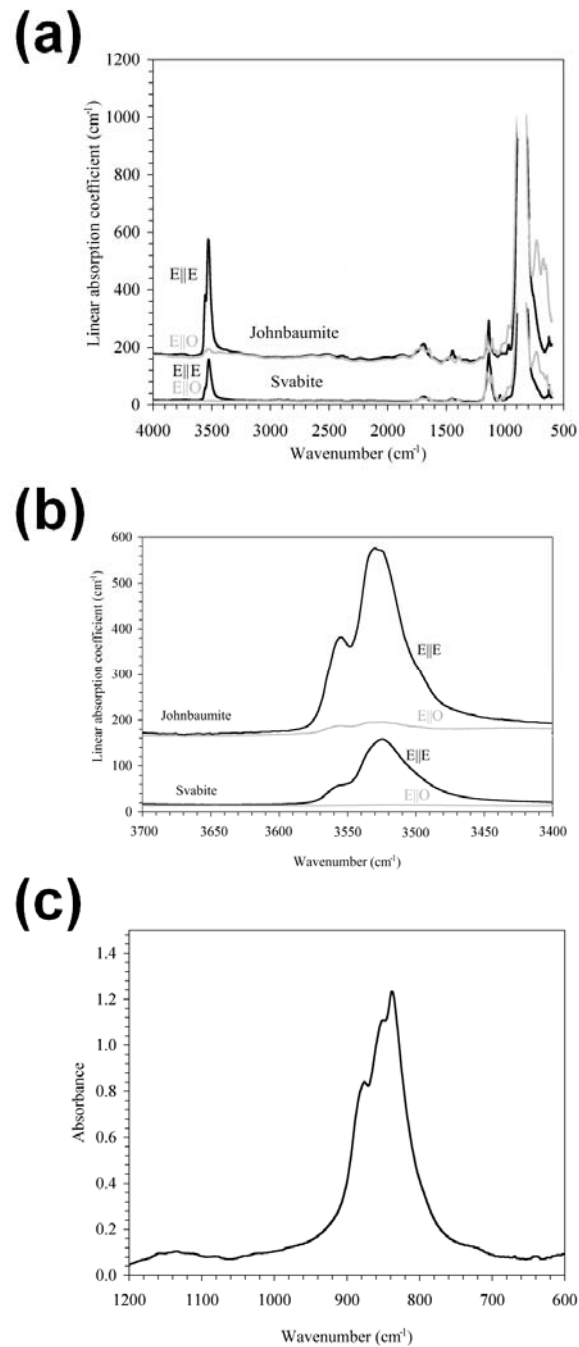
Note: left and right superscripts indicates the number of equivalent bonds involving cations and anions, respectively.

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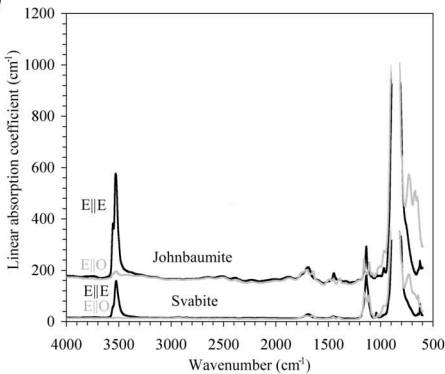
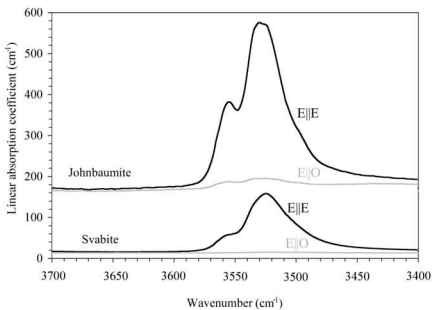
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416 spectra of svabite and johnbaumite; (b) polarised single-crystal IR-spectra of svabite and
417 johnbaumite in the OH stretching region; (c) unpolarised IR-spectrum of powdered svabite in a
418 pressed KBr disc.



419

(a)**(b)****(c)**