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**Bulachite, [Al 6 (AsO 4) 3 (OH) 9 (H 2 O) 4]·2H 2 O
from Cap Garonne, France: Crystal structure and
formation from a higher hydrate**

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1 **Bulachite, $[\text{Al}_6(\text{AsO}_4)_3(\text{OH})_9(\text{H}_2\text{O})_4]\cdot 2\text{H}_2\text{O}$ from Cap Garonne, France: Crystal**
2 **structure and formation from a higher hydrate .**

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10

11 **Abstract**

12 Bulachite specimens from Cap Garonne, France, comprise two intimately mixed hydrated
13 aluminium arsenate minerals with the same Al:As ratio of 2:1 and with different water contents.

14 The crystal structures of both minerals have been solved using data from low-dose electron
15 diffraction tomography combined with synchrotron powder X-ray diffraction. One of the

16 minerals has the same PXRD pattern as for published bulachite. It has orthorhombic symmetry,

17 space group *Pnma* with unit cell parameters $a = 15.3994(3)$, $b = 17.6598(3)$, $c = 7.8083(1)$ Å

18 and $Z = 4$, with the formula $[\text{Al}_6(\text{AsO}_4)_3(\text{OH})_9(\text{H}_2\text{O})_4]\cdot 2\text{H}_2\text{O}$. The second mineral is a higher

19 hydrate with composition $[\text{Al}_6(\text{AsO}_4)_3(\text{OH})_9(\text{H}_2\text{O})_4]\cdot 8\text{H}_2\text{O}$. It has the same *Pnma* space group

20 and unit cell parameters $a = 19.849(2)$, $b = 17.6903(4)$ and $c = 7.7788(3)$ Å. i.e. almost the

21 same b and c parameters but a much larger a parameter. The structures are based on polyhedral

22 layers, parallel to (100), of composition $[\text{Al}_6(\text{AsO}_4)_3(\text{OH})_9(\text{H}_2\text{O})_4]$ and with H-bonded H_2O

23 between the layers. The layers contain [001] spiral chains of edge-shared octahedra, decorated

24 with corner connected AsO_4 tetrahedra that are the same as in the mineral liskeardite. The spiral

25 chains are joined together by octahedral edge-sharing to form layers parallel to (100).

26 Synchrotron PXRD patterns collected at different temperatures during heating of the specimen

27 show that the higher-hydrate mineral starts transforming to bulachite when heated to 50°C, and

28 the transformation is complete between 75 and 100°C.

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30

31 **Introduction**

32 Bulachite, from Neubulach, northern Black Forest, Germany was first described by Walenta
33 (1983). It occurs as aggregates of fine white needles encrusting quartz and associated with
34 arsenocrandallite, malachite, bariopharmacosiderite and goethite. Walenta provided results
35 from chemical and thermogravimetric analyses and powder X-ray diffraction (PXRD), that
36 established the ideal composition as $\text{Al}_2(\text{AsO}_4)(\text{OH})_3(\text{H}_2\text{O})_3$ and the symmetry as orthorhombic
37 with unit cell parameters $a = 15.53$, $b = 17.78$ and $c = 7.03$ Å. A second occurrence of bulachite
38 from Sardinia, Italy, was reported by Frau and Da Pelo (2001). The Sardinian specimens were
39 collected at a mine dump from old workings in an arsenopyrite lens in the Sa Bidda Beccia
40 area located about 20 km southwest of Cagliari in southern Sardinia. Here the mineral occurs
41 as whitish, satiny, polycrystalline aggregates, usually on dark-brown layers of mansfieldite and
42 goethite encrusting quartzite clasts. Scanning electron microscope (SEM) images show that the
43 bulachite occurs as sub-parallel groups of very thin fibres, to 150 µm long and less than 0.25
44 µm in diameter. Frau and Da Pelo (2001) indexed the PXRD pattern using the unit cell reported
45 by Walenta (1983). They suggested that bulachite could have formed by direct precipitation
46 from iron-depleted drainage waters, or alternatively, from the hydration of mansfieldite in the
47 presence of aqueous aluminium. The most recent occurrence of bulachite is from the South
48 mine of the Cap Garonne (CG) old copper mine near the town of Le Pradet in the Var,
49 southeastern France, where it occurs in close association with bariopharmacoalumite- $Q2a2b2c$
50 (Grey *et al.*, 2014).

51 As part of an ongoing characterisation of hydrated Al arsenate minerals (Grey *et al.*, 2013,
52 2014, 2015, 2016*a,b*) we studied specimens of bulachite from Cap Garonne where the mineral
53 forms patchy crusts of ultrathin lath-like crystals on yellow crystals of pharmacoalumite
54 (Figure 1). The ruler-shaped laths are typically up to 50 µm long by 0.4 µm wide and only 0.1
55 µm thick. A surprising result was that PXRD patterns of the specimens, while having a number

56 of sharp peaks in common with the pattern reported by Walenta (1987), did not have the
57 strongest bulachite peak at 7.78 Å but had a number of broad peaks not present in the Walenta
58 pattern, including a strong peak at $d \sim 10$ Å. Electron diffraction (ED) patterns on flat laths
59 gave in-plane orthogonal dimensions of 17.7 Å x 7.8 Å with the 7.8 Å axis aligned along the
60 long dimension. The ED patterns assisted in the indexing of the PXRD pattern, giving an
61 orthorhombic unit cell with $a \approx 19.9$, $b \approx 17.7$ and $c \approx 7.8$ Å and possible space groups $Pnma$
62 or $Pn2_1a$.

63 An exception to the PXRD findings was obtained in a synchrotron PXRD data collection
64 made on small clumps of crystal aggregates packed in a capillary. Rotation of the capillary
65 during the experiment accidentally caused the bulk of the sample to move along the capillary
66 out of the beam, so the diffraction pattern was obtained only for crystals from the outer surface
67 of the small clumps that had adhered to the inner wall of the capillary. The resulting PXRD
68 pattern was the same as that reported by Walenta (1983) for bulachite. This experiment
69 suggested that the crusts of crystals have bulachite only at the surface and a different phase in
70 the bulk, with the possibility that bulachite has formed from the bulk specimen by reaction at
71 the surface. To test this hypothesis we obtained synchrotron PXRD data collections on a
72 specimen that was heated at different temperatures. Above 50°C the diffraction pattern
73 corresponding to the above-reported cell started changing and between 75°C and 100°C it had
74 transformed completely to the pattern reported by Walenta (1983) for bulachite.

75 ED patterns obtained for the sample heated to 100°C gave an orthorhombic cell with $a \approx 15.4$,
76 $b \approx 17.7$ and $c \approx 7.8$ Å and possible space groups $Pnma$ or $Pn2_1a$. i.e. the unit cell is the same
77 as for the phase before heating, except for a large decrease in a . The a axis is normal to the
78 ruler-shaped laths. The large decrease in a under very mild heating conditions is consistent
79 with a layer structure having interlayer water molecules which are evolved on heating above
80 $\sim 50^\circ$ C, resulting in a contraction of the interlayer separation.

81 We report here the application of synchrotron PXRD and precession ED methods to determine
82 the structures of both bulachite and the higher-hydrate precursor mineral that transforms to
83 bulachite on dehydration.

84 **Experimental**

85 The specimens for study were collected by GF in Salle B, South mine, Cap Garonne, Var,
86 France (43°4'53"N, 6°1'55"E; Favreau and Galea-Cloulus, 2014). The specimens were checked
87 for chemical purity by energy-dispersive X-ray analysis in a scanning electron microscope
88 (Figure 2). The only metals detected were Al and As, in an atomic ration of 2:1, consistent with
89 the formula obtained by Walenta (1983). The sample is preserved in the mineralogical
90 collections of Geosciences, Museums Victoria, registration number M55455. A sample of the
91 type specimen of bulachite that was studied by Walenta (1983) was supplied by Thomas Theye.
92 It was in the form of sub-millimetre tufts of densely packed fibrous crystals, see Figure 4 in
93 Walenta (1983).

94 **PXRD**

95 Laboratory PXRD scans showed that even light grinding of the specimens resulted in loss of
96 long-range ordering (severe peak broadening) so for the synchrotron experiments, small
97 unground clumps of subparallel fibres, such as shown in Figure 2 were packed into a 0.5 mm
98 diameter quartz capillary. In one of the earlier data collects, it was found that during rotation
99 of the capillary the clumps moved along the capillary and out of the beam. Subsequent samples
100 were prepared by packing a few mm of small clumps in a 0.5 mm quartz capillary then inserting
101 a 0.3 mm capillary to the edge of the specimen, to stop any movement. The data collections
102 were conducted on the powder diffraction beamline at the Australian Synchrotron (Wallwork
103 *et al.*, 2007). High energy 21 keV X-rays were used to reduce fluorescence due to As. The
104 wavelength was 0.59028(6) Å, calibrated to NIST standard LaB₆ 660b. The capillary was
105 positioned in the diffractometer rotation centre and spun at ca. 1 Hz. The X-ray beam was

106 aligned to coincide with the diffractometer centre and slits were used to restrict the beam width
107 to 2 mm. The data were collected using a Mythen position sensitive detector (Schmitt *et al.*,
108 2003) covering 80° in 2θ with a step size of 0.00375° in 2θ . Heating was supplied by an Oxford
109 Cryostream system. The first data collection was at close to ambient (25°C). The temperature
110 was then increased in steps of 25°C to 100°C and at each temperature pairs of data sets were
111 collected at two detector positions 0.5° apart in order to cover the gaps between the detector
112 modules. Acquisition time at each position was 300 seconds. The data pairs were merged into
113 single files using in-house data processing software, PDViPcR, available at the beamline. After
114 the 100°C collect the sample was cooled to ambient and a dataset obtained. A dataset was also
115 collected on an empty capillary so that correction for the capillary contribution could be applied
116 in the calculation of pair distribution functions (PDF) from the datasets.

117 Le Bail fitting of the PXRD data to obtain refined unit cell parameters was made using
118 JANA2006 (Petříček *et al.*, 2014). Manual backgrounds were used with interpolation between
119 40 points and a pseudo-Voigt peak shape function. It was necessary to include a parameter for
120 selective peak broadening for reflections with $h = 2n+1$.

121 Pair distribution functions (PDFs) were generated from the synchrotron datasets, with $Q_{\text{max}} =$
122 16.9 \AA^{-1} . The raw diffraction data were corrected for capillary contribution, reduced to structure
123 functions and then Fourier transformed to the PDFs, $G(r)$ (Egami and Billinge, 2003). PDF
124 calculations were conducted using PDFgui (Farrow *et al.*, 2007).

125 Gandolfi PXRD patterns were obtained on small clumps of crystals of the Neubulach type
126 specimen studied by Walenta (1983). The Gandolfi patterns were obtained on a Rigaku
127 XtaLAB Synergy diffractometer at the School of Chemistry, University of Melbourne. The
128 instrument employs a HiPix CCD Plate detector and $\text{CuK}\alpha$ radiation.

129

130

131 ***Transmission electron microscopy***

132 Crystal aggregates were sonicated in ethanol and the suspension was dispersed onto a holey
133 carbon grid for transmission electron microscopy (TEM). The TEM studies were conducted
134 using a JEOL 4000EX microscope with a LaB₆ source and a spherical aberration coefficient of
135 1.06 mm. The microscope was operated at 400 kV, using parallel illumination geometry to
136 minimise beam damage. TEM images were recorded on a Gatan slow scan CCD camera.

137 The new technique of low-dose electron diffraction tomography (Kodjikian and Klein, 2019)
138 was applied to crystals from a specimen that had been heated to 100°C and had a PXRD pattern
139 corresponding to bulachite (Walenta, 1983). Crystal aggregates were lightly crushed in an agate
140 mortar in absolute ethanol and a droplet of the suspension was deposited on carbon-coated
141 copper grid. The ED data collection was made using a Philips CM300ST TEM, equipped with
142 a TVIPS F416 CMOS camera, a Nanomegas Spinningstar device and a Bruker Silicon Drift
143 Detector for EDS. The diffraction intensities were measured on one selected particle (atomic
144 composition from EDS: Al:64.6% and As: 35.3%, Oxygen was detected but not quantified).

145 The tilt step between two frames of the tomography was chosen as 1°, the precession angle was
146 1.05°. A data set of 105 frames with an exposure time of 0.5 s per frame was recorded from a
147 single crystal of approximate size of 1 µm * 0.5 µm. During the automated data acquisition the
148 beam was blanked from the sample between the exposures in order to irradiate the crystal only
149 during the exposure time of the diffraction patterns. The dose rate was 0.056 electrons.s⁻¹.Å⁻²
150 and the total dose was 3 electrons.Å⁻². Data analysis of the recorded patterns was performed
151 with the software PETS2.0 (Palatinus *et al.*, 2019) and Jana2006 (Petříček *et al.*, 2014).

152 ***Crystal structure determinations***

153 The crystal structure of the sample heated to 100°C (= bulachite) was independently solved
154 from the low-dose electron diffraction tomography data and from the synchrotron PXRD data.

155 The individual ED patterns of the tomography series were treated for data reduction in PETS

156 2.0. Sections of the reciprocal lattice showed reflection conditions leading to the extinction
157 symbol $Pn\bar{a}$ consistent with space groups $Pnma$ and $Pn2_1a$.

158 Superflip in JANA2006 (Petříček *et al.*, 2014) was used to obtain a model in space group $Pn2_1a$
159 from the PXRD data whereas the ED data were used in Superflip and in SIR2014 (Burla *et al.*,
160 2015) where both space groups were tested and the best fit was found for a $Pnma$ model. Both
161 the ED and PXRD-derived models had the same topology of edge-shared Al-centred octahedra
162 connected to AsO₄ tetrahedra by corner-sharing. Based on the ED model, a centre of symmetry
163 was located for the $Pn2_1a$ model and the atomic coordinates were transformed to the
164 centrosymmetric space group setting for refinement against the synchrotron PXRD data.

165 The crystal structure of the higher-hydrate mineral was established by recognising that it had
166 the same polyhedral layers as in bulachite, but with an increased layer separation due to the
167 presence of interlayer water molecules. The x coordinates for the bulachite model were scaled
168 by the ratio of the two a axes to establish the polyhedral layers in the $a = 19.9$ Å cell. The
169 PXRD pattern for this model was calculated and found to have only a fair agreement with the
170 experimental pattern. We examined the possibility that the transformation of the $a = 19.9$ Å
171 phase to the $a = 15.4$ Å phase involved not only a contraction of the interlayer spacing but also
172 a sliding of the layers relative to one another, as we found in heating studies on other hydrated
173 aluminium arsenate minerals (Grey *et al.*, 2016b). In space group $Pnma$, the layers can be
174 displaced relative to one another along [001], with no distortion of the polyhedra, by changing
175 the z coordinate for all atoms by the same amount. We ran a series of tests where the z
176 coordinate for all atoms was changed in increments of 0.01. It was found that changing z in a
177 positive sense improved the fit to the experimental PXRD pattern, and the profile R factors
178 decreased with increasing Δz up to 0.09 then increased with further change in z . The value of
179 Δz was then fixed at 0.09, and difference-Fourier maps were used to locate the interlayer water
180 molecules.

181 ***Structure refinements***

182 The *Pnma* structural model for bulachite was refined both with the synchrotron PXRD data
183 and by dynamical refinement of the ED data. The latter will be reported separately. Here we
184 describe the PXRD refinement, using the synchrotron data to a resolution of 1.0 Å (the peaks
185 become very weak and broad at higher resolutions). The Rietveld data collection and
186 refinement conditions are given in Table 1.

187 The profile parameters were established using a Le Bail structureless fit to the PXRD pattern.
188 Manual backgrounds were automatically located at 40 positions in JANA2006. The unit-cell
189 parameters, a zero-shift, the Lorentzian parameters *LX* and *LY*, and a parameter to deal with
190 anisotropic peak broadening for reflections *hkl* with $h = 2n+1$ were refined, giving Le Bail fit
191 indices of $R_p = 2.60$, $R_{wp} = 3.73$ and Goodness of fit, $GoF = 3.13$.

192 The atomic coordinates were refined using soft distance restraints for the As–O and Al–O
193 distances of 1.670(1) Å and 1.900(5) Å, respectively. The restrained distances used are the
194 mean of As–O and Al–O distances obtained from single-crystal refinements of other
195 aluminium arsenate minerals (Grey *et al.*, 2013, 2015, 2016a). Angle restraints were also used,
196 for the AsO₄ tetrahedra, O–As–O = 109.47(2)°. Group isotropic displacement parameters, *B*,
197 for the metal atoms, polyhedral anions and interlayer water molecule oxygen atoms were
198 refined. Rietveld refinement in JANA2006 converged at fit indices of $R_p = 3.73$, $R_{wp} = 5.09$
199 and $GoF = 4.29$. The refined structural parameters are reported in Table 2. The atom labels are
200 the same as used for other hydrated Al arsenate minerals (Grey *et al.*, 2015, 2016a) where OH
201 = hydroxyl, Ow = coordinated H₂O and W = H-bonded H₂O. Polyhedral bond distances, cation-
202 cation distances and likely H-bonded pairs are given in Table 3.

203 For the higher-hydrate mineral the structural parameters were not refined, apart from
204 establishing the magnitude of layer sliding along [001] as discussed above. The synchrotron
205 PXRD pattern for this mineral (Figure 1) is of lower quality than that for bulachite. In

206 particular, all reflections with non-zero h are broadened and the reflections with h odd are
207 broader than those with h even. This was dealt with by combining anisotropic Lorentzian
208 particle size broadening (parameter LXe) with anisotropic peak broadening for reflections with
209 $h = 2n+1$. As for bulachite, the PXRD data was truncated at 1 Å resolution, 40 manual
210 backgrounds were located and profile parameters were established with a Le bail fit, giving fit
211 indices of $R_p = 2.88$, $R_{wp} = 4.06$ and $GoF = 3.40$. The interlayer water molecules were located
212 in difference-Fourier maps. The agreement factors for the Rietveld fitting of the PXRD data
213 are $R_p = 5.57$, $R_{wp} = 7.43$ and $GoF = 6.23$. Because the polyhedral layers are built from the
214 refined bulachite structure, the polyhedral bond distances are the same as reported in Table 2
215 for bulachite. The higher hydrate is a potential new mineral and further crystallochemical
216 details await the preparation of a new mineral proposal to the International Mineralogical
217 Association Commission on New Minerals, Nomenclature and Classification
218 (IMA–CNMNC).

219

220 **Results**

221 The low-angle region of the PXRD pattern for the Cap Garonne specimen is shown in Figure
222 3. The indexed sharp peaks in the pattern are also present in the bulachite pattern reported by
223 Walenta (1983) but the other peaks, which are much broader, have no counterpart in the
224 bulachite pattern. The sharp reflections all correspond to a single reciprocal lattice section,
225 $(0kl)$. This was the most commonly encountered pattern in ED studies of the sample. The ED
226 $(0kl)$ pattern is shown in Figure 4a. It is obtained when the platy laths lie flat on the TEM grid.
227 Indexing of the ED pattern gives cell parameters $b = 17.7$ Å and $c = 7.8$ Å. Systematic absences
228 in the pattern for $(0kl)$ reflections with $k+l = 2n+1$ indicate an n -glide plane. The associated
229 image of the diffracting crystal is shown in Figure 4b. It confirms that the direction of the 7.8
230 Å axis is parallel to the long dimension of the lath. Aided by the ED results the PXRD could

231 be fully indexed and a Le Bail refinement gave the orthorhombic unit-cell parameters $a =$
232 $19.849(2)$, $b = 17.6903(4)$ and $c = 7.7788(3)$ Å, with possible space groups $Pnma$ or $Pn2_1a$.

233 PXRD patterns corresponding to heating of the Cap Garonne specimen are presented in Figure
234 5. At 50°C there is the appearance of a peak at $d = 7.8$ Å (arrowed), which is the strongest peak
235 in the pattern of bulachite (Walenta, 1983). Note that this peak is present in the room
236 temperature pattern but it is very weak and broad. At 75°C there is a dramatic change in the
237 pattern with a strong increase in the 7.8 Å peak and a marked diminution in the 10 Å peak and
238 other peaks present in the room temperature pattern. At 100°C the transformation is complete
239 and all peaks present match those reported by Walenta (1983) for bulachite.

240 ED patterns obtained on the sample heated to 100°C were indexed with unit-cell parameters
241 $a = 15.4$, $b = 17.7$ and $c = 7.8$ Å. Using these as starting parameters in a Le Bail fit to the 100°C
242 PXRD pattern gave the refined unit cell parameters $a = 15.3994(3)$, $b = 17.6598(3)$ and $c =$
243 $7.8083(1)$ Å. The systematic extinctions in the ED patterns correspond to space groups $Pnma$
244 or $Pn2_1a$, the same as for the $a = 19.9$ Å mineral. As mentioned in the previous section the fit
245 indices were $R_p = 2.60$, $R_{wp} = 3.73$ and $GoF = 3.13$. For comparison we re-ran the Le Bail
246 fitting to the 100°C dataset starting with the unit cell parameters reported by Walenta (1983).
247 There was a marked deterioration to the fit, with fit indices $R_p = 6.17$, $R_{wp} = 10.49$ and GoF
248 $= 9.76$. With the higher resolution of the synchrotron data (Walenta used a Debye-Scherrer
249 camera with $FeK\alpha$ radiation), serious misfits are evident using the Walenta cell, due to the
250 incorrect c parameter.

251 The possibility existed that the bulachite specimen from Cap Garonne was crystallochemically
252 different from the bulachite from Neubulach. To check this we obtained a portion of the
253 specimen characterised by Walenta (1983). We were able to confirm, by obtaining Gandolfi
254 PXRD patterns on different crystal aggregates, that both the $a = 19.9$ Å and $a = 15.4$ Å phases
255 are present in the Neubulach sample, as shown in Figure 6. For the 19.9 Å phase, the reflections

256 involving h are very broad, including the strong characteristic (200) reflection at $d \sim 10 \text{ \AA}$, so
257 small amounts of this phase are difficult to detect. Frau and da Pelo (2001) noted that their
258 PXRD pattern had an anomalously high background suggestive of the presence of amorphous
259 phase and broad peaks. Our PXRD heating experiments (Figure 5) show that the 19.9 \AA phase
260 begins to transform to bulachite within a few minutes at 50°C , so it is likely that at suitable
261 humidity conditions, the transformation could occur at ambient temperatures over long periods.
262 The dehydration of the 19.9 \AA phase will start at the surface of the mineral crusts and move
263 inwards under diffusion control, so it is not unexpected to find a mix of the two phases in the
264 crusts. It is possible that the specimen that Walenta used to obtain a PXRD pattern came from
265 the upper region of the surface aggregates where dehydration of the 19.9 \AA phase had occurred.

266 As described in the Experimental section, the crystal structure of bulachite was determined
267 in space group $Pnma$ using low-dose electron tomography data and refined using Rietveld
268 treatment of synchrotron PXRD data. The data collection and refinement details are given in
269 Table 1 and the Rietveld fit to the PXRD data is shown in Figure 7.

270 Projections of the crystal structures along the 7.8 \AA axis are shown in Figures 8 and 9 for
271 bulachite and the higher hydrate, respectively, while Figure 10 shows a view of the structures
272 normal to the (100) layers. This Figure shows that the polyhedral layers are built from edge-
273 shared Al-centred octahedra that form spiral chains along [001], the same as occurs in
274 liskeardite (Grey *et al.*, 2013). The spirals are joined together along [010] by edge-sharing of
275 octahedra in the mirror plane at $y = \frac{1}{4}$. The spirals are decorated with AsO_4 tetrahedra that
276 corner-connect to the AlO_6 octahedra in the same manner as in liskeardite.

277 The close relationship of the two structures to that of liskeardite is illustrated by comparing
278 the PDFs for the three minerals in Figure 11. The first three strong peaks in the PDFs, at 1.8.
279 2.7 and 3.2 \AA correspond to As–O + Al–O, O–O and As–Al + Al–Al distances, respectively.

280 The O–O at 2.7 Å is strong despite the low scattering of oxygen, because fortuitously the O–O
281 distances in both the AsO₄ tetrahedra and the AlO₆ octahedra are almost the same.

282 The composition of the layers is readily established from the refinement using bond valence
283 sums (BVS) to distinguish the different anions. BVS values were calculated using the
284 parameters of Gagné and Hawthorne (2015). The values, in valence units, are given in Table
285 2. Taking into account the site multiplicities, they show clearly that the layers contain 12
286 oxygens, 9 hydroxyls and 4 coordinated H₂O. The O2 and O6 sites, which contain unshared
287 tetrahedral oxygen atoms, have low BVS values of 1.32, while the sites O4 and O7 are also
288 slightly low. However, as shown by the H-bond couples in Table 3, oxygen atoms at these sites
289 are acceptor atoms for several H-bonds from OH, Ow and W donor atoms. Taking into account
290 the numbers of O, OH and Ow gives the layer formula Al₆(AsO₄)₃(OH)₉(H₂O)₄, with Z = 4.
291 The same layer formula applies to the higher hydrate mineral. Adding in the H-bonded H₂O
292 (=W) gives the overall formula for bulachite of [Al₆(AsO₄)₃(OH)₉(H₂O)₄]₂H₂O, while the
293 formula for the higher hydrate is [Al₆(AsO₄)₃(OH)₉(H₂O)₄]₈H₂O.

294 A search of the literature failed to find any related PXRD pattern or unit cell that matched
295 those for the higher hydrate. The Cap Garonne specimen appears to be a new mineral which
296 eventually will require a proposal to be prepared to the IMA–CNMNC for validation.

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299 SEM image, Anita d'Angelo for help with the synchrotron PXRD data collects. Thanks also to
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303

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351 Table 1. Synchrotron PXRD data collection and Rietveld refinement details for bulachite.

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Formula	$[\text{Al}_6(\text{AsO}_4)_3(\text{OH})_9(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$
Unit-cell parameters (Å)	$a = 15.3994(3)$ $b = 17.6598(3)$ $c = 7.8083(1)$
Volume (Å ³), <i>Z</i>	2123.46(7), 4
Space group	<i>Pnma</i>
X-ray radiation source, wavelength (Å)	Australian Synchrotron, 0.59028(6)
2θ range, step size (°)	1.50 to 104.82, 0.00375
Resolution for structure analysis (Å), number of contributing reflections	1.0, 1158
Number of profile parameters	8
Number of structural parameters/restraints	63/38
Profile function	Pseudo-Voigt
Background	Interpolation between 40 selected points
<i>R_p</i> , <i>R_{wp}</i> , <i>GoF</i> , <i>R_F</i>	3.73, 5.09, 4.29, 10.7

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361 Table 2. Refined atomic coordinates, isotropic displacement parameters and calculated bond
362 valence sums (BVS) for bulachite.

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Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)	BVS
As1	0.82245(18)	0.00921(19)	0.3827(4)	0.0368(6)	5.22
As2	0.9057(3)	0.25	0.5824(6)	0.0368(6)	5.24
Al1	0.6329(6)	0.0696(5)	0.2444(17)	0.0368(6)	3.11
Al2	0.8397(6)	0.0964(5)	0.7535(16)	0.0368(6)	2.96
Al3	0.7207(6)	0.1692(6)	0.4971(16)	0.0368(6)	2.70
O1	0.7276(5)	-0.0061(6)	0.2856(14)	0.0186(15)	2.19
O2	0.9002(6)	0.0190(6)	0.2359(12)	0.0186(15)	1.32
O3	0.8160(7)	0.0885(5)	0.5006(13)	0.0186(15)	2.00
O4	0.8459(7)	-0.0642(5)	0.5099(13)	0.0186(15)	1.86
O5	0.8043(5)	0.25	0.5078(18)	0.0186(15)	2.28
O6	0.9752(8)	0.25	0.4186(14)	0.0186(15)	1.32
O7	0.9217(6)	0.17267(14)	0.7019(7)	0.0186(15)	1.82
OH1	0.7085(9)	0.1522(7)	0.250(2)	0.0186(15)	0.98
OH2	0.6300(10)	0.0952(9)	0.4819(19)	0.0186(15)	0.98
OH3	0.9259(8)	0.0208(7)	0.772(3)	0.0186(15)	1.10
OH4	0.7386(8)	0.1541(7)	0.740(2)	0.0186(15)	1.01
OH5	0.6390(13)	0.25	0.511(3)	0.0186(15)	1.00
Ow1	0.5229(9)	0.1135(7)	0.226(3)	0.0186(15)	0.55
Ow2	0.8415(13)	0.1119(9)	0.9944(19)	0.0186(15)	0.51
W1	0.93	0.25	0.018	0.074(11)	
W2	0.3652	0.75	0.0187	0.074(11)	

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368 Table 3. Polyhedral bond distances, cation-cation distances and likely H-bonded pairs in
 369 bulachite.

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As1–O1	1.667(8)	Al2–O1	1.918(13)
As1–O2	1.667(9)	Al2–O3	2.014(16)
As1–O3	1.679(9)	Al2–O7	1.890(11)
As1–O4	1.672(10)	Al2–OH3	1.889(16)
Mean	1.671	Al2–OH4	1.864(16)
As2–O5	1.666(10)	Al2–Ow2	1.900(19)
As2–O6	1.668(12)	Mean	1.912
As2–O7	1.673(5)	Al3–O3	2.046(14)
Mean	1.670	Al3–O5	1.924(11)
Al1–O1	2.005(13)	Al3–OH1	1.96(2)
Al1–O4	1.862(17)	Al3–OH2	1.917(18)
Al1–OH1	1.868(15)	Al3–OH4	1.94(2)
Al1–OH2	1.91(2)	Al3–OH5	1.905(17)
Al1–OH3	1.847(15)	Mean	1.949
Al1–Ow1	1.869(16)		
Mean	1.894	As1–Al1	3.290(10)
Potential H-bonded pairs		As1–Al1	3.223(13)
Donor...Acceptor		As1–Al2	3.291(12)
Ow1...O2	2.55	As1–Al2	3.276(10)
Ow1...O4	2.77	As1–Al3	3.352(10)
Ow1---O6	2.77	As2–Al2	3.190(10)
Ow2...O2	2.65	As2–Al2	3.190(10)
Ow2...O4	2.99	As2–Al3	3.255(10)
Ow2...O7	2.82	As2–Al3	3.255(10)
W1...O7	2.82	Al1–Al2	2.962(12)
W2...O6	2.58	Al1–Al3	2.970(16)
OH2...O2	2.84	Al2–Al3	3.004(15)
OH3...O2	2.79	Al3–Al3	2.854(14)
OH4...O4	2.92		
OH4...O7	2.86		
OH5...O2	2.55		
OH5...O4	2.77		
OH5...O6	2.77		

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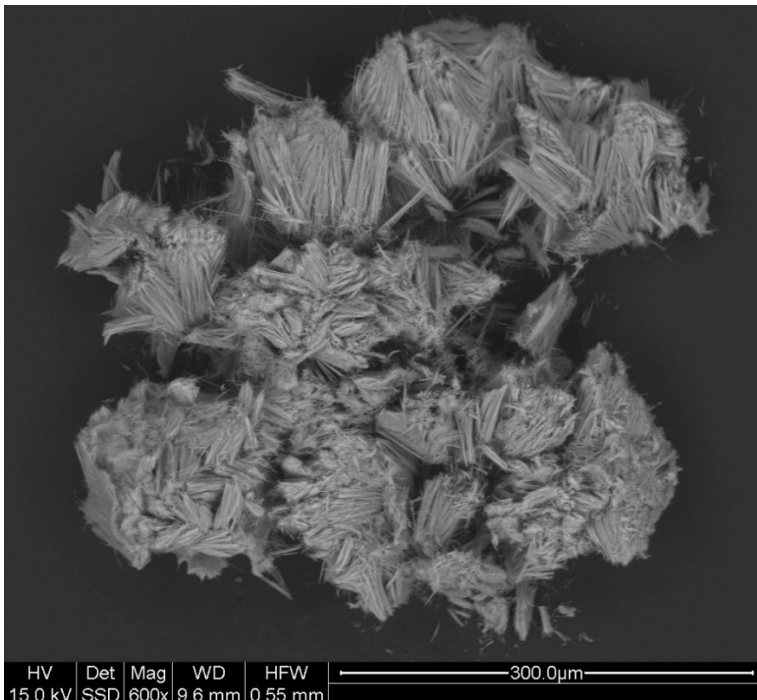
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373 Figure 1. Patchy regions of bulchite (white) on yellow pharmacalumite from Cap Garonne.

374 FOV 15 mm. Museums Victoria specimen M55455.

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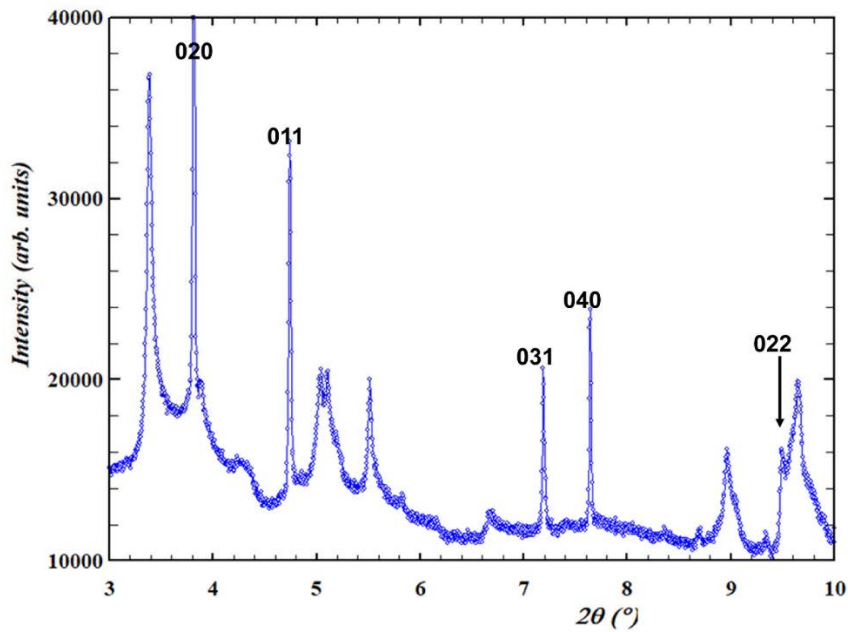
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378 Figure 2. SEM back-scattered electron image of clumps of fibrous bulchite crystals from

379 Cap Garonne. Museums Victoria specimen M55455.

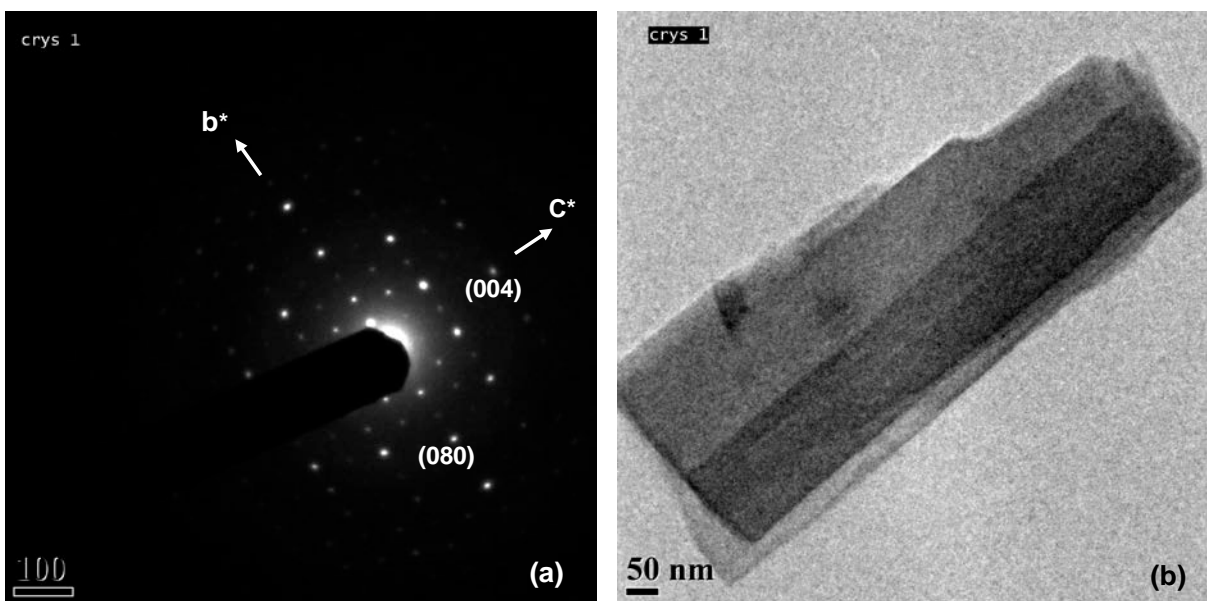


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381 Figure 3. Low-angle region of the synchrotron PXRD pattern for the Cap Garonne specimen.

382 The sharp reflections all index as $(0kl)$ based on cell parameters $b = 17.7$ and $c = 7.8$ Å. The
 383 first reflection is (200) where $a = 19.9$ Å.

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387 Figure 4. Electron diffraction $(0kl)$ reciprocal lattice section for the Cap Garonne specimen.

388 (b) Image of flat lath crystal used to obtain the ED pattern. Museums Victoria specimen

389 M55455.

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392 Figure 5. Low-angle region of synchrotron PXRD patterns for the Cap Garonne specimen
393 heated at temperatures 25, 50, 75 and 100°C. Indexing of the 100°C pattern shown.

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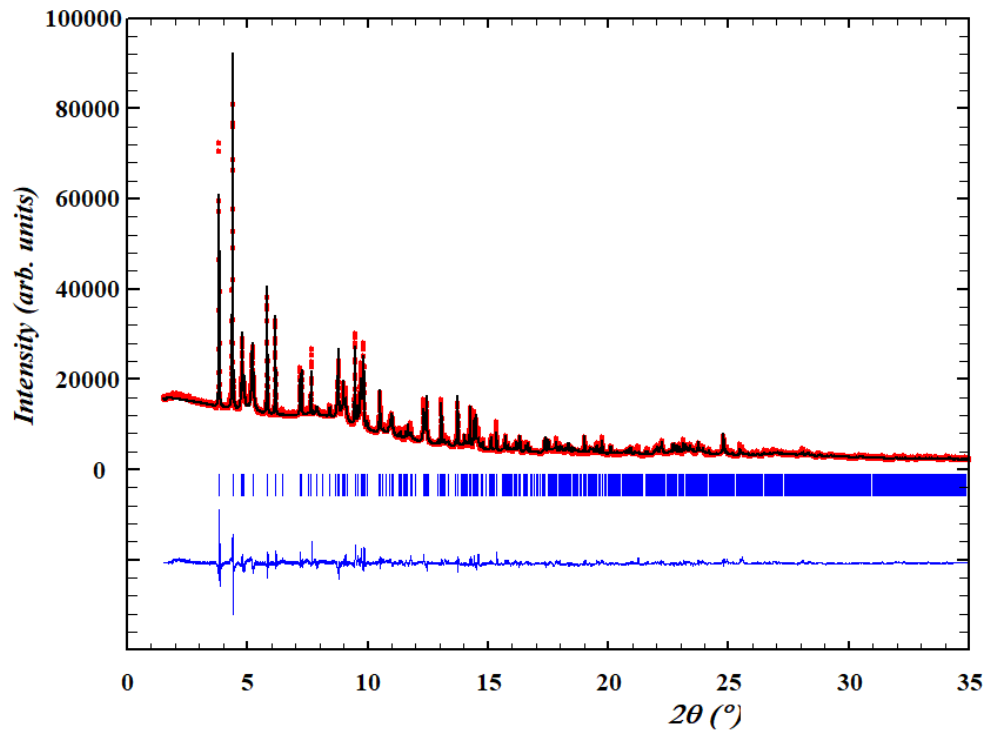
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Figure 6. Gandolfi PXR patterns for two separate tufts of the Neubulach type specimen of bulachite ($\text{CuK}\alpha$ radiation).



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426 Figure 7. Rietveld observed (red points) and calculated (black line) PXRD patterns for
427 bulachite from Cap Garonne. Short bars show the positions of the Bragg reflections. The
428 difference plot is in blue.

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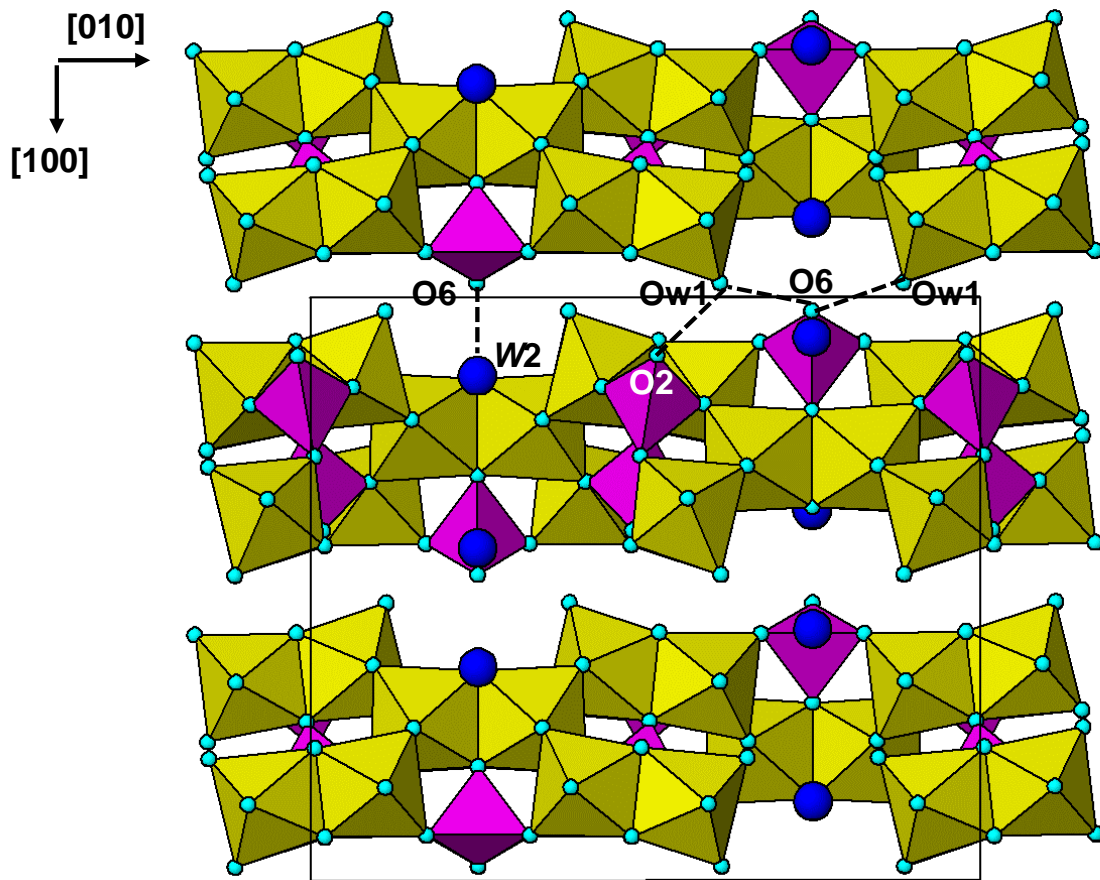
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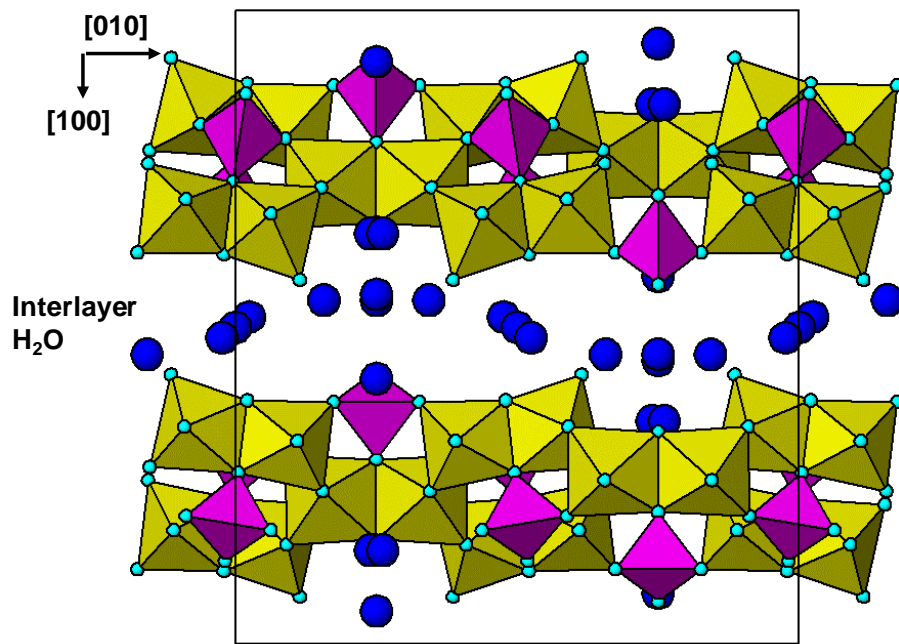
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441 Figure 8. [001] projection of the layer structure for bulachite. Dotted lines show likely
442 interlayer H-bonds. Dark blue spheres are water molecules, Al-centred octahedra are yellow
443 and AsO₄ tetrahedra are mauve.

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448 Figure 9. [001] projection of the layer structure for the higher hydrate mineral. Blue spheres

449 are interlayer water molecules, Al-centred octahedra are yellow and AsO₄ tetrahedra are

450 mauve.

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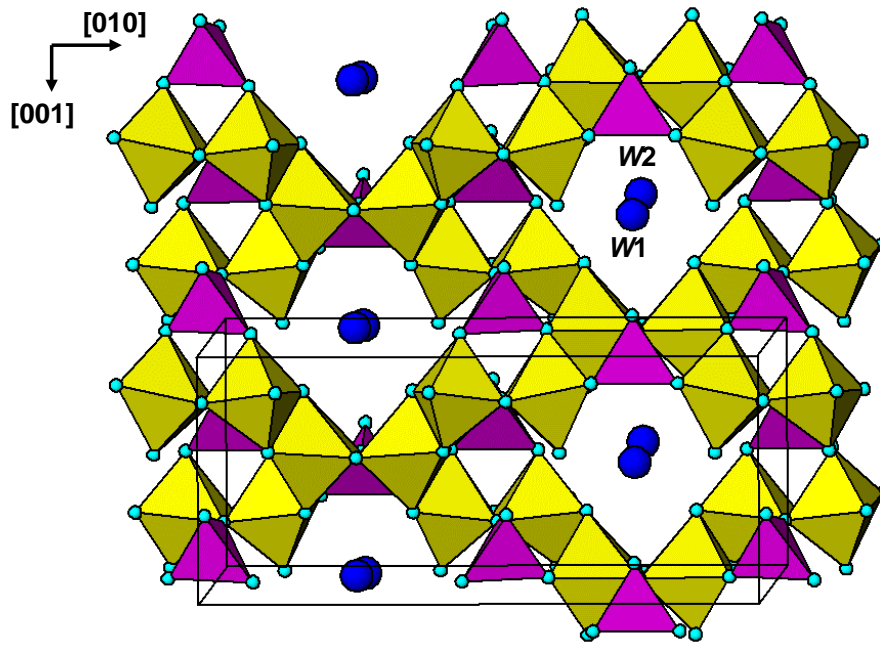
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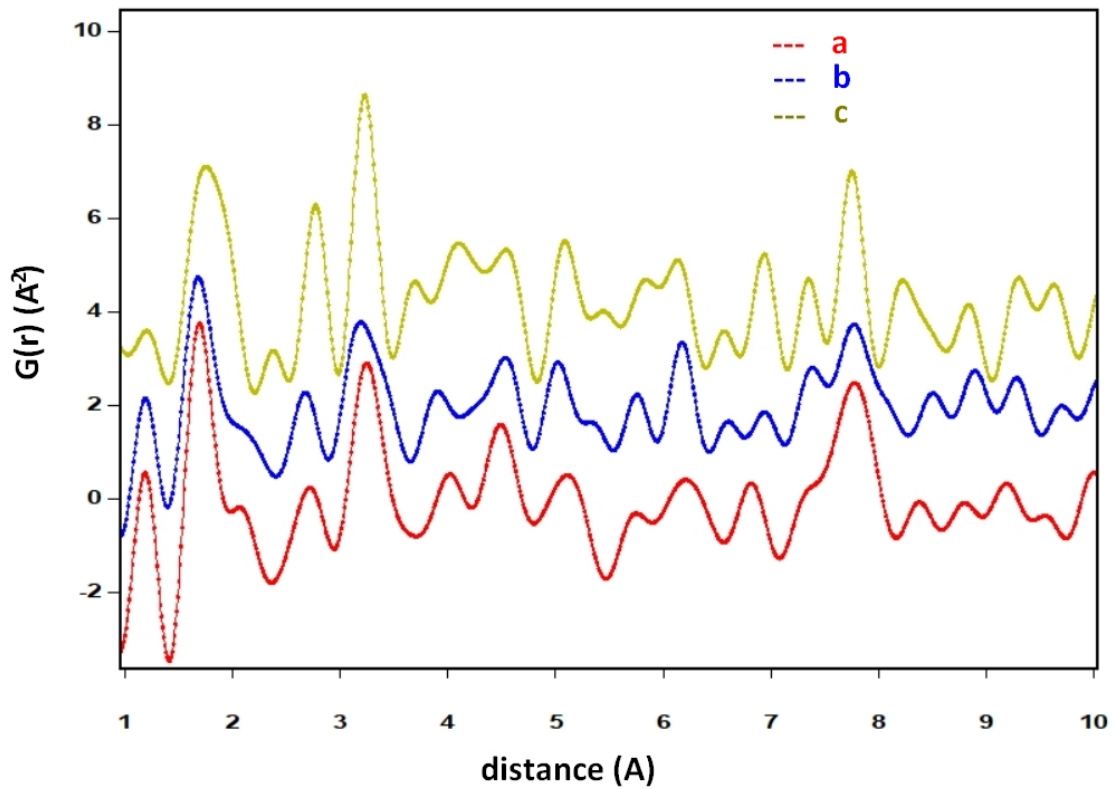
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459 Figure 10. Projection approximately along [100] of the structure of bulachite, showing spirals

460 along [001] of edge-shared Al-centred octahedra (yellow) and corner-connected AsO₄

461 tetrahedra (mauve).

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Figure 11. Experimental PDFs for (a) the higher hydrate mineral and (b) bulachite formed at 100°C, compared with the calculated PDF for liskeardite (c).