

Physics and Chemistry of Minerals

Crystal-chemistry of sulfates from Apuan Alps (Tuscany, Italy). IV. Giacobazzoite, $K_5Fe_3+3O(SO_4)_6(H_2O)_9 \cdot H_2O$, the natural analogue of the β -Maus's Salt and its dehydration product --Manuscript Draft--

Manuscript Number:	PCMI-D-19-00115R1	
Full Title:	Crystal-chemistry of sulfates from Apuan Alps (Tuscany, Italy). IV. Giacobazzoite, $K_5Fe_3+3O(SO_4)_6(H_2O)_9 \cdot H_2O$, the natural analogue of the β -Maus's Salt and its dehydration product	
Article Type:	Original paper	
Keywords:	Giacobazzoite; new mineral; Sulfate; crystal structure; Maus's salt	
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Funding Information:	Università di Pisa (PRA_2018_41)	Not applicable
Abstract:	<p>The new mineral giacobazzoite, $K_5Fe_3+3O(SO_4)_6(H_2O)_9 \cdot H_2O$, has been discovered in the Monte Arsiccio mine, Apuan Alps, Tuscany, Italy. It occurs as orange-brown prismatic crystals, up to 0.1 mm long, with yellowish streak and vitreous luster. It is brittle, with a perfect {100} cleavage. Associated minerals are alum-(K), krausite, gypsum, scordariite, and magnanelliite. Electron microprobe analysis (WDS mode) gave (in wt%): SO_3 45.82, Fe_2O_3 22.67, K_2O 22.72, H_2O_{calc} 17.18, total 108.39. The high total, after the addition of calculated H_2O (based on structural results), is due to the dehydration of the sample during analysis. The corresponding empirical chemical formula, on the basis of 25 anions and 10 H_2O groups, is $K_{5.06}Fe_3+2.98O(SO_4)_6 \cdot 10H_2O$. Giacobazzoite is monoclinic, space group $P2_1/c$, with unit-cell parameters $a = 9.4797(2)$, $b = 18.4454(5)$, $c = 18.0540(4)$ Å, $\beta = 92.626(2)^\circ$, $V = 3153.55(13)$ Å³, $Z = 4$. Its crystal structure was refined to $R_1 = 0.0587$ for 10254 reflections with $F_o > 4\sigma(F_o)$ and 511 refined parameters. It is formed by a structural unit, represented by a heteropolyhedral $[Fe_3+3O(SO_4)_6(H_2O)_3]^{5-}$ cluster, and an interstitial complex, having composition $\{K_5(H_2O)_7\}^{5+}$. The $[Fe_3+3O(SO_4)_6(H_2O)_3]^{5-}$ clusters form layers parallel to {100} which are bonded in this plane by K atoms. Successive layers are bonded, along c, through H-bonds, and by K atoms. The heteropolyhedral cluster occurring in giacobazzoite is known in the crystal structures of metavoltine, scordariite, carlsonite, and a series of synthetic compounds. Among them, the β-Maus's salt has isotypic relationships with giacobazzoite. This latter mineral easily dehydrates and its dehydrated product has been investigated.</p>	



November 16th, 2019

Manuscript

Dear Prof. Rieder,

we have taken into account the comments and corrections of the two reviewers improving the manuscript. We have accepted all the suggestions of reviewer #1 and we have replaced the term “metagiacovazzoite” with other terms indicating its dehydrated nature. As regards the suggestions given by reviewer #2, we briefly added some comments about the changes in the H-bond system in the dehydrated phase.

Yours sincerely,

Cristian Biagioni

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REVISION 1

Cristian Biagioni^{a,*}, Luca Bindi^b, Daniela Mauro^a, Marco Pasero^a**Crystal-chemistry of sulfates from the Apuan Alps
(Tuscany, Italy). IV. Giacovazzoite,
 $\text{K}_5\text{Fe}^{3+}_3\text{O}(\text{SO}_4)_6(\text{H}_2\text{O})_9 \cdot \text{H}_2\text{O}$, the natural analogue of the
 β -Maus's Salt and its dehydration product**^a *Dipartimento di Scienze della Terra, Università di Pisa, Via S. Maria 53, I-56126 Pisa, Italy*^b *Dipartimento di Scienze della Terra, Università di Firenze, Via La Pira 4, I-50121 Firenze, Italy**e-mail address: cristian.biagioni@unipi.it

Abstract The new mineral giacovazzoite, $\text{K}_5\text{Fe}^{3+}_3\text{O}(\text{SO}_4)_6(\text{H}_2\text{O})_9 \cdot \text{H}_2\text{O}$, has been discovered in the Monte Arsiccio mine, Apuan Alps, Tuscany, Italy. It occurs as orange-brown prismatic crystals, up to 0.1 mm long, with yellowish streak and vitreous luster. It is brittle, with a perfect {100} cleavage. Associated minerals are alum-(K), krausite, gypsum, scordariite, and magnanelliite. Electron microprobe analysis (WDS mode) gave (in wt%): SO_3 45.82, Fe_2O_3 22.67, K_2O 22.72, $\text{H}_2\text{O}_{\text{calc}}$ 17.18, total 108.39. The high total, after the addition of calculated H_2O (based on structural results), is due to the dehydration of the sample during analysis. The corresponding empirical chemical formula, on the basis of 25 anions and 10 H_2O groups, is $\text{K}_{5.06}\text{Fe}^{3+}_{2.98}\text{O}(\text{SO}_4)_{6.00} \cdot 10\text{H}_2\text{O}$. Giacovazzoite is monoclinic, space group $P2_1/c$, with unit-cell parameters $a = 9.4797(2)$, $b = 18.4454(5)$, $c = 18.0540(4)$ Å, $\beta = 92.626(2)^\circ$, $V = 3153.55(13)$ Å³, $Z = 4$. Its crystal structure was refined to $R_1 = 0.0587$ for 10254 reflections with $F_o > 4\sigma(F_o)$ and 511 refined parameters. It is formed by a structural unit, represented by a heteropolyhedral $[\text{Fe}^{3+}_3\text{O}(\text{SO}_4)_6(\text{H}_2\text{O})_3]^{5-}$ cluster, and an interstitial complex, having composition $\{\text{K}_5(\text{H}_2\text{O})_7\}^{5+}$. The $[\text{Fe}^{3+}_3\text{O}(\text{SO}_4)_6(\text{H}_2\text{O})_3]^{5-}$ clusters form layers parallel to {100} which are bonded in this plane by K atoms. Successive layers are bonded, along **c**, through H-bonds, and by K atoms. The heteropolyhedral cluster occurring in giacovazzoite is known in the crystal structures of metavoltine, scordariite, carlsonite, and a series of synthetic compounds. Among them, the β -Maus's salt has isotypic relationships with giacovazzoite. This latter mineral easily dehydrates and its dehydrated product has been investigated.

Keywords Giacovazzoite · New mineral · Sulfate · Crystal structure · Maus's salt

32 **Introduction**

33 The system $K_2O-Fe_2O_3-SO_3-H_2O$ is currently composed by few mineral species: goldichite, $KFe(SO_4)_2 \cdot 4H_2O$
34 (Rosenzweig and Gross 1955), jarosite, $KFe_3(SO_4)_2(OH)_6$ (Bayliss et al. 2010), krausite, $KFe(SO_4)_2 \cdot H_2O$ (Foshag 1931),
35 and yavapaiite, $KFe(SO_4)_2$ (Hutton 1959). These minerals are usually the result of the interaction of acidic solutions,
36 derived from the pyrite oxidation, with K-bearing rocks, or they can be observed in fumarolic environments.

37 The occurrence of sulfate assemblages from the pyrite ore deposits from the Apuan Alps (northern Tuscany, Italy) has
38 been known since the 19th Century (D'Achiardi 1872). However, modern mineralogical data were collected only since
39 the mid-2000s, when the presence of sulfate piles in the old tunnels of the Fornovolasco mining complex was first
40 described (Biagioni et al. 2008), allowing the finding of the new mineral species volaschioite (Biagioni et al. 2011) as
41 well as the crystal-chemical study of other sulfates (Mauro et al. 2018a, 2018b). The study of samples from other mining
42 sites from the same kind of ore deposits led to the description of another new mineral, the ferric iron hydrated sulfate-
43 phosphate bohoslavite (Mauro et al. 2019). Recently, the identification of a complex sulfate assemblage from the Monte
44 Arsiccio mine, where Ti-rich pyrite orebodies are hosted within a Paleozoic phylladic complex, allowed the further
45 identification of three new K-Fe³⁺ sulfates: giacovazzoite (IMA 2018-165), magnanelliite (IMA 2019-006), and
46 scordariite (IMA 2019-010 – Biagioni et al. 2019).

47 This paper deals with the description of giacovazzoite, the natural analogue of synthetic β -Maus's salt (Mereiter and
48 Völlenkne 1978). This mineral honours Carmelo Giacovazzo (b. 1940), full professor of Mineralogy and Crystallography
49 at the University of Bari from 1975 up to his retirement, for his outstanding contribution to crystallography. Prof.
50 Giacovazzo is author of more than 300 papers and six books on crystallographic topics. He is very well-known in the
51 scientific community for his contribution to the direct methods and to the solution of the phase problem in crystallography.
52 It is noteworthy that Prof. Giacovazzo was the recipient of the 2011 Ewald Prize of the International Union of
53 Crystallography. The mineral and its name have been approved by the Commission on New Minerals, Nomenclature and
54 Classification of the International Mineralogical Association (IMA-CNMNC). Holotype material is deposited in the
55 mineralogical collection of the Museo di Storia Naturale of the University of Pisa, under catalogue number 19896.

57 **Occurrence and mineral properties**

58 Giacovazzoite was found in a specimen from the Monte Arsiccio mine (latitude 43°58'N, longitude 10°17'E), Apuan
59 Alps, Tuscany, Italy. The Monte Arsiccio mine exploited a pyrite + baryte + iron oxide (magnetite, hematite) ore deposit
60 located in the NE sector of the Sant'Anna tectonic window, in southern Apuan Alps (Costagliola et al. 1990). The
61 orebodies are located close to the contact between a Paleozoic metavolcanic-metasedimentary sequence, locally
62 tourmalinized, and Triassic metadolostone belonging to the Grezzoni Formation. The weathering of microcrystalline
63 pyrite occurring in these orebodies, enriched in several environmentally critical elements (D'Orazio et al. 2017; George
64 et al. 2018) gives rise to acid mine drainage, negatively affecting the area (e.g., Perotti et al. 2017).

65 The studied sulfate assemblage occurs in an old stope of the mine, where a pyrite orebody is exposed and it is deeply
66 weathered, with the formation of cm-thick veins of light blue melanterite and colorless alum-(K). Other common sulfates
67 occur (e.g., römerite, halotrichite, coquimbite, voltaite, gypsum, alunogen, jarosite), as well as some rarer minerals
68 (krausite, goldichite, khademite). In the sampling site, the measured air temperature (*T*) was 17 °C. Minerals directly
69 associated with giacovazzoite include alum-(K), krausite, gypsum, scordariite, and magnanelliite.

70 Giacovazzoite occurs as orange-brown prismatic crystals, up to 0.1 mm in length (Fig. 1), with a yellowish streak. It is
71 transparent with vitreous luster and displays no fluorescence. Mohs hardness could be close to 2, in agreement with related
72 minerals (e.g., carlsonite – Kampf et al. 2016). Giacovazzoite is brittle, with a perfect cleavage on {100} and imperfect

73 on {001}; fracture is irregular. Density, calculated on the basis of the empirical formula and unit-cell volume refined from
74 single-crystal X-ray diffraction measured at room temperature, is 2.392 g/cm³. Crystals are slowly soluble in H₂O at room
75 temperature. Giacovazzoite is distinctly pleochroic, from tan to brownish. Mean refractive index, calculated according to
76 the Gladstone–Dale relationship (Mandarino 1979, 1981), is 1.564. This value agrees with the refraction indices reported
77 by Mereiter and Völlenkle (1978) for synthetic β-Maus’s salt.

78

79 Micro Raman spectroscopy

80 Micro-Raman spectra were collected on an unpolished sample of giacovazzoite in nearly back-scattered geometry with a
81 Horiba Jobin-Yvon XploRA Plus apparatus, equipped with a motorized *x-y* stage and an Olympus BX41 microscope with
82 a 10× objective. The 532 nm line of a solid-state laser was used. The minimum lateral and depth resolution was set to a
83 few μm. The system was calibrated using the 520.6 cm⁻¹ Raman band of silicon before each experimental session. Spectra
84 were collected in the range 200–4000 cm⁻¹ through multiple acquisitions with single counting time of 60 s, with laser
85 power filtered to 10% (2.5 mW) in order to avoid sample burning and hematite formation, as observed by Kampf et al.
86 (2016) for carlsonite. Figure 2 shows the Raman spectrum of giacovazzoite. Bands related to the SO₄ group modes occur
87 in the range 400 – 1200 cm⁻¹ (e.g., Myneni 2000). In agreement with Kampf et al. (2016), bands between ~1000 and
88 ~1200 cm⁻¹ are due to the *v*₁ and *v*₃ modes, whereas those in the range between 400 and 600 cm⁻¹ are related to the *v*₂ and
89 *v*₄ modes. Bands occurring at wavenumbers lower than 300 cm⁻¹ are interpreted as due to Fe–O modes and lattice
90 vibrations. The stretching of O–H bonds is represented by relatively weak and broad bands between 3000 and 3600 cm⁻¹,
91 whereas the bending modes can be observed at ~1625 cm⁻¹. It is worth noting that the Raman spectrum of giacovazzoite
92 shares some similarity with that of carlsonite (Kampf et al. 2016).

93

94 Chemistry

95 The chemical composition of giacovazzoite was determined from one polished crystal using a JEOL JXA 8200 electron
96 microprobe operating in WDS mode at 8 kV and 20 nA, with the beam diameter defocused to 15 μm in order to reduce
97 sample damage. The following standards and emission lines were used: synthetic MgSO₄ (*SKα*), hematite (*FeKα*), and
98 sanidine (*KKα*). The crystal was found homogeneous within analytical error, although only three spot analyses were
99 obtained owing to the small size of the polished surface. Table 1 gives the results of the chemical analysis.

100 However, the measurements were done under unfavourable conditions, because giacovazzoite slightly decomposed under
101 the electron beam. Indeed, high analytical totals after addition of calculated H₂O content, based on structural data, are
102 likely related to the partial dehydration of the sample under vacuum during carbon coating or during electron microprobe
103 analysis. Such a dehydration is manifested by the appearance of fractures on the sample surface.

104 The empirical formula of giacovazzoite, based on 25 anions per formula unit and 10 H₂O groups, is
105 K_{5.06}Fe³⁺_{2.98}O(SO₄)_{6.00}·10H₂O. The ideal formula is K₅Fe³⁺₃O(SO₄)₆·10H₂O, corresponding to (in wt%): SO₃ 42.30, Fe₂O₃
106 21.09, K₂O 20.74, H₂O 15.87, sum 100.00.

107

108 X-ray crystallography and structure refinement

109 Giacovazzoite was initially identified as a potential new mineral through X-ray powder diffraction, using a 114.6 mm
110 Gandolfi camera and Ni-filtered CuKα radiation. The mineral was found to be the natural counterpart of the synthetic β-
111 Maus’s salt (Mereiter and Völlenkle 1978). Unit-cell parameters refined from X-ray powder data (Table 2), on the basis
112 of 19 unequivocally indexed reflections, using the software UnitCell (Holland and Redfern 1997), are: *a* = 9.459(2), *b* =

113 18.445(9), $c = 18.130(4)$ Å, $\beta = 92.47(2)^\circ$, $V = 3160.2(12)$ Å³. These values fairly well match those of synthetic β -Maus's
114 salt: $a = 9.491(3)$, $b = 18.474(6)$, $c = 18.109(6)$ Å, $\beta = 92.38(5)^\circ$, $V = 3172.4$ Å³ (Mereiter and Völlenklee 1978).

115 A first data collection of giacovazzoite using a Bruker D8 Venture fitted with an air-cooled Photon II detector and
116 monochromatized MoK α radiation, performed at room T , resulted in a rapid dehydration of the mineral, forming a
117 compound having a smaller unit cell, with unit-cell parameters $a \sim 9.36$, $b \sim 18.17$, $c \sim 17.76$ Å, $\beta \sim 96.44^\circ$, $V \sim 3000$ Å³.
118 The analysis of the reflection conditions suggested the same space group of giacovazzoite, i.e., $P2_1/c$. Consequently, a
119 new crystal, previously identified through a Gandolfi pattern, was used and fragmented in three portions. The first one
120 was used for data collection using an Oxford Diffraction Excalibur PX Ultra diffractometer fitted with a 165 mm diagonal
121 Onyx CCD detector and CuK α radiation at room T . Refined unit-cell parameters agree with those of the synthetic β -
122 Maus's salt: $a = 9.4797(2)$, $b = 18.4454(5)$, $c = 18.0540(4)$ Å, $\beta = 92.626(2)^\circ$, $V = 3153.55(13)$ Å³. The reflection
123 conditions suggested the space group $P2_1/c$. The crystal structure was refined using Shelxl-2018 (Sheldrick 2015) starting
124 from the atomic coordinates of the synthetic β -Maus's salt given by Mereiter and Völlenklee (1978). Some H atoms showed
125 negative or too high displacement parameters, and therefore were removed from the structural model. The refinement
126 converged to $R_1 = 0.0442$ for 2072 reflections with $F_o > 4\sigma(F_o)$ and 506 refined parameters.

127 The second fragment was used for a data collection with the Bruker D8 Venture fitted with the air-cooled Photon II
128 detector and MoK α radiation at room T ; again, a rapid dehydration of the mineral, within 3 minutes from the beginning
129 of the data collection, was observed. Refined unit-cell parameters are $a = 9.3434(3)$, $b = 18.1838(5)$, $c = 17.7702(7)$ Å, β
130 $= 96.3810(10)^\circ$, $V = 3000.43(17)$ Å³. Its crystal structure was solved through direct methods using Shelxs-97 (Sheldrick
131 1997) and refined using Shelxl-2018 (Sheldrick 2015) to $R_1 = 0.0404$ for 6672 reflections with $F_o > 4\sigma(F_o)$ and 453
132 refined parameters.

133 Finally, the third fragment was used for the data collection using this same experimental apparatus at low T conditions
134 (100 K). The unit-cell volume was contracted with respect to that observed at room T ($\Delta V = -1.4\%$), but no dehydration
135 occurred. Unit-cell parameters are: $a = 9.4480(5)$, $b = 18.3183(9)$, $c = 17.9825(7)$ Å, $\beta = 92.274(2)^\circ$, $V = 3109.8(3)$ Å³.
136 The position of H atoms was refined starting from the atomic coordinates of the synthetic β -Maus's salt (Mereiter and
137 Völlenklee 1978); however, three H atoms [bonded to Ow(30) and Ow(31)] had too high displacement parameters and
138 were removed from the structural model. Soft restraints on the O–H bond distances were applied. The refinement
139 converged to $R_1 = 0.0587$ for 10254 reflections with $F_o > 4\sigma(F_o)$ and 511 refined parameters.

140 Details of data collections and refinements are given in Table 3. In this paper, the structural data collected at low T are
141 used, since they have a higher completeness than those collected at room T using CuK α radiation. Finally, the structural
142 details of the dehydration product of giacovazzoite are also briefly discussed. CIF of the crystal structures of giacovazzoite
143 (refined using low T data) and its dehydration product are available as Supplementary Material.

144

145 **Crystal structure description**

146 Sites, fractional atomic coordinates, and displacement parameters for giacovazzoite are reported in Table 4, whereas Table
147 5 gives selected bond distances. Bond-valence sums (BVS) are shown in Table 6. In agreement with Schindler et al.
148 (2006), the crystal structure of giacovazzoite can be described as a bipartite structure, consisting of a structural unit and
149 an interstitial unit. The former is defined by the $[\text{Fe}^{3+}_3\text{O}(\text{SO}_4)_6(\text{H}_2\text{O})_3]^{5-}$ cluster, whereas the latter, having formula
150 $\{\text{K}_5(\text{H}_2\text{O})_7\}^{5+}$, balances the negative charges of the structural unit and links the clusters together. Figure 3 shows the
151 crystal structure of giacovazzoite.

152 Ferric iron atoms are hosted at three independent sites, namely Fe(1), Fe(2), and Fe(3). Their bond distances range
153 between 1.910 Å and 2.079 Å. In each octahedron, the longer distance is formed with H₂O groups hosted at Ow(26),

154 Ow(27), and Ow(28), whereas the shorter distance is formed with the shared oxygen atom hosted at the O(25) site.
155 Average $\langle\text{Fe}-\text{O}\rangle$ distances are in the very narrow range between 2.003 and 2.005 Å. BVS range between 3.11 and 3.14
156 valence unit (v.u.). The cluster formed by these three Fe-centered octahedra sharing O(25) is connected, through corner-
157 sharing, with six independent SO_4 groups. The S–O bond distances range between 1.448 and 1.504 Å, with average $\langle\text{S}-$
158 $\text{O}\rangle$ values between 1.473 and 1.480 Å, to be compared with the grand value given by Hawthorne et al. (2000), i.e., 1.473
159 Å. BVS at the S sites range between 5.90 and 6.02 v.u.

160 Potassium atoms occupy five independent sites, with eight- [K(1), K(3), and K(4)], nine- [K(2)], and ten-fold coordination
161 [K(5)]. Bond distances range between 2.658 and 3.350 Å, with average bond distances ranging from 2.891 Å for the
162 eight-fold coordinated K(4) site to 3.006 Å for the ten-fold coordinated K(5) site. BVS at the K site range between 1.07
163 and 1.17 v.u.

164 The examination of the BVS at the O sites shows the occurrence of several underbonded atoms. This agrees with the
165 occurrence of H_2O groups, involved in H-bonding. Indeed, O atoms belonging to SO_4 groups usually are acceptors of one
166 or two H-bonds from H_2O groups, the only exception being represented by O atoms bonded to S(2) that are not involved
167 in any H-bond. Table 7 gives the geometrical features and the bond strength, calculated according to Ferraris and Ivaldi
168 (1988), of H-bonds in the crystal structure of giacovazzoite.

169 As highlighted above, the main structural feature of giacovazzoite is represented by isolated heteropolyhedral clusters
170 $[\text{Fe}^{3+}_3\text{O}(\text{SO}_4)_6(\text{H}_2\text{O})_3]^{5-}$. These clusters are connected along **b** through K atoms hosted at K(1), whereas along **c** the
171 connection is favoured by K atoms hosted at K(2), K(3), and K(5). Finally, the K atoms hosted at the K(4) site allowed
172 the connection of the $[\text{Fe}^{3+}_3\text{O}(\text{SO}_4)_6(\text{H}_2\text{O})_3]^{5-}$ clusters along **a**. This scaffolding results in channels running along **b** and
173 hosting H_2O groups at fractional atomic coordinates $x/a \sim 0$, $z/c \sim 0$ and $x/a \sim 0$ and $z/c \sim 1/2$. Among H_2O groups not
174 belonging to the heteropolyhedral $[\text{Fe}^{3+}_3\text{O}(\text{SO}_4)_6(\text{H}_2\text{O})_3]^{5-}$ clusters, six are bonded to K atoms, whereas one, occurring at
175 the Ow(31) site, is isolated, only being involved in H-bonds with other H_2O groups. Consequently, the structural formula
176 of giacovazzoite is $\text{K}_5[\text{Fe}^{3+}_3\text{O}(\text{SO}_4)_6(\text{H}_2\text{O})_3](\text{H}_2\text{O})_6 \cdot \text{H}_2\text{O}$.

177

178 **The dehydration product of giacovazzoite**

179 Giacovazzoite rapidly dehydrates under the microfocused X-ray beam, using $\text{MoK}\alpha$ radiation at room T . Unit-cell
180 parameters are contracted, showing the following variations: $\Delta a = -1.44\%$, $\Delta b = -1.42\%$, $\Delta c = -1.57\%$, and $\Delta V = -4.86\%$.
181 In addition, the β angle increases, passing from 92.63° at room T to 96.38° in the dehydrated compound. The crystal
182 structure of this latter phase has been solved and it is here compared with that of giacovazzoite. Atomic coordinates and
183 other structural details are reported in the CIF, available as Supplementary Material.

184 The general structural features of the dehydrated product are the same as those shown by giacovazzoite. The
185 $[\text{Fe}^{3+}_3\text{O}(\text{SO}_4)_6(\text{H}_2\text{O})_3]^{5-}$ clusters display the same geometrical features, with bond distances ranging between 1.908 and
186 2.094 Å, the shorter distances formed with the shared oxygen atom at the O(25) site and the longer ones with H_2O groups
187 hosted at Ow(26), Ow(27), and Ow(28) sites. Average $\langle\text{Fe}-\text{O}\rangle$ distances range between 1.996 and 2.010 Å, with BVS
188 between 3.08 and 3.18 v.u. Similarly, the dehydration does not affect the geometry of the SO_4 groups, with S–O distances
189 in the range 1.432–1.501 Å ($\langle\text{S}-\text{O}\rangle$ distances between 1.465 and 1.472 Å). BVS at the S sites range between 6.04 and
190 6.16 v.u.

191 Whereas the geometrical features of the structural unit are preserved, a reorganization of the interstitial unit occurs. Figure
192 4 shows the comparison between $\{100\}$ heteropolyhedral layers in giacovazzoite and its dehydration product, showing a
193 different arrangement of K atoms. The channels, running along **b** and hosting seven H_2O groups in giacovazzoite, host
194 one K atom in the dehydrated compound, along with ~ 2.5 H_2O groups. These H_2O groups are hosted at three positions:

195 one of them is a split position [Ow(31) – see CIF], with two sub-sites having a site occupancy of 0.76(1) and 0.24(1),
196 whereas another [Ow(32)] is only partially occupied (site occupancy 0.52). The split nature of the Ow(31) site, as well as
197 the partial occupancy at the Ow(32) position, may be related to some kind of disorder occurring during the dehydration
198 process and related to the reorganization of the H-bond system. Indeed, the structural investigation of the dehydration
199 product of giacovazzoite allowed the location of the H atoms of the H₂O groups belonging to the [Fe³⁺₃O(SO₄)₆(H₂O)₃]⁵⁻
200 clusters [Ow(26), Ow(27), and Ow(28) sites] and those of the isolated H₂O group hosted at Ow(29). This latter site occurs
201 in the space separating successive [Fe³⁺₃O(SO₄)₆(H₂O)₃]⁵⁻ clusters along *c*. As in giacovazzoite, O atoms of the (SO₄)
202 groups are acceptors of H-bonds, although the different arrangement of K atoms gives rise to new K–O bonds, favouring
203 higher BVS values at several O positions, in agreement with the lower number of H-bonds occurring in the dehydrated
204 compound. The structural formula of this dehydration product can be written as K₅[Fe³⁺₃O(SO₄)₆(H₂O)₃](H₂O)_{2.52}·H₂O.
205

206 **Origin of giacovazzoite and relationships with other metavoltine-related sulfates**

207 Giacovazzoite seems to be a late-stage mineral in the sulfate assemblage from Monte Arsiccio, having been found only
208 on the outer portion of the deeply altered pyrite orebody embedded in schist. In particular, in the studied samples, it is
209 always associated with alum-(K). According to Mereiter and Völlenkle (1978), synthetic β-Maus's salt formed through
210 decomposition of KFe(SO₄)₂·12H₂O. Indeed, this latter compound is not stable at room *T* and it transforms into β-Maus's
211 salt and a yellowish acid solution, according to the reaction: 5KFe(SO₄)₂·12H₂O → K₅Fe₃O(SO₄)₆·10H₂O + 2Fe³⁺ +
212 4SO₄²⁻ + 2H⁺ + 49H₂O. Consequently, giacovazzoite may form through the decomposition of Fe-rich domains within
213 alum-(K). The refinement of the crystal structure of alum-(K) from Monte Arsiccio through single-crystal X-ray
214 diffraction data points to a site occupancy, at the Al site, of (Al_{0.86}Fe_{0.14}) (unpublished data).

215 Giacovazzoite fits the 7.DF subdivision of the Nickel-Strunz classification (Strunz and Nickel 2001), i.e., Sulfates with
216 additional anions, with H₂O, with large and medium-sized cations. It shares the same [Fe³⁺₃O(SO₄)₆(H₂O)₃]⁵⁻ clusters with
217 a series of synthetic compounds (e.g., Scordari et al. 1994a) as well as natural phases, i.e., metavoltine (Giacovazzo et al.
218 1976), carlsonite (Kampf et al. 2016), and scordariite (Biagioni et al. 2019) (Table 8). Following Mills et al. (2009), these
219 minerals may be considered as members of the metavoltine family, where the term “family” can be applied to groups or
220 supergroups having similar structural and/or chemical features. Indeed, notwithstanding the occurrence of the same
221 heteropolyhedral [Fe³⁺₃O(SO₄)₆(H₂O)₃]⁵⁻ cluster, every mineral species shows peculiar topological features and belongs
222 to different supergroups. Taking into account the chemical variability shown by natural and synthetic compounds, mainly
223 related to different hydration states and the replacement of K⁺ by other large monovalent cations (e.g., Na⁺, NH₄⁺), it is
224 not unlikely that additional researches further expand the mineral systematic of the metavoltine family.
225

226 **Acknowledgments**

227 Two anonymous reviewers are thanked for their constructive comments on the manuscript. Mario Bianchini provided us
228 with the first specimen of giacovazzoite. CB acknowledges financial support from the University of Pisa through the
229 project P.R.A. 2018-2019 “Georisorse e Ambiente” (Grant No. PRA_2018_41).
230

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 308

309 **Table captions**

310 Table 1 – Electron microprobe data (in wt%) for giacovazzoite.

311 Table 2 – X-ray powder diffraction data (d in Å) for giacovazzoite. Only reflections with $I_{\text{calc}} > 5$ are given, if not observed.

312 Observed intensities were visually estimated: vs = very strong; s = strong; m = medium; mw = medium-weak; w
313 = weak; vw = very weak. The six strongest reflections are given in bold. The symbol * indicates the reflections
314 used for unit-cell refinement.

315 Table 3 – Crystal and experimental data for giacovazzoite and its dehydration product.

316 Table 4 – Sites, fractional atomic coordinates, and isotropic (*) or equivalent isotropic displacement parameters (in Å²)
317 for giacovazzoite.

318 Table 5 – Selected bond distances (in Å) for giacovazzoite.

319 Table 6 – Bond-valence sums (in valence units) for giacovazzoite.

320 Table 7 – Hydrogen bond lengths (in Å), bond angles (in °), and bond strengths (in valence units, v.u.) for giacovazzoite.

321 Table 8 – Selected compounds characterized by the $[\text{Fe}^{3+}_3\text{O}(\text{SO}_4)_6(\text{H}_2\text{O})_3]^{5-}$ cluster.

322

323 **Figure captions**

324 Figure 1 – Giacovazzoite, as orange prismatic crystals on whitish alum-(K) (FOV = 2 mm) (a) and back-scattered electron
325 image showing prismatic crystals on deeply altered microcrystalline pyrite.

326 Figure 2 – Raman spectrum of giacovazzoite in the range 200 – 4000 cm⁻¹.

327 Figure 3 – Crystal structure of giacovazzoite, as seen down **a** (a), **b** (b), and **c** (c). Brown and yellow polyhedra represent
328 Fe- and S-centered polyhedra, respectively. Light blue, pink, purple, and red circles represent Ow, H, K, and O
329 sites. Thick lines indicate O–H bonds, whereas dotted light blue lines are H···O bonds.

330 Figure 4 – Comparison between the crystal structure of giacovazzoite, as seen down **a** (a) and **b** (b), and its dehydrated
331 product, as seen down **a** (c) and **b** (d). Same symbols as in Figure 3. H-bonds are not shown in the dehydrated
332 phase.

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Table 1 – Electron microprobe data (in wt%) for giacovazzoite.

Constituent	Mean	Range	Stand. Dev. (σ)
K ₂ O	22.72	21.98 – 23.33	0.68
Fe ₂ O ₃	22.67	22.05 – 23.21	0.58
SO ₃	45.82	44.99 – 46.49	0.76
Sum	91.21	89.02 – 93.03	2.03
H ₂ O _{calc} *	17.18		
Total	108.39		

337

338

339 Table 2 – X-ray powder diffraction data (d in Å) for giacovazzoite. Only reflections with $I_{\text{calc}} > 5$ are given, if not observed.
 340 Observed intensities were visually estimated: vs = very strong; s = strong; m = medium; mw = medium-weak; w
 341 = weak; vw = very weak. The six strongest reflections are given in bold. The symbol * indicates the reflections
 342 used for unit-cell refinement.

I_{obs}	d_{obs}	I_{calc}	d_{calc}	$h k l$	I_{obs}	d_{obs}	I_{calc}	d_{calc}	$h k l$
s	9.1	100	9.47	1 0 0					
		35	9.02	0 0 2	mw	2.901	5	2.904	-1 0 6
vs	8.2*	62	8.21	0 2 1	w	2.842*	16	2.886	-2 5 1
vw	7.5*	3	7.51	1 1 1	w	2.800*	10	2.834	2 3 4
w	6.6*	6	6.61	1 2 0			6	2.808	3 3 0
w	6.2*	9	6.27	-1 2 1	w	2.717	3	2.722	-3 2 3
vw	5.4*	1	5.41	-1 2 2	mw	2.634*	4	2.713	-3 3 2
vw	4.99*	1	4.991	-1 1 3	w	2.575*	6	2.626	-1 3 6
w	4.73*	9	4.735	2 0 0			2	2.569	1 3 6
w	4.51*	4	4.493	-2 1 1			2	2.510	1 7 1
mw	4.15*	11	4.145	-1 0 4	mw	2.496	1	2.505	3 3 3
mw	4.02*	8	4.000	1 0 4			4	2.492	-1 1 7
		6	3.796	-1 4 2			2	2.487	2 0 6
mw	3.761	10	3.751	2 3 0	mw	2.294	2	2.305	3 1 5
		7	3.739	1 4 2			3	2.298	-4 1 2
w	3.678*	7	3.659	0 4 3			2	2.293	4 2 0
w	3.507*	6	3.509	-2 3 2	vw	2.260*	5	2.290	-2 1 7
m	3.442*	16	3.437	-1 3 4			2	2.261	-3 3 5
m	3.371	7	3.359	0 2 5	w	2.221	2	2.222	-4 1 3
		19	3.353	1 3 4	w	2.163	1	2.219	1 8 1
		3	3.236	-2 3 3	w	2.079			
mw	3.220	3	3.230	-1 5 2	w	2.053			
		5	3.209	-1 2 5	w	1.966			
mw	3.147*	11	3.157	3 0 0	w	1.908			
m	3.005	9	3.006	0 0 6	w	1.851			
		21	3.006	-1 5 3	w	1.814			
		28	2.963	1 5 3					
m	2.968	9	2.938	3 0 2					
		6	2.937	-2 3 4					

343

344

345 Table 3 – Crystal and experimental data for giacovazzoite and its dehydration product.

	Giacovazzoite <i>LT</i>	Giacovazzoite room <i>T</i>	Dehydration product
Crystal data			
Crystal size (mm)	0.060 × 0.055 × 0.030	0.050 × 0.045 × 0.030	0.065 × 0.050 × 0.040
Cell setting, space group	Monoclinic, <i>P2₁/c</i>	Monoclinic, <i>P2₁/c</i>	Monoclinic, <i>P2₁/c</i>
<i>a</i> (Å)	9.4480(5)	9.4797(2)	9.3434(3)
<i>b</i> (Å)	18.3183(9)	18.4454(5)	18.1838(5)
<i>c</i> (Å)	17.9825(7)	18.0540(4)	17.7702(7)
β (°)	92.274(2)	92.626(2)	96.3810(10)
<i>V</i> (Å ³)	3109.8(3)	3153.55(13)	3000.43(17)
<i>Z</i>	4	4	4
Data collection and refinement			
Radiation, wavelength (Å)	MoKα, 0.71073	CuKα, 1.54178	MoKα, 0.71073
Temperature (K)	100	293	293
2θ _{max} (°)	70.93	90.60	61.02
Measured reflections	43069	5495	33961
Unique reflections	14085	2568	9152
Reflections with <i>F_o</i> > 4σ(<i>F_o</i>)	10254	2072	6672
<i>R</i> _{int}	0.0678	0.0409	0.0521
<i>R</i> σ	0.0810	0.0593	0.0570
Range of <i>h, k, l</i>	-15 ≤ <i>h</i> ≤ 13, -29 ≤ <i>k</i> ≤ 23, -28 ≤ <i>l</i> ≤ 29	-7 ≤ <i>h</i> ≤ 8, -12 ≤ <i>k</i> ≤ 16, -16 ≤ <i>l</i> ≤ 10	-13 ≤ <i>h</i> ≤ 12, -25 ≤ <i>k</i> ≤ 25, -25 ≤ <i>l</i> ≤ 25
<i>R</i> [<i>F_o</i> > 4σ(<i>F_o</i>)]	0.0587	0.0442	0.0404
<i>R</i> (all data)	0.0887	0.0609	0.0654
<i>wR</i> (on <i>F_o</i> ²)	0.1556	0.1213	0.0981
Goof	1.058	0.902	1.060
Number of least-squares parameters	511	506	453
Maximum and minimum residual peak (<i>e</i> Å ⁻³)	1.42 [at 0.74 Å from Fe(2)] -1.32 [at 0.67 Å from Fe(1)]	0.71 [at 1.36 Å from K(2)] -0.66 [at 0.17 Å from H(321)]	0.73 [at 1.47 Å from Ow(31)a] -0.68 [at 0.71 Å from K(3)]

346

347

348 Table 4 – Sites, fractional atomic coordinates, and isotropic (*) or equivalent isotropic displacement parameters (in Å²)
 349 for giacovazzoite.

Site	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> _{eq}
K(1)	0.54415(8)	0.15573(4)	0.24416(4)	0.01300(13)
K(2)	0.63785(9)	0.22595(4)	0.03564(5)	0.01687(15)
K(3)	0.26611(9)	0.10184(4)	0.04798(4)	0.01583(15)
K(4)	0.12505(9)	0.20433(4)	0.27235(5)	0.01689(15)
K(5)	0.32617(9)	0.11271(4)	0.44081(4)	0.01598(15)
Fe(1)	0.31621(5)	0.41663(3)	0.25801(3)	0.00789(9)
Fe(2)	0.63609(5)	0.40773(3)	0.34320(3)	0.00819(9)
Fe(3)	0.59944(5)	0.39646(3)	0.15778(3)	0.00847(9)
S(1)	0.39126(9)	0.52165(4)	0.39297(4)	0.00851(14)
S(2)	0.39806(9)	0.29491(4)	0.38371(4)	0.00901(14)
S(3)	0.78161(9)	0.52346(4)	0.24106(5)	0.00932(14)
S(4)	0.81673(9)	0.29379(4)	0.24349(4)	0.00920(14)
S(5)	0.36450(9)	0.51371(4)	0.10715(4)	0.00941(14)
S(6)	0.31440(9)	0.29483(4)	0.12870(4)	0.00908(14)
O(1)	0.3330(3)	0.51081(13)	0.31504(13)	0.0106(4)
O(2)	0.5094(3)	0.46856(14)	0.40712(14)	0.0120(5)
O(3)	0.2797(3)	0.50662(14)	0.44520(14)	0.0124(5)
O(4)	0.4442(3)	0.59605(14)	0.40020(14)	0.0133(5)
O(5)	0.3076(3)	0.35512(13)	0.35081(13)	0.0108(4)
O(6)	0.5500(3)	0.31631(14)	0.37780(15)	0.0136(5)
O(7)	0.3680(3)	0.28700(15)	0.46209(14)	0.0145(5)
O(8)	0.3743(3)	0.22766(14)	0.34214(15)	0.0146(5)
O(9)	0.7352(3)	0.50089(13)	0.31633(14)	0.0124(5)
O(10)	0.7679(3)	0.45952(13)	0.18991(13)	0.0104(4)
O(11)	0.9320(3)	0.54472(14)	0.24815(14)	0.0122(4)
O(12)	0.6962(3)	0.58470(13)	0.21386(14)	0.0128(5)
O(13)	0.7938(3)	0.34690(14)	0.30513(14)	0.0128(4)
O(14)	0.6978(3)	0.30248(13)	0.18645(14)	0.0119(4)
O(15)	0.9524(3)	0.31061(14)	0.21054(14)	0.0126(4)
O(16)	0.8144(3)	0.21918(14)	0.27127(15)	0.0140(5)
O(17)	0.5112(3)	0.48214(15)	0.10742(14)	0.0134(5)
O(18)	0.2841(3)	0.47660(15)	0.16563(14)	0.0130(5)
O(19)	0.2937(3)	0.50093(14)	0.03541(14)	0.0132(5)
O(20)	0.3787(3)	0.59139(14)	0.12256(15)	0.0165(5)
O(21)	0.4500(3)	0.33140(15)	0.10840(14)	0.0146(5)
O(22)	0.2710(3)	0.32571(14)	0.20116(13)	0.0116(4)
O(23)	0.2070(3)	0.31122(15)	0.07069(14)	0.0140(5)
O(24)	0.3376(3)	0.21723(14)	0.13912(15)	0.0176(5)
O(25)	0.5174(3)	0.40817(13)	0.25241(13)	0.0097(4)
Ow(26)	0.0990(3)	0.42464(14)	0.27070(14)	0.0113(4)
Ow(27)	0.7620(3)	0.40300(14)	0.43961(14)	0.0130(5)
Ow(28)	0.7038(3)	0.38409(14)	0.05968(14)	0.0127(4)
Ow(29)	-0.0024(4)	0.0701(2)	0.1013(2)	0.0388(9)
Ow(30)	0.9195(5)	0.2133(2)	0.0743(2)	0.0414(9)
Ow(31)	0.9775(3)	0.40551(15)	0.05600(16)	0.0163(5)
Ow(32)	0.9556(4)	0.55378(17)	0.08561(17)	0.0210(6)
Ow(33)	0.9251(3)	0.72919(17)	0.07272(17)	0.0196(6)
Ow(34)	0.9614(3)	0.88056(16)	0.06621(16)	0.0172(5)

Ow(35)	0.7890(3)	0.20698(16)	0.42857(16)	0.0180(5)
H(261)	0.049(6)	0.387(3)	0.246(3)	0.05(2)*
H(262)	0.057(7)	0.463(3)	0.244(3)	0.06(2)*
H(271)	0.751(9)	0.438(3)	0.478(3)	0.07(3)*
H(272)	0.861(2)	0.403(4)	0.433(4)	0.05(2)*
H(281)	0.804(2)	0.384(3)	0.058(3)	0.022(14)*
H(282)	0.717(9)	0.427(2)	0.032(4)	0.06(2)*
H(291)	-0.009(8)	0.065(4)	0.1543(13)	0.06(2)*
H(292)	-0.088(5)	0.052(5)	0.075(4)	0.08(3)*
H(311)	0.055(4)	0.381(2)	0.076(2)	0.015(12)*
H(321)	0.024(6)	0.565(4)	0.051(3)	0.06(2)*
H(322)	0.023(5)	0.564(3)	0.124(2)	0.027(15)*
H(331)	0.882(7)	0.732(4)	0.0248(18)	0.046(19)*
H(332)	0.020(3)	0.719(3)	0.060(3)	0.024(14)*
H(341)	0.970(8)	0.8296(12)	0.069(4)	0.07(2)*
H(342)	0.926(6)	0.904(3)	0.107(2)	0.037(17)*
H(351)	0.795(7)	0.225(3)	0.3796(16)	0.036(17)*
H(352)	0.715(7)	0.173(4)	0.430(5)	0.11(4)*

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352 Table 5 – Selected bond distances (in Å) for giacovazzoite.

K(1)	–O(20)	2.743(3)	K(2)	–Ow(30)	2.733(4)	K(3)	–O(3)	2.720(3)	K(4)	–O(8)	2.658(3)
	–O(12)	2.749(3)		–Ow(35)	2.734(3)		–O(24)	2.743(3)		–O(15)	2.746(3)
	–O(8)	2.764(3)		–O(4)	2.769(3)		–O(7)	2.753(3)		–O(12)	2.772(3)
	–O(4)	2.823(3)		–O(7)	2.835(3)		–Ow(29)	2.809(4)		–Ow(33)	2.881(3)
	–O(16)	2.830(3)		–O(21)	2.963(3)		–O(4)	2.858(3)		–O(22)	2.936(3)
	–O(24)	2.890(3)		–Ow(28)	2.991(3)		–Ow(34)	2.931(3)		–O(16)	2.947(3)
	–O(1)	3.102(3)		–O(6)	3.026(3)		–O(9)	3.062(3)		–O(11)	2.993(3)
	–O(14)	3.245(3)		–O(14)	3.085(3)		–O(2)	3.313(3)		–O(24)	3.195(3)
	average	2.893		–Ow(27)	3.178(3)		average	2.898		average	2.891
				average	2.924						
K(5)	–O(19)	2.713(3)	Fe(1)	–O(25)	1.914(3)	Fe(2)	–O(25)	1.943(2)	Fe(3)	–O(25)	1.910(3)
	–O(8)	2.802(3)		–O(22)	1.992(2)		–O(6)	1.973(3)		–O(17)	1.979(3)
	–O(12)	2.828(3)		–O(18)	2.005(3)		–O(13)	2.003(3)		–O(14)	2.014(3)
	–Ow(32)	2.895(3)		–O(1)	2.010(2)		–O(9)	2.014(3)		–O(21)	2.026(3)
	–O(23)	2.979(3)		–O(5)	2.018(2)		–O(2)	2.026(3)		–O(10)	2.032(3)
	–O(17)	2.990(3)		–Ow(26)	2.079(3)		–Ow(27)	2.065(3)		–Ow(28)	2.067(3)
	–O(20)	3.078(3)		average	2.003		average	2.004		average	2.005
	–Ow(33)	3.194(3)									
	–O(7)	3.238(3)	S(1)	–O(4)	1.456(3)	S(2)	–O(8)	1.454(3)	S(3)	–O(12)	1.455(3)
	–O(21)	3.350(3)		–O(3)	1.466(3)		–O(7)	1.456(3)		–O(11)	1.474(3)
	average	3.006		–O(2)	1.495(3)		–O(6)	1.496(3)		–O(10)	1.492(2)
				–O(1)	1.498(2)		–O(5)	1.502(2)		–O(9)	1.498(3)
				average	1.479		average	1.477		average	1.480
			S(4)	–O(16)	1.456(3)	S(5)	–O(19)	1.448(2)	S(6)	–O(24)	1.449(3)
				–O(15)	1.466(3)		–O(20)	1.455(3)		–O(23)	1.457(3)
				–O(13)	1.497(3)		–O(18)	1.486(3)		–O(22)	1.493(3)
				–O(14)	1.499(2)		–O(17)	1.502(3)		–O(21)	1.504(3)
				average	1.480		average	1.473		average	1.476

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Table 6 – Bond-valence sums (in valence units) for giacovazzoite.

	K(1)	K(2)	K(3)	K(4)	K(5)	Fe(1)	Fe(2)	Fe(3)	S(1)	S(2)	S(3)	S(4)	S(5)	S(6)	Σ anions	H bonds	Σ anions ¹
O(1)	0.07					0.51			1.41						1.99		1.99
O(2)			0.04				0.49		1.41						1.94		1.94
O(3)			0.20						1.53						1.73	+0.23 +0.14	2.10
O(4)	0.15	0.18	0.14						1.57						2.04		2.04
O(5)						0.50				1.39					1.89		1.89
O(6)		0.09					0.56			1.41					2.06		2.06
O(7)		0.15	0.19		0.05					1.58					1.97		1.97
O(8)	0.18			0.24	0.16					1.58					2.16		2.16
O(9)			0.08				0.50				1.41				1.99		1.99
O(10)								0.48			1.43				1.91		1.91
O(11)				0.10							1.50				1.60	+0.21 +0.18 +0.14	2.13
O(12)	0.19			0.18	0.15						1.58				2.10		2.10
O(13)							0.52					1.40			1.92		1.92
O(14)	0.05	0.08						0.50				1.40			2.03		2.03
O(15)				0.19								1.53			1.72	+0.22 +0.12	2.06
O(16)	0.15			0.11								1.57			1.83	+0.16	1.99
O(17)					0.10			0.55					1.39		2.04		2.04
O(18)						0.52							1.45		1.97		1.97
O(19)					0.21								1.60		1.81	+0.22	2.03
O(20)	0.19				0.08								1.58		1.85	+0.19	2.04
O(21)		0.11			0.04			0.49						1.38	2.02		2.02
O(22)				0.11		0.53								1.42	2.06		2.06
O(23)					0.10									1.57	1.67	+0.19 +0.15	2.01
O(24)	0.13		0.19	0.06										1.61	1.99		1.99
O(25)						0.66	0.61	0.66							1.93		1.93
Ow(26)						0.42									0.42	-0.22 -0.21 +0.11	0.10
Ow(27)		0.06					0.43								0.49	-0.23 -0.25	0.01
Ow(28)		0.10						0.43							0.53	-0.22 -0.27	0.04
Ow(29)			0.16												0.16	-0.14 -0.18 +0.20	0.04
Ow(30)		0.20													0.20	-0.12 -0.20	-0.12
Ow(31)															0.00	-0.19 -0.19 +0.27 +0.20	0.09
Ow(32)					0.12										0.12	-0.14 -0.20 +0.20	-0.02
Ow(33)				0.13	0.06										0.19	-0.15 -0.21 +0.18	0.01
Ow(34)			0.11												0.11	-0.11 -0.18 +0.25	0.07
Ow(35)		0.20													0.20	-0.16 -0.19 +0.21	0.06
Σ cations	1.11	1.17	1.11	1.12	1.07	3.14	3.11	3.11	5.92	5.96	5.92	5.90	6.02	5.98			

Note: ¹ after H-bond correction.

Table 7 – Hydrogen bond lengths (in Å), bond angles (in °), and bond strengths (in valence units, v.u.) for giacovazzoite.

Donor (<i>D</i>) – H	<i>D</i> –H	Acceptor (<i>A</i>)	H... <i>A</i>	<i>D</i> –H... <i>A</i> angle	<i>D</i> ... <i>A</i>	<i>v.u.</i>
Ow(26)–H(261)	0.93(2)	O(15)	1.78(2)	173(6)	2.708(2)	0.22
Ow(26)–H(262)	0.93(2)	O(11)	1.91(4)	145(6)	2.728(4)	0.21
Ow(27)–H(271)	0.94(2)	O(3)	1.76(2)	173(8)	2.693(4)	0.23
Ow(27)–H(272)	0.95(2)	Ow(34)	1.73(3)	164(7)	2.652(4)	0.25
Ow(28)–H(281)	0.953(19)	Ow(31)	1.69(2)	166(5)	2.619(4)	0.27
Ow(28)–H(282)	0.95(2)	O(19)	1.79(3)	165(7)	2.714(4)	0.21
Ow(29)–H(291)	0.96(2)	O(11)	1.91(4)	153(7)	2.800(4)	0.18
Ow(29)–H(292)	0.97(2)	O(3)	2.02(3)	161(7)	2.956(5)	0.14
Ow(30)	-	O(15)	-	-	3.036(5)	0.12
Ow(30)	-	Ow(29)	-	-	2.763(6)	0.20
Ow(31)–H(311)	0.916(19)	O(23)	1.93(3)	152(4)	2.777(4)	0.19
Ow(31)	-	Ow(32)	-	-	2.751(4)	0.20
Ow(32)–H(321)	0.94(2)	Ow(31)	2.00(5)	136(6)	2.751(4)	0.20
Ow(32)–H(322)	0.937(19)	O(11)	2.45(5)	113(4)	2.945(4)	0.14
Ow(33)–H(331)	0.94(2)	O(23)	2.04(3)	154(6)	2.916(4)	0.15
Ow(33)–H(332)	0.951(19)	Ow(35)	1.82(3)	160(5)	2.733(4)	0.21
Ow(34)–H(341)	0.94(2)	Ow(33)	1.89(3)	162(7)	2.797(4)	0.18
Ow(34)–H(342)	0.923(19)	Ow(26)	2.25(3)	155(5)	3.116(4)	0.11
Ow(35)–H(351)	0.943(19)	O(16)	1.97(3)	157(6)	2.857(4)	0.16
Ow(35)–H(352)	0.94(2)	O(20)	1.96(7)	145(9)	2.779(4)	0.19

Table 8 – Selected compounds characterized by the $[\text{Fe}^{3+}_3\text{O}(\text{SO}_4)_6(\text{H}_2\text{O})_3]^{5-}$ cluster.

Name	Chemical formula	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	α (°)	β (°)	γ (°)	s.g.	Ref.
α -Maus's Salt	$\text{K}_2[\text{K}_{0.5}(\text{H}_2\text{O})_{0.5}]_6(\text{H}_3\text{O})_2[\text{Fe}^{3+}_3\text{O}(\text{SO}_4)_6(\text{H}_2\text{O})_3](\text{OH})_2$	9.71	9.71	18.96	90	90	120	$P6_3/m$	[1]
Metavoltine	$\text{K}_2\text{Na}_6\text{Fe}^{2+}[\text{Fe}^{3+}_3\text{O}(\text{SO}_4)_6(\text{H}_2\text{O})_3]_2 \cdot 12\text{H}_2\text{O}$	9.58	9.58	18.17	90	90	120	$P3$	[2]
β -Maus's Salt	$\text{K}_5[\text{Fe}^{3+}_3\text{O}(\text{SO}_4)_6(\text{H}_2\text{O})_3] \cdot 7\text{H}_2\text{O}$	9.49	18.47	18.11	90	92.4	90	$P2_1/c$	[3]
Salt X	$\text{K}_2[\text{K}_{0.41}(\text{H}_2\text{O})_{0.59}]_6\text{Na}_{3.98}(\text{H}_3\text{O})_{0.78}\text{X}^{+0.68}(\text{Fe}^{2+}_{0.05}\square_{0.95})[\text{Fe}^{3+}_3\text{O}(\text{SO}_4)_6(\text{H}_2\text{O})_3]_2 \cdot 5.91\text{H}_2\text{O}$	9.64	9.64	18.02	90	90	120	$P3$	[4]
Synthetic	$\text{K}_3[\text{K}_{0.33}(\text{H}_2\text{O})_{0.67}]_6\text{Na}_2[\text{Na}_{0.38}(\text{H}_3\text{O})_{0.12}(\text{H}_2\text{O})_{0.50}][\text{Fe}^{3+}_3\text{O}(\text{SO}_4)_6(\text{H}_2\text{O})_3]_2$	9.59	9.59	51.96	90	90	120	$R-3$	[5]
Synthetic	$[\text{Na}_{0.33}(\text{H}_2\text{O})_{0.67}]_{12}\text{Na}[\text{Fe}^{3+}_3\text{O}(\text{SO}_4)_6(\text{H}_2\text{O})_3]$	15.02	11.15	18.38	90	90	90	$Cmcm$	[6]
Synthetic	$[(\text{H}_2\text{O})_{0.50}(\text{H}_3\text{O})_{0.38}\text{Na}_{0.12}]_6[\text{Na}_{0.12}(\text{H}_3\text{O})_{0.88}]\{\text{K}_2[\text{K}_{0.33}(\text{H}_2\text{O})_{0.67}]\text{Na}_2[\text{Fe}^{3+}_3\text{O}(\text{SO}_4)_6(\text{H}_2\text{O})_3]_2\}$	9.62	9.62	35.97	90	90	120	$P-31c$	[7]
Synthetic	$\text{K}_{3.86}\text{Na}_{5.30}(\text{H}_3\text{O})_{0.84}[\text{Fe}^{3+}_3\text{O}(\text{SO}_4)_6(\text{H}_2\text{O})_3]_2 \cdot 11.08\text{H}_2\text{O}$	9.61	9.61	17.83	90	90	120	$P-3$	[8]
Carlsonite	$(\text{NH}_4)_5[\text{Fe}^{3+}_3\text{O}(\text{SO}_4)_6(\text{H}_2\text{O})_3] \cdot 4\text{H}_2\text{O}$	9.59	9.77	18.40	93.2	95.3	118.0	$P-1$	[9]
Giacovazzoite	$\text{K}_5[\text{Fe}^{3+}_3\text{O}(\text{SO}_4)_6(\text{H}_2\text{O})_3] \cdot 7\text{H}_2\text{O}$	9.48	18.45	18.05	90	92.6	90	$P2_1/c$	[10]
Scordariite	$\text{K}_8(\text{Fe}^{3+}_{0.67}\square_{0.33})[\text{Fe}^{3+}_3\text{O}(\text{SO}_4)_6(\text{H}_2\text{O})_3]_2 \cdot 8\text{H}_2\text{O}$	9.75	9.75	53.52	90	90	120	$R-3$	[11]

[1] Giacovazzo et al. (1975); [2] Giacovazzo et al. (1976); [3] Mereiter and Völlenkle (1978); [4] Scordari (1980); [5] Scordari (1981); [6] Scordari et al. (1994b); [7] Scordari and Milella (1983); [8] Scordari and Stasi (1990); [9] Kampf et al. (2016); [10] this work; [11] Biagioni et al. (2019).



Figure 1 – Giacovazzoite, as orange prismatic crystals on whitish alum-(K) (FOV = 2 mm).

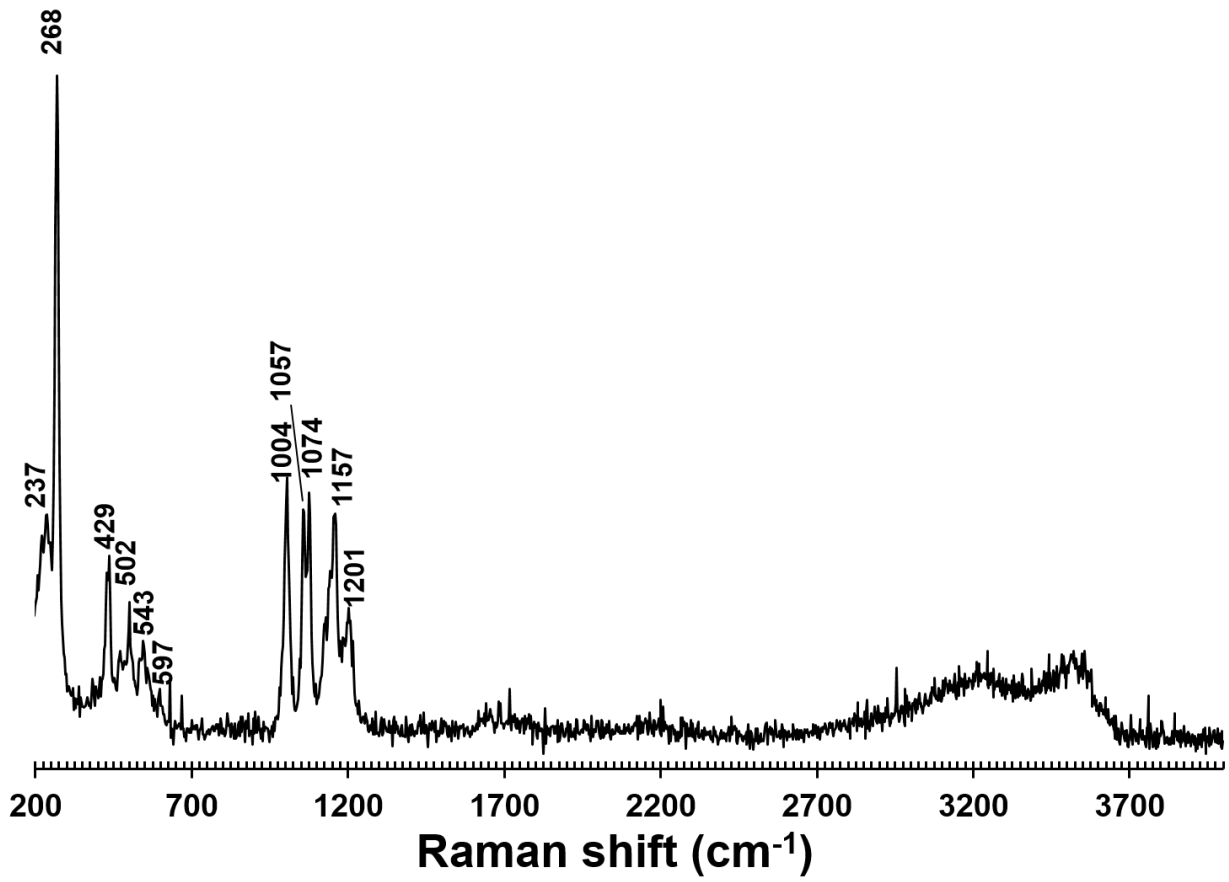


Figure 2 – Raman spectrum of giacovazzoite in the range 200 – 4000 cm^{-1} .

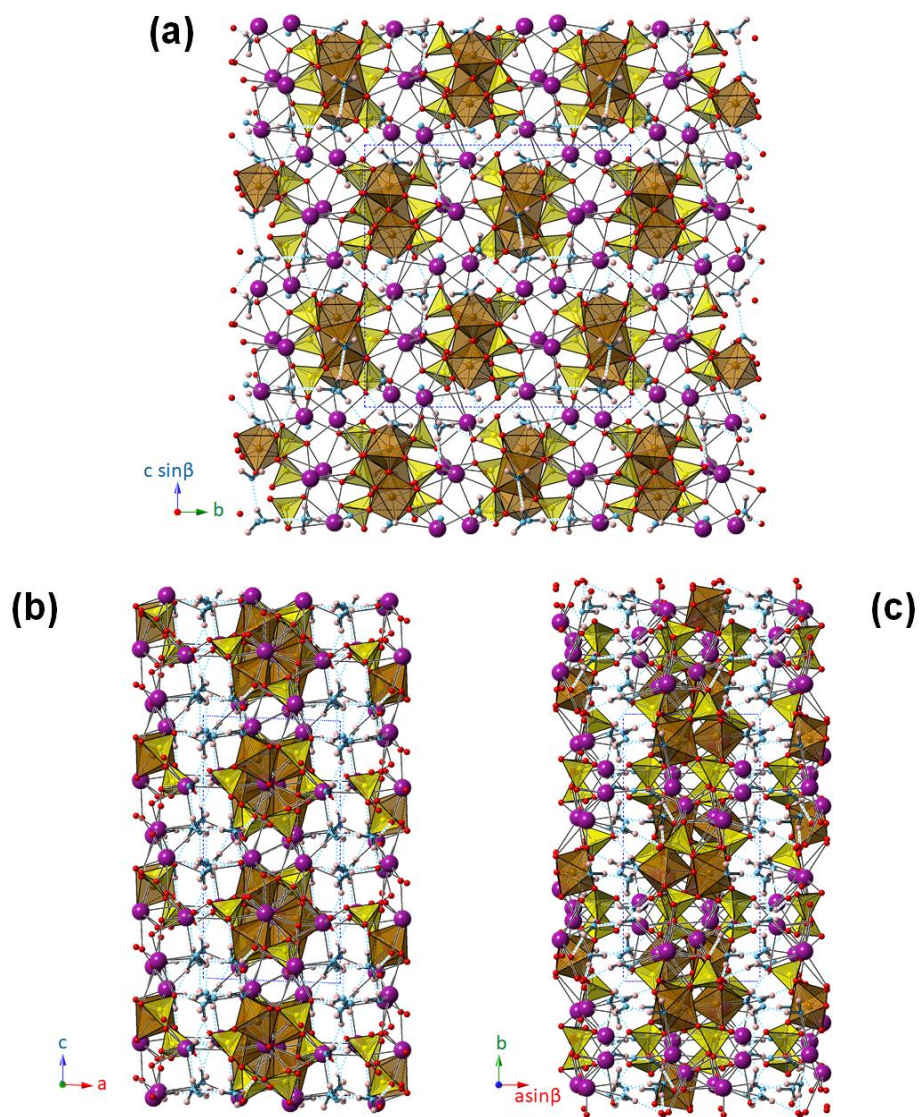


Figure 3 – Crystal structure of giacovazzoite, as seen down **a** (a), **b** (b), and **c** (c). Brown and yellow polyhedra represent Fe- and S-centered polyhedra, respectively. Light blue, pink, purple, and red circles represent Ow, H, K, and O sites. Thick lines indicate O–H bonds, whereas dotted light blue lines are H···O bonds.

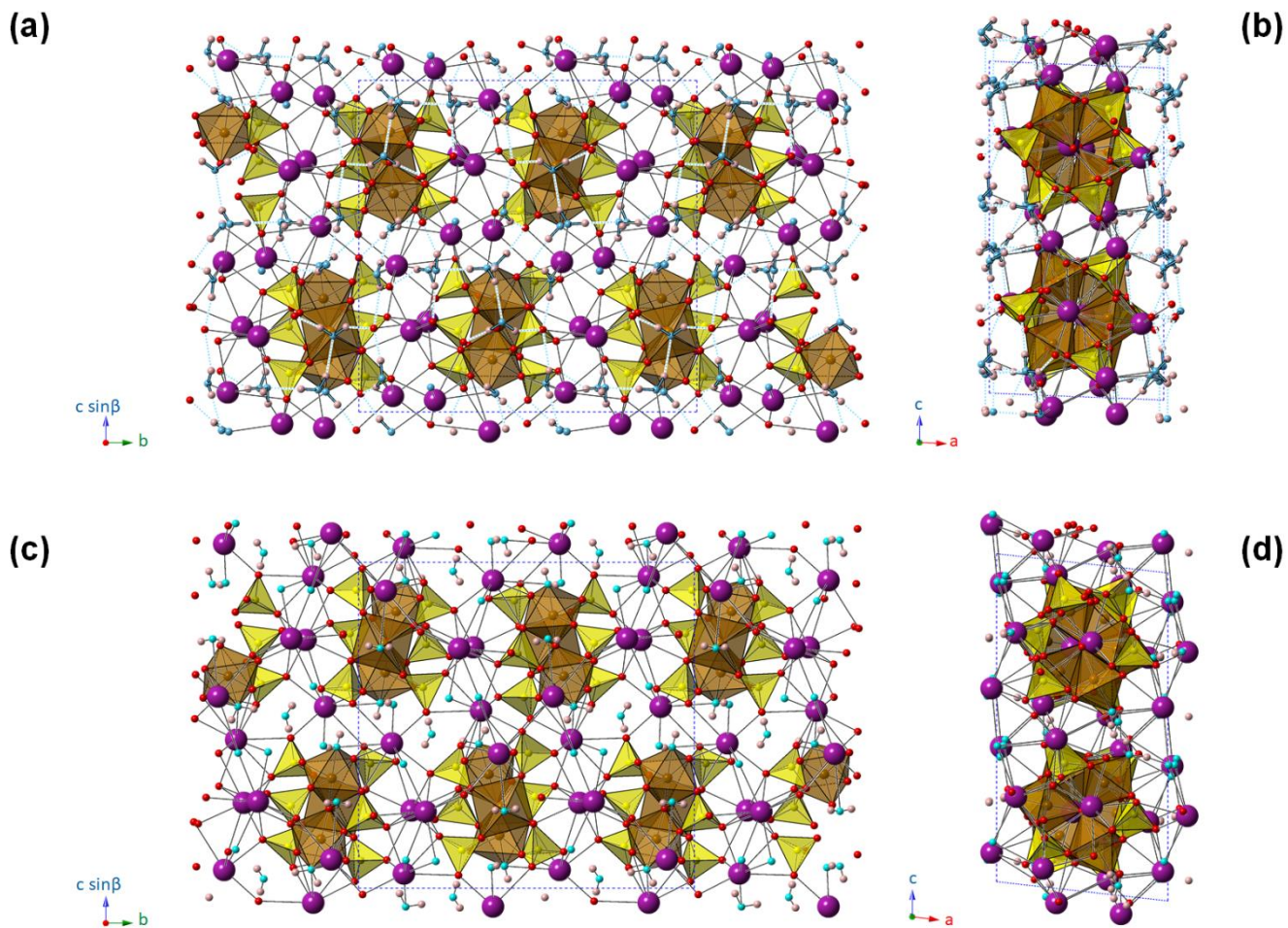
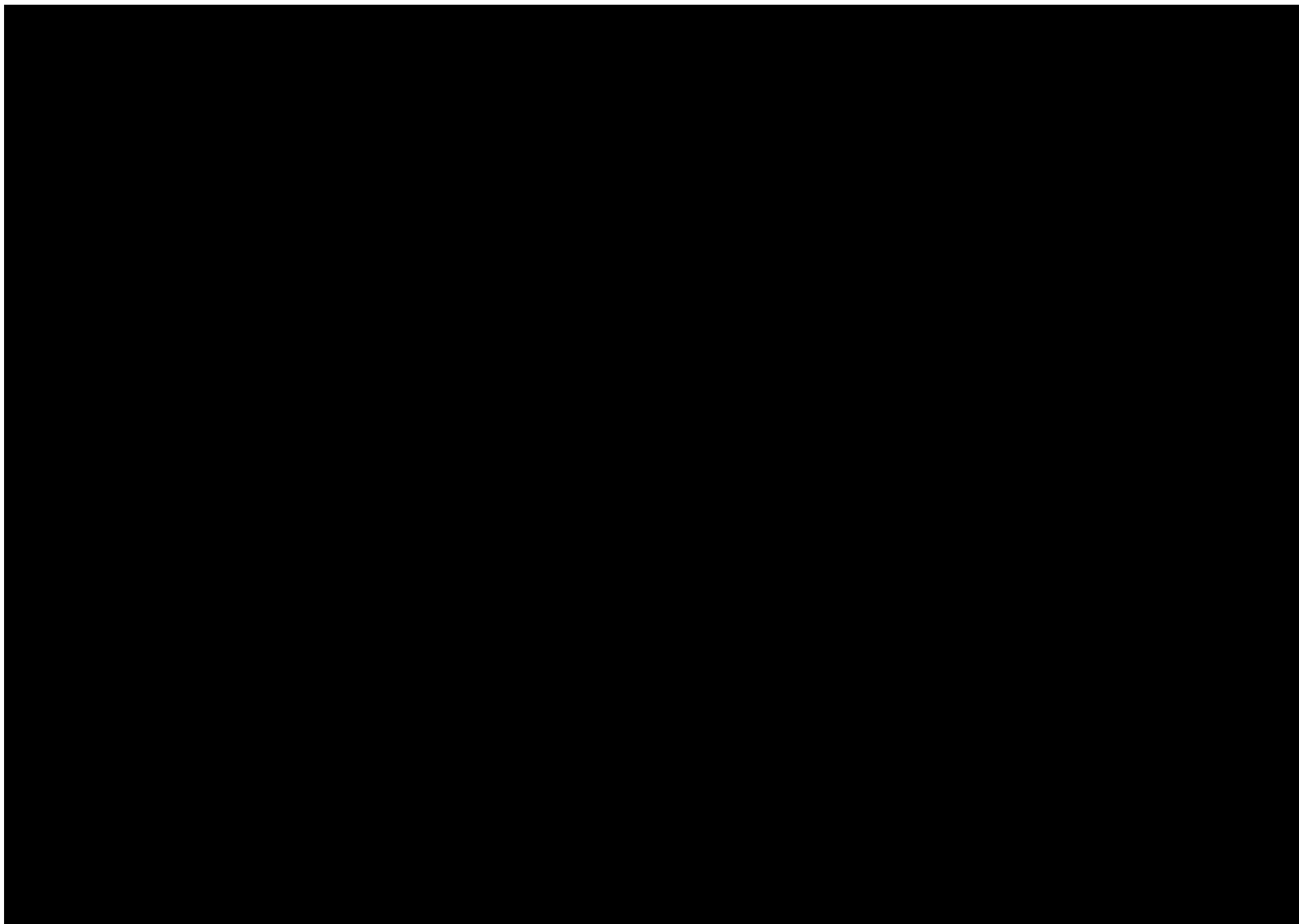
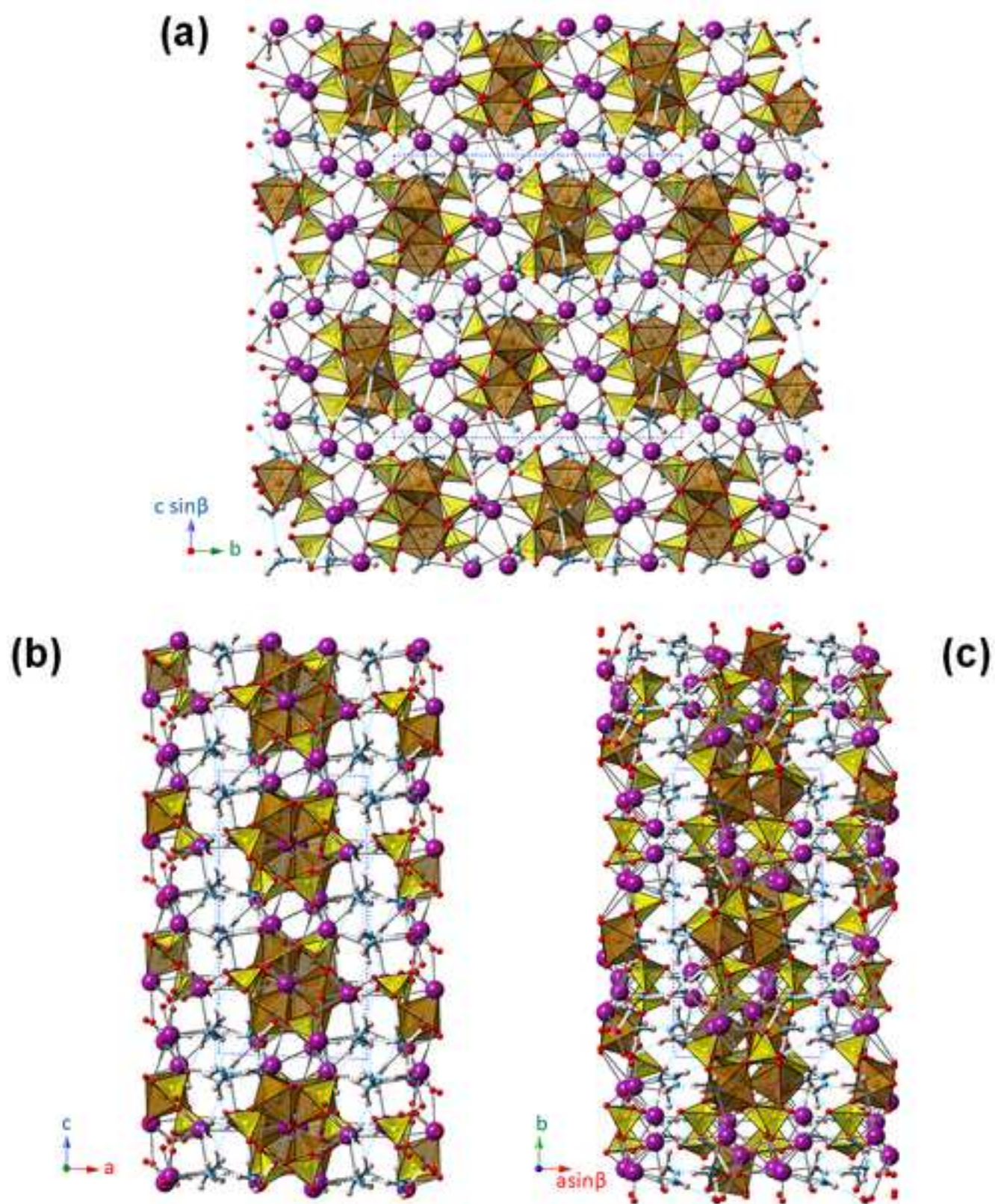


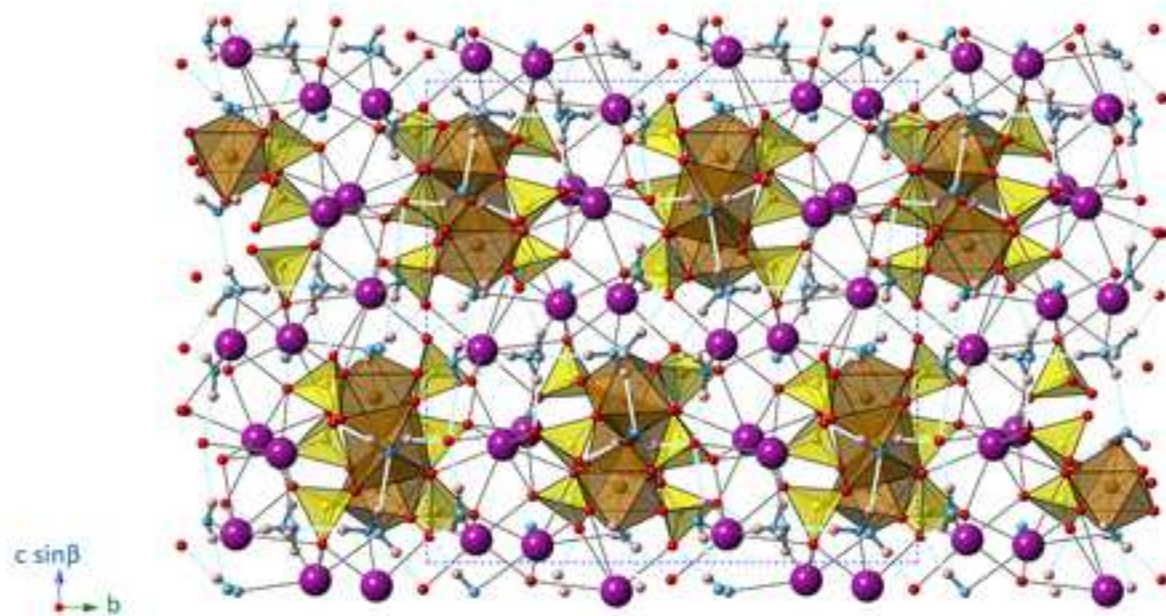
Figure 4 – Comparison between the crystal structure of giacovazzoite, as seen down **a** (a) and **b** (b), and its dehydrated product, as seen down **a** (c) and **b** (d). Same symbols as in Figure 3. H-bonds are not shown in the dehydrated phase.



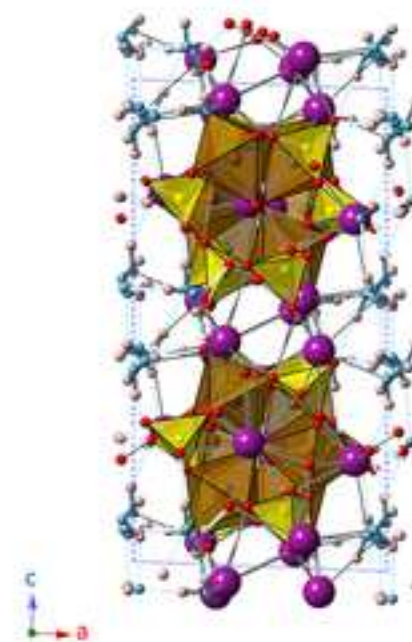




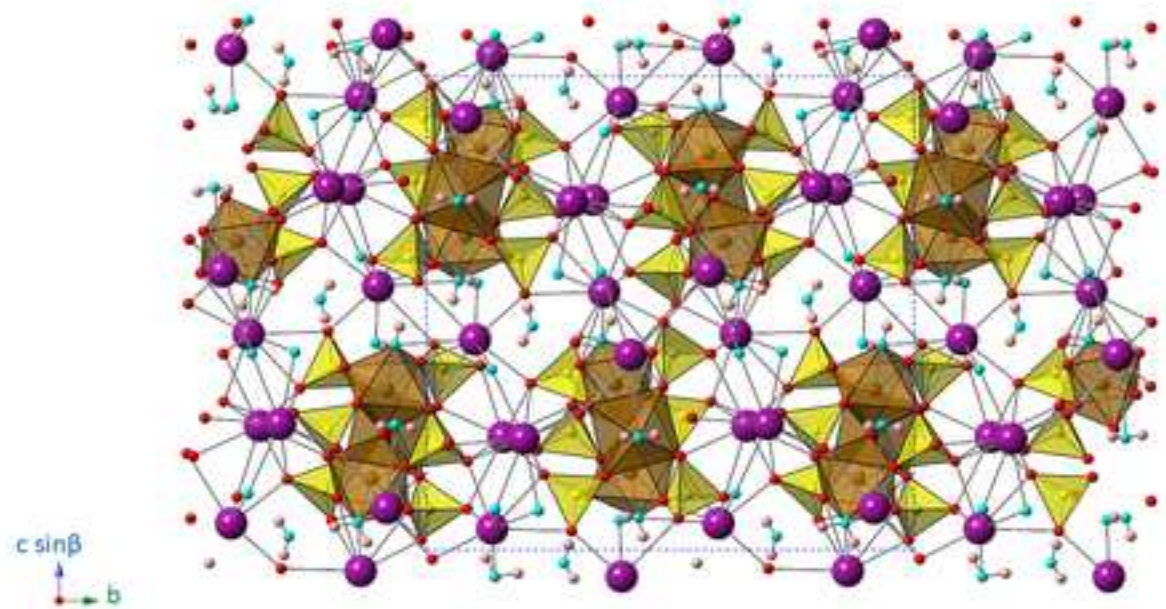
(a)



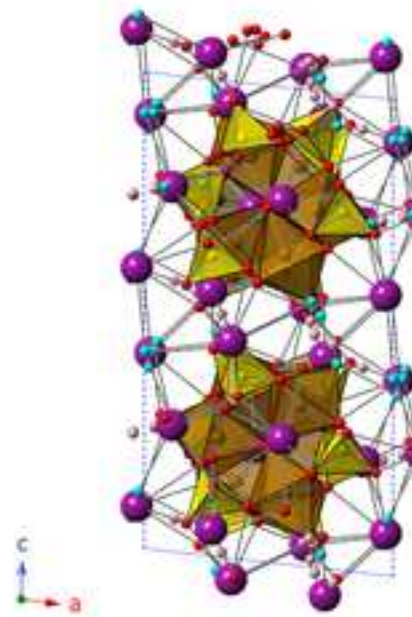
(b)

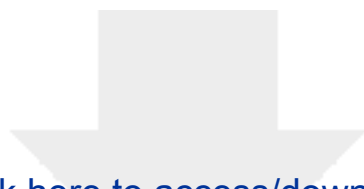


(c)



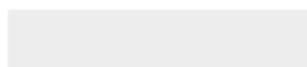
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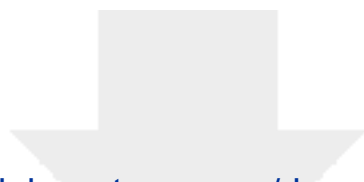




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