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New Crystal-Structure Data on Bohuslavite, $Fe^{3+}_4(PO_4)_3(SO_4)(OH)(H_2O)_{10} \cdot nH_2O$

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Abstract: Bohuslavite, $Fe^{3+}_4(PO_4)_3(SO_4)(OH)(H_2O)_{10} \cdot nH_2O$, was first described from the Buca della Vena mine (Apuan Alps, Tuscany, Italy) and from the Horní Město deposit (northern Moravia, Czech Republic). Its full characterization was a difficult task, owing to the very low diffraction quality of available material. Notwithstanding a physically reasonable structural model, some issues remained uncertain. A new intensity data collection on a sample from the Buca della Vena mine allowed us to improve our knowledge of the crystal structure of bohuslavite. This mineral is triclinic, $P1$, with unit-cell parameters a = 13.3722(15), b = 13.3488(18), c = 21.585(3) Å, α = 92.345(6), β = 90.153(8), γ = 120.34(2)°, V = 3321.2(11) Å^3, Z = 4. The crystal structure of bohuslavite has been refined to R_1 = 0.1498 on the basis of 19,578 unique reflections with $F_o > 4\sigma(F_o)$ and 773 refined parameters. The actual (SO_4) distribution is clarified, as well as the role of some H_2O groups, whereas some minor details remain to be solved.

Keywords: bohuslavite; sulfate; phosphate; iron; crystal structure; Buca della Vena mine; Apuan Alps; Italy

1. Introduction

Secondary mineral assemblages deriving from the alteration of pyrite ore deposits in the southern Apuan Alps have been known since the 19th Century (e.g., [1]), but only in the last decade have some mineralogical investigations focused on their characterization (e.g., [2]). These studies revealed a quite interesting mineralogical complexity coupled with the occurrence of well-crystallized specimens allowing an improvement in the crystal-chemical knowledge of this mineral class; for instance, a better definition of coquimbite was provided [3], and new data on the rare fluo-sulfates khademite and wilcoxite were collected [4,5]. Moreover, some new mineral species were discovered and described: the K-Fe^{3+} sulfates giacovazzoite, magnanelliite, and scordariite [6–8], as well as the Fe^{3+} hydrated hydroxy-sulfate-phosphate bohuslavite [9].

Among these new species, bohuslavite could be relatively widespread in several acid mine drainage systems associated with P-bearing rocks, as suggested by its further findings at Horní Město (Czech Republic) and at the Jeremias Glück mine (Germany) [9]; probably, its identification can be biased by its association with other Fe^{3+}-phosphate-sulfate minerals (e.g., destinezite and diadochite) and the small size of its crystals. Indeed, the type description of this species was made problematic by the relatively bad quality of the available material, requiring a multi-technique approach for its characterization. Electron microprobe analysis and X-ray powder diffraction data suggested the uniqueness of this compound, but the unsatisfying quality of its crystal structure model made necessary the collection of other data in order to confirm some structural features. Notwithstanding these efforts, some details remain poorly constrained, for instance, the actual configuration of SO_4 groups. Recently, new X-ray intensity data were collected on a small crystal of

bohuslavite from its type locality, the Buca della Vena mine (Apuan Alps, Tuscany, Italy). These new data improved our picture of this mineral and are reported in this paper.

2. Experimental

A thin pseudo-hexagonal crystal of bohuslavite was picked up from the holotype specimen # 19899 kept in the mineralogical collection of the Museo di Storia Naturale of the Università di Pisa. Intensity data were collected using a Bruker D8 Venture operating at 50 kV and 1.4 mA and equipped with an air-cooled Photon III CCD detector (Centro per l'Integrazione della Strumentazione dell'Università di Pisa, CISUP, Pisa, Italy). Graphite-monochromatized Mo$K\alpha$ radiation was used. The detector-to-crystal working distance was set to 38 mm. A total of 2633 frames was collected using φ and ω scan modes, with an exposure time of 90 s per frame. Intensity data were integrated and corrected for the Lorentz-polarization factor, background effects, and absorption using the software package Apex 4 [10]. The reduced unit-cell is triclinic, with a = 13.2915(18), b = 13.3488(18), c = 21.585(3) Å, α = 87.655(6), β = 87.491(6), γ = 60.258(4)°, V = 3321.2(8) Å^3. In order to compare this cell with that reported by [9], the transformation matrix [$\bar{1}$ 1 0 | 0 $\bar{1}$ 0 | 0 0 1] was applied, obtaining the following cell: a = 13.3722(15), b = 13.3488(18), c = 21.585(3) Å, α = 92.345(6), β = 90.153(8), γ = 120.34(3)°, V = 3321.2(11) Å^3. These unit-cell parameters can be compared with those given by [9] for the samples from Buca della Vena mine and Horní Město: a = 13.376(3), b = 13.338(3), c = 10.863(4) Å, α = 92.80(2), β = 91.03(2), γ = 119.92(2)°, V = 1675.7(9) Å^3, and a = 13.393(8), b = 13.349(7), c = 21.525(14) Å, α = 92.509(9), β = 92.293(12), γ = 119.839(6)°, V = 3326(3) Å^3, respectively. It is worth noting that a doubling of the c parameter was also reported for the Italian sample, but the reflections were usually too weak and diffuse to be accurately measured. On the contrary, as shown in Figure 1, the new crystal studied in this work was characterized not only by sharp reflections in the *hk*0 reciprocal lattice layer but also by the reflections in the *h0l* and *0kl* layersbeinge relatively sharp. At higher resolution, reflections are diffuse, probably owing to stacking disorder along the **c*** of the studied crystal.
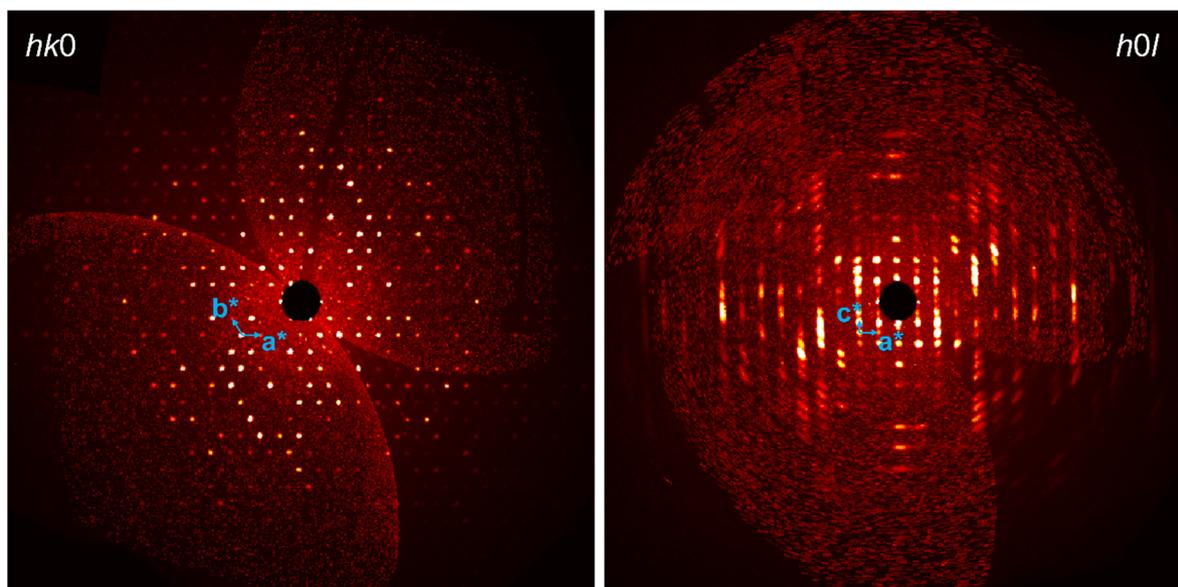
Figure 1. Reconstructed precession images of *hk*0 and *h0l* reciprocal lattice layers of the studied crystal.

The statistical tests on the distribution of $|E|$ values ($|E^2-1|$ = 0.992) suggested a centric nature of bohuslavite, in agreement with what was observed by [9] for the crystal structure solution performed in the $P\bar{1}$ space group, with c ~ 10.8 Å. The crystal structure was solved using ShelxTL [11]. However, whereas one structural layer was

relatively well-defined, being formed by Fe-centered octahedra and P-centered tetrahedra, as in Mauro et al. [9]'s structural model, the other layer was poorly defined, with atomic distances physically unsound. Consequently, the solution in the acentric space group $P1$ was tried. After having located heavy atoms (Fe and P), the positions of S and O atoms were found through successive difference-Fourier maps. Both structural layers stacked along **c** are relatively well-defined, with physically reasonable bond distances. Finally, several maxima located in the interlayer and within structural channels were interpreted as due to H_2O groups. The structural model was refined using Shelxl-2018 [11]. Neutral scattering factors for Fe, P, S, and O atoms were taken from the *International Tables of Crystallography* [12]. Anisotropic displacement parameters were modeled for cations, whereas anions were refined isotropically. In the final stages of the refinement, some restraints were imposed on P–O and S–O bond distances. Some constraints on the values of the anisotropic displacement parameters for some Fe and P sites were added in order to avoid negatively defined values. Three maxima interpreted as H_2O groups were found to be split and the sum of the occupancy of the split positions was constrained to full occupancy. After several cycles of refinement, the R value converged to 0.1498 for 19,578 unique reflections with $F_o > 4\sigma(F_o)$ and 773 refined parameters. Table 1 gives details of data collection and refinement. Atom coordinates, site occupancy factors, and displacement parameters are reported in the Crystallographic Information File (CIF), made available as Supplementary Material linked to this article.

Table 1. Crystal and experimental details for bohuslavite.

Crystal Data	
Crystal size (mm)	$0.060 \times 0.040 \times 0.010$
Cell setting, space group	Triclinic, $P1$
a (Å)	13.3722(15)
b (Å)	13.3488(18)
c (Å)	21.585(3)
α (°)	92.345(6)
β (°)	90.153(8)
γ (°)	120.34(2)
V (Å^3)	3321.2(11)
Z	4
Data Collection and Refinement	
Radiation, wavelength (Å)	Mo$K\alpha$, 0.71073
Temperature (K)	293(2)
$2\theta_{max}$ (°)	57.34
Measured reflections	107166
Unique reflections	29739
Reflections with $F_o > 4\sigma(F_o)$	19578
R_{int}	0.0726
$R\sigma$	0.0761
Range of h, k, l	$-17 \leq h \leq 17$, $-17 \leq k \leq 17$, $-28 \leq l \leq 28$
$R\ [F_o > 4\sigma(F_o)]$	0.1498
R (all data)	0.1968
wR (on $F_o{}^2$)	0.4527
Goof	1.089
Absolute structure parameter [13]	0.47(6)
Number of least-squares parameters	773
Maximum and minimum residual peak (e Å^{-3})	4.69 [at 1.92 Å from O(29)] -2.07 [at 1.25 Å from O(75)]

3. Crystal Structure Description

The crystal structure of bohuslavite is characterized by sixteen independent Fe sites, twelve P sites, four S positions, and 128 anion positions. Selected bond distances and bond-valence sums (BVS) for Fe-, P-, and S-centered polyhedra are given in Table 2. The main structural features previously described in [9] are confirmed. The crystal structure of bohuslavite is formed by {001} heteropolyhedral layers, formed by the connection of Fe-centered octahedra and P-centered tetrahedra. Sulfate groups are corner-bonded to these layers, decorating them on both sides (Figure 2). The refinement of the crystal structure allowed the identification of 20 additional atom positions located in the interlayers and in the channels running along **c**. These atoms were interpreted as O atoms of H_2O groups.

Table 2. Selected bond distances (Å) and bond-valence sums (BVS, in valence units) for cation sites in bohuslavite.

Fe(11)	–O(5)	1.907(18)	Fe(21)	–O(9)	1.957(18)	Fe(31)	–O(14)	1.93(2)	Fe(41)	–O(16)	1.946(16)
	–O(2)	1.938(18)		–O(10)	1.960(18)		–O(15)	1.955(18)		–O(19)	1.95(2)
	–O(3)	1.959(19)		–O(8)	1.972(18)		–O(17)	1.97(2)		–O(24)	1.971(16)
	–O(6)	2.05(2)		–O(12)	2.04(3)		–O(22)	2.01(3)		–O(21)	2.03(2)
	–O(4)	2.09(2)		–O(11)	2.04(3)		–O(23)	2.08(3)		–O(20)	2.08(3)
	–O(7)	2.14(3)		–O(13)	2.10(3)		–O(18)	2.08(3)		–O(25)	2.10(3)
	average	2.01		average	2.01		average	2.00		average	2.01
	BVS	3.09		BVS	3.06		BVS	3.13		BVS	3.06
Fe(51)	–O(27)	1.916(17)	Fe(61)	–O(42)	1.903(18)	Fe(71)	–O(32)	1.899(16)	Fe(81)	–O(37)	1.906(18)
	–O(26)	1.918(18)		–O(31)	1.923(15)		–O(46)	1.911(18)		–O(36)	1.913(19).
	–O(40)	1.961(19)		–O(30)	1.926(19)		–O(33)	1.945(19)		–O(48)	1.94(2)
	–O(28)	2.03(2)		–O(45)	2.04(3)		–O(35)	2.07(3)		–O(47)	2.02(3)
	–O(29)	2.07(3)		–O(44)	2.06(2)		–O(34)	2.07(3)		–O(39)	2.04(2)
	–O(41)	2.09(3)		–O(43)	2.14(2)		–O(1)	2.08(2)		–O(38)	2.08(2)
	average	2.00		average	2.00		average	2.00		average	1.98
	BVS	3.21		BVS	3.22		BVS	3.24		BVS	3.33
P(11)	–O(5)	1.515(17)	P(21)	–O(37)	1.513(16)	P(31)	–O(2)	1.510(16)	P(41)	–O(15)	1.507(17)
	–O(32)	1.517(15)		–O(27)	1.519(16)		–O(9)	1.524(16)		–O(36)	1.522(17)
	–O(26)	1.545(16)		–O(31)	1.536(14)		–O(17)	1.537(17)		–O(46)	1.536(16)
	–O(8)	1.551(16)		–O(19)	1.538(16)		–O(42)	1.544(16)		–O(30)	1.544(16)
	average	1.532		average	1.526		average	1.529		average	1.527
	BVS	4.86		BVS	4.93		BVS	4.91		BVS	4.93
P(51)	–O(40)	1.509(16)	P(61)	–O(24)	1.503(15)	S(11)	–O(39)	1.466(18)	S(21)	–O(6)	1.48(2)
	–O(3)	1.516(16)		–O(33)	1.514(17)		–O(50)	1.48(2)		–O(53)	1.48(2)
	–O(16)	1.520(15)		–O(10)	1.528(16)		–O(49)	1.49(2)		–O(54)	1.48(2)
	–O(14)	1.533(18)		–O(48)	1.531(18)		–O(51)	1.49(2)		–O(52)	1.49(2)
	average	1.520		average	1.519		average	1.48		average	1.48
	BVS	5.03		BVS	5.04		BVS	5.88		BVS	5.86
Fe(12)	–O(102)	1.89(3)	Fe(22)	–O(62)	1.89(3)	Fe(32)	–O(67)	1.89(4)	Fe(42)	–O(72)	1.87(3)
	–O(56)	1.89(3)		–O(57)	1.96(3)		–O(68)	1.93(3)		–O(91)	1.93(3)
	–O(58)	1.97(3)		–O(65)	1.98(4)		–O(55)	1.96(2)		–O(75)	1.95(3)
	–O(59)	2.06(3)		–O(64)	1.99(3)		–O(70)	2.02(4)		–O(74)	2.05(5)
	–O(60)	2.12(3)		–O(63)	2.02(5)		–O(69)	2.05(4)		–O(77)	2.11(3)
	–O(61)	2.13(3)		–O(66)	2.04(4)		–O(71)	2.12(4)		–O(76)	2.11(4)
	average	2.01		average	1.98		average	2.00		average	2.00
	BVS	3.16		BVS	3.33		BVS	3.24		BVS	3.20
Fe(52)	–O(79)	1.86(3)	Fe(62)	–O(84)	1.86(2)	Fe(72)	–O(90)	1.87(3)	Fe(82)	–O(96)	1.84(2)
	–O(78)	1.88(3)		–O(85)	1.89(3)		–O(92)	1.92(3)		–O(97)	1.91(3)
	–O(81)	1.97(3)		–O(86)	1.93(4)		–O(73)	1.93(3)		–O(98)	1.94(3)
	–O(80)	2.04(3)		–O(88)	2.01(4)		–O(93)	2.01(4)		–O(99)	2.00(4)
	–O(83)	2.11(4)		–O(87)	2.02(4)		–O(94)	2.11(3)		–O(100)	2.05(4)
	–O(82)	2.13(3)		–O(89)	2.06(2)		–O(95)	2.22(4)		–O(101)	2.11(3)
	average	2.00		average	1.96		average	2.01		average	1.98
	BVS	3.27		BVS	3.54		BVS	3.20		BVS	3.45

Table 2. *Cont.*

| P(12)	–O(92)	1.51(2)	P(22)	–O(78)	1.52(2)	P(32)	–O(81)	1.52(2)	P(42)	–O(90)	1.50(2)
	–O(55)	1.52(2)		–O(98)	1.52(2)		–O(91)	1.53(2)		–O(62)	1.52(2)
	–O(86)	1.54(2)		–O(84)	1.53(2)		–O(58)	1.53(2)		–O(85)	1.52(2)
	–O(97)	1.54(2)		–O(75)	1.55(2)		–O(67)	1.53(3)		–O(72)	1.57(2)
	average	1.53		average	1.53		average	1.53		average	1.53
	BVS	4.92		BVS	4.89		BVS	4.92		BVS	4.93
P(52)	–O(68)	1.52(2)	P(62)	–O(79)	1.51(2)	S(12)	–O(103)	1.47(2)	S(22)	–O(106)	1.46(2)
	–O(56)	1.52(2)		–O(73)	1.51(2)		–O(104)	1.47(2)		–O(107)	1.47(2)
	–O(96)	1.52(2)		–O(64)	1.53(2)		–O(89)	1.48(2)		–O(59)	1.48(2)
	–O(57)	1.53(2)		–O(102)	1.54(2)		–O(105)	1.49(2)		–O(108)	1.48(2)
	average	1.52		average	1.52		average	1.48		average	1.47
	BVS	4.99		BVS	4.99		BVS	5.94		BVS	6.03
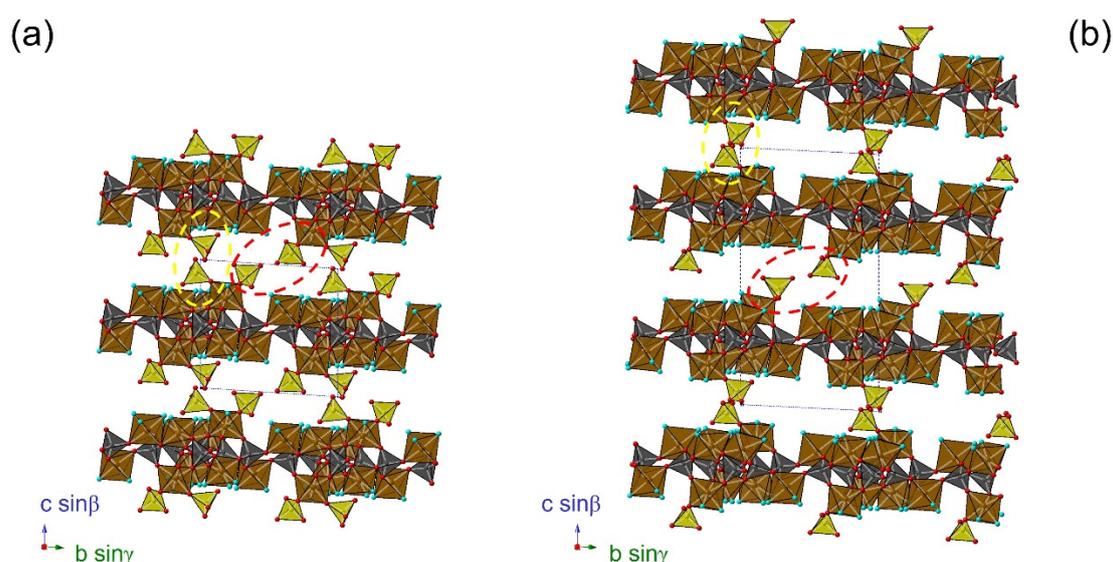
Figure 2. Comparison between the $c \sim 10.8$ Å (**a**) and $c \sim 21.6$ Å (**b**) crystal structure of bohuslavite, seen down **a**. Brown, dark grey, and yellow polyhedra are Fe-, P-, and S-centered. Red and light blue circles represent O^{2-} and $[H_2O,(OH)^-]$ groups. Interlayer H_2O groups are not shown.

Iron is hosted in octahedral coordination. Average bond distances range between 1.96 and 2.01 Å, with values varying between 1.84 and 2.22 Å; the observed average distances are in keeping with the ideal $<Fe^{3+}–O>$ distance of 2.015 Å, calculated using the bond parameters of Brese and O'Keeffe [14]. In the structural model of Mauro et al. [9], such average bond distances were slightly shorter, ranging between 1.94 and 1.99 Å. As a consequence, the BVS of the Fe atoms was higher than the theoretical values, varying between 3.21 and 3.66 valence units (v.u.). This overbonding is less pronounced in the new crystal structure refinement, with values ranging between 3.06 and 3.54 v.u., with an average value of 3.23 v.u. The deviations from the ideal value are probably related to the distortion shown by the Fe-centered octahedra, with some relatively short distances increasing the BVS value.

As in Mauro et al. [9], bond distances for P and S-centered tetrahedra were restrained using the average values observed for $<P–O>$ and $<S–O>$ by previous authors, i.e., 1.537 and 1.473 Å, respectively [15,16]. Consequently, the BVS agrees with the theoretical ones. Indeed, the BVS at the P sites ranges between 4.86 and 5.04 v.u., whereas at the S sites, BVS values vary between 5.86 and 6.03 v.u. It is worth noting that whereas in the previous structural model, the position of some O atoms belonging to the SO_4 groups was calculated in order to achieve reasonable S–O and O–O distances, in the current refinement, all the O positions were located in the difference-Fourier maps.

The crystal structure of bohuslavite is characterized by 128 anion positions. Among them, 108 belong to the heteropolyhedral layers. These anions can be divided into three different groups. The first one is represented by those O atoms bonded only to one Fe atom; their BVS is usually around 0.5 v.u. and they probably belong, usually, to H_2O groups. The second group is composed of O atoms bonded to one Fe and one P or S atom; their BVS is close to ~ 1.75–2 v.u. and they can be considered O^{2-} anions. Finally, the last group of O atoms is constituted by those atoms bonded to S atoms only. In this case, they achieve a total BVS ~ 1.5 v.u, and are probably acceptors of two H-bonds from H_2O groups. The O atoms belonging to the two structural layers can thus be divided into these three groups: for every layer, 22 belong to the first group, 26 to the second one, and 6 to the last one. In this way, the chemical formula of every layer is $Fe^{3+}_8(PO_4)_6(SO_4)_2\varphi_{22}$, where φ = (H_2O, OH) (see below).

The crystal structure refinement allowed the location of 20 additional electron density maxima located in the interlayer and the structural channels. These maxima were interpreted as O atoms belonging to H_2O groups; in some cases, these O atoms are split, probably because of structural disorder. The isotropic displacement parameters of these O atoms are usually larger than those of the O atoms belonging to the heteropolyhedral layers, and this structural feature may have both a structural origin, being related to the positional disorder, as well as to the relatively low quality of experimental data.

4. Discussion

Mauro et al. [9] highlighted two main shortcomings in their study of bohuslavite. The first one was represented by the actual unit-cell parameters; indeed, weak and some diffuse reflections were observed in both Italian and Czech type material, suggesting a doubling of the *c* parameter. The other question was about the number of H_2O groups occurring in bohuslavite. The collection of better structural data, with the resolution of its ~21.6 Å crystal structure, allowed us to improve the knowledge of the crystal chemistry of this phosphate-sulfate, suggesting some solutions to the previous questions.

4.1. Ordering of SO_4 Groups

All investigated samples of bohuslavite studied through single-crystal X-ray diffraction showed the occurrence of weak and diffuse reflections giving a periodicity $c' = 2c = 2 \times 10.8$ Å [9]. Mauro et al. [9] hypothesized that this doubling may be related to the ordering, along $\mathbf{c^*}$, of the two statistically occupied S sites found in the $c = 10.8$ Å crystal structure.

As displayed in Figure 1, in the sample studied in this work such reflections doubling the *c* parameter were relatively strong and sharp and allowed the solution and refinement of the ~21.6 Å superstructure. Figure 2 compares the crystal structures of bohuslavite of Mauro et al. [9] and of this work, as seen down **a**.

As stated above, heteropolyhedral layers are decorated, on both sides, by SO_4 groups. In the $c \sim 10.8$ Å crystal structure, two half-occupied S sites occur, giving rise to two mutually exclusive configurations (Figure 2a). The solution of the $c \sim 21.6$ Å crystal structure clearly indicates that these two configurations regularly alternate along **c** and are fully ordered in different structural layers. Consequently, the structure solved by Mauro et al. [9] was only an "average" structure: it contains all the structural features, but some details were not fully solved. For instance, the actual orientation of SO_4 tetrahedra is slightly different from that proposed by previous authors, and this is due to the uncertainties in the correct location of half-occupied O atoms in the $c \sim 10.8$ Å crystal structure.

Bohuslavite is not the first example of a sulfate-bearing mineral showing a doubling of the unit-cell parameters owing to SO_4 ordering. For instance, the ordering of SO_4 and H_2O groups along the **b** direction of volaschioite resulted in the appearance of superstructure reflections doubling the $b \sim 3.06$ Å parameter. However, such ordered sequences are not long-range related, and the superstructure reflections appear as continuous streaks of diffuse intensity [17]. On the contrary, in bohuslavite no streaking was observed and

probably the main shortcoming is due to the quality of available material, showing stacking disorder in the small platelets used for single-crystal X-ray diffraction. Indeed, using a smaller individual for this new data collection ($0.060 \times 0.040 \times 0.010$ mm, to be compared with $0.180 \times 0.120 \times 0.020$ mm in [9]) helped in improving the quality of the refinement.

4.2. H_2O Content in Bohuslavite

Infrared spectroscopy and crystal structure solution indicate that H_2O is hosted in bohuslavite in two different environments [9]. Some H_2O groups are directly bonded to Fe^{3+} atoms, forming their coordination polyhedra. In agreement with [9], there are 10 H_2O groups per formula unit belonging to the heteropolyhedral layers. Other H_2O groups are located within the [001] channels as well as in the interlayers. According to [9], this latter kind of H_2O could be gained or lost by bohuslavite, probably as a function of the relative humidity; for these reasons, these H_2O groups are indicated as "zeolitic".

Different amounts of H_2O were reported by Mauro et al. [9]. The measured densities of the Italian and Czech type materials fit with a number of "zeolitic" H_2O groups ranging between 13 and 14. On the contrary, the empirical formulae of bohuslavite seem to indicate a content of H_2O ranging between 5 (for the Czech bohuslavite) and 8 (for the Italian one) H_2O groups per formula unit. These latter values are based on thermogravimetric data. Finally, the solution and refinement of the crystal structure by Mauro et al. [9] allowed the distinction of only 3 H_2O groups within channels and interlayers.

The current structure solution and refinement allowed to locate 10 "zeolitic" H_2O groups per formula unit. An examination of the possible H-bonds involving the undersaturated O atoms belonging to SO_4 groups revealed three different configurations:

(i)   two O atoms are H-bonded to one "zeolitic" H_2O group and one H_2O belonging to the heteropolyhedral layers, whereas the third O atom is an acceptor of H-bonds from H_2O bonded to the layers;

(ii)   all three O atoms are bonded to one "zeolitic" and one layer-bonded H_2O group;

(iii)   two O atoms are bonded to one "zeolitic" and one layer-bonded H_2O group, whereas one O is bonded to only one H_2O group belonging to the heteropolyhedral layers.

As discussed above, it is probable that the O atoms bonded only to S atoms are involved in two H-bonds. Consequently, case (iii) could actually indicate the missing location of an additional H_2O group, likely of the "zeolitic" type. If so, there are 5 "zeolitic" H_2O groups per formula unit H-bonded to SO_4 groups. It is worth noting that this value corresponds to the lower hydration state proposed by Mauro et al. [9] on the basis of thermogravimetric data.

There are some implications deriving from this observation. These 5 H_2O groups may play an important structural role and may correspond to the lower hydration state of this mineral. Probably, they cannot be defined as "zeolitic", since their loss could promote a structural rearrangement of bohuslavite. Higher hydration states are possible, with H_2O groups mainly hosted in structural channels. Other H_2O groups in the interlayer play a less-defined role that is not fully understood, owing to the uncertainty in the correct location of some of them.

Different hydration states do not affect the *c* spacing of bohuslavite, i.e., there is no evidence for expandability. Indeed, the stacking of successive heteropolyhedral layers is mediated through H-bonds involving H_2O located in the interlayer or bonded to Fe atoms (Figure 3). This succession of layers is very probably ordered, being ruled by the H-bond system. This is the reason for the absence of any evidence of streaking in the X-ray diffraction patterns of bohuslavite: the crystal structure is well-ordered, and the low quality of the diffraction data is simply due to the misorientation of the crystallites forming the studied grains.
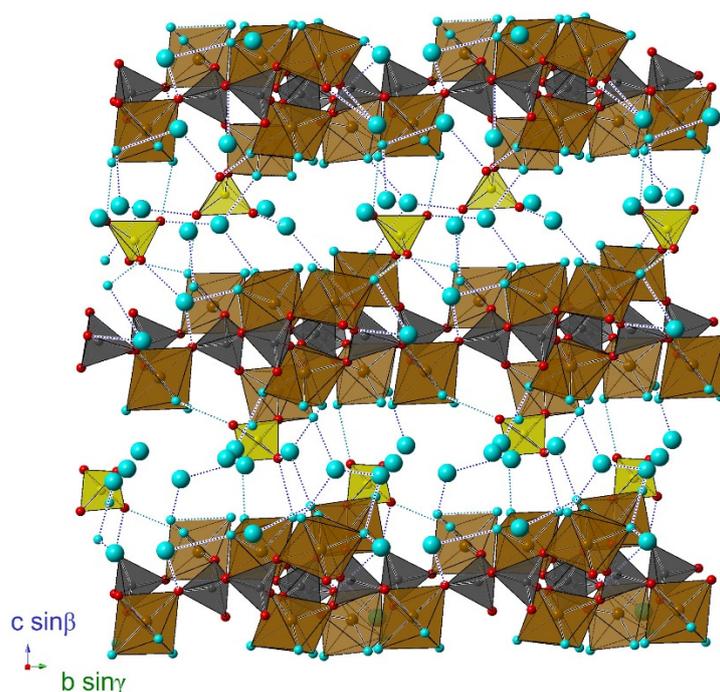
Figure 3. Detail of the crystal structure of bohuslavite showing interlayer H_2O groups with dotted lines indicating O···O distances shorter than 3 Å. Same symbols as in Figure 2. Interlayer H_2O groups are shown as light blue circles larger than those used for Fe-bonded H_2O.

4.3. Looking for the Position of (OH) Groups

The chemical formula of bohuslavite is given as $Fe^{3+}_4(PO_4)_3(SO_4)(OH)(H_2O)_{10}\cdot nH_2O$ (Z = 4). It is worth noting that the actual location of the OH groups was only hypothesized, but no experimental evidence for its occurrence was found. Mauro et al. [9] proposed that the OH group could occupy the anion positions statistically bonded to S: these positions were occupied by O^{2-} when bonded to S, and they host $(OH)^-$ when they are non-bonded. However, their BVS (0.65 and 0.61 v.u.) was comparable to other (H_2O)-bearing sites.

The current solution of the $c \sim 21.6$ Å crystal structure does not allow us to solve this question. No anion sites characterized by a BVS suggesting their occupancy by OH groups were found. Consequently, several hypotheses were checked, in order to achieve the electrostatic balance. Indeed, every structural layer has the formula $Fe^{3+}_8(PO_4)_6(SO_4)_2\varphi_{22}$, with 24 positive charges and 22 negative ones; for this reason, φ_{22} should be represented by 10 H_2O and 2 monovalent anions.

A first possibility is that these monovalent anions may be represented by F^-, possibly acting as an acceptor of H-bonds. In accord with Mauro et al. [9], bohuslavite is probably the result of the interaction between H_2SO_4, released from pyrite oxidation, and P-bearing rocks. The coexistence with gypsum at both the Italian and Czech type localities may suggest a possible reaction involving the dissolution of some apatite-group minerals, for instance, fluorapatite, as proposed by Peacor et al. [18] for destinezite. These latter authors discussed the possible precipitation of fluorite, but this mineral was not observed in bohuslavite-bearing assemblages, although some very rare fluo-sulfates have been reported from the Apuan Alps (e.g., wilcoxite, khademite [4,5]). Notwithstanding this possibility, chemical data did not support the occurrence of F in bohuslavite.

Another possible mechanism could be a reduction of the total positive charges, through the substitution of Fe^{3+} by Fe^{2+}, the occurrence of a vacancy, or the P^{5+}-to-S^{6+} substitution. Mössbauer spectroscopy did not reveal any evidence for the occurrence of Fe^{2+} [9]; moreover, the substitution of Fe^{3+} by Fe^{2+} should increase the size of octahedral sites. On the contrary, the oversaturation of Fe atoms indicates that Fe-centered polyhedra are smaller than the ideal ones. Finally, the occurrences of vacancies or the P-to-S replacement are not supported by chemical data [9].

As a matter of fact, the only explanation is that OH groups occur in the crystal structure of bohuslavite. Possibly, some O atoms bonded to Fe-atoms only could be the acceptor of two relatively strong H-bonds (bond strength in the range 0.25–0.30 v.u.) and the donor of a weak H-bond (~0.10 v.u.), satisfying the bond strength requirements. Unfortunately, the quality of the refinement is not good enough to allow an accurate description of the H-bonds in bohuslavite and this issue remains to be solved if better crystals will be found.

5. Conclusions

Bohuslavite is an interesting kind of microporous mineral, according to the IUPAC definition [19], having large [001] channels. The new structural data reported in this work refine the knowledge of this mineral. Indeed, the actual unit-cell has a doubled *c* parameter, related to the alternation of two different SO_4 configurations along **c***. Undersaturated O atoms belonging to the SO_4 group, moreover, are acceptors in H-bonds with H_2O groups; among the latter, some are hosted within interlayers. Consequently, even if they are not bonded to Fe atoms, these H_2O groups cannot be considered as "zeolitic" and their occurrence seems to be necessary for the stabilization of bohuslavite. Notwithstanding such improvements in our understanding of the crystal chemistry of this mineral, some details regarding the actual H-bond system and the position of OH groups still remain unknown, and further investigations will be required.

Bohuslavite may be not only one of the several mineral species formed during pyrite oxidation, through the interaction between H_2SO_4 and P-bearing country rocks. As for the chemically related minerals destinezite and diadochite [18], bohuslavite could be a minor but not rare mineral constituent in soils formed under low pH conditions. In this respect, considering the high S and P contents detected in Martian soils formed in acid environments [20,21], these Fe^{3+}-phosphate/sulfate minerals could play a hitherto unknown role in the mineralogical evolution of Mars.

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