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Crystal structure of tooeleite, $Fe_6(AsO_3)_4SO_4(OH)_4{\cdot}4H_2O$, a new iron arsenite oxyhydroxy-sulfate mineral relevant to acid mine drainage

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ABSTRACT

The crystal structure of tooeleite, $Fe_6(AsO_3)_4(SO_4)(OH)_4{\cdot}4H_2O$, has been solved from high-resolution synchrotron XRD powder data recorded on a sample from Tooele county, Utah. The structure is monoclinic, space group $C2/m$, a = 8.9575(1), b = 6.4238(1), c = 9.7912(1) Å, β = 96.032(1)°, V = 560.27(3) Å^3, d_{calc} = 3.16 g/cm^3. The structure was solved by direct methods and atomic positions, site occupancies, and isotropic displacement parameters were refined by the Rietveld method. The AsO_3 pyramids bond to FeO_6 octahedra by both edge- and corner-linkage, forming layers that intercalate SO_4 groups. Assignment of structural H_2O and OH groups were done from bond-valence analysis. Tooeleite is the only arsenite-sulfate mineral known and has been recently identified as the main constituent of stromatolite-like deposits in the Carnoulès acid mine, Gard, France.

Keywords: Crystal structure, tooeleite, XRD data, synchrotron powder diffraction, new minerals, geomicrobiology, acid mine drainage

INTRODUCTION

In acid mine drainage (AMD), and in hot springs, microbiological oxidation of Fe(II) to Fe(III) plays a key role in immobilizing toxic elements such as arsenic, by co-precipitation (and adsorption) with (onto) iron oxy-hydroxide and iron-hydroxysulfate minerals (Bigham and Nordstrom 2000). A recent study of bacterial accumulations from the Carnoulès AMD, France, has shown that they consist mainly of a rare arsenic iron mineral, tooeleite. Laboratory experiments showed that specific bacterial strains from *Acidithiobacillus ferrooxidans* sp. isolated from Carnoulès induced formation of nanocrystalline tooeleite, via oxidation of dissolved Fe(II) to Fe(III), in the presence of high dissolved As(III) (Morin et al. 2003). Hydrochemistry budgets on the Carnoulès AMD indicate that formation and sedimentation of tooeleite, in association with poorly ordered Fe^{3+}-$As^{3+/5+}$ hydroxy-sulfates, promotes an efficient natural bio-remediation (Leblanc et al. 1996; Casiot et al. 2003; Duquesne et al. 2003).

XANES data indicate that tooeleite is an iron arsenite mineral, i.e., As^{3+}, (Morin et al. 2003), although it was originally described as an iron arsenate, i.e., As^{5+}, when discovered by Cesbron and Williams (1992). Determination of the structure of this mineral is necessary to interpret XRD and EXAFS data from biogenic precipitates forming at Carnoulès and to better understand their mechanisms of formation.

MATERIAL AND EXPERIMENTAL METHODS

The sample from Tooele County, Utah (Cesbron and Williams 1992), kindly provided by F.P. Cesbron, was used for structure determination. This sample was chosen because it has much larger crystallite dimensions (a few hundreds of nanometer thick and a few micrometers long) than samples from the Carnoulès AMD (<10 nm thick platelets). The Utah sample consists of a fibro-radial coating of tooeleite crystals, filling the pores (voids of millimeter size) of a scorodite-arsenopyrite assemblage. Individual crystals are a few micrometers long and less than one micrometer wide. Tooeleite powder separated from this sample exhibits a well-resolved X-ray powder diffraction pattern (Cesbron and Williams 1992). Approximately 50 mg of high-purity tooeleite was carefully hand picked from this sample. The chemical composition of the sample was determined by electron microprobe analysis (EPMA) at CAMPARIS/UPMC using a SX50 CAMECA microprobe on few grains embedded in resin and prepared as a polished section. A high-resolution X-ray powder diffraction-pattern of the Utah tooeleite was recorded in 3 h in transmission Debye-Scherrer geometry at the DW22 wiggler-beamline at LURE, Orsay, France. The sample was mounted in a rotating silica capillary 0.3 mm in diameter. The wavelength of 0.6926 Å was extracted from the white beam by means of a double crystal Si(111) monochromator. The diffracted beam was collected using a Ge(111) analyzer leading to an instrumental resolution of less than 0.03 °2θ, which was evaluated by recording a few Bragg peaks of the LaB6 powder diffraction standard.

RESULTS AND DISCUSSION

Chemical formula

XANES investigation of tooeleite samples, including the one of the present study, has shown that arsenic is only present in the As(III) state in this mineral (Morin et al. 2003). Hence, the structural formula proposed by Cesbron and Williams (1992) is erroneous because these authors assumed that tooeleite was an As^{5+} mineral. Mössbauer data on nano-crystalline tooeleite from Carnoulès, France indicates that more than 95% of the total iron is present as Fe^{3+}. Twenty-seven electron microprobe analyses of tooeleite were averaged and normalized to an H_2O content of 9.8 wt%, as measured by Cesbron and Williams (1992) using the Penfield method. The result of this procedure gave the following composition: 44.3 (0.6) wt% Fe_2O_3, 36.2 (0.6) wt% As_2O_3,

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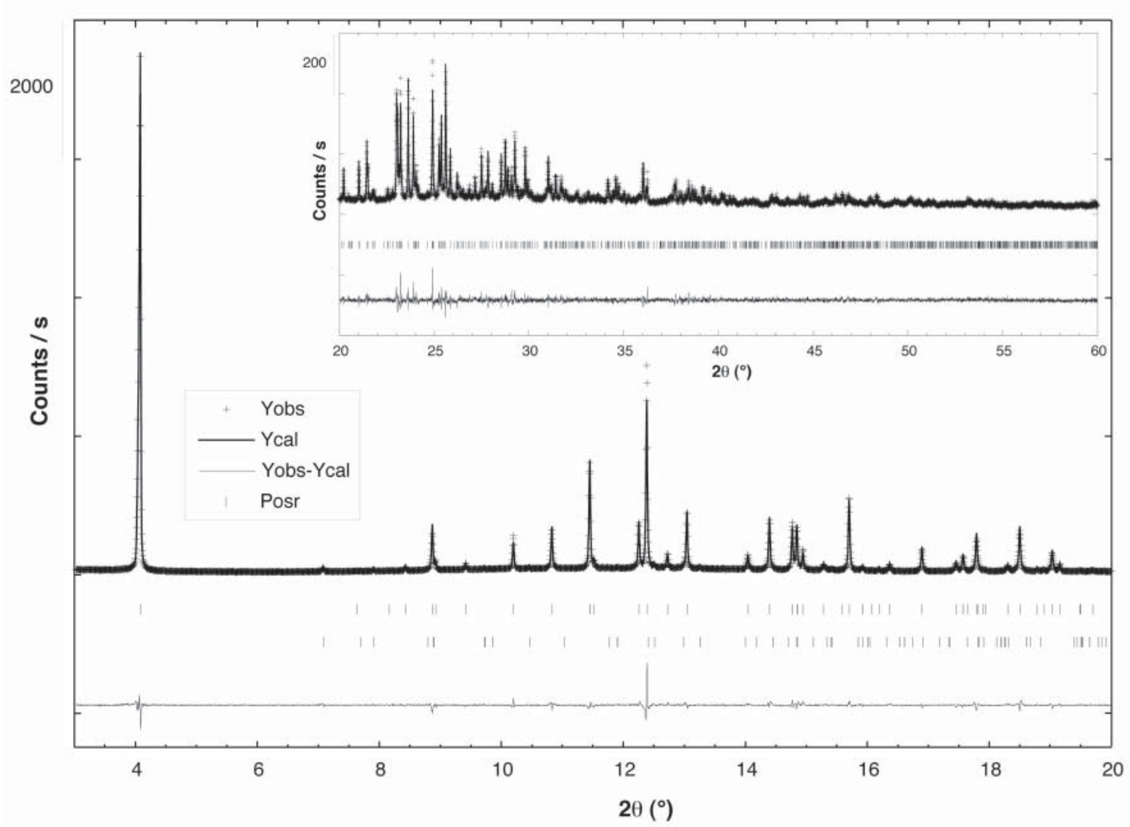

FIGURE 1. Rietveld refinement of the synchrotron XRD powder pattern of the Utah tooeleite sample. Yobs, Ycal, and Yobs-Ycal = experimental, calculated, and difference pattern, respectively. Posr = positions for tooeleite (98 wt%) and scorodite (2 wt%). Detail of the high angle region (20–60° 2θ) is displayed in the inset.

and 9.7 (0.4) wt% SO_4, giving a total of 90.2 (0.7) wt%. These values agree well with those of Cesbron and Williams (1992), when normalized to the same H_2O content: 46.0 wt% Fe_2O_3, 35.1 wt% As_2O_3, and 9.2 wt% SO_4, total 85.5 wt%. However, the Fe/As and Fe/S molar ratios are slightly over-estimated in this latter analysis, suggesting the presence of higher amount of scorodite impurity in the powder sample analyzed by Cesbron and Williams (1992) than in the present one, as shown thereafter. From the present electron microprobe analysis and the knowledge that only As^{3+} is present, the structural formula of tooeleite is $Fe_6(AsO_3)_4SO_4(OH)_4·4–5H_2O$.

Powder-pattern indexing

The powder-pattern was indexed using the program DICVOL91 (Louer and Louer 1972; Boultif and Louer 1991), and the 35 most intense reflections. Only one solution was found in monoclinic symmetry with cell parameters very close to the final ones determined from Rietveld refinement of the full structure. All attempts to index the pattern in higher symmetry failed. Note that the monoclinic cell determined in the present work is close to half the orthorhombic cell proposed by Cesbron and Williams (1992), taking $a_{mono} = b_{ortho}/2$, $b_{mono} = a_{ortho}$, and $c_{mono} = c_{ortho}$. However, attempts to extract structure factors using this orthorhombic cell yielded severe discrepancies between experimental and calculated patterns.

Extraction of integrated intensities

Integrated intensities were extracted using the FullProf program of Rodriguez-Carvajal (1993), following the method of Le Bail et al. (1988, 2001), fitting simultaneously the integrated intensities, cell parameters, and width and shape parameters of a pseudo-Voigt line-profile function. Absorption for Debye Scherrer geometry (Rouse et al. 1970) was negligible for $\mu r = 0.7$ cm^{-1} (assuming that the apparent density of the powder would be half that of the mineral).

Rietveld profile-fitting assuming a monoclinic cell indicated the presence of a few very weak, unexplained reflections, which were related to about 2 wt% of scorodite impurity in the sample studied. Existence of these lines with higher relative intensities in the Bragg reflection list given by Cesbron and Williams (1992) indicates that their powder sample contained a higher amount of this impurity. Scorodite was included in the fitting procedure using the single-crystal structure data of Hawthorne (1976), varying only the scale factor. Line-width parameters were constrained to follow those of tooeleite. Integrated intensities of 952 reflections from tooeleite were extracted in the 5–60° 2θ range after full-pattern profile matching.

Structure solution

The structure was solved by direct methods using the program SHELX-86 (Sheldrick 1990). The reflection condition $h+k = 2n$

suggested the space groups *C*2 or *C*2/*m*. Attempts to solve the structure in *C*2 failed, probably because of a lack of independent observed reflections. By contrast, chemically sensitive structural fragments were obtained in *C*2/*m*. Attempts to solve the structure with a high-angle limit larger than 55° 2θ failed to give realistic oxygen positions, likely because of too many overlapping reflections at high angle. A high-angle limit lower than 50° 2θ also failed to give useful oxygen positions, probably because of lack of information. A reliable and chemically realistic structural fragment was obtained when the high-angle limit was between 50° 2θ and 55° 2θ, the value of 55° 2θ giving the best result. In this latter case, based on 671 observed reflections, 167 positive unique triplets, and 65 negative quartets were retained for tangent refinement. The best solution with CFOM = 0.1021 was retained for *E*-map interpretation and Fourier recycling, resulting in the location of 15 sites. The 3 sites with the highest peak-height values on the Fourier map were assigned as Fe or As. All other atoms were considered as O atoms. Among them, 8 atoms were deleted to produce octahedral coordination for Fe^{3+} and pyramidal coordination for As^{3+}. In agreement with the structural formulae, $Fe_6(AsO_3)_4SO_4(OH)_4·4–5H_2O$ ($Z = 1$), one Fe atom occupies a 2(*c*) position and the other occupies a 4(*i*) position; the As atom is at the 4(*i*) position. Sulfate groups and H_2O groups were not identified at this stage. Structure expansion based on the initial structural model indicated high electron-density at the 2(*a*) position (0,0,0), which was due to a S atom. However this model failed to reveal the oxygen positions for the corresponding sulfate groups.

Structure refinement

Rietveld refinement of the structure was carried out using the synchrotron X-ray powder-diffraction data and the program FullProf in the range 3-60° 2θ. The structure solution derived from SHELX-86 reasonably matched the experimental XRD pattern without fitting any atom parameter.

As oxygen atoms of the sulfate groups were not located via structure expansion, their initial positions were estimated with the constraint that they form a regular tetrahedron around the S atom at the 2(*d*) position. However, the (010) mirror in *C*2/*m* is not compatible with an SO_4 tetrahedron centered on the 2(*d*) position, suggesting lower symmetry or disorder. As a first approach, the SO_4 tetrahedra were considered as being randomly distributed over two orientations symmetrically oriented with respect to the (010) mirror. Based on average S-O distances in sulfate tetrahedra (Hawthorne et al. 2000), an SO_4 tetrahedron was built around the S atom at 2(*d*) by adding two oxygen atoms, O5 and O6, in positions satisfying an S-O bond length of 1.47 Å and S-O-S angles of 109°. These oxygen positions were chosen so that transforming the O5 and O6 atoms by the twofold axis generated a tetrahedron centered on the S atom. Subsequent transformation by the (010) mirror generated a symmetrical tetrahedron centered on the same S atom. Random distribution over these two orientations of the SO_4 group was taken into account by halving the site occupancies of O5 and O6 and constraining the site occupancy of S to be half those of O5 and O6. All atom positions were refined simultaneously, together with site occupancies of the SO_4 group. Displacement parameters were constrained to be equal for each type of atom. The best fit was obtained by including preferred orientation along the [010] direction. The G1 parameter of the March-Dollase function reached a value of 0.961, accounting for a slight elongation of the tooeleite crystallites in the **b** direction. Such a crystal shape is in agreement with SEM microphotographs reported by Cesbron and Williams (1992). The R_{wp} parameter for the pattern and the R_{Bragg} parameter for tooeleite reached final values of 0.088 and 0.045, respectively (Fig. 1, Table 1). Final atom positions, displacement parameters, and site occupancies are reported in Table 2.

Final positions of the O5 and O6 atoms did not vary significantly from their initial estimated values, giving an almost regular SO_4 tetrahedra with classical bond lengths and angles (Table 3; Hawthorne et al. 2000). The final value of the SO_4 site occupancies was 0.653(8). This corresponds to 1.30(1) SO_4 per unit cell, slightly higher that the value of 1.0 expected from the structural formula derived from EPMA. This discrepancy is not yet explained, but could be accounted for by an excess of about 0.3 H^+ per unit cell.

Describing the structure in *C*2 or *P*2 could account for possible ordering of sulfate group orientation with respect to the (010) mirror. In *C*2, all SO_4 would have the same orientation, whereas in *P*2, there may be alternating orientations between

Table 1. Chemical formula, crystallographic data and refinement parameters for tooeleite

Formula	$Fe_6(AsO_3)_4(SO_4)(OH)_4·4H_2O$
Formula weight (g/mol)	1064
No. of structural formula in cell unit	1
No. of structural formula in asymmetric unit	0.5
Space group	Monoclinic *C*2/*m*
Refined unit-cell parameters	
a (Å)	8.9575(1)
b (Å)	6.4238(1)
c (Å)	9.7912(1)
β (°)	96.032(1)
Unit-cell volume, *V* (Å^3)	560.27(3)
Temperature	Ambient
Wavelength (Å)	0.6926
Step increment (2θ)	0.005
Geometry	Debye-Scherrer
Preferred-orientation function	March-Dollase
Direction	[010]
G_1	0.961
Background	Spline
Profile function	pseudo-Voigt
Pattern range (2θ)	3–60
Number of reflections	1009
Refined parameters	35
Profile *R* values	
R_{wp} (%)	8.8
R_p (%)	6.8
R_{Bragg} (%)	4.5
$R_{expected}$	6.8

Table 2. Atomic parameters for tooeleite in space group *C*2/*m*: fractional coordinates, isotropic displacement parameter (B_{iso}), occupancy factor (Occ), and site multiplicity (Mult)

Atom	*x*/*a*	*y*/*b*	*z*/*c*	B_{iso} (Å^2)	Occ	Mult
As	0.7396(5)	0	0.2990(4)	0.84(8)	1	4(*i*)
Fe1	0	0	1/2	0.66(9)	1	2(*c*)
Fe2	0.3675(7)	0	0.3802(5)	0.66(9)	1	4(*i*)
O1	0.866(2)	–0.196(2)	0.375(2)	0.30(6)	1	8(*j*)
HO2	0.378(2)	0	0.159(2)	0.30(6)	1	4(*i*)
H_2O3	0.596(2)	0	0.413(2)	0.30(6)	1	4(*i*)
O4	0.146(2)	0	0.355(2)	0.30(6)	1	4(*i*)
S	0	0	0	1.6(5)	0.65(2)	2(*a*)
O5	0.014(5)	–0.141(6)	0.114(5)	0.3(2)	0.325(10)	8(*j*)
O6	0.123(5)	0.151(2)	0.0106(17)	0.3(2)	0.325(10)	8(*j*)

Note: Standard deviations on the last digit are in parentheses.

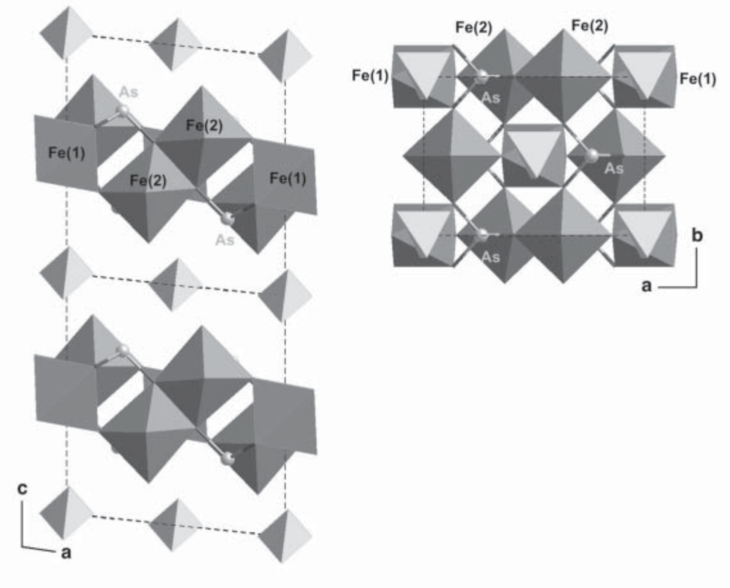

FIGURE 2. The crystal structure of tooeleite, viewed down the [010] and the [001] directions, on the left and right, respectively. The layers are composed of corner and edge sharing FeO_6 octahedra linked by corners and edges to AsO_3 pyramids. Isolated sulfate tetrahedra occupy the interlayer space. Only one possible orientation of the sulfate groups with respect to the (010) mirror is represented. In addition, whatever the orientation, only one half of the represented sulfate site is occupied.

(0,0,0) and (1/2,1/2,0). The XRD pattern calculated in *C*2 matched the experimental data, as well as the random model described previously. This option was not retained because the structure with all sulfate groups having the same orientation with respect to the (010) plane would be chiral, which is uncommon in sulfate minerals (Hawthorne et al. 2000). On the other hand, the *P*2 model did not satisfy the condition $h+k = 2n$ and thus yields poorer agreement with the experimental data. A freely rotating SO_4 group might also be consistent with the data. These ambiguities clearly indicate that the orientation of the sulfate groups is poorly constrained in the present structure refinement, likely because the X-ray powder-diffraction pattern of tooeleite is dominated by As and Fe contributions. Consequently, in the absence of experimental evidence supporting ordering of the sulfate groups, *C*2/*m* was retained, with SO_4 groups randomly distributed over two possible orientations, and symmetric with respect to the (010) mirror. Disordered sulfate tetrahedra showing two possible orientations occur in orschallite, $Ca_3(SO_3)_2(SO_4)·12(H_2O)$ (Weidenthaler et al. 1993). Further analysis of tooeleite using neutron powder diffraction may help to better locate the SO_4 groups within the structure.

Description of the structure

The structure is layered with positively charged iron-arsenic oxyhydroxide layers and sulfate groups within the interlayer space (Fig. 2). Iron ions are six-coordinated with average Fe-O distances and bond-valence sums in good agreement with Fe^{3+} (Table 3). Arsenic is three-coordinated to oxygen as expected for As^{3+} with a bond valence sum of 2.9(1). The S atoms are four-coordinated to oxygen with a valence sum of 6.5(3), close to the expected value of 6. All oxygen atoms have valence sums close to the expected value of 2, but O2 and O4 atoms that exhibit lower values (0.32 and 1.04, respectively). Accordingly, O2 and O4 are H_2O and OH groups, respectively. The low valence sum at O2 is related to the fact that O2 is bonded to only one iron with a long Fe2-O2 distance (2.18 Å). Assignment of O2 to a water molecule suggests that the structural formula actually contains four water molecules. Further work is needed to accurately locate the H atoms in the vicinity of the O2 and O4 atoms. Hydrogen bonds might link the H_2O2 and OH4 groups (belonging to the layers), to the O5 and O6 oxygen atoms belonging to the interlayer sulfate groups.

TABLE 3. M-O).67⌧2(⌧6(=,).⌧ 32⌧) ⌧) O-M-O ⌧, 0⌧6⌧ +35F⌧O_6, A6O_3, ⌧) SO_4 430⌧- ⌧) 5⌧ (M F F⌧, A6, S) .2 733⌧0⌧.7⌧

A6	O1 .	O1 .9	O3.			
O1.	1.81(1)	A9⌧5⌧, ⌧) .67⌧2(⌧D1.80(1)				
O1 .9	89(1)	1.81(1)	Δ F 0.17 ×G-04			
O3 .	102(1)	102(1)	1.79(2)	B.⌧. S81 D2.9(1)		
F⌧1	O1 .	O1 ..	O1 ...	O1.9	O4.	O4..
O1.	2.05(2)	A9⌧5⌧, ⌧) .67⌧2(⌧D2.05(2)				
O1 ..	104(1)	2.05(2)	Δ= 0.22 ×G-04			
O1 ...	180(2)	76(1)	2.05(2)	B.⌧. S81 D2.8(1)		
O1 .9	76(1)	180(2)	104(1)	2.05(2)		
O4 .	88(1)	92(2)	92(2)	88(1)	2.03(2)	
O4 ..	92(2)	88(1)	88(1)	92(2)	180(2)	2.03(2)
F⌧2	O1 9	O1 9...	O2 .	O3 .	O3 ..	O4.
O19	1.95(2)	A9⌧5⌧, ⌧) .67⌧2(⌧D2.02(1)				
O1 9...	177(1)	1.95(2)	Δ= 15.2 ×G-04			
O2 .	89(1)	89(1)	2.18(2)	B.⌧. S81 D3.1(1)		
O3 .	91(2)	91(1)	91(2)	2.04(2)		
O3 ..	91(1)	91(1)	168(2)	78(2)	2.02(2)	
O4 .	90(1)	90(1)	91(2)	178(2)	101(2)	1.97(2)
S	O5 .	O5 ..	O6.	O6..		
O5.	1.43(3)	A9⌧5⌧, ⌧) .67⌧2(⌧D1.45(3)				
O5 ..	101(4)	1.43(3)	Δ= 1.2 ×G-04			
O6 .	111(4)	119(4)	1.46(3)	B.⌧. S81 D6.5(3)		
O6 ..	119(4)	111(4)	97(4)	1.46(3)		

Notes: -⌧⌧9⌧5⌧, ⌧M-O) .67⌧2(⌧6⌧5⌧⌧63 5⌧4357⌧) ,⌧6: ⌧0⌧67- ⌧⌧32) 9⌧0⌧2(⌧ 681 (B.⌧. S81)(⌧0 80⌧7⌧) 86.2, 7- ⌧H⌧(-⌧5.⌧6⌧2 +351 80⌧D B.⌧. S81 F $\Sigma_{⌧F1,N}$⌧; 4⌧(d_0 − d)/0.37% -⌧5⌧d .67- ⌧M-O_i) .67⌧2(⌧: .7- .2 7- ⌧MO_N (335) .2⌧7.32 430⌧- ⌧) 532, ⌧) d_0 .67- ⌧(-⌧5⌧(7⌧5.67.(4⌧5⌧1 ⌧7⌧5+357- ⌧M-O 4⌧.55⌧4357⌧) ⌧⌧B53: 2 ⌧2) A0 ⌧51 ⌧77 (1985). -⌧) .67357.32 4⌧5⌧1 ⌧7⌧5Δ 3+7-⌧ MO_N (335) .2⌧7.32 430⌧- ⌧-)532 .6)⌧ fi2⌧) ⌧D Δ F (1 /N) $\Sigma_{.F1,N}$⌧d − ⟨d⟩)/ ⟨d⟩%:-⌧ 5⌧d .67-⌧ M-O⌧). 67⌧2(⌧⌧) ⟨d⟩ .67- ⌧⌧9⌧5⌧, ⌧M-O) .67⌧2(⌧39⌧57- ⌧N fi5672⌧., -⌧356. S7⌧2) ⌧5)) ⌧9.⌧7.326 32 7- ⌧0⌧67) ., .7⌧5⌧ .2 4⌧5⌧27- ⌧6⌧6.

. F x,y,zE.. F ⌧x,⌧y,⌧zE... F ⌧x,⌧y,⌧zE.9 F x,⌧y,z E9 F xC1/2,yC1/2,zE9. F ⌧xC1/2,yC1/2,⌧zE 9.. F ⌧xC1/2,⌧yC1/2,⌧zE9... F xC1/2,⌧yC1/2,z. A((35) .2, 73 385) ⌧6(547.32 3+7- ⌧ 6758(785⌧ .2 64⌧ ⌧, 5384 *C*2/*m*, 7: 3 ⌧⌧8.9⌧0⌧27 SO_4 7⌧75⌧- ⌧) 5⌧ ⌧5⌧ 6⌧1 1 ⌧75.(: .7- 5⌧64⌧(773 7- ⌧(010) 1 .553540⌧2⌧ ⌧2) ⌧37- ⌧5⌧ -⌧0+3((84.⌧) .

In tooeleite, AsO_3 groups are not polymerized together and share an edge with an FeO_6 octahedron. Although this arrangement is also observed in schneiderhöhnite (site As5; Hawthorne 1985), it contrasts with that in most of the iron arsenite minerals, where AsO_3 pyramids are polymerized. They form dimers in schneiderhöhnite (sites As1-As3 and As2-As4; Hawthorne 1985) and fetiasite (Graeser et al. 1994), chains in ludlockite (Cooper and Hawthorne 1996), and rings in stenhuggarite (Coda et al. 1977).

Tooeleite is the first arsenite-sulfate mineral described in the literature (Hawthorne et al. 2000; Ralph and Chau 2006). The crystal structure reported here will be used to interpret XRD data of samples from the Carnoulès AMD, and from in vitro biogenic precipitates synthesized using strains of *Thiobacillus ferrooxydans*. Preliminary Rietveld refinement confirms the occurrence of nanocrystalline tooeleite in both natural and synthetic samples, and yields an estimate of its crystal size and shape. Combined Rietveld and XAFS analysis indicates that tooeleite is associated with various amounts of amorphous Fe^{3+}-As^{3+} hydroxysulfates in these samples, whose role in the formation of tooeleite is still unknown.

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