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Švenekite, $Ca[AsO_2(OH)_2]_2$, a new mineral from Jáchymov, Czech Republic

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ABSTRACT

Švenekite (IMA 99-007), $Ca[AsO_2(OH)_2]_2$, is a rare supergene arsenate mineral occurring in the Geschieber vein, Jáchymov ore district, Western Bohemia, Czech Republic. It grows directly on the granite rocks and occurs isolated from other arsenate minerals otherwise common in Jáchymov. Švenekite usually forms clear transparent coatings composed of indistinct radiating to rosette-shaped aggregates up to 3 mm across. They are composed of thin lens- or bladed-shaped crystals, usually 100–150 μm long. Švenekite is transparent to translucent and has a white streak and a vitreous lustre; it does not fluoresce under ultraviolet light. Cleavage is very good on {010}. The Mohs hardness is ~2. Švenekite is biaxial, non-pleochroic. The refractive indices are $\alpha' = 1.602(2)$, $\gamma' = 1.658(2)$. The empirical formula of švenekite (based on As + P + S = 2 a.p.f.u., an average of 10 spot analyses) is $(Ca_{1.00}Mg_{0.01})_{\Sigma 1.01}[AsO_2(OH)_2]_{1.96}[PO_2(OH)_2]_{0.03}(SO_4)_{0.01}$. The simplified formula is $Ca[AsO_2(OH)_2]_2$ and requires CaO 17.42, As_2O_5 71.39, H_2O 11.19, total 100.00 wt.%. Raman and infrared spectroscopy exhibit dominance of O–H vibrations and vibration modes of distorted tetrahedral $AsO_2(OH)_2$ units. Švenekite is triclinic, space group $P\bar{1}$, with $a = 8.5606(5)$, $b = 7.6926(6)$, $c = 5.7206(4)$ Å, $\alpha = 92.605(6)$, $\beta = 109.9002(6)$, $\gamma = 109.9017(6)^{\circ}$, and $V = 327.48(4)$ Å^3, $Z = 2$, $D_{calc} = 3.26$ g·cm^{-3}. The *a:b:c* ratio is 0.7436:1:1.1082 (for single-crystal data). The six strongest diffraction peaks in the X-ray powder diffraction pattern are [*d* (Å)/*I*(%)/(*hkl*)]: 3.968(33)($2\bar{1}0$); 3.766(35)($2\bar{1}\bar{1}$); 3.697(49)(101); 3.554(100)(020); 3.259(33)($2\bar{2}0$); 3.097(49)($1\bar{2}1$). The crystal structure of švenekite was refined from single-crystal X-ray diffraction data to $R_1 = 0.0250$ based on 1309 unique observed, and to $wR_2 = 0.0588$, for all 1588 unique reflections (with $GOF_{all} = 1.20$). The structure of švenekite consists of sheets of corner-sharing CaO_8 polyhedra and AsO_2OH_2 groups, stacked parallel to (001). Adjacent sheets are linked by hydrogen bonds. The švenekite structure possesses very short symmetrical hydrogen bonds (with the *D*–H lengths ~1.22 Å). The mineral is named to honour Jaroslav Švenek, the former curator of the mineralogical collection of the National Museum in Prague, Czech Republic.

Keywords: švenekite, new mineral, calcium bis (dihydrogen-arsenate), crystal structure, Jáchymov.

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Introduction

THE compound $Ca[AsO_2(OH)_2]_2$ was first described from nature as an unnamed mineral phase from the Jáchymov ore district under the acronym "CAS" (Ondruš *et al.*, 1997). Further detailed investigation led to a submission of this mineral with the name švenekite to the IMA Commission on New Minerals and Mineral Names and subsequently the mineral was approved (IMA 99-007). Later, a short note about the occurrence of švenekite was published by Ondruš *et al.* (2003*a*) and this mineral was also mentioned briefly in a book by Sejkora and Kouřimský (2005) and a paper by Tvrdý and Plášil (2010). However, a complete description of this mineral phase has not yet been published. In the present paper we report new microprobe chemical data from a holotype and one additional sample, a Raman spectrum and new powder data, as well as the crystal structure refined from single-crystal X-ray diffraction (XRD) data.

The name švenekite honours the Czech mineralogist Dr Jaroslav Švenek (1927–1994) for both his professional and human qualities. Dr Švenek was a long-time curator of the mineralogical collection at the National Museum in Prague. The holotype specimen of švenekite has been deposited in the mineral collection of the National Museum in Prague, Czech Republic (catalogue number P1p 2/99).

Occurrence

Švenekite was found in the Jáchymov ore district, Western Bohemia, Krušné hory Mts, Czech Republic. This ore district is a classic example of Ag + As + Co + Ni + Bi + U vein-type hydrothermal mineralization. The ore veins cut a complex of medium-grade metamorphosed sedimentary rocks of Cambrian to Ordovician age, in the contact aureole of a Variscan granite pluton. The majority of ore minerals were deposited during Variscan mineralization from mesothermal fluids (Ondruš *et al.*, 2003*b*). Primary and supergene mineralization in this district resulted in an extraordinarily rich mineral association; more than 420 mineral species have been described to date (Ondruš *et al.*, 1997, 2003*a*,*b*; Tvrdý and Plášil, 2010).

Švenekite was found at the Geschieber vein (12th level, Svornost/Einigkeit mine; 50° 22′ 21.138″ N, 12° 54′ 46.251″ E) in the vicinity of the Běhounek (HG-1) radioactive spring. It is a very rare supergene mineral and was found only once, but in considerable amounts. Švenekite grows directly on the granite rocks and occurs isolated from other arsenates, which are common in Jáchymov. It crystallized from concentrated, strongly acidic solution with a strong circulation, which carried arsenic acid produced by decomposition of native arsenic or arsenides common in the Geschieber vein.

Physical and optical properties

Švenekite forms clear transparent coatings composed of indistinct radiating to rosette-shaped aggregates up to 3 mm across with a glassy lustre. It also forms hollow white botryoidal crusts with a mat or lustrous surface (Fig. 1). Secondary electron images taken with a TESCAN VEGA3XM scanning electron microscope show that the rosettes are composed of thin lens- to blade-shaped crystals (Fig. 2*a*,*b*). Individual crystals are up to 100–150 μm long; their thickness is variable but always significantly smaller than length. Some of the crystals were found to display faint striations and/or minute hollows (Fig. 2*b*).

Švenekite is transparent to translucent and has a white streak and a vitreous lustre; it does not fluoresce under ultraviolet light. There is one cleavage, very good on {010}. The Mohs hardness is ~2; švenekite is brittle with an uneven fracture. The density was measured by floating in a solution of methylene iodide-benzyl benzoate and Clerici solution and it is 3.16(1) g/cm^3. The calculated density based on the unit-cell dimensions from

FIG. 1. Švenekite of typical appearance from Jáchymov: crystalline aggregates of strong glassy lustre and whitish powder-like aggregates. FOV 5 mm, holotype specimen, photo by J. Sejkora.

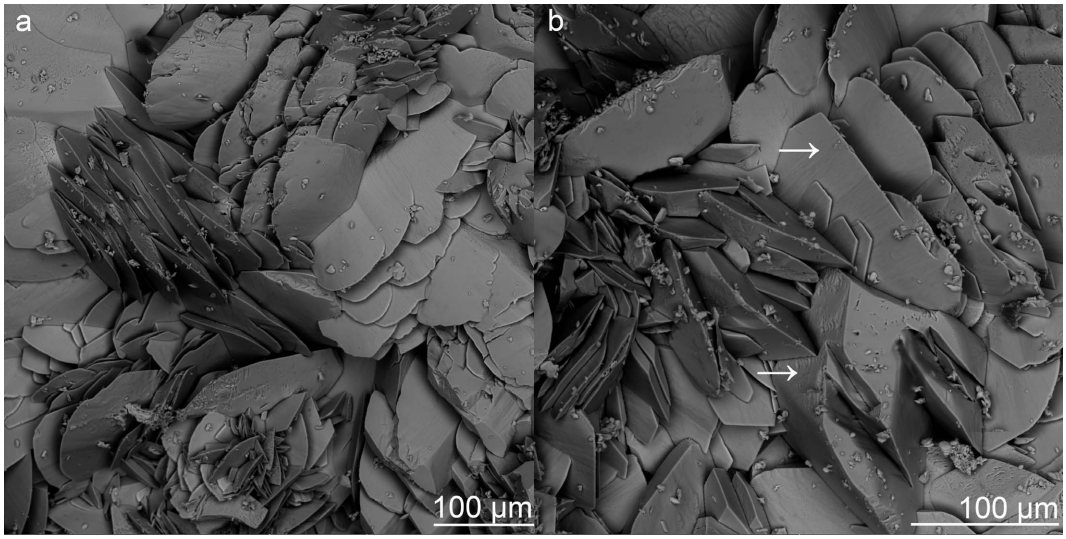

FIG. 2. Scanning electron microscope images of platy švenekite crystals with multiple intergrowths (a), showing striations (marked by arrows) on particular faces (b).

single-crystal X-ray data and electron microprobe results is 3.26 g/cm^3. Švenekite is slightly soluble in water.

Optical properties were measured for the wavelength of 589 nm. Švenekite is optically biaxial and non-pleochroic. The measured refractive indices are $\alpha' = 1.602(2)$, $\gamma' = 1.658(2)$. The third refractive index could not be measured due to the absence of suitably oriented mineral grains and fragments. Hence, due to incomplete optical data, a Gladstone-Dale compatibility index could not be calculated. The theoretical mean refraction index is 1.62, well between the two measured indices.

Chemical composition

Two distinct types of of švenekite crystals were analysed using a CAMECA SX-100 electron microprobe (Laboratory of electron microscopy and microanalysis of Masaryk University and the Czech Geological Survey, Brno). A crystal of the first type was removed from the holotype specimen of švenekite, and a crystal of the second type was picked from the crystal aggregate used for the single-crystal diffraction experiment. Analyses were carried out under following conditions: wavelength-dispersive mode was used with an accelerating voltage of 15 kV, a specimen current of 10 nA and a beam diameter of 10 μm. The following spectral lines and standards were used: $K\alpha$: andradite (Ca, Fe), baryte (S), Co (Co), fluorapatite (P), Ni (Ni), Mg_2SiO_4 (Mg), albite (Na), sanidine (Si, K), gahnite (Zn); $L\alpha$: lammerite (As). Peak-counting times were 20 s for main elements and 60 s for minor elements, counting time for background was ½ of the peak counting-time. Raw intensities were converted to concentrations using automatic *PAP* (Pouchou and Pichoir, 1985) matrix correction software. The elements Fe, Co, Ni, K and Zn were sought, but found to be below the detection limit (~0.01–0.03 wt.%). The presence and quantity of (OH) groups were established by crystal-structure solution and refinement.

Electron microprobe analyses revealed a near-ideal stoichiometry of both analysed types of švenekite. The empirical formula of the švenekite holotype specimen is $(Ca_{1.00}Mg_{0.01})_{\Sigma 1.01}[AsO_2(OH)_2]_{1.96}[PO_2(OH)_2]_{0.03}(SO_4)_{0.01}$ (average of 10 spot analyses, calculated on the basis of As + P + S = 2 a.p.f.u.), and the empirical formula of the second type of švenekite studied is $(Ca_{0.99}Mg_{0.01}Na_{0.01})_{\Sigma 1.01}[AsO_2(OH)_2]_{1.99}[PO_2(OH)_2]_{0.01}(SiO_4)_{0.01}(SO_4)_{0.01}$ (average of 5 spot analyses, calculated on the basis of As + P + Si + S = 2 a.p.f.u.). Both types contain minor amounts of Mg (up to 0.01 a.p.f.u.) and P and S (both up to 0.04 a.p.f.u.). The second type was found to contain also minor Na (up to 0.02 a.p.f.u.) and Si (up to 0.01 a.p.f.u.) (see

TABLE 1. Chemical composition (wt.%) of švenekite from Jáchymov.

	H	H1	H2	H3	H4	H5	H6	H7	H8	H9	H10	S	S1	S2	S3	S4	S5
Na_2O	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	0.12	0.11	0.11	0.15	0.13	0.08
CaO	17.51	17.03	17.29	17.28	17.63	17.40	17.70	17.46	17.76	17.70	17.87	17.26	17.27	17.34	16.96	17.32	17.43
MgO	0.12	0.19	0.14	0.00	0.00	0.15	0.17	0.13	0.13	0.14	0.12	0.17	0.14	0.14	0.25	0.17	0.18
SiO_2	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	0.10	0.04	0.09	0.22	0.11	0.05
As_2O_5	70.56	70.67	70.18	70.77	71.48	71.64	69.21	71.31	69.40	71.05	69.91	71.27	72.37	71.45	71.18	70.51	70.83
P_2O_5	0.64	0.75	0.85	0.73	0.67	0.55	0.65	0.50	0.67	0.61	0.39	0.08	0.05	0.04	0.12	0.11	0.10
SO_3	0.18	0.08	0.91	0.10	0.09	0.13	0.16	0.13	0.13	0.05	0.05	0.15	0.14	0.21	0.22	0.12	0.07
H_2O*	11.22	11.27	11.22	11.28	11.38	11.37	11.01	11.31	11.05	11.29	11.06	11.19	11.36	11.21	11.19	11.08	11.13
Total	100.23	99.98	100.59	100.16	101.26	101.24	98.89	100.84	99.14	100.84	99.40	100.35	101.47	100.59	100.29	99.56	99.86
Na^{+}	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.012	0.011	0.011	0.015	0.014	0.008
Ca^{2+}	0.999	0.969	0.973	0.982	0.994	0.981	1.029	0.990	1.030	1.006	1.038	0.985	0.973	0.987	0.964	0.999	1.003
Mg^{2+}	0.009	0.015	0.011	0.000	0.000	0.012	0.013	0.010	0.011	0.011	0.010	0.014	0.011	0.011	0.020	0.014	0.014
ΣM	1.008	0.984	0.984	0.982	0.994	0.993	1.042	1.000	1.041	1.017	1.047	1.011	0.995	1.010	0.998	1.026	1.026
Si^{4+}	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.005	0.002	0.005	0.012	0.006	0.003
As^{5+}	1.964	1.963	1.926	1.963	1.966	1.970	1.964	1.972	1.964	1.971	1.980	1.985	1.990	1.985	1.974	1.984	1.990
P^{5+}	0.029	0.034	0.038	0.033	0.030	0.025	0.030	0.023	0.031	0.027	0.018	0.004	0.002	0.002	0.006	0.005	0.005
S^{6+}	0.007	0.003	0.036	0.004	0.004	0.005	0.007	0.005	0.005	0.002	0.002	0.006	0.006	0.008	0.009	0.005	0.003
ΣT	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000
H^{+}	3.984	3.994	3.929	3.993	3.993	3.990	3.985	3.991	3.990	3.995	3.997	3.976	3.986	3.973	3.959	3.978	3.990

H – mean of ten point analyses of the holotype sample; S – mean of five point analyses of the sample used for the single-crystal study; Bdl – analyzed content below the limit of detection; H_2O* content was calculated on the basis of stoichiometry; coefficients of empirical formula were calculated on the basis (As + P + S + Si) = 2.

Table 1). The simplified formula of švenekite is $Ca[AsO_2(OH)_2]_2$ and requires CaO 17.42, As_2O_5 71.39, H_2O 11.19, total 100.00 wt.%.

For thermal analysis of švenekite, a Stanton Redcroft Thermobalance TG 750 apparatus was employed under the following conditions: heating rate 10ºC/min, dynamic air atmosphere 10 ml/min and sample weight 2.35 mg. According to the thermogravimetric (TG) curve, švenekite decomposes in several steps. It loses mass corresponding to two H_2O molecules (equivalent to 4 OH) in the temperature range 250–340ºC (weight loss of 0.263 mg; 11.17 wt.%$_{meas.}$, 11.23 wt.%$_{calc}$; 35.875 atomic mass units measured, 36.030 atomic mass units calculated). Weight loss of 0.113 mg in the temperature range 340–900ºC (4.97 wt.%$_{calc.}$, 4.79 wt.%$_{meas.}$; 15.375 atomic mass units measured, 15.999 atomic mass units calculated) may be assigned to the release of ½O_2. Thermal decomposition of švenekite may be described schematically as follows: $Ca(H_2AsO_4)_2 \rightarrow Ca(AsO_3)_2 \rightarrow CaAs_2O_5 \rightarrow CaO$. Decomposition of $CaAs_2O_5$ to CaO accompanied by the release of As_2O_3 and O_2 proceeds at temperatures >900ºC.

Infrared and Raman spectroscopy

A Raman spectrum of švenekite (Fig. 3) covering the range 50–6400 cm^{-1} (with spectral resolution of 2 cm^{-1}) was collected using a DXR dispersive Raman spectrometer (Thermo Scientific) mounted on a confocal Olympus microscope (100 × objective). The Raman signal was excited by a 532 nm laser and detected by a CCD detector. Experimental parameters: exposure time: 5 s; number of exposures: 32; grating: 400 lines/mm; spectrograph aperture: 50 μm slit; camera temperature: 50ºC; laser power level: 3.0 mW. The infrared spectrum of švenekite was measured using a Nicolet 740 type apparatus in the range 4000–400 cm^{-1}. The sample for analysis was prepared as a KBr disk. Spectra were processed (background correction, fitting) using the *OMNIC* Spectral tool software v.7.3 (ThermoElectron Corp.).

Raman and infrared (IR) spectra of švenekite were tentatively interpreted following published interpretations given by Keller (1971) in particular, Vansant *et al.* (1973), Myneni *et al.* (1998) and references therein.

Exact interpretation of vibrational behaviour of arsenate groups in the solid state is still not straightforward. According to Myneni *et al.* (1998), the tetrahedral T_d symmetry of the uncoordinated $(AsO_4)^{3-}$ groups is very rarely preserved in natural samples because of its strong affinity to protonation, hydration and formation of complexes with metal cations. The tetrahedral symmetry is therefore reduced to C_{3v}/C_3, C_{2v}/C_2 or C_1/C_s symmetry.

Raman bands at 929, 901, 871 and 840 cm^{-1} and IR bands at 913, 882 and 807 cm^{-1} are

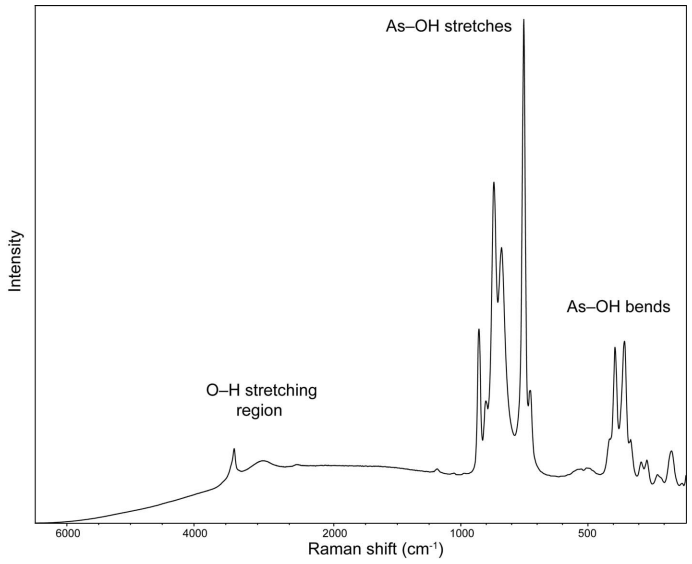

FIG. 3. Raman spectrum of švenekite.

assigned to the ν_3 antisymmetric and the ν_1 symmetric As–O vibrations of the $[(AsO_2(OH)_2]^-$ groups, respectively. However, they may also be related to the ν As–O–Ca stretching vibrations. Raman bands at 753 and 726 cm^{-1} and IR bands at 745 and 711 cm^{-1} are attributed to the ν_3 antisymmetric and ν_1 symmetric As–OH stretching vibrations. Raman bands at 541 and 498 cm^{-1} and IR bands and shoulders at 600, 536 and 490 cm^{-1} are related to δ As–OH out-of-plane bending vibrations. Raman bands at 417, 393 and 358 cm^{-1} and those at 330 and 289 cm^{-1} may be assigned to the ν_4 (δ) O–As–O and ν_2 (δ) O–As–O bending vibrations, respectively. The Raman bands at 268 and 223 cm^{-1} are attributed to the ν (OH···O) vibrations and the band at 172 cm^{-1} is assigned to the lattice modes.

Raman bands at 3368, 2917 and 2385 cm^{-1} and IR bands and shoulders at 3400, 3371, 2965, 2930 and 2386 cm^{-1} are associated with the ν O–H stretching vibrations of hydrogen-bonded hydroxyl ions. There is a weak IR band present at 1635 cm^{-1}, which may be attributed to the ν_2 (δ) bending vibration of the H_2O. As švenekite is a nominally anhydrous phase and is not expected to contain H_2O in its crystal structure, it is suggested that the presence of those vibration bands of molecular H_2O may originate from moisture in the KBr used for the pellet preparation. This conclusion is further supported by the TG curve of švenekite giving no evidence for release of H_2O. According to Libowitzky's empirical relation (Libowitzky, 1999), O···O separation distances in corresponding hydrogen bonds vary in the range 2.5–2.9 Å.

X-ray crystallography and crystal-structure determination

Single-crystal XRD

A single crystal of švenekite, with dimensions 0.13 mm × 0.04 mm × 0.02 mm, was examined using an Oxford Diffraction Gemini single-crystal diffractometer with an Atlas CCD detector using monochromatized Mo*K*α radiation, with a fibre-optics Mo-Enhance collimator. The unit cell was refined from 2232 reflections by the least-squares algorithm with the *CrysalisPro* package (Agilent Technologies, 2010). From the total 4557 measured reflections, merging of equivalent reflections gave 1588 independent reflections, 1309 of them were classified as observed with the criterion $[I_{obs} > 3\sigma(I)]$. An empirical correction for absorption was applied using the ABSPACK algorithm implemented in the RED routine of *CrysAlis* (Agilent Technologies, 2010), leading to R_{int} of 0.0317. Other details of data collection are given in Table 2.

The crystal structure of the synthetic analogue of švenekite is well known (Chiari and Ferraris, 1971; Ferraris *et al.*, 1972), thus the structure model of synthetic švenekite provided by Chiari and Ferraris (1971) based on single-crystal XRD data was used for structure refinement of the natural mineral using *Jana2006* software (Petříček *et al.*, 2006). Hydrogen atoms were localized from difference Fourier maps and treated by mixed refinement comprising constraints on bond-length and riding commands for atomic displacement parameters (ADP). The isotropic ADP of hydrogen atoms were evaluated as $1.2 \times U_{eq}$ of the parent atom; O–H bond lengths were treated by the soft-constraints of 0.90 Å and 1.10 Å (with a constraint's weight of 0.10). All other atomic types were refined anisotropically. Refinement converged quickly to final indices $R_1 = 0.0250$, $wR_2 = 0.0344$ for 1309 observed reflections (with $GOF_{obs} = 1.22$) and $wR_2 = 0.0588$ for all 1588 unique reflections (with $GOF_{all} = 1.20$). Details on the refinement are given in Table 2. Atomic positions and displacement parameters are provided in Table 3, selected geometrical parameters and bond lengths are given in Table 4. Bond-valence analysis for the crystal structure of švenekite was carried out according to Brown (2002), using bond strengths of Brown and Altermatt (1985) (for Ca^{2+}–O, As^{5+}–O), and Brown (2002) (for H–O) (Table 5).

Powder diffraction

Powder diffraction data of švenekite were collected on a Bruker D8 Discover powder diffractometer equipped with a primary focusing Johansson Ge(111) monochromator producing Cu$K\alpha_1$ radiation. Data were collected in reflecting geometry with a sample deposited on a zero-background silicon holder. Powder diffraction data (for Cu$K\alpha_1$) are listed in Table 6. Positions of diffraction maxima were obtained by profile fitting performed with *TOPAS* software (Bruker, 2008) employing the pseudo-Voigt profile shape function. To assess low-angle peak asymmetry, a split type of function was used to fit low-angle reflections. The unit cell was refined utilizing software by Burnham (1962) correcting for the

TABLE 2. Summary of data collection conditions and refinement parameters for švenekite.

Structural formula	$Ca[AsO_2(OH)_2]_2$
Crystal data	
a (Å)	8.5606(5)
b (Å)	7.6926(6)
c (Å)	5.7206(4)
α (°)	92.605(6)
β (°)	109.9002(6)
γ (°)	109.9017(6)
V (Å^3)	327.48(4)
Z	2
D_{calc} (g/cm^3)	3.264
Space group	$P\bar{1}$
Data collection	
Temperature	293 K
Detector; wavelength	Atlas CCD; MoK_α (0.71073 Å)
Crystal dimensions	0.13 × 0.04 × 0.02 mm
Collection mode	ω rotational scans to fill Ewald sphere
Limiting θ angles	3.12−29.14°
Limiting Miller indices	$-11 < h < 10$, $-10 < k < 10$, $-7 < l < 7$
No. of reflections	4557
No. of unique reflections	1588
No. of observed reflections (criterion)	1309 [$I_{obs} > 3\sigma(I)$]
R_{int}, coverage	0.0317, 99.85%
Absorption correction (mm^{-1}), method,	10.99, multiscan,
T_{min}/T_{max}	0.595/1
F_{000}	308
Refinement by *Jana2006* on F^2	
Parameters refined, constraints, restraints	109, 5, 5
R_1, wR_2 (obs)	0.0250, 0.0539
R_1, wR_2 (all)	0.0344, 0.0588
GOF obs/all	1.22/1.20
$\Delta\rho_{min}$, $\Delta\rho_{max}$ (eÅ^{-3})	−0.46, 0.55
Weighting scheme, details	σ, $w = 1/(\sigma^2(I) + 0.0004I^2)$

sample height error. Diffraction maxima were indexed in accordance with a simulated powder pattern calculated using *PowderCell* software (Kraus and Nolze, 2000) from the structure model obtained by single-crystal XRD. Unit-cell parameters refined from the powder data are a = 8.5482(3) Å, b = 7.6945(3) Å, c = 5.7180(2) Å, α = 92.602(2) °, β = 109.867(2) °, γ = 109.910(2) ° and V = 327.01(3) Å^3.

Description of the švenekite crystal structure and its relationship to other inorganic structures

The crystal structure of švenekite from Jáchymov is identical to that described for the synthetic analogue by Chiari and Ferraris (1971) and Ferraris *et al.* (1972). There is one unique Ca atom, two As, eight O and four H atoms in the asymmetric unit. Švenekite possesses a sheet structure, which is built up from the chains of edge-sharing CaO_8 polyhedra (the distorted square-antiprisms) interconnected by the AsO_2OH_2 groups. Each As group is linked to the three distinct CaO_8 polyhedra. The distortion of the $Ca\Phi_8$ polyhedra occurs due to the substantial variation in Ca−Φ bond lengths (Table 4). The reason for this variation may be found in differences in the coordination environment of these ligand atoms with respect to their role in H bonds. The longest Ca−O bonds correspond to atoms O2 and O7 where hydrogen atoms are located. The linkage of the chains into the sheet is provided by an As2 tetrahedron,

TABLE 3. Atomic positions, occupancies, equivalent displacement parameters (U_{eq}) and anisotropic displacement parameters for švenekite.

	x	y	z	U^*(eq)	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ca	0.08168(9)	0.18648(11)	0.31266(13)	0.0127(3)	0.0119(4)	0.0150(4)	0.0105(3)	0.0044(3)	0.0041(3)	0.0022(3)
As1	0.34172(5)	0.23993(5)	0.98495(6)	0.01135(15)	0.0091(2)	0.0136(2)	0.0103(2)	0.0021(2)	0.0045(1)	0.0019(1)
As2	−0.18668(5)	0.23399(5)	0.66951(7)	0.01220(15)	0.0108(2)	0.0129(2)	0.0126(2)	0.0040(2)	0.0046(1)	0.0009(2)
O1	−0.1744(3)	−0.0618(4)	−0.0028(5)	0.0149(10)	0.011(1)	0.015(1)	0.017(1)	0.000(1)	0.008(1)	0.003(1)
O2	0.3771(4)	0.4001(4)	1.2362(5)	0.0207(12)	0.0200(16)	0.0204(17)	0.0178(14)	0.0009(12)	0.0105(13)	−0.0042(12)
O3	0.5416(4)	0.2079(5)	1.0750(5)	0.0211(12)	0.0149(14)	0.0351(17)	0.0168(15)	0.0120(13)	0.0076(11)	0.0061(14)
O4	0.3116(3)	0.3252(4)	0.7213(4)	0.0152(10)	0.0143(13)	0.0159(14)	0.0113(12)	0.0015(11)	0.0037(10)	0.0049(10)
O5	−0.0457(3)	0.3292(4)	−0.0304(4)	0.0168(10)	0.0197(14)	0.0112(13)	0.0124(13)	0.0037(11)	0.0001(10)	−0.0010(10)
O6	−0.1254(3)	0.0935(4)	0.5244(4)	0.0144(10)	0.0155(13)	0.0151(13)	0.0153(13)	0.0067(11)	0.0082(10)	0.0006(10)
O7	−0.1691(4)	0.4339(4)	0.5344(5)	0.0206(12)	0.0172(16)	0.0232(16)	0.0157(14)	0.0068(13)	0.0000(11)	0.0051(13)
O8	−0.3974(3)	0.1412(4)	0.6588(5)	0.0186(11)	0.0117(13)	0.0227(15)	0.0199(13)	0.0029(12)	0.0088(11)	−0.0042(11)
H2	−0.229(6)	0.410(7)	0.431(8)	0.0248*						
H3	0.449(6)	0.463(7)	1.253(9)	0.0248*						
H5	0.559(7)	0.202(8)	0.983(9)	0.0253*						
H7	0	0.5	0	0.0202*						
H8	0.5	1	0.5	0.0223*						

* U (eq) is defined as a third of the trace of the orthogonalized U_{ij} tensor.

TABLE 4. Selected bond distances in the crystal structure of švenekite.

As1−O1	1.648(2)	As2−O5	1.677(3)
As1−O2	1.721(3)	As2−O6	1.653(3)
As1−O3	1.718(4)	As2−O7	1.735(4)
As1−O4	1.647(3)	As2−O8	1.678(3)
<As1−O>	1.684	<As2−O>	1.686
V_P	2.403	V_P	2.438
σ^2	53.816	σ^2	27.134
Δ	0.021	Δ	0.015
ECoN	3.931	ECoN	3.952
Ca−O1	2.420(2), 2.452(3)	Ca−O7	2.773(3)
Ca−O2	2.697(3)	<Ca−O>	2.503
Ca−O4	2.385(2)	V_P	27.21
Ca−O5	2.409(3)	Δ	0.047
Ca−O6	2.408(3), 2.479(3)	ECoN	7.184
H−bonds			
	H···A	D−A	D−H···A angle
O2−H2···O4	2.09(5)	2.703(4)	175(6)
O3−H3···O3	2.07(6)	2.668(5)	172(7)
O5−H5···O5	1.221(1)	2.442(1)	180
O7−H7···O3	2.30(4)	2.878(3)	158(7)
O8−H8···O8	1.222(1)	2.443(2)	180

Δ, Bond-length distortion after Brown and Shannon (1973); σ^2, bond-angle distortion after Robinson *et al.* (1971); ECoN, an effective coordination number after Hoppe (1979); V_P, polyhedral volume (in $Å^3$). Calculations by Vesta (Momma and Izumi, 2008).

which interlinks two adjacent chains (bridging O7 atom). The sheets are stacked parallel to (001), the linkage between adjacent sheets is provided by hydrogen bonds (Fig. 4). The following hydrogen bonds are proposed to be involved in the linkage of adjacent sheets: O7−H7···O3, O3−H3···O8, O2−H2···O4 and also two symmetrical H bonds O5−H5−O5 and O8−H8−O8 (Table 4).

There are few known minerals for which the crystal structures contain the doubly-protonated As tetrahedra. Such minerals usually form from strong acidic solutions. To date, the following minerals are known: kaatialaite, $Fe[AsO_2(OH)_2]_3(H_2O)_5$ (Raade *et al.*, 1984; Boudjada and Guitel, 1981), andyrobertsite, ideally $KCd[Cu_5^{2+}(AsO_4)_4\{AsO_2(OH)_2)\}](H_2O)_2$

TABLE 5. Bond-valence analysis for švenekite.

	Ca	As1	As2	H2	H3	H5	H7	H8	ΣBV
O1	0.29, 0.27	1.38							1.94
O2	0.14	1.13		0.96					2.23
O3		1.14			0.97		0.16		2.27
O4	0.32	1.38		0.20					1.90
O5	0.30		1.28			0.50, 0.50			2.08
O6	0.30, 0.25		1.36						1.92
O7	0.11		1.09				0.96		2.16
O8			1.28		0.20			0.50, 0.50	1.98
ΣBV	2.00	5.04	5.00	1.16	1.17	1.00	1.12	1.00	

Values are expressed in valence units (v.u.). ΣBV, bond-valence sums.

TABLE 6. Powder XRD data for švenekite.

I_{rel}	d_{obs}	d_{calc}	I_{calc}	h	k	l	I_{rel}	d_{obs}	d_{calc}	I_{calc}	h	k	l	I_{rel}	d_{obs}	I_{calc}	d_{calc}	h	k	l
5.9	7.425	7.440	6.6	1	0	0	3.5	1.9099	1.9107	3.2	2	$\bar{4}$	0	2.4	1.40986	0.4	1.40998	2	4	0
13.5	7.100	7.113	12.6	0	1	0	2.3	1.9055	1.9060	2.1	2	$\bar{2}$	2			2.5	1.40980	3	1	2
11.8	6.510	6.522	10.8	1	$\bar{1}$	0	3.2	1.9017	1.9022	3.3	1	$\bar{3}$	2	0.9	1.40874	0.2	1.40849	3	0	$\bar{4}$
0.4	5.369	5.376	0.2	1	0	$\bar{1}$	0.7	1.8839	1.8847	0.5	4	$\bar{2}$	$\bar{2}$	3.8	1.40634	3.5	1.40648	1	$\bar{5}$	$\bar{1}$
2.5	5.280	5.288	1.9	0	0	1	1.9	1.8792	1.8798	1.5	4	$\bar{3}$	$\bar{1}$	0.8	1.40075	0.6	1.40091	2	0	3
7.5	4.665	4.671	7.0	0	$\bar{1}$	1	11.4	1.8716	1.8720	9.7	1	3	$\bar{2}$			0.3	1.40064	5	$\bar{4}$	$\bar{2}$
24.5	4.479	4.484	24.3	1	$\bar{1}$	$\bar{1}$	2.7	1.8687	1.8691	2.9	3	2	$\bar{1}$	2.5	1.39433	1.7	1.39444	6	$\bar{1}$	$\bar{1}$
22.8	4.113	4.117	23.0	1	1	$\bar{1}$	5.1	1.8598	1.8600	3.3	4	0	0			1.2	1.39443	2	$\bar{3}$	3
32.6	3.968	3.972	32.7	2	$\bar{1}$	0	6.5	1.8463	1.8467	5.7	1	$\bar{4}$	1	2.1	1.38995	2.1	1.38999	5	$\bar{3}$	1
5.6	3.912	3.916	5.9	0	1	1	4.1	1.8407	1.8409	3.7	4	$\bar{3}$	0	2.2	1.38658	1.8	1.38683	6	$\bar{3}$	$\bar{1}$
15.8	3.808	3.812	15.5	1	$\bar{1}$	1	0.7	1.8331	1.8337	0.6	3	$\bar{3}$	$\bar{2}$	6.5	1.38412	2.8	1.38433	0	$\bar{4}$	3
14.8	3.788	3.791	17.0	2	0	$\bar{1}$	1.2	1.8287	1.8289	0.3	2	$\bar{1}$	$\bar{3}$			2.7	1.38404	5	$\bar{1}$	1
34.9	3.766	3.769	33.6	2	$\bar{1}$	$\bar{1}$	0.9	1.8188	1.8191	1.1	2	2	1	1.5	1.37977	2.1	1.37992	1	$\bar{5}$	2
6.2	3.717	3.720	7.4	2	0	0	6.2	1.8126	1.8129	6.3	2	3	$\bar{1}$	0.5	1.37235	0.8	1.37241	3	3	$\bar{3}$
49.0	3.697	3.700	46.5	1	0	1	2.3	1.8046	1.8049	2.4	3	$\bar{4}$	0	2.2	1.34608	2.1	1.34620	1	5	$\bar{1}$
100.0	3.554	3.557	100.0	0	2	0	2.2	1.7975	1.7979	2.1	2	$\bar{4}$	1	0.4	1.34406	0.1	1.34400	4	0	$\bar{4}$
33.0	3.259	3.261	33.0	2	$\bar{2}$	0	4.2	1.7957	1.7961	4.4	2	$\bar{4}$	$\bar{1}$	0.7	1.33910	0.2	1.33918	1	$\bar{1}$	$\bar{4}$
3.8	3.234	3.237	4.4	0	$\bar{2}$	1	8.1	1.7777	1.7784	3.9	0	4	0	0.5	1.32853	0.8	1.32869	3	$\bar{5}$	$\bar{2}$
48.6	3.097	3.099	50.1	1	$\bar{2}$	1			1.7776	2.3	3	2	$\bar{2}$	1.3	1.32363	1.3	1.32367	6	0	$\bar{1}$
15.9	3.037	3.039	16.7	2	1	$\bar{1}$	5.0	1.7623	1.7626	4.8	0	0	3	0.4	1.32197	0.7	1.32216	3	$\bar{4}$	$\bar{3}$
13.6	3.003	3.005	13.5	2	$\bar{2}$	$\bar{1}$	6.7	1.7594	1.7597	6.3	1	3	1			0.0	1.32192	0	0	4
21.1	2.924	2.9256	21.5	1	1	1	2.3	1.7570	1.7574	2.5	3	$\bar{4}$	$\bar{1}$	0.9	1.31920	0.2	1.31908	3	$\bar{2}$	$\bar{4}$
16.6	2.8772	2.8788	16.3	2	1	0	1.1	1.7509	1.7513	1.4	2	$\bar{3}$	2	0.8	1.31782	0.7	1.31785	5	$\bar{5}$	$\bar{1}$
9.2	2.8536	2.8552	7.6	1	0	$\bar{2}$	2.1	1.7248	1.7251	2.3	2	3	0	0.6	1.30915	0.3	1.30907	4	$\bar{4}$	$\bar{3}$
0.5	2.8184	2.8200	0.7	1	2	0	5.5	1.7078	1.7080	4.8	0	$\bar{2}$	3	1.2	1.30611	0.8	1.30647	5	2	$\bar{2}$
6.4	2.8029	2.8043	6.5	3	$\bar{1}$	$\bar{1}$	1.2	1.7023	1.7024	1.2	3	1	$\bar{3}$			0.1	1.30637	4	0	2
3.1	2.7283	2.7298	3.4	0	2	1	2.0	1.6990	1.6988	1.9	5	$\bar{2}$	$\bar{1}$	0.1	1.30216	0.1	1.30193	2	$\bar{2}$	$\bar{4}$
8.6	2.6967	2.6981	8.2	1	1	$\bar{2}$	0.7	1.6695	1.6697	0.2	2	$\bar{2}$	$\bar{3}$	3.5	1.30028	2.6	1.30032	1	5	$\bar{2}$
1.8	2.6869	2.6880	1.6	2	0	$\bar{2}$	1.2	1.6664	1.6666	1.6	2	1	2			0.2	1.30028	6	$\bar{2}$	$\bar{3}$
22.7	2.6652	2.6663	21.6	3	0	$\bar{1}$	3.6	1.6625	1.6628	3.3	3	$\bar{4}$	1	0.2	1.29830	0.9	1.29833	2	4	$\bar{3}$
0.8	2.6429	2.6438	0.6	0	0	2	7.1	1.6526	1.6528	7.9	4	1	0	1.2	1.29616	0.8	1.29581	4	$\bar{4}$	2
3.4	2.6389	2.6403	2.8	0	$\bar{1}$	2	5.3	1.6438	1.6441	5.8	5	$\bar{1}$	$\bar{2}$	0.4	1.27827	0.6	1.27840	2	$\bar{6}$	0
3.6	2.6115	2.6127	3.3	2	0	1	0.9	1.6402	1.6402	0.9	4	$\bar{1}$	$\bar{3}$	0.2	1.27609	0.4	1.27603	2	3	2
0.2	2.6021	2.6039	0.2	1	$\bar{1}$	$\bar{2}$	3.2	1.6355	1.6357	3.3	4	$\bar{4}$	$\bar{1}$	1.4	1.27381	1.0	1.27381	3	$\bar{6}$	0
8.8	2.5904	2.5916	7.7	2	$\bar{2}$	1	2.6	1.6321	1.6321	4.4	3	$\bar{2}$	2	0.4	1.26721	1.0	1.26702	6	$\bar{4}$	0
7.3	2.5539	2.5550	6.2	3	$\bar{2}$	$\bar{1}$	5.4	1.6306	1.6305	4.1	4	$\bar{4}$	0	1.7	1.26524	0.5	1.26516	3	2	2

1.4	2.5332	2.5341	0.7	3	$\bar{2}$	0	3.1	1.6250	1.6255	1.9	3	$\bar{1}$	2	0.1	1.26174	0.2	1.26191	2	$\bar{6}$	1
4.4	2.4668	2.4677	3.4	2	$\bar{3}$	0	2.6	1.5994	1.5998	2.1	0	4	1	0.7	1.25603	0.4	1.25606	0	$\bar{3}$	4
5.3	2.3701	2.3712	4.1	0	3	0	0.8	1.5814	1.5815	0.7	5	$\bar{1}$	0			0.3	1.25597	1	$\bar{1}$	4
3.5	2.3632	2.3643	3.5	1	$\bar{3}$	1	0.1	1.5778	1.5777	0.4	4	0	1	1.0	1.25455	0.7	1.25453	5	$\bar{5}$	$\bar{2}$
0.4	2.3416	2.3427	0.3	0	1	2	1.1	1.5754	1.5756	1.2	4	$\bar{2}$	$\bar{3}$	2.7	1.25132	0.7	1.25179	2	3	$\bar{4}$
7.0	2.3266	2.3277	6.9	0	$\bar{3}$	1	2.8	1.5573	1.5576	1.4	3	$\bar{4}$	$\bar{2}$			1.9	1.25124	4	3	0
5.1	2.3147	2.3155	4.2	2	2	$\bar{1}$			1.5569	1.0	0	$\bar{3}$	3	1.9	1.24958	0.9	1.24986	1	$\bar{2}$	4
8.9	2.2897	2.2906	7.0	2	$\bar{3}$	$\bar{1}$	0.9	1.5495	1.5497	1.0	2	$\bar{4}$	2			1.2	1.24955	1	$\bar{6}$	1
4.1	2.2837	2.2846	4.1	1	2	$\bar{2}$	3.0	1.5457	1.5461	0.6	3	3	$\bar{1}$	1.9	1.24760	1.7	1.24742	4	3	$\bar{3}$
1.9	2.2714	2.2722	1.2	3	1	$\bar{1}$			1.5456	2.0	1	4	$\bar{2}$	0.4	1.24702	0.1	1.24650	1	$\bar{6}$	0
2.6	2.2431	2.2441	1.8	1	$\bar{3}$	$\bar{1}$	1.4	1.5396	1.5392	1.1	4	2	$\bar{1}$	0.8	1.23993	0.8	1.24000	6	0	0
1.4	2.2374	2.2384	1.4	1	0	2	8.1	1.5365	1.5364	5.9	5	$\bar{3}$	$\bar{2}$	1.0	1.23879	1.4	1.23880	3	$\bar{6}$	1
1.4	2.2346	2.2354	1.2	1	2	1	1.4	1.5281	1.5283	2.2	4	1	$\bar{3}$	1.2	1.23818	1.2	1.23796	3	$\bar{6}$	$\bar{1}$
3.6	2.2102	2.2109	3.0	2	1	1	0.5	1.5094	1.5095	1.0	3	3	$\bar{2}$	0.7	1.23752	0.3	1.23782	5	$\bar{2}$	$\bar{4}$
0.3	2.1888	2.1896	0.2	2	2	0	2.2	1.5068	1.5069	2.1	3	2	1	1.4	1.23389	1.5	1.23386	4	$\bar{6}$	0
2.3	2.1849	2.1855	1.8	2	$\bar{3}$	1	0.4	1.4950	1.4947	0.3	3	$\bar{3}$	$\bar{3}$	0.5	1.23277	0.4	1.23245	2	5	$\bar{1}$
18.4	2.1721	2.1727	15.7	1	$\bar{2}$	$\bar{2}$	1.7	1.4818	1.48195	2.1	2	3	$\bar{3}$	0.9	1.22449	0.0	1.22414	2	$\bar{6}$	$\bar{1}$
0.2	2.1372	2.1382	0.1	3	$\bar{3}$	$\bar{1}$	1.4	1.4777	1.47776	1.9	2	$\bar{3}$	$\bar{3}$			0.3	1.22421	1	0	4
0.1	2.1313	2.1317	0.0	4	$\bar{1}$	$\bar{1}$	5.7	1.4758	1.47586	3.2	1	$\bar{4}$	$\bar{2}$	0.1	1.22215	0.2	1.22198	4	2	$\bar{4}$
4.1	2.1210	2.1216	4.1	3	$\bar{2}$	$\bar{2}$			1.47590	3.1	0	2	3	1.6	1.22072	1.1	1.22059	5	$\bar{5}$	1
0.2	2.1170	2.1168	0.0	3	$\bar{1}$	1	1.9	1.4744	1.47468	1.2	5	$\bar{4}$	$\bar{1}$	1.0	1.21831	0.0	1.21818	5	2	0
2.3	2.1060	2.1068	2.2	3	1	0	1.2	1.4596	1.45971	1.2	3	3	0			1.4	1.21822	4	$\bar{6}$	$\bar{1}$
1.1	2.1014	2.1019	1.1	1	3	$\bar{1}$	0.4	1.4560	1.45617	0.5	2	$\bar{1}$	3	0.6	1.21753	0.3	1.21736	1	$\bar{5}$	3
3.4	2.0855	2.0860	2.9	3	$\bar{2}$	1	1.9	1.4535	1.45415	0.8	5	1	$\bar{1}$	0.5	1.21606	0.4	1.21591	7	$\bar{2}$	$\bar{2}$
2.2	2.0764	2.0772	1.9	4	$\bar{2}$	$\bar{1}$			1.45374	0.6	2	$\bar{2}$	3	<0.1	1.21077	0.0	1.21057	4	1	2
0.9	2.0685	2.0690	0.7	3	1	$\bar{2}$			1.45338	0.7	4	$\bar{3}$	$\bar{3}$	1.3	1.20942	1.6	1.20940	6	$\bar{5}$	$\bar{1}$
1.2	2.0582	2.0586	0.8	2	2	$\bar{2}$	2.8	1.4518	1.45192	2.8	5	1	$\bar{2}$	1.6	1.20857	1.3	1.20859	5	1	1
0.2	2.0295	2.0299	0.1	0	3	1	1.2	1.4454	1.44557	1.7	1	3	2	1.3	1.20641	1.9	1.20635	1	5	1
1.1	2.0081	2.0085	0.8	4	0	$\bar{1}$	0.5	1.4331	1.43314	0.9	3	$\bar{5}$	1	0.7	1.18720	1.1	1.18720	2	5	0
11.7	1.9932	1.9939	10.4	4	$\bar{1}$	0	2.5	1.4316	1.43164	2.4	3	$\bar{4}$	2	0.6	1.18564	0.8	1.18558	0	6	0
3.1	1.9855	1.9859	2.7	4	$\bar{2}$	0	0.7	1.4266	1.42620	0.4	2	4	$\bar{2}$			0.2	1.18561	4	$\bar{6}$	1
1.7	1.9757	1.9762	1.7	3	0	1	1.7	1.4226	1.42270	1.4	0	5	0	0.9	1.18268	0.4	1.18269	6	$\bar{4}$	$\bar{3}$
1.0	1.9605	1.9607	0.9	4	$\bar{1}$	$\bar{2}$	1.8	1.4185	1.41885	0.9	4	$\bar{5}$	0	0.0		0.0	1.18256	2	$\bar{5}$	3
4.1	1.9457	1.9463	4.0	2	$\bar{1}$	2			1.41798	0.4	6	$\bar{2}$	$\bar{1}$	0.2	1.18199	0.0	1.18214	7	$\bar{1}$	$\bar{1}$
							2.0	1.4137	1.41377	1.1	2	1	$\bar{4}$	0.6	1.16934	0.5	1.16939	5	$\bar{6}$	$\bar{1}$

Unit-cell dimensions refined from the above data employing the cosine term to correct sample displacement: a = 8.5482(3) Å, b = 7.6945(3) Å, c = 5.7180(2) Å, α = 92.602(2)°, β = 109.867(2)°, γ = 109.910(2)°, V = 327.01(3) Å^3.

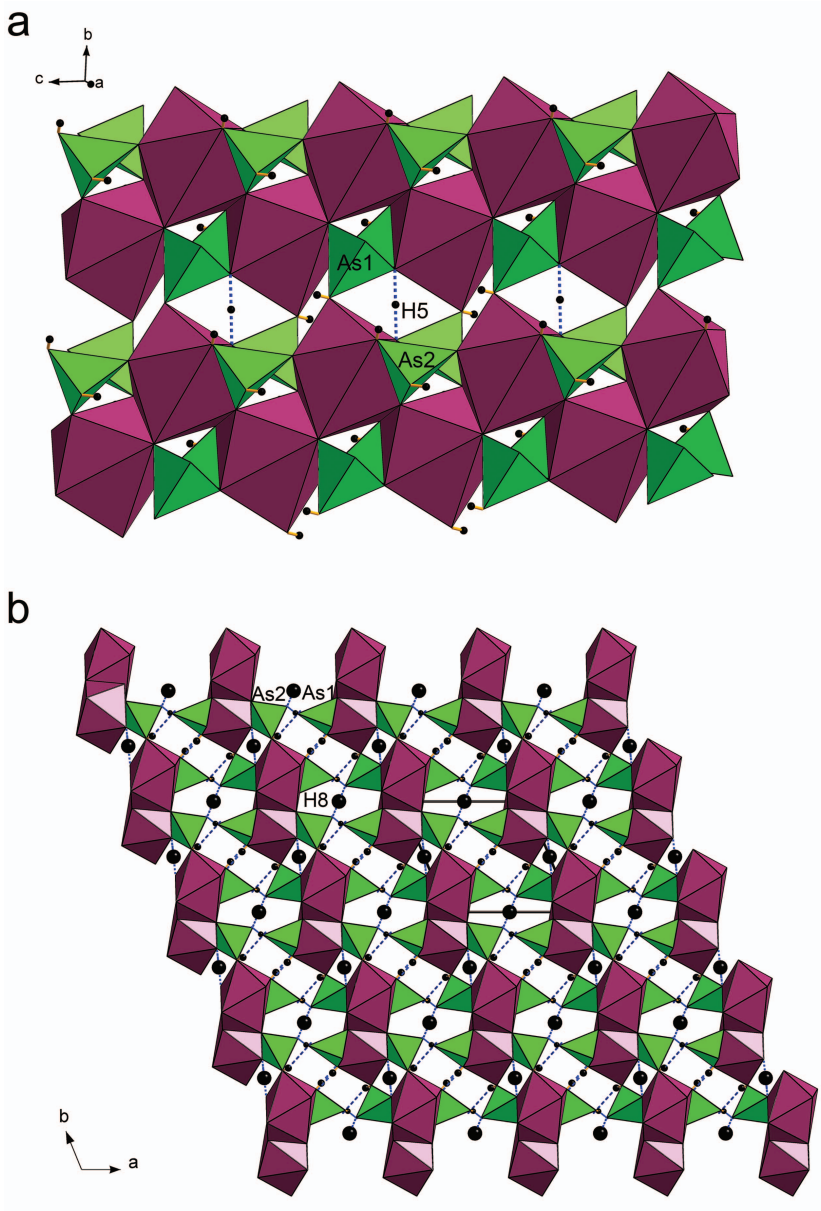

FIG. 4. (*a*) Sheet of polyhedra in the structure of švenekite (projected slightly inclined to [100]). The symmetrical hydrogen bond (blue dashed) O5-H5-O5 extends an inter-sheet linkage. An As1 tethrahedron links the adjacent chains of edge-sharing Ca-polyhdera (violet) into the sheets, while the As2 tetrahedron is linked to the neighouring Ca-polyhedra within the same chain. (*b*) View of the structure parallel to the sheets (along *c*) linked by the network of hydrogen bonds.

(Cooper *et al.*, 1999; Cooper and Hawthorne, 2000), and the mineral calcio-andyrobertsite (Cooper *et al.*, 1999), which forms two polytypes – calcio-andyrobertsite-1*O*, $KCa[Cu_5^{2+}(AsO_4)_4\{AsO_2(OH)_2)\}](H_2O)_2$ (Cooper and Hawthorne, 2000) and calcio-andyrobertsite-2*M*, $KM[Cu_5^{2+}(AsO_4)_4\{AsO_2(OH)_2)\}](H_2O)_2$, where M = Ca, Cd, Mn (Sarp and Černý, 2004). The

other mineral known to contain doubly-acid arsenate groups is the mineral manganlotharmeyerite, $Ca(Mn^{3+},\square,Mg)_2$ $[AsO_4,\{AsO_2(OH)_2\}]_2(OH,H_2O)_2$ (Brugger *et al.*, 2002). However, švenekite represents different topological type from all these minerals.

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