BURGESSITE, Co_2 $(H_2O)_4$ $[AsO_3(OH)]_2$ (H_2O), A NEW ARSENATE MINERAL SPECIES FROM THE KEELEY MINE, SOUTH LORRAIN TOWNSHIP, ONTARIO, CANADA

Jiří SEJKORA

Department of Mineralogy and Petrology, National Museum, Václavské náměstí 68, CZ–115 79, Praha 1, Czech Republic

Frank C. HAWTHORNE[§] AND Mark A. COOPER

Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada

Joel D. GRICE

Research Division, Canadian Museum of Nature, PO Box 3443, Station "D", Ottawa, Ontario K1P 6P4, Canada

Josef VAJDAK

342 Forest Avenue, Massapequa, New York 11758–5707, U.S.A.

John L. JAMBOR[†]

136 Rosehill Wynd, Tsawwassen, British Columbia V4M 3L9, Canada

ABSTRACT

Burgessite, Co_2 $(H_2O)_4$ $[AsO_3(OH)]_2$ (H_2O), is a new mineral species of supergene origin from the Keeley mine, South Lorrain Township, Timiskaming District, Ontario, Canada. Burgessite forms rosettes up to 0.8 mm across consisting of prismatic crystals up to 0.1 mm long, elongate along **a**, with the following forms: {011} >> {h0l}, and no observable twinning. It is associated with primary skutterudite, cobaltite and bismuth, and supergene arsenolite, bismutoferrite and erythrite. Burgessite is transparent, purplish pink with a slight brown tint, and has a colorless to pale pink streak and a vitreous luster; it does not fluoresce under ultraviolet light. It exhibits two cleavages, {010} good and {001} fair. The Mohs hardness is ~3; burgessite is brittle with a hackly fracture, and has measured and calculated densities of 2.93(2) and 2.94 g/cm³, respectively. Burgessite is biaxial positive with α 1.596, β 1.604, γ 1.628, all ±0.002, with a $2V_{obs}$ of 70(2)° and $2V_{calc}$ = 61°. It is nonpleochroic, with an optic orientation X = **b**, Y ∧ **c** = 29° (in β obtuse), Z ∧ **a** = 20° (in β acute). Burgessite is monoclinic, space group $P2_1/n$, *a* 4.7058(12), *b* 9.299(3), *c* 12.738(4) Å, β 98.933(8)°, *V* 550.6(5) Å³, Z = 2, *a:b:c* = 0.5061:1:1.3698. The strongest seven lines in the X-ray powder-diffraction pattern [*d* in Å(I)(*hkl*)] are: 7.446(100)(011), 6.267(44)(002), 3.725(29)(022), 3.260(25)(12$\bar{1}$), 2.998(31)(031), 2.970(21)(014) and 2.596(23)(024). A chemical analysis with an electron microprobe gave As_2O_5 47.91, P_2O_5 0.03, CoO 27.31, NiO 3.52, ZnO 0.04, CaO 0.18, SO_3 0.13, H_2O (calc.) 22.65, for a sum of 101.77 wt.%; the valence states of As and Co, and the amount of H_2O, were determined by crystal-structure analysis. The resulting empirical formula on the basis of 13 (O, OH, H_2O) anions is $(Co_{1.75}$ $Ni_{0.23}$ $Ca_{0.02})_{\Sigma2.00}$ $(AsO_3OH)_{\Sigma2.00}$ $(H_2O)_5$. The crystal structure of burgessite consists of chains of the form $[Co_2(H_2O)_4(As^{5+}O_3(OH))_2]$ that extend in the **a** direction and are linked by hydrogen bonds, and is closely related to that of erythrite.

Keywords: burgessite, new mineral species, arsenate, chemical analysis, X-ray powder-diffraction pattern, optical properties, erythrite, Keeley mine, Ontario.

SOMMAIRE

Nous décrivons la burgessite, Co_2 $(H_2O)_4$ $[AsO_3(OH)]_2$ (H_2O), nouvelle espèce minérale d'origine supergène provenant de la mine Keeley, canton de South Lorrain, district de Timiskaming, Ontario, Canada. La burgessite se présente en rosettes mesurant jusqu'à 0.8 mm de diamètre, composées de petits cristaux prismatiques atteignant une longueur de 0.1 mm, allongés selon **a**, avec

[†]   Deceased.
[§]   *E-mail address*: frank_hawthorne@umanitoba.ca

les formes suivantes; {011} >> {*h*0*l*}, et sans macle observable. Lui sont associés skutterudite primaire, cobaltite et bismuth, et comme phases supergènes, arsénolite, bismutoferrite et érythrite. La burgessite est transparente, rose violacé avec une légère teinte brune; elle possède une rayure incolore à rose pâle et un éclat vitreux. Elle ne montre aucune fluorescence en lumière ultra-violette. Elle possède deux clivages, {010} bon et {001} imparfait. La dureté de Mohs est environ 3. La burgessite est cassante avec une fracture hachée; la densité mesurée et calculée est 2.93(2) et 2.94 g/cm^3, respectivement. Elle est biaxe positive, avec α 1.596, β 1.604, γ 1.628, tous ±0.002, avec un $2V_{obs}$ de 70(2)° et $2V_{calc}$ de 61°. Elle est non pléochroïque, avec une orientation optique X = **b**, Y $\wedge$ **c** = 29° (dans l'angle β obtus), Z $\wedge$ **a** = 20° (dans l'angle β aigu). La burgessite est monoclinique, groupe spatial $P2_1/n$, a 4.7058(12), b 9.299(3), c 12.738(4) Å, β 98.933(8)°, V 550.6(5) Å^3, Z = 2, a:b:c = 0.5061:1:1.3698. Les sept raies les plus intenses du spectre de diffraction X (méthode des poudres) [d en Å(I)(hkl)] sont: 7.446(100)(011), 6.267(44)(002), 3.725(29)(022), 3.260(25)(12$\bar{1}$), 2.998(31)(031), 2.970(21)(014) et 2.596(23)(024). Une analyse chimique avec une microsonde électronique a donné As$_2$O$_5$ 47.91, P$_2$O$_5$ 0.03, CoO 27.31, NiO 3.52, ZnO 0.04, CaO 0.18, SO$_3$ 0.13, H$_2$O (calc.) 22.65, pour une somme de 101.77% (poids); la valence de l'arsenic et du cobalt, et la teneur en H$_2$O, découlent de l'analyse de la structure. La formule empirique qui en résulte, calculée sur une base de 13 (O, OH, H$_2$O) anions, est (Co$_{1.75}$ Ni$_{0.23}$ Ca$_{0.02}$)$_{\Sigma2.00}$ (AsO$_3$OH)$_{\Sigma2.00}$ (H$_2$O)$_5$. La structure cristalline de la burgessite contient des chaînes de la forme [Co$_2$(H$_2$O)$_4$(As^{5+}O$_3$(OH))$_2$] allongées selon la direction **a** et connectées l'une à l'autre par liaisons hydrogène; elle montre une relation étroite avec l'érythrite.

(Traduit par la Rédaction)

Mots-clés: burgessite, nouvelle espèce minérale, arsenate, analyse chimique, spectre de diffraction X sur poudre, propriétés optiques, érythrite, mine Keeley, Ontario.

INTRODUCTION

The Keeley mine, located in South Lorrain Township, Timiskaming District, Ontario, Canada, was a significant producer of silver and cobalt from 1908 to 1942 and from 1963 to 1965. The area consists of early Precambrian folded metavolcanic rocks cut by a thick (250–300 m) domed sill of Nipissing diabase. Mineralization is associated with the diabase and calcite veins containing native silver, skutterudite (variety "smaltite"), nickeline, proustite and many other sulfides and sulfosalts; in particular, the locality is well known for fine wire silver (Boyle & Dass 1971a). Moreover, the primary mineralization has been affected by subsequent supergene alteration (Boyle & Dass 1971b). Mr. David Burgess of Newington, Connecticut, U.S.A., purchased a mineral specimen labeled "erythrite" from a mineral dealer; the sample consists of pink rosettes on matrix and was collected in the 1920s. Mr. Burgess brought this specimen to the attention of the authors. The X-ray powder-diffraction pattern of the pink rosettes did not correspond to that of any known mineral, and a complete description resulted in approval of the new mineral by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA 2007–055). The mineral is named *burgessite* after David S. Burgess (born April 18, 1951) of Newington, Connecticut, U.S.A. The holotype specimen of burgessite has been deposited in the mineral collection of the Canadian Museum of Nature, catalogue number CMNMC 86051.

PHYSICAL PROPERTIES

Burgessite consists of purplish pink (with a slight brown tint) rosettes (up to 0.8 mm across) scattered across a surface of primary skutterudite, cobaltite and bismuth, and supergene arsenolite, bismutoferrite and erythrite (Fig. 1). At higher magnifications (Fig. 2), individual lath-like crystals with a strong vitreous luster are apparent. Individual crystals are prismatic, up to 0.1 mm long, elongate along **a** (Fig. 3), with the following forms: {011} >> {*h*0*l*}; no twinning was observed. Burgessite is transparent and has a colorless to pale pink streak and a vitreous luster; it does not fluoresce under ultraviolet light. There are two cleavages, {010} good and {001} fair. The Mohs hardness is ~3; burgessite is brittle with a hackly fracture. The density measured by suspension in a bromoform-acetone mixture is 2.93(2), and the calculated density is 2.94 g/cm^3. Optical properties were measured with the Bloss spindle stage for the wavelength 590 nm using a gel filter. The indices of refraction are α 1.596, β 1.604, γ 1.628, all ±0.002, the calculated birefringence is 0.032, $2V_{obs}$ = 70(2)°, $2V_{calc}$ = 61°, burgessite is nonpleochroic, and the optic orientation is as follows: X = **b**, Y $\wedge$ **c** = 29° (in β obtuse).

CHEMICAL COMPOSITION

Crystals were analyzed with a Cameca SX–100 electron microprobe (Laboratory of electron microscopy and microanalysis of Masaryk University and Czech Geological Survey, Brno) operating in the wavelength-dispersion mode with an accelerating voltage of 15 kV, a specimen current of 4–10 nA, and a beam diameter of 5–20 μm. The following lines and standards were used: $K\alpha$: andradite (Ca), barite (S), CoO (Co), apatite-(CaF) (P), NiO (Ni), ZnO (Zn); $L\alpha$: InAs (As). Peak-counting times were 20 s for main elements and 60 s for minor elements. The time spent counting the background was half of the time spent counting the peak. Raw intensities were converted to concentrations using the

FIG. 1. Round rosettes of burgessite dispersed on the rock surface; the field of view is 0.4 cm. National Museum Prague (Czech Republic) collection, photo J. and E. Sejkora.

FIG. 2. Rosettes of burgessite showing the individual lath-like crystals and their adamantine luster; the field of view is 1.1 mm. National Museum Prague (Czech Republic) collection, photo J. and E. Sejkora.
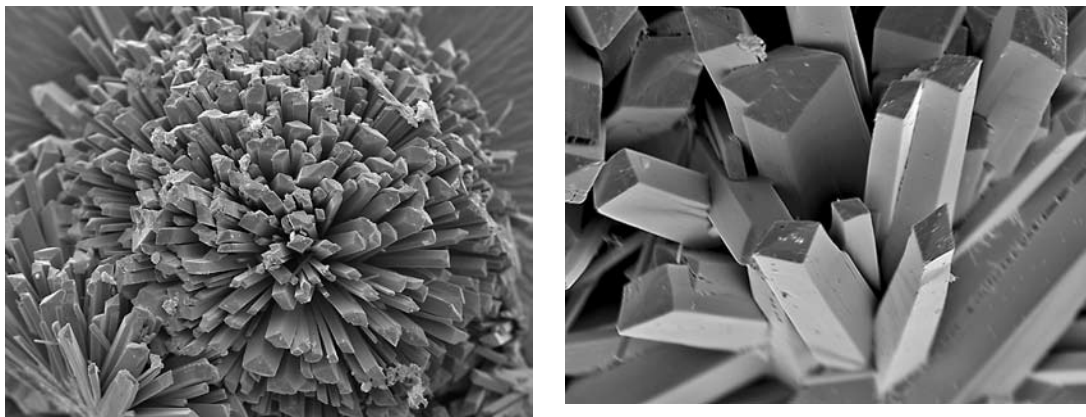
FIG. 3. SEM photographs of a rosette of burgessite: the field of view is as follows: (a) 200 μm, (b) 50 μm.

PAP (Pouchou & Pichoir 1985) software package for matrix correction. The presence and quantity of (OH) and (H_2O) groups were established by crystal-structure solution and refinement. In addition, infrared spectroscopy indicated a broad intense band centered at ~3400 cm^{-1} and a band at 1635 cm^{-1}, indicative of H_2O. Table 1 gives the chemical composition (mean of eight determinations) and formula unit based on 13 (O, OH, H_2O) anions [including two (OH) groups and 5 (H_2O) groups per formula unit (*pfu*)]. The excess of wt.% total over 100 is probably caused by slight dehydration of the mineral during electron-microprobe analysis, which would increase the percentages of non-H_2O components. The end-member formula for burgessite is Co_2 ($H_2O)_4$ [(AsO_3OH)]$_2$ (H_2O), where the (H_2O) groups before the arsenate bond to Co and the (H_2O) group after the arsenate is held in the structure solely by hydrogen bonds.

INFRARED ABSORPTION SPECTROSCOPY

The infrared-absorption spectrum of pulverized burgessite (KBr disk) was recorded with a Nicolet FTIR 740 spectrophotometer in the range 4000–400 cm^{-1} (Fig. 4). It differs distinctly from the spectrum of the hydrated Co arsenate mineral erythrite (Farmer 1974). Tentative assignment of observed infrared bands of burgessite is based on the data published by Keller (1971) and Farmer (1974), and on the fact that the crystal-structure solution of burgessite shows the presence of both ($AsO_3OH)^{2-}$ and (H_2O) groups.

The band at 3392 cm^{-1} (with a shoulder at 3588 cm^{-1}) was assigned to the ν OH stretching vibrations of (H_2O) groups, and those in the range 1600–1750 cm^{-1} (with a maximum at 1635 cm^{-1}) were assigned to the δ H–O–H bending vibration of (H_2O) groups. A shoulder in this region of the infrared spectrum may indicate that two structurally nonequivalent (H_2O) groups are present in the structure of burgessite, in accord with the results of the crystal-structure study (Cooper & Hawthorne 2009).

The ($AsO_3OH)^{2-}$ tetrahedron in the crystal structure of burgessite is distorted from its holosymmetric point-symmetry (C_{3v}), and all vibrations may become active in the infrared spectrum, and degenerate vibrations may split. The stretching vibration ν (OH) in the (AsO_3OH) group can be related to shoulders in the range 3000–2700 cm^{-1}, with a maximum at 2895 cm^{-1}. The δ (As–OH) in-plane bending vibrations, overtones and combination bands were observed in the range 1500–1100 cm^{-1}, with maxima at 1427, 1236, 1166, 1119 and 1054 cm^{-1}. Weak bands in the range 700–600 cm^{-1} with maxima 689, 675 and 654 cm^{-1} can be related to the stretching vibration ν (As–OH), the out-of-plane bending vibrations δ (As–OH), and libration modes of (H_2O) groups. Strong bands at 868 and 837, and 806 cm^{-1} were assigned to the triply degenerate antisymmetric-stretching vibration ν_3 (As–O) and the ν_1 (As–O) symmetric-stretching vibration, respectively.

TABLE 1. CHEMICAL COMPOSITION OF BURGESSITE

	mean	range	**	
CaO wt.%	0.18	0.05–0.28	Ca *apfu*	0.015
NiO	3.52	2.67–4.93	Ni	0.225
CoO	27.31	25.46–28.76	Co	1.742
ZnO	0.04	0.00–0.10	Zn	0.002
P_2O_5	0.03	0.00–0.06	P	0.002
As_2O_5	47.91	46.62–49.11	As	1.992
SO_3	0.13	0.06–0.23	S	0.008
H_2O*	22.65		OH	1.994
			H_2O	5.010
total	101.77			

* The content of H_2O was calculated from formula derived from crystal-structure analysis. ** Atom proportions are calculated on the basis (O,OH,H_2O) = 13.
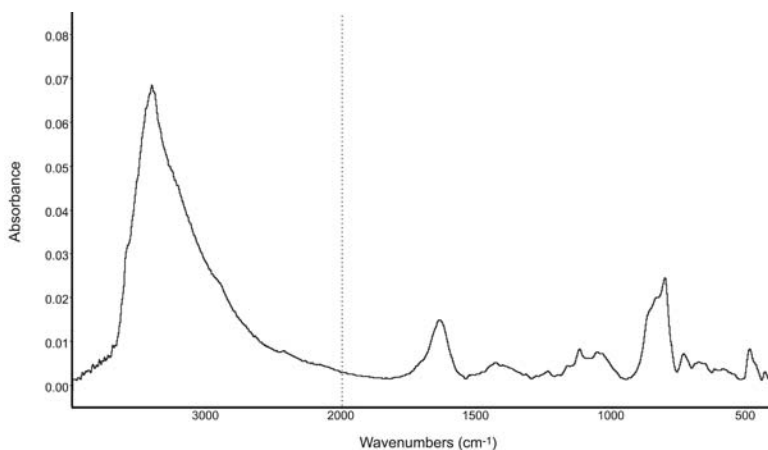
FIG. 4.   The infrared spectrum of burgessite.

TABLE 2. X-RAY POWDER-DIFFRACTION PATTERN OF BURGESSITE
FROM THE KEELEY MINE, ONTARIO

h k l	d_{obs}	d_{calc}	I_{obs}	h k l	d_{obs}	d_{calc}	I_{obs}	h k l	d_{obs}	d_{calc}	I_{obs}
0 1 1	7.446	7.452	100	1 3 2	2.3100	2.3099	2	2 3 1	1.8034	1.8029	1
0 0 2	6.267	6.274	44	2 0 $\bar{2}$	2.2973	2.2957	4	1 4 $\bar{4}$	1.7873	1.7869	1
0 1 2	5.189	5.194	9	1 1 $\bar{5}$	2.2940	2.2932	1	2 3 $\bar{3}$	1.7799	1.7797	2
1 0 $\bar{1}$	4.588	4.591	7	2 1 $\bar{1}$	2.2788	2.2761	1	0 5 2	1.7762	1.7766	15
0 2 1	4.343	4.345	9	2 1 $\bar{2}$	2.2322	2.2283	1	0 1 7	1.7593	1.7599	7
1 1 0	4.146	4.149	12	0 2 5	2.2060	2.2064	4	1 1 $\bar{7}$	1.7367	1.7358	2
1 0 1	"	4.148		0 3 4	2.2019	2.2005	2	1 3 5	1.7222	1.7231	3
1 1 $\bar{1}$	4.117	4.114	5	0 4 2	2.1687	2.1724	1	2 3 2	"	1.7216	
0 1 3	3.809	3.812	8	2 1 1	2.1599	2.1597	2	2 2 $\bar{5}$	1.7205	1.7208	5
1 1 1	3.787	3.786	4	1 2 4	2.1519	2.1515	5	1 5 0	"	1.7205	
0 2 2	3.725	3.726	29	1 3 3	2.1115	2.1104	3	0 5 3	1.6932	1.6938	1
1 0 $\bar{3}$	3.379	3.379	11	1 2 $\bar{5}$	2.1094	2.1076	4	2 3 $\bar{4}$	1.6899	1.6915	1
1 2 $\bar{1}$	3.260	3.261	25	2 2 $\bar{1}$	2.0943	2.0943	2	1 5 $\bar{2}$	1.6843	1.6842	2
1 1 2	"	3.259		1 3 $\bar{4}$	2.0775	2.0780	1	1 4 4	1.6756	1.6762	5
1 1 $\bar{3}$	3.173	3.175	15	1 0 5	2.0763	2.0765	1	0 2 7	1.6724	1.6717	7
0 0 4	3.132	3.137	1	2 0 2	2.0740	2.0740	2	2 1 $\bar{6}$	1.6629	1.6623	4
1 2 1	3.089	3.090	20	1 4 0	2.0719	2.0720	8	2 4 $\bar{1}$	1.6492	1.6487	1
1 2 $\bar{2}$	3.045	3.046	12	1 4 $\bar{1}$	2.0674	2.0675	2	2 4 0	1.6389	1.6391	7
0 3 1	2.998	2.998	31	0 1 6	2.0402	2.0400	7	1 5 2	1.6370	1.6353	1
0 1 4	2.970	2.971	21	1 1 5	2.0257	2.0262	17	2 2 4	1.6290	1.6293	2
1 0 3	2.893	2.891	9	0 4 3	"	2.0258		2 3 3	1.6221	1.6226	8
1 2 2	2.781	2.783	1	1 4 1	2.0219	2.0219	4	2 2 $\bar{6}$	1.5967	1.5873	4
0 3 2	2.775	2.770	2	2 2 1	2.0041	2.0025	1	2 4 $\bar{3}$	"	1.5865	
1 1 3	2.761	2.760	17	1 1 $\bar{6}$	1.9817	1.9815	2	0 5 4	1.5954	1.5951	7
1 2 $\bar{3}$	2.729	2.730	13	2 1 $\bar{4}$	1.9734	1.9755	3	2 3 $\bar{5}$	1.5891	1.5891	2
1 1 $\bar{4}$	2.689	2.689	10	0 3 5	1.9476	1.9474	13	0 0 8	1.5687	1.5685	2
0 2 4	2.596	2.597	23	1 4 2	1.9275	1.9280	3	1 1 7	"	1.5681	
1 3 0	2.571	2.571	19	0 2 6	1.9061	1.9060	5	1 3 6	1.5583	1.5579	1
0 3 3	2.4838	2.4840	15	2 2 2	1.8918	1.8928	6	0 1 8	1.5468	1.5465	5
1 3 1	2.4752	2.4767	11	1 3 $\bar{5}$	1.8768	1.8784	2	1 5 $\bar{4}$	"	1.5466	
1 3 $\bar{2}$	2.4544	2.4540	6	2 2 $\bar{4}$	1.8520	1.8531	5	1 4 5	1.5463	1.5459	8
1 2 3	"	2.4526		2 3 $\bar{2}$	1.8408	1.8422	2	0 6 0	1.5439	1.5437	3
1 0 $\bar{5}$	2.3672	2.3669	9	0 5 1	1.8332	1.8326	15	1 1 $\bar{8}$	1.5404	1.5397	2
1 1 4	2.3476	2.3500	1	2 1 $\bar{5}$	1.8172	1.8175	3	1 4 $\bar{6}$	1.5257	1.5258	6
2 0 0	2.3206	2.3205	3	1 4 3	1.8079	1.8074	1	2 2 5	1.4988	1.4998	4

Philips X'Pert MPD X-ray powder diffractometer, operated at 40kV and 40mA; Cu$K\alpha$ radiation with a graphite secondary monochromator.

Bands at 493 and 432 cm^{-1} are connected with the bending vibrations ν_4 and ν_2 (As–O), respectively. A digitized version of the spectrum is available from the Depository of Unpublished Data on the MAC website [document Burgessite CM47_165].

X-Ray Powder Diffraction

The powder-diffraction pattern was recorded with graphite-monochromated Cu*K*α X-radiation (λ = 1.54178 Å) and a Philips X'Pert powder diffractometer (40 kV, 40 mA). To minimize the complicated shape of the background, the sample studied was placed on a flat low-background silicon wafer. The powder pattern of burgessite (Table 2) was collected in the range from 3 to 63° 2θ with a step size of 0.02° 2θ and an exposure time of 42 s per step. Positions and intensities of reflections were calculated using the Pearson VII profile-shape function with the ZDS program package (Ondruš 1995). The unit-cell parameters, refined with the least-squares refinement program of Burnham (1962), are: *a* 4.6982(7), *b* 9.262(1), *c* 12.702(1) Å, β 98.95(1)°, *V* 546.0(1) Å^3.

Acknowledgements

References

Boyle, R.W. & Dass, A.S. (1971a): The origin of the native silver veins at Cobalt, Ontario. *Can. Mineral.* **11**, 414-429.

Boyle, R.W. & Dass, A.S. (1971b): The geochemistry of the supergene processes in the native silver veins of the Cobalt – South Lorrain area, Ontario. *Can. Mineral.* **11**, 358-390.

Burnham, C.W. (1962): Lattice constant refinement. *Carnegie Inst. Wash., Yearbook* **61**, 132-135.

Cooper, M.A. & Hawthorne, F.C. (2009): The crystal structure of burgessite, $Co_2(H_2O)_4AsO_3(OH)]_2(H_2O)$, and its relation to erythrite. *Can. Mineral.* **47**, 165-172.

Farmer, V.C., ed. (1974): *The Infrared Spectra of Minerals. Mineralogical Society Monograph* **4**.

Keller, P. (1971): Die Kristallchemie der Phosphat- und Arsenatminerale unter besonder Berücksichtigung der Kationen-Koordinationspolyeder und des Kristallwassers. I. Die Anionen der Phosphat- und Arsenatminerale. *Neues Jahrb. Mineral., Monatsh.*, 491-510.

Ondruš, P. (1995): *ZDS – Software for Analysis of X-ray Powder Diffraction Patterns. Version 6.01. User's guide*.

Pouchou, J.L. & Pichoir, F. (1985): "PAP" (ϕ–ρ–Z) procedure for improved quantitative microanalysis. *In* Microbeam Analysis. San Francisco Press, San Francisco, California (104-106).