The Canadian Mineralogist
Vol. 42, pp. 963-972 (2004)

PHOSPHOWALPURGITE, THE (PO_4)-DOMINANT ANALOGUE OF WALPURGITE, FROM SMRKOVEC, SLAVKOVSKÝ LES MOUNTAINS, CZECH REPUBLIC

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ABSTRACT

Phosphowalpurgite, ideally $(UO_2)Bi_4O_4(PO_4)_2{\bullet}2H_2O$, is the (PO_4)-dominant analogue of walpurgite. It occurs at old mine dumps of an abandoned small ore deposit near Smrkovec, located 10 km NNE of Mariánské Lázně, Slavkovský Les Mountains, western Bohemia, Czech Republic. Associated minerals include: "apatite", atelestite, bismutoferrite, bismutite, eulytite, hechtsbergite, metatorbernite, mixite, petitjeanite, preisingerite, pucherite, retgersite, schumacherite, smrkovecite and walpurgite. Phosphowalpurgite crystallized during the supergene alteration of primary bismuth and uraninite in hydrothermal quartz veins. It occurs as subhedral to euhedral tabular crystals, flattened on {010}, up to 1 mm in size, randomly growing in crystalline crusts, up to 1 cm^2 in size, within small fissures and cavities in the quartz gangue. Brownish grey, translucent crystals, which average 0.1–0.3 mm, have a vitreous to adamantine luster and a light brownish grey streak. The mineral is biaxial with high indices of refraction (1.9–2.0) and moderate to high birefrigence; the Mohs hardness is <5; it is nonfluorescent under both short- and long-wave UV radiation. Phosphowalpurgite has perfect cleavage on {010}, shows simple twinning, and is brittle with an uneven to conchoidal fracture. The calculated density (for the empirical formula) is 6.36 g/cm^3. Phosphowalpurgite is triclinic, space group $P\bar{1}$. The unit-cell parameters, refined from powder data, are: *a* 7.060(3), *b* 10.238(4), *c* 5.464(3) Å, α 101.22(4), β 109.93(3), γ 87.93(4)°, *V* 364.0(3) $Å^3$, *a*:*b*:*c* = 0.6896:1:0.5337, *Z* = 1. The strongest seven X-ray powder-diffraction lines [*d* in Å(I)(*hkl*)] are: 10.059(100)(010), 3.346(43)(030,$20\bar{1}$), 3.251(72)(021,$1\bar{2}\bar{1}$), 3.125(86)(210), 3.084(95)($1\bar{2}1$,$2\bar{1}\bar{1}$), 3.005(52)($13\bar{1}$), 2.726(42)(220,$11\bar{2}$). The average results of eight electron-microprobe analyses are: CaO 0.04, Cu 0.30, PbO 0.24, Fe_2O_3 0.40, Bi_2O_3 65.39, SiO_2 0.18, P_2O_5 7.65, V_2O_5 0.12, As_2O_5 4.15, UO_3 18.73, H_2O (2.59), total (100.09), corresponding to $[(UO_2)_{0.91}Ca_{0.08}Fe_{0.07}Cu_{0.05}Pb_{0.01}]_{\Sigma 1.12}$ $Bi_{3.91}O_{3.91}[(PO_4)_{1.50}(AsO_4)_{0.50}(SiO_4)_{0.04}(VO_4)_{0.02}]_{\Sigma 2.06}{\bullet}2.00H_2O$ (basis: 16 O atoms per formula unit). The ideal formula $(UO_2)Bi_4O_4(PO_4)_2{\bullet}2H_2O$ requires Bi_2O_3 66.76, P_2O_5 10.17, UO_3 20.49, H_2O 2.58, total 100.00 wt.%. We provide a detailed tentative interpretation of infrared-absorption spectra and other properties of the walpurgite – phosphowalpurgite series.

Keywords: phosphowalpurgite, new mineral species, tetrabismuthyl uranyl diphosphate dihydrate, walpurgite, uranyl, infrared spectroscopy, Smrkovec, Slavkovský Les Mountains, Czech Republic.

SOMMAIRE

La phosphowalpurgite, dont la formule idéale est $(UO_2)Bi_4O_4(PO_4)_2{\bullet}2H_2O$, est l'analogue phosphaté de la walpurgite. On la trouve dans les haldes d'un petit gîte minéral abandonné près de Smrkovec, situé à 10 km au nord–nord-ouest de Mariánské Lázně, montagnes Slavkovský Les, en Bohème occidentale, République Tchèque. Lui sont associés, entre autres, "apatite", atelestite, bismutoferrite, bismutite, eulytite, hechtsbergite, métatorbernite, mixite, petitjeanite, preisingerite, pucherite, retgersite,

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schumacherite, smrkovecite et walpurgite. La phosphowalpurgite a cristallisé au cours de l'altération épigénétique du bismuth et de l'uraninite primaires dans des veines de quartz hydrothermales. Elle se présente en cristaux sub-idiomorphes à idiomorphes, en plaquettes applaties sur {010} jusqu'à 1 mm de taille, en croûtes de cristaux d'orientation quelconque, recouvrant jusqu'à 1 cm^2 de surface, dans de petites fissures et dans des cavités dans les veines de quartz. Les cristaux gris brunâtres translucides, de 0.1 à 0.3 mm, en moyenne, possèdent un éclat vitreux à adamantin et une rayure gris brunâtre pâle. Il s'agit d'un minéral biaxe ayant des indices de réfraction élevés (1.9–2.0) et une biréfringence moyenne à élevée. La dureté de Mohs est inférieure à 5; elle est non fluorescente en lumière ultraviolette (ondes courtes et longues). La phosphowalpurgite possède un clivage {010} parfait, est simplement maclée, et cassante, avec une fracture inégale ou conchoïdale. La densité calculée (avec la formule empirique) est 6.36 g/cm^3. Elle est triclinique, groupe spatial $P\bar{1}$. Les paramètres réticulaires, affinés à partir du spectre de diffraction (méthode des poudres) sont: a 7.060(3), b 10.238(4), c 5.464(3) Å, α 101.22(4), β 109.93(3), γ 87.93(4)°, V 364.0(3) $Å^3$, a:b:c = 0.6896:1:0.5337, Z = 1. Les sept raies les plus intenses du spectre de diffraction [d en Å(I)(hkl)] sont: 10.059(100)(010), 3.346(43)($030,20\bar{1}$), 3.251(72)($021,1\bar{2}\bar{1}$), 3.125(86)(210), 3.084(95)($1\bar{2}1,2\bar{1}\bar{1}$), 3.005(52)($13\bar{1}$), 2.726(42)($220,11\bar{2}$). Les résultats moyens de huit analyses obtenues avec une microsonde électronique sont: CaO 0.04, Cu 0.30, PbO 0.24, Fe_2O_3 0.40, Bi_2O_3 65.39, SiO_2 0.18, P_2O_5 7.65, V_2O_5 0.12, As_2O_5 4.15, UO_3 18.73, H_2O (2.59), total (100.09%), ce qui correspond à $[(UO_2)_{0.91}Ca_{0.08}Fe_{0.07}Cu_{0.05}Pb_{0.01}]_{\Sigma 1.12}Bi_{3.91}O_{3.91}[(PO_4)_{1.50}(AsO_4)_{0.50}(SiO_4)_{0.04}(VO_4)_{0.02}]_{\Sigma 2.06}\bullet 2.00H_2O$ (sur une base de 16 atomes d'oxygène par formule unitaire). La formule idéale, $(UO_2)Bi_4O_4(PO_4)_2\bullet 2H_2O$, requiert Bi_2O_3 66.76, P_2O_5 10.17, UO_3 20.49, H_2O 2.58, total 100.00% (poids). Nous présentons une interprétation détaillée provisoire du spectre d'absorption infrarouge et des autres propriétés de la série walpurgite – phosphowalpurgite.

(Traduit par la Rédaction)

Mots-clés: phosphowalpurgite, nouvelle espèce minérale, diphosphate de tétrabismuthyle uranylé dihydraté, walpurgite, uranyle, spectroscopie infrarouge, Smrkovec, montagnes Slavkovský Les, République Tchèque.

Introduction

Recent investigations of walpurgite-type minerals, identified from the small abandoned ore deposit near Smrkovec, in western Bohemia, Czech Republic, reveal a broad variation in $(AsO_4)^{3-}$ and $(PO_4)^{3-}$ content. Electron-microprobe analyses show that both As- and P-dominant phases occur at this locality and that walpurgite with some (PO_4) content is the more abundant (Sejkora *et al.* 2002). We name the (PO_4)-dominant analogue *phosphowalpurgite* on the basis of its chemical composition and structural relationship to walpurgite.

The Commission on New Minerals and Mineral Names of the IMA has approved the mineral and mineral name (IMA 2001–062). Type material has been deposited under number P1p 10/2001 at the Department of Mineralogy and Petrology, National Museum, Prague, Czech Republic.

Background Information

Walpurgite is a rare uranium-bearing mineral; only a few localities have been reported in the literature. It was originally described from a unique occurrence of U and Bi minerals in the Walpurgis vein of the Weisser Hirsch mine at Schneeberg–Neustädtel, Saxony, Germany, associated with trögerite, zeunerite, uranospinite and uranosphaerite (Weisbach 1871, 1877). Walpurgite was studied as "waltherite" from Jáchymov, Czech Republic by Fischer (1955), and more recently by Sejkora (1992a) and Ondruš *et al.* (1997a). Walpurgite has also been documented to occur at Dalbeattie, southern Scotland (Braithwaite & Knight 1990), the Adam Heber mine, Schneeberg, Saxony (Haacke *et al.* 1994), the "Schurfschacht 14" mine of SDAG Wismut near Geyer, Saxony (Haacke *et al.* 1994), at Wittichen, Schwarzwald, Germany (Walenta 1972, Krause *et al.* 1995), the Hilfe Gottes mine, near Schiltach, Schwarzwald (Markl 1992), the uranium occurrence Rýžovištì near Harrachov (Sejkora *et al.* 1994b), and the small ore deposit near Smrkovec (Sejkora *et al*. 2002), both in the Czech Republic.

The orthorhombic analogue of walpurgite, orthowalpurgite, was described by Krause *et al.* (1995) as transparent yellow tabular crystals on quartz at the type locality, Schmiedestollen, Wittichen, Schwarzwald, Germany.

Minor to substantial amounts of phosphorus substituting for arsenic were reported in walpurgite from the following localities: Schneeberg, Saxony: 9 mol.% (Fischer 1948) and 43 mol.% (Evans 1950), and Smrkovec: 23 to 48 mol.% (Sejkora *et al*. 2002); a minor content of P was reported in walpurgite from Jáchymov (Ondruš *et al.* 1997a).

A mineral phase close to phosphowalpurgite was described as "phosphate–walpurgite" from Jáchymov by Ondruš *et al.* (1997b); however, no quantitative chemical data were given. The unnamed phase "hydrated uranophosphate of bismuth", which we can consider a phosphate analogue of walpurgite, was published by Melkov (1945); however, neither quantitative chemical nor X-ray data were published. Because of significant differences in optical data, this phase is very likely not identical to phosphowalpurgite; however, it was called "walpurgite(P)" by Smith (1984), "Phosphat-Walpurgin" by Strunz (1982), and "unnamed phosphate analogue of walpurgite" by Finch & Murakami (1999). On the other hand, this phase was not included in the compilations of valid mineral species (*e.g.*, Gaines *et al.* 1997, Mandarino 1999, Anthony *et al.* 2000).

Occurrence and Associated Minerals

The small ore deposit near Smrkovec is situated about 10 km NNE of Mariánské Lázně, western Bohemia, in the Czech Republic, in rocks of the crystalline complex of the Slavkovský Les Mountains. Veins of hydrothermal ore are located in a fault zone between a granite body (petrological type "Ovčák") and the surrounding metamorphic rocks (Fiala 1959). This rock complex includes chlorite – white mica phyllites, metamorphosed along the granite contact into two-mica gneisses and massive hornfels with sillimanite, andalusite and garnet. Phosphorus-rich rocks, which may be related to metamorphosed phosphorites, also occur in this complex (Fiala 1975).

Mining of silver ore at Smrkovec is known to have occurred in the 16^{th} century (Fiala 1959); prospecting was carried out in the 18^{th} and 19^{th} centuries, without any significant results, however. In 1917–1918, the old mine dumps apparently yielded 200 kg of bismuth, and the locality was prospected for uranium ores between 1950 and 1955. All mine workings have recently caved in. Therefore, our knowledge of the ore mineralization is solely based on the study of rare ore samples collected and preserved from these mine dumps. It appears that the mineralization is related to thin hydrothermal quartz veins and alteration zones along those veins where impregnations of bismuth, bismutite and bismutoferrite occur (Sejkora 1992a).

Primary mineralization is represented by irregularly disseminated aggregates of ore minerals (especially bismuth, galena, Ag-bearing sulfides, Ni–Co arsenides and uraninite) enclosed in a medium- to fine-grained quartz gangue. Grains of massive grey sillénite, up to several cm in size and probably of primary origin (Sejkora *et al.* 1993a), were identified sporadically.

The short list of secondary minerals reported from Smrkovec by Kratochvíl (1963), Tuček (1970) and Bernard (1981), metatorbernite, autunite and zippeite, has been significantly extended on the basis of results of recent research: retgersite (Sejkora 1992b), atelestite-group minerals (atelestite, hechtsbergite and smrkovecite) (Řídkošil *et al.* 1996), preisingerite-group minerals (preisingerite and petitjeanite), and Bi–Mn oxides (Sejkora 1992a), eulytite (Sejkora *et al.* 1993b), bismutite (Sejkora & Řídkošil 1994), bismutoferrite (Sejkora *et al.* 1994a), mixite (Sejkora *et al.* 1997), pucherite (Sejkora *et al.* 1998), and (PO_4)-rich walpurgite (Sejkora *et al.* 2002). Besides abundant arsenates, we observed closely associated subordinate phosphates and rare vanadates with extensive As–P–V substitution in some minerals (*e.g.,* minerals of the preisingerite group and the atelestite groups: Figs. 1a, b). These substitution reflect elevated concentrations of P and V in the host rocks.

Appearance and Physical Properties

Phosphowalpurgite occurs as small clusters of irregular crystals (Fig. 2), up to 1 cm^2 in size, within small fissures and cavities in the quartz gangue. Subhedral to euhedral tabular crystals with the {010} form dominant do not exceed 1 mm in size and average 0.1–0.3 mm. The mineral is brownish grey, translucent, with a light brownish grey streak. It exhibits a vitreous to adamantine luster, an uneven to conchoidal fracture, and is nonfluorescent under both long- and short-wave ultraviolet radiation. Phosphowalpurgite is brittle, shows

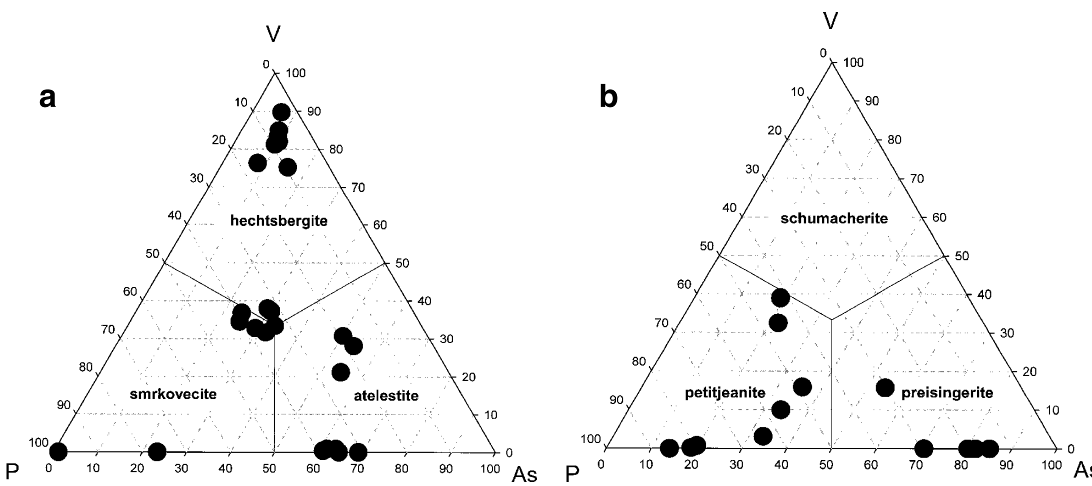

FIG. 1. As – P – V plots of members of (a) the atelestite group $[Bi_2O(XO_4)(OH)$, X = As, P, V] and (b) the preisingerite group $[Bi_3O(XO_4)_2(OH)$, X = As, P, V] minerals from Smrkovec (in molar proportions).

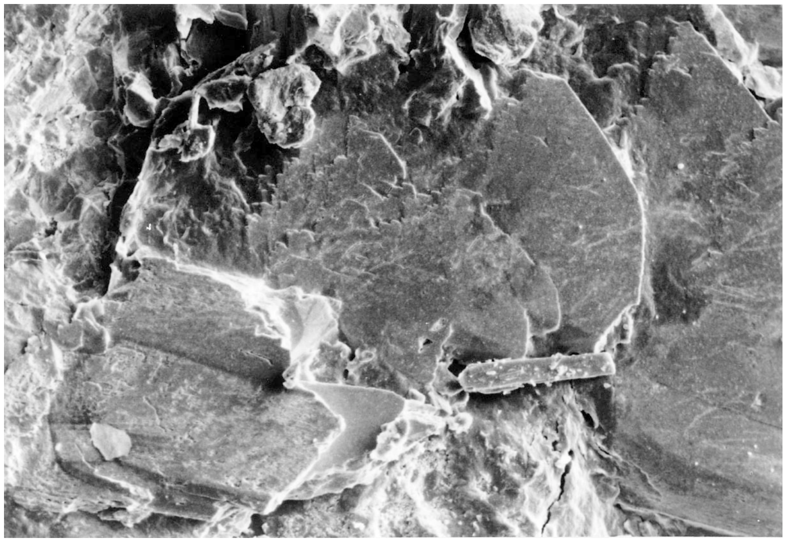

FIG. 2. Scanning electron photomicrograph of tabular crystals (up to 330 μm) of phosphowalpurgite, Smrkovec (Tesla BS 320, J. Sejkora and A. Gabašová; field of view 515 μm).

simple twinning, the cleavage on {010} is perfect, and the Mohs hardness is < 5. The density was not determined owing to the dearth of pure material available for study; the calculated density (based on the empirical formula and refined unit-cell parameters) is 6.36 g/cm^3. Phosphowalpurgite is biaxial with high indices of refraction (1.9–2.0) and with moderate to high birefringence (0.05–0.1). It is heterogeneous; the indices of refraction vary slightly within a given crystal. The calculated average index of refraction based on the Gladstone–Dale equation is 2.01.

CRYSTALLOGRAPHY

Crystals of phosphowalpurgite of appropriate quality for a single-crystal investigation were not found; it forms multiple subparallel intergrowths. The powder X-ray-diffraction pattern of phosphowalpurgite was obtained from a hand-picked sample using a Philips APD diffractometer in step-scanning mode. For the calculation of unit-cell parameters, the step-scanned (0.02°/8 s) X-ray powder-diffraction pattern was collected over the range 2–68° 2θ with Co$K\alpha$ radiation (Table 1). The positions and intensities of all reflections were calculated using the Pearson VII profile-shape function in the ZDS computer program (Ondruš 1995). The experimental data were indexed by analogy with the isotypic walpurgite (Mereiter 1981, 1982). The possibility of an orthorhombic unit-cell [*Pbcm*, orthowalpurgite, Krause *et al.* (1995)] was checked using the same experimental data but did not yield satisfactory results. Therefore, we

TABLE 1. POWDER X-RAY-DIFFRACTION DATA FOR PHOSPHOWALPURGITE

I_{rel}	d_{obs}	d_{calc}	*h k l*	I_{rel}	d_{obs}	d_{calc}	*h k l*
100	10.059	10.037	0 1 0	17	2.414	2.416	2 $\bar{1}$ 1
28	5.630	5.619	1 $\bar{1}$ 0	25	2.370	2.373	1 $\bar{4}$ 0
18	5.467	5.452	1 1 0	5	2.324	2.320	1 3 $\bar{2}$
7	5.058	5.040	0 0 1	7	2.314	2.317	2 3 0
21	5.014	5.018	0 2 0	11	2.306	2.306	3 1 $\bar{1}$
28	4.902	4.896	1 0 $\bar{1}$	13	2.249	2.249	1 3 1
11	4.730	4.716	1 1 $\bar{1}$	9	2.193	2.193	1 $\bar{2}$ $\bar{2}$
16	4.066	4.067	1 $\bar{2}$ 0	21	2.175	2.174	3 $\bar{1}$ 0
28	3.952	3.961	0 2 $\bar{1}$	15	2.051	2.048	3 $\bar{2}$ 0
6	3.476	3.482	1 0 1	17	2.005	2.007	0 5 0
19	3.461	3.455	1 $\bar{1}$ 1			2.003	0 5 $\bar{1}$
43	3.346	3.346	0 3 0	16	1.9782	1.9814	3 2 $\bar{2}$
		3.342	2 0 $\bar{1}$	4	1.9549	1.9533	3 $\bar{1}$ $\bar{2}$
31	3.266	3.266	2 1 $\bar{1}$	22	1.9047	1.9041	1 5 0
72	3.251	3.254	0 2 1	20	1.8582	1.8592	2 3 1
		3.248	1 $\bar{2}$ $\bar{1}$	16	1.8129	1.8126	3 $\bar{1}$ 1
86	3.125	3.119	2 1 0	12	1.7599	1.7602	3 4 $\bar{1}$
95	3.084	3.088	1 $\bar{2}$ 1	13	1.7520	1.7525	3 1 1
		3.084	2 $\bar{1}$ $\bar{1}$	15	1.6793	1.6813	4 2 $\bar{1}$
52	3.005	3.001	1 3 $\bar{1}$			1.6808	2 $\bar{1}$ $\bar{3}$
42	2.726	2.726	2 2 0	11	1.6732	1.6733	2 1 2
		2.721	1 1 $\bar{2}$			1.6710	4 0 $\bar{2}$
8	2.577	2.572	1 $\bar{3}$ $\bar{1}$	5	1.6500	1.6475	2 4 1
11	2.567	2.567	0 3 1	3	1.6404	1.6418	2 $\bar{5}$ 1
		2.564	0 1 $\bar{2}$	9	1.6295	1.6319	3 0 $\bar{3}$
15	2.518	2.520	0 0 2				

Philips APD powder X-ray diffractometer, step-scanning 0.02°/8 s, 2 – 68°2θ, Co$K\alpha$ radiation.

assume the triclinic space group $P\bar{1}$ with $Z = 1$ for phosphowalpurgite.

The unit-cell parameters of phosphowalpurgite were refined with the computer program of Burnham (1962): a 7.060(3), b 10.238(4), c 5.464(3) Å, α 101.22(4), β 109.93(3), γ 87.93(4)°, V 364.0(3) Å^3, $a:b:c$ = 0.6896:1:0.5337. The relation of mean phosphate content *versus* unit-cell parameters in the walpurgite – phosphowalpurgite solid-solution series is given in Figure 3. A decrease of unit-cell parameters and unit-cell volume with increasing phosphate content can be inferred. This decrease results from differences in the ionic radius of As^{5+} and P^{5+} (0.46 and 0.38 Å, respectively; Shannon 1976) and corresponding As–O and P–O bond lengths (~1.70 and ~1.55 Å, respectively) observed in arsenates and phosphates (*e.g.*, Pushkin *et al.* 2000, Wells 1986).

The unit-cell parameters of walpurgite from Jáchymov (Ondruš *et al.* 1997a) and Harrachov (Sejkora *et al.* 1994b) indicate the presence of $(PO_4)^{3-}$ substituting for $(AsO_4)^{3-}$. However, the crystallographic data for unnamed "phosphate-walpurgite" from Jáchymov (Ondruš *et al.* 1997b) exhibit wide variability and are significantly different from those discussed in this paper. These differences may be caused by poor crystallinity or sample purity (*e.g.*, broadened diffraction-profiles and absence of some diffraction maxima).

Chemical Composition

The polished flat surface of a phosphowalpurgite sample was chemically analyzed with a JEOL JXA–50A electron microprobe (EDAX PV 9400) using the energy-dispersion mode with a beam diameter of 1–2 μm, an operating voltage of 30 kV and a beam current of 5.7 nA; the raw data were corrected with a conventional ZAF 4 program. The following standards were used: pyroxene (Ca), libethenite (Cu, P), crocoite (Pb), synthetic Fe_2O_3 (Fe), pucherite (Bi), synthetic SiO_2 (Si), clinoclase (As), walpurgite (U). A direct determination of H_2O was not possible owing to the dearth of pure material (only a few mg), but the presence of structural H_2O was confirmed by infrared spectroscopy (see below), and the H_2O content was calculated from the empirical formula (H_2O = 2.00).

TABLE 2. CHEMICAL COMPOSITION OF PHOSPHOWALPURGITE

	mean	range	*2	*3
CaO wt.%	0.34	0.25 - 0.41	0.084	
CuO	0.30	0.17 - 0.53	0.053	
PbO	0.24	0.09 - 0.42	0.015	
Fe_2O_3	0.40	0.12 - 0.69	0.070	
Bi_2O_3	65.39	64.74 - 66.37	3.910	66.76
SiO_2	0.18	0.04 - 0.34	0.042	
P_2O_5	7.65	6.73 - 8.80	1.501	10.17
V_2O_5	0.12	0.03 - 0.28	0.018	
As_2O_5	4.15	3.47 - 5.73	0.503	
UO_3	18.73	18.53 - 18.92	0.912	20.49
H_2O *1	(2.59)		4.004	2.58
Total	(100.09)			100.00

*1 calculated amount of H_2O on the basis of H_2O = 2.00 in empirical formula
*2 atom ratios on the basis (O,H_2O) = 16
*3 composition of ideal formula $(UO_2)Bi_4O_4(PO_4)_2{\bullet}2H_2O$

Results of the electron-microprobe study are given in Table 2. The empirical formula, calculated from the average results of eight electron-microprobe analyses and based on 16 atoms of oxygen per formula unit, is $[(UO_2)_{0.91}Ca_{0.08}Fe_{0.07}Cu_{0.05}Pb_{0.01}]_{\Sigma 1.12}Bi_{3.91}O_{3.91}$ $[(PO_4)_{1.50}(AsO_4)_{0.50}(SiO_4)_{0.04}(VO_4)_{0.02}]_{\Sigma 2.06}{\bullet}2.00\ H_2O$. This formula is close to the ideal composition $(UO_2)Bi_4O_4(PO_4)_2{\bullet}2H_2O$, but with an elevated amount of As.

Phosphowalpurgite crystals exhibit a weak As-for-P zoning, which varies within the range of 20–33 mol.%. Minor to substantial P substituting for As was found in some samples of walpurgite from Schneeberg (Fischer 1948, Evans 1950) and (PO_4)-rich walpurgite from Smrkovec (Sejkora *et al.* 2002). Compositions of members of the phosphowalpurgite – walpurgite solid-solution series are plotted in Figure 4; they indicate good miscibility between end-members.

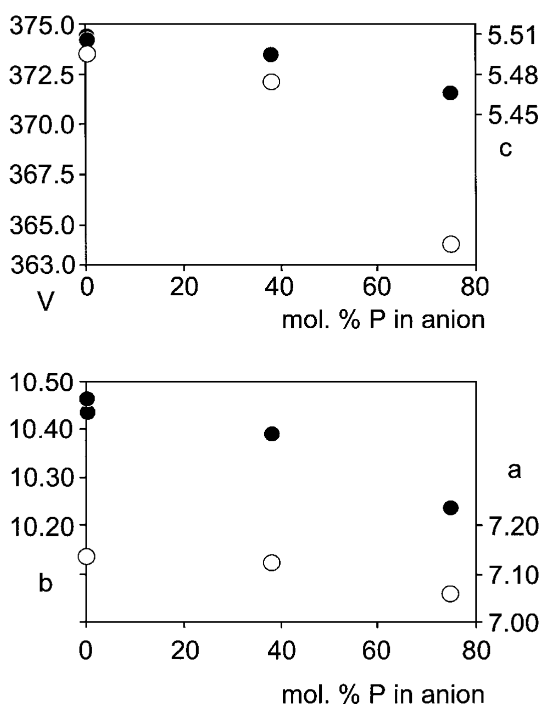

FIG. 3. The relation of phosphate content *versus* unit-cell parameters in the walpurgite – phosphowalpurgite solid-solution series (walpurgite: Mereiter 1982, Sejkora *et al.* 1994b; (PO_4)-rich walpurgite: Sejkora *et al.* 2002; phosphowalpurgite: this paper). Filled circles: b and c (Å); open circles: a (Å) and V (Å^3).

Infrared Spectroscopy

The infrared-absorption spectrum of phosphowalpurgite in a KBr disk was measured with a Nicolet 740 instrument in the range 4000–400 cm^{-1}. The spectrum is shown in Figure 5, and observed wavenumbers and characteristics of the bands are given in Table 3, along with the IR spectra of (PO_4)-rich walpurgite from Smrkovec (Sejkora *et al.* 2002) and walpurgite from Harrachov (Sejkora *et al.* 1994b).

The crystal structures of walpurgite (Mereiter 1982) and orthowalpurgite (Krause *et al.* 1995) are based upon chains containing $UO_2\Phi_4$ (Φ: anions in the uranyl equatorial plane) square bipyramids and AsO_4 tetrahedra. According to Burns (1999), each $UO_2\Phi_4$ square bipyramid shares all four corners with AsO_4 tetrahedra, which provides the linkages between adjacent uranyl polyhedra along the chain length. The uranyl ions of the $UO_2\Phi_4$ square dipyramids are oriented roughly perpendicular to the chain length. Both structures contain two symmetrically distinct Bi polyhedra, which are coordinated by six or seven ligands. The $Bi\Phi_2$ polyhedra link to form sheets that are in turn linked by the uranyl arsenate chains. Walpurgite and orthowalpurgite are dimorphs that differ mainly in the alignment of adjacent uranyl arsenate chains (Burns 1999). A similar structure may be inferred for phosphowalpurgite, which contains PO_4 polyhedra; however, the PO_4 polyhedra may be partly replaced by AsO_4 polyhedra.

Absorption bands at 885 cm^{-1} (phosphowalpurgite, P), 890 cm^{-1} (P-rich walpurgite, WP) and 888 cm^{-1} (walpurgite, W) are assigned to the antisymmetric stretching ν_3 $(UO_2)^{2+}$. According to empirical relations [$\nu_1 = 0.939\nu_3$ cm^{-1} (McGlynn *et al.* 1961); $\nu_1 = 0.89\nu_3 + 21$ cm^{-1} (McGlynn *et al.* 1961); $\nu_1 = 0.89\nu_3 + 30.8$ cm^{-1} (Bullock 1969); $\nu_1 = 0.912\nu_3 - 1.04$ cm^{-1} (Bagnall & Wakerley 1975); for details see, for example, Bullock (1969) and Čejka (1999)], the symmetric stretching vibration ν_1 $(UO_2)^{2+}$, if IR active, may be located close to the region 806–837 cm^{-1}. A weak band at 829 cm^{-1} (P) and a shoulder at 830 cm^{-1} (WP) are assigned to this vibration. This vibration was not observed in walpurgite (W). However, an overlap or coincidence of ν_1 $(UO_2)^{2+}$ with the split triply degenerate antisymmetric stretching vibration ν_3 $(AsO_4)^{3-}$ cannot be excluded.

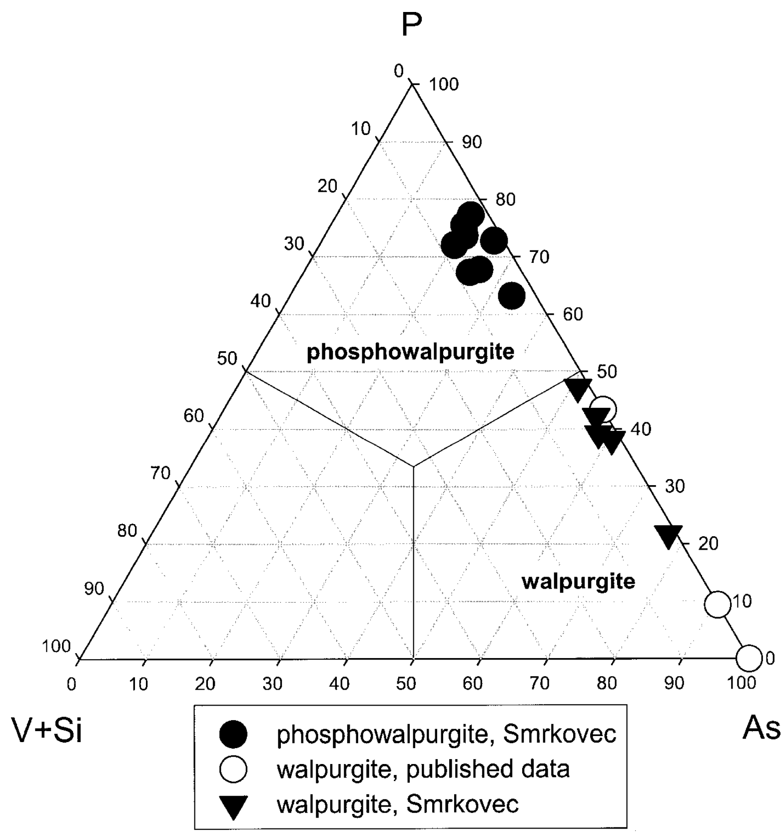

FIG. 4. As – P – (V+Si) plot of members of the phosphowalpurgite – walpurgite solid-solution series (in molar proportions).

The wavenumbers of the antisymmetric stretching vibration ν_3 $(UO_2)^{2+}$ were used to calculate the U – O_I (uranium – oxygen in uranyl) bond lengths with different empirical relations $R_{U–OI} = ax + b$ Å, where $x = [\nu_3(UO_2)^{2+}]^{-2/3}$ (Table 4). The calculated results agree with the U–O_I bond length derived from the crystal structure of walpurgite [1.784(14) Å: Mereiter (1982)], but differ from those derived from the crystal structure of orthowalpurgite [1.88(3) and 1.94(3) Å: Krause *et al.* (1995)].

The pattern of the recorded spectra indicates that the ideal T_d symmetry of $(PO_4)^{3-}$ and $(AsO_4)^{3-}$ tetrahedra is lowered. The ν_1 symmetric and ν_2 bending vibrations become infrared active, and doubly degenerate ν_2 bending and triply degenerate ν_3 antisymmetric and ν_4 bending vibrations split (Nakamoto 1986, Myneni *et al.* 1998). Six (C_{3v} symmetry), eight (C_{2v} symmetry) or nine (C_s symmetry) bands or shoulders may be observed to become IR active with respect to the site symmetry of these $(PO_4)^{3-}$ and $(AsO_4)^{3-}$ anions. Shoulders at 946 cm^{-1} (P) and 943 cm^{-1} (WP) may be assigned to the symmetric stretching vibration ν_1 $(PO_4)^{3-}$. This vibration was not observed in the infrared spectrum of walpurgite. An absorption band at 778–779 cm^{-1}, observed in the infrared spectra of all walpurgite-group minerals, may be due to the symmetric stretching vibration ν_1 $(AsO_4)^{3-}$. However, a partial overlap with absorption bands related to the split ν_3 $(AsO_4)^{3-}$ vibration cannot be excluded. Weak absorption bands in the range 429–476 cm^{-1} are assigned to the split ν_2 $(PO_4)^{3-}$ and ν_4 $(AsO_4)^{3-}$ bending vibrations. The antisymmetric stretching vibration ν_3 $(AsO_4)^{3-}$ exhibits absorption bands in the range 796–871 cm^{-1}, and the antisymmetric stretching vibration ν_3 $(PO_4)^{3-}$ exhibits absorption bands in the range 964–1152 cm^{-1}. Both vibrations are split owing to lower symmetry.

According to Hazra *et al.* (1997), Szaller *et al.* (2000), and Sreenivasu & Chandramouli (2000), the stretching vibrations of Bi–O and Bi–O–Bi polyhedra may be observed in the range 370–620 cm^{-1}; however, they may partly overlap and coincide with corresponding split ν_2 $(PO_4)^{3-}$, ν_4 $(PO_4)^{3-}$ and ν_4 $(AsO_4)^{3-}$ vibrations.

The OH-stretching vibrations of H_2O molecules are located in the region 2862–3520 cm^{-1}, and the δ H_2O bending vibrations are located in the region 1604–1634 cm^{-1}. Aditional vibration modes of H_2O molecules (libration) may be also observed near 700 cm^{-1}. From the

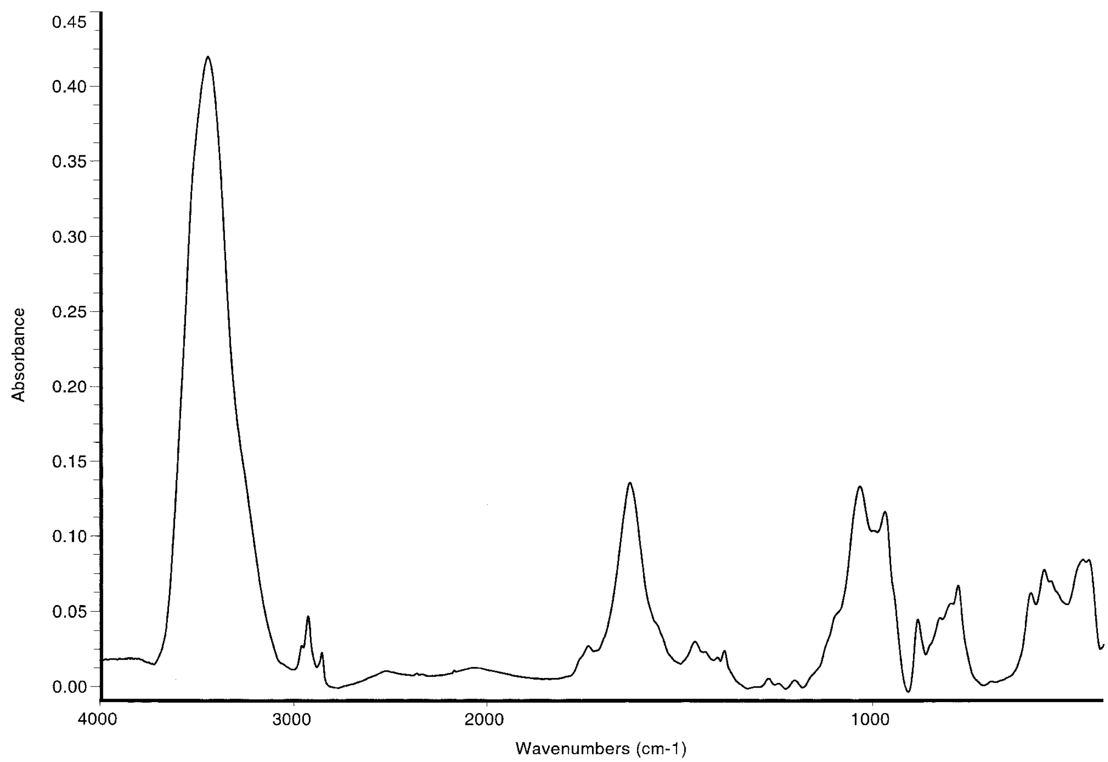

FIG. 5. Infrared-absorption spectrum of phosphowalpurgite.

wavenumbers of these vibrations, we can infer that some weak hydrogen bonds are involved in the crystal structure of all members of the phosphowalpurgite – walpurgite series, with the weakest bonding in walpurgite (*e.g.*, Čejka 1999, Sejkora *et al.* 2002).

The infrared spectra of phosphowalpurgite, (PO_4)-rich walpurgite and walpurgite are similar, which indicates that the crystal structures of these minerals are closely related.

Acknowledgements

The authors thank Andrew J. Locock, Andrew C. Roberts and Associate Editor Peter C. Burns for comments that substantially improved this manuscript. We express our thanks to the State Department of Culture of the Czech Republic and the Academy of Science of the Czech Republic, both of which have supported this research with their grants RK01P03OMG009, MK0CEZ99F0201 and IRSM 340.410. We gratefully acknowledge the help of Miroslava Novotná and Ananda Gabašová with portions of the analytical study.

TABLE 4. THE U–O$_I$ (URANYL) BOND LENGTH (Å) CALCULATED FROM ν_3 $(UO_2)^{2-}$

Reference	a	b	Pwl 885 cm^{-1}	Wl-P 888 cm^{-1}	Wl 890 cm^{-1}
Veal *et al.* (1975)	81.20	0.895	1.776	1.774	1.773
Carnall *et al.* (1965)	53.30	1.17	1.748	1.747	1.746
Serezhkin & Serezhkina (1984)	50.02	1.236	1.779	1.777	1.777
Bartlett & Cooney (1989)	91.43	0.804	1.796	1.794	1.792
Glebov (1989)	68.20	1.050	1.790	1.788	1.787
Syt´ko *et al.* (2001a)	218.50	-0.56	1.810	1.805	1.802
Syt´ko *et al.* (2001b)	71.70	1.0	1.778	1.776	1.775

a, b: $R_{U-OI} = ax + b$ Å, where $x = (\nu_3(UO_2)^{2+})^{-2/3}$, expressed in cm^{-1}. Symbols: Pwl: phosphowalpurgite, Wl-P: phosphate-rich walpurgite, Wl: walpurgite.

TABLE 3. INFRARED-ABSORPTION DATA FOR MEMBERS OF THE PHOSPHOWALPURGITE–WALPURGITE SOLID-SOLUTION SERIES

Pwl Smrkovec		Wl-P Smrkovec		Wl Harrachov		Tentative assignments	
439	m	429	wm	432	ms	ν_2 $(PO_4)^{3-}$ bending vibrations	ν_4 $(AsO_4)^{3-}$ bending vibrations
456	m	458	wm				
		476	w				
		500	vw				
		524	mw				ν Bi–O or ν Bi–O–Bi stretching vibrations (or both)
538	m	545	w			ν_4 $(PO_4)^3$ bending vibrations	
557	m	563	w	560	w		
591	vw	583	w				
		623	sh				
		669	vw			L H_2O libration modes	
		695	vw				
779	m	778	ms	778	s	ν_1 $(AsO_4)^{3-}$ symmetric stretching vibration	
802	sh	802	m	796	s	ν_3 $(AsO_4)^{3-}$ antisymmetric stretching vibrations	$\nu_1(UO_2)^{2+}$ stretching vibration (?)
829	wm	830	m sh				
855	sh						
		871	wm				
885	wm	890	wm	888	ms	ν_3 $(UO_2)^{2+}$ antisymmetric stretching vibration	
946	sh	943	sh			ν_1 $(PO_4)^{3-}$ symmetric stretching vibration	
969	s	964	sh				
998	sh						
		1000	sh				
1035	s	1027	wm	1028	ms	ν_3 $(PO_4)^{3-}$ antisymmetric stretching vibrations	
		1058	sh				
1088	sh						
1102	sh	1101	w				
		1121	w				
1150	sh	1152	w				
1205	vw						
1271	vw	1274	vw			overtones or combination bands (or both)	
1387	w	1390	vw				
1463	w						
1630	s	1634	s	1604	w	δ H_2O bending vibration	
1739	vw					overtone or combination bands (or both)	
2862	w	2862	w				
2928	w	2934	w			ν OH stretching vibrations in H_2O molecules	
				3380	ms		
3442	vs	3449	vs	3520	w		

Nicolet 740 FTIR spectrophotometer. Intensity and character of absorption bands: vs: very strong, s: strong, m: medium, w: weak, vw: very weak, sh: shoulder, b: broad. Pwl: phosphowalpurgite (this work), Wl-P: phosphate-rich walpurgite (Sejkora *et al.* 2002), Wl: Sejkora *et al.* (1994).

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Received September 7, 2003, revised manuscript accepted April 30, 2004.