PHOSPHOWALPURGITE, THE (PO4)-DOMINANT ANALOGUE OF WALPURGITE, FROM SMRKOVEC, SLAVKOVSKÝ LES MOUNTAINS, CZECH REPUBLIC

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ABSTRACT

Phosphowalpurgite, ideally (UO2)Bi4O4(PO4)2•2H2O, is the (PO4)-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 cm2 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 birefringence; 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/cm3. Phosphowalpurgite is triclinic, space group P1̅. 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) Å3, a/b/c = 0.6896:1:0.5337, Z = 1. The strongest seven X-ray powder-diffraction lines [d in Å(hkl)] are: 10.059(100)(010), 3.346(43)(030,20 ¯1), 3.251(72)(021,12 —1), 3.125(86)(210), 3.084(95)(1 ¯21,21—1), 3.005(52)(13 ¯1), 2.726(42)(220,11¯2). The average results of eight electron-microprobe analyses are: CaO 0.04, Cu 0.30, PbO 0.24, Fe2O3 0.40, Bi2O3 65.39, SiO2 0.18, P2O5 7.65, V2O5 0.12, As2O5 4.15, UO3 18.73, H2O (2.59), total (100.09), corresponding to [(UO2)0.91Ca0.08Fe0.07Cu0.05Pb0.01]1.12 Bi3.91O3.91[(PO4)1.50(AsO4)0.50(SiO4)0.04(VO4)0.02]2.06•2.00H2O (basis: 16 O atoms per formula unit). The ideal formula (UO2)Bi4O4(PO4)2•2H2O requires Bi2O3 66.76, P2O5 10.17, UO3 20.49, H2O 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 (UO2)Bi4O4(PO4)2•2H2O, 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-ouest de Mariánské Lázně, montagnes Slavkovský Les, en Bohême occidentale, République Tchèque. Lui sont associés, entre autres, “apatite”, atelestite, bismutoferrite, bismutite, eulytite, hechtsbergite, métatorbernite, mixite, petitjeanite, preisingerite, pucherite, retgersite, schumacherite, smrkovecite et walpurgite.

Sommaire

La phosphowalpurgite, dont la formule idéale est (UO2)Bi4O4(PO4)2•2H2O, 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-ouest de Mariánské Lázně, montagnes Slavkovský Les, en Bohême occidentale, République Tchèque. Lui sont associés, entre autres, “apatite”, atelestite, bismutoferrite, bismutite, eulytite, hechtsbergite, métatorbernite, mixite, petitjeanite, preisingerite, pucherite, retgersite, schumacherite, smrkovecite et walpurgite.
schumacherite, smrkovecite and walpurgite. La phosphowalpurgite a cristallisé à l’aide 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 aplatis sur [010] jusqu'à 1 mm de taille, en cristaux de cristaux d'orientation quelconque, recouvrant jusqu'à 1 cm² 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 vitreuse à adamantine et une rayere grise brunâtre pâle. Il s'agit d’un minéral biaxie 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/cm³. Elle est triclinique, groupe spatial P. Les paramètres réticulaires, affinés à partir du spectre de diffraction (méthode des poudres) sont: a = 7.060(3), b = 10.258(4), c = 5.464(3) Å, α = 101.22(4), β = 109.93(3), γ = 87.93(4)°. V = 364.0(3) Å³. a/b/c = 0.6896:1:0.5337, Z = 1. Les sept raies les plus intenses du spectre de diffraction [d en Å(hkl)] sont: 10.059(100)(010), 3.346(43)(030,201), 3.251(72)(021,121), 3.125(86)(210), 3.084(95)(121,211), 3.005(52)(131), 2.726(42)(220,112). Les résultats moyens de huit analyses obtenues avec une microsonde électronique sont: CaO 0.04, Cu 0.30, PbO 0.24, Fe2O3 0.40, Bi2O3 65.39, SiO2 0.18, P2O5 7.65, V2O5 0.12, As2O5 4.15, UO3 18.73, H2O (2.59), total (100.09%), ce qui correspond à [(UO2)0.91Ca0.08Fe0.07Cu0.05Pb0.01]Bi3.91O3.91[(PO4)1.50(AsO4)0.50(SiO4)0.04(VO4)0.02]•2H2O (sur une base de 16 atomes d’oxygène par formule unitaire). La formule idéale, (UO2)Bi4O4(PO4)2•2H2O, requiert Bi2O3 66.76, P2O5 10.17, UO3 18.73, H2O (2.59), total 100.00% (poids). Nous présentons une interprétation détaillée provisoire du spectre d’absorption infrarouge et des autres propriétés de la série walpurgite – phosphowalpurgite.

**Introduction**

Recent investigations of walpurgite-type minerals, identified from the small abandoned ore deposit near Smrkovec, in western Bohemia, Czech Republic, reveals a broad variation in (AsO₄)³⁻ and (PO₄)³⁻ content. Electron-microprobe analyses show that both As- and P-dominant phases occur at this locality and that walpurgite with some (PO₄) content is the more abundant (Sejkora et al. 2002). We name the (PO₄)-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–Neustäteld, Saxony, Germany, associated with trägerite, zeunerite, uranospinite and uranospheerite (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 (Brathwaite & Knight 1990), the Adam Heber mine, Schneeberg, Saxony (Haacke et al. 1994), the “Schurfshacht 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 Ryžovištì 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 16th century (Fiala 1959); prospecting was carried out in the 18th and 19th 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 smrkovcetc) (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 (PO₄)-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 cm² 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 \(\text{Bi}_2\text{O}(\text{XO}_4)_2(\text{OH})\), \(\text{X} = \text{As}, \text{P}, \text{V}\) and (b) the preisingerite group \(\text{Bi}_3\text{O}(\text{XO}_4)_2(\text{OH})\), \(\text{X} = \text{As}, \text{P}, \text{V}\) minerals from Smrkovec (in molar proportions).](image-url)
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/cm³. 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 CoKα 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

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Philips APD powder X-ray diffractometer, step-scanning 0.02°/8 s, 2–68° 2θ, CoKα radiation.
assume the triclinic space group $P\overline{1}$ 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, $\alpha = 101.22(4)$, $\beta = 109.93(3)$, $\gamma = 87.93(4)^\circ$, $V = 364.0(3)$ 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$_2$O$_3$ (Fe), pucherite (Bi), synthetic SiO$_2$ (Si), clinoclase (As), walpurgite (U). A direct determination of H$_2$O was not possible owing to the dearth of pure material (only a few mg), but the presence of structural H$_2$O was confirmed by infrared spectroscopy (see below), and the H$_2$O content was calculated from the empirical formula (H$_2$O = 2.00).

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 

\[(\text{UO}_2)_{0.91}\text{Ca}_{0.08}\text{Fe}_{0.07}\text{Cu}_{0.05}\text{Pb}_{0.01}\text{Bi}_{3.91}\text{O}_{3.91}\] 

\[(\text{PO}_4)_{1.50}(\text{AsO}_4)_{0.50}(\text{SiO}_4)_{0.04}(\text{VO}_4)_{0.02}\text{H}_2\text{O}.

This formula is close to the ideal composition (UO$_2$)$_2$Bi$_4$O$_4$(PO$_4$)$_2$•2H$_2$O, 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.

**TABLE 2. CHEMICAL COMPOSITION OF PHOSHOWALPURGITE**

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<td>0.39</td>
<td>0.17 - 0.55</td>
<td>0.033</td>
<td></td>
</tr>
<tr>
<td>PbO</td>
<td>0.24</td>
<td>0.09 - 0.42</td>
<td>0.015</td>
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<tr>
<td>FeO$_3$</td>
<td>0.40</td>
<td>0.12 - 0.69</td>
<td>0.070</td>
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<tr>
<td>Bi$_2$O$_3$</td>
<td>65.39</td>
<td>64.74 - 66.37</td>
<td>3.910</td>
<td>66.76</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>0.18</td>
<td>0.04 - 0.34</td>
<td>0.042</td>
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<tr>
<td>P$_2$O$_5$</td>
<td>7.65</td>
<td>6.73 - 8.80</td>
<td>1.501</td>
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<tr>
<td>V$_2$O$_5$</td>
<td>0.12</td>
<td>0.03 - 0.58</td>
<td>0.018</td>
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<tr>
<td>As$_2$O$_3$</td>
<td>4.15</td>
<td>3.87 - 5.73</td>
<td>0.503</td>
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<tr>
<td>UO$_2$</td>
<td>18.75</td>
<td>18.55 - 18.92</td>
<td>0.912</td>
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<tr>
<td>H$_2$O *1</td>
<td>2.59</td>
<td>4.04</td>
<td>2.58</td>
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<tr>
<td>Total</td>
<td>100.09</td>
<td></td>
<td>100.00</td>
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</tr>
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</table>

*1 calculated amount of H$_2$O on the basis of H$_2$O = 2.00 in empirical formula

*2 atom ratios on the basis of 0(3) = 10

*3 composition of ideal formula (UO$_2$)$_2$Bi$_4$O$_4$(PO$_4$)$_2$•2H$_2$O.

![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$^3$).](image-url)
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 (PO₄)-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 UO₂(H₂O)₄ (H₂O anions in the uranyl equatorial plane) square bipyramids and AsO₄ tetrahedra. According to Burns (1999), each UO₂(H₂O)₄ square bipyramid shares all four corners with AsO₄ tetrahedra, which provides the linkages between adjacent uranyl polyhedra along the chain length. The uranyl ions of the UO₂(H₂O)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(H₂O)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 PO₄ polyhedra; however, the PO₄ polyhedra may be partly replaced by AsO₄ 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 \( \nu_3 (\text{UO}_2)^{2+} \). According to empirical relations [\( \nu_1 = 0.939 \nu_3 \text{ cm}^{-1} \) (McGlynn et al. 1961); \( \nu_1 = 0.89 \nu_3 + 21 \text{ cm}^{-1} \) (McGlynn et al. 1961); \( \nu_1 = 0.89 \nu_3 + 30.8 \text{ cm}^{-1} \) (Bullock 1969); \( \nu_1 = 0.912 \nu_3 - 1.04 \text{ cm}^{-1} \) (Bagnall & Wakerley 1975); for details see, for example, Bullock (1969) and Čejka (1999)], the symmetric stretching vibration \( \nu_1 (\text{UO}_2)^{2+} \), 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 \( \nu_1 (\text{UO}_2)^{2+} \) with the split triply degenerate antisymmetric stretching vibration \( \nu_3 (\text{AsO}_4)^{2-} \) cannot be excluded.

![As – P – (V+Si) plot of members of the phosphowalpurgite – walpurgite solid-solution series (in molar proportions).](image)

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 $v_3$ ($\text{UO}_2^{2+}$) were used to calculate the U–O bond lengths with different empirical relations $R_{\text{U-OI}} = ax + b$ Å, where $x = [v_3(\text{UO}_2^{2+})]^{-2/3}$ (Table 4). The calculated results agree with the U–O 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 ($\text{PO}_4$)$^{3-}$ and ($\text{AsO}_4$)$^{3-}$ tetrahedra is lowered. The $v_1$ symmetric and $v_2$ bending vibrations become infrared active, and doubly degenerate $v_3$ antisymmetric and $v_4$ 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 ($\text{PO}_4$)$^{3-}$ and ($\text{AsO}_4$)$^{3-}$ anions. Shoulders at 946 cm$^{-1}$ (P) and 943 cm$^{-1}$ (WP) may be assigned to the symmetric stretching vibration $v_1$ ($\text{PO}_4$)$^{3-}$. 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 $v_1$ ($\text{AsO}_4$)$^{3-}$. However, a partial overlap with absorption bands related to the split $v_3$ ($\text{AsO}_4$)$^{3-}$ vibration cannot be excluded. Weak absorption bands in the range 429–476 cm$^{-1}$ are assigned to the split $v_2$ ($\text{PO}_4$)$^{3-}$ and $v_4$ ($\text{AsO}_4$)$^{3-}$ bending vibrations. The antisymmetric stretching vibration $v_3$ ($\text{AsO}_4$)$^{3-}$ exhibits absorption bands in the range 796–871 cm$^{-1}$, and the antisymmetric stretching vibration $v_3$ ($\text{PO}_4$)$^{3-}$ 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 $v_2$ ($\text{PO}_4$)$^{3-}$, $v_4$ ($\text{PO}_4$)$^{3-}$ and $v_4$ ($\text{AsO}_4$)$^{3-}$ vibrations.

The OH-stretching vibrations of H$_2$O molecules are located in the region 2862–3520 cm$^{-1}$, and the $\delta$ H$_2$O bending vibrations are located in the region 1604–1634 cm$^{-1}$. Additional vibration modes of H$_2$O molecules (libration) may be also observed near 700 cm$^{-1}$. From the
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, (PO₄)-rich walpurgite and walpurgite are similar, which indicates that the crystal structures of these minerals are closely related.

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