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PHILIPSBURGITE, A NEW COPPER ZINC ARSENATE HYDRATE RELATED TO KIPUSHITE, FROM MONTANA

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ABSTRACT

Philipsburgite, $(Cu,Zn)_6(AsO_4,PO_4)_2(OH)_6{\cdot}H_2O$, is monoclinic, space group $P2_1/c$, with a 12.33(8), b 9.20(4), c 10.69(3) Å, β 96.92(35)°, V 1204 Å^3, $Z = 4$. The strongest six lines in the X-ray powder-diffraction pattern [d in Å(I) (hkl)] are: 12.2(80)(100), 4.05(90)(300,121), 3.405(50)(122,311,221), 2.666(60)(412,123,104,032), 2.559(100)(132,114,014), 1.534(60)(not indexed). Microprobe and DTA–TGA analyses yield CuO 46.3, ZnO 18.2, P_2O_5 8.7, As_2O_5 16.3, H_2O 9.9, Σ = 99.4 wt. %. Philipsburgite is bright green, without apparent cleavage; the hardness is approximately 3–4 (Mohs); D_{meas} 4.07(10), D_{calc} 4.04 g/cm^3. It is biaxial negative, $2V_x$ 16(2)°, with indices of refraction α 1.729, β 1.774, and γ 1.775 (all ± 0.002). $2V_x$ (calc.) = 17°. Philipsburgite is moderately pleochroic, with $Y = Z$ medium green, X pale green; absorption is $Y = Z > X$; orientation is $b \parallel Z$, $c \wedge Y = 7°$. Philipsburgite is found in a late-stage druse on bayldonite, mimetite and quartz from the Black Pine mine, near Philipsburg, Montana. It is isostructural with kipushite.

Keywords: philipsburgite, new mineral species, kipushite, copper, zinc, arsenate, Montana.

SOMMAIRE

La philipsburgite, $(Cu,Zn)_6(AsO_4,PO_4)_2(OH)_6{\cdot}H_2O$, est monoclinique, groupe spatial $P2_1/c$, a 12.33(8), b 9.20(4), c 10.69(3) Å, β 96.92(35)°, V 1204 Å^3, $Z = 4$. Les six raies les plus intenses du cliché de poudre [d en Å(I)(hkl)] sont: 12.2(80)(100), 4.05 (90)(300,121), 3.405 (50)(122,311,221), 2.666(60)(412,123,104,032), 2.559(100)(132,114,014), 1.534(60)(raie non indexée). Les analyses à la microsonde, thermique différentielle et thermogravimétrique donnent: CuO 46.3, ZnO 18.2, P_2O_5 8.7, As_2O_5 16.3, H_2O 9.9, total 99.4% (en poids). C'est un minéral vert brillant, sans clivage évident; sa dureté Mohs est de 3 à 4. Densité mesurée 4.07(10), calculée 4.04. Biaxe négatif, $2V_x$ 16(2)°, indices de réfraction α 1.729, β 1.774, γ 1.775 (±0.002); $2V_x$ (calc.)17°. Pléochroïsme modéré, $Y = Z$ vert moyen, X vert pâle; absorption $Y = Z > X$; orientation $b \parallel Z$, $c \wedge Y = 7°$. La philipsburgite cristallise tardivement sur bayldonite, mimetite et quartz dans une cavité dans la mine Black Pine, près de Philipsburg (Montana); elle possède la structure de la kipushite.

(Traduit par la Rédaction)

Mots-clés: philipsburgite, nouvelle espèce minérale, kipushite, cuivre, zinc, arsenate, Montana.

INTRODUCTION

The new mineral species described herein was noted as an unknown in the course of a detailed study of the mineralogy of the Black Pine mine, near Philipsburg, Montana, by LGZ. Preliminary examination of this mineral suggested it is a new species, and our subsequent study has borne out that assumption. We have named this new species *philipsburgite* for the town of Philipsburg, near which the Black Pine mine is located. The mineral and the name were approved by the Commission on New Minerals and Mineral Names, IMA. Type material is preserved at the Smithsonian Institution (NMNH #161201) and the Royal Ontario Museum (#M41000).

CRYSTALLOGRAPHY

Single crystals of philipsburgite were studied using Weissenberg (Cu$K\alpha$, Ni-filtered radiation) and precession (Mo$K\alpha$, Zr-filtered radiation) methods. Philipsburgite is monoclinic, space group $P2_1/c$, with unit-cell parameters a 12.33(8), b 9.20(4), c 10.69(3) Å, β 96.92(35)°, V 1204 Å^3, $Z = 4$. These data are very similar to those for the mineral kipushite (a 12.197, b 9.156, c 10.667 Å, β 96.77° (Piret *et al.* 1985). This, combined with an apparent equivalence with all other properties of kipushite, shows that these minerals are isostructural. The cell

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

I/Io	d (obs.)	d (calc.)	hkl	I/Io	d (obs.)
80	12.2	12.24	100	20	2.441
5	6.96	6.95	011	5	2.385
40	6.21	6.26	$11\bar{1}$	10	2.361
2	5.84	5.85	111	10	2.331
20	5.09	5.10	$10\bar{2}$	5	2.289
		5.10	210		
2	4.67	4.67	102	40	2.167
40	4.29	4.31	120	20	2.136
		4.27	$20\bar{2}$	20	2.068
90	4.05	4.08	300	1	2.024
		4.05	$12\bar{1}$	30	1.946
10	3.76	3.79	202	2	1.853
		3.73	310	1	1.822
40	3.56	3.56	$22\bar{1}$	2	1.780
50	3.405	3.416	$12\bar{2}$	10	1.749
		3.404	311	5	1.720
		3.400	221		
2	3.306	3.303	013	10	1.695
1	3.224	3.223	$31\bar{2}$	2	1.666
2	3.046	3.061	302	5	1.610
		3.060	400	5	1.572
		3.053	$21\bar{3}$	60	1.534
		3.053	320		
30	2.874	2.887	$13\bar{1}$	10	1.503
		2.886	$41\bar{1}$	5	1.490
		2.866	321	2	1.472
60	2.666	2.680	$41\bar{2}$	5	1.450
		2.679	123	5	1.436
		2.661	$10\bar{4}$		
		2.656	032		
100	2.559	2.564	132	2	1.415
		2.556	$11\bar{4}$	5	1.381
		2.550	014	10	1.330
10	2.497	2.492	$23\bar{2}$	5	1.313
				2	1.303
				2	1.286
				2	1.276
				1	1.195
				2	1.178
				2	1.147
				1	1.137
				2	1.095
				5	1.082

parameters were refined from the X-ray powder-diffraction data, as obtained using a 114.6-mm-diameter Gandolfi powder camera, a polycrystalline sample, Cu*Kα* Ni-filtered radiation, and Si as an internal standard. The powder data are presented in Table 1. The standard errors in the cell parameters are unusually large in this case because very few (8) unambiguously indexed reflections could be obtained and used in the refinement, even with the aid of single-crystal photographs.

Morphologically, philipsburgite crystals are slightly curved, elongate on [010], and have a composite large face (100) as the dominant form. Scanning-electron photomicrographs of some philipsburgite crystals are shown in Figure 1, which clearly reveals the nature of the aggregates and the slight curvature of the crystals, and Figure 2, which illustrates the chisel-like terminations of the crystals.

PHYSICAL AND OPTICAL PROPERTIES

Philipsburgite is bright emerald-green in color and has a light green streak. The mineral is transparent in small crystals but semi-opaque in massive aggregates. The lustre is vitreous on both crystal faces and fracture surfaces. These is no discernible cleavage or parting. The hardness (Mohs) is approximately 3–4; philipsburgite is not particularly brittle. The density, measured using a Berman balance and employing a temperature correction, is 4.07 (± 0.10) g/cm^3, compared with the calculated value of 4.04 g/cm^3 based on the empirical formula. There is no discernible fluorescence in ultraviolet radiation.

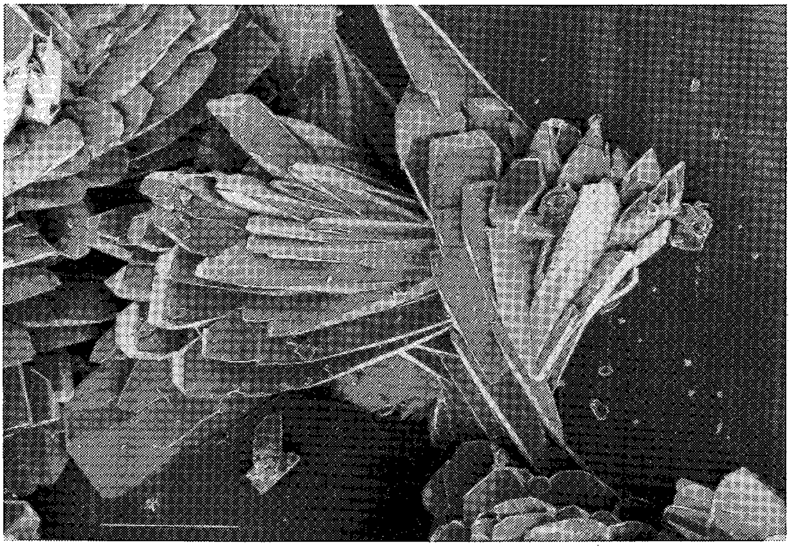

FIG. 1. Cluster of philipsburgite crystals showing the slightly curved, subparallel habit of the crystals. Scale bar 100 μm.

Optically, philipsburgite is biaxial negative, with $2V_x = 16(2)°$, and indices of refraction α 1.729, β 1.774 and γ 1.775 (all ± 0.002). Pleochroism is moderate: $Y = Z$ medium green, X pale green. Absorption is $Y = Z > X$. Dispersion of the optic axes is strong, $r > v$. The orientation is b parallel to Z, $c \wedge Y = 7°$ in the acute angle between crystallographic axes a and c. The edges of some grains have areas where the mineral appears almost uniaxial; this area is also distinguished by an anomalous blue interference-color observed when (100) lies in the plane of the microscope stage. We have no explanation for this optical anomaly; we report these properties for completeness. Calculation of the Gladstone-Dale relationship using the constants of Mandarino (1981) yields a compatibility relation of "superior" agreement between physical and chemical data.

CHEMICAL COMPOSITION

Philipsburgite was chemically analyzed using an ARL-SEMQ electron microprobe utilizing an operating voltage of 15 kV and a sample current of 0.025 μA, measured on brass. A wavelength-dispersion microprobe scan indicated the absence of any elements with atomic number greater than 8, except those reported herein. The following standards were used: olivenite (As), ZnO (Zn), Cu_2O (Cu), and fluorapatite (P,F). The data were corrected using a modified version of the *MAGIC*-4 computer program. Water was determined *in vacuo* by simultaneous TGA-EGA with a Mettler TA-1 Thermoanalyzer / Inficon IQ200 mass-spectrometer system. Water was lost between 150 and 610°C, with maximum evolution at 415°C. The 10.0% weight loss recorded for this interval includes an estimated O_2 loss of 0.1%; the water content is reported as 9.9%. The resultant analytical data are CuO 46.3, ZnO 18.2, P_2O_5 8.7, As_2O_5 16.3 H_2O 9.9, sum = 99.4 weight %. Calculation of unit-cell contents, using the refined cell-parameters and the observed density, yields: $Cu_{17.18}Zn_{6.60}(AsO_4)_{4.19}(PO_4)_{3.62}(OH)_{24.13}\cdot 4.16H_2O$. This is interpreted, ideally, as $(Cu,Zn)_6(AsO_4,PO_4)_2(OH)_6\cdot H_2O$.

This formula is equivalent to that of kipushite, $(Cu,Zn)_6(PO_4)_2(OH)_6\cdot H_2O$. The structure of kipushite was determined by Piret *et al.* (1985), who showed that the 24 (Cu, Zn) per cell are distributed over 6 general positions. One is tetrahedrally co-ordinated and is occupied only by Zn. The other five positions are octahedrally co-ordinated. Because two are severely distorted, as consistent with a Jahn–Teller effect, and three have more regular octahedral co-ordination, these sites are assumed to accommodate only Cu, and Cu + Zn, respectively. The 6.60 Zn per cell of philipsburgite must occupy equivalent sites, *i.e.,* four are tetrahedrally co-ordinated and 2.60 per cell occur in solid solution with Cu on the three regular octahedrally co-ordinated sites.

In the structure of kipushite, tetrahedrally co-ordinated P occupies two general positions of rank four. As there are 4.19 As and 3.62 P per cell in philipsburgite, this implies the possibility of ordering of As on one site, with solid solution of As for P on another. Complete random solid-solution of As and P on both of these sites is still possible, of course.

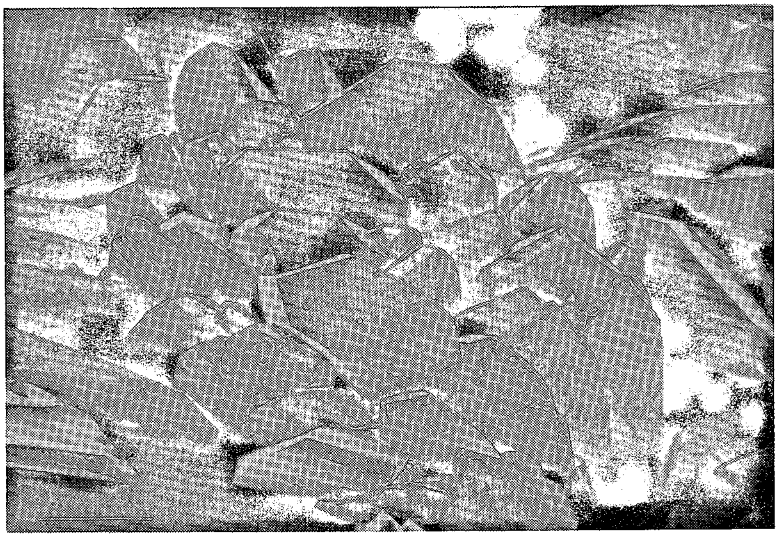

FIG. 2. Cluster of philipsburgite crystals showing chisel-shaped terminations. Scale bar 50 μm.

OCCURRENCE

Philipsburgite occurs in a secondary assemblage from the Black Pine mine, located in the Flint Creek Valley, in the John Long Mountains, approximately 14.5 km northwest of Philipsburg, Montana. The orebodies at the Black Pine mine are fissure veins generally conformable to, but locally low-angle crosscutting, the bedding of the Mount Shields Formation (quartzite) of the Missoula Group of the Precambrian Belt Supergroup (Wallace *et al.* 1981, Emmons & Calkins 1913, Harrison 1972, Winston 1984). All exploration, to date, appears to have been confined to the Mount Shields Formation. The vein dips 10 to 20° SW and is from 15 cm to 1.3 m wide. It consists principally of comb quartz, commonly vuggy, with the principal primary minerals being silver-bearing tetrahedrite, huebnerite and pyrite; galena, sphalerite, chalcopyrite and native elements are minor constituents.

Faults and fracture zones have provided access to ground water, which has brought about oxidation of the primary minerals, resulting in an assemblage of unusual Cu–Pb–Zn arsenates and phosphates, such as arthurite, bayldonite, duftite, tsumebite and veszelyite, as well as more common carbonates, arsenates, phosphates, sulfates, silicates and antimonates. Tetrahedrite presumably provided the Cu and As for philipsburgite; Zn could have been provided by available sphalerite. Philipsburgite appears to be rare and, in the arsenate assemblage, usually occurs in microscopic spherules with crystal terminations providing a rough exterior surface. In all specimens seen to date, philipsburgite appears to be the youngest mineral except for very late microdruse quartz, "limonite gel", and chrysocolla, which covers many of the secondary minerals. It is usually found on quartz or mimetite crystals.

The holotype specimen consists of bright green druses of philipsburgite crystals that coat vugs in quartz. The druse varies from sparse coatings, which are composed of isolated clusters of crystals (Fig. 1) to thick (0.5 mm) coatings that completely conceal the underlying quartz. This material is free of physically admixed phases. On another sample, philipsburgite occurs as small (0.2 mm) spherules that occur on the surface of thin druses of bayldonite, which encrusts light yellow mimetite crystals, which in turn coat euhedral quartz crystals approximately 2–3 cm in length. Philipsburgite spherules are not monomineralic; some examined by powder-diffraction techniques are aggregates of philipsburgite (dominant) and minor to moderate amounts of bayldonite.

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