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VASILITE, $(Pd,Cu)_{16}(S,Te)_7$, A NEW MINERAL SPECIES FROM NOVOSELTSI, BULGARIA

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Abstract

Vasilite, $(Pd,Cu)_{16}(S,Te)_7$, a new mineral species, is found in heavy-mineral concentrates obtained from Priabonian clastic sediments near the village of Novoseltsi, Bourgas region, southeastern Bulgaria. Vasilite is an opaque mineral with a metallic luster. Its color is steel grey, and its streak is black. VHN_{10} = 486.1 (467.2 - 505.9) and VHN_{20} = 490.4 (473.5 - 507.3). The mineral is brittle and has no cleavage. The fracture is uneven. Under reflected light, vasilite is creamy with a yellowish tint where it is adjacent to bowieite and isoferroplatinum. It has no internal reflections, anisotropism, bireflectance or pleochroism. The reflectance values (air, oil) interpolated for the COM wavelengths are: 41.2, 25.6% (470 nm), 37.7, 22.1% (546 nm), 38.6, 32.0% (589 nm) and 43.1, 27.6% (650 nm). Vasilite is cubic, space group $I\bar{4}3m$, with a 8.922(1) Å, Z = 2. The strongest six powder-diffraction lines [d in Å(I)(hkl)] are: 3.64(8)(211), 2.389(10)(321), 2.100(8)(330), 1.446(8)(532), 1.214(7)(552) and 1.010(7)(752). D_{calc} = 8.796(2) g/cm^3. Vasilite is named after Dr. Vasil Atanasov, Associate Professor of mineralogy, Higher Institute of Mining and Geology, Sofia. Both the mineral and name have been approved by the IMA Commission on New Minerals and Mineral Names.

Keywords: vasilite, palladium sulfide, new mineral species, platinum-group minerals, Novoseltsi, Bulgaria.

Sommaire

La vasilite, $(Pd,Cu)_{16}(S,Te)_7$, nouvelle espèce minérale, a été découverte dans des concentrés de minéraux lourds provenant des sédiments clastiques priaboniens près du village de Novoseltsi, région de Bourgas, dans le sud-est de la Bulgarie. C'est un minéral opaque à éclat métallique. Sa couleur est gris acier, et sa rayure, noire. VHN_{10} = 486.1 (467.2 - 505.9), et VHN_{20} = 490.4 (473.5 - 507.3). La vasilite est cassante et sans clivage; les cassures sont irrégulières. En lumière réfléchie, elle possède une couleur crème avec teinte jaunâtre où elle est contiguë à la bowieïte et à l'isoferroplatine. Elle est sans réflections internes, anisotropisme, biréflectance ou pléochroïsme. Les valeurs de réflectance (dans l'air et dans l'huile), obtenues par interpolation aux longueurs d'onde standards de la COM, sont: 41.2, 25.6% (470 nm), 37.7, 22.1% (546 nm), 38.6, 32.0% (589 nm), et 43.1, 27.6% (650 nm). Elle est cubique, groupe spatial $I\bar{4}3m$, a 8.922(1) Å, Z = 2. Les six raies les plus intenses du cliché de diffraction [d en Å(I)(hkl)] sont: 3.64(8)(211), 2.389(10)(321), 2.100(8)(330), 1.446(8)(532), 1.214(7)(552) et 1.010(7)(752). D_{calc} 8.796(2) g/cm^3. Le nom honore Vasil Atanasov, professeur agrégé de minéralogie à l'Institut supérieur des Mines et Géologie, à Sofia. Le minéral et le nom ont reçu l'approbation de la commission des nouveaux minéraux et des noms de minéraux de l'IMA.

(Traduit par la Rédaction)

Mots-clés: vasilite, sulfure de palladium, nouvelle espèce minérale, minéraux du groupe du platine, Novoseltsi, Bulgarie.

Introduction

Vasilite is found in the heavy-mineral concentrates obtained from the Priabonian clastic sediments near the village of Novoseltsi, Bourgas region, southeastern Bulgaria. The host rocks are gravels, sands and bentonite clays. The main clastic mineral in the gravels and sands is quartz. The most common minerals in the heavy concentrates are magnetite, chromite, garnet, zircon, rutile, ilmenite, pyroxene, amphibole, native gold, Au_3Pd and platinum-group minerals and alloys: platinum, isoferroplatinum, palladium, iridium and iridosmine. These phases occur as individual grains up to 3–4 mm in size. Cooperite, malanite, braggite, vysotskite, vasilite, osmium, Ir-bearing osmium, iridosmine, Pt-bearing osmium, erlichmanite, laurite, hollingworthite, prassoite, bowieite, bornite, Rh-bearing pyrrhotite, Pd-bearing troilite, chromite and augite are found as inclusions in all these grains. Vasilite is found as a component of oval or spherical polymineralic inclusions, together with bowieite and Pd-bearing troilite, in a matrix of isoferroplatinum. The form of the vasilite grains is irregular or platy, up to 100 μm in length and 35 μm in width (Fig. 1).

Physical Properties

Under reflected light, vasilite is creamy with a yellowish tint, where adjacent to isoferroplatinum and bowieite. It is brittle, with a metallic luster, and has a black streak. Microhardness measurements (VHN) were made with 10 g and 20 g indentations; with 10 g, the microhardness is 486.1 (3 indentations, range: 467.2–504.9) and with 20 g, it is 490.4 (4 indentations, range: 473.5–507.3). These values correspond approximately to 4.5 - 5 on the Mohs scale. The 100 g indentation recommended by the International Mineralogical Association's Commission on Ore Microscopy was not applied because of the small

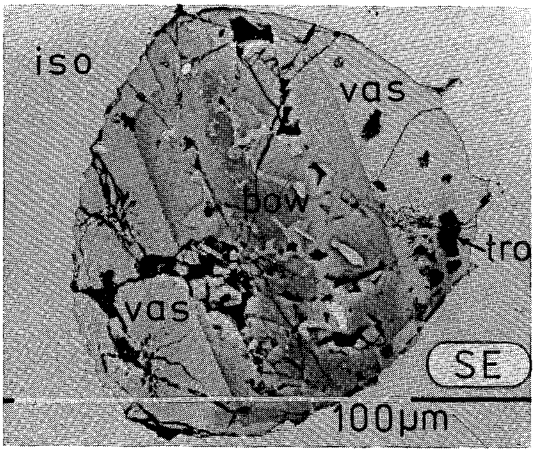

FIG. 1. Secondary electron (SE) image of a polymineralic inclusion of vasilite (vas), bowieite (bow) and Pd-bearing troilite (tro) in a matrix of isoferroplatinum (iso). Scale bar is 100 μm.

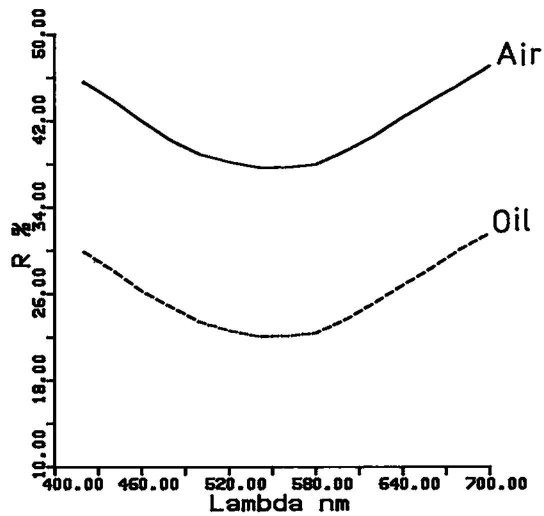

FIG. 2. Quantitative reflectance spectra for vasilite in air (———) and in oil (- - - -).

TABLE 1. REFLECTANCE VALUES FOR VASILITE

λ nm	R% in air	R% in oil	λ nm	R% in air	R% in oil
400	----	----	560	37.7	22.1
420	45.6	29.9	580	38.0	22.4
440	43.9	28.2	600	39.2	23.6
460	42.0	26.3	620	40.6	25.1
480	40.2	24.8	640	42.3	26.8
500	38.9	23.4	660	43.9	28.4
520	38.2	22.6	680	45.4	30.1
540	37.7	22.1	700	47.1	31.6

TABLE 2. COLOR VALUES FOR VASILITE (A ILLUMINANT)

	x	y	Y%	P_e%	λ_d
in air	0.4493	0.3977	38.84	1.47	564
in oil	0.4523	0.3895	23.06	2.97	563

λ_d in nm.

TABLE 3. ELECTRON-MICROPROBE DATA FOR VASILITE

	PdLα	CuLα₁	SKα	TeLα₁	Total*	Pd	Cu	S	Te
1.	76.91	9.65	10.66	2.50	99.72	13.55	2.85	6.23	0.37
2.	77.59	8.03	10.98	3.89	100.49	13.65	2.37	6.41	0.57
3.	77.03	8.45	10.97	3.33	99.78	13.59	2.50	6.42	0.49
4.	77.31	7.98	10.92	3.87	100.08	13.41	2.91	6.28	0.40
5.	77.13	10.01	11.78	2.76	101.68	13.11	2.85	6.65	0.39

Empirical formulas

1. $(Pd_{13.55}Cu_{2.85})_{\Sigma 16.40}(S_{6.23}Te_{0.37})_{\Sigma 6.60}$
2. $(Pd_{13.65}Cu_{2.37})_{\Sigma 16.02}(S_{6.41}Te_{0.57})_{\Sigma 6.98}$
3. $(Pd_{13.59}Cu_{2.50})_{\Sigma 16.09}(S_{6.42}Te_{0.49})_{\Sigma 6.91}$
4. $(Pd_{13.41}Cu_{2.91})_{\Sigma 16.32}(S_{6.28}Te_{0.40})_{\Sigma 6.68}$
5. $(Pd_{13.11}Cu_{2.85})_{\Sigma 15.96}(S_{6.65}Te_{0.39})_{\Sigma 7.04}$

Conditions: Philips SEM 515 equipped with EDAX 9100 and WDS fully computerized system of analysis using X-ray spectrometry. Standards used: pure metals for Pd, Cu and Te, and marcasite for S. Acceleration voltage: 20 kV. * in wt. %.

TABLE 4. X-RAY POWDER-DIFFRACTION PATTERN OF VASILITE

I	d_{meas}	h	k	l	d_{calc}	I	d_{meas}	h	k	l	d_{calc}
2	6.35	1	1	0	6.309	3	1.288	4	4	4	1.288
3	4.471	2	0	0	4.461	5	1.262	5	4	3	1.262
8	3.638	2	1	1	3.643	7	1.214	5	5	2	1.214
2	3.155	2	2	0	3.155	5	1.171	7	3	0	1.172
3	2.822	3	1	0	2.822	5	1.098	5	5	4	1.098
6	2.575	2	2	2	2.576	3	1.052	6	6	0	1.052
10	2.389	3	2	1	2.385	2	1.037	7	4	3	1.037
6	2.230	4	0	0	2.231	5	1.024	6	6	2	1.023
8	2.100	3	3	0	2.103	7	1.010	7	5	2	1.010
3	1.995	4	2	0	1.995	5	0.962	6	5	5	0.962
3	1.901	3	3	2	1.902	1	0.940	7	5	4	0.940
6	1.822	4	2	2	1.821	2	0.920	7	6	3	0.920
6	1.747	4	3	1	1.750	3	0.911	8	4	4	0.911
3	1.630	5	2	1	1.629	5	0.901	7	7	0	0.901
6	1.577	4	4	0	1.577	1	0.883	7	7	2	0.883
6	1.530	4	3	3	1.530	5	0.875	8	6	2	0.875
3	1.487	4	4	2	1.487	7	0.851	7	6	5	0.851
8	1.446	5	3	2	1.447	2	0.828	8	6	4	0.828
1	1.377	5	4	1	1.377	1	0.815	10	4	2	0.814
2	1.345	6	2	2	1.345	7	0.808	8	7	3	0.808
6	1.316	6	3	1	1.316	7	0.795	9	6	3	0.795

Crystal system: cubic; space group: $I\bar{4}3m$; *a* 8.922(1) Å, *V* 710.21(24) Å^3, *Z* = 2, D_{calc} 8.796(2) g/cm^3. Cu*K*α radiation, λ 1.54187 Å. d_{meas} and d_{calc} are expressed in Å.

grain-size and the brittleness of vasilite. An indentation with 20 g produced small fractures at the corners of the indentations. The fracture is uneven.

OPTICAL PROPERTIES IN REFLECTED LIGHT

Under reflected light, there is no visual difference between the color of vasilite in air and in oil. Neither bireflectance nor anisotropism was observed. The mineral takes a good polish. The polishing hardness is lower than that of isoferroplatinum and bowieite. The experimental conditions for acquisition of reflectance data are: NU-2 microscope (GDR), multiplier M 12FS35, monochromator with a band width of

10 nm, illuminant HBO 50, reflector-plane glass; the aperture used in the measurements was 0.8 (for 50× objective) in air and 1.3 (for 100× objective) in oil. Spot sizes were 6 μm (for 50 × objective) and 3 μm (for 100× objective). A Si standard, tested in the National Physics Laboratory, Cambridge, U.K., was used. Immersion oil: PCB-Frei (GDR), N_D (20°C) = 1.515. Reflectance data (average from 3 measurements) for vasilite and quantitative color values referred to CIE, illuminant A are shown in Tables 1 and 2. The quantitative reflectance spectra for vasilite in air and in oil are shown in Figure 2.

Composition

The chemical composition of vasilite was determined by quantitative electron-microprobe analysis; five different grains were analyzed using wavelength dispersion and, as standards, pure metals for Pd, Cu and Te, and marcasite for S (53.56 wt.%; Table 3). The simplified formula of vasilite is $Pd_{16}S_7$, and its proposed empirical formula is $(Pd,Cu)_{16}(S,Te)_7$, calculated on the basis of a total of 23 atoms.

Crystallography

A single-crystal study of vasilite was not carried out because of its small grain-size. The material was extracted after optical studies, microprobe analysis and microhardness indentations and mounted for X-ray diffraction using a Gandolfi camera 57.3 mm in diameter. The material analyzed is from grain No. 2, Table 3. Forty-two lines of vasilite were obtained and indexed on the basis of the cubic cell $I\bar{4}3m$, for the structure type $Pd_{16}S_7$ of Matković *et al.* (1976). All calculations were made using the PDI program (Macicek 1988). The X-ray powder-diffraction pattern of vasilite is shown in Table 4.

Discussion

In chemical composition, X-ray-diffraction pattern and some physical properties, vasilite is identical to the compound $Pd_{16}S_7$, synthesized by Matković *et al.* (1976), and to the compound $Pd_{2.20}S$, synthesized by Grønvold & Rost (1956). It is similar to the unnamed Pd_4CuS_2, found by Rudashevsky & Zhdanov (1983), which also occurs as oval polymineralic inclusions (2–80 μm in size) together with bornite, chalcopyrite and $(Cu,Rh)_3S_4$ in an isoferroplatinum matrix. This unnamed Pd_4CuS_2 contains (in wt.%): Pd 76.1, Cu 10.2, Rh 0.24, Fe 0.21, Ir 0.68, Pt 0.44 and S 12.6. A recalculation of this composition according to the stoichiometry of $Pd_{16}S_7$ gives the following empirical formula: $(Pd_{12.77}Cu_{2.87}Rh_{0.17}Fe_{0.07}Ir_{0.06}Pt_{0.04})_{\Sigma 15.98}S_{7.02}$.

Vasilite is named after my father, Dr. Vasil Atanasov Atanasov, Associate Professor in Mineralogy, Higher Institute of Mining and Geology, Sofia. He was born on April 8, 1933. The original Cyrillic spelling is Василит. The type material of vasilite is deposited in the National Museum of Earth and Man, Sofia, Bulgaria (sample No. 10 213). The origin of the platinum-group minerals (*PGM*) has not been clearly established. The primary source may be deep-seated chromite-bearing basic and ultrabasic rocks, which appear as inclusions in the Upper Cretaceous andesites, trachyandesites and basaltic andesites of the region. The morphology of the *PGM*, their aggregates and associated minerals suggests remobilization and secondary melting of the *PGM* and their host rocks during Upper Cretaceous magmatic activity. The Cu- and Te-bearing minerals associated with the *PGM* show a geochemical relationship with the Bourgas copper deposits, located in the Upper Cretaceous volcanic rocks. The mineralogy of the *PGM* in the Priabonian sediments shows features of magmatic contamination and redeposition.

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