Mineralogical Magazine, February 2002, Vol. 66(1), pp. 173–179

Verbeekite, monoclinic $PdSe_2$, a new mineral from the Musonoi Cu-Co-Mn-U mine, near Kolwezi, Shaba Province, Democratic Republic of Congo

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ABSTRACT

Verbeekite, ideally $PdSe_2$, monoclinic with space-group choices $C2/m$, $C2$ or Cm; a = 6.659(7), b = 4.124(5), c = 4.438(6) Å, ß = 92.76(3)°, V = 121.7(4) Å^3; a:b:c = 1.6147:1:1.0761, Z = 2, is a new, very rare, primary mineral, intimately associated with secondary oosterboschite [$(Pd,Cu)_7Se_5$], from the Musonoi Cu-Co-Mn-U mine, near Kolwezi, Shaba Province, Democratic Republic of Congo. Additional associated minerals are Cu- and Pd-bearing trogtalite [$(Co,Cu,Pd)Se_2$], Se-bearing digenite and Se-bearing covellite. The strongest five lines of the X-ray powder-diffraction pattern [d in Å (I) (hkl)] are: 4.423(30)(001), 3.496 (30)(110), 2.718(100)(111), 1.955(50)(310) and 1.896(50)($\bar{1}$12). The mineral has also been identified, as a single anhedral 25 µm-sized grain, from Hope's Nose, Torquay, Devon, England where it is associated with native gold, chrisstanleyite $Ag_2Pd_3Se_4$, oosterboschite(?), unnamed Pd_2HgSe_3 and cerussite. At Musonoi, altered verbeekite grains do not exceed 200 µm in size and are anhedral, black, with a black streak and a metallic lustre. The mineral is opaque, brittle, has an uneven fracture, and lacks discernible cleavage. The VHN_5 ranges 490–610, mean 550 kp/mm^2 (2 indentations), roughly approximating a Mohs' hardness of 5½. $D_{calc.}$ = 7.211 g/cm^3 for the ideal formula. Electron-microprobe analyses (mean of 4 spot analyses) yielded Pd 39.6, Cu 0.5, Se 58.8, total 98.9 wt.%. The empirical formula is $(Pd_{0.99}Cu_{0.02})_{\Sigma 1.01}Se_{1.99}$, based on Pd+Cu+Se = 3. In plane-polarized reflected light, the mineral is a nondescript grey and is neither pleochroic nor perceptibly bireflectant. Anisotropy is moderate with rotation tints in varying shades of brown. Reflectance spectra and colour values are tabulated. The name honours Dr Théodore Verbeek (1927–1991) who was the first geoscientist to study the Musonoi palladium mineralization in the Democratic Republic of Congo (1955–1967) and who co-discovered this new mineral phase.

KEYWORDS: verbeekite, palladium diselenide, X-ray data, electron-microprobe data, reflectance data, Musonoi Cu-Co-Mn-U mine, Kolwezi, Shaba Province, Democratic Republic of Congo, Hope's Nose, Torquay, Devon, England.

Introduction

SPECIMENS containing the new mineral, verbeekite, were collected by amateur mineralogist Ing. R. Coussement in 1963–1964 from the dumps of the Musonoi Cu-Co-Mn-U mine. This mine, situated in the western portion of Shaba (formerly Katanga) Province, near Kolwezi, Democratic Republic of Congo (formerly Zaïre) at approximate latitude 10°44′S and approximate longitude 25°26′E, is well known internationally for its diverse suite of colourful secondary U-Se

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DOI: 10.1180/0026461026610020

minerals. It is the type locality for derriksite (Cesbron *et al.*, 1971), demesmaekerite (Cesbron *et al.*, 1965), guilleminite (Pierrot *et al.*, 1965) and marthozite (Cesbron *et al.*, 1969). They and other secondary uranium minerals are hosted within a Se-rich lens; a metallurgical nightmare, but a mineralogical treasure chest. Lens material was found to be too radioactive and too complex to process and was thus piled up, dumped and buried by 1964. Less well known within the lens are the suite of primary Se-rich metallic phases, several of which are Pd-bearing. It is one of these rare less-colourful platinum group mineral (PGM) phases which is the topic of this paper. While Musonoi is considered the type locality for verbeekite, it should be noted that it has also been identified at Hope's Nose, Torquay, Devon, England, UK (lat. 58°28′N, long. 3°28′W) (Paar *et al.*, 1998 and references therein which describe the mineralization found at Hope's Nose). The mineral name honours Dr Théodore Verbeek (1927–1991) who was the first geoscientist to study the Musonoi Se-bearing lens mineralization (1955–1967) and who, along with Dr R. Oosterbosch, first documented (in internal mining reports) the existence of palladium selenides. Verbeekite is probably the unidentified mineral mentioned briefly in the paper dealing with the formal description of oosterboschite, $(Pd,Cu)_7Se_5$, (Johan *et al.*, 1970). The mineral and mineral name have been approved by the Commission on New Minerals and Mineral Names, of the International Mineralogical Association (IMA). The holotype polished section (Musonoi) containing remnant verbeekite grains is registered in the mineral collections at The Natural History Museum in London as BM2001, 4.

Occurrence and association

The Musonoi mine resides within the richly mineralized Kolwezi overthrust. The ore bodies belong stratigraphically to the Roan System (Mines Series, also known as the Rhodesian Mines Series) and are of late Precambrian age. The deposits and the surrounding country rock show sedimentary-hydrothermal affiliations, and are deeply faulted, folded and altered (Oosterbosch, 1962; Demesmaeker *et al.*, 1963; François, 1987). An overview (in English) of the geology and mineralogy of the Musonoi deposit is given by Gauthier *et al.* (1989). A comprehensive study of PGM mineralogy of the Shaba Province has recently been published by Jedwab (1997), based, in part, on the specimens collected by Ing. R. Coussement during the early 1960s. Verbeekite is considered to be a primary phase both at Musonoi and at Hope's Nose and has formed from hydrothermal solutions at temperatures up to 120°C (based on fluid-inclusion studies at Hope's Nose). At Musonoi, the principle verbeekite grain is highly fractured and secondary replacement oosterboschite (verified by routine X-ray film methods) 'heals' these fractures. The mineral must be considered extremely rare at both localities; virtually all mineralogical studies reported in this paper (except reflectance) were carried out on this single anhedral grain that initially measured approximately 200 × 200 µm (Fig. 1) and is composed of a 50:50 mixture of primary verbeekite and secondary oosterboschite. Other closely associated metallic minerals at Musonoi include Cu- and Pd-bearing trogtalite $[(Co,Cu,Pd)Se_2]$, Se-bearing digenite and Se-bearing covellite.

At Hope's Nose, the mineral has been found as a single anhedral 25 µm-sized grain enclosed within native gold, associated with chrisstanleyite $Ag_2Pd_3Se_4$, oosterboschite(?), unnamed Pd_2HgSe_3 and cerussite. In the formal descriptive paper dealing with chrisstanleyite (Paar *et al.*,

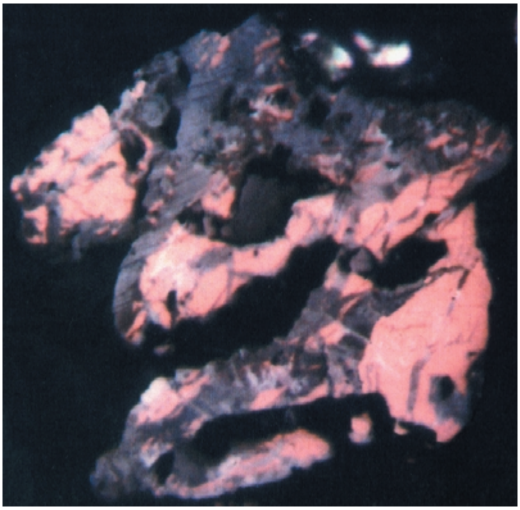

FIG. 1. Photomicrograph of composite verbeekite-oosterboschite grain before initial X-ray study. The verbeekite appears pinkish and the oosterboschite is dark grey in this photomicrograph. Grain measures approximately 200 × 200 µm.

1998), verbeekite is referred to as "uk2" and a photomicrograph depicting it and several of the other unknown phases is presented in Figure 4 of that paper. We attempted to extract this grain for routine X-ray study and were largely unsuccessful, in part due to extraneous contamination from native gold and cerussite. We did observe, however, the most intense reflection (2.72 Å) characteristic of verbeekite on a 57.3 mm Debye-Scherrer powder film.

Appearance and physical properties

Verbeekite occurs as altered anhedral grains which, upon extraction from polished section, are black with a black streak. It possesses a metallic lustre, is opaque, brittle, has an uneven fracture and no observable cleavage. There was no evidence of twinning in either the reflectance study or the precession single-crystal study. Vickers microhardness measurements were determined using a Leitz Miniload 2 Hardness tester and gave the following results: VHN_5 (2 determinations) mean 550, range 490–610 kPa/mm^2. This corresponds to a calculated Mohs' hardness of ~5½. A dearth of pure unaltered material prevented us from attempting to determine the measured density; calculated densities with Z = 2 are as follows: 7.211 g/cm^3 (ideal formula and unit-cell parameters derived from CCD-equipped four-circle diffractometer); 7.199 g/cm^3 (ideal formula and unit-cell parameters refined from powder data); 7.196 g/cm^3 (empirical formula and unit-cell parameters derived from CCD-equipped four-circle diffractometer); 7.186 g/cm^3 (empirical formula and unit-cell parameters refined from powder data).

X-ray studies

Two verbeekite fragments from the composite grain were dug out of the polished section and studied using X-ray single-crystal methods (Ottawa). The larger fragment was studied by precession camera employing unfiltered Mo radiation. This fragment was, unfortunately, orientated with 111* parallel to the dial axis and, as such, only $c^* \wedge 110^*$, a reciprocal-lattice level containing *b**, and a reciprocal-lattice level containing 310* were evident from numerous preliminary orientation photographs. The smaller fragment, ~20 μm in size, was mounted on a Bruker *P*4 four-circle diffractometer equipped with a CCD detector (Winnipeg). A complete sphere of intensity data was collected using a 0.1° frame width, a 4 min per frame count time, and a 4 cm crystal-to-detector distance. Only 33 reflections were observed, but this entire data set could be successfully indexed on a *C*-centred monoclinic cell with the following unit-cell parameters:

TABLE 1. X-ray powder-diffraction data for verbeekite.

	$I_{\text{est.}}$	$d_{\text{meas.}}$ (Å)	$d_{\text{calc.}}$ (Å)	*hkl*		$I_{\text{est.}}$	$d_{\text{meas.}}$ (Å)	$d_{\text{calc.}}$ (Å)	*hkl*
	30	4.423	4.435	001	*	20	1.645	1.646	$\bar{2}21$
*	30	3.496	3.508	110	*	3	1.617	1.617	221
*	100	2.718	2.717	111	*	20	1.533	1.532	401
*	20	2.063	2.065	020		3	1.494	1.498	$\bar{3}12$
*	50	1.955	1.953	310	*	10	1.478	1.478	003
*	50	1.896	1.897	$\bar{1}12$	*	10	1.394	1.393	$\bar{2}22$
*	5	1.870	1.872	021	*	5	1.376	1.375	$\bar{1}13$
*	5	1.851	1.853	112		20	1.361	1.363	$\bar{4}02$
*	20	1.815	1.817	$\bar{3}11$				1.358	222
*	20	1.805	1.804	202	*	20	1.233	1.233	$\bar{5}11$
*	5	1.661	1.662	400	*	20	1.204	1.204	$\bar{3}13$

114.6 mm Debye-Scherrer powder camera; Cu radiation, Ni filter (λ Cu-$K\alpha$ = 1.54178 Å)
Intensities estimated visually
Not corrected for shrinkage and no internal standard
* = lines used for unit-cell refinement
Diffraction lines ascribable to admixed oosterboschite have been deleted from the powder data
Indexed with *a* = 6.657(2), *b* = 4.129(2), *c* = 4.440(1) Å, ß = 92.83(3)°

TABLE 2. Electron microprobe analyses of verbeekite.

Constituent	Wt.%[1]	Range	Std. dev.	Atoms per unit
Pd	39.6	39.0–39.8	0.4	0.99
Cu	0.5	0.3–0.7	0.2	0.02
Se	58.8	58.2–59.2	0.4	1.99
Total	98.9			

[1] Average of 4 analyses

a = 6.659(7), b = 4.124(5), c = 4.438(6) Å, ß = 92.76(3)°, V = 121.7(4) Å^3, a:b:c = 1.6147:1:1.0761. The permissible space-group choices are $C2/m$, $C2$ or Cm. This highly impoverished data set did not give a meaningful structure refinement. However, these calculated intensities, combined with the precession film data, were more than adequate to satisfactorily index the powder-diffraction pattern.

Fully indexed 114.6 mm Debye-Scherrer camera X-ray powder data are presented in Table 1. The refined unit-cell parameters: a = 6.657(2), b = 4.129(2), c = 4.440(1) Å, ß = 92.83(3)°, V = 121.9(1) Å^3, a:b:c = 1.6123:1:1.0753 are based on 19 reflections, between 3.496 and 1.204 Å, in the X-ray powder pattern for which unambiguous indexing was possible. Diffraction lines ascribable to oosterboschite contamination have been omitted. The data are unique and do not bear resemblance to any mineral or inorganic compound listed in the PDF up to and including Set 50.

Verbeekite is the monoclinic polymorph of orthorhombic synthetic PdSe$_2$ (Grønvold and Røst, 1957; PDF 11-453, 72-1197] and is chemically the Pd-analogue of sudovikovite (hexagonal PtSe$_2$). Monoclinic PdSe$_2$ has not previously been recognized in the Pd-Se binary phase diagram. The Pearson Symbol Code (PSC) is $mC6$ and verbeekite may have calaverite (AuTe$_2$) as its prototype structure. We intend to test this hypothesis in the near future, once a new generation high-sensitivity CCD detector has been installed on the four-circle diffractometer.

Electron microprobe analyses

Prior to extraction for X-ray studies, the dominant verbeekite-bearing grain from Musonoi was analysed using a JEOL Superprobe JXA-8600 electron microprobe equipped with an ELX-Link system (Salzburg). Operating conditions were as follows: 25 kV; 30 nA; counting time 20 s (peak), 7 s (background); 1 μm beam-size. The

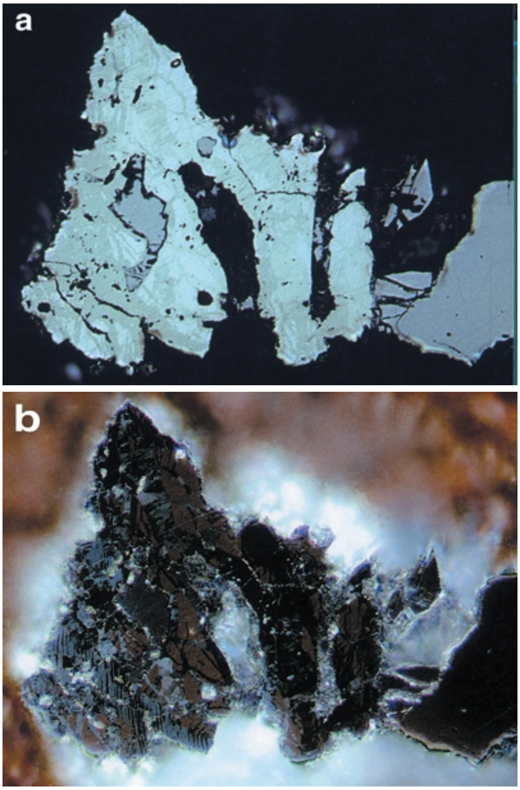

FIG. 2. Verbeekite photomicrographs in (*a*) plane-polarized light (upper image) and (*b*) between crossed polars (lower image). The horizontal dimension is 275 μm for both photomicrographs. In the lower image, verbeekite is a bronzy brown colour and the associated oosterboschite shows obvious lamellar twinning and is grey in colour. Both photomicrographs are oriented for the position of maximum anisotropy for verbeekite.

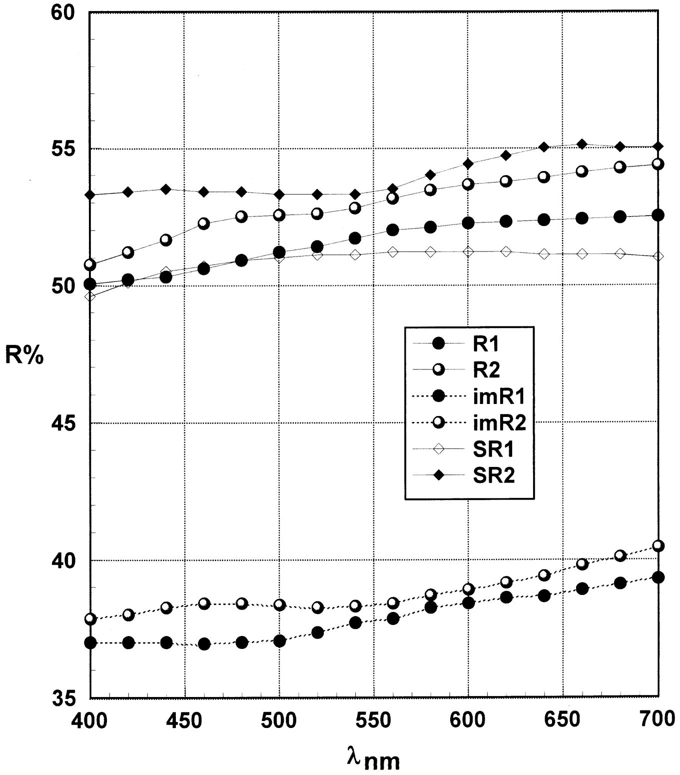

FIG. 3. Reflectance spectra for verbeekite in air and in oil (N_D = 1.515). [Footnote: The air and oil curves measured in London are R1 and R2 for air, and imR1 and imR2 for oil. The air curves measured in Salzburg are SR1 and SR2.]

accumulated raw data were then processed with the Link ZAF-4 computer program. Natural Cu_3Se_2 (umangite) (Cu-*K*α and Se-*K*α) and synthetic Pd metal (Pd-*L*α) were used as suitable standards. The results of the probe study are given in Table 2. The empirical formula derived from these 4 analyses corresponds to $(Pd_{0.99}Cu_{0.02})_{\Sigma 1.01}Se_{1.99}$ on the basis of Pd+Cu+Se = 3. The ideal formula, $PdSe_2$, requires Pd 40.26, Se 59.74, total 100.00 wt.%.

Optical properties

In plane-polarized light (at a colour temperature of ~3200 K), verbeekite is a nondescript grey; it is neither pleochroic nor perceptibly bireflectant. The sample available in polished section appears to consist of a single grain, fractured and infilled with another mineral which is very slightly greenish grey by comparison with the remaining verbeekite (Fig. 2*a*). Between crossed polars, verbeekite is moderately anisotropic but its only rotation tints are varying shades of brown. Figure 2*b* shows that all of the fragments of remnant verbeekite have the same intensity and colour of rotation tint, i.e. they are in optical continuity, and therefore suggest that it was originally a single grain. The other mineral present is lamellar twinned and its rotation tints are grey – this mineral has a composition corresponding approximately to that of oosterboschite. Uncontaminated grains of verbeekite large enough for reflectance measurement were few.

Reflectance measurements were made initially at Salzburg (Austria) in the wavelength range 400–700 nm. These suggested that the mineral was moderately bireflectant and weakly pleochroic – neither of which could be quantified. Consequently, the material was re-measured at The Natural History Museum (NHM) in London, England. Here, the two most anisotropic grains

TABLE 3. Reflectance percentages and colour values relative to CIE (1931) (as explained by Criddle (1980) and Henry (1980)) illuminants for verbeekite.

λ (nm)	R1	R2	imR1	imR2	SR1	SR2
400	50.05	50.75	37.00	37.85	49.60	53.30
420	50.20	51.20	37.00	38.00	50.10	53.40
440	50.30	51.65	37.00	38.25	50.50	53.50
460	50.60	52.25	36.95	38.40	50.70	53.40
480	50.90	52.50	37.00	38.40	50.90	53.40
500	51.20	52.55	37.05	38.35	51.00	53.30
520	51.40	52.60	37.35	38.25	51.10	53.30
540	51.70	52.80	37.70	38.30	51.10	53.30
560	52.00	53.15	37.85	38.40	51.20	53.50
580	52.10	53.45	38.25	38.70	51.20	54.00
600	52.25	53.65	38.40	38.90	51.20	54.40
620	52.30	53.75	38.60	39.15	51.20	54.70
640	52.35	53.90	38.65	39.40	51.10	55.00
660	52.40	54.10	38.90	39.80	51.10	55.10
680	52.45	54.25	39.10	40.10	51.10	55.00
700	52.50	54.35	39.30	40.45	51.00	55.00
COM:						
470	50.80	52.30	37.00	38.40	50.80	53.40
546	51.85	52.90	37.75	38.30	51.20	53.40
589	52.20	53.55	38.50	38.60	51.20	53.20
650	52.40	54.00	38.80	39.60	51.10	55.10
CIE A:						
x	0.450	0.450	0.451	0.450	0.448	0.450
y	0.409	0.408	0.408	0.407	0.408	0.407
Y%	52.0	53.3	38.0	38.7	51.2	53.9
λ_d	585	588	590	616	579	616
P_e%	2.5	2.3	2.8	0.9	1.0	1.0
CIE C:						
x	0.313	0.313	0.314	0.312	0.311	0.312
y	0.320	0.319	0.319	0.317	0.318	0.317
Y%	51.8	53.1	37.9	38.6	51.1	53.7
λ_d	576	578	582	591	570	595
P_e%	1.8	1.6	1.8	0.8	0.8	0.8

Measurement conditions (London, R1, R2, imR1, imR2): Zeiss MPM 800; reflectance standard WTiC (Zeiss) no. 314; levelling superstage (Lanham); objectives, air and oil × 50, effective numerical apertures 0.28. SR1 and SR2 reflectance data in air were measured in Salzburg.

provided spectra that conformed with observation (Fig. 3). The discrepancy between the measurements from the two laboratories was sufficient that the sample was returned to Salzburg and re-measured. The reflectance spectra obtained were similarly dispersed to the first Salzburg set, but they are less bireflectant; nevertheless, they still bracket the set from the NHM (Fig. 3). Table 3 lists these data and adds colour values relative to the CIE (1931) (see Criddle (1980) and Henry (1980) for an explanation) illuminants A (2856 K) and C (6774 K). Taking the A illumination values as corresponding most closely to the conditions of observation and measurement, these show that the luminance values (Y%) for R1 and R2 obtained in the two laboratories are very similar – Salzburg: 51.2 and 53.9, London: 52.0 and 53.3. The bireflectance for the Salzburg set is greater at 2.7% than the London value of 1.3%. The excitation purity values (P_e%) are vanishingly low for the Salzburg set at 1% and a little higher for the London set at 2.3–2.5%. These figures prove that the grains measured in both laboratories would appear to be very weakly bireflectant, if at all, and non-pleochroic.

Acknowledgements

The senior author thanks Ms Kathryn Mooney (GSC) for typing numerous revisions of the manuscript and Ms Rachel Lacroix (GSC) for digitizing Fig 1. J.J. thanks Ing. R. Coussement, for donating his verbeekite-bearing specimens to the Université Libre de Bruxelles. Major Equipment Research and Major Facilities Access Grants to Prof. F.C. Hawthorne helped to finance the X-ray studies at the University of Manitoba. The sample was polished for optical work and photography by Dr Chris Stanley without whose expertise the characterization of the mineral would have been incomplete. The authors thank Drs Alan Pring and Nigel Cook for their constructive reviews.

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[*Manuscript received 6 June 2001:*
revised 15 October 2001]