NEW DATA ON VINCENTITE

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Abstract

Vincentite was described in 1974 as a new palladium-bearing mineral species in platinum–gold concentrates from the Riam Kanan River, southeastern Borneo. Because of its small grain-size, it was not possible at that time to obtain satisfactory X-ray data. The mineral has now been re-investigated. In reflected light, it is light brownish grey; pleochroism and anisotropy are weak. Maximum and minimum values of reflectance in air for standard wavelengths (470, 546, 589 and 650 nm) are: 38.8/43.1; 45.4/51.3; 48.0/54.2 and 50.8/55.9, respectively. New electron-microprobe analyses confirm the formula $(Pd,Pt)_3(As,Sb,Te)$ attributed earlier. The X-ray powder-diffraction patterns obtained with a microdiffractometer were indexed on a monoclinic cell with a 11.226(3), b 6.318(2), c 8.047(2) Å, β 100.95(4)°, V 560.4(2) Å³; a:b:c = 1.776:1:1.273. For Z = 8, the calculated density is 10.86 g/cm³. The strongest five lines in the X-ray pattern [d in Å(I)(hkl)] are: 1.800(10)($\bar{6}$02), 1.775(9)($\bar{4}$04), 1.758(8)($\bar{4}$23), 1.745(8)(331) and 1.838(6)(600).

Keywords: vincentite, Pd mineral, new data, spectral reflectance, X-ray-diffraction pattern, unit-cell parameters.

Sommaire

La vincentite a été décrite en 1974 comme nouvelle espèce minérale de palladium provenant de concentrés alluvionnaires de platine–or prélevés dans la rivière Riam Kanan, secteur sud-est de Bornéo. Vu la taile infime des grains, il n'était pas possible alors d'obtenir des données en diffraction X convenables. Nous avons maintenant ré-étudié la vincentite. En lumière réfléchie, elle est gris brunâtre; le pléochroïsme et l'anisotropie sont faibles. Les valeurs maximum et minimum de la réflectance dans l'air aux longueurs d'ondes standard (470, 546, 589 et 650 nm) sont: 38.8/43.1, 45.4/51.3, 48.0/54.2 et 50.8/55.9, respectivement. De nouvelles données obtenues avec une microsonde électronique confirment la formule $(Pd,Pt)_3(As,Sb,Te)$ attribuée antérieurement. Le spectre de diffraction X obtenu avec un microdiffractomètre a été indexé sur une maille monoclinique ayant comme paramètres a 11.226(3), b 6.318(2), c 8.047(2) Å, β 100.95(4)°, V 560.4(2) Å³; a:b:c = 1.776:1:1.273. Avec Z = 8, la densité calculée est de 10.86 g/cm³. Les cinq raies les plus intenses du spectre de diffraction X [d en Å(I)(hkl)] sont: 1.800(10)($\bar{6}$02), 1.775(9)($\bar{4}$04), 1.758(8)($\bar{4}$23), 1.745(8)(331) et 1.838(6)(600).

(Traduit par la Rédaction)

Mots-clés: vincentite, minéral de Pd, nouvelles données, réflectance spectrale, spectre de diffraction X, paramètres réticulaires.

Introduction

Vincentite was discovered as a new mineral with the formula $(Pd,Pt)_3$ (As,Sb,Te) in platinum–gold concentrates from the Riam Kanan River, southeastern Borneo; it was named in honor of Professor E.A. Vincent of the University of Oxford (Stumpfl & Tarkian 1974). It was accepted by the International Mineralogical Associa-tions Commission on New Mineral and Mineral Names, but because of the small grain-size, the X-ray data presented at that time were judged not to be satisfactory. In the present paper, we report results of new investigations of vincentite using a microdiffractometer. In addition, complete reflectance curves and new chemical data have been obtained.

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OPTICAL PROPERTIES

Vincentite occurs as inclusions in Fe-bearing platinum. The maximum grain-size is in the order of 40 μm (Fig. 1). In reflected light, the mineral is light brownish grey with a weak bireflectance. The anisotropism is weak, from greenish grey to dark brown. Polishing hardness is somewhat higher (VHN$_{15}$ 494 kg/mm^2) than that of the platinum matrix. A computerized Zeiss MPM microphotometer and WTiC standard (R$_{589}$ in air = 49.5%) were used for reflectance measurements (Table 1, Fig. 2).
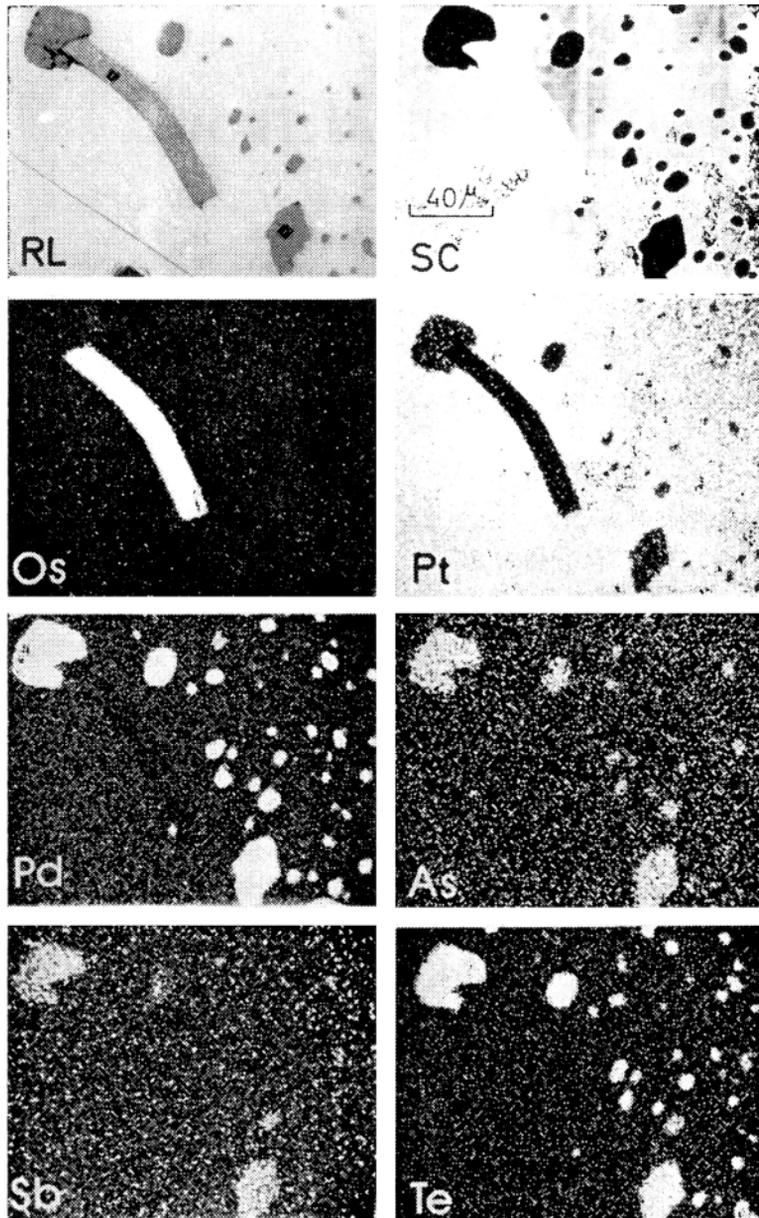
FIG. 1. Inclusions of vincentite and a lamella of native osmium in iron-bearing platinum. RL = reflected light; SC = sample current picture. Single-element scans for Os, Pt, Pd, As, Sb and Te are shown.

CHEMICAL COMPOSITION

Several grains of vincentite were analyzed using a Cameca Camebax Microbeam wavelength–dispersion electron microprobe at the Department of Mineralogy and Petrology, University of Hamburg. The accelerating voltage was 20 kV, the beam current, 22.8 nA, and the beam diameter, 1 μm.

For all elements the $L\alpha$ X-ray line was used. Pure elements (for Pd and Pt) as well as stibnite (for Sb), synthetic PdBiTe (for Te) and AsGa (for As) were used as standards. Matrix corrections were applied using the PAP program (Pouchou & Pichoir 1991). Representative compositions are given in Table 2. Results of new electron-microprobe analyses (Table 2, Nos. 3, 4) confirm the formula $(Pd,Pt)_3(As,Sb,Te)$ originally established for vincentite.

X-RAY DATA

The two largest grains of vincentite analyzed by microprobe (Fig. 1), were studied on a Rigaku X-ray microdiffractometer PSPC/MDG (Cr$K\alpha$ radiation, operated at 50 kV and 200 nA, diameter of diaphragm 10 μm). The PSPC/MDG is specifically designed to facilitate X-ray-diffraction analysis of extremely small areas. The use of a curved PSPC (position-sensitive proportional counter) on a dedicated goniometer with a three-axis sample-oscillation mechanism produces high detection-sensitivities from a microsample while at the same time permitting detection of all reflections from a very wide angle (0 to 150° 2θ). Areas as small as 11 μm in diameter can be measured with high accuracy. A zoom optical microscope with X–Y–Z adjusting stage enables easy positioning of the sample for irradiation of a spot 10 μm in diameter (Rigaku 1994). Diffraction lines were measured between 20° and 145° 2θ. There were 29 sharp reflections of vincentite; in addition, four lines (d 2.230, 1.938, 1.721 and 1.366 Å) of the Pt–Fe matrix were recorded. The latter were subtracted from the spectrum. The X-ray pattern obtained for vincentite is presented in Table 3. The pattern was indexed on a monoclinic cell. Refinement of the data using the program of Holland & Redfern (1997) yielded: a 11.226(3), b 6.318(2), c 8.047(2) Å, β 100.95(4)°, V 560.4(2) Å^3, a:b:c = 1.776:1:1.273. For Z = 8, the density calculated

TABLE 1. REFLECTANCE DATA FOR VINCENTITE

λ nm	R_1 (air)	R_2 (air)	λ nm	R_1 (air)	R_2 (air)
400	36.0	36.5	560	46.3	52.2
420	36.4	37.3	580	47.6	53.8
440	36.4	38.7	**589**	**48.0**	**54.2**
460	38.0	41.8	600	48.4	54.8
470	**38.8**	**43.1**	620	48.9	55.8
480	40.5	44.2	640	50.4	55.9
500	42.0	46.1	**650**	**50.8**	**55.9**
520	43.4	48.9	660	51.6	56.0
540	45.1	51.1	680	53.1	55.8
546	**45.4**	**51.3**	700	54.2	56.2

Color values (C illuminant)

	x	y	y%	Pe%	λd
R_1	0.332	0.338	45.8	11.7	577
R_2	0.335	0.343	51.6	14.0	576
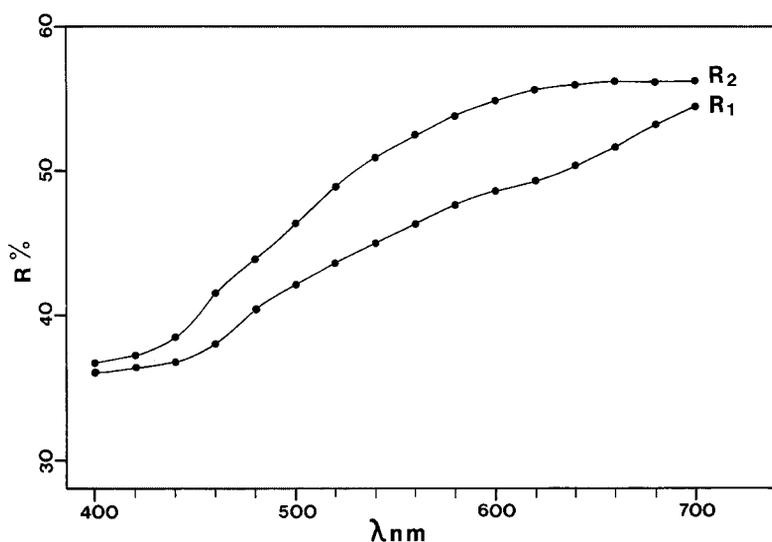
FIG. 2.   Reflectance spectra for vincentite in air.

TABLE 2. ELECTRON-MICROPROBE DATA FOR VINCENTITE

No.	1*	2*	3	4
Pd wt%	61.3	59.6	61.63	60.31
Pt	14.4	17.6	14.91	16.70
As	7.3	7.2	7.51	6.99
Sb	6.3	9.3	7.42	9.18
Te	8.9	6.3	7.89	7.12
Total	98.2	100.0	99.36	100.30
Atom proportions (Σ atoms = 4)				
Pd *apfu*	2.65	2.57	2.64	2.59
Pt	0.34	0.41	0.35	0.39
ΣMe	2.99	2.98	2.99	2.98
As	0.45	0.44	0.45	0.43
Sb	0.24	0.35	0.28	0.34
Te	0.32	0.23	0.28	0.25
Σ	1.01	1.02	1.01	1.02

* Stumpfl & Tarkian (1974). Atom proportions are quoted in atoms per formula unit, *apfu*.

TABLE 3. X-RAY DATA FOR VINCENTITE

I_{est}	d_{meas}	d_{calc}	hkl	I_{est}	d_{meas}	d_{calc}	hkl
<1	5.912	5.911	$\overline{1}$01	8	1.758	1.757	$\overline{4}$23
<1	4.987	4.986	$\overline{2}$01	8	1.745	1.744	331
2	4.299	4.316	111	4	1.697	1.696	$\overline{1}$24
2	4.147	4.153	210	3	1.674	1.674	024
3	3.951	3.950	002	1	1.601	1.599	431
1	3.340	3.349	012	<1	1.470	1.470	$\overline{6}$23
3	2.934	2.933	021	<1	1.458	1.458	$\overline{4}$15
4	2.888	2.885	$\overline{1}$21	<1	1.431	1.429	721
2	2.043	2.043	$\overline{1}$23	3	1.360	1.360	$\overline{1}$43
1	2.009	2.005	$\overline{4}$13	1	1.346	1.346	810
1	1.983	1.983	$\overline{2}$04	1	1.317	1.316	006
6	1.838	1.836	600	<1	1.279	1.279	106
10	1.800	1.801	$\overline{6}$02	<1	1.268	1.268	$\overline{8}$22
9	1.775	1.772	$\overline{4}$04	<1	1.254	1.253	116
				<1	1.236	1.235	151

Rigaku microdiffractometer PSPC/MDG. Cr$K\alpha$ radiation, voltage 50 kV, current 200nA, diameter of diaphragm 10 µm. Unit-cell parameters: *a* 11.226(3), *b* 6.318(2), *c* 8.047(2) Å, β 100.95(4)°.

for a composition given in Table 2 (anal. 2) is 10.86 g/cm^3. The strongest five lines in the X-ray pattern [*d* in Å (I)($hk\overline{l}$)] are: 1.800(10)($\overline{6}$02), 1.775(9)($\overline{4}$04), 1.758(8)($\overline{4}$23), 1.745(8)(331) and 1.838(6)(600).

DISCUSSION

The optical data of vincentite are now completely defined by reflectance spectra, and the color values are given. The new chemical data confirm the stoichiometry of vincentite; its formula is (Pd,Pt)$_3$(As,Sb,Te). In the IMA approval, vincentite was defined as (Pd,Pt)$_3$(As,Sb,Te) with Pd>Pt and As:(Sb,Te) ≈ 1:1 (Stumpfl & Tarkian 1974). In the literature, there are two unnamed minerals with a (Pd,Pt)$_3$ (X,Y) stoichiometry, where X and Y are either As > Sb (Johan *et al.* 1990, Distler *et al.* 1999) or Te > As (Augé & Legendre 1992, Weiser & Schmidt-Thomé 1993). But there are none with (As,Sb,Te). However, neither of these minerals can be vincentite, as defined, on compositional grounds. Their composition, however, reveals the presence of mixed crystals in the system Pd$_3$As–Pd$_3$Sb–Pd$_3$Te; part of the Pd may also be replaced by Pt. Phase relationships, stabilities and extents of solid solution are, however, still unknown. Cabri *et al.* (1975) have discussed the field of stability of several palladium arsenides and antimonides in relation to experimental results in some detail. End members in the above system occurring in nature are limited to "guanglinite", Pd$_3$As (Chao & Cabri 1976), which has been discredited as probably the equivalent of isomertiite (Cabri 1980), and keithconnite, Pd$_{3-x}$Te (Cabri *et al.* 1979). The X-ray pattern of vincentite, however, does not show any similarity with either "guanglinite" or keithconnite, nor

with synthetic Pd$_3$As (Saini *et al.* 1964); nor is the pattern of vincentite similar to the X-ray pattern of other minerals in the system Pd–As–Sb, such as arsenopalladinite, Pd$_8$(As,Sb)$_3$ (Cabri *et al.* 1977), mertieite I, Pd$_{11}$(Sb,As)$_4$ and mertieite II, Pd$_8$(Sb,As)$_3$ (Desborough *et al.* 1973, Cabri *et al.* 1975), isomertieite, Pd$_{11}$Sb$_2$As$_2$ (Clark *et al.* 1974), stibiopalladinite, Pd$_5$Sb$_2$ (Cabri & Chen 1976) and stillwaterite, Pd$_8$As$_3$ (Cabri *et al.* 1975).

Out of six X-ray lines attributed to vincentite in the original paper (Stumpfl & Tarkian 1974), only two (*d* 3.951 and 1.749 Å) are close to the newly recorded lines. This discrepancy is due to the fact that in the Gandolfi spectrum used at that time, the reflections of vincentite were suppressed by those of the Pt–Fe matrix and osmium; the volume ratio of the Pt–Fe matrix to vincentite inclusions is approximately 30:1 (Fig. 1). The X-ray pattern of vincentite can be indexed with a monoclinic cell with considerable accuracy. There are two PDF cards for vincentite (nos. 26–1452, 44–1432), that carry incomplete and inaccurate data. Both cards should be deleted and replaced by a new file based on the data presented in this note.

REFERENCES

AUGÉ, T. & LEGENDRE, O. (1992): Pt–Fe nuggets from alluvial deposits in eastern Madagascar. *Can. Mineral*. **30**, 983-1004.

CABRI, L.J. (1980): New mineral names. *Am. Mineral*. **65**, 184.

_____ & CHEN, T.T. (1976): Stibiopalladinite from the type locality. *Am. Mineral*. **61**, 1249-1254.

_____, CLARK, A.M. & CHEN, T.T. (1977): Arsenopalladinite from Itabira, Brazil, and from the Stillwater Complex, Montana. *Can. Mineral*. **15**, 70-73.

_____, LAFLAMME, J.H.G., STEWART, J.M., ROWLAND, J. F. & CHEN, T.T. (1975): New data on some palladium arsenides and antimonides. *Can. Mineral*. **13**, 321-335.

_____, ROWLAND, J.F., LAFLAMME, J.H.G. & STEWART, J.M. (1979): Keithconnite, telluropalladinite and other Pd–Pt tellurides from the Stillwater complex, Montana. *Can. Mineral*. **17**, 589-594.

CHAO, G.Y. & CABRI, L.J. (1976): New mineral names. *Am. Mineral*. **61**, 184.

CLARK, A.M., CRIDDLE, A.J. & FEJER, E.E. (1974): Palladium arsenide–antimonides from Itabira, Minas Gerais, Brazil. *Mineral. Mag*. **39**, 528-543.

DESBOROUGH, G.A., FINNEY, J.J. & LEONARD, B.F. (1973): Mertieite, a new palladium mineral from Goodnews Bay, Alaska. *Am. Mineral*. **58**, 1-10.

DISTLER, V.V., SLUZHENIKIN, S.F., CABRI, L.J., KRIVOLUTSKAYA, N.A., TUROVTSEV, D.M., GOLOVANOVA, T.A., MOKHOV, A.V., KNAUF, V.V. & OLESHKEVICH, O.I. (1999): Platinum ores of the Noril'sk layered intrusions: magmatic and fluid concentration of noble metals. *Geology of Ore Deposits* **41**(3), 214-237 (in Russ.).

JOHAN, Z., OHNENSTETTER, M., FISCHER, W. & AMOSSÉ, J. (1990): Platinum-group minerals from the Durance River alluvium, France. *Mineral. Petrol*. **42**, 287-306.

HOLLAND, T.J.B. & REDFERN, S.A.T. (1997): Unit cell refinement from powder diffraction data: the use of regression diagnostics. *Mineral. Mag*. **61**, 65-77.

POUCHOU, J.-L. & PICHOIR, F. (1991): Quantitative analysis of homogenous or stratified microvolumes applying the model "PAP". *In* Electron Probe Quantitation (K.F.J. Heinrich & D.E. Newbury, eds.). Plenum Press, New York, N.Y. (31-75).

RIGAKU (1994): Curved PSPC/MDG system. Rigaku position Sensitive Proportional Counter X-ray Micro Diffraction Unit. *The Rigaku Journal* **11**, 2, 39-43, Tokyo, Japan.

SAINI, G.S., CALVERT, L.D., HEYDING, R.D. & TAYLOR, J.B. (1964): Arsenides of the transition metals.VII. The palladium – arsenic system. *Can. J. Chem*. **42**, 620-629.

STUMPFL, E.F. & TARKIAN, M. (1974): Vincentite, a new palladium mineral from south-east Borneo. *Mineral. Mag*. **39**, 525-527.

WEISER, T. & SCHMIDT-THOMÉ, M. (1993): Platinum-group minerals from the Santiago River, Esmeraldas Province, Ecuador. *Can. Mineral*. **31**, 61-73.