# The new mineral insizwaite (PtBi<sub>2</sub>) and new data on niggliite (PtSn)

## L. J. CABRI and D. C. HARRIS

Mineral Sciences Division, Department of Energy, Mines and Resources, Mines Branch, 555 Booth Street, Ottawa, Canada. K1A oG1

SUMMARY. Insizwaite from Waterfall Gorge, Insizwa, is a new mineral with the composition Pt<sub>1.00</sub>Bi<sub>1.35</sub>Sb<sub>0.57</sub>. The name is for the locality and is to be applied to the end member PtBi<sub>2</sub>. The analysed material is an antimonian variety. The mineral is cubic, the unit-cell for the antimonian variety has a 6·625 (2) Å, probable space group Pa<sub>3</sub>, calc. D 12·8 g/cm³. The strongest lines on the X-ray diffraction powder pattern are: 2·96 (8) 210; 2·70 (8) 211; 2·34 (5) 220; 1·99 (10) 311; 1·774 (7) 321; 1·433 (5) 421; 1·277 (6) 511, 333; 1·171 (6) 440; and 0·862 (7) 731. Under reflected light the mineral is white (in air and in oil) and is isotropic. Reflectance measurements at 470, 546, 589, and 650 nm gave 61·1, 60·0, 60·6, and 61·7 %. Micro-indentation hardness values range from 488 to 540 (av. 519) kg/mm² with a 25 g load.

New data are presented for niggliite from the type locality and for synthetic PtSn.

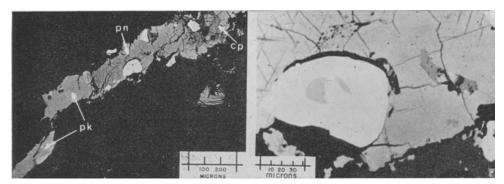
A SAMPLE of massive pyrrhotine ore from the Insizwa deposit, Waterfall Gorge, Pondoland and East Griqualand areas (Transkei), South Africa, was kindly provided by Prof. D. L. Scholtz. The geology and mineralogy are well described by Scholtz (1936). The new mineral and name were approved by the Commission on New Minerals and Mineral Names, I.M.A. The name insizwaite is for the locality and is pronounced insizwa-ait. Type material is preserved in the National Mineral Collection (No. 10,400), Ottawa.

The new mineral was found in a vein associated with pentlandite (containing exsolved chalcopyrite) and chalcopyrite (containing exsolved bornite) and with parkerite and niggliite (fig. 1). Insizwaite occurs as small rounded grains, varying in area up to  $70 \times 120 \mu$  (fig. 2). The parkerite in this section has been described and analysed (Petruk *et al.*, 1969). The niggliite has maximum areas up to  $25 \times 75 \mu$  (fig. 3) and occurs as inclusions in parkerite or in insizwaite (fig. 1) as well as in pentlandite. Niggliite has been studied in some detail because it has not been reexamined by modern techniques from the type locality and since there are some conflicting reports on its composition in the literature.

## Materials and method of investigation

The minerals were studied by ore microscopy, X-ray diffraction analysis, and by the electron-probe microanalyser. X-ray diffraction powder data were obtained by the film method using 57·3 and 114·6 mm Gandolfi and Debye–Scherrer cameras. Film shrinkage corrections were applied, and the unit-cell parameters were refined by a least-squares computer programme.

© Crown Copyright reserved.



Figs. 1 and 2: Fig. 1 (left), Pentlandite (pn)-chalcopyrite (cp)-parkerite (pk) vein with inclusions of insizwaite (white) and niggliite (grey within insizwaite). Fig. 2 (right). Largest insizwaite grain (from fig. 1) showing details of niggliite inclusions and exsolved chalcopyrite lamellae in the pentlandite.

The compositions were determined using a Materials Analysis Company model 400 electron-probe microanalyser; both metals and synthetic Pt-Bi-Sb and PtSn were used as standards. Corrections were applied using Edition VII of the programme by Rucklidge (1967).

The sample was mounted in cold-setting plastic, polished on lead laps and lightly buffed on a cloth lap using  $0-0\cdot 2\mu$  alumina. The reflectance values were obtained with a Leitz MPE microscope photometer equipped with a Dumont 6467 photomultiplier tube and a continuous-band interference filter. A silicon standard calibrated by the National Physical Laboratory, Great Britain, was used as a reference. A  $16\cdot 5:1$  objective with a numerical aperture of 0.40 was used. The micro-indentation hardness was measured with a Leitz Durimet tester.

# Optical, physical, and chemical properties

Insizwaite. In reflected light the mineral is white both in air and under oil immersion. It is isotropic and no bireflectance is observed. The reflectance was measured for the four wavelengths 470, 546, 589, and 650 nm giving the values 61·1, 60·0, 60·6, and 61·7 %, respectively. The reflectance values are the mean for five measurements on one grain. Reflectance was also measured for the high- and low-temperature polymorphs of synthetic PtBi<sub>2</sub>. Values obtained for the same four wavelengths were 55·2, 57·3, 58·4, and 59·7 % for high-PtBi<sub>2</sub> and 58·6, 59·7, 61·7, and 66·3 % for low-PtBi<sub>2</sub>.

The micro-indentation hardness values were obtained from seven measurements on the largest grain (no. 1 in table I) with a 25 g load. The range of micro-indentation hardness is 488 to 540, with an average value of 519 kg/mm². Synthetic insizwaite (Pt<sub>1.00</sub>Bi<sub>1.40</sub>Sb<sub>0.60</sub>) has a range in values of 441 to 576 and a mean of 503 kg/mm² for the same load. Synthetic PtBi<sub>2</sub> gave quite different micro-indentation hardness values for the two polymorphs. Low temperature PtBi<sub>2</sub> had VHN<sub>25</sub> = 437 to 459 (av. 450) kg/mm² while the high-temperature form exhibited hardness anisotropy and much lower values. One diagonal had VHN<sub>25</sub> = 102 to 128 (av. 114) and the other VHN<sub>25</sub> = 131 to 188 (av. 166).

The results of the microanalyses for five grains are given in table I, and the average formula for insizwaite from the above analyses is  $Pt_{1.00}Sb_{1.35}Sb_{0.57}$ .

The unit-cell of synthetic low-temperature  $PtBi_2$  was reported by Wallbaum (1943) as  $a \cdot 6 \cdot 695$  (5) Å and we have obtained  $a \cdot 6 \cdot 691$  (2) Å. Our pattern is included in table II for comparison because it is more complete than the earlier published pattern. The unit-cell of insizwaite (Grain no. 1) has  $a \cdot 6 \cdot 625$  (2) Å and we obtained  $a \cdot 6 \cdot 614$  (2) Å for a synthetic insizwaite ( $Pt_{1.00}Bi_{1.40}Sb_{0.60}$ ).

		Pt	Bi	Sb	Sn	Total	Atomic ratios			
							Pt	Bi	Sb	Sn
		36·o	52.7	12.5	-	101.5	I.00	1.37	0.55	
	2	35.6	53.0	11.9		100.2	1.00	1.40	0.54	
Insizwaite	{ 3	35.9	54.6	10.7	-	101.2	1.00	1.43	0.52	
	14	36.4	50.2	14.5		101.1	1.00	1.29	0.64	
	(5	36.4	49.6	14.8	_	100.8	1.00	1.28	0.65	
Niggliite	/ I	61.0	2.2	4.7	31.4	99.3	1.00	0.035	0.15	0.84
	2	60.8	2.9	6.5	29.4	99.6	1.00	0.045	0.17	0.79

Table I. Microanalyses of insizwaite and niggliite in weight %

Niggliite. Confusion regarding the composition of niggliite began with the preliminary report by Scholtz (1936) that platinum and tellurium were present. The close similarity of niggliite to synthetic PtTe, both in X-ray diffraction pattern and in optical properties, led Groeneveld Meijer (1955) to suggest that they were identical. Ramdohr (1960) suggests that the formula is Pt<sub>2</sub>Sn<sub>3</sub> but in Ramdohr (1969) the composition is given as 'PtTe, perhaps a mixed crystal with isostructural PtSn'. Scholtz (pers. comm. 23 Jan. 1971) reports that re-examination showed niggliite is essentially PtSn.

Under reflected light the mineral is characterized by very high bireflectance, from pinkish-cream to pale cobalt-blue. The anisotropism is intense, from bright pinkish-cream to very dark-blue or black. The reflectance for the four wavelengths 470, 546, 589, and 650 nm was 46·5, 42·6, 40·6, and 38·4 % for the minimum position (blue) and 63·5, 62·8, 61·8, and 63·9 % for the maximum position (pinkish-cream), all respectively. The values represent the mean of three separate measurements on Grain no. I in table I. Niggliite exhibits hardness anisotropy. For Grain no. I VHN<sub>25</sub> = 585 to 612 (av. 599) and 642 to 673 (av. 657) kg/mm² for five indentations. A second grain gave VHN<sub>25</sub> = 572 to 612 (av. 590) and 657 to 673 (av. 670) kg/mm² for four indentations.

The compositions for two grains of niggliite are given on table I, other grains microanalysed were found to be inhomogenous and had larger quantities of Sb.

The X-ray diffraction data for PtSn are very unsatisfactory, with no powder pattern in the literature. Harris *et al.* (1968) report that PtSn has hexagonal symmetry, with cell dimensions  $a ext{ 4.1013}$  (2) and  $c ext{ 5.4403}$  (2) Å and space group  $P6_3/mmc$ . Our synthetic PtSn has the unit-cell  $a ext{ 4.100}$  (1) and  $c ext{ 5.432}$  (2) Å (table III). The PtSn was carefully examined microscopically and with the electron-probe and found to be

Table II. X-ray diffraction data for synthetic  $PtBi_2$  and insizwaite  $(Pt_{1\cdot 00}Bi_{1\cdot 35}Sb_{0\cdot 5\cdot 7})$ 

PtB	i <sub>2</sub> , <i>a</i> 6·691(2	) Å		Insizwaite, a 6.625(2) Å				
I	$d_{ m meas}$	$d_{ m ealc}$	hkl	I	$d_{ m meas}$	$d_{ m calc}$		
3	3·856 Å	3·862 Å	III	1/2*	3·79 Å	3·825 Å		
5	3.343	3.345	200	2*	3.31	3.313		
10	2.996	2.992	210	8*	2.96	2.963		
8	2.732	2.731	211	8*	2.70	2.705		
5	2.365	2.365	220	5*	2.34	2.342		
2	2.231	2.230	300, 221	1/2	2.20	2.208		
9	2.017	2.017	311	10	1.998	1.998		
3	1.932	1.931	222	2	1.915	1.913		
4	1.854	1.855	320	4	1.836	1.838		
6	1.788	1.788	321	7	1.774	1.771		
3	1.672	1.672	400	Í	1.655	1.656		
4	1.494	1.496	420	4	1.484	1.482		
5	1.459	1.460	421		1.443	1.446		
4	1.426	1.426	332	5 3	1.414	1.413		
3	1.366	1.366	422	3	1.354	1.352		
5	1.288	1.287	333, 511	3	1.277	1.275		
4	1.242	1.242	520, 432	4	1.231	1.230		
3	1.221	1.221	521	3	1.210	1.210		
4	1.182	1.182	440	6	1.171	1.171		
2	1.114	1.115	600, 442	2	1.103	1.104		
2	1.099	1.100	610	1/2	1.085	1.089		
4	1.086	1.085	611, 532	3	1.074	1.075		
4 I	1.028	1.028	620	1/2	1.048	1.048		
4	1.020	I ·020	533	3	1.010	1.010		
4 I	1.008	1.008	622	I	0.998	0.999		
4	0.997	0.997	630, 542	3	0.988	0.988		
3	0.987	0.987	631	2	0.976	0.977		
3	0.919	0.919	720, 641	2	0.909	0.910		
3	0.911	0.910	721, 633	3	0.901	0.902		
2	0.895	0.894	642	I	0.884	0.885		
	0.872	0.871	731, 553	7	0.862	0.863		
5 2	0.857	0.857	650, 643		0.848	0.848		
	0.851	0.849	732, 651	3	0.841	0.841		
3			732, US1 800	4 2	0.841	0.828		
2	0·837 0·811	0·836 0·811			0.803	0.804		
3	0.806	0.805	820, 733	I 2				
4			821, 742		0.797	0.798		
3	0.800	0.799	653	I	0.791	0.792		
2	0.788	0.788	822					
5	0.772	0.772	750, 831, 743					

Both patterns obtained using Ni-filtered Cu-radiation: 114.6 mm Debye-Scherrer for PtBi<sub>2</sub> and 57.3 mm Gandolfi for insizwaite. All intensities visually estimated. \*Measured from a 114.6 mm Gandolfi camera film because the smaller film was too dark in the low  $2\theta$  region.

a homogeneous phase. We were unable to obtain a powder pattern of niggliite free of minor parkerite impurities, but this pattern is obviously closely related to that of synthetic PtSn and to the niggliite pattern reported by Scholtz (1936) (table III). Some of the strongest reflections for parkerite coincide or are close enough to those of

niggliite to affect the relative intensity or even the d-value measured. There are seven extra reflections if Scholtz's pattern is compared to that of synthetic PtSn, three of

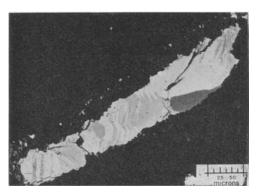


Fig. 3. Parkerite vein (lower left-hand in fig. 1) showing details of parkerite twinning and largest grain of niggliite (dark grey). A few degrees from extinction.

which correspond to parkerite while the other four are unaccountable. It is likely that these extra reflections represent another mineral impurity. Indexing our niggliite pattern in the same manner as for PtSn gives a unit-cell of a + 106 (2) c + 5.43 (8) Å.

#### Discussion

The name insizwaite is proposed for the composition PtBi<sub>2</sub> and the type specimen is an antimonian insizwaite. The maximum extent of Sb substitution for Bi has not been determined. The Pt:(Bi,Sb) ratio ranged from I-9I to I-94 and the mean was I-92. It is not certain if this ratio indicates a real

deficiency in the structure or if it is due to minor errors in the corrections applied. Prior to using the synthetic homogeneous standard of composition  $Pt_{1\cdot00}Bi_{1\cdot60}Sb_{0\cdot40}$ , analyses using metal standards gave a ratio ranging from 1·76 to 1·79. This suggests that the required corrections brought about by the programme were insufficient and that analyses of minerals containing these elements should be viewed with caution if they were derived by using metal standards.

Elliott (1965), in his review of the Bi-Pt system, indicates that  $PtBi_2$  transforms to a high-temperature form at about 270 °C and that it melts incongruently at about 660 °C. We have synthesized the high-temperature form at 600° and quenched it successfully; this form exhibits significantly different VHN values from the low-temperature form. The composition  $Pt_{1\cdot00}Bi_{1\cdot60}Sb_{0\cdot40}$  synthesized at 600 °C, however, had the X-ray diffraction pattern of low-temperature  $PtBi_2$  as well as similar VHN values. The addition of Sb either raises the temperature of this inversion or prevents the preservation of the high form.

Niggliite from the type locality has been shown to be an antimonian-bismuthian variety of PtSn.

Acknowledgements. We wish to thank Dr. D. L. Scholtz, Stellenbosch University, for the sample and Messrs. J. M. Stewart and E. J. Murray for the measurement of the X-ray films as well as the members of the technical support staff of the Mineral Sciences Division.

# REFERENCES

ELLIOTT (R. P.), 1965. Constitution of Binary Alloys, first supplement, New York (McGraw-Hill). Groeneveld Meijer (W. O. J.), 1955. Niggliite, a monotelluride of platinum? Amer. Min. 40, 693-6. Harris (I. R.), Norman (M.), and Bryant (A. W.), 1968. A study of some palladium-indium, platinum-indium and platinum-tin alloys. Journ. Less-Common Metals, 16, 427-40.

TABLE III. X-ray diffraction data for niggliite and synthetic PtSn

	iite Itz, 1936)	Niggliite a 4·106(2) Å c 5·43(8)				PtSn a 4·100(1) Å c 5·432(2)			
I	$d_{ m meas}$	$\overline{I}$	$d_{ m meas}$	$d_{ m calc}$	hkl	$\overline{I}$	$d_{ m meas}$	$d_{\mathrm{calc}}$	
			8		001	1/2***	5·42 Å	5·432 Å	
		6	4·02 Å*			<u></u>			
m	3·54 Å	5	3.57	3.556	100	O	3.548	3.220	
w w	3.31			_		_			
	3·03 2·96	_	2.98	2.975	011	7	2.971	2.972	
mw mw	2.83	7 9	2.82**	2·716	002	ĭ	2.718	2.716	
w?		5	2.327*	2 /10				2 /10	
w?	2.33		2.273*	_					
	2.27	5 10	2.158	2.158	012	10	2.157	2.157	
S	2.15		2.055	2.053	110	8	2.050	2.050	
S	2.05	7 2	2.025*	2.053	110		2 030	2 030	
	_		1.983*					_	
		5	1.787	1.778	020	3	1.774	1.775	
mw	1·773 1·685	4b	1·/6/ 1·692	1.690	021		1.686	1.687	
mw	1.638	I	1.641**	1.638	112	4 2	1.635	1.636	
W		3	1.610	1.613	013	3	1.612	1.613	
w	1.609	3 6		1.488	022	8	1.485	1.486	
S	1.486	0	1.487	1.400	022	0	— 403 —	1 400	
W	1.438	_		_		_	_		
W	1.412	4	1.412*	T-258	004		1.358	1.358	
mw	1.358	I I	1.357	1.358	120	3 3	1.341	1.342	
mw	1.343	1	1.344	1.344	-	<u> </u>		1 342	
w	1.326		1.300	1.305	121	4	1.302	1.302	
m	1·304 1·268		1.266	1.363	023	4	1.267	1.267	
m	1.205	3 6	1.205	1.205	122	9	1.203	1.203	
s m	1.186	2	1.187	1.185	030	4b	1.183	1.183	
mw	1.134	4	1.133	1.133	114	46 6b	1.132	1.132	
ww ww	1.089	4	1-133		032	1	1.084	1.085	
mw	1.081	3	I·075	1.079	132,	4	1.077	1.078	
11174	1 001	3	10/3	10/9	024	4	10//	1070	
w	1.041	2	1.033	1.039	015	2	1.038	1.038	
m	1.028				220	4	1.025	1.025	
111	1 020	_	_		130	2	0.9848	0.9848	
		_			131	3	0.9692	0.9690	
		_	_	Non-constitution of the Constitution of the Co	124	3	0.9550	0.9546	
		3	0.927	0.927	025	6	0.9267	0.9267	
		2	0.893	0.893	034	5	0.8930	0.8923	
		~	0 093	0 093	016	4	0.8776	0.8773	
					133	2	0.8653	0.8655	
					125	5	0.8449	0.8444	
					116	ĭ	0.8285	0.8283	
					224	6	0.8184	0.8182	
					230	ī	0.8145	0.8146	
					026	5	0.8069	0.8066	
					134	3 4	0.7981	0.7973	
					232	10b	0.7810	0.7803	
					007	8b	0.7758	0.7760	

All patterns obtained with Ni-filtered Cu-radiation.  $57\cdot3$  mm Gandolfi and 114·6 mm Debye-Scherrer cameras used in this study for niggliite and PtSn, respectively. Intensities visually estimated in this study (b = broad): w = weak, m = medium, s = strong reported by Scholtz.

<sup>\*</sup> Reflections due to parkerite.

\*\* Reflections due to parkerite plus niggliite.

\*\*\* Only observed on 57·3 mm Debye-Scherrer film.

Petruk (W.), Harris (D. C.), and Stewart (J. M.), 1969. Langisite, a new mineral, and the rare minerals cobalt pentlandite, siegenite, parkerite and bravoite from the Langis Mine, Cobalt-Gowganda Area, Ontario. Canad. Min. 9, Pt. 5, 597-616.

RAMDOHR (P.), 1960. Die Erzmineralien und ihre Verwachsungen. Berlin (Akad. Verlag).

—— 1969. The ore minerals and their intergrowths. Oxford (Pergamon Press).

RUCKLIDGE (J.), 1967. A computer program for processing microprobe data. Journ. Geol. 75, 126.

SCHOLTZ (D. L.), 1936. The magmatic nickeliferous ore deposits of East Griqualand and Pondoland. Trans. Geol. Soc. S. Africa, 39, 81–210.

Wallbaum (H. J.), 1943. Die Kristallstrukturen von Bi<sub>2</sub>Pt und Sn<sub>2</sub>Pt. Zeits. Metallkunde, 35, 200-1.

[Manuscript received 7 February 1972]