

The new mineral insizwaite (PtBi_2) and new data on niggliite (PtSn)

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SUMMARY. Insizwaite from Waterfall Gorge, Insizwa, is a new mineral with the composition $\text{Pt}_{1.00}\text{Bi}_{1.35}\text{Sb}_{0.57}$. The name is for the locality and is to be applied to the end member PtBi_2 . 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 $Pa\bar{3}$, 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.

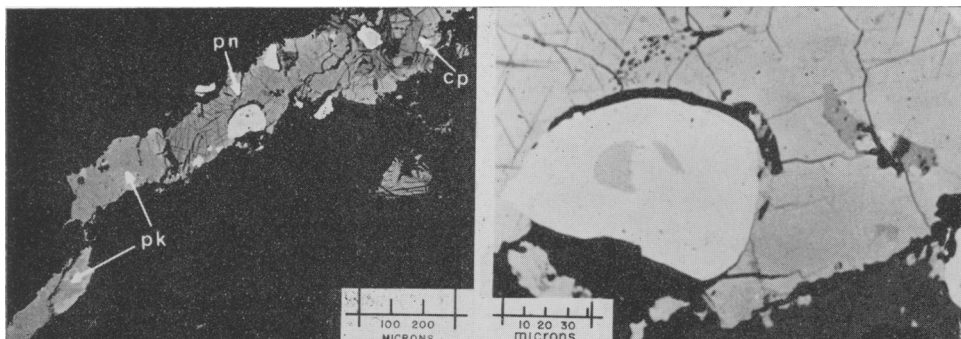
New data are presented for niggliite from the type locality and for synthetic PtSn .

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 re-examined 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.



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 $0.02\ \mu$ 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 16.5:1 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 birefractance 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_2 . Values obtained for the same four wavelengths were 55.2, 57.3, 58.4, and 59.7 % for high- PtBi_2 and 58.6, 59.7, 61.7, and 66.3 % for low- PtBi_2 .

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/mm^2 . Synthetic insizwaite ($\text{Pt}_{1.00}\text{Bi}_{1.40}\text{Sb}_{0.60}$) has a range in values of 441 to 576 and a mean of 503 kg/mm^2 for the same load. Synthetic PtBi_2 gave quite different micro-indentation hardness values for the two polymorphs. Low temperature PtBi_2 had $\text{VHN}_{25} = 437$ to 459 (av. 450) kg/mm^2 while the high-temperature form exhibited hardness anisotropy and much lower values. One diagonal had $\text{VHN}_{25} = 102$ to 128 (av. 114) and the other $\text{VHN}_{25} = 131$ 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 $\text{Pt}_{1.00}\text{Sb}_{1.35}\text{Sb}_{0.57}$.

The unit-cell of synthetic low-temperature PtBi_2 was reported by Wallbaum (1943) as a 6.695 (5) Å and we have obtained a 6.691 (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 6.625 (2) Å and we obtained a 6.614 (2) Å for a synthetic insizwaite ($\text{Pt}_{1.00}\text{Bi}_{1.40}\text{Sb}_{0.60}$).

TABLE I. *Microanalyses of insizwaite and niggliite in weight %*

		Pt	Bi	Sb	Sn	Total	Atomic ratios			
							Pt	Bi	Sb	Sn
Insizwaite	1	36.0	52.7	12.5	—	101.2	1.00	1.37	0.55	—
	2	35.6	53.0	11.9	—	100.5	1.00	1.40	0.54	—
	3	35.9	54.6	10.7	—	101.2	1.00	1.43	0.52	—
	4	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	1	61.0	2.2	4.7	31.4	99.3	1.00	0.035	0.12	0.85
	2	60.8	2.9	6.5	29.4	99.6	1.00	0.045	0.17	0.79

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_2Sn_3 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. 1 in table I. Niggliite exhibits hardness anisotropy. For Grain no. 1 $\text{VHN}_{25} = 585$ to 612 (av. 599) and 642 to 673 (av. 657) kg/mm^2 for five indentations. A second grain gave $\text{VHN}_{25} = 572$ to 612 (av. 590) and 657 to 673 (av. 670) kg/mm^2 for four indentations.

The compositions for two grains of niggliite are given on table I, other grains micro-analysed 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 4.1013 (2) and c 5.4403 (2) Å and space group $P6_3/mmc$. Our synthetic PtSn has the unit-cell a 4.100 (1) and c 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 PtBi₂ and insizwaite (Pt_{1.00}Bi_{1.35}Sb_{0.57})

PtBi ₂ , <i>a</i> 6.691(2) Å				Insizwaite, <i>a</i> 6.625(2) Å		
<i>I</i>	<i>d</i> _{meas}	<i>d</i> _{calc}	<i>hkl</i>	<i>I</i>	<i>d</i> _{meas}	<i>d</i> _{calc}
3	3.856 Å	3.862 Å	111	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	1	1.655	1.656
4	1.494	1.496	420	4	1.484	1.482
5	1.459	1.460	421	5	1.443	1.446
4	1.426	1.426	332	3	1.414	1.413
3	1.366	1.366	422	3	1.354	1.352
5	1.288	1.287	333, 511	6	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
1	1.058	1.058	620	1/2	1.048	1.048
4	1.020	1.020	533	3	1.010	1.010
1	1.008	1.008	622	1	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	1	0.884	0.885
5	0.872	0.871	731, 553	7	0.862	0.863
2	0.857	0.857	650, 643	3	0.848	0.848
3	0.851	0.849	732, 651	4	0.841	0.841
2	0.837	0.836	800	2	0.828	0.828
3	0.811	0.811	820, 733	1	0.803	0.804
4	0.806	0.805	821, 742	2	0.797	0.798
3	0.800	0.799	653	1	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 PtBi₂ 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 2θ 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

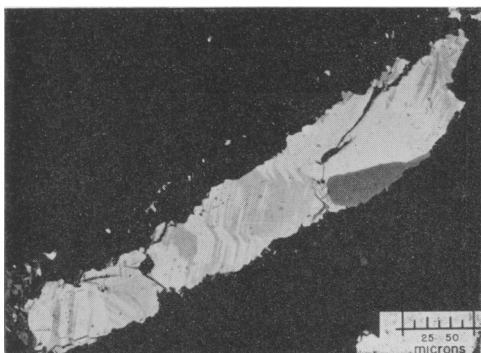


FIG. 3. Parkerite vein (lower left-hand in fig. 1) showing details of parkerite twinning and largest grain of niggliite (dark grey). A few degrees from extinction.

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 4.106 (2) c 5.43 (8) Å.

Discussion

The name insizwaite is proposed for the composition PtBi_2 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 1.91 to 1.94 and the mean was 1.92. 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 $\text{Pt}_{1.00}\text{Bi}_{1.60}\text{Sb}_{0.40}$, 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 $\text{Pt}_{1.00}\text{Bi}_{1.60}\text{Sb}_{0.40}$ 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.

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

Niggliite (Scholtz, 1936)		Niggliite <i>a</i> 4·106(2) Å <i>c</i> 5·43(8)			PtSn <i>a</i> 4·100(1) Å <i>c</i> 5·432(2)			
<i>I</i>	<i>d</i> _{meas}	<i>I</i>	<i>d</i> _{meas}	<i>d</i> _{calc}	<i>hkl</i>	<i>I</i>	<i>d</i> _{meas}	<i>d</i> _{calc}
—	—	—	—	—	001	1/2***	5·42 Å	5·432 Å
—	—	6	4·02 Å*	—	—	—	—	—
m	3·54 Å	5	3·57	3·556	100	6	3·548	3·550
w	3·31	—	—	—	—	—	—	—
w	3·03	—	—	—	—	—	—	—
mw	2·96	7	2·98	2·975	011	7	2·971	2·972
mw	2·83	9	2·82**	2·716	002	1	2·718	2·716
w?	2·33	5	2·327*	—	—	—	—	—
w?	2·27	5	2·273*	—	—	—	—	—
s	2·15	10	2·158	2·158	012	10	2·157	2·157
s	2·05	7	2·055	2·053	110	8	2·050	2·050
—	—	2	2·025*	—	—	—	—	—
—	—	5	1·983*	—	—	—	—	—
mw	1·773	4b	1·787	1·778	020	3	1·774	1·775
mw	1·685	1	1·692	1·690	021	4	1·686	1·687
w	1·638	3	1·641**	1·638	112	2	1·635	1·636
w	1·609	3	1·610	1·613	013	3	1·612	1·613
s	1·486	6	1·487	1·488	022	8	1·485	1·486
w	1·438	—	—	—	—	—	—	—
w	1·412	4	1·412*	—	—	—	—	—
mw	1·358	1	1·357	1·358	004	3	1·358	1·358
mw	1·343	1	1·344	1·344	120	3	1·341	1·342
w	1·326	—	—	—	—	—	—	—
m	1·304	1	1·300	1·305	121	4	1·302	1·302
m	1·268	3	1·266	1·269	023	4	1·267	1·267
s	1·205	6	1·205	1·205	122	9	1·203	1·203
m	1·186	2	1·187	1·185	030	4b	1·183	1·183
mw	1·134	4	1·133	1·133	114	6b	1·132	1·132
ww	1·089	—	—	—	032	1	1·084	1·085
mw	1·081	3	1·075	1·079	132,	4	1·077	1·078
—	—	—	—	—	024	—	—	—
w	1·041	2	1·033	1·039	015	2	1·038	1·038
m	1·028	—	—	—	220	4	1·025	1·025
—	—	—	—	—	130	2	0·9848	0·9848
—	—	—	—	—	131	3	0·9692	0·9690
—	—	—	—	—	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
—	—	—	—	—	016	4	0·8776	0·8773
—	—	—	—	—	133	2	0·8653	0·8655
—	—	—	—	—	125	5	0·8449	0·8444
—	—	—	—	—	116	1	0·8285	0·8283
—	—	—	—	—	224	6	0·8184	0·8182
—	—	—	—	—	230	1	0·8145	0·8146
—	—	—	—	—	026	5	0·8069	0·8066
—	—	—	—	—	134	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. 57·3 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.

* Reflections due to parkerite.

** Reflections due to parkerite plus niggliite.

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

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