The occurrence of platinoid bismuthotellurides in the Merensky Reef at Rustenburg platinum mine in the western Bushveld

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(With Plate XII)

[Read 29 April 1965]

Summary. Four different palladium and platinum bismuthotellurides, one containing major mercury, have been identified in the ore from Rustenburg mine on the Merensky Reef. The composition of each phase was determined by electron-probe microanalysis, and X-ray powder data are presented for three of these phases. Quantitative spectral reflectivity values at 470, 546, 589, and 650 mμ were obtained on areas of 1–10μ. Similar phases have been located in the ore from Union mine.

Two of these phases are shown to be moncheïte and kotulskite. From two electron-probe microanalyses, kotulskite is shown to be Pd(Te,Bi). The other two phases are new minerals: analysis of one of them gives the composition $(Pd,Pt)(Te,Bi)_2$, containing 23·1 % Pd, 1·8 % Pt, 50·8 % Te, 14·2 % Bi, with strongest X-ray powder lines at 2·92 (10), 2·10 (6), 2·02 (3), and 1·54 Å (3), and cell parameters a $3{\cdot}978 \pm 0{\cdot}001$, c $5{\cdot}125 \pm 0{\cdot}002$; it is probably isostructural with moncheïte, and an isomorphous series may exist between them; the name ***merenskyite*** is proposed for this mineral, after Dr. Hans Merensky who was mainly responsible for discovering the platinoid bearing 'reef'; it is commonly intergrown with kotulskite. For the second new phase (*Mineral A*), no X-ray data could be obtained, but a single electron-probe microanalysis gave a composition of Pd 27·8 %, Hg 12 %, Te 38·5 % and Bi 1·6 % suggesting the empirical formula (Pd,Hg)(Te,Bi).

THE Merensky Reef, named after the geologist Dr. Hans Merensky who was responsible for the prospecting programme that led to its discovery in 1924, is a layer of feldspathic pyroxenite containing economic amounts of copper, nickel, and platinoid elements. It occurs in the lower part of the intrusive norite or mafic zone of the Bushveld Igneous Complex, which is a vast composite body of extrusive, hypabyssal, and plutonic rocks in the central Transvaal of South Africa. The Merensky Reef or Merensky Horizon forms a generally continuous layer that has been located and followed around most of the norite outcrop. It is at present being exploited in the western sector of this mafic zone at Rustenburg mine, about 50 miles west of Pretoria, and also at Union mine, 55 miles north of Rustenburg and about 6 miles west of Northam.

The Merensky Reef at Rustenburg is a composite layer at the base of which is a thin chromite band, resting on an undulating but sharp contact with the footwall spotted anorthositic norite. The chromite band, about one inch in thickness, grades rapidly up into a coarse feldspathic pyroxenite commonly known to those exploiting this horizon as the 'Reef', averaging about one foot in thickness. The Reef or pegmatoid (as suggested by Willemse (1964)) contains disseminated interstitial segregations of copper–iron–nickel sulphides with which the platinum group minerals are commonly associated. At or near the top of the Reef is found a thin irregular and discontinuous chromite band of about $\frac{1}{4}$ in. thickness. The Reef or pegmatoid is overlain by a less coarse feldspathic pyroxenite known to the miners as the 'Merensky'. The contact between the two is sometimes sharp and sometimes gradational. The 'Merensky' pyroxenite is also gradational into the overlying hangingwall spotted anorthosite, although generally the top of it is about two feet above the Reef.

In the northern outcrop of the Merensky Reef at Union mine these units are still present although considerably thicker. The bottom one-inch thick chromite band, resting on the undulating surface of the footwall spotted anorthosite, is overlain by a very coarse feldspathic pyroxenite of 10 to 18 feet in thickness that can be equated to the 'Reef' pegmatoid at Rustenburg. A continuous one-inch thick chromite band occurs at the top of this coarse pyroxenite, and is overlain by up to 20 feet of a finer grained pyroxenite similar to the 'Merensky' pyroxenite at Rustenburg. This grades upwards, after about 75 feet, into a spotted anorthosite. It is of interest to note that whereas at Rustenburg mine the entire width of the pegmatoid, including the top and bottom chromite bands, is mined, at Union mine a combination of the great width of the pegmatoid and the generally much lower platinoid content of the bottom chromite seam renders the extraction of the whole 'Reef' uneconomic (Beath, Cousins, and Westwood, 1961). Fairly typical geological sections through the Merensky Reef at Rustenburg and Union mines are illustrated in fig. 1.

Up to the commencement of the author's investigations in 1962, the platinoid mineralogy of the Merensky Reef was generally thought to be fairly simple, consisting of five or six major platinoid minerals together with a large proportion of platinum metal content accounted for by Schneiderhohn (1929) as occurring in solid solution in the base metal sulphides pyrite, pyrrhotine, pentlandite, and chalcopyrite. However workers on other platiniferous deposits, in particular Stumpfl (1961), Borovskii *et al.* (1959), and Genkin *et al.* (1961, 1963), have described a great variety of new platinoid minerals and it was thus reasonable to suspect that many of these new phases, together with other unreported ones, were present in the Merensky Reef. During the present study all the previously recorded platinoid minerals from this deposit have been recognized, and their identification confirmed with the electron-probe microanalyser and X-ray powder analysis. A number of new phases were identified, the most interesting of which are the platinoid bismuthotellurides. The frequencies of occurrence of the platinoid minerals in polished sections of the ore from Rustenburg mine and Union mine are:

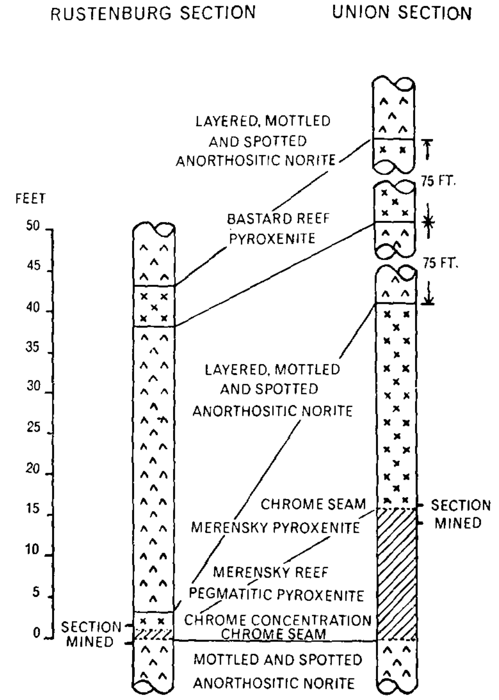

FIG. 1. Geological sections through the Merensky Reef zone at Rustenburg and Union mines (after Beath, Cousins, and Westwood, 1961).

	Rustenburg	*Union*
ferroplatinum (Pt,Fe)	minor	common
palladic gold (Au,Pd)	rare	rare

	Rustenburg	*Union*
palladic electrum (Au,Ag,Pd)	minor	minor
cooperite PtS	common	minor
braggite (Pt,Pd,Ni)S	common	minor
laurite RuS_2	rare	common
sperrylite $PtAs_2$	minor	minor
arsenopalladinite Pd_3As	v. rare	not located
stibiopalladinite Pd_xSb	v. rare	not located
moncheïte $(Pt,Pd)(Te,Bi)_2$	rare	rare
kotulskite Pd(Te,Bi)	rare	rare
merenskyite $(Pd,Pt)(Te,Bi)_2$	rare	rare
mineral A $(Pd,Hg)_x(Te,Bi)_y$	v. rare	not located

More phases are undoubtedly present. Iridium, osmium, and rhodium are known to be present in appreciable quantities but have not yet been detected as separate mineral phases in the ore although minor quantities do occur in most of the above minerals.

Determinative techniques

Electron-probe microanalysis. The electron-probe microanalyser used in this study is a Cambridge Microscan Mark 1. This is a scanning analyser with a vertically incident electron beam and X-ray detection at an angle of 20° to the surface of the specimen. It does not have paraxial optics, but positioning is facilitated by the use of a back-scattered electron image also obtained at an angle of 20° to the surface.

The counts for the characteristic radiation are detected with a semi-focusing spectrometer that incorporates a flow-proportional counter with a 'dead time' of 5 μsec. A pulse-height analyser is used for discrimination against unwanted noise while scanning photographs are being taken, but it is rarely used while counting in order to avoid errors due to pulse-height depression.

The count rates were corrected for statistical errors due to the 'dead time' of the electronics, and also for counts due to the background radiation. The apparent mass percentages given by these corrected count rates were further corrected to allow for the following phenomena: absorption of the characteristic X-rays by the matrix (using the method proposed by Philibert (1962)); fluorescence produced by the characteristic radiation (using Castaing's formula (1951)); the effect of the difference in atomic number of the constituent atoms of the mineral (using Ziebold's correction method (1964)); and a correction for overvoltage was made by a modification to Philibert's formula made by Duncumb (1964). Background fluorescence effects were ignored. The values of the absorption coefficients used in the above corrections were those given by Kelly (1966).

The standards used in the present investigation were an analysed 50/50 Pt:Pd alloy (kindly given by Johnson and Matthey & Co., Ltd.), an analysed specimen of calaverite, $(Au,Ag)Te_2$, for tellurium, an analysed specimen of coloradoite, HgTe, for mercury determinations, and spectrographically pure bismuth. All specimens for analysis were polished using diamond abrasives on cloth laps as described by Barringer (1953). They were subsequently cut down to size and coated with a 50–75 Å thick film of aluminium to render the surface electrically conducting to the electron beam.

X-ray diffraction. In this particular investigation a procedure was required which would enable a very small (0·3–0·01 mm) and previously analysed grain to be extracted, with minimum contamination from the enclosing silicates and sulphides, and to be suitably mounted for X-ray powder analysis. A steel needle, a tungsten carbide pick, and a microdrill were found too unmanageable and not practical for extracting such small grains. However, by using a diamond marker in the way described by Williams (1962) it was found that with practice very small areas can be removed with some precision. A method devised by A. P. Millman (*pers. comm.*), which entails using the Leitz Durimet microscope fitted with a standard Leitz wedge-type scratch diamond, was found to have a much greater precision of positioning.

The diamond, after being lowered on to the required spot, is moved, using the micrometer stage, in the opposite direction to the normal one used for scratch purposes. A mound of mineral powder is formed at the end of the scratch, the length of which can be very precisely controlled. The mineral powder is mounted as follows: a clean glass slide is taken and a spot of 'Cow' gum or other rubber solution is allowed to adhere to it; the slide is then inverted and held over the polished section whilst still observing the powdered area under the ore microscope with a low-power objective (some refocussing is required because of the intervening glass slide); the rubber-cement spot, which can now be seen through the back of the glass, is lowered on to the powdered area to engulf the fragments of broken mineral. After a short while the solvent begins to evaporate and the cement can be rolled into a ball containing the mineral powder. The slide and adhering rubber ball are then raised from the surface of the polished section. Further grinding of the powder can be accomplished between two slides, as described by Hiemstra (1956), followed by the mounting of the ball on the end of a glass fibre. The ball should generally not be greater than 0·5 mm in diameter. The larger the ball the more scattering of X-rays occurs with consequent fogging of the film. An X-ray photograph of a globule of pure cement should be taken first since some varieties yield lines in the front reflection region.

Before destroying the rare mineral grains of these bismuthotellurides some preliminary experiments, similar to those by Hiemstra (1956), and Genkin and Korolev (1961), were carried out on cleavage fragments of galena to determine approximately the minimum quantity of material required to produce a distinct powder pattern. It was found that a cleavage fragment of dimensions 0·06 × 0·05 × 0·025 mm and of approximate weight 0·6 μg produced a weak but measurable pattern.

Spectral reflectivity measurements. Quantitative spectral reflectivity values at wavelengths of 470, 546, 589, and 650 mμ were obtained with the Reichert reflex spectral microphotometer, which incorporates a photomultiplier tube and wedge dielectric filter. A description of this together with the results of standardization experiments are given by Santokh Singh (1965). This instrument enables rapid and accurate spectral reflectivity measurements to be made on areas down to 1μ diameter and is invaluable for routine determinative work on opaque minerals. In the present context the size of the area used for any particular mineral grain corresponded to the maximum flawless and flat area available and ranged from 1 to 10μ diameter. The rarity of grains of a suitable size and having a flat area limited the number of reflectivity values that could be made.

The author is indebted to S. H. U. Bowie of the Atomic Energy Division for the loan of an N.P.L. Measured pyrite (N.1915.1), which was used in the present study as a standard.

Indentation microhardness values were obtained where possible with a Durimet hardness tester fitted with a Vickers diamond, as described by Young and Millman (1964). Because of the general by small grain size of these platinoid bismuthotelluride phases in polished sections of the ore, only a 15 g load could be used to produce a reliable indentation value. The relative hardness, deduced from the polishing relief, was assessed for each phase.

Bismuthotellurides of platinum and palladium

Although this is the first time that platinoid minerals of tellurium and bismuth have been found and described in the Merensky Reef, the presence of a Pd–Bi–Te compound was demonstrated in 1952 by chemical analyses of a non-magnetic portion of a concentrate from the northern extension of this horizon at Union Mine by F. M. Lever, R. Todd, and A. R. Powell of Johnson and Matthey Ltd. (*pers. comm.*). In 1962, in a preliminary investigation of the platinoid minerals with the electron-probe microanalyser, the author found a number of white strongly anisotropic laths, occurring in chalcopyrite and at the margins of the iron–copper–nickel sulphide segregations, to be bismuthotellurides of platinum and palladium. No X-ray powder data at that time could be obtained for any of these phases because of their small size. Meanwhile in 1961 Genkin and Korolev, in a paper describing a procedure for the identification of small mineral grains by X-ray powder analysis and microspectrographic methods, described the occurrence of similar phases from the Monchegorsk deposit. In 1963 Genkin *et al.* defined these minerals more precisely, naming two of them *moncheïte*, $(Pt,Pd)(Te,Bi)_2$, and *kotulskite*, $Pd(Te,Bi)_{1-2}$, as well as giving more data on *michenerite*,

$PdBi_2$, which was shown to contain tellurium as a major constituent. Recently Stumpfl (*pers. comm.* 1965) has also detected by electron-probe microanalysis the presence of a platinum bismuthotelluride from the Dreikop platinum pipe in the eastern Bushveld.

The results of the present study confirm the presence of moncheïte and kotulskite in the Merensky Reef at Rustenburg mine. Two other bismuthotellurides are shown to be new platinoid phases: one of composition $(Pd,Pt)(Te,Bi)_2$, named *merenskyite* after Dr. Hans Merensky, is possibly isostructural with moncheïte and an isomorphous series may exist between the palladium and platinum end members; the second new phase (*Mineral A*), for which no X-ray data are yet available, is a grey isotropic mineral having a composition close to (Pd,Hg)(Te,Bi). A preliminary investigation of the ore from Union mine has also revealed the presence of moncheïte and a palladium bismuthotelluride phase optically similar to merenskyite. A more detailed electron-probe study has still to be completed. It is hoped that more occurrences of these phases will be found at Union mine so that a comprehensive study can be made of them.

These bismuthotellurides occur late in the paragenesis as equant grains 1–3 μ in size enclosed partially or completely by chalcopyrite and occasionally pentlandite (pl. XII, fig. A). Larger euhedral to subhedral lamellae of 0·3 to 0·6 mm are more rarely found. Often clusters of small grains are to be found isolated in microveinlets in the silicates together with disseminated blebs of chalcopyrite. Except for the mercury phase (*Mineral A*) all these platinoid minerals are white to cream in colour, are anisotropic, and crystallize in the hexagonal system.

Moncheïte

Moncheïte (Genkin *et al.* 1961, 1963) was reported to occur as minute grains in chalcopyrite, pyrrhotine, and occasionally violarite in the upper sectors of vertical veins of the Monchegorsk platinum deposits, commonly intergrown with michenerite and kotulskite. Moncheïte from the Merensky Reef at Rustenburg mine is similarly associated with kotulskite and other platinum tellurides enclosed by or adjoining chalcopyrite. Generally it is in the form of blebs or fine laths of the order of 1 to 10 μ in size (pl. XII, fig. A). Only one large lath of sufficient size to enable its extraction for X-ray powder analysis ($200 \times 60 \mu$) has so far been located. This occurred at a sulphide: silicate contact as a subhedral lath penetrating pyrrhotine along a pentlandite: pyrrhotine boundary (fig. 2); pl. XII, fig. D).

Optical and physical properties. Moncheïte from Rustenburg is a bright

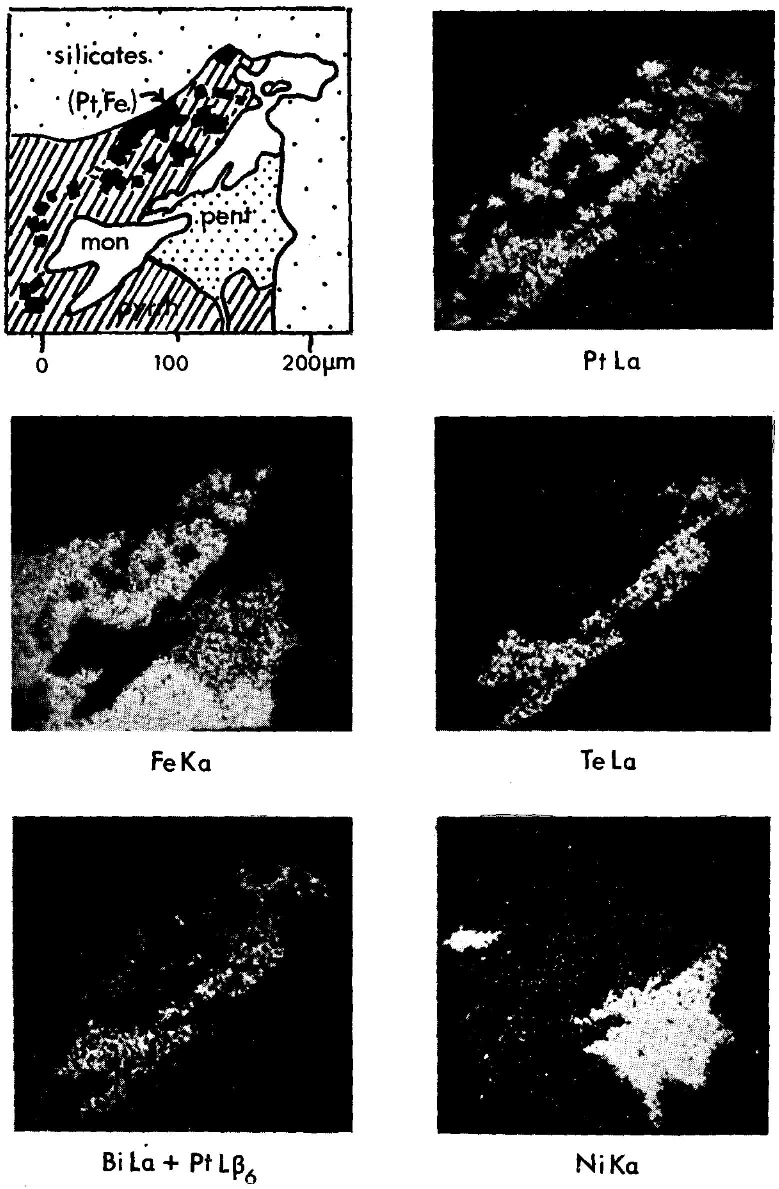

FIG. 2. X-ray scanning micrographs showing the distribution of platinum, iron, tellurium, bismuth, and nickel in an intergrowth of moncheïte $Pt(Te,Bi)_2$ (mon) and ferroplatinum (Pt,Fe) in pyrrhotine (pyrrh) and pentlandite (pent) in a polished section of the 'Reef' pyroxenite.

greyish-white mineral showing weak pleochroism in air. Under oil immersion it is a light grey and exhibits a distinct pleochroism. Compared with ferroplatinum it appears more grey and less creamy especially under oil. When enclosed by braggite it appears greyish white but is a bright white against chalcopyrite. Its anistropy is from distinct to strong in air, according to orientation with light yellowish brown to dark brown polarization colours. Although a reliable indentation microhardness measurement was not obtained, it was seen to be approximately of the same hardness as pentlandite when applying the pseudo-Becke line test. Its reflectivity in sodium light, by visual comparison, was between pentlandite and ferroplatinum and very much greater than braggite or cooperite. Accurate measurements are given in table II. The measurements were made in air using a × 60 objective and 2 mm mirror diaphragm. Two of the largest grains were measured.

Composition. The results of quantitative microspectrographic analyses of four grains of moncheïte from the Monchegorsk deposit by Genkin *et al.*, and the results of electron-probe microanalyses of moncheïte from Rustenburg are tabulated for comparison in table I. The analyses 1, 2, 3, and 4 were under conditions of constant specimen-current, and after correction for absorption, using a correction procedure by Tong (*pers. comm.*), they were still far from satisfactory but sufficiently accurate to illustrate substitutional trends in the moncheïte members.

One of the grains (table I, anal. 3; pl. XII, fig. D; fig. 2), confirmed by X-ray powder analysis to be moncheïte, was reanalysed at constant beam-current. The analysis was corrected for absorption, atomic number and fluorescence by the method previously outlined. This is presented in table I under analysis 5. The empirical formula from this approximates to that of the type moncheïte, $(Pt,Pd)(Te,Bi)_2$.

The X-ray data for the Rustenburg moncheïte are given in table II together with the type moncheïte and the probable palladium end-member merenskyite. The unindexed spacings may be due in part to contamination by pyrrhotine and pentlandite during extraction from the polished section. Of the eleven indexed lines, nine agree closely with those for the type moncheïte. The discrepancies in intensity towards the back reflection region are probably the result of the minute quantity of powder available and also possible disorder in the lattice.

Kotulskite

Kotulskite was first reported from the Monchegorsk deposit by Genkin *et al.* (1961, 1963) and an approximate formula given, $Pd(Te,Bi)_{1-2}$.

Table I. Results of electron-probe microanalyses and reflectivity values of some platinoid bismuthotellurides from Rustenburg Mine, and quantitative microspectrographic analyses of moncheïte and kotulskite from the Monchegorsk deposit by Genkin *etal.*, 1963.

	Moncheïte									*Kotulskite*			*Merenskyite*		*Mineral A*	*Mineral C*
	Rustenburg					*Monchegorsk*				*Rustenburg*		*Monchegorsk*	*Rustenburg*		*Rustenburg*	*Rustenburg*
Element	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
% *before correction*																
Pt	17·2	26·2	34·9	39·4	41·0					—	1·0		1·5	—	—	1·2
Pd	6·7	2·5	—	—	—					56·8	47·0		27·5	40·7	31·5	30·0
Bi	9·9	7·2	16·7	17·0	16·0					18·3	21·0		14·2	15·7	1·5	29·6
Te	38·6	39·8	30·8	35·6	45·0					32·1	31·0		50·2	54·0	35·3	17·2
Hg	—	—	—	—	—					—	—		—	—	11·9	—
(Fe,Cu,Ni)	5·0	6·0	3·0	3·0	—					—	—		—	—	—	trace
% *after correction*																
Pt	18·6	28·4	37·0	42·0	38·4	22·3	27·4	25·9	30·8	—	1·1	—	1·8	—	—	1·3
Pd	9·3	3·7	—	—	—	7·0	9·2	6·9	4·6	45·9	38·8	31·1	23·1	33·2	27·8	40·0
Bi	10·2	7·5	17·0	17·0	16·2	31·7	29·9	12·9	9·2	17·2	20·1	24·9	14·2	15·1	1·6	30·6
Te	40·3	40·7	35·1	35·3	45·8	39·0	33·5	54·3	55·4	38·0	36·1	44·0	50·8	56·3	38·5	23·3
Hg	—	—	—	—	—	—	—	—	—	—	—	—	—	—	12·0	—
(Fe,Cu,Ni)	7·0	8·0	3·0	3·0	—	—	—	—	—	—	—		—	—	—	trace
Reflectivity %																
λ mμ																
470	—	53·0	—	—	53·9	—	—	—	—	55·1	53·0	—	61·8	60·9	48·8	—
		56·8			56·5					57·3	53·4		62·2	61·4		
546	—	53·2	—	—	53·7	—	—	—	—	60·9	58·7	—	64·3	63·2	53·3	—
		58·8			56·6					64·4	61·1		65·2	64·4		
589	—	52·9	—	—	53·3	← 56 60 →				63·3	61·7	66 %	65·7	64·4	55·6	—
		58·1			56·1					65·6	63·2	max.	67·0	66·0		
650	—	52·7	—	—	52·7	—	—	—	—	65·2	64·1	—	65·9	64·3	53·9	—
		59·6			54·9					67·9	66·2		67·4	66·6		

TABLE II. X-ray powder data for moncheïte $(Pt,Pd)(Te,Bi)_2$ and merenskyite $(Pd,Pt)(Te,Bi)_2$ from Rustenburg mine (Cu radiation, Ni filter and 11·483 cm and 6 cm diameter cameras respectively), and for moncheïte from Monchegorsk (Genkin *et al.*, 1963) and artificial $PdTe_2$ (Thomassen, 1929)

	Moncheïte					*Merenskyite*				*Artificial* $PdTe_2$		
	Rustenburg			*Monchegorsk*								
Hexagonal cells	*a*	*c*		*a*	*c*	*a*		*c*		*a*	*c*	
	4·062	5·346		4·049	5·288	3·978		5·125		4·028	5·118	
	±0·002	±0·003		±0·004	±0·005	±0·001		±0·002		±0·003	±0·004	
hkil	*d calc.*	*d obs.*	*I obs.*	*d obs.*	*I obs.*	*hkil*	*d calc.*	*d obs.*	*I obs.*	*hkil*	*d obs.*	*I obs.*
0001*	5·325	5·25	50	5·32	60	—	—	—	—	—	—	—
—	—	3·02	40	3·07	20	—	—	3·07	30	—	—	—
$10\bar{1}1$*	2·932	2·94	100	2·93	100	$10\bar{1}1$*	2·921	2·92	100	$10\bar{1}1$	2·89	60
—	—	2·73	10	—	—	—	—	—	—	—	—	—
0002	—	—	—	2·66	10	—	—	2·51	20	0002	2·56	20
$10\bar{1}2$*	2·124	2·12	60	2·11	80	$10\bar{1}2$*	2·088	2·10	60	$10\bar{1}2$	2·07	60
—	—	2·08	20	—	—	—	—	—	—	—	—	—
$11\bar{2}0$*	2·028	2·03	60	2·02	70	$11\bar{2}0$*	2·015	2·02	30	$11\bar{2}0$	2·02	40
$11\bar{2}1$*	1·896	1·885	20	1·888	40	—	—	—	—	—	—	—
—	—	1·798	40	1·712	20	—	—	—	—	—	—	—
0003	—	—	—	—	—	0003*	1·726	1·73	20	0003	1·71	20
—	—	1·728	30	—	—	—	—	—	—	—	—	—
$20\bar{2}1$*	1·668	1·668	40	1·664	60	—	—	1·67	30	$20\bar{2}1$	1·65	30
$10\bar{1}3$*	1·587	1·588	20	1·575	50	—	—	1·61	20	$11\bar{2}2$	1·59	20
—	—	1·534	20	—	—	$10\bar{1}3$*	1·543	1·54	30	$10\bar{1}3$	1·54	70
$20\bar{2}2$*	1·467	1·471	20	1·462	70	—	—	1·46	10	$20\bar{2}2$	1·44	50
0004	—	—	—	1·324	40	—	—	—	—	—	—	—
$21\bar{3}0$*	1·328	1·328	20	—	—	—	—	1·39	10	$11\bar{2}3$	1·30	20
$21\bar{3}1$*	1·289	1·289	40	1·282	70	0004*	1·288	1·29	10	0004	1·28	80
$20\bar{2}3$	—	—	—	1·242	30							
$10\bar{1}4$*	1·247	1·248	10	—	—							
$21\bar{3}2$	—	—	—	1·182	50							

* These indices were checked, assuming a hexagonal symmetry, using a modified version of a computer programme by W. D. Hoff *et al.* (1965). In this programme the indices were accepted if $|(\sin^2\theta_0 - \sin^2\theta_c)| \leqslant 0{\cdot}003$. The drift constant K (Hess, 1951) was assumed proportional to $\frac{1}{2}(\cos^2\theta/\sin\theta + \cos^2\theta/\theta)$. Standard deviations of *a* and *c* were also determined. All reflections indexed were included in the determination of the cell parameters.

A similar phase from Rustenburg mine, considered to be kotulskite from the evidence of the X-ray powder data (table III), is shown to be Pd(Te,Bi) from two accurate quantitative electron-probe microanalyses. Kotulskite occurs in the Monchegorsk platinum deposit intergrown with moncheïte and michenerite, and as separate grains enclosed in chalcopyrite. At Rustenburg mine it also occurs enclosed by or adjoining chalcopyrite, especially at the periphery of the chalcopyrite where it abuts against the silicates. It is along the sulphide–silicate boundaries that the larger grains of this phase and the other tellurides occur. Kotulskite is also invariably intergrown with the new palladium bismuthotelluride, *merenskyite,* which occasionally replaces it but often shows mutual boundary relationships (fig. 3; pl. XII, fig. c).

TABLE III. X-ray powder data for kotulskite (Pd,Pt)(Te,Bi) from Rustenburg mine (copper radiation, Ni filter and 11·483 cm diameter camera), kotulskite $Pd(Te,Bi)_{1-2}$ from Monchegorsk (Genkin *et al.*, 1963), and artificial PdTe (Thomassen, 1929)

	Kotulskite							
	Rustenburg			*Monchegorsk*			*Artificial PdTe*	
Hexagonal cell	*a* 4·145 ±0·005	*c* 5·67 ±0·01			*a* 4·19 ±0·01	*c* 5·67 ±0·01	*a* 4·127 ±0·004	*c* 5·663 ±0·005
hkil	*d calc.*	*d obs.*	*I obs.*	*hkil*	*d obs.*	*I obs.*	*d obs.*	*I obs.*
†	—	—	—	$10\bar{1}0$	3·65	30	3·58	10
$10\bar{1}1$*	3·032	3·03	100	$10\bar{1}1$	3·05	100	3·03	40
—	—	—	—	0002	2·85	10	—	—
$10\bar{1}2$*	2·224	2·22	90	$10\bar{1}2$	2·24	90	2·22	80
$11\bar{2}0$*	2·071	2·08	70	$11\bar{2}0$	2·09	90	2·07	60
$20\bar{2}1$*	1·711	1·72	20	$20\bar{2}1$	1·73	60	1·71	40
$10\bar{1}3$*	1·671	1·67	20	$10\bar{1}3$	1·68	60	1·67	50
$11\bar{2}2$	1·672							
$20\bar{2}2$*	1·515	1·52	30	$20\bar{2}2$	1·53	70	1·51	80
—	—	1·41	5	0004	1·42	20	1·42	25
$10\bar{1}4$*	1·318	1·32	10	$10\bar{1}4$	1·33	70	1·32	50
$21\bar{3}2$	1·319							
—	—	1·23	10	$20\bar{2}3$	1·31	30	1·30	25
$30\bar{3}1$	1·170	1·17	10	$21\bar{3}2$	1·24	80	1·22	100
$11\bar{2}4$*	1·169							
				$30\bar{3}0$	1·19	70	1·21	50
				$20\bar{2}4$	1·17	80	1·17	100

* See footnote to table II. † Strong blackening of the film in this region due to rubber.

Optical and physical properties. Kotulskite from Rustenburg is a cream or pale yellow mineral in air and exhibits a distinct pleochroism from a light cream to a slightly darker greyish cream. In oil it appears more yellow and the pleochroism is more distinct. Moncheïte and merenskyite compared with pale yellow kotulskite appear white and are easily distinguished. Chalcopyrite against kotulskite appears greenish yellow. It exhibits a strong anisotropy with polarization effects from grey to dark bluish grey with the nicols completely crossed. Its polishing relief, compared with associated minerals, indicated it to be harder than chalcopyrite and softer than pentlandite and merenskyite. One grain of this phase was large enough to obtain two Vickers indentation microhardness values using a 15 g load. The average of the two indentations gave a value of $VMH_{15} = 236$. The indentation shape for kotulskite was symmetrical with no fractures and straight to very weakly concave sides. Accurate quantitative measurements of reflectivity are given in table I. The measurements were made in air using a ×32 objective and 2 mm mirror diaphragm.

Composition. Two grains of kotulskite from Rustenburg mine were quantitatively analysed with the electron-probe microanalyser using constant beam-current conditions, and the initial percentages were corrected for absorption, atomic number, and fluorescence as outlined previously. The results are presented in table I together with the semi-quantitative microspectrographic analysis of kotulskite from Monchegorsk by Genkin *et al.* X-ray scanning micrographs showing the distribution of palladium, tellurium, and bismuth in an intergrowth of kotulskite and merenskyite are presented in fig. 3.

A phase, Mineral C, with similar optical and physical properties to kotulskite, and which with stibiopalladinite formed a small composite grain of about 30μ diameter in a late stage microveinlet cutting the early formed matrix silicates, showed, on analysis under conditions of constant specimen-current (table I), a large bismuth content compared to the previous analyses of kotulskite; tellurium was correspondingly lower.

The X-ray data for the Rustenburg kotulskite are tabulated in table III together with the type kotulskite and artificial PdTe for comparison. Although the powder was exposed for 26 hr at 40 kV and 22 mA only ten lines could be measured to a reasonable degree of accuracy. The fall-off in line intensity towards the back reflection region is again probably caused by the extremely small quantity of powdered mineral available. The close agreement with artificial PdTe strongly supports the empirical formula Pd(Te,Bi) for kotulskite derived by electron-probe microanalysis. This is further emphasized by the lack of agreement with the powder data for artificial $PdTe_2$.

Merenskyite[1]

Merenskyite occurs in the same manner as kotulskite with which it is very commonly intergrown (fig. 3; pl. XII, fig. c). In reflected light it is

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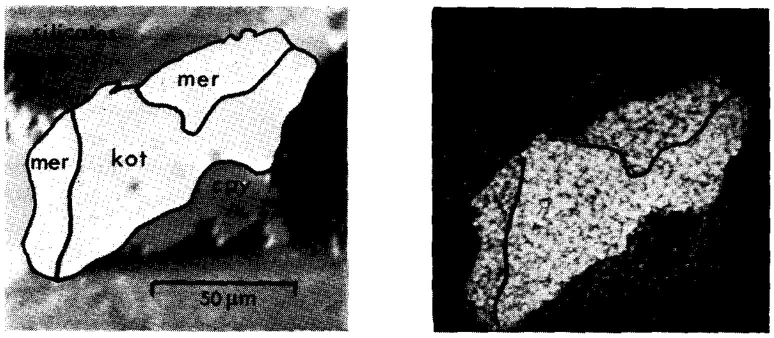
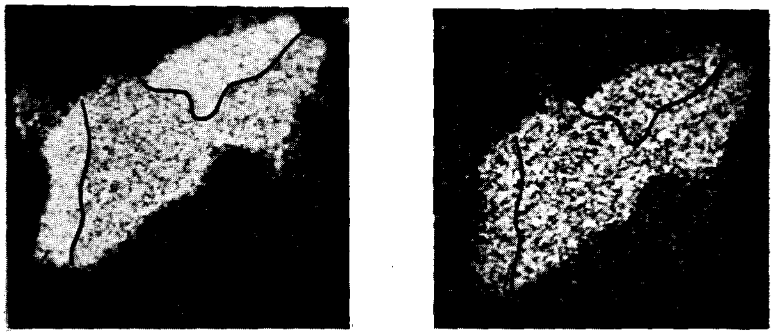
[1] Name approved before publication by the Commission on New Minerals and Mineral Names, International Mineralogical Association, June 1965.

easily distinguished from kotulskite, which is pale yellow in colour, whereas merenskyite is white in comparison. Moncheïte and merenskyite are not easily distinguished from each other, unless in close proximity, when merenskyite can be seen to have a higher reflectivity and appears slightly more creamy.



Electron Image Pd La



Te La Bi La

FIG. 3. X-ray scanning micrographs showing the distribution of palladium, tellurium and bismuth in a composite grain of merenskyite $Pd(Te,Bi)_2$ (mer) and kotulskite Pd(Te,Bi) (kot) intergrown with chalcopyrite (cpy). Because of poor contrast the respective phases have been outlined.

Optical and physical properties. In air merenskyite is white with a weak pleochroism from white to greyish white. In oil the reflection pleochroism is more distinct, from white with a slight creamy tint to light greyish white. It is distinctly to strongly anisotropic, according to orientation, with dark brown to light greenish grey polarization colours. No Vickers indentation microhardness values were obtained for this phase because of the small size of the grains. The polishing relief indicated its polishing hardness to be less than pentlandite, greater than chalcopyrite, and just greater than kotulskite. Precise reflectivity values are given in table I; measurements were made in air using a ×32 objective and 2 mm mirror diaphragm.

Composition. An electron-probe microanalysis of a large grain (fig. 3) of this phase, from which X-ray powder data were later obtained, was made using constant beam-current conditions and correcting the initial percentages for absorption, atomic number, and fluorescence. This analysis (table I, anal. 13) gives a (Pd,Pt): (Te,Bi) ratio of 1·0: 2·06 indicating the empirical formula $(Pd,Pt)(Te,Bi)_2$. The X-ray data for this phase are presented in table II together with artificial $PdTe_2$ and moncheïte for comparison. As with previous phases only a minute quantity of powder could be obtained and a 30-hr exposure at 40 kV and 22 mA with Cu-$K\alpha$ radiation was needed to obtain a reasonable photograph. The similarity of the patterns for merenskyite and moncheïte suggests that they are probably isostructural, merenskyite being the palladium end-member of a possible solid solution series, and the close agreement of both patterns with that for artificial $PdTe_2$ helps to confirm the above formula. The X-ray data compared with those for artificial PdTe do not show such a close similarity.

A further electron-probe microanalysis (table I, analysis 14) of a phase optically identified as merenskyite and intimately intergrown with kotulskite (pl. XII, fig. c) suggested the empirical formula $Pd_3(Te,Bi)_5$. This may be an error, probably present in many probe analyses of chemically similar phases complexly intergrown, caused by the inclusion of sub-outcropping kotulskite in the irradiated zone of the analysis. However, in an equilibrium diagram for Pd–Te alloys (fig. 4) (Z. S. Medvedeva *et al.* (1961)) it is significant that in the $PdTe_2$–PdTe region, in the range 640–690° C, the alloys form a continuous series of solid solutions, which break down below 640° C into a mixture of two solid solutions based on PdTe and $PdTe_2$. This could account for the $Pd_3(Te,Bi)_5$ phase as consisting of merenskyite with PdTe or Pd(Te,Bi) in solid solution. This relationship also helps to account for the invariable occurrence of kotulskite, equivalent to PdTe, as an intimate intergrowth with merenskyite.

In conclusion it appears that merenskyite is the palladium end-member of a possible solid-solution series with the platinum end-member moncheïte. It may also form a complete solid-solution series with kotulskite at high temperatures and only a partial one at normal temperatures, an indication being the possible existence of $Pd_3(Te,Bi)_5$.

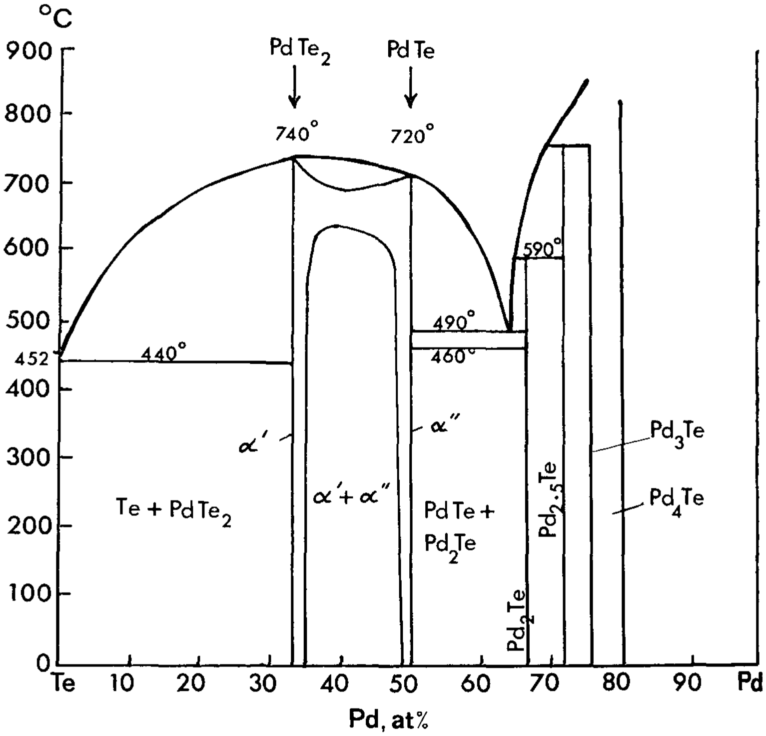


FIG. 4. Equilibrium diagram for Pd-Te alloys (after Medvedeva, Klochko, Kuznetsov, and Andreeva, 1961).

Mineral A, $(Pd,Hg)_x(Te,Bi)_y$

This phase has so far only been located as four blebs, ranging from 2 to 5 μ in diameter, intergrown with merenskyite. Its colour in air is light grey but under oil immersion it is slightly darker with a brownish tint. It appears to be isotropic. Values of reflectivity for this phase are presented in table II. From an examination of polishing relief it is softer than merenskyite and chalcopyrite.

The composition of this phase as determined with the electron-probe microanalyser is at present only semiquantitative because of the small grain size and the consequent errors involved in such an analysis (table I, anal. 15). This suggests a (Pd,Hg) : (Te,Bi) ratio of 1 : 1. The only other palladium–mercury minerals reported in the literature are potarite, PdHg, and allopalladium, whose exact composition is uncertain but which appears to contain palladium and mercury.

Paragenetic considerations

Although the mode of emplacement and the details of the subsequent differentiation of the mafic zone of the Bushveld Igneous Complex are still somewhat controversial, there are few who would not concede that it was produced from a melt of basaltic composition, which did undergo at least part of its differentiation *in situ.* Thus the paragenesis of the minerals composing the Merensky Reef can be considered in the light of fractional crystallization and sulphide immiscibility in an oxide-silicate melt. One can envisage, as a result of these two processes combined with gravity settling and related phenomena, the formation at one stage of a compact coarsely crystalline aggregate of mainly pyroxenes with subordinate feldspars, with a sulphide melt rich in volatiles filling the interstices. Reaction takes place between this sulphide melt and the early silicates producing reaction minerals such as hornblende and biotite. Graphite may also be formed at this time. Meanwhile from the interstitial sulphide melt the base metal sulphides and platinoid minerals begin to crystallize out in a certain order. In the Rustenburg mine this order is relatively simple and early pyrite is followed by pyrrhotine, exsolution pentlandite and primary pentlandite, and finally chalcopyrite with exsolved cubanite and mackinawite. One of the earliest formed platinum minerals is ferro-platinum, which is commonly associated with pyrrhotine either as a fine graphic intergrowth, suggesting a eutectic relationship, or as euhedral partially corroded grains. The platinoid sulphides and arsenides are slightly later and generally occur as euhedral aggregates or isolated grains enclosed in pentlandite but often fractured and veined by chalcopyrite. The bismuthotellurides, stibiopalladinite, and arsenopalladinite are the latest formed platinoid minerals and are commonly associated with chalcopyrite as included blebs and laths or as discrete grains along sulphide–silicate boundaries. They are also found as clusters or small grains in microveinlets along partings in the altered early silicates. These microveinlets may have been formed by reaction of residual fugitive constituents with the early silicates. Thus the platinoid bismuthotellurides appear to be of late crystallization and may be associated with the residual 'pegmatitic' phase after the formation of the main bulk of the sulphides as postulated by Schneiderhohn (1929).

The tendency at present is to allocate platinum minerals to a later stage of crystallization (Stumpfl, 1962) than was envisaged in past conceptions of the geochemical behaviour of the platinum metals by Schneiderhohn (1929) and Rankama and Sahama (1950). This trend of opinion began as a result of the location of numerous new platinoid phases in deposits and ores that from field evidence were of a relatively late stage of crystallization compared to the early magmatic sulphides of the Merensky Reef. Notable among these discoveries are those from the Dreikop dunite pipe in the eastern Bushveld by Stumpfl (1961), from the Urals, Norilsk, and Monchegorsk by Borovskii (1959), Genkin (1959, 1961, 1963), and Betechtin (1961), and from Sudbury by Hawley and Berry (1958). However, as regards the Merensky Reef it is apparent that not all the platinum minerals are of a late stage of crystallization as has been suggested by Willemse (1964). In fact, the chief platinoid minerals at Rustenburg mine, cooperite and braggite, appear to have crystallized early from the interstitial magmatic sulphides.

The presence of these platinoid bismuthotellurides is of interest as regards the geochemical behaviour of tellurium during the fractional crystallization of the sulphides. Their occurrence is in agreement with investigations by Sindeeva (1959) and others who have demonstrated that tellurium, although a close analogue of sulphur and selenium, tends to form independent minerals even when present in very low concentrations rather than to form solid solutions in the base metal sulphides. This is explained as a result of the quite different atomic size and electronegativity of tellurium compared to sulphur. Selenium readily substitutes for sulphur, as shown by Zaryan (1962) and others, and where the concentration of selenium is low, independent selenium minerals will be unlikely to form. In the Merensky Reef no selenides have yet been found, although traces of selenium are probably present in the sulphides. Platinoid selenides were reported from the Urals in the copper–nickel sulphide ores of the Norilsk region by Zainullin and Pashinkin (1960), but compared with the platinoid tellurides they were rare even though there was more selenium than tellurium present in the ore. The results of microscopic and chemical investigations of the distribution of tellurium in ores related to basic and ultrabasic intrusives by Zainullin (1960), Pshenichnii (1961), Zaryan (1962), and others, show that tellurium is concentrated in the later stages of crystallization and in particular in the chalcopyrite-rich ores. The tellurium in the Merensky Reef appears to follow this trend. Bismuth appears to behave in a similar way and in these ores substitutes for tellurium as demonstrated in the various analyses of moncheïte in table I. This substitution would be expected from the close similarity in atomic radius of bismuth (1·55 Å) and tellurium (1·43 Å).

Acknowledgements. This paper constitutes part of a research programme into the mineralogy of the Merensky Reef of the Western Bushveld. I am very grateful for financial assistance from the Vernon Hobson Bequest Fund of the Institution of Mining and Metallurgy and the Hilary Bauerman grant from Imperial College. I am also indebted to Johannesburg Consolidated Investment Co. Ltd. for their help and permission to study the field relations and collect specimens of this platiniferous horizon at Rustenburg and Union mines from July to September of 1962. I would especially like to thank Dr. J. Zermatten of J.C.I. for his kindness and assistance and his generous provision of a comprehensive collection of polished sections of concentrates and ore from the two mines.

I would like to express my sincere thanks to Dr. A. P. Millman for his helpful suggestions and criticisms during the course of this investigation and in the preparation of this paper.

I am grateful to Mr. T. K. Kelly for his help in the electron probe microanalysis of these minerals and for correcting the initial results for absorption, atomic number, and fluorescence. In connexion with the electron probe microanalysis, Messrs. Johnson and Matthey Ltd. very generously provided standard platinoid alloys. Thanks are also owed to Mr. R. Curtis and Mr. M. T. Frost for their help in obtaining and processing the X-ray data.

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[*Manuscript received 2 September 1965.*]

Explanation of Plate XII

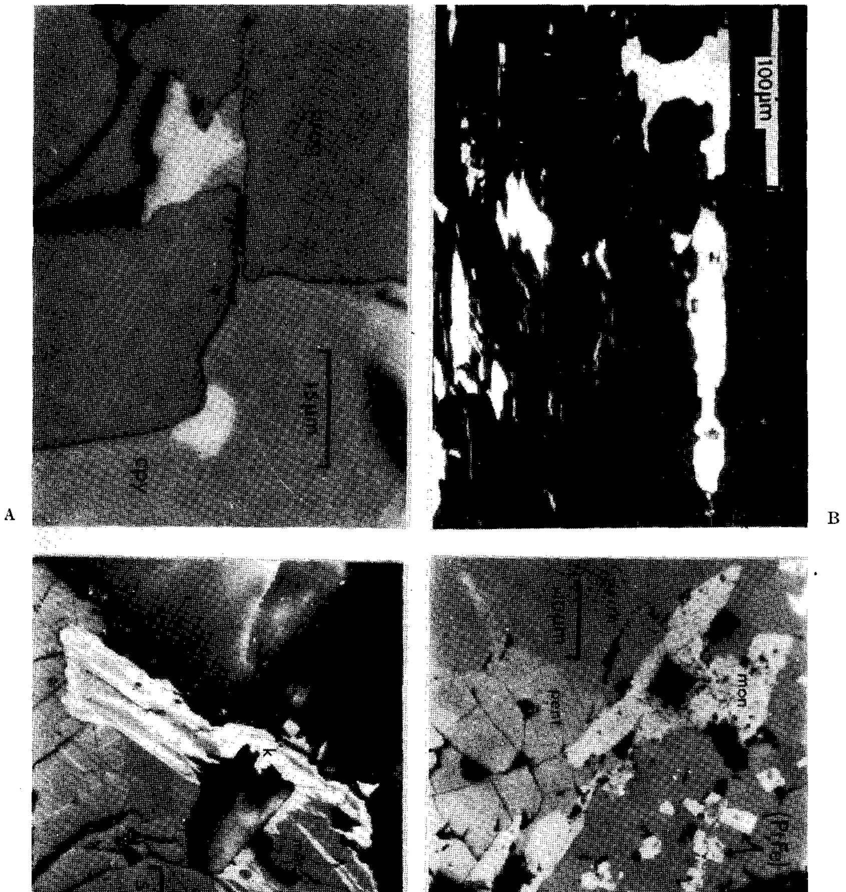
Fig. a. Two grains of moncheïte $Pt(Te,Bi)_2$ (white) associated with chalcopyrite (cpy) which encloses fractured braggite (Pt,Pd,Ni)S (brag).

Fig. b. Platinoid bismuthotelluride grains (white) associated with chalcopyrite (light grey) in microveinlets in the silicates (dark grey).

Fig. c. A subhedral lath of merenskyite (mer) along a pentlandite: silicate contact showing partial replacement by kotulskite (k) Pd(Te,Bi). Crossed nicols.

Fig. d. A lath of moncheïte $Pt(Te,Bi)_2$ (mon) and euhedral crystals of ferroplatinum (Pt,Fe) showing cubic outline, intergrown with pyrrhotine (pyrrh) and pentlandite (pent).

[*Note*: μm, on the scales on Plate XII, is a micro-metre, equal to a micron (μ), and not to be confused with a millimicron, mμ.—*Ed.*]



G. A. Kingston: Platinoid Bismuthotellurides