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RUSTENBURGITE AND ATOKITE, TWO NEW PLATINUM-GROUP MINERALS FROM THE MERENSKY REEF, BUSHVELD IGNEOUS COMPLEX

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Abstract

Microprobe analyses of two grains gave Pt 53.44, Pd 28.28, Sn 17.70, sum 99.43, and Pt 43.74, Pd 38.35, Sn 18.65, sum 100.75 wt. %. These correspond to $Pt_{0.398}Pd_{0.386}Sn_{0.217}$ (palladian rustenburgite) and $Pd_{0.486}Pt_{0.302}Sn_{0.212}$ (platinian atokite) respectively. Experimental work done by the authors on the platinum-palladium-tin ternary system delineates the rustenburgite-atokite field and indicates a limited solid-solution field that allows a deviation from the ideal stoichiometry of $(Pt,Pd)_3Sn$. Both natural grains fall very close to, but slightly outside, this experimentally determined solid-solution boundary, probably owing to pressure/temperature differences between natural and experimental conditions. The name *rustenburgite* is proposed for the platinum end-member and *atokite* for the palladium end-member.

X-ray study shows the minerals to be face centered cubic (disordered as a result of strain) with probable space group F*m*3*m*. Z = 4, G_{calc} = 15.08 (palladian rustenburgite) and 14.19 (platinian atokite). *a* (for both grains, within experimental error) = 3.991Å. The strongest lines are 2.295 (10) (111), 1.408(9) (220), 1.202(10) (311), 0.9153(9) (422). Synthetic material has the ordered, *Pm*3*m* structure.

The minerals occur in concentrates from the Rustenburg and Atok Platinum mines in the Bushveld Igneous Complex, South Africa. Colour light cream in polished section; slightly anisotropic due to strain; reflectance varies between 59.2 and 65.1 in air at 546nm. VHN_{25} = 365 (palladian rustenburgite) and 357 (platinian atokite).

The rustenburgite-atokite series is related to the mineral zvyagintsevite, which is the lead-rich equivalent of atokite.

Introduction

During the examination of concentrates of some platinum telluride minerals from the Merensky Reef, Bushveld Igneous Complex, South Africa, two new platinum-palladium-tin minerals were discovered. The one mineral, $(Pt,Pd)_3Sn$ with Pt>Pd, is named after the Rustenburg Platinum Mine, and the other, $(Pd,Pt)_3Sn$ with Pd>Pt, after tthe Atok Platinum Mine, (some 30 miles SE of Pietersburg), both mines exploiting the Merensky Reef. The names rustenburgite and atokite have been approved by the Commission on New Minerals and Mineral Names, I.M.A. The minerals are scarce; only two small grains (~100 micron diameter) among several so far encountered were of sufficient size to permit quantitative investigation.

In order to characterise these minerals, the Pt-Pd-Sn ternary system was investigated and part of the equilibrium diagram constructed.

The Pt-Pd-Sn Ternary System

No information on the ternary phase relationships among these elements is available from the literature. The Pt-Sn and Pd-Sn binary diagrams were described by several investigators — Hansen (1958), Nowotny *et al.* (1946), Schubert *et al.* (1959), Schubert & Jahn (1949), Schubert & Pfisterer (1949) and Knight & Rhys (1959) — and the existence of the Pt_3Sn and Pd_3Sn compounds noted by them. However, whether a stable field existed between these two end-members, and the relationship between this possible field and the Pt-Pd-Sn solid-solution field, were uncertain.

With this in mind, Specpure platinum, palladium, and tin were weighed out in the proportions shown in Table 1, sealed in evacuated silica tubes, and heated in an oxy-acetylene flame close to the softening point of silica. The sealed tubes were then annealed in a furnace from a maximum temperature of 1100°C according

TABLE 1. COMPOSITIONS OF BEADS USED TO DELINEATE THE Pt-Pd-Sn TERNARY DIAGRAM

Bead no.	Amount used (grams)				Calculated composition (at. proportion)			Final wt. of bead after annealing
	Pt	Pd	Sn	Total	Pt	Pd	Sn	
1	0.07835	0.04700	0.02500	0.15035	0.381	0.419	0.200	0.15035
2	0.06895	0.03795	0.03760	0.14450	0.344	0.347	0.308	0.145005
3	0.05875	0.03230	0.04810	0.13915	0.298	0.301	0.401	0.13915
5	0.09735	0.04700	0.01000	0.15435	0.487	0.431	0.082	0.15330
6	0.04110	0.07270	0.01790	0.13170	0.202	0.654	0.144	0.13170
7	0.13600	0.01810	0.01680	0.17090	0.691	0.169	0.140	0.17065
9	0.03620	0.06110	0.06200	0.15930	0.145	0.448	0.407	0.15930
10	0.13320	0.00970	0.02880	0.17170	0.672	0.090	0.239	0.17180
11	0.12220	0.00920	0.00975	0.14120	0.788	0.109	0.103	0.14120
12	0.03585	0.05765	0.03375	0.12730	0.182	0.536	0.282	0.12720
13	0.04020	0.05960	0.02995	0.12980	0.202	0.550	0.248	0.12985
14	0.10040	0.01070	0.04930	0.16040	0.499	0.098	0.403	0.16040
15	0.11500	0.02140	0.02800	0.16440	0.574	0.196	0.230	0.16440
16	0.06360	0.04725	0.02920	0.14005	0.321	0.437	0.242	0.14010
17	0.08860	0.04250	0.01760	0.14870	0.453	0.399	0.148	0.14870

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to the cooling curve shown in Figure 1. The beads formed were used in the preparation of polished sections. Optical investigation showed most beads to consist of two phases, some of only one phase, and one bead of three phases. All the phases present were analyzed with an ARL EMX electron microprobe, the single-phase beads 13 and 16 being used as standards. The resulting ternary phase diagram is shown in Figure 2. Beads falling in the tin-rich portion of the diagram (numbers 4, 8, 18, and 19) were not equilibrated even after prolonged annealing, and this portion of the diagram is therefore not shown.

The existence of a Pt_3Sn-Pd_3Sn field, separated by miscibility gaps from the Pt-Pd-Sn solid-solution field and from the paolovite (Pd_2Sn) and niggliite (PtSn) fields is clearly established. The Pt_3Sn-Pd_3Sn field is arbitrarily divided into four: Pt_3Sn to $Pt_{2.25}Pd_{0.75}Sn$ is called rustenburgite, $Pt_{2.25}Pd_{0.75}Sn$ to $Pt_{1.5}Pd_{1.5}Sn$ is palladian rustenburgite, $Pt_{1.5}Pd_{1.5}Sn$ to $Pt_{0.75}Pd_{2.25}Sn$ is platinian atokite, and $Pt_{0.75}Pd_{2.25}Sn$ to Pd_3Sn is atokite. These compounds can deviate from ideal stoichiometry by a few atomic per cent tin, as shown in Figure 2.

PROPERTIES OF THE NATURAL MINERALS

Physical properties

Under the microscope, both palladian rustenburgite and platinian atokite are light cream in colour and have high reflectance. No bireflection could be observed. However, on a Leitz MPV photometer birereflection was revealed. Slight anisotropism was observed in both, and is slightly more distinct in oil.

A WC-standard, purchased from Carl Zeiss in Göttingen and calibrated by that firm, was used for the determination of reflectances of the two minerals studied. The microhardness of each was measured with a Leitz 'Miniload' Vickers hardness tester, using a weight of 25 grams and a single indent on each grain. The results of the above are listed in Table 2.

The grains were too small for density determination, but the calculated densities for the compositions found are 15.08 g/cc for the palladian rustenburgite and 14.19 for the platinian atokite, using the constants proposed by Schlecht (1944).

TABLE 2. REFLECTANCE AND MICROHARDNESS MEASUREMENTS

Mineral	Reflectance								Micro-hardness
	480nm		546nm		589nm		656nm		VHN$_{25}$
	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	
Palladian rustenburgite	55.6	56.8	59.3	60.3	59.9	60.9	61.2	62.1	365
Platinian atokite	57.4	60.8	59.2	65.1	60.4	63.5	62.2	65.8	357

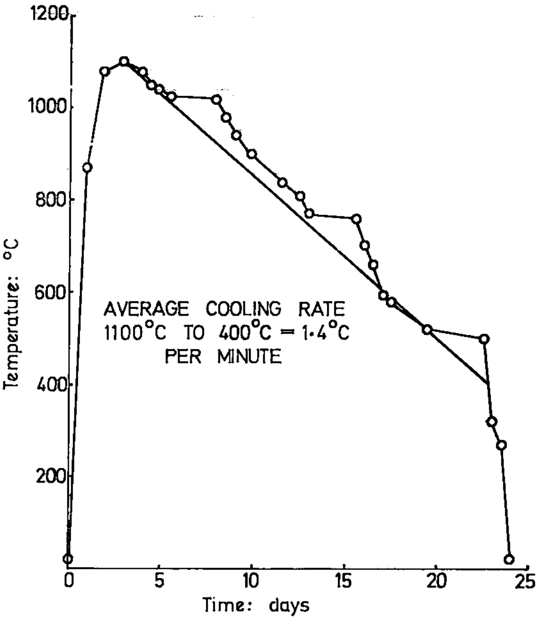

FIG. 1. Cooling curve showing heat treatment of Pt-Pd-Sn beads.

Chemical compositions

The following standards were used during the electron microprobe analysis of the two grains: for Pt and Pd, a synthetically prepared platinum-palladium-bismuth telluride, and for Sn the pure metal. The excitation voltage was 25kV and the sample current 0.02μA. Pulse-height discrimination was used, and the raw data were corrected by means of a computer program devised by Beeson (1969). The results are listed in Table 3, and show one grain to be palladian rustenburgite and the other platinian atokite. Both grains fall very close to, but slightly outside, the experimentally determined boundary, probably because of pressure/temperature differences between natural and experimental conditions.

X-ray study

Powder diffraction photographs were prepared by means of a 114.6mm Gandolfi camera. The unit cells were determined from Nelson-Riley

TABLE 3. ELECTRON MICROPROBE ANALYSES OF PALLADIAN RUSTENBURGITE AND PLATINIAN ATOKITE

	Palladian rustenburgite			Platinian atokite		
	Raw data wt %	Corrected wt %	Atomic prop.	Raw data wt %	Corrected wt %	Atomic prop.
Pt	57.08	53.44	0.398	45.58	43.74	0.302
Pd	27.34	28.28	0.386	38.33	38.35	0.486
Sn	12.51	17.70	0.217	12.96	18.65	0.212
Total		99.42			100.74	
Formula:	$(Pt,Pd)_3Sn_{0.83}$			$(Pd,Pt)_3Sn_{0.81}$		

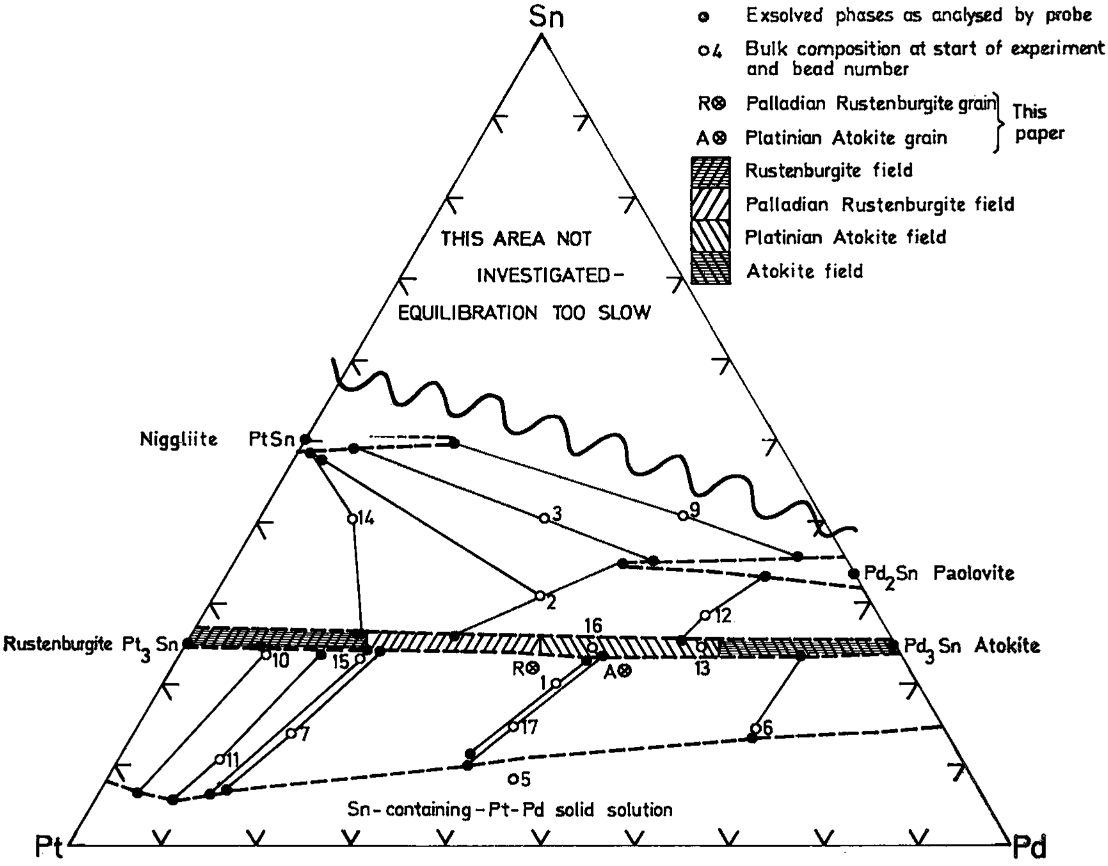

FIG. 2. Ternary diagram showing phase relationships in the Pt, Pd-rich portion of the Pt-Pd-Sn system, at room temperature. (Atom %).

plots and agree within experimental error. Only one set of *d*-values and one unit-cell value is therefore given in Table 4, and it applies to both our platinian atokite and palladian rustenburgite grains. Two crystal faces were noted on the one grain, shown to be the (100) faces after orientation in a Weissenberg camera. The diffraction spots were very diffuse, indicating that the minerals were in a strained condition. This is presumably due to physical damage acquired during the lengthy physical beneficiation procedures used in obtaining the concentrate. Because of this condition, no unambiguous choice of space group could be made, other than the presence of face-centering, that is, *Fm3m*. However, synthetic Pt_3Sn and Pd_3Sn both have the ordered primitive Cu_3Au *Pm3m* structure (Nowotny *et al.* 1946; Schubert & Pfisterer 1949), and it can therefore be assumed that the Sn in rustenburgite-atokite, when these minerals are in an unstrained state, is ordered. Physical damage of these minerals presumably changes the *Pm3m* to the *Fm3m* structure. It is also possible that the weak superstructure reflections indicating ordering were just not visible on the Gandolfi films. However, the Weissenberg photographs also provided no evidence for the *Pm3m* space group in these strained grains.

TABLE 4. X-RAY POWDER DATA FOR RUSTENBURGITE - ATOKITE SERIES, $(Pt,Pd)_3Sn$

d_{meas}Å	d_{calc}Å	I/I_1	*hkl*
2.295	2.304	100	111
1.992	1.996	80	200
1.408	1.411	90	220
1.202	1.203	100	311
1.150	1.152	40	222
0.9975	0.9978	20	400
0.9153	0.9156	90	331
0.8922	0.8925	80	420
0.8145	0.8147	90	422

114.6mm Gandolfi camera, Ni-filtered Cu*K*α radiation, λ=1.5405, I/I_1 visual.

Indexed with a=3.991Å, space group *Fm3m*.

The diffraction pattern of strained rustenburgite-atokite differs from that of the Pt-Pd-Sn solid solution only quantitatively, *i.e.* in unit-cell value, but giving similar spacings and intensities for the diffraction lines. This does not imply that the rustenburgite-atokite series is isostructural with the Pt-Pd-Sn solid-solution, in which the tin is not ordered, but merely that the tin in the former easily reverts to the disordered state, and that the mineral grains have to be annealed for a correct structure determination. Unfortunately, our grains were too small for this.

Related Minerals

Previously described Pt-Pd-Sn minerals such as paolovite, Pd_2Sn, (Genkin *et al.* 1974), and niggliite, PtSn, (Cabri & Harris 1972), contain the same elements, but are not structurally related to rustenburgite or atokite. However, zvyagintsevite as described by Genkin *et al.* (1966) and also by Cabri & Traill (1966) — see discussion by J. A. Mandarino, *Amer. Mineral.*, vol. 52, p. 1588 — seems to be the lead-bearing equivalent of the atokite side of the rustenburgite-atokite series. Our proposed scheme illustrating this relationship is shown in Figure 3. Whether a continuous transition from the lead-rich to the tin-rich portion is possible was not experimentally determined. However, *x*-ray evidence would suggest this to be possible as the structures are the same. Furthermore, the zvyagintsevite described by Genkin *et al.* (1966) and one of the minerals described by Razin & Bykov (1971) contain both lead and tin.

The two unnamed minerals described by Razin & Bykov (1971), and referred to by Cabri (1972) (see also discussion by L. J. Cabri, *Amer. Mineral.*, vol. 57, p. 596 & 597) as 'unnamed minerals S and R', are without a doubt palladian rustenburgite and atokite respectively.

It would appear that rustenburgite, atokite, and zvyagintsevite are closely related, and that these minerals can contain, in addition to major Pt, Pd, Sn, or Pb, minor amounts of any of the following elements: Au, Ag, Rh, Cu, and possibly also Fe and Ni, though the last two are more doubtful. The positions of these related minerals, as projected onto the $(Pt,Pd)_3(Sn,Pb)$ plane of Figure 3, is indicated in Figure 4. We thus have plotted two palladian rustenburgites, a platinian atokite, an atokite, and two zvyagintsevites.

In conclusion, the proposal of Genkin *et al.* (1969) that the name zvyagintsevite be reserved for the compositions of $(Pd,Pt)_3(Pb,Sn)$, where Pd>Pt and Pb>Sn, is supported. However, when Pb<Sn, then the names rustenburgite or atokite apply, depending on whether Pt > or < Pd.

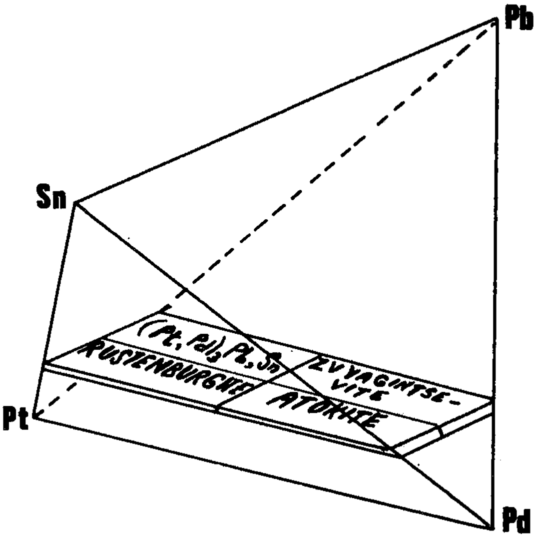

FIG. 3. Tetrahedron showing the relationships between zvyagintsevite, rustenburgite, and atokite. The extent of the zvyagintsevite field is uncertain. The name is probably valid to $Pd_{1.5}Pt_{1.5}Pb$.

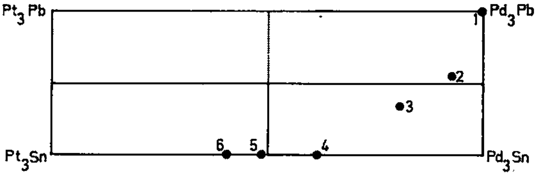

FIG. 4. Compositions of described minerals plotted on the $(Pt,Pd)_3(Sn,Pb)$-plane of the tetrahedron shown in Figure 3.

(1) Zvyagintsevite, Cabri & Traill (1966). (2)Zvyagintsevite, Genkin *et al.* (1966). (3) Unnamed mineral, Razin & Bykov (1971). (4) Platinian atokite, this paper. (5) Palladian rustenburgite, this paper. (6) Unnamed mineral, Razin & Bykov (1971).

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