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MINERALOGIE UND PETROGRAPHIE

Platinum-Group Minerals (PGM) from placer deposits in the mineral collection of the Museum of Natural History, Vienna, Austria

By T.W. WEISER¹

(With 8 figures and 2 tables)

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Abstract

Ten samples of platinum-group minerals (PGM) from placer deposits around the world from the mineral collection of the Museum of Natural History, Vienna, Austria, including the large nugget on display, were analyzed by electron microprobe for the first time. The samples originate from Nizhni Tagil, Urals and Kuzenelig, Altai in Russia; California and Rogue River, Oregon in the USA; Serro, Minas Gerais (MG) and three others, not exactly localized occurrences in Brazil. All samples from the various localities are mainly Pt-Fe- and Os-Ir-Ru alloys, whereas laurite and gold are subordinate and occur as single grains in only few samples. Apart from Pt-Fe- and Os-Ir-Ru- alloys and laurite, the PGM hongshiite, potarite, tulameenite, laurite, erlichmanite, bowieite, irarsite, hollingworthite, cuprorhodsite, sperrylite, cherepanovite, rhodarsenite-palladodymite, and the unnamed phases (Rh,Pt)S, Rh₂S₄, (Os,Ir)₂CuS, and Ru oxide were observed as inclusions, crack fillings or rims. One of the most interesting samples from Serro, Minas Gerais (MG), Brazil consists of dendritic alloys of Pt-Pd- and Pt-Pd-Hg alloys with colloidal texture.

Zusammenfassung

Platingruppenminerale (PGM) aus Seifenlagerstätten in der Sammlung des Naturhistorischen Museums in Wien, Österreich

Zehn Proben von Platingruppenmineralen (PGM) verschiedener Seifenlagerstätten, einschliesslich des grossen ausgestellten Nuggets, aus der umfangreichen Sammlung des Naturhistorischen Museums in Wien wurden erstmals mit der Elektronenstrahl-Mikrosonde untersucht. Die Proben stammen aus Nizhni Tagil, Ural und Kuzenelig, Altai in Russland; Kalifornien und Rogue River, Oregon in den USA; Serro, Minas Gerais (MG) und weiteren nicht exakt lokalisierten Vorkommen in Brasilien. Die Proben bestehen überwiegend aus Pt-Fe- und Os-Ir-Ru-Legierungen. Laurit und Gold treten in den Proben selten als Einzelkörner auf. Neben Pt-Fe- und Os-Ir-Ru-Legierungen und Laurit finden sich Hongshiit, Potarit, Tulameenit, Laurit, Erlichmanit, Irarsit, Hollingworthit, Cuprorhodsit, Sperrylith, Cherepanovit, Rhodarsenit-Palladodymit und die unbekannt Phasen (Rh,Pt)S, Rh₂S₄, (Os,Ir)₂CuS und Ru-Oxid als Einschlüsse, Rissfüllungen oder Verwitterungskrusten. Eine der interessantesten Proben von Serro, Minas Gerais (MG), Brasilien enthält dendritische Verwachsungen von Pt-Pd-Legierungen und kolloidale Verwachsungen von Pt-Pd-Hg-Legierungen.

¹ T.W. WEISER, Federal Institute for Geosciences and Natural Resources, Hannover, Germany. Author's address: Rischkamp 63, D-30659 Hannover, Germany, e-mail: weiser@wald-info.de

Introduction

In 1752, the medical doctor and scientist Nicolaus Joseph VON JACQUIN entered emperor FRANZ STEPHAN von Lothringen's service for leading an expedition to Central America to collect rarities of the nature for the court in Vienna. In 1759, he brought back samples from platinum occurrences in Colombia for the imperial mineral collection, labeled as "Platinum in granis solitis a ferro magnetico ... ex Santa Fe di Bogoda" in the first catalogue of the mineral collection, called "Catalogus Stützianus" (SCHOLLER 1958). These are presumably the first samples of "platinum" in the mineral collection of the museum in Vienna and one of the first in Europe. In 1807, the museum received additional samples of platinum from Colombia and in 1888 two private collections were purchased. In 1997, a donation of samples from the Rio Cauca and Rio Condoto, Colombia was made by the author.

The first samples of platinum-bearing gravels from Brazil were acquired in 1816. One of the samples from Minas Gerais, Brazil, collected by E. HUSSAK in 1904, will be described in this paper.

Curious is the notice in the catalogue from 1807 about platinum in the Urals and that a collector from London presented another sample from the Urals in 1816, because only rumours had been circulating in 1806 and 1810 about platinum in Siberia (MCDONALD & HUNT 1982). Not until 1819, small pieces of platinum from the Urals were brought to the attention of anyone in authority (MCDONALD & HUNT 1982). A large collection of samples from placer deposits in the Urals together with other Russian minerals and rocks was donated by tsar NIKOLAUS I. to the Austrian emperor FERDINAND III., in 1836. The gift of a 6.2 kg platinum nugget from Nizhni Tagil, Urals, by Count Nikolai Nikitich DEMIDOV, the owner of several platinum mines, to Dr. Moritz HOERNES, director of the mineral cabinet of the emperor, in 1859, is the most spectacular acquisition of the mineral collection (HAIDINGER 1859). This nugget ranks as one of the largest nuggets ever found, apart from another one from the Urals in the collection of the Kremlin and the largest described nugget of the world of 11.6 kg from Colombia in the museum of Madrid, Spain (QUIRING 1962).

In 1892, the museum got two samples of platinum from placer deposits in the Altai, Russia. The first analyses of these samples will be discussed in this paper.

Samples from placer deposits in California and Oregon, USA, acquired in 1856 and 1870, are also described.

The museum came into possession of further samples of PGM, e.g., from the hortonolite-dunite pipe of Onverwacht, Bushveld, South Africa, and from placer deposits in Burma and Ecuador in the last century.

Altogether, more than 50 samples of PGM from various deposits worldwide are in the collection of the Mineralogical-Petrographical Department of the Museum of Natural History, Vienna, thus being certainly one of the largest of the world.

Sample Selection

Ten different samples of PGM from placer deposits worldwide, including small pieces of the large nugget from Nizhni Tagil, Urals, were analyzed (Tab. 1). The chosen samples

Tab. 1: Mineralogy of the analyzed samples

No.	Locality	grains	analyses	Groundmass	Inclusions, rims etc.
A.i. 731	Russia, Urals, Nizhni Tagil	8	32	Pt-Fe alloys	iridium, laurite cuproiridsite
G 656	Russia, Altai, Kuzenelig	1	11	iridium	Pt-Fe alloys rutheniridosmine
		1	44	ruthenium	Pt-Fe alloys, laurite irarsite-hollingworthite-series, Ru-oxide
		1	23	Pt-Fe alloys	osmium, sperrylite
G 657	Russia, Altai, Kuzenelig	4	31	ruthenium	Pt-Fe alloys laurite, erlichmanite
		4	26	Pt-Fe alloys	osmium, iridium, rutheniridosmine laurite, erlichmanite rhodarsenite-palladodymite-series cherepanovite, sperrylite
A.a. 3586	USA, California	8	10	osmium	—
		7	13	ruthenium	osmium, irarsite
		3	7	iridium	osmium, irarsite
A.a. 5432	USA, Oregon, Rogue River	12	28	osmium	Pt-Fe alloys irarsite, "(Os,Ir) ₂ (Cu,Fe)S"
		11	19	iridium	Pt-Fe alloys, osmium
		2	3	ruthenium	—
		1	3	laurite	—
A.a. 5431	USA, Oregon, Rogue River	13	59	Pt-Fe alloys	cuprorhodsite "(Rh,Pt)S", "Rh ₃ S ₄ "
		2	7	osmium	—
		2	2	iridium	Pt-Fe alloys
		6	22	laurite	osmium
		8	11	gold	—
A.a. 2047	Brazil	3	38	Pt-Fe alloys	osmium, hongshiite, tulameenite bowieite, chalcocite, silicate
A.a. 2687	Brazil	5	37	native Platinum	osmium
		1	5	Pt-Fe alloys	osmium, hongshiite
M 7203	Brazil	2	14	osmium	laurite, erlichmanite
		1	10	ruthenium	Os-Ir-Ru-Pt alloys
H 2340	Brazil, Minas Gerais, Serro	2	21	Pt-Pd-Hg alloys	—
		1	11	Pt-Pd-Au-Hg alloys	potarite

Note: The minerals are listed in the following order: alloys – sulphides – sulpharsenides – arsenides – oxides – unnamed phases

were mainly from localities which were not described previously in the extensive paper by CABRI et al. (1996), or which showed an unusual morphology. It is understandable that not the whole sample of the mineral collection could be analyzed. Therefore the selection under the stereo microscope was somewhat biased towards grains with different external appearance or colour.

The following samples were analyzed:	no. of grains	no. of analyses
no. A.i. 731 Russia, Urals, Nizhni Tagil (nugget)	8	32
no. G 656 Russia, Altai, Kuzenelig	3	78
no. G 657 Russia, Altai, Kuzenelig	8	57
no. A.a. 3586 USA, California	18	30
no. A.a. 5432 USA, Oregon, Rogue River	26	53
no. A.a. 5431 USA, Oregon, Rogue River	31	101
no. A.a. 2047 Brazil	3	38
no. A.a. 2687 Brazil	6	42
no. M 7203 Brazil	3	24
no. H 2340 Brazil, Minas Gerais, Serro	3	32

Analytical Methods

The selected grains were first mounted as SEM stubs to examine the morphology and to obtain preliminary information on the composition. A Philips 525M scanning electron microscope (SEM) equipped with an EDAX DX4 energy-dispersive system was used for qualitative analyses. Later, the grains were embedded in araldite and polished with diamond powder on a Dürener polisher for optical examination and quantitative analyses, using a CAMECA CAMEBAX Microbeam electron microprobe. The analytical conditions were: accelerating voltage 20 kV, specimen current 30 nA and measurement time 10 s. The following X-ray lines and standards were used: Ru L α , Rh L α , Os M α , Ir L α , Au L α , Ag L β , Cu K α , Ni K α , Co K α , Se L α , Te L α , Bi M α (metal), Pt L α , Fe K α (synthetic Pt₃Fe alloy), Pd L α (synthetic PdS), Pb M α (galena [PbS]), Hg M α (synthetic HgS), S K α (synthetic PtS), As L α (synthetic GaAs), and Sb L α (stibnite [Sb₂S₃]). Raw data were corrected using the PAP program supplied by CAMECA. Additional corrections were performed for enhancement of the elements Rh, Pd, Ag, Cu, As, and Sb by secondary lines. Detection limits of the analyzed elements were 0.05 wt.%.

In total, 487 quantitative electron-microprobe analyses were carried out on 109 selected grains of the 10 samples.

Mineralogy and Discussion

Sample no. A.i. 731 Russia, Urals, Nizhni Tagil

From the most important platinum producing region of the world until the beginning of the 20th century (WEISER 2002) this nugget is the most spectacular specimen of the whole PGM collection of the museum (Fig. 1a). The sample, labeled as platinum, weighs 6200 g, is 9 cm across, well rounded, and in depressions intergrown with chromite or partly covered with thin layers of iron oxide/hydroxide. It is obvious that it was not possible to analyze a large piece of this specimen for the exact identification of the texture and chemical composition. The microprobe analyses were carried out on small pieces of the rim, up to several hundred μm in size.

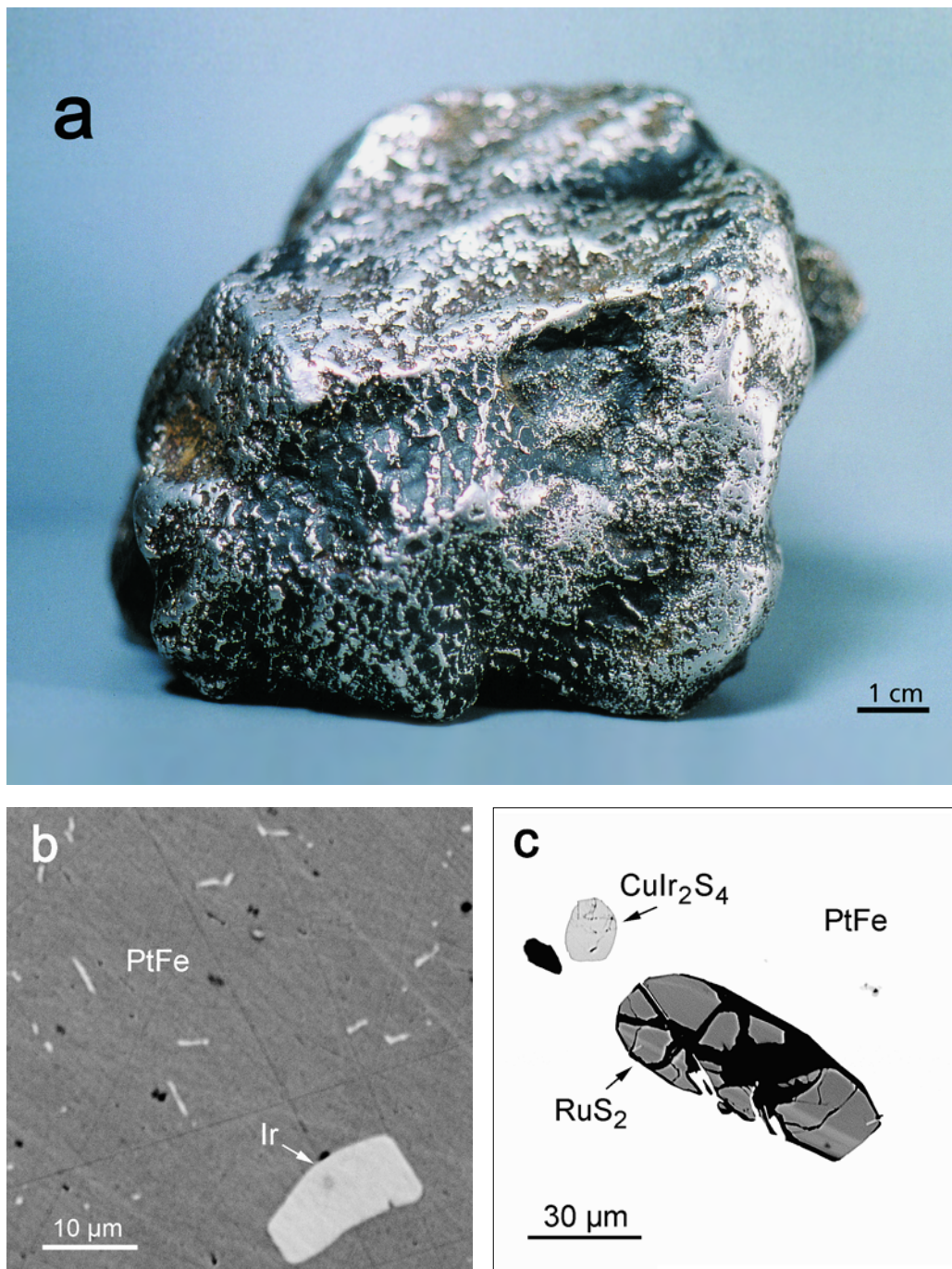


Fig. 1: (a) Giant Pt-Fe nugget from Nizhni Tagil, Urals (no. A.i. 731). (b) Back scattered electron image (BSE) of tabular inclusions of iridium (Ir). (c) BSE of rounded inclusions of laurite (RuS_2) and cuproiridsite (CuIr_2S_4).

Tab. 2: Selected electron microprobe analyses of PGM

No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
weight per cent																
Ru	0	0,28	36,19	0	0	0	0	0	0	0	0	0,71	0	0,63	0,38	0,89
Rh	0,37	1,72	0,67	12,33	0	0	0	0	0	0	0	25,21	33,04	45,02	61,71	0
Pd	0,21	0	0	0	33,90	37,52	19,51	50,79	50,99	45,61	41,19	16,46	30,86	2,75	0,41	0
Os	0	26,47	22,64	0	0	0	0	0	0	0	0	0	0	0	0,27	44,08
Ir	2,64	62,53	5,34	45,20	0	0	0	0	0	0	0	6,83	0,47	0,65	0,21	33,03
Pt	87,36	8,08	0,63	5,40	64,31	61,79	79,55	0,25	35,22	44,81	54,39	17,67	10,47	30,07	7,47	0
Fe	6,99	0	0,16	0,18	0	0	0	0	0	0	0	0	0	2,12	0,60	2,04
Cu	2,01	0	0	10,55	0	0	0	0	0	0	0	0	0	0,20	0,40	12,04
Ni	0,31	0	0	1,04	0	0	0	0	0	0	0	0	0	0,47	0	0
S	0	0	32,46	23,70	0	0	0	0	0	0	0	3,30	0	17,10	26,85	8,23
Se	0	0	0	0	0	0	0	0	0,17	0,24	0	0	0	0	0	0
As	0	0	0	0	0	0	0	0	0	0	0	29,54	24,99	0	0	0
Ag	0	0	0	0	0	0,25	0,23	1,06	0	0	0,23	0	0	0	0	0
Au	0	0	0	0	0	0	0	3,45	0	0	0	0	0	0	0	0
Hg	0	0	0	0	1,41	0	0	44,32	13,36	8,82	4,11	0	0	0	0	0
Total	99,89	99,08	98,09	98,40	99,62	99,56	99,29	99,62	99,74	99,48	99,92	99,72	99,83	99,01	98,30	100,31
atomic proportions																
Ru	0	0,005	0,702	0	0	0	0	0	0	0	0	0,014	0	0,026	0,018	0,039
Rh	0,006	0,032	0,013	0,641	0	0	0	0	0	0	0	0,476	0,962	0,718	2,791	0
Pd	0,003	0	0	0	0,486	0,524	0,469	0,657	0,658	0,607	0,562	0,300	0,870	0,042	0,018	0
Os	0	0,265	0,233	0	0	0	0	0	0	0	0	0	0	0	0,007	1,036
Ir	0,022	0,619	0,055	1,258	0	0	0	0	0	0	0	0,069	0,007	0,006	0,005	0,768
Pt	0,712	0,079	0,006	0,148	0,503	0,472	0,527	0,002	0,248	0,325	0,405	0,176	0,161	0,253	0,178	0
Fe	0,199	0	0,006	0,017	0	0	0	0	0	0	0	0	0	0,062	0,050	0,163
Cu	0,050	0	0	0,888	0	0	0	0	0	0	0	0	0	0,005	0,029	0,888
Ni	0,008	0	0	0,095	0	0	0	0	0	0	0	0	0	0,013	0	0
S	0	0	1,985	3,953	0	0	0	0	0	0	0	0,200	0	0,875	3,904	1,147
Se	0	0	0	0	0	0	0	0	0,003	0,004	0	0	0	0	0	0
As	0	0	0	0	0	0	0	0	0	0	0	0,766	1,000	0	0	0
Ag	0	0	0	0	0	0,004	0,004	0,013	0	0	0,003	0	0	0	0	0
Au	0	0	0	0	0	0	0	0,024	0	0	0	0	0	0	0	0
Hg	0	0	0	0	0,011	0	0	0,304	0,091	0,062	0,030	0	0	0	0	0

Analyses no. 1-4 nugget, Nizhni Tagil, Urals (sample no. A.i. 731): no. 1 matrix, no. 2 inclusion of iridium, no. 3 inclusion of laurite, no. 4 inclusion of cuproiridsite; no. 5-7 dendritic grain of Pt-Pd-Hg alloys from Serro, Minas Gerais, Brazil (sample no. H 2340): no. 5 core, no. 6 inclusion, no. 7 margin; no. 8-11 botryoidal grain of Pt-Pd-Hg alloys from Serro, Minas Gerais, Brazil (sample no. H 2340): no. 8 core, no. 9 inner zone, no. 10 outer zone, no. 11 margin; no. 12 cherepanovite, Altai, Russia (sample no. G 657); no. 13 rhodarsenite-palladodymite, Altai, Russia (sample no. G 657); no. 14 unnamed phase (Rh,Pt)As, Rogue River, Oregon, USA (sample no. A.a. 5431); no. 15 unnamed phase Rh₃S₄, Rogue River, Oregon, USA (sample no. A.a. 5431); no. 16 unnamed phase (Os,Ir)₂CuS, Rogue River, Oregon, USA (sample no. A.a. 5432)

The analyses confirm the description of the nugget as platinum. The matrix is homogeneous in some parts, but in others it contains euhedral to subhedral inclusions of iridium, up to 75 μm in size. The matrix contains between 86.8 and 88.2 wt.% Pt, 6.4-7.8 wt.% Fe, up to 3.3 wt.% Ir, up to 2.2 wt.% Cu, traces of Rh, Pd, and Ni, but no Ru and Os. This corresponds to "isoferroplatinum" with the general formula $\text{Pt}_{73.1-75.2}\text{Fe}_{24.8-26.9}$ (Table 2, no. 1). According to the nomenclature of platinum-iron alloys (CABRI & FEATHER 1975), this identification is uncertain because only compositional data are known, but not the crystal structure, so it has to be named platinum-iron alloy or Pt-Fe alloy.

The predominant inclusions are droplets, needles and euhedral crystals of iridium (Fig. 1b), irregularly distributed and up to 75 μm in size. The grains contain between 0.0 and 30.7 wt.% Os, 89.9 and 57.7 wt.% Ir, 6.8 and 10.0 wt.% Pt, 1.5 and 3.1 wt.% Rh, traces of Ru, but no Pd (Table 2, no. 2). The analyses with the calculated formula $[\text{Ir}_{58.8-63.2}\text{Os}_{0.0-31.6}\text{Pt}_{8.0-10.0}]$ plot in the triangular diagram Ir-Os-Pt. Notably, WYSSOTZKY (1913) already found hexagonal platelets of osmium, oriented parallel to the crystal faces, and intergrown lamellae of iridium by etching euhedral platinum grains from Nizhni Tagil.

Subordinately there are up to 100 μm large tabular inclusions of laurite with the composition of $[(\text{Ru}_{0.61-0.78}\text{Os}_{0.17-0.32}\text{Ir}_{0.04-0.07})\text{S}_2]$ (Fig. 1c, Table 2, no. 3). Laurite grains contain up to 1.3 wt.% Pt and 0.9 wt.% Rh. One 15 μm large rounded inclusion is a rhodium-rich cuproiridsite with the formula $[(\text{Cu}_{0.89}\text{Ni}_{0.10}\text{Fe}_{0.02})_{1.01}(\text{Ir}_{1.26}\text{Rh}_{0.64}\text{Pt}_{0.15})_{2.05}\text{S}_{3.94}]$ (Fig. 1c, Table 2, no. 4).

The composition of the nugget and the properties of the inclusions are a clear evidence for their primary origin. The results of the analyses are also in good agreement with the detailed description of the placer deposits of Nizhni Tagil area by several authors, like WYSSOTZKY (1913), DUPARC & TIKONOWITCH (1920), RAZIN (1976), STUMPF & TARKIAN (1976), CABRI et al. (1996) and WEISER (2002). All of them found that Pt-Fe alloys are the main PGM in the placers of the Ural Mountains, associated with Alaskan-type ultramafic complexes.

Sample no. G 656 Russia, Altai, Kuzenelig

The sample is labeled "sisserskite" and was collected in 1892. "Sisserskite" or "sysstertskite" ("osmium" after the classification by HARRIS & CABRI 1991) was discovered in the Urals in 1834-1835 and described by HAIDINGER in 1845. The sample weighs 11.3 g and contains up to 5 mm large knobby, rounded and partly flattened grains with a metallic or dark lustre. Qualitative analyses showed that the sample consists of approximately equal parts of Os-Ir-Ru- and Pt-Fe alloys.

One lobate grain, 2 mm in size, is iridium (Fig. 2a) with the composition $[\text{Ir}_{53.8}\text{Os}_{27.4}\text{Ru}_{18.8}]$ and contains up to 13.4 wt.% Pt and up to 1.4 wt.% Rh, but no Pd. The analysis plots in the miscibility gap of the Os-Ir-Ru diagram (Fig. 3). The grain contains drop-like inclusions of Pt-Fe alloy with the composition of $[\text{Pt}_{70}\text{Fe}_{30}]$, so that the high Pt content of the matrix could base on submicroscopic inclusions of Pt-Fe alloy. On the other hand the Fe content of the iridium grain is only 0.8 wt.%. This is similar to Pt-free flame-like exsolution lamellae of rutheniridosmine of the same grain (Fig. 4a). Similar relationships of Pt-rich iridium were reported by KRSTIĆ & TARKIAN (1997) from Yugoslavia and by WEISER & BACHMANN (1999) from Papua New Guinea, explained by the latter to be the result of formation at higher temperature, or to the fact that the miscibility gap in the systems Ru-Ir (RAUB 1964) and Os-Ir (RUDMAN 1967) applies to Pt-free systems.

The second analyzed grain, 4 mm in size and rounded with lobed outlines, is ruthenium with the composition of 27.7 at.% Os, 27.1 at.% Ir, and 45.2 at.% Ru, containing up to 5.0 wt.% Pt, 1.6 wt.% Rh, but no Pd (Fig. 3). Most frequent are tabular inclusions in the centre and flame-like inclusions on the grain boundary, up to 250 μm in length, of Pt-Fe alloys with a composition $[\text{Pt}_{70-73}\text{Fe}_{30-27}]$, containing up to 2.3 wt.% Ir, traces of Rh, Ru, Ni and Cu, but no Pd and Os (Fig. 4a). Other inclusions are tabular grains of laurite, in which Os presumably is substituted by Rh $[(\text{Ru}_{0.92}\text{Rh}_{0.05}\text{Ir}_{0.03})\text{S}_2]$, and drop-like grains of hollingworthite $[(\text{Rh}_{0.54}\text{Ir}_{0.30}\text{Ru}_{0.19})_{1.03}\text{As}_{0.97}\text{S}]$. Alteration rims consist of an inner zone of ruarsite and an outer one of irarsite. Inhomogeneous rims with numerous cracks have low optical reflectivity, show low contrast of the BSE pictures, a low total of the microprobe analyses (58.4 and 62.0 wt.%) and might be a Ru oxide.

The last analyzed grain of the sample is rounded and 2.5 mm in size. The grain is Pt-Fe alloy with a step faced surface, partly intergrown with sperrylite (Fig. 2c) and has a composition of $[\text{Pt}_{77-80}\text{Fe}_{23-20}]$, containing 4.4 wt.% Ir, 4.2 wt.% Os, 2.2 wt.% Ru, and 1.6 wt.% Cu, but no Rh, Pd and Ni. Inclusions are tabular, partly zoned crystals of osmium with a core of approximately $[\text{Os}_{85.3}\text{Ir}_{12.2}\text{Ru}_{2.5}]$ and a rim of $[\text{Os}_{78.3}\text{Ir}_{11.7}\text{Ru}_{10.0}]$. Porous, multi-phase sperrylite in which As is partly substituted by S occurs in fractures and rims. The sperrylite is presumably the product of later low-temperature alteration.

Sample no. G 657 Russia, Altai, Kuzenelig

The sample is labeled with "newjanskite" and the collection date of 1892. This mineral – "iridium" according to the classification by HARRIS & CABRI (1991) – was also first discovered in the Ural Mountains and described by HÄIDINGER (1845). The sample weighs 9.7 g, consists of up to 4 mm large, rounded platelets of metallic or grey colour and has equal parts of Os-Ir-Ru- and Pt-Fe alloys.

All analyzed grains of Os-Ir-Ru-alloys are ruthenium, flattened with lobed outlines and up to 3 mm in size, (Fig. 2b). The individual grains are homogeneous in composition, but compositions differ from grain to grain. The compositions vary between 24.6 and 32.1 at.% Os, 21.3 and 24.6 at.% Ir and 46.6 and 51.6 at.% Ru (Fig. 3). The grains also contain minor amounts of up to 5.0 wt.% Pt, 3.6 wt.% Rh, and 0.2 wt.% Pd (in one grain only). Some of the ruthenium grains are characterized by parallel schlieren of ruthenium $[\text{Ru}_{46.5}\text{Os}_{32.4}\text{Ir}_{21.1}]$ and Pt-Fe alloy $[\text{Pt}_{67.4}\text{Fe}_{32.6}]$. Inclusions are rounded tabular grains, up to 100 μm in size, of Pt-Fe alloy $[\text{Pt}_{76.4}\text{Fe}_{23.6}]$, containing up to 4.7 wt.% Rh and up to 4.1 wt.% Ni. Alteration rims of ruthenium have mostly an inner zone of erlichmanite $[(\text{Os}_{0.46}\text{Ru}_{0.34}\text{Ir}_{0.21})_{1.01}\text{S}_{1.99}]$ and an outer zone of laurite $[(\text{Ru}_{0.76}\text{Ir}_{0.23}\text{Os}_{0.01})_1\text{S}_2]$. Occasionally, the alteration rim is a network of needles built of erlichmanite (Fig. 4b).

The small Pt-Fe alloy grains are lobed, up to 150 μm in size, with a composition of $[\text{Pt}_{71.0}\text{Fe}_{29.0}]$ and contain up to 2.8 wt.% Ir, up to 2.0 wt.% Rh, and 0.8 wt.% Ni. The core of one of the grains, and droplet inclusions of a second, are enriched in Fe ($\text{Pt}_{67.0}\text{Fe}_{33.0}$), Rh (4.8 wt.%), and Ni (2.4 wt.%). The largest grain of Pt-Fe alloy is elongated, 700 μm in size, and has a composition of $[\text{Pt}_{78.3}\text{Fe}_{21.7}]$, containing up to 10.0 wt.% Ir, 3.3 wt.% Os, 1.6 wt.% Ru, 1.2 wt.% Cu, but no Rh and Ni, compared with the smaller grains. Inclusions are mainly tabular grains of osmium $[\text{Os}_{60.2}\text{Ir}_{33.6}\text{Ru}_{6.2}]$, iridium $[\text{Ir}_{46.6}\text{Os}_{32.1}\text{Ru}_{21.3}]$, and rutheniridosmine $[\text{Ir}_{47.3}\text{Os}_{43.3}\text{Ru}_{9.4}]$. Also common as inclusions are euhedral to anhedral, partly zoned grains of laurite $[(\text{Ru}_{0.89}\text{Os}_{0.04}\text{Ir}_{0.10})_{1.03}\text{S}_{1.97}]$ and erlichmanite $[(\text{Os}_{0.68}\text{Ru}_{0.29}\text{Ir}_{0.08})_{1.05}\text{S}_{1.95}]$.

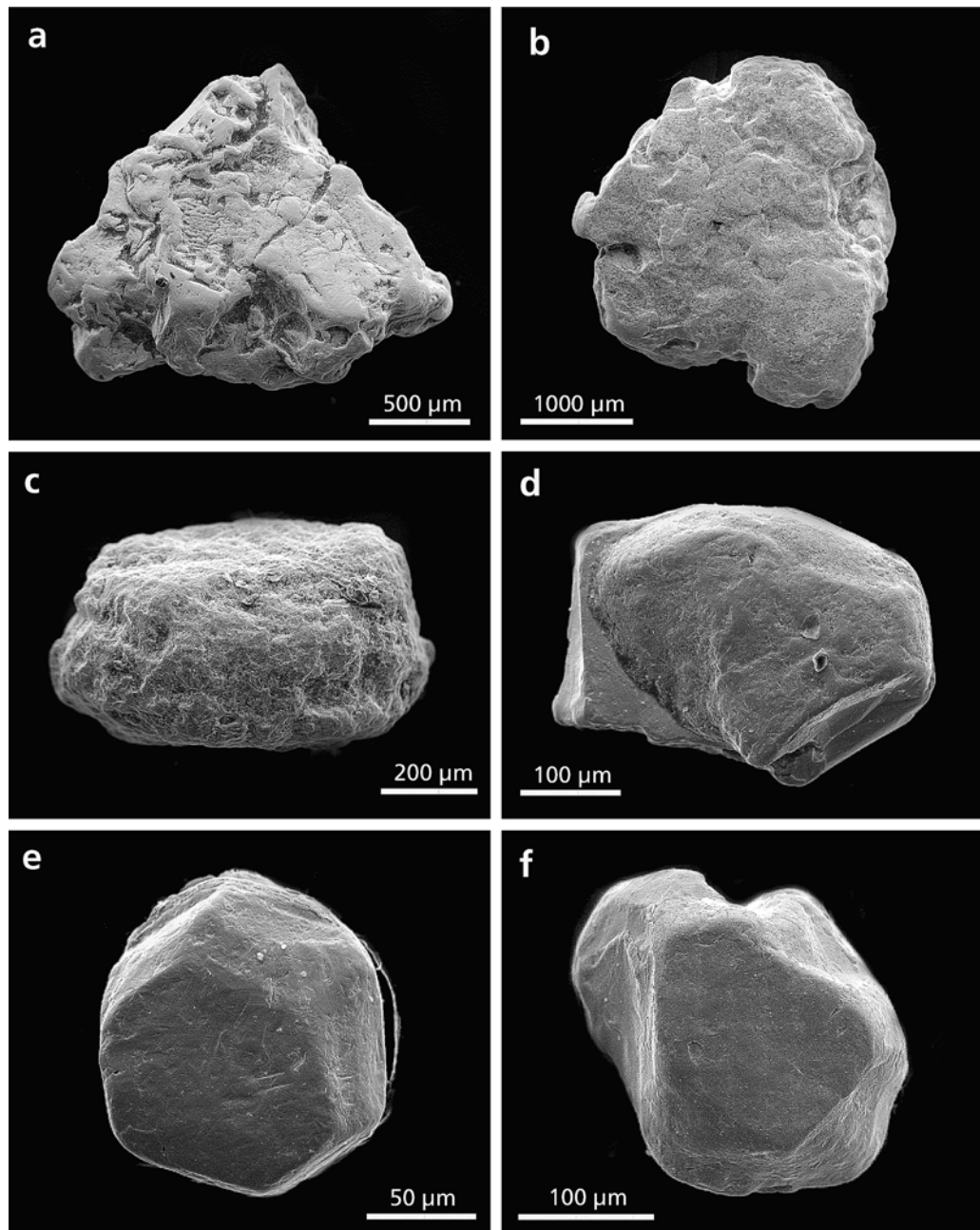


Fig. 2: Scanning electron images of Os-Ir-Ru alloys. (a) Angular grain of iridium (Altai, Russia, no. G 656). (b) Flattened grain of ruthenium (Altai, Russia, no. G 657). (c) Rounded step-faced grain of Pt-Fe alloy, partly covered by sperrylite (Altai, Russia, no. G 656). (d) Platelet of osmium covered with iridium (California, USA, no. A.a. 3586). (e) Euohedral crystal of ruthenium with partly rounded edges (California, USA, no. A.a. 3586). (f) Rounded grain of osmium with partly well preserved crystal faces (California, USA, no. A.a. 3586).

Few drop-like inclusions, up to 25 µm in size, are minerals of the rhodarsenite [(Rh,Pd)₂As] – palladodymite [(Pd,Rh)₂As] solid solution series with the composition [(Rh_{0.97}Pd_{0.87}Pt_{0.16})₂As] (Table 2, no. 13). The inner part of the thin alteration crust of the Pt-Fe alloys has a composition of [(Rh_{0.48}Pd_{0.30}Pt_{0.18}Ir_{0.07})_{1.03}(As_{0.77}S_{0.20})_{0.97}] or generally [(Rh,Pd)As] (Table 2, no. 12). This could be cherepanovite, first described from Kamchatka by RUDASHEVSKY et al. (1985). However, the high contents of Pd, Pt, and S are conspicuous, compared with the nearly pure RhAs described by RUDASHEVSKY et al. (1985). The outer part of the alteration rim is sperrylite with traces of Rh, Pd, and Ir and As partly substituted by S. Sperrylite also occurs in fractures of the Pt-Fe alloy grain.

There is no reference in the literature on the locality "Kuzenelig" in the Altai. According to TOLSTYKH (pers. comm., 2002), this may be due to an incorrect transcription of the Kuznetsk-Alatau, where many PGM occurrences are well-known, e.g., in the placers of the Taidon, Nizhnyaya Ters', Srednyaya Ters', Us, Kondoma, Mrassu, Lebed', Kiya, Kundat, Sarala rivers. It seems, that there hardly exists a river in some areas of the Kuznetsk-Alatau, in which no PGM were found during gold mining (KRIVENKO et al. 1994). One of the first descriptions of PGM in the Kuznetsk-Alatau area was by WYSSOTZKY (1933). More detailed information has come from microprobe analyses (e.g., KRIVENKO et al. 1994; TOLSTYKH & KRIVENKO 1994; TOLSTYKH et al. 1997; TOLSTYKH et al. 2002).

KRIVENKO et al. (1994) found in PGM-bearing gold placers of the Altai-Sayan region three different types of PGM associations: (1) Ru-Ir-Os alloys, related to ultramafic rocks of ophiolite belts; (2) Pt-Fe alloys, related to zoned Alaskan-type intrusions; and, (3) sperrylitic assemblages, related to hydrothermal alteration of gabbroic complexes. This model is modified and extended for Sibiria and Russian Far East by TOLSTYKH et al. (2002). In their opinion the Ru-Ir-Os assemblage, related to ophiolitic complexes, consists of an early Os-Ir and a later Pt-Fe – Ru association. Their second association dominantly consists of Ru-Os-Ir alloys and subordinately of Pt-Fe alloys. The source of this association is still unknown. The third association are Pt-Fe alloys, related to Alaskan-type complexes, with Pt₃Fe as the dominant phase. An early isoferroplatinum – osmium and a later isoferroplatinum – iridium paragenesis is reported from the source rocks of this association. Typical alteration products are PGE sulpharsenides and laurite in the Os-Ir-Ru association and cooperite and sperrylite in the Pt-Fe alloys association (TOLSTYKH et al. 2002).

Due to the similar composition of the analyzed PGM of the samples G 656 and G 657 and of the PGM in the large data base by TOLSTYKH et al. (2002) it can be assumed that the samples G 656 and G 657 presumably originate from placer deposits related to ophiolite complexes in the Kuznetsk-Alatau region.

Sample no. A.a. 3586 USA, California

The sample is labeled "osmiridium". The grains of the sample are mainly platelets (Fig. 2d) or euhedral to subhedral with rounded edges (Figs. 2e, f) mainly up to 250 µm and occasionally up to 500 µm in size. The surface is smooth and has a silvery lustre. Rounded grains of chromite and ilmenite occur subordinately.

All analyzed grains are Os-Ir-Ru alloys, dominantly osmium (8) and ruthenium (7); two grains are iridium and one is a platelet of osmium covered with a rounded grain of iridium (Fig. 2d).

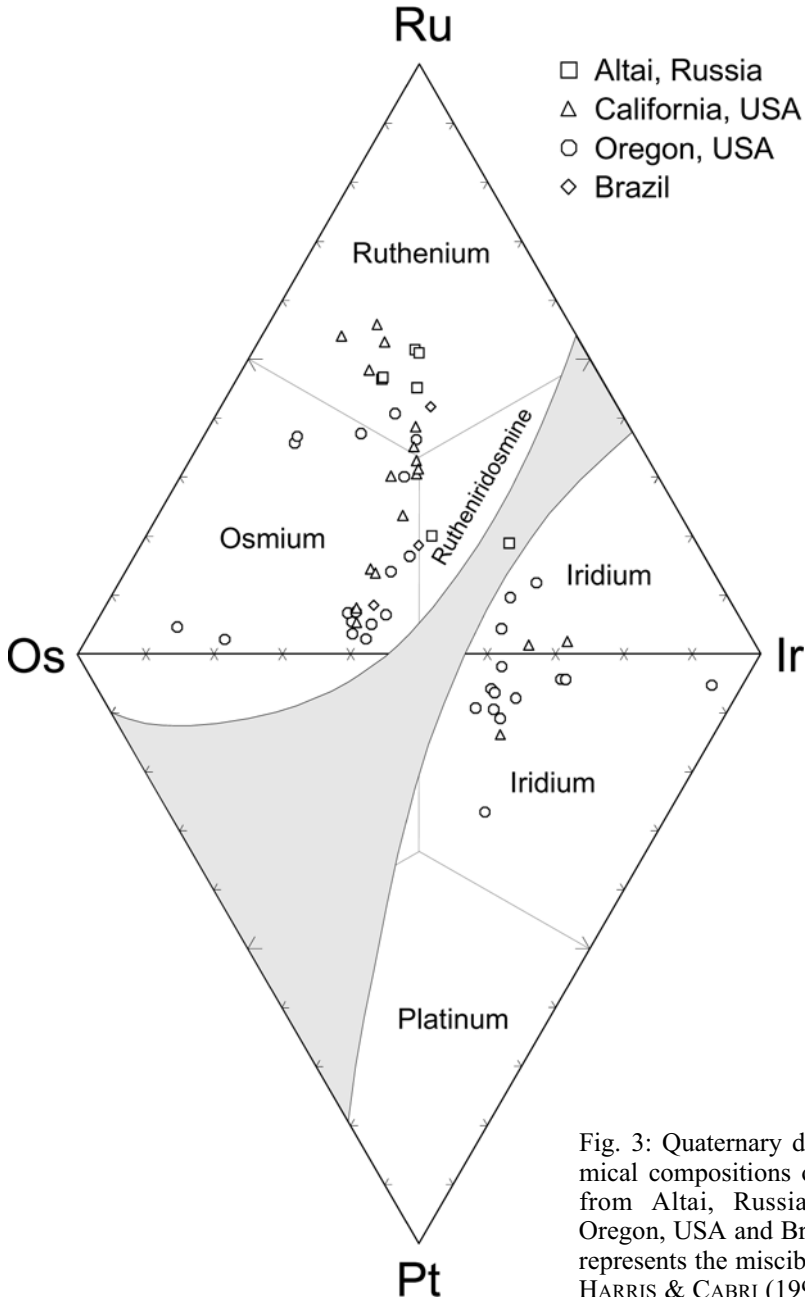


Fig. 3: Quaternary diagram showing chemical compositions of Os-Ir-Ru-Pt alloys from Altai, Russia; California, USA; Oregon, USA and Brazil. The shaded area represents the miscibility gap proposed by HARRIS & CABRI (1991).

The grains of osmium are homogeneous in composition and free of inclusions. However, compositions vary from grain to grain. A first group of PGM grains has an average composition of 53.8 at.% Os, 36.9 at.% Ir, and 9.2 at.% Ru, and a second one has 36.6 at.% Os, 33.7 at.% Ir, and 29.7 at.% Ru (Fig. 3). The Ir content is nearly constant whereas the

content of Os can be substituted by Ru, or vice versa. The osmium grain rimmed with iridium (Fig. 2d) contains 49.5 at.% Os, 36.7 at.% Ir, and 13.8 at.% Ru. All analyzed grains contain up to 4.8 wt.% Pt and up to 0.8 wt.% Rh, but only two 0.2 wt.% Pd.

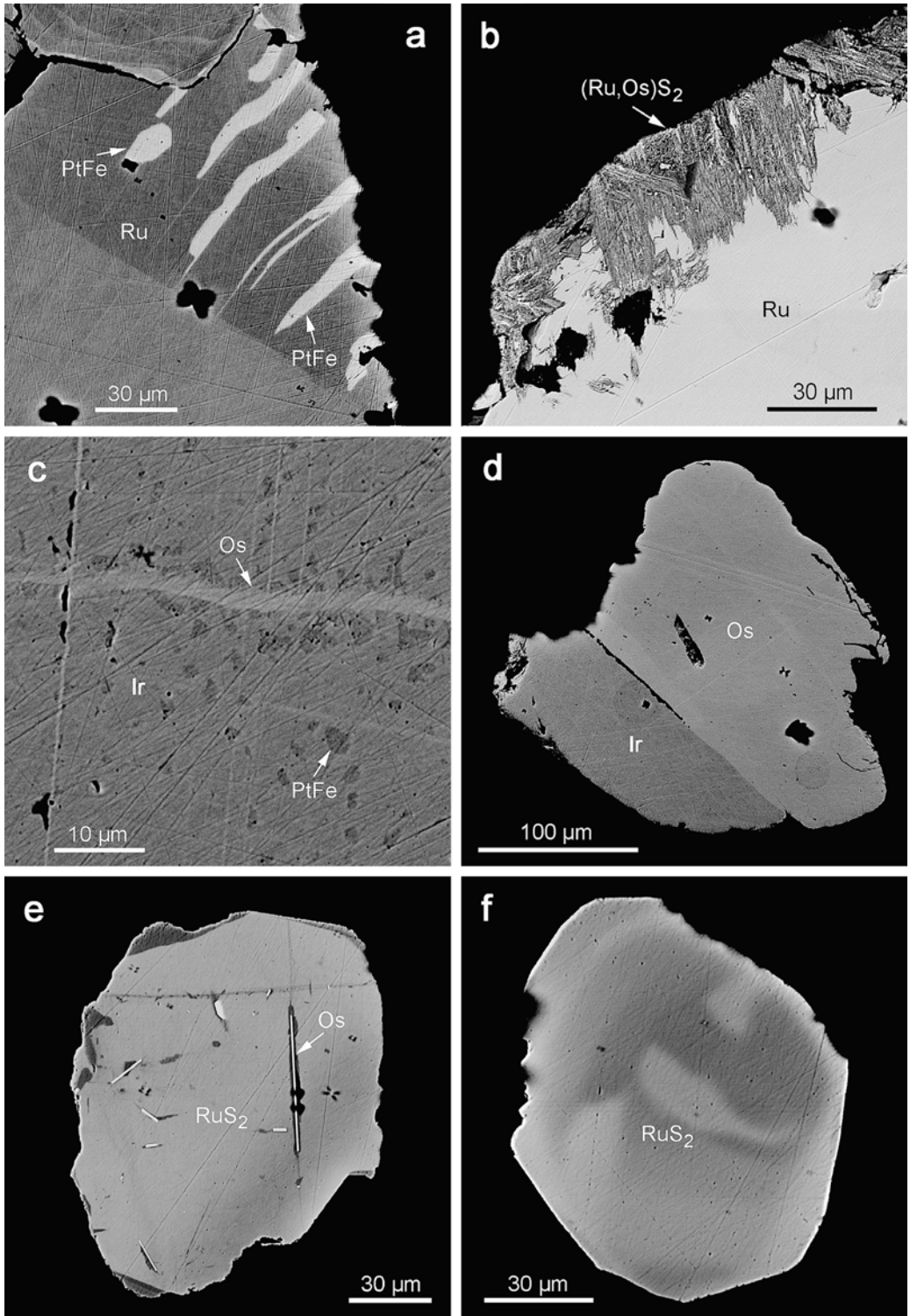
Ruthenium is also homogeneous; only droplets of osmium up to 15 µm in size were found in one grain. The composition of ruthenium varies between the grains, similar to osmium. One group has a higher content of ruthenium [Ru_{52.7}Os_{31.1}Ir_{16.2}] than the other one [Ru_{36.8}Os_{32.2}Ir_{31.0}] (Fig. 3), but all grains contain up to 5.0 wt.% Pt, 1.6 wt.% Rh, and 0.4 wt.% Pd. In one grain of ruthenium, Pt is a major component instead of Ir. Therefore, the analysis [Ru_{66.4}Os_{22.2}Pt_{11.4}] plots in the Os-Ru-Pt diagram. It also contains 10.0 wt.% Ir, 1.0 wt.% Rh, and 0.4 wt.% Pd. Few grains show small rims of irarsite with the composition [(Ir_{0.61}Ru_{0.21}Pt_{0.20})_{1.02}AsS_{0.98}] as alteration products.

The two analyzed grains of iridium are very similar in composition and contain 67.9 at.% Ir, 30.2 at.% Os, 1.9 at.% Ru, traces of Pt (1.6 wt.%), and Rh (0.2 wt.%), but no Pd (Fig. 3). Small inclusions in one of the iridium grains are osmium with 62.4 at.% Os and 37.6 at.% Ir, but without any other PGE. The same grain contains inclusions of irarsite with the formula [(Ir_{0.90}Ru_{0.08}Os_{0.04})_{1.02}As_{0.84}S_{1.14}]. The iridium grain covering osmium (Fig. 2d) contains more Pt than Ru. Therefore, the analysis with the formula [Ir_{55.3}Os_{31.0}Pt_{13.7}] plots in the Os-Ir-Pt diagram.

Since mid 1800, platinum was produced as a byproduct of gold placer mining in several counties in California west of the Sierra Nevada (QUIRING 1962). MERTIE (1969) reported the presence of large nuggets of platinum from the Trinity River, but precise mineralogical and chemical investigations of the platinum-bearing placers are scarce. SNETSINGER (1971a, 1971b, 1972) described the new minerals erlichmanite and osarsite from the Trinity River and Gold Bluff, respectively, Humboldt County; and also a Pt-Fe alloy nugget with lamellae of ruthenium from the Trinity River. LEGENDRE & AUGÉ (1993) carried out a mineralogical study of a PGM concentrate from Trinity County and found that Os-Ir- and Pt-Fe alloys are the main minerals, whereas laurite-erlichmanite are less common. The inclusions of base-metal sulphides in the main PGM indicate a primary origin, probably from the ophiolitic complex of Trinity County. CABRI et al. (1996) reported Pt-Fe alloys with exsolution lamellae of osmium and iridium of a sample from California whose exact origin is unknown. Osmium isotope measurements on PGM from Mariposa County by LYON et al. (1997) evidence a mantle origin of the PGM from ultramafic intrusions followed by weathering, transport and deposition in placers.

The composition of the analyzed Os-Ir-Ru alloys is similar to the results by LEGENDRE & AUGÉ (1993) and CABRI et al. (1996) and suggest a primary origin from ophiolitic complexes.

Fig. 4: Back scattered electron images of PGM. (a) Flame-like lamellae and drop-like inclusions of Pt-Fe alloys (PtFe) in ruthenium (Altai, Russia, no. G 656). (b) Alteration rim of needle-like network of erlichmanite [(Ru,Os)S₂] on ruthenium (Ru) (Altai, Russia, no. G 657). (c) Tabular and drop-like inclusions of Pt-Fe alloys (PtFe) and lamellae of osmium (Os) in iridium (Ir) (Rogue River, Oregon, USA, no. A.a. 5432). (d) Composite grain of osmium (Os) and iridium (Ir) (Rogue River, Oregon, USA, no. A.a. 5432). (e) Laurite (RuS₂) with inclusions of needle-like osmium (Os) (Rogue River, Oregon, USA, no. A.a. 5431). (f) Schlieren-like variation in composition of laurite (RuS₂) (Rogue River, Oregon, USA, no. A.a. 5431).



Sample no. A.a. 5432 USA, Oregon, Rogue River

The fine-grained sample is labeled "iridosmine" and contains euhedral to anhedral grains, partly rounded or with rounded edges, up to 350 μm in size (Figs. 5a-c). The smooth surface of the PGM shows silvery or dark lustre. Monazite, ilmenite, titanite, and cassiterite are also present in the concentrate.

The dominant analyzed PGM are osmium (11) and iridium (10) in nearly equal proportions, followed by composite grains of osmium and iridium (2), ruthenium (2), and laurite (1). The Os-Ir-Ru alloys are homogeneous in composition, and with the exception of one grain of osmium and of iridium, they are free of inclusions. The chemical compositions of iridium vary from grain to grain, but all grains are characterized by very low Ru contents.

Most osmium grains have a composition of $[\text{Os}_{53.2}\text{Ir}_{38.9}\text{Ru}_{7.9}]$, two are richer in Os $[\text{Os}_{80.1}\text{Ir}_{16.3}\text{Ru}_{3.6}]$, two others are enriched in Ru $[\text{Os}_{50.1}\text{Ir}_{13.7}\text{Ru}_{36.2}]$ (Fig. 3) and constantly contain up to 2.2 wt.% Rh, sporadically up to 4.7 wt.% Pt, whereas only two grains have up to 0.3 wt.% Pd. One osmium grain contains cubic inclusions of Pt-Fe alloys with a composition close to Pt_3Fe and drop-like inclusions of irarsite with the composition $[(\text{Ir}_{0.97}\text{Rh}_{0.01}\text{Pt}_{0.01})_{0.99}\text{As}_{1.04}\text{S}_{0.97}]$ and that of an unnamed Os-Ir-Fe-S phase with the generalized formula $[(\text{Os},\text{Ir})_2(\text{Cu},\text{Fe})\text{S}]$ (Table 2, no. 16).

Only one grain of iridium with the composition $[\text{Ir}_{58.6}\text{Os}_{31.9}\text{Ru}_{9.6}]$ plots in the Os-Ir-Ru diagram (Fig. 3). Predominantly in all other grains Ru is substituted by Pt leading the analyses with the average composition $[\text{Ir}_{60.4}\text{Os}_{33.0}\text{Pt}_{6.6}]$ to plot in the Os-Ir-Pt diagram (Fig. 3). Figure 5b shows a rounded grain of nearly pure iridium with the composition of $[\text{Ir}_{90.2}\text{Os}_{4.5}\text{Pt}_{5.3}]$. The iridium grains contain minor amounts of Ru (0.2-6.7 wt.%) and Rh (0.2-4.4 wt.%), but no Pd. One grain of iridium contains lamellae of osmium and drop-like inclusions of Pt-Fe alloys with a composition close to Pt_3Fe (Fig. 4c).

The composite grains of osmium and iridium (Fig. 4d) have the same composition as the discrete grains of osmium and iridium.

The two analyzed grains of ruthenium are free of inclusions. Chemical analyses showed that ruthenium itself has a Ru content similar to these of Os and Ir. Therefore, the mean composition $[\text{Ru}_{38.6}\text{Os}_{32.6}\text{Ir}_{28.7}]$ plots in the Os-Ir-Ru diagram close to the boundary of osmium and rutheniridosmine (Fig. 3). Both ruthenium grains contain up to 3.6 wt.% Pt, 1.4 wt.% Rh, and 0.3 wt.% Pd.

The rounded grain of laurite, 150 μm in size, is homogeneous, free of inclusions, has the composition of $[(\text{Ru}_{0.86}\text{Os}_{0.11}\text{Ir}_{0.04})_{1.01}\text{S}_{1.99}]$ and contains 0.6 wt.% Pd, but no Rh and Pt.

Sample A. a. 5431 USA, Oregon, Rogue River

The sample is labeled "laurite and chrome-iron". The grains are mainly dark, rounded cubic crystals, partly with well preserved crystal faces (Fig. 5e) and subordinate platelets with metallic lustre (Fig. 5d), up to 400 μm in size. From the 31 analyzed grains, 13 are Pt-Fe alloys, two osmium, two iridium, six laurite, and eight gold. Chromite, ilmenite, and cassiterite occur subordinately.

The Pt-Fe alloys are euhedral to subhedral with rounded edges and up to 400 μm in size (Fig. 5f). The dominantly homogeneous grains are rich in platinum with 87.9 to 94.4 wt.% Pt, corresponding to 72.2 to 87.4 at.% and a maximum between 82.0 and 84.0 at.%. The

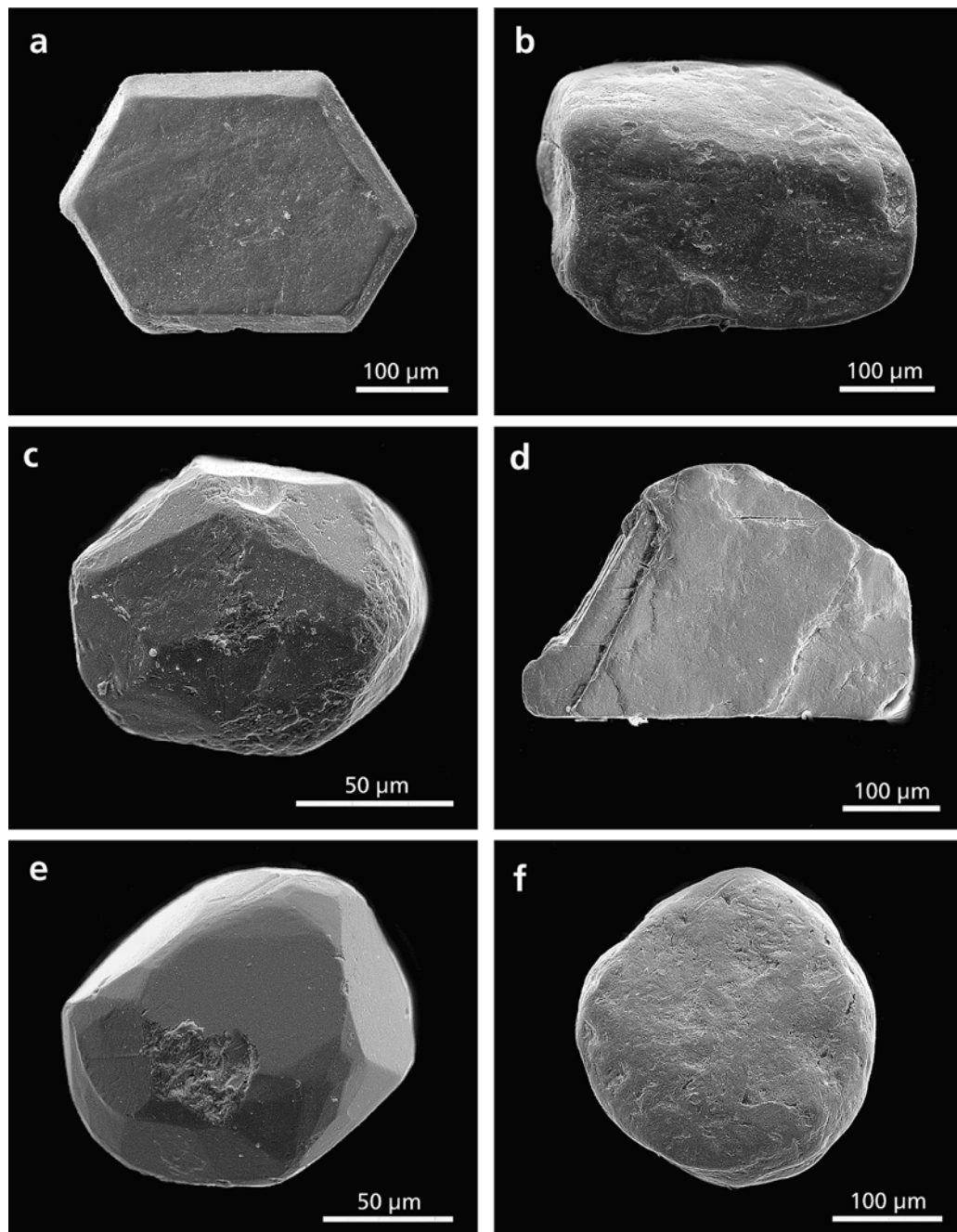


Fig. 5. Scanning electron images of PGM of the Rogue River, Oregon, USA. (a) Euhedral crystal of osmium (no. A.a. 5432). (b) Euhedral crystal of pure iridium with rounded edges (no. A.a. 5432). (c) Rounded crystal of laurite with clear visible crystal faces (A.a. 5432). (d) Platelet of osmium (no. A.a. 5431). (e) laurite crystal with partly rounded edges (no. A.a. 5431). (f) Rounded grain of Pt-Fe alloy (A.a. 5431).

content of Fe varies between 3.6 and 9.6 wt.%, and Cu between 0.2 and 0.9 wt.%, whereas the amount of Ni is close to or below the detection limit. The Pt-Fe alloys always contain up to 5.0 wt.% Ir, 4.0 wt.% Rh, whereas Pd (<1.0 wt.%) and Os (<0.7 wt.%) only occur sporadically. Few grains contain rare, drop-like inclusions of cuprorhodsite with the composition $[(\text{Cu}_{0.86}\text{Fe}_{0.11}\text{Ir}_{0.97})(\text{Rh}_{1.20}\text{Pt}_{0.84}\text{Ir}_{0.07})_{2.11}\text{S}_{3.92}]$, and one Pt-Fe alloy grain contains roundish inclusions consisting of Rh, Pt, Pd, Ru, S and traces of Ir with the formula $[(\text{Rh}_{0.75}\text{Pt}_{0.27}\text{Pd}_{0.04}\text{Ru}_{0.01})_{1.08}\text{S}_{0.92}]$ or (Rh,Pt)S (Table 2, no. 14). A similar unnamed phase, but without Pt, was described by FEATHER (1976) from the Witwatersrand, South Africa. Another observed unnamed phase detected here corresponds to Rh_3S_4 (Table 2, no. 15).

The osmium grains are euhedral to anhedral platelets up to 400 μm in size (Fig. 5d). The grains are homogeneous, free of inclusions, and vary in composition from grain to grain between $[\text{Os}_{39.8}\text{Ir}_{22.8}\text{Ru}_{37.4}]$ and $[\text{Os}_{54.4}\text{Ir}_{40.6}\text{Ru}_{5.0}]$ (Fig. 3), and contain small amounts of Pt (4.3 wt.%), Pd (0.3 wt.%), and Rh (0.2 wt.%).

The iridium grains are rounded and up to 75 μm in size. A homogeneous grain has the composition $[\text{Ir}_{59.9}\text{Os}_{35.8}\text{Ru}_{4.3}]$ (Fig. 3) and contains small amounts of Pt (2.8 wt.%) and Rh (0.7 wt.%), but no Pd. The second analyzed grain contains numerous drop-like inclusions of platinum, <1 μm in size. The analysis gave a composition of $[\text{Ir}_{57.6}\text{Os}_{35.8}\text{Pt}_{6.6}]$ (Fig. 3). In the calculation of the formula Ru is probably "substituted" by Pt due to possible submicroscopic inclusions of Pt-Fe alloys.

The grains of laurite are euhedral to anhedral, partly rounded and up to 120 μm in size (Fig. 5e). Their compositions vary widely from grain to grain between $[(\text{Ru}_{0.58}\text{Os}_{0.37}\text{Ir}_{0.05})_{1.00}\text{S}_{2.00}]$ and $[(\text{Ru}_{0.89}\text{Os}_{0.09}\text{Ir}_{0.05})_{1.01}\text{S}_{1.99}]$. Few grains show distinct zoning with a core richer in Os $[(\text{Ru}_{0.70}\text{Os}_{0.26}\text{Ir}_{0.05})_{1.01}\text{S}_{1.99}]$ than the margin $[(\text{Ru}_{0.74}\text{Os}_{0.20}\text{Ir}_{0.05})_{1.01}\text{S}_{1.99}]$. More common are schlieren-like grains (Fig. 4f) with variable compositions between $[(\text{Ru}_{0.85}\text{Os}_{0.11}\text{Ir}_{0.05})_{1.01}\text{S}_{1.99}]$ and $[(\text{Ru}_{0.99}\text{Os}_{0.02}\text{Ir}_{0.01})_{1.02}\text{S}_{1.98}]$. Only one grain contains needles of osmium as inclusions (Fig. 4e).

The gold grains are lobate, partly porous, up to 100 μm in size, and have many cracks. The analyses show compositions close to $[\text{Au}_{0.89}\text{Ag}_{0.11}]$ with traces of Cu and Bi (0.3 wt.%). Some grains have a rim depleted in Ag, with a composition of $[\text{Au}_{0.98}\text{Ag}_{0.02}]$, and also contain traces of Cu and Bi (0.3 wt.).

In 1852, Au- und PGE-bearing beach placers were discovered along the Oregon coast (PARDEE 1934) and stream placers in the hinterland in the mid 1910s (MERTIE 1969). In 1944, mining took place on the Applegate River, a tributary of the Rogue River. The chemical analysis of a concentrate showed 29.7 wt.% Pt, 32.0 wt.% Ir, 25.6 wt.% Os, 12.8 wt.% Ru, whereas Rh was not determined (MERTIE 1969). This represents a mixture of Os-Ir-Ru- and Pt-Fe alloys. The first detailed analyses of PGM from placers of Josephine Creek, close to Rogue River, were reported by BIRD & BASSETT (1980). They found osmium, iridium and ruthenium as the main minerals, and concluded that the alloys were the result of melting in the lower mantle "when the earth had temperatures higher than at present or that they melted at depths greater than 2900 km" (BIRD & BASSETT 1980). STOCKMAN & HLAVA (1984) described laurite, porous Ru-rich alloy, Os-Ir- and Pt-Fe alloys as inclusions in chromite of the Josephine Peridotite and the Onion Mountain ophiolite. In their opinion, the primary PGM were formed before or during the crystallization of the chromite grains. LYON et al. (1997) suggested by using osmium iso-

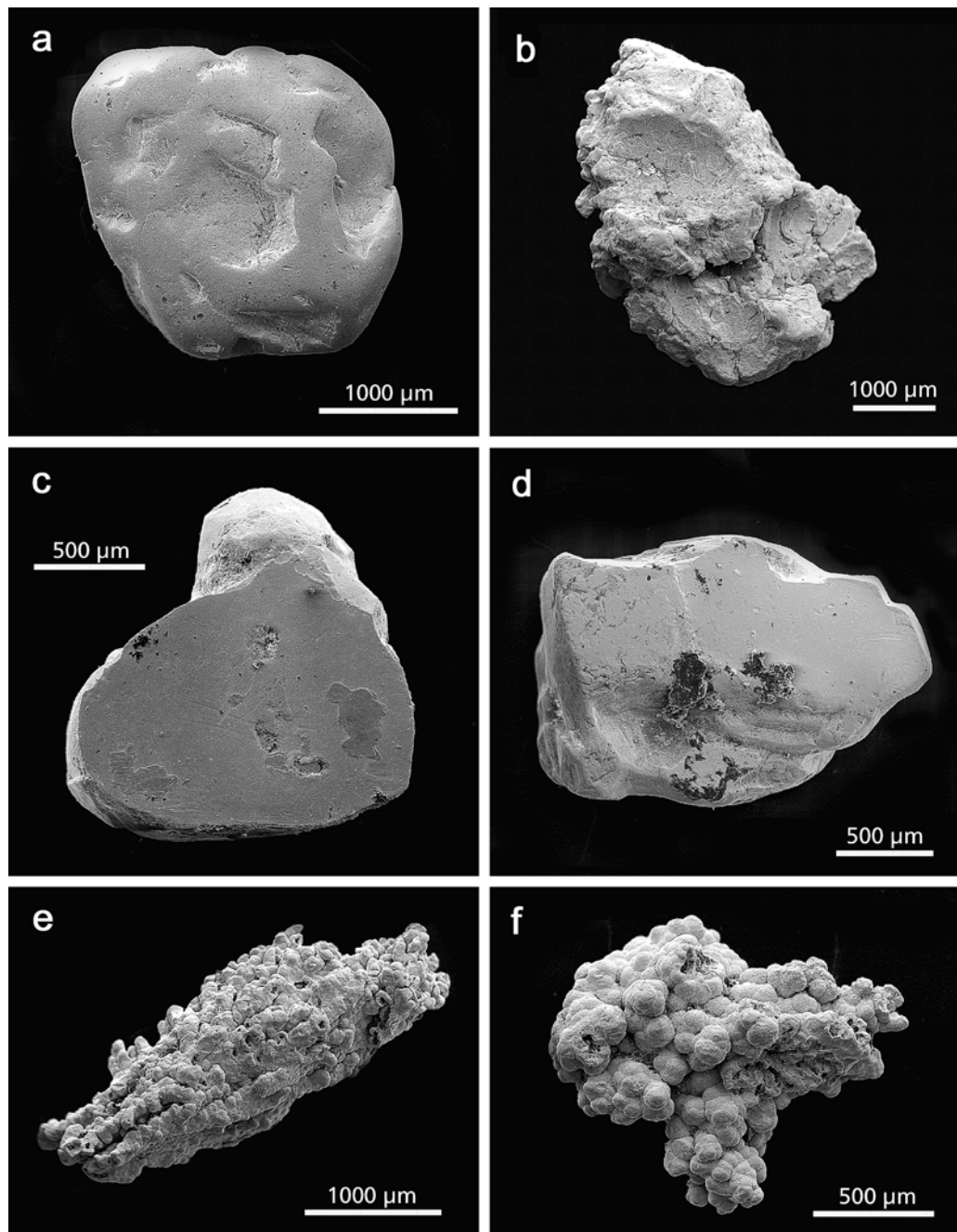


Fig. 6. Scanning electron images of Pt-Fe-, Os-Ir-Ru- and Pt-Pd-Hg alloys from Brazil. (a) Rounded grain of Pt-Fe alloy with negative crystals (no. A.a. 2047). (b) Squeezed grain of Pt-Fe alloy (no. A.a. 2687). (c) Rounded platelet of osmium (no. M 7203). (d) Rounded grain of ruthenium with bent edges (no. M 7203). (e) Dendritic nugget of stick-shaped Pt-Pd alloys (Serro, Minas Gerais, no. H 2340). (f) Botryoidal nugget of Pt-Pd-Hg alloys (Serro, Minas Gerais, no. H 2340).

tope measurements on Os-Ir-Ru alloys from the Applegate River that the grains are detrital and were released from ultramafic host rocks without significant chemical modification.

All these data are in good agreement with the analyses of the samples from the Rogue River. The composition of the analyzed Os-Ir-Ru alloys also shows a nearly vertical trend from Os to Ru for the hexagonal alloys confirmed by the experimental work of BIRD & BASSETT (1980) on Os-Ir-Ru alloys. This points to a primary origin related to an ophiolitic complex (KRIVENKO & TOLSTYKH 1994), probably the Josephine Peridotite.

MEIBOM & FREI (2002) recently measured three osmium grains of sample no. A.a. 5432 by negative thermal ionization mass spectrometry (NTI-MS). Calculated $^{187}\text{Os}/^{188}\text{Os}$ ages of these PGM gave estimates between 256 and 1437 Ma, implying that they are much older than the time of emplacement of Josephine Peridotite (~160 Ma). The osmium isotopic composition of the osmium grains indicates in their opinion a PGE reservoir with a supra-chondritic Pt/Os ratio. This could be produced in the outer core as result of crystallization of the inner core with fractionation of Os from Pt. In this case the inner core would have formed very early, within several hundred millions of years after the accretion of Earth (MEIBOM & FREI 2002).

Sample no. A.a. 2047 Brazil

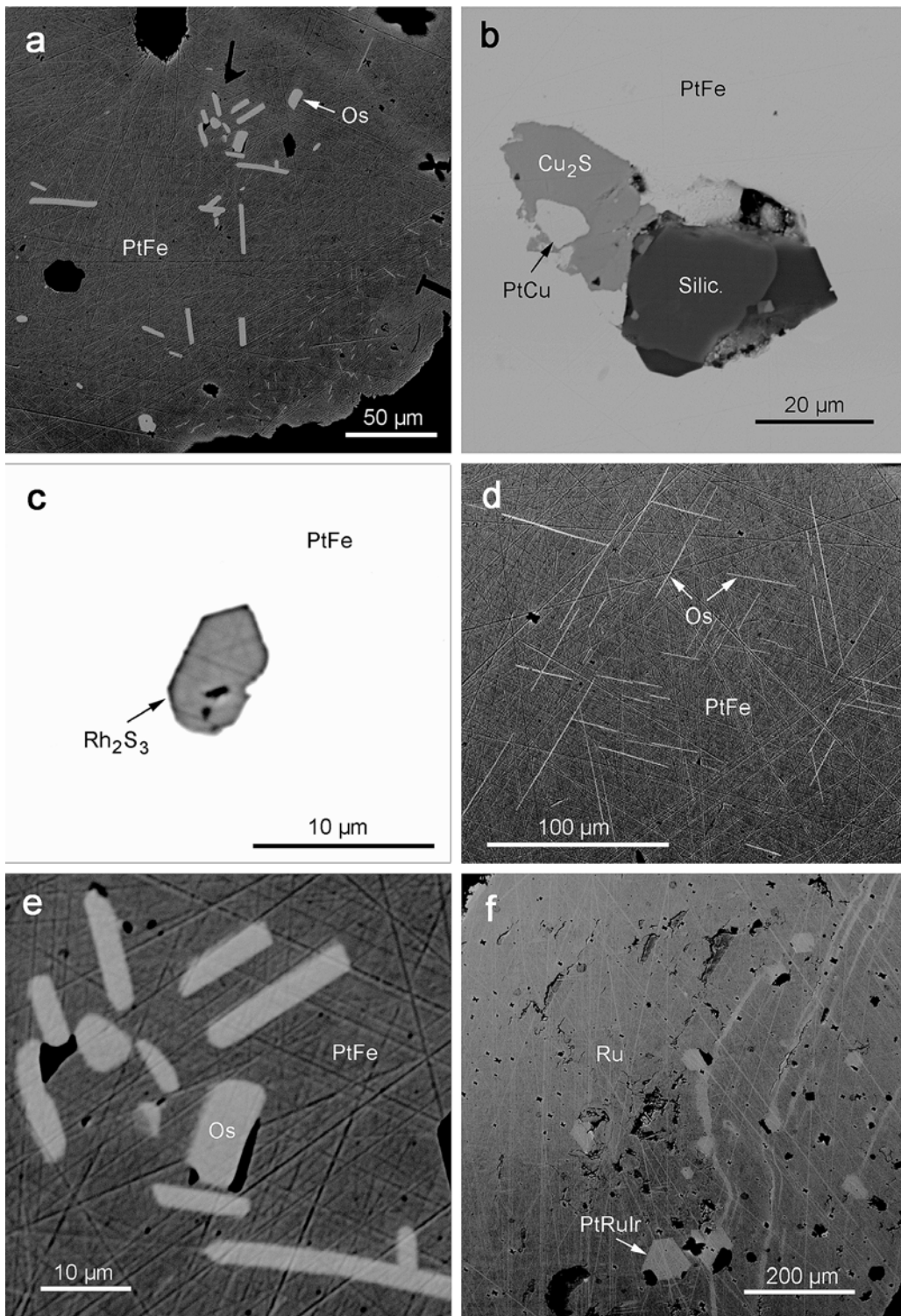
The sample weighs 25 g and contains elongated or rounded grains with knobby surfaces and a silvery or darkbrown lustre, up to 6 mm in size. Some grains show cavities or negative cubic crystals on the surface (Fig. 6a).

All analyzed grains are homogeneous Pt-Fe alloys and very similar in composition. The contents of the main elements vary between 85.6 and 86.9 wt.% Pt, 5.2 and 5.8 wt.% Fe and 0.6 and 3.8 wt.% Cu, whereas Ni is absent. The grains contain small amounts of Ir (up to 3.4 wt.%), Os (up to 1.9 wt.%) and Rh (up to 1.7 wt.%), but only traces of Ru and Pd, corresponding to the formula $[\text{Pt}_{76.8}\text{Fe}_{23.2}]$. The Pt-Fe alloys contain numerous needle-like or tabular grains of osmium, up to 30 μm in size (Fig. 7a). The osmium grains are very rich in Os (up to 96.4 wt.%), contain Pt and Rh, but no Ir and Ru $[\text{Os}_{97.0}\text{Pt}_{1.9}\text{Rh}_{1.1}]$. Figure 7b shows a complex inclusion of hongshiite $[\text{Pt}_{0.98}\text{Cu}_{1.02}]$, chalcocite $[\text{Cu}_{2.02}\text{S}_{0.98}]$, and silicate, and Figure 7c a euhedral inclusion of bowieite, containing 2.1 wt.% Pt, but no other traces $[(\text{Rh}_{1.52}\text{Ir}_{0.49}\text{Pt}_{0.04})_{2.05}\text{S}_{2.95}]$. Tulameenite forms alteration rims around one of the analyzed Pt-Fe grains.

Sample no. A.a. 2687 Brazil

The sample weighs 20.2 g. The grains are mostly well rounded with lobate outlines and up to 5.5 mm in size. The grains partly show a lamellar structure of the surface or deep cavities and are covered with a thin crust of iron hydroxide (Fig. 6b).

Fig. 7. Back scattered electron images of PGM from Brazil. (a) Needle-like and tabular inclusions of osmium (Os) in Pt-Fe alloy (PtFe) (no. A.a. 2047). (b) Polymineralic inclusion of hongshiite (PtCu), chalcocite (Cu_2S) and silicate (Silic) in Pt-Fe alloy (Pt-Fe) (no. A.a. 2047). (c) Inclusion of bowieite (Rh_2S_3) in Pt-Fe alloy (PtFe) (no. A.a. 2687). (d) Oriented exsolution laths of osmium (Os) in Pt-Fe alloy (PtFe) (no. A.a. 2687). (e) Tabular inclusions of osmium (Os) in Pt-Fe alloy (PtFe) (no. A.a. 2687). (f) Euhedral and schlieren-like inclusions of Pt-Ru-Ir alloy (PtRuIr) in ruthenium (Ru) (no. M 7203).



All analyzed grains are Pt-Fe alloys with silicate-filled holes and cracks. The grains are homogeneous and contain between 89.1 and 91.0 wt.% Pt, 4.8 and 5.4 wt.% Fe, and up to 0.7 wt.% Cu. This corresponds to native platinum with the formulae $[\text{Pt}_{81.8}\text{Fe}_{18.2}]$ and $[\text{Pt}_{84.0}\text{Fe}_{16.0}]$, respectively. One grain has a remarkably lower Pt content (72.9 wt.%), and an appropriately higher Fe content with 8.9 wt.%. This corresponds to Pt-Fe alloy with the formula $[\text{Pt}_{72.9}\text{Fe}_{27.1}]$. All grains contain small amounts of Rh (up to 2.1 wt.%), Os (up to 1.2 wt.%), and traces of Ru, Pd, and Ir (< 0.5 wt.%). Oriented inclusions of osmium in the form of up to 100 μm long needle-like exsolution lamellae (Fig. 7d) and tabular grains of 30 μm in size (Fig. 7e) are very frequent. The osmium grains are rich in Os (89.4 – 96.3 wt.%) and contain varying amounts of Ir (up to 8.2 wt.%), Pt (up to 3.4 wt.%), Rh (up to 1.5 wt.%), and Ru (up to 1.3 wt.%), but no Pd, so that the analyses plot in several diagrams of the Os-Ir-Ru-Pt-Rh system (Os-Ir-Ru, Os-Ir-Rh, Os-Ir-Pt, Os-Ru-Pt, Os-Ru-Rh, and Os-Pt-Rh). Hongshiite with the general formula $[\text{Pt}_{1.03}\text{Cu}_{0.97}]$, containing traces of Pd, fills cracks and builds alteration rims around the grains of Pt-Fe alloys.

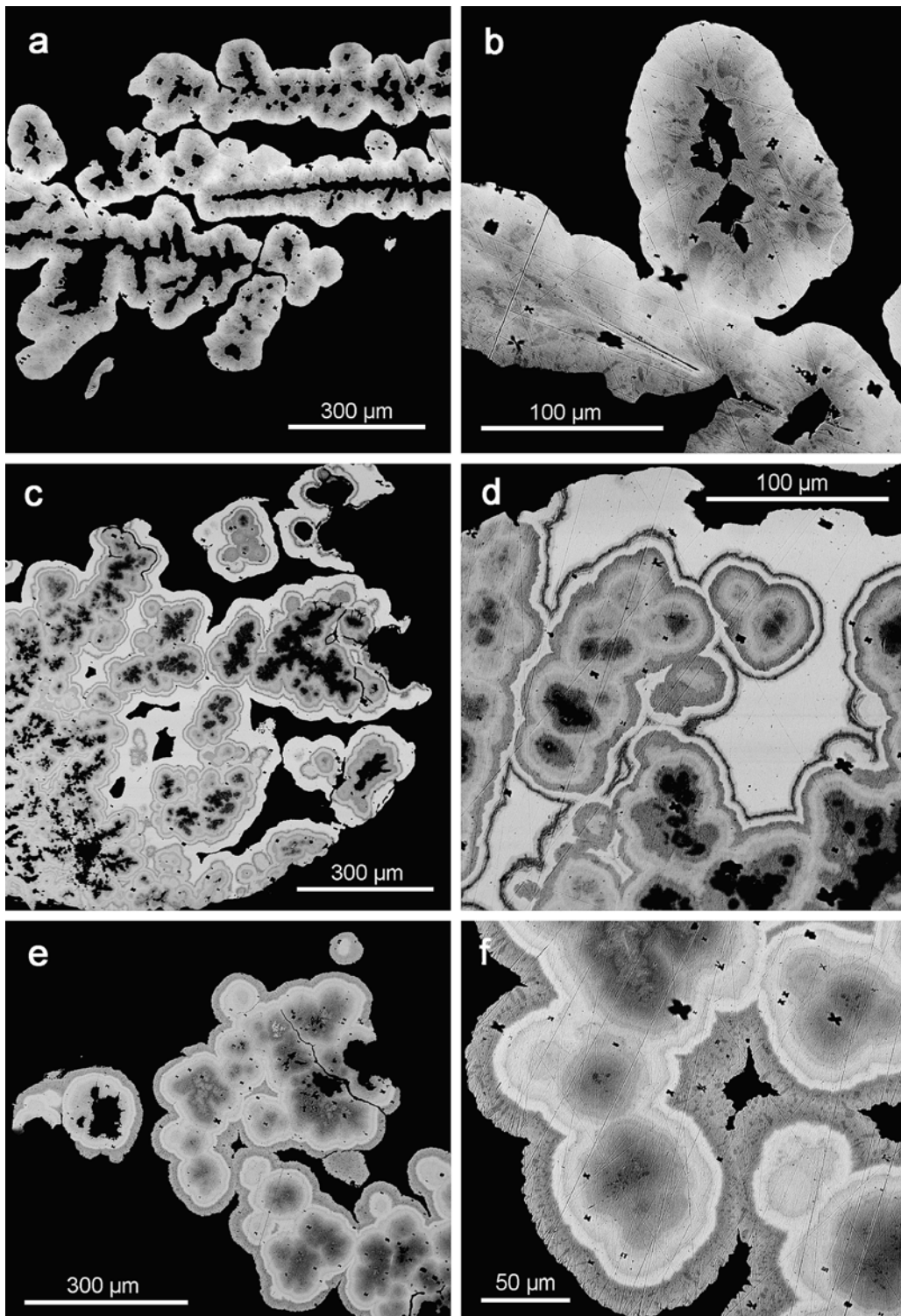
Sample no. M 7203 Brazil

The sample is labeled "osmium iridium" and dated in 1819 and 1821. The grains are up to 4 mm in size and rounded with a platy side (Figs. 6c-d). Few grains show striations due to crystallinity or cleavage, cavities and a metallic lustre of the surface.

Two grains are osmium. They are homogeneous and have the composition of $[\text{Os}_{52.5}\text{Ir}_{39.2}\text{Ru}_{8.3}]$ and $[\text{Os}_{40.9}\text{Ir}_{40.7}\text{Ru}_{18.4}]$, respectively (Fig. 3). One grain contains euhedral inclusions of laurite, up to 15 μm in size with the composition of $[(\text{Ru}_{0.99}\text{Os}_{0.04}\text{Ir}_{0.03})_{1.06}\text{S}_{1.94}]$. Zoned alteration rims of the grains consist in the inner part of As-bearing erlichmanite $[(\text{Os}_{0.49}\text{Ru}_{0.38}\text{Ir}_{0.16})_{1.03}(\text{S}_{1.96}\text{As}_{0.49})_{1.97}]$ and of As-free laurite $[(\text{Ru}_{0.61}\text{Os}_{0.23}\text{Ir}_{0.21})_{1.05}\text{S}_{1.95}]$ in the outer zone.

The third analyzed grain is ruthenium with the composition $[\text{Os}_{27.4}\text{Ir}_{30.6}\text{Ru}_{42.0}]$ (Fig. 3). It contains up to 5.2 wt.% Pt, 2.2 wt.% Rh, and 0.2 wt.% Pd. Inclusions are euhedral grains and schlieren of Os-Ir-Ru-Pt alloy (Fig. 7f) with the composition of 35.8 wt.% Pt, 30.1 wt.% Ir, 17.3 wt.% Ru, 11.5 wt.% Os, 4.8 wt.% Rh, and only traces of Pd and Fe. This corresponds to the formula $[\text{Pt}_{35.9}\text{Ru}_{33.5}\text{Ir}_{30.6}]$ and plots in the Ir-Ru-Pt diagram.

Fig. 8: Back scattered electron images of sample no. H 2304 (Serro, Minas Gerais, Brazil). (a) Dendritic grains with empty tubes in the centre, partly filled with angular quartz. The darker zone around the core is palladian platinum with the composition close to $\text{Pt}_{50}\text{Pd}_{50}$. The composition gradually changes to the broad margin of palladian platinum with $\text{Pt}_{67.5}\text{Pd}_{32.5}$. (b) Closeup of the grain on the left side of Fig. 8a, showing spotted grains of platinumian palladium $[\text{Pd}_{52.7}\text{Pt}_{47.3}]$. (c) Arborescent nugget with cores of Pt-Pd-Hg alloys or cavities, partly filled with quartz, surrounded by several zones of Pt-Pd alloys with various composition and a broad margin of pure platinum. (d) Botryoidal grains with cores of palladian platinum surrounded by oscillatory zones of Pt-Pd alloys, partly containing Hg, and a broad margin of platinum. (e) Botryoidal aggregate of Pt-Pd-Hg alloys with cores of potarite. (f) Closeup of Fig. 8e showing cores of potarite surrounded by several zones of Pt-Pd-Hg alloys with increasing Pt content and a margin of Ag-bearing platinumian palladium with the highest Pt content (see Table 2, no. 8-11).



Sample no. H 2340 Brazil, Minas Gerais, Serro

The sample, collected by HUSSAK in 1904, weighs 0.38 g and is labeled "platinum". The grains are up to 5 mm in size and show a distinct wide variation in morphological features. The habit is very different from those of all other analyzed samples. The grains are dendritic or stalactital (Fig. 6e), botryoidal or mamillary (Fig. 6f), reniform or coraloidal with a knobby surface and often implanted quartz grains and have a metallic lustre and no abrasion. The inner structure of the grains is commonly radial-columnar with an empty tube in the centre.

All grains are alloys of Pt and Pd, partly containing Hg, Au, Ag and Se. The other measured PGE, and Fe, Cu, Ni, Co, S, Te, As, Sb, Bi, and Pb are under the detection limit. The grains show an oscillatory zoning or a gradual change in the composition and are free of inclusions.

The dendritic or stalactital aggregate is built up by grown stick-like single grains with an empty tube in the centre (Figs. 6e, 8a). The surface and the cavities of the grains contain angular grains of quartz, up to 100 µm in size. The broad inner zone around the cavities consists of a Pt-Pd alloy with 64.3 wt.% Pt, 33.9 wt.% Pd, and 1.4 wt.% Hg corresponding to mercury-bearing palladian platinum with the formula $[\text{Pt}_{50.3}\text{Pd}_{48.6}\text{Hg}_{1.1}]$ (Table 2, no. 5). Spotted grains of platiniferous palladium occur in this zone, up to 30 µm in size, containing 61.8 wt.% Pt and 37.5 wt.% Pd with the corresponding formula $[\text{Pd}_{52.4}\text{Pt}_{47.2}]$ (Table 2, no. 6). The inner zone gradually changes to the broad margin of palladian platinum with 79.6 wt.% Pt and 19.5 wt.% Pd corresponding to the formula $[\text{Pt}_{52.7}\text{Pd}_{46.9}]$ (Table 2, no. 7). All parts of the dendritic grain are free of Au and only the inner zone contains small amounts of Hg (up to 1.4 wt.%).

The second analyzed aggregate is mamillary and has a botryoidal internal structure with oscillatory zoning (Figs. 8c-d). Larger cavities can be filled by angular grains of quartz up to 60 µm in size. The composition of the different grains of the aggregate varies widely. In general two types of compositional zoning were observed. The core of the first type contains 49.9 wt.% Pt, 43.1 wt.% Pd, 5.0 wt.% Hg, 1.8 wt.% Au and traces of Ag and Se (0.2 wt.%). This corresponds to Hg-Au-Ag-Se-bearing platiniferous palladium with the formula $[\text{Pd}_{59.1}\text{Pt}_{32.9}\text{Hg}_{3.7}\text{Au}_{3.6}\text{Ag}_{0.2}\text{Se}_{0.5}]$. The core is surrounded by a broad rim of palladian platinum with 80.4 wt.% Pt and 19.3 wt.% Pd and the formula $[\text{Pt}_{69.5}\text{Pd}_{30.5}]$. The following outer rim is mercury-rich (11.7 wt.%) and contains 60.3 wt.% Pt and 28.2 wt.% Pd. This corresponds to Hg-bearing palladian platinum with the formula $[\text{Pt}_{48.8}\text{Pd}_{41.9}\text{Hg}_{9.3}]$. The next outer rim contains only Pt (89.5 wt.%) and Pd (10.0 wt.%) with the formula $[\text{Pt}_{82.9}\text{Pd}_{17.1}]$ and is surrounded by a narrow rim with a lower content of Pt (70.7 wt.%) and a higher content of Pd (29.3 wt.), respectively. This is palladian platinum with the formula $[\text{Pt}_{56.8}\text{Pd}_{43.2}]$. The broad margin consists of pure platinum (99.6 wt.%) without any traces of other elements. In contrast, the core of the second type of zoning only contains Pt (80.7 wt.%) and Pd (18.9 wt.), which corresponds to palladian platinum with the formula $[\text{Pt}_{70.0}\text{Pd}_{30.0}]$. The broad surrounding rim consists of Hg-bearing palladian platinum with 65.5 wt.% Pt, 26.5 wt.% Pd, and 8.5 wt.% Hg and the formula $[\text{Pt}_{53.5}\text{Pd}_{39.7}\text{Hg}_{6.8}]$. It follows a broad Hg-free zone of palladian platinum with 94.0 wt.% Pt and 6.0 wt.% Pd and the formula $[\text{Pt}_{89.5}\text{Pd}_{10.5}]$. This zone is bordered by a narrow rim (1-10 µm) with a lower Pt content (69.8 wt.%) and a higher Pd content (30.3 wt.%), corresponding to $[\text{Pt}_{55.5}\text{Pd}_{44.5}]$. The broad margin consists of pure platinum without any measurable amounts of other elements (Fig. 8d).

The third analyzed botryoidal aggregate of 1.5 mm in size consists of orbicular grains up to 150 µm in size (Fig. 6f). Figures 8e and 8f show the internal structure with typical zoning. The chemical composition of the different grains varies widely. The profile across one grain shows a Hg-bearing platinian palladium core with 47.5 wt% Pt, 47.0 wt.% Pd, 5.1 wt.% Hg, and 0.3 wt.% Se and the formula $[\text{Pd}_{61.8}\text{Pt}_{34.1}\text{Hg}_{3.6}\text{Se}_{0.5}]$ and in the outer zones a gradually increasing content of Pt and decreasing amounts of Pd and Hg up to 79.3 wt.% Pt, 19.3 wt.% Pd, 0.4 wt.% Hg, and 0.2 wt.% Se, which corresponds to palladian platinum with the formula $[\text{Pt}_{68.5}\text{Pd}_{30.7}\text{Hg}_{0.3}\text{Se}_{0.5}]$. The margin consists of Hg- and Ag-bearing Pt-Pd alloy (62.8 wt.% Pt, 35.5 wt.% Pd, 0.8 wt.% Hg, 0.3 wt.% Ag) with the formula $[\text{Pd}_{50.4}\text{Pt}_{48.6}\text{Hg}_{0.6}\text{Ag}_{0.4}]$. Another analyzed grain of the aggregate comprises of an arborescent core of an Au- and Ag-bearing Pd-Hg alloy with the composition of 0.2 wt.% Pt, 50.8 wt.% Pd, 44.3 wt.% Hg, 3.4 wt.% Au, and 1.1 wt.% Ag, corresponding to the formula $[\text{Pd}_{65.7}\text{Hg}_{30.4}\text{Au}_{2.4}\text{Ag}_{1.3}\text{Pt}_{0.2}]$ or $[(\text{Pd}_{1.31}\text{Au}_{0.05}\text{Ag}_{0.02}\text{Pt}_{0.01})_{1.39}\text{Hg}_{0.61}]$ (Fig. 8.d, Table 2, no. 8). This could be potarite, a mineral poorly documented (CABRI 2002). A similar phase, but with higher Hg contents, was described by CASSEDANNE et al. (1996) and FLEET et al. (2002) from the Bom Sucesso Stream, Minas Gerais. The surrounding zones are characterized by a continuously increasing Pt content resp. decreasing contents of Hg and partly of Pd from the inner to the outer zones. The inner zone contains 35.2 wt.% Pt, 51.0 wt.% Pd, 13.4 wt.% Hg and 0.2 wt.% Se, corresponding to the formula $[\text{Pd}_{65.8}\text{Pt}_{24.8}\text{Hg}_{9.1}\text{Se}_{0.3}]$ (Table 2, no. 9). The outer zone however contains 44.8 wt.% Pt, 45.6 wt.% Pd, 8.8 wt.% Hg and 0.2 wt.% Se, corresponding to the formula $[\text{Pd}_{60.7}\text{Pt}_{32.5}\text{Hg}_{6.2}\text{Se}_{0.4}]$ (Table 2, no. 10). The margin contains 54.4 wt.% Pt, 41.2 wt.% Pd, 4.1 wt.% Hg, and 0.2 wt.% Ag, but no Au. This corresponds to platinian palladium with the formula $[\text{Pd}_{56.2}\text{Pt}_{40.5}\text{Hg}_{3.0}\text{Ag}_{0.3}]$ (Table 2, no. 11).

Since the beginning of the 19th century the occurrence of platinum in Brazil has been known from Minas Gerais (HUSSAK 1904). In 1805 and 1809, WOLLASTON described platinum from Brazil as small fragments of a spongy substance with a surface consisting of small spherical protuberances which contain Ir. HUSSAK (1904) suspected that these grains originated from Corrego das Lagens near Conceicao do Serro, Minas Gerais. In 1904 and 1906, HUSSAK described the occurrences of palladium and platinum from Brazil in great detail. Apart from the grains with botryoidal or stalactital texture he described euhedral or rounded grains of platinum and "osmiridium" similar to the Uralian platinum. In the past forty years numerous examinations of Pd-bearing minerals from Minas Gerais were reported (e.g., CASSEDANNE & CASSEDANNE 1974; CLARK et al. 1974; STUMPFL 1974; CASSEDANNE & ALVES 1992; OLIVO & GAUTHIER 1995; CASSEDANNE et al. 1996; CABRAL et al. 2001; FLEET et al. 2002).

The analyzed samples no. A.a. 2047, A.a. 2687 and M 7203 are only labeled "Brazil" without any exact locality. They contain Pt-Fe and Os-Ir-Ru alloys free of Pd. A sample of similar composition with Pd-free Pt-Fe alloys, rimmed by tulameenite, was described by CABRI et al. (1996) from the collection of the Mining Academy of Freiberg/Saxony, Germany. HUSSAK (1904, 1906a, b) only described botryoidal or fibrous grains of Pt-Pd alloys from the localities Condado, Serro and Corrego das Lagens at Conceicao, Minas Gerais. On the other hand, he found platelets of osmium ordered parallel to the octahedral crystal faces of platinum by etching Pd-free grains of Pt-Fe alloys from the Rio Abaete, southern Minas Gerais. HUSSAK (1904, 1906a, b) regards dunites of the neighbourhood as the source rocks of these PGM. The similarity in chemical compositions

and textures of the analyzed grains of the samples no. A.a. 2047 and A.a. 2687 with the data of HUSSAK (1904, 1906a, b) may indicate that these samples originate from Rio Abaete, southern Minas Gerais.

The above described analytical examination on some grains of sample no. H 2340 from Serro, Minas Gerais, collected by HUSSAK, confirm not only his description about the habit but also of the chemical composition. Similar internal structures of dendritic grains with palladium-rich cores and margins of platinum (Figs. 8a, 8b) were reported by CASSEDANNE & CASSEDANNE (1974) and later confirmed by CASSEDANNE & ALVES (1992). In 1996, CASSEDANNE et al. described dendritic PGM with a core of Pt-bearing potarite, surrounded by platinian palladium, palladian platinum and a margin of Hg-bearing palladian platinum. The first occurrence of potarite, with coating of native platinum, from Brazil was reported by STUMPFL (1974) from placer deposits at Morro de Pilar, Minas Gerais. He explained the intergrowth of Pt- and Pd-Hg alloys as a secondary accretion process during transportation in the rivers. FLEET et al. (2002) recently described arborescent nuggets with a core of massive auriferous potarite from the Bom Sucesso Stream at Serro, Minas Gerais. A similar mineralization of gold-bearing potarite, together with platinum and palladian gold, was reported by LEAKE et al. (1991) from south Devon, England.

The comparison of the analyzed grains from Serro with the results by CASSEDANNE et al. (1996) and FLEET et al. (2002) shows a wide variation of the texture and the composition of the PGM from these placer deposits. The analyzed dendritic or stalactital aggregate (Figs. 6c, 8a) contains in the core only small amounts of Hg, and no Au, in contrast to the results by CASSEDANNE et al. (1996) and by FLEET et al. (2002). This could be an indication for an extensive alteration of potarite of the analyzed grain. Conspicuous is also the gradual change in the composition from the core to the margin (Fig. 8b) compared with the sharp zoning observed by CASSEDANNE et al. (1996) and FLEET et al. (2002). On the contrary the analyzed mamillary or botryoidal grains show a sharp zoning and partly cores with small amounts of Hg and Au, but higher contents of Hg in outer zones. While one of the analyzed grains contains a broad margin of pure platinum (Figs. 8c-d), the other has a margin of Hg- and Ag-bearing Pt-rich palladium (Figs. 8e-f). The core of this grain is auriferous potarite. The analyses confirm the observations by FLEET et al. (2002), that the potarite from Serro, Minas Gerais contains more Pd (up to 65.6 at.%) than stoichiometric potarite and is auriferous (up to 3.6 at.%).

HUSSAK (1904, 1906a, b) already proposed that the morphology of the PGM grains and their quartz inclusions are an indication for a precipitation of PGE from solutions. In his opinion the source of PGE could be the decomposition of platinum-bearing pyrite or inclusions of Pt-Pd alloys in sperrylite from nearby tourmaline-bearing quartz veins or micaceous quartzites. CASSEDANNE & CASSEDANNE (1974) and CASSEDANNE & ALVES (1992) confirmed HUSSAK's observation (1904, 1906a, b) and found locally outcropping mafic and ultramafic rocks with chromite, which could contain PGE as a possible source for the alluvial PGM. FLEET et al. (2002) suggest that the PGM derived from a high level episodic hydrothermal alteration of mafic or ultramafic rocks within the drainage basin with remobilized Pt and Pd precipitated in either open spaces or carbonate veins in the surrounding metaquartzites.

Summary

The present examination provides exact descriptions and analyses of PGM samples of various placer deposits from the collection of the Museum of Natural History, Vienna, collected during the past two centuries. The analyses broadens the information on the mineralogy of PGM from placer deposits of the Altai, Russia, of California and Oregon, USA, and of Minas Gerais, Brazil although the samples contain only little information about the exact localities, sources or composition. The results are a good completion of the extensive detailed data base on worldwide PGM placer deposits by CABRI et al. (1996) and the detailed description of the mineralogy of the most important PGM placer deposits given by WEISER (2002).

One of the spectacular nuggets from Nizhni Tagil, Urals was analyzed for the first time. The analyses confirmed the description as Pt-Fe alloy with the formula close to Pt_3Fe . Additionally, inclusions of iridium, laurite, and cuproiridsite were detected.

The two analyzed samples no. G 656 and G 657 from Altai, Russia are mixtures of Pt-Fe- and Os-Ir-Ru alloys. They contain inclusions of laurite, in which Os mainly is probably substituted by Rh, erlichmanite, minerals of irarsite-hollingworthite solid-solution, sperrylite, the rare minerals cherepanovite and rhodarsenite-palladodymite solid-solution, and possibly Ru-oxide. The paragenesis is similar to that described of placer deposits of the Kuznetsk-Alatau by TOLSTYKH et al. (2002). Therefore, the analyzed PGM most probably originate from placer deposits associated with ophiolite complexes of this region.

Sample no. A.a. 3586 from California only consists of Os-Ir-Ru alloys. Os-Ir-Ru alloys are described in the literature mainly from Trinity County (e.g., SNETSINGER 1971a, b, 1972; LEGENDRE & AUGÉ 1993; CABRI et al. 1996). The analyzed sample could also originate from this locality and the PGM have a primary origin and might derive from ophiolitic complexes.

Both samples from Rogue River, Oregon, USA (A.a. 5431, A.a. 5432) mainly consist of Os-Ir-Ru alloys, Pt-Fe alloys, laurite, and gold, and contain only few inclusions of irarsite, cuprorhodsite and the unnamed phases $[(Rh,Pt)S]$, $[Rh_3S_4]$ and $[(Os,Ir)_2(Fe,Cu)S]$. The samples have a similar composition as described from placers of Josephine Creek by BIRD & BASSETT (1980) and of chromite of the Josephine Peridotite and the Onion Mountain by STOCKMAN & HLAVA (1984). Therefore, it can be assumed that the analyzed samples probably originate from the Josephine Peridotite in the neighbourhood of the Rogue River.

The samples no. A.a. 2047 and A.a. 2687 from Brazil only contain Pt-Fe alloys with few inclusions of osmium, bowieite, hongshiite, chalcocite and alteration rims of tulameenite; sample no. M 7203 is dominated by Os-Ir-Ru alloys with inclusions of laurite and erlichmanite. Minerals with a similar composition and habit are described by HUSSAK (1904, 1906a, b) from the Rio Abaete, southern Minas Gerais, probably deriving from dunites in the neighborhood.

Sample no. H 2340 from Serro, Minas Gerais, Brazil is remarkable for the unusual morphology of the dendritic or stalactital and mamillary or botryoidal grains without any abrasion. The grains consist of zoned Pt-Pd alloys of various composition and partly containing potarite in the core. The habit and the chemical composition indicate, accord-

ing to HUSSAK (1904, 1906a, b), a precipitation of PGE from solutions. CASSEDANNE & CASSEDANNE (1974), CASSEDANNE & ALVES (1992) and recently FLEET et al. (2002) essentially confirmed the observation by HUSSAK. The PGM from Serro, Minas Gerais are, apart from the Au-Pd-Pt grains from south Devon, England described by LEAKE et al. (1991) and explained as grown from oxidizing saline fluids at about 100°C, the only known example for a formation of PGM of placer deposits at low temperatures (CABRI et al. 1996; WEISER 2002).

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Autor(en)/Author(s): Weiser T.W.

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