

## EXCERPTS and NOTES (Section 5b: from Jedwab 1995 to Zavaridsky)

### Jedwab 1995

[Microscopical and chemical properties of UPGM from Cauè (Minas Gerais, Brazil), Zabargad (Egypt, Shinkolobwe and Ruwe (Katanga, Congo): ouro preto, anatase/native platinum mixtures, Pt-Mg-Cr-Fe-oxide, Pt-Ru-Ir-heterogenite, Ce-Pd oxide. Chemical analysis of the heart of Pt grains rimmed by Pt-anatase and Pt-Cu shows minor amounts of Ti. A tentative generalization of the observations reveals the possible existence of a large group of ternary compounds (PGE-Transition Elements-oxygen).]

### Jedwab 1997

[A review paper of all PGM and PGE-containing compounds and ores, found by the previous and present authors. The newer findings, amounting to over 25 defined species and undefined compounds, are described. Five mineralization stages are proposed to explain the diversity of compounds and parageneses. Similarities between the Katangian Copper Belt and West-Australia evaporitic-bound unconformity-related deposits are evoked.]

### Jedwab & Cassedanne 1998

[A review paper on the early observations of Brazilian dark-brown to black compounds (ouro preto and palladinite p. parte), associated with gold in itabirites. The odds of the definition of the species "palladinite", from which the major component iron has been skipped over, are detailed.]

Fig. 1: "*Ouro preto grain composed of gold, isomertieite and black Pt-Cu-Au-Fe-Mn oxide.*"

### Jedwab et al. 1999

[Description of a bitumen containing high concentrations (up to several wt.%) of non-particulate Pd, Pt, Au, Hg, Fe and S (down to the nanometric scale), found in association with potarite and Pd-Pt-Au-Bi-containing plumbojarosite.]

### Jedwab 2004

[Several Ru-Ir-Pt-Ti-Cr-Fe oxide/hydroxide compounds (sometimes well crystallized), Pt-Ir-K chlorocompounds, and Pt-Ir-Ru-K-Cl-containing opal have been found in museum samples. The two last groups are considered as artifacts generated by the hydrometallurgy of the Pt ores].

### Johnson & Lampadius 1837

p. 310: [Item b, probably a concentrate from jacotinga]: "*The palladian gold occurred partly as powder, and partly as rounded grains of a dark-brown colour. A few metallic particles of dark-coloured gold were obvious in the powder. The rounded grains could be crushed between the fingers and disclose thereafter gold particles in flakes and a few rounded nuclei. When powdered and digested in hydrochloric acid, they leave a dark-brown solution, and also gold of a colour corresponding to 20-21 carats cleared of its crust of brown powder. This gold is malleable, but becomes more and more flaky when hammered.*"

p. 311: "'I think" says Mr. Johnson, "that palladium occurs in the zacotinga partly in the native state in combination with gold, partly as oxide\*\*".

"\*\* I found that indication by Mr. Johnson so interesting that I undertook immediately an investigation in relation with it. I had observed previously that the palladian gold could be liberated from the brown powder with the aid of hydrochloric acid."

p. 312: "*It occurred thus to me without doubt that the palladian gold obtained from the zacotinga by discoloration was a mixture of native palladian gold and of an iron-rich palladium oxidate (probably an oxide). We have here as a novelty the first occurrence of a metal connected with platinum in the oxidized state. I shall disclose in the near future an analysis of the quantitative proportions of the components of this iron-containing oxydate.*" [There is no ambiguity at all about the concomitant determination of iron and palladium in one same palladian compound. These right analysis and conclusion have been systematically overlooked or misinterpreted by all followers.]

### Kepper 2000

Fig. p. 8: "*Gypsum twin containing native iridium dust showing as bright white specks, jarosite plates surround twin. Boss Mine. SEM photograph by J.J.2000.*"

**Knopf 1915a**

[The only detailed description of the Boss Mine and its PG mineralogy. Knopf describes the isolation of a black platinum-containing substance, insoluble in hydrofluoric acid, but he does not come to the right conclusion that it is carbonaceous. ]

**Knopf 1915b**

[The author states that Bi, Si, Ti..., and the precious metals Au, Pt, Pd and Ag found by R. C. Wells in the analysis of plumbojarosite are to be considered as impurities. (cf. Jedwab et al., 1999)].

**Knopf 1915c** [Same data as in Knopf 1915a and 1915b].

[These three papers rehearse the same superior chemical analysis by R.C.Wells (USGS), made on “the purest obtainable material (plumbojarosite)”. Results are the following (in wt %): Au 0.79, Pt 0.05, Pd 0.22. These data have frequently been borrowed by later authors, and used as a proof of Precious Metals Au-Pd-Pt entering jarosite. However, Knopf is more cautious when stating that “platinum and palladium occur in extremely small particles”, nearly impossible to separate by panning. Our own SEM/EMP analyses confirm the absence of the Precious Metals Au-Pd-Pt in the jarosite, and their occurrence as micrometric to sub-micrometric PGM particles of several species, and as Au-Pd-Pt-Hg-S bitumen (cf. Jedwab et al.1999). The use of the mineral name “jarosite” instead of “jarositic ore” is probably at the root of the confusion.]

**Kokscharow 1866**

p. 179: Chapter 103: Native platinum [mostly Uralian] *"Colour: steel-grey to silver white, sometimes discoloured to brownish."*

[p. 184: Quotation of the work by Muchin, J. von- (1842): [in Russian] Chemical study of the platinum varieties of the Urals Range. Trud. Miner. Obsh. S. Petersb., part II, p. 101.]: *"Black native platinum from Nishne-Tagilsk. If, following a remark by von Muchin, one cleans the non-magnetic grains of this platinum with hydrochloric acid or aqua regia, their surface is liberated from a black, earthy substance, leaving three kinds of grains: very bright grains of near silver-white colour; less bright; grey; graphite-like grains; and dull black grains. When hit, these black grains decay into smaller grains and a black powder."*

[p. 185-186: Chemical analyses of non-magnetic and magnetic grains, as-found and acid-treated. Grains remaining black after acid-treatment, both magnetic and non-magnetic, have relatively higher iron and more insoluble contents, but the differences are not large.]

**Krstic & Tarkian 1997**

p. 15 and Table 5: *"Ruthenium oxide (?). A fine-grained phase, occurring as pseudo-morph after several grains of laurite, was identified. In reflected light, this mineral is dark grey with a faint brownish tinge, and strongly bireflectant and anisotropic, with rotation colors that range from dark grey to bronze-yellow...The concentration of Fe varies between 5 and 10 wt. %. Other elements (S, As, Sb, Cu, Ni, Co, Ca) are present in negligible quantities ....Recalculation of the compositions into oxide components provides a clue that this phase appears to be RuO<sub>2</sub>. However, at the moment we cannot rule out the presence of OH."*

**Kucha 1993**

From the Abstract: *"The clay-organic matrix of the [Kupferschiefer] contains small accumulations of Au, Pt and Pd, probably as organometallic compounds ....The optic-ally homogeneous organic matrix of the thucholite contains discrete inclusions of UO<sub>2</sub>, brannerite and organic compounds of U, Au, Pt, and Ni varying in size from 0.008 to 0.02 μm, as shown by electron microscopy...During replacement of thucholite by calcite at the boundary of the two minerals, native Au, Ag, Bi, PbBi, AuPb<sub>2</sub>, Pb, Pd-arsenides, Bi-sulfides, PbSe, and TiO<sub>2</sub> developed."*

**Kucha et al. 1993**

From the abstract: *"A tightly intermixed clay-organic matrix of the noble metal-bearing shale contains small accumulations of Au, Pt and Pd presumably as organometallic compounds. Thucholite is present locally...The optically homogenous organic matrix of the thucholite contains discrete inclusions of UO<sub>2</sub>, brannerite, electrum and organic compounds of Au, U, Pt and Ni varying in size from 0.008 to 0.025 μm as shown by TEM."*

**Kucha & Przybylowicz 1999**

From the abstract: "The noble metals content in the organic matrix of thucholite reaches 2,528 ppm Au, 5,000 ppm Pd, and 1,770 ppm Pt. Pt is probably bound to tetrapyrrole rings, with Ni and V as vanadyl."

**Lampadius & Plattner 1833**

p. 356: "This analysis [of separate fractions] thus corroborates the former assumption and the visual impression, that the platinum and its normal associates are not chemically bound to the gold in the studied ore, but instead, that the native argentian gold [sic: Silbergold] and the platinum ore occur mingled one close to the other in the iron ore."

p. 358-9: "Considering that the mechanical separation of the gold from the hematite yielded no visible native platinum at all, that on the other hand hematite contained platinum according to the analyses, but that separate crystals of the same were entirely devoid of platinum, according to blow-pipe assay, the following must consequently be assumed: either the platinum occurs in the native state and is very finely dispersed in the iron ore, or it forms in combination with other materials a brittle, pulverizable material, which colour resembles that of hematite, and can thus difficultly be discerned by eye from the same".

**Lechler et al. 1988**

[High concentrations of Pt, Pd and Rh are found in the Gibellini mine, where a Mn, Ni, Zn, V mineralization is associated with kerogenous black shales. The authors favour a hydrothermal origin for the PGE and Ni, Zn and V. PGM have not been sought for or observed.]

**Legendre & Augé 1993a**

[The presence of several PGE oxides is mentioned without analyses or descriptions].

**Legendre & Augé 1993b**

p. 924: "Photograph. Inclusion of iridium oxide within a Pt<sub>3</sub>Fe nugget...Note the presence of osmium at the ends of the inclusion." [The black stuff wrapping the fragmented Ir-oxide has unfortunately not been analysed. The picture shows also inclusions of soft materials with a lighter elemental composition and crystalline outlines which are not discussed.] [A complex inclusion of (Ir, Pt, Ru, Fe)O<sub>2</sub> and (Os, Ir, Ru, Pt) alloy in isoferroplatinum is interpreted as of primary, probably magmatic, origin.]

**Logan 1918**

p. 78-79: "Michigan Salmon or Red Hill Mine: Probably a large percentage of that [platinum] present has been lost, as no great care seems to be given to its recovery. The bulk of the metal is in small scales and nuggets but there are many larger pieces, the biggest one saved weighing 1/8 ounce. The small scales are bright but the larger pieces are rough and coated with a blackish film."

p. 79: "Last year several nuggets of a metal looking a good deal like dirty lead were picked out of the box at clean-up time and put aside. The man who leased the property recognized them as platinum metals....The largest nugget was reported to weigh one-half ounce, and the bulk of that saved was in nuggets from a pennyweight upward."

North Fork, Peterson Mine, Eddy's Gulch".

p. 80: "The gold found here is rusty, rough and coarse, often with quartz attached. The few pieces of platinum saved are rough and covered with a black and rusty coating. This material shows few signs of erosion. The largest nugget weighed 23 grains. The nuggets have flat, angular shapes and are probably osmiridium."

p. 82: "North Fork, bench mine at the mouth of Jessop's Gulch: The largest piece shows a rounded surface but most of the metal is in irregular unworn nuggets and in jagged scales exhibiting perfect basal cleavage faces, indicating osmiridium. Boiling in conc-entrated acid readily removed the black coating and accentuated the sharp, unworn character of the material."

p. 109, Table: Analyses of Platinum Group Metals from California. Column: "Percentage gold". "Note 1: In most cases, this is probably black or rusty gold which will not amalgamate."

**McCallum et al. 1976**

p. 1427: "The PdTe<sub>2</sub> mineral is provisionally referred to as Pd phase C. In addition, a light coffee-brown, extremely anisotropic Pd-Bi-Te mineral of indeterminate stoichiometry occurs as thin rims replacing

*michenerite (and rarely merenskyite) in weakly oxidized ore. This supergene Pd mineral is here referred to as Pd phase D (Fig. 4A)."*

p. 1440: *"Pd phase A [Pd<sub>5</sub>(Bi,Sb)<sub>2</sub>Te<sub>4</sub>] generally shows supergene alteration of variable degree to a dull gray-brown substance that qualitative microprobe examination shows to be an inhomogeneous, compositionally complex material containing appreciable Pd, Bi and Te, but also much Cu and Fe. Microscopic inspection suggests that the alteration material is either amorphous or a mixture of several minerals with grain size below the limits of optical resolution."*

#### **McDonald et al. 1999a**

From the abstract: *"Mineralogical investigation of the UM2 core reveals that a small number of low reflecting, Pd-bearing PGM are present—always in association with a poorly characterized Pd stibioarsenide [Pd<sub>3</sub>(Sb,As)] phase—in the shallowest of the three zones. Electron microprobe analysis of these PGM indicates the presence of oxygen and that of at least two species exist. The resulting stoichiometries suggest that at least one species could be a hydrated form of palladinite [PdO.(H<sub>2</sub>O)<sub>n</sub>]. The other phase could be a hydroxide [Pd(OH)<sub>2</sub>] or a less strongly hydrated form of palladinite."*

#### **McDonald et al. 1999b**

From the abstract: *"Increase in pH generated by wall-rock reactions is seen as an important mechanism in Pt precipitation, and the presence of reniform mixtures of platinum, Pt-Pd alloy, and Pt-O species are believed to reflect annealing of metal and alloy from an originally amorphous, hydrated Pt-O precursor (possibly resembling PtO.nH<sub>2</sub>O)."*

p. 187 and Table 2: Six analyses of a porous Pt-bearing, oxygen-containing material. *"The analyses cluster into two groups; one material containing approximately 91 wt.% Pt, and another containing approximately 85 wt.% Pt....The more Pt-rich Pt-O species has a stoichiometric formula close to PtO, while the Pt-poor species has a stoichiometry close to PtO<sub>2</sub>, Pt(OH)<sub>2</sub>, or PtO.H<sub>2</sub>O....[The oxygen-bearing material] "occurs irregularly throughout the whole of the mass of metal, is intimately mixed with both platinum and Pt-Pd alloy, and appears to be a primary feature."*

#### **Milliotti & Stumpfl 1996**

p. 173: *"Ruthenium oxide minerals are widespread in the chromitite and occur as alteration rims of Os-laurite crystals enclosed in either chromite or goethite and limonitic material. The thickness of these rims varies from 1 to 5 μm depending on the degree of laurite alteration...In reflected light, they are brownish grey phases and can be distinguished by their low reflectance similar to spinels and isotropic character. The ruthenium oxides approach the composition RuO<sub>4</sub>, with variable Ru, Fe and Ir content."*

p. 174. *"The palladium iodide phase. A Pd-iodine phase occurs at the rim of a subhedral PtFe alloy grain in goethite within chromite. It displays irregular shape and is approximately 10 μm long and 2-3 μm across. The mineral appears anisotropic, with low reflectance comparable to that of goethite. Semi-quantitative microprobe analyses show large variation in Pd and Fe, and the best compositional formula obtained approximates a Pd<sub>2</sub>FeI composition."*

#### **Mingaye 1916**

[Pt, Pd, Ir and Rh (?) found in ironstone gossan, copper carbonates and chloritic schists by chemical analyses.]

#### **Moreno et al. 1999**

p. 373: *"Pt- and Pd-bearing oxides occur on the edges of chromite grains and have average sizes of 2x3 μm but may be up to 10 μm across. They are very irregular in shape and chemically inhomogeneous with cracks and lineations across their surfaces. They give dull back-scattered images on the SEM and commonly contain relicts of Pt- and Pd-sulphides in their centres or form mosaics with them. These oxides have analyses containing Pt, Pd, Fe, O with minor S, Ni and Si."*

#### **Muchin 1842: [cf. Koksharov, 1866].**

#### **Nickel 2002**

[Color pictures, EMP analyses and XR diffraction lines of several unidentified Pd and Pt oxides, some of which contain additional Se, Hg and/or Cu. Behaviour under the probe suggests the presence of hydroxyl. ]

**Nixon et al. 1990**

p. 531: *"The formation of rare Pt oxide (e.g. Figs. 7C, D) shows clear evidence of alteration under conditions of locally high  $f(O_2)$ ."*

Fig. 7C: *"Compound zoned grain of geversite and breithauptite with a Pt oxide rim enclosed in serpentine."*

Fig. 7D: *"Composite grain of predominantly Pt oxide with relict geversite enclosed in a vein of serpentine in chromite."*

p. 516. Table 5: *"Electron microprobe data on platinum oxide (?) in chromitite (Oxygen by difference)."*

[The Pt oxides quoted in the body of the text and in the tables are not outlined in the abstract, not in the discussion or the conclusions. Several figures suggest the presence of PGE-oxides]

**Oberthür et al. 2000**

p. 3: *"The PGM [in the oxidized Main Sulfide Zone] mostly show no features of alteration besides being black in colour due to a thin surface coating....The suite of PGM is largely identical to that of the pristine, sulfide MSZ, however, many (Pt,Pd)-bismutho-telluride grains show alteration zones along their rims. Microprobe analyses of these altered zones indicate that they consist of still ill-defined mixtures of (Pt,Pd)-oxides-hydroxides."*

p. 4: *"It is evident that the "missing" PGE contents in the pervasively oxidized ores are either dispersed in iron-hydroxides, or in smectites, or are present as distinct PGE-oxides-hydroxides, at still unknown relative proportions."*

**Olivo et al. 1994**

Figs. 5 & 6: *"Back-scattered electron image of gold with small inclusions of Pd-Cu oxides" and "Enlargement of area showing Pd-Cu oxide inclusion in the gold grain."*

Fig. 8. *Scanning electron micrograph of gold grain from Corpo X orebody with a Pd-Cu-oxide inclusion.*

**Olivo & Gauthier 1995**

p. 459: [Description, optical properties and EMP-analyses of palladium-copper oxide (Pd,Cu, Hg, Au, Fe, Se, Sb)O conformable with hematite lamellae. Oxygen calculated by stoichiometry (?).]

**Olivo & Gammons 1996**

p. 549: [Pictures showing several in-situ (Pd,Cu)O lamellae in jacutinga].

ibid.: *"In contrast, at low temperature, any fluid that equilibrated with atmospheric oxygen would lie well within the PdO stability field, suggesting that PdO at the Cauê mine probably formed at low temperature by interaction with near-surface waters".*

**Oman et al. 1997**

p. 3: *"One coal waste sample from Coleman County Texas (an area that experienced silver mineralization) had 42 ppb Ru and 1900 ppb Pt! Because two other coal waste samples from this site had no more than ppb levels of the PGEs, these exceptionally high values are suspect."*

**Parnell 1988**

From the abstract: *"Native platinum occurs as submicrometer-scale inclusions in pyrobitumen at Fonda, New York."*

p. 1170: *"The occurrence of platinum grains in crosscutting fractures in the pyrobitumen could be interpreted (1) as precipitation from organometallic compounds as the pyrobitumen was progressively carbonized or (2) as precipitation from later migrating fluids, induced by the reducing environment of the organic material."*

**Peterson 1994**

p. A8: *"In a retrieval of PGE analyses from the PLUTO geochemical data base of the USGS, five samples of the Meade Peak Phosphatic Shale Member of the Phosphoria Formation are reported to contain 1.6 to 2.0 ppm Pd; the accuracy of this information has not been verified".*

**Prichard et al. 1994**

p. 285-286: "Many of the assemblages of Pt- and Pd-bearing PGM include low-reflectance minerals that form composite grains with other PGM. Their textural associations suggest that they are products of alteration of earlier PGM; [EMP] analyses show that they contain oxygen. Detected compounds [are] Pt, As, Cr, Fe, Ni, Cu and Rh oxide associated with hollingworthite, geversite, hongshiite and genkinite; Pt, As, Ni, Cu and Fe oxide associated with sperrylite; Pd oxide associated with Pd antimonides....All these examples emphasize the wide distribution of ochres throughout the PGE-bearing lithologies in this ophiolite complex." [Fig. 14]

p. 290: "The low-reflectance Pt- and Pd-bearing oxides or ochres...are shown here to be quite widespread in this ophiolite and present wherever Pt- and Pd-rich PGM occur. They take a poor polish and are friable. Texturally, they occur around the other PGM, suggesting that they were the last PGM to form. They are considered to be products of oxidation formed by present-day weathering, characterized by high fugacity of oxygen."

**Przybyłowicz et al. 1990**

[Pd and Pt, respectively 310 and 270 ppm wt., determined by micro-PIXE in thucholite].

**Rose 1842**

v. 2, p. 386-388: "NATIVE PLATINUM - Steel grey to silver white, with metallic shine, but sometimes altered to dull brown." [...] "[Platinum is] soluble in boiling aqua regia, normally with a residue of osmium-iridium flakes, which are frequently admixed to Uralian platinum, according to Berzelius."

**Rosenblum et al. 1986**

p. 30 and Fig. 19: "...we discovered that platinum was held in the magnetite lattice near the borders with Pt-Fe alloy. The results shown by contour lines in Fig. 19 indicate a range of ratios from Fe 10:Pt 0 to Fe 10:Pt 7.5. Similarly, in grain 2 of the same sample, we discovered that magnetite near the borders with PGE phases contained small amounts of rhodium and iridium. In all such border areas of magnetite, we inferred that there was a considerable amount of PGE and that such magnetite grains constitute a source of PGE that should not be ignored". "Contour lines of platinum : iron ratios [in magnetite] show that platinum has diffused into magnetite near the borders of Pt-Fe alloy."

p. 25-29 : "Unknown phases: Four unknown phases could correspond to oxidic compounds, although the authors do not consider that possibility. The needle or blade habits, the reflected light properties (strong anisotropism, bronze colour) and the complex chemistry strongly suggest that possibility:

U. A (Ir-Fe) and Figs. 12 and 14.

U. B (Ir-Rh-Pt-Fe-As) and Figs. 4 and 9.

U. C (Rh-Pd-Ni-As-S) and Figs. 7 and 9.

U. D (Pb-Rh-Fe-Ir-S) and Figs. 13 and 14."

**Salpéteur et al. 1995**

[Passim: Observations, figures and analyses acknowledge the probable presence of Pt-Pd oxides and hydroxides, here interpreted as aggregates of supergene origin. However, the authors' efforts are mainly devoted to demonstrate the possible formation of secondary Pt-Fe alloys at low temperatures.]

p. 35: "Ovoid micronodules with smooth surfaces or covered by a microporous rusty FePt crust (Fig. 7.8 and 7.9) containing trace amounts of Pd, Co, Cr and Si."

p. 38: "A similar spongy area has lost its As content and the resulting analysis shows a weight deficit that could indicate a mixing of two phases: the Pd oxide (PdO recalculated ...after Fe correction) and a Pd(Cu, Ni, Au, Sn) alloy. Optical observation of the spongy material shows the vugs filled with a black material very similar to the recently described occurrences of palladinite."

p. 38: "Spot microprobe analysis of the crystal edge shows a considerable weight deficit...that could indicate a mixing of several mineral phases: relict of a vincentite type mineral mixed with a Pd, Fe, Cu oxide phase and alloy....This occurrence indicates that a secondary alloy of Pd and palladinite (a Pd oxide) may coexist in ferrallitic soils."

**Seredin & Evstigneeva 1997**

p. 109: "The native metals [are] associate[d] with various sulfides, halogenides (chlorides, bromides, iodides and fluorides) and halogen-bearing phases (oxyhalogen-ides, chalcogenides, fluorine- and

chlorine-carbonates) of most of the elements detected as native metals. These minerals are in aggregates with various native metals, and are included in them." [These observations would strongly support a natural origin of the detected PG native metals and alloys, also described in Seredin (1997), but the possible presence of oxygen is never addressed. The extraordinary list of observed native metals should have been supported by a regard for a possible anthropogenic origin.]

#### **Shepard 1857**

p. 144: "Sp.9. Palladium-ochre. Occurs in very small spherical masses, with a radiated, fibrous structure. C[olour]. yellowish, or greyish white. B[lowpipe]. acts like telluric acid. Found very rarely at Fauberg and Zalathna in Siebenburg. [An obvious confusion with data from another locality, where palladium has never been described, but telluric acid well.]

#### **Stribrny et al. 2000**

p. 263: "Great Dyke, Zimbabwe. Oxidized Main Sulfide Zone-MSZ: ...the fate of the "missing" Pt (ca. 75%) and Pd (100%) not present in a particulate form remains open. Both elements appear to be dispersed either in iron hydroxides or in smectites, prob-ably also in the form of " PGE oxides".

#### **Tamana 1994**

Fig. 4.19: [Esterly Mine, pit 1, Oregon; Sample BM1982,320]: "A SEM photomicro-graph of a cross section of the grain shown in Fig. 4.18. The grain exhibited a complex alteration. The iridium bulk was replaced along cleavage boundaries by iron and iridium oxide."

#### **Thoreau & du Trieu 1933**

p. 14: "PRECIOUS METALS-The presence of Precious Metals in the Shinkolobwe deposit has been recorded at the very beginning of the investigations. Gold flakes can be obtained by panning the hard rocks, either in the uranium mineralized zone or elsewhere. Pitchblende shows sometimes native gold as coatings and as thin crevice fillings. The analysis of the residues of ore treatment shows that there is additional Pd and accessory, Pt. One has also recently found a faulted zone, slightly mineralized in U, Cu, Co and Ni, and showing noteworthy contents of Au and Pd. Au is in its native state, but as for Pd, it has not been possible until now to determine its speciation."

#### **Timofeeva 1968**

p. 461: "One observes palladite in close association with iron hydroxides in the oxidation zone of the sulfidic body."

p. 464: "Porpezite (Au, Pd), potarite (PdHg<sub>3</sub>) and allopalladium have been found in the primary ores and in their oxidation zones; palladite has been found in the iron hydroxides."

#### **Timofeeva 1975**

p. 42-43: "Platinum: Occurrences of platinum minerals were met with in contiguous areas of the Kyrgyz SSR, near the border of Uzbekistan. Indeed, polyxen and porpezit have been found in the Kurutegerek deposit (Sandalashskii Range), for the first time in Central Asia. According to T.S. Timofeeva (1968, 1971), here were found native platinum, cuproplatinum, cooperite, niggliite, sperrylite, allopalladium, potarite and pallad-ite." [The properties of palladite are not whatsoever described, but the locality is here better indicated than in the preceding reference].

#### **Tolstykh et al. 1996**

p. 39: "A peculiar feature of Fe-bearing platinum from the placer of the Tyulenevsky Spring is the presence of rims tentatively consisting of platinum carbide. These rims occasionally contain segregations of native gold (Fig.5: Pt<sub>2</sub>C<sub>3</sub>)."

p. 35 From the abstract: "The Pt-Fe solid solutions might undergo alteration under postmagmatic conditions to form copper-bearing platinum and hongshiite...as well as reactional metasomatic rims composed of sperrylite, cooperite, and platinum carbide."

Fig. 5: "Rh-bearing Pt(Fe) with Pt<sub>2</sub>C<sub>3</sub> rim and Au(Ag) segregation. Placers of the spring Tyulenevsky."

**Tolstykh et al. 2000**

From the abstract: "*Pd-Sb-Bi oxides occur in the exocontact sulphide ores of the Chiney anorthosite-gabbro-norite massif. Three types of oxides have been distinguished: Pd-Sb, Pd-Sb-Bi, and Pd-Bi oxides... The formation of Pd-Sb-Bi-O minerals may have been due to a high-temperature fluid influencing the host sandstones of the exocontact ores.*"

p. 438-439: "*Discussion. The supergene hypothesis of the formation of PGE oxides is hardly probable in this case because: (1) the samples in which the investigated oxides were found are not oxidized, and (2) these minerals have not been found in the oxidation zone of sulphide ores from the Chiney massif. Properties of the discovered oxides are supported by numerous photographs, chemical analyses (including oxygen), and measured optical properties.*"

[p. 438-439: The stoichiometric formulas calculated by the authors are as follows:

-Pd<sub>5</sub>Sb<sub>2</sub> to Pd<sub>5</sub>Sb<sub>2</sub>O<sub>4</sub>, with unaccounted Fe (up to 8.21 wt. %) and Cu (up to 2.66 %)

-Pd<sub>2</sub>(Sb,Bi)O to Pd(Sb,Bi)O<sub>2</sub>,

-Bi<sub>2</sub>O<sub>3</sub> (with a few unit % Pd)-Pd<sub>3</sub>Bi<sub>3</sub>O<sub>4</sub>.]

**Urashima et al. 1974**

From the abstract: "*Platinum grains from Yubdo, western Ethiopia... occur in lateritic layers covering ultrabasic rocks and birbirites. Most of the grains are subangular and are coated by iron hydroxides and iron oxides.*"

p. 409, Fig. 5: "*Platinum (white) coated by iron oxides (pale gray). Yubdo.*" [This figure shows a thick crust of variable shades of gray, following the exact shape of the platinum grain. Although this crust has not been analysed for PGE, the morphology is reminding of several cases of Fe-PGE crusts observed elsewhere.]

**Urashima et al. 1977**

"*This [Ru-Mn-O] mineral occurs in elongate crystals of 20x30 micrometer of a white-metallic colour, and is associated with Pt-Fe and an unknown Ir mineral. The relative hardness is lower than that of the Pt-Fe, it is putty-coloured, and it shows a weak opt-ical anisotropism. The main components are Ru, Mn and O, with minor Ir, Pd, Fe, Ni, Cu, Si, Al, Ca, Na, etc. This mineral has a probable formula close to RuMnO<sub>4</sub>. Previous reports of either Platinum Group Minerals with a major Mn content, or localities of oxide minerals of the Platinum Group Elements have not been found in the literature.*" [Transl. M. Nespolo et al.] [SEM picture and EMP maps for Ru, Mn and O.]

**Varajao et al. 1999**

From the Abstract: "*Xenomorphous particles of an undefined Pd-Cu rich phase associated with palladian-gold... reveal by EMP analysis that it contains approximately 7.5 wt-% of oxygen. The mean chemical formula is Pd<sub>5</sub>(Cu,As)O<sub>3</sub>.*"

**Vuorelainen et al. 1982**

p. 1517 "*A dark grayish palladium arsenate with distinct anisotropy occurs as an alteration product of the phase (Pd,Cu)<sub>7</sub>(As,Sb)<sub>2</sub>. The phase is oxygen bearing and, if interpreted as hydrated arsenate, has a formula of (Pd,Cu,Ni)<sub>18</sub>AsO<sub>4</sub>·4H<sub>2</sub>O.*"

Fig. 5. "*Back-scattered electron image of an arsenopalladinite or an unknown Pd<sub>5</sub>As<sub>2</sub> crystal which is replaced by unreproted phases of (Pd,Cu)<sub>7</sub>(As,Sb)<sub>2</sub> and palladium arsenate.*"

**Weiser 1992**

p. 52: "*During our work on platinum-group minerals (PGM) in placer deposits from world-wide occurrences we rarely observed inclusions with a very low reflectivity in Pt-Fe alloys under the microscope. Microprobe analyses for 15 elements gave only a total between 84 and 93 wt.%. The qualitative and quantitative analyses for oxygen showed that the difference to 100 wt.% is really oxygen. Probably two or three different Pt-oxides and one Ir-Pt-oxide exist.*"

Poster explanatory text: "*EMP analyses (including oxygen) of inclusions with unusual optical properties. Platinum and iridium oxides: Pt<sub>2</sub>O<sub>3</sub>, Pt<sub>3</sub>O<sub>2</sub> (Chidwin Riv. placer, Burma) and (Ir,Pt)O (Condoto Riv. placer, Colombia).*" [Although most of the analyses yielded minor to major concentrations of Fe, this was not accounted for.]

**Weiser & Bachmann 1999**

p. 1143 and Fig. 9d: *"Undefined Ru-Os-Ir oxide: One grain of osmium from the Aikora area contains an unknown mineral in fractures and at the grain boundary. The phase looks grey with a brownish tinge, is weakly anisotropic, and shows undulatory extinction under reflected light in oil immersion...The calculated formula corresponds to (Ru,Os,Ir)O for the grain within the Os-Ir-Ru alloy, and (Ru,Os,Ir)O<sub>2</sub> for the grain at the boundary of the alloy."*

**Westland 1981**

p. 9-10: Platinum-Group Elements and oxygen: *"Several of the PGE oxides, e.g. IrO<sub>3</sub>, have only marginal stability, but incorporation into ternary systems makes them quite stable."*

p. 12: Solution species. *"Reducing agents are capable of reducing the PGE to oxidation states of 2, 1 and 0, but usually, ligands of the so-called "back-bonding" type, such as carbon monoxide, must be present except for Pd(II) and Pt(II). A few such ligand substances may occur in ground water containing humic matter, but the reducing conditions are rarely, if ever, present. Hydrocarbons are another possible source of such ligand substances.... Complexing substances other than water and chloride which may be important under natural circumstances are ammonia, amino-acids, other organic nitrogen compounds and sulphide. Important ammine complexes are [Pt(NH<sub>3</sub>)<sub>6</sub>]Cl<sub>4</sub> and [Pd(NH<sub>3</sub>)<sub>2</sub>]Cl<sub>2</sub>. Organic amines, purines, etc. can form compounds analogous to these. These would be expected to occur in the presence of decaying organic matter. Sulphides of the Os-Pt triad dissolve in alkaline solutions, possibly by forming thioanions such as [Pt(SH)<sub>x</sub>(OH)<sub>4-x</sub>]<sup>2-</sup>. The dissolved species may be more complex, however, and some of them may be colloids."*

p. 13. Redox reactions. *"The PGE's display their so-called noble character only in the absence of strongly complexing species....Because the oxides have not been observed as minerals, the reader will perhaps be more interested in the redox behaviour of the chalcogenides."*

p. 16-17. The geochemical cycle. *"The writer (unpublished work) has combined ruthenium with silica in the form of alkali ruthenosilicate. Thus, the PGE in ultramafic rocks may be in the form of metallosilicate anions, a postulate that requires further work for verification.... Weathering by oxidation of natural metal alloys is undoubtedly slow. It has been pointed out above that moderately strong oxidizing solutions that contain complexing agents, chloride or possibly humic matter, could accomplish the dissolving process....Once rendered soluble, the PG complexes would probably have but a brief existence as solutes. Like gold, they would be easily reduced or adsorbed physically or chemically in organic matter. Redeposition of placers and compound minerals a little distance from the primary ore is common."*

**Wilde et al. 2003**

[Review paper mainly devoted to mineralization processes and to prospection aspects, with generous reference section.]

p. 11 : *"...in Jabiluka...[where high Pd concentrations are spatially coincident with high Au and U grades within brecciated carbonaceous schist] no discrete Pd-bearing minerals have not been identified."*

**Wright & Fleischer 1965**

p. A7 and Table 5: *"Oxides: Pd (palladinite)(?). Uncertain."* [no references].

p. A10: *"Oxide minerals that have been reported to contain more than 1 ppm of total platinum metals are pyrolusite, psilomelane, cassiterite, columbite and chromite."*

p. A20: *"Suggestions for future study: Detailed study of the mineralogy of the platinum metals is just now beginning. The electron microprobe should be used to determine the limits of solid solution of platinum metals in natural alloys, the composition variations of platinum-metal compounds, and the extent to which trace amounts of platinum metals in rock-forming minerals are present as discrete inclusions or as substituting ions."*

**Zavaridsky 1928**

p. 53. [Zav. translation]: *"Platinum of the primary deposits after its formation was submitted to secondary alterations. On the outward surface of the grains thin rims were formed. They are easily etched by acids and contain, besides platinum and iron, a certain amount (up to 13 %) of copper. The structure of these rims is different [sic] (see fig.2-6, Plate IV)".*