

Dedicated to the memory of Dr A. J. Criddle, Natural History Museum, London, who died in May 2002

'Irite' (Hermann, 1836/1841) from the Urals

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ABSTRACT

A reappraisal of Hermann's 'irite', described in 1836 and 1841, has been attempted by examining and analysing three museum samples, accessioned before 1865. The three samples were determined to be mixtures of chromite, native Os and Ir, rutheniridosmine, platinum, laurite, hongshiite, irarsite, cuprorhodsite, iridsite, prassoite, hollingworthite, erlichmannite, 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. The latter two are considered as artifacts generated by the hydrometallurgical processes applied to the crude platinum ores. Individual particles of native iridium and osmium display baroque crystal habits (filaments, leaves, blades, hollow crystals) that could be their natural, although rarely observed, states. There is still doubt about the origin (either natural or artificial) of all Ru-Ir-Pt-Ti-Cr-Fe oxides, but they can be compared with those found in several pristine placer and hard-rock deposits worldwide and in the Urals.

KEYWORDS: 'irite' Urals, PGE oxides, platinum group minerals.

Introduction

IN an endeavour to assess the earliest records of oxide and other platinum group minerals and mineraloids, intriguing references (often relegated to footnotes) were found to 'irite', a supposed oxide compound of iridium, discovered in the Urals by Hermann (1836, 1841). Claus (1860) dismissed that discovery as being a mixture, and further, considered such a natural compound as improbable. This position was adopted by subsequent authors and consequently, no reappraisal of 'irite' has been attempted until now. However, several oxide compounds of the Ru-Os-Ir series have now been described from the Urals and elsewhere and a reappraisal is required, as 'irite' samples have been preserved in museum collections from the time of Hermann and Claus.

The present paper has the following purposes: (1) to collect and revise the literature on 'irite'; (2) to present several key texts, which were

published in journals and books, presently not easily accessible, and written in French, German and Russian. Excerpts of these key texts are collected in the Appendix, and referred to in the text as "Exc."; (3) to extend this revision toward works not explicitly dealing with 'irite', but with laboratory experiments and hydrometallurgical procedures, tentatively explaining 'irite's' peculiarities; (4) to report microscopical observations, emphasizing the optical, morphological and paragenetic aspects, supported by chemical compositions; and (5) to discuss the results with regard to the earlier observations and writings, and to what is presently known about PGE oxides, either natural or artificial.

Historical landmarks

The discoveries of the new elements iridium and osmium (1803/4), rhodium and palladium (1804/5), ruthenium (1828/1844), and the Uralian platinum deposits (1819/1825) induced very active scientific and ore-dressing (hydrometallurgy) studies. Analytical difficulties and the race to discover new chemical elements chal-

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lenged several distinguished minds (Howe and Holtz, 1919). In particular, the discovery and mining of the very rich placer deposits of platinum in the Urals involved relatively easy access to a continental ore field and to large quantities of ores, important since earlier studies on South American platinum ores (Colombia and Brazil) had been hampered by various colonial interests. In addition, the then useless residues left behind after the aqua regia extraction of platinum were recognized by several authors as a good starting material for the discovery of new elements, and generated several papers (Charonnat, 1958; Pitchkov, 1996; Exc. 1 and 4).

Hermann (1836)

These circumstances are at the root of Hermann's involvement with the worthless Ir-Os-rich residue obtained at the Imperial Mint, in St. Petersburg (Hermann, 1836; Exc.1; Pitchkov, 1996). Hermann's first paper was devoted to the isolation by levigation and to the chemical analysis of a light fraction from this residue. He found that it was an Ir-Os-Fe-Cr sub-oxide ("oxydul") which he called "Irit" ("irite" in English and French), and even recognized in it shiny black octahedra which he considered as the main compounds. He claimed forcefully to be the first to have discovered a natural oxidic compound of a platinum metal, one year in advance of the discovery by Johnson and Lampadius (1837) of a palladium-iron oxide in Brazil (Jedwab and Cassedanne, 1998).

The chemical analyses performed by Hermann on his lighter fraction yielded the following composition (given as wt.% oxides (oxyduls): iridiusesquioxidul = 62.85; osmiumoxydul = 10.18; ironoxydul = 13.31; chromiumoxydul = 13.66; + tr. Mn. A recalculated composition in wt.% of the metals + oxygen is to be found in Dana (1892): "Ir 56.04, Os 9.53, Fe 9.72, Cr 9.40, tr. of Mn, with a loss of 15.25, which [Hermann] reckoned as oxygen".

The same 1836 paper also contained an important chapter on the chlorides and ammoniochlorides of Ir and Pt, formed during the aqua regia treatment of the platinum ores, and the subsequent reprecipitation of pure platinum by ammonium chloride (Exc.2). Hermann noted that these salts of Ir and of Ir-Pt were often formed during the evaporation to dryness of the final liquor. This statement will prove to be of direct relevance for observations presented here. In

time, Hermann's 1836 paper sank into oblivion in favour of the 1841 paper, probably because in the latter Hermann did not refer to the 1836 paper. Howe and Holtz (1919), Swjagintzeff (1932; Exc. 13) and Yushkin *et al.* (1986; Exc. 14) are the only authors to have quoted that 1836 paper.

Hermann (1841)

Shortly after his first paper, Hermann published another on nearly the same topic, apparently with some bitterness, since the earlier paper did not receive the attention he considered it to deserve (Hermann, 1841; Exc. 3). Indeed, according to Howe and Holtz (1919) who record all follow-ups and references to each paper, Hermann's 1836 paper received no citation, whereas the 1841 paper received six citations in the following years. Hermann (1841) does not acknowledge Johnson and Lampadius (1837), who fail to cite Hermann (1836). This is normal, considering the narrow time span; but the claims made separately by Hermann and by Johnson and Lampadius indicate a concern for, and an overjoyed astonishment at, finding oxides of the platinum metals, reputedly unalterable.

There is a notable difference between Hermann's two papers: when in the first, he positively states that 'irite' is the separated residue of chemical extraction of platinum, in the later one he states that 'irite' is already present and discernable as a black, fine powder in the cavities of the larger [untreated] native platinum pieces, and especially in the most iron-rich ones (Exc. 3). But he does not give an analysis of this powder, which could belong to the pervasive black oxide crusts found on platinum nuggets in placers. Hermann also stresses here that several others had already observed 'irite', but that they erroneously equated it to osmium-iridium, or a mixture of osmium-iridium and chromite.

Other contributions to the 'irite' problem

A search for other first-hand examinations by knowledgeable scientists disclosed only two papers: Kennigott (1849; Exc. 5) and Claus (1860; Exc. 8). Interestingly, a nearly contemporary paper by von Muchin (1842) dealing with a related subject (the chemical analysis of black and magnetic platinum grains from the same Uralian locality) does not mention Hermann's works, nor does Rose (1842; Exc. 4) or von Kokscharow (1866) in the platinum and iridium

sections of his monumental work, in which von Muchin is largely quoted. *Dufrénoy*

Kenngott

Kenngott (1849; Exc. 5) examined two samples belonging to one Dr Schneider, in which he observed, under medium magnification, three types of particles: shiny flakes, irregular grains, and small crystals of octahedral habit. He also noted a large difference in the proportions of the three particle types between the available samples (fully confirmed by present observations). This is Kenngott's only published contribution to the 'irite' problem, as far as can be judged from his bibliography (Grubenmann, 1897).

Claus

Claus is celebrated for his discovery of Ru and for the establishment of its analytical properties (Pitchkov, 1996). We know from Rose (1842; Exc. 4) that Berzelius was already familiar with the residues of dissolution of Uralian platinum. But the latter's works await a reappraisal from the point of view of the 'irite' problem.

Claus' starting materials were two bulk samples of aqua regia leach residues of the Nishnij Tagil platinum ores, the very same from which Hermann separated 'irite' (Pitchkov, 1996). The latter work depicts a flow sheet of Claus' operations leading to the separation of metallic ruthenium, giving an insight into the several stages (and chemicals) to which the aqua regia residues were submitted, before being circulated as "irit". The first steps of this flow sheet are the same as those used by Berzelius for the analysis of platinum ores. One of the first products of the aqua regia treatment, separated by the Berzelius process, were the "sands", which were discarded, and not even mentioned again (Duparc and Tikonowitch, 1920).

Claus was naturally aware of Hermann's work, ([Claus, 1844, work known by a quotation in Pitchkov, 1996]; Claus, 1860; Exc.8). He recognized the mixed character of an 'irite' sample prepared by himself using Hermann's procedures, and disputed giving a mineral name to a mixed levigation fraction. Indeed, Claus was among the first to observe minerals under the microscope (Pitchkov, 1996) and the mixed character of 'irite' was thus obvious to him. More oddly, Claus considered the possible existence of an oxidic compound of Ir, Os, Fe and Cr, claimed by Hermann, as improbable ("unwarscheinlich").

Dufrénoy (1859; Exc. 7) published a section on 'irite', quoting in the body of the text the name of Hermann with reference to a footnote. But the latter gives the title of an 1833 paper by Rose, antedating Hermann's papers, and dealing with a different, although related subject. Moreover, Dufrénoy focuses mainly on hard, black octahedra, more likely to be chromite than Hermann's graphite-like material. Rose (1833) has yet to be checked to see if the confusion with chromite was due to a misreading by Rose (who was fluent in German) or by Dufrénoy. In any case, Dufrénoy had some involvement with 'irite', since his name appears as the first owner of the sample from the Museum of Paris studied here, but there is no evidence he studied it himself.

Later literature

Several later mineralogy handbooks and treatises relied on Claus' opinion to dismiss 'irite' as a mineral species (Dana, 1892; Swjagintzeff, 1932, Exc. 13; Palache *et al.*, 1946; Chuboda, 1960; Hey, 1962; Yushkin *et al.*, 1986, Exc. 14; Clark, 1993), whereas others merely reproduced Hermann's analysis describing shiny octahedra, which were actually chromite, as crystalline 'irite' (Dana, 1851). 'Irite' does not seem to have been studied again by modern Russian mineralogists (Chukhrov and Bonstedt-Kupletskaya, 1967; Yushkin *et al.*, 1986; Begizov, 1986).

The hydrometallurgy of the crude platinum ores

Since 'irite' is an artifact, both in its chemical procurement and its physical separation, the processing of the crude platinum head-ore must be considered (Duval, 1958). A few points may be highlighted.

(1) The processes of selective dissolution of platinum and palladium from the crude ores with aqua regia, and the subsequent selective precipitation of platinum from the acid solutions by sal-ammoniac were well established since Berzelius (Duparc and Tikonowitch, 1920). Berzelius also observed the insolubility and thus, the concentration of native iridium, osmium and their alloys resulting from these two stages of head-ore treatment (Rose, 1842, Exc. 4).

(2) The aqua regia treatment was not carried out in the Urals, but the concentrates were

transported to the St. Petersburg Mint, where the worthless insolubles were piled up (Pitchkov, 1996). Later, the concentrates were sent abroad (to Germany, Great Britain, and to France after 1896, de Hautpick, 1910; Merz, 1918). This explains why and how 'irite' ended up at several places outside Russia, and why the samples appear so different.

(3) Several details concerning 'irite' may be found in the detailed accounts of the hydro-metallurgical operations given by Duparc and Tikonowitch (1920) and by Pitchkov (1996). Flow sheets of the various analytical schemes and extraction procedures are given here but after Berzelius, the "sands" were not considered.

(4) Duparc and Tikonowitch (1920) stated that native platinum could not be completely dissolved in one operation, which was repeated (partly in the dark), and that several intermediary products ("noirs" = blacks) were progressively generated when extracting and purifying the five other PGE.

(5) Numerous chemicals were used at each stage, and traces of these could remain in the intermediary products if the latter were washed without care. This could easily happen when eliminating these worthless products, particularly since several of the PGE-containing artificial components were difficult to dissolve and to eliminate, especially the chlorocompounds. It was only at the end of the 19th century that the commercial value of the residues was recognized, and more care was given to their elimination (Exc. 12).

(6) One point still unclear is the composition of the first insoluble residue. Duparc and Tikonowitch (1920), following Berzelius, refer to it as "sands", containing chromite, native iridium and osmium, and the "osmiures" (a name given by Berzelius to the insoluble Ir-Os-Pt alloys). However, nowhere is it stated that they also contained quartz, opal and silicates, only suggested by the use of the word "sands". Hermann seems to be the first to have insisted on the presence of large amounts of Ir-Os-compounds in the sands.

(7) It is well known that the aqua regia treatment dissolves a part of the silicates, which forms a gel, later insolubilized as silica (opal) when the highly acid solution is heated and brought to dryness (Hillebrand and Lundell, 1953). According to the latter, opal precipitated in the course of regular chemical analyses contains several minor elements, like Al, Fe, PO₄, Ti, but no analyses of the "sands" left by the

aqua regia treatment of the platinum concentrates were found. It is reasonable to consider that PGE, Cl and K are adsorbed on the colloidal silica formed during the ore treatment.

Samples studied

The following museum samples were studied:

(1) *Naturhistorisches Museum-Vienna, Austria*

#? Printed label: "Irite (Hermann). Feiner Sand aus den Höhlungen des gediegen Platin. Tajilk [sic], Ural. Acq. Post. 1865.XVI.44. A. Krantz in Berlin". [Irite (Hermann). Fine sand from the cavities of the native platinum].

Excerpt from the register: "8. Mai 1865, im Kauf von Hr. August Krantz, Mineralienhändler in Bonn-am-Rhein, um 525 fl. aus dem Extraordinarium". [8 May 1865, bought from Mr. August Krantz, mineral dealer in Bonn-on-the-Rhein, at 525 fl. on the extraordinary [budget?]]. The labels refer literally to the kind of material described by Hermann (1841), and not to the aqua regia residue. But this is not as stated. This sample is fine-grained, black and powdery, and contains numerous fragile aggregates. Abbreviated as NHMV in this work.

(2) *Muséum National d'Histoire Naturelle-Paris, France*

Label: #52.657. "Irite de Hermann. Tagilsk, Russie. Coll. Dufrénoy, 1865. Orig.: Dr. Krantz." The sample is composed of a fine powder. Abbreviated as MNHN in this work.

(3) *Ecole Nationale Supérieure des Mines-Paris, France*

Label: #6774. "Iridosmine, Variété: Irite. Taguilsk, Oural, URSS".

An old printed label by "Dr Krantz-Berlin" is identical to the one from Vienna. Register: "6774. Irite, chromite. Nijni-Taghil, Sverdlosk, Oural, Fédér. de Russie. Echange Dr. F. Krantz, Bonn 1856 (7092 Adam)." The sample is composed of grey to black, submillimetric nuggets, flakes and fragments. Abbreviated as ENSM in this work.

(4) *Natural History Museum, London, United Kingdom*

Label: # BM.1982.320: Mertie Collection. Klamath Mountains, SW Oregon, USA). J. B. Mertie Jr. (Mertie, 1969) collected this placer sample. It was lent to the author through Alan

Criddle. The collection was studied by Tamana (1994), who observed in passing a particle of iridium-iron oxide, which is not the same as that illustrated in this work. Mertie's sample has apparently not been subjected to any aqua regia treatment, and may thus be considered as pristine placer material, suitable for comparison purposes. Abbreviated as NHML in this work.

It is remarkable that Dr Krantz distributed all the 'irite' samples over a short time span, although being physically different. However, they did not come directly from Russia in the hands of the famous mineral dealer, as stated above. Indeed, and according to the archives preserved at the "Dr Krantz-Mineralien-Kontor", somebody from the firm was sent to Russia in 1847 on a trip to buy minerals, but 'irite' does not appear in the records (Ms U. Mueller-Krantz, pers. comm.). The Paris samples passed through the hands of the systematic mineralogists Adam, Dufrenoy and Blum. The pre-registration whereabouts of the Vienna sample are not known, but could be related somehow to Kenngott, who studied 'irite' in Breslau (Kenngott, 1849), and who sojourned in Vienna from 1850 onwards, where he studied at the Hofmineralienkabinett with Partsch and Haidinger, and acted as custodian-assistant in this same museum from 1852 to 1856 (Grubenmann, 1897). However, the dates do not match the date of acquisition from Krantz.

Methods of study

Sample preparation

The three samples were hand-picked under a binocular microscope and selected particles were mounted on SEM/EDS stubs with double-sided adhesive tape. Also, bulk powders and separate grains (hand-picked or sifted) were embedded in epoxy or bakelite, ground with silicon carbide papers, and polished on synthetic cloth with alumina.

Microscope observations

Preparations were observed under the reflected polarizing light microscope (RLM) with dry and oil immersion objectives, and particles of interest were located with an object marker. The scanning electron microscope-SEM (JEOL-S733) was used in its back scattered (BS) and secondary electron (SM) modes to study the particles of interest located by RLM, and otherwise interesting particles selected by their BS yield.

The main mineralogical difference of interest in this work is between the metal/sulphide and oxide states. RLM was used to determine properties of opaque minerals and also of semi-transparent and transparent minerals. Under the SEM(BS), the correct balance of contrast and brightness on associated metal or sulphide phases, combined with fast EDS analysis of dark phases, enabled oxide phases to be located.

Chemical analyses

Qualitative and semi-quantitative (standardless) chemical analyses were obtained with a X-ray energy dispersive spectrometer (EDS) NORAN-VOYAGER (spectral range: 0.1 to 20 keV; acceleration voltage: 25 kV; beam intensity: 10^{-9} A; spot diameter: 100–1000 Å). Chemical data are unreliable for oxygen, water, hydroxyl and nitrogen (ammonium). Nitrogen is not detectable by this method and under these conditions, and gaseous oxygen is easily absorbed by the PGE in their metallic state. Even the highest reflecting native Ir and Os and their alloys show noteworthy and variable oxygen in their analyses (Tables 1 and 3). This may be due either to gas absorption (Duval, 1958), or to incipient oxidation, suggested by the presence in the spectra of incompatible elements like Ca, Ti, Cr. In the case of partly oxidized laurite (Fig. 4e), both S and O occur.

The tables display the values in wt.% and at.% of triplicate spot analyses. Standard deviations are generally satisfactory for major elements, but less so for minor elements. Sought for but not detected elements are represented by "0.00". Although it is probable that the elements in the oxidic compounds are mostly present as oxides/hydroxides, they have been calculated as elements, due to their variable valencies (Augé and Legendre, 1994a,b; Legendre and Augé, 1993; McDonald *et al.*, 1999a,b), and their state (ionized and/or metallic). An enduring problem is the presence in the oxidic masses (either massive, weblike or crystallized) of minute residues of alloys and primary minerals. (Fig. 4c).

For the PGE-chlorocompounds it was impossible to distinguish between simple chlorides, oxychlorides, ammonium chlorocompounds, and double salts of potassium-ammonium with the methods used. The latter salts are probably present and indicated by deficient or absent K in the spectra.

It was difficult to distinguish the PGE oxides on a purely chemical basis for two reasons: 'pure' metals

TABLE 1. Electron microprobe data (wt.% and at.%) for metals with topochemical alterations.

Wt.% <i>n</i> = 3 cryst.	1 Fig. 3a,b Metal	2 Fig. 3c,d Oxide cryst.	3 Fig. 4a Metal	4 Fig. 4a Lamellar oxide	5 Fig. 4c Metal	6 Fig. 4d Oxide
Ru	2.68±0.62	2.56±0.92	31.75±1.22	14.24±1.89	5.78±0.64	5.51±0.93
Os	7.26±0.28	1.11±0.82	25.77±2.03	2.59±1.22	53.50±2.34	4.27±2.68
Ir	76.94±0.64	78.31±2.61	28.18±1.57	58.96±4.00	34.24±2.14	73.71±3.39
Pt	8.31±1.36	2.53±2.86	11.02±1.58	9.44±2.81	2.65±0.42	2.57±2.09
Fe	2.08±0.25	0.88±0.28	0.00	0.17±0.17	0.21±0.21	1.11±0.31
Ti	0.03±0.03	0.06±0.06	0.11±0.11	0.00	0.25±0.13	0.12±0.12
Cr	0.00	0.00	0.00	0.00	0.13±0.13	0.21±0.21
Cu	0.00	0.00	0.00	0.00	0.00	0.12±0.12
Ca	0.00	0.00	0.00	0.00	0.10±0.10	0.34±0.18
Cl	0.44±0.33	0.58±0.07	0.31±0.31	0.48±0.48	0.00	0.21±0.21
K	0.30±0.22	0.45±0.20	0.18±0.18	3.62±0.21	0.21±0.22	3.29±0.18
O	1.94±0.39	13.27±1.22	2.64±0.75	10.49±1.48	2.90±1.11	8.56±1.50
Total	100.00	100.00	100.00	100.00	100.00	100.00
Ru	3.86±0.89	1.92±0.69	37.71±1.44	11.08±1.47	7.92±0.86	4.81±0.81
Os	5.58±0.21	0.44±0.32	16.26±1.28	1.07±0.50	38.26±1.68	1.97±1.24
Ir	58.32±0.48	30.99±1.03	17.59±0.98	24.14±1.63	24.69±1.52	33.81±1.55
Pt	6.21±1.01	0.99±1.11	6.77±0.97	3.80±1.13	1.94±0.29	1.15±0.94
Fe	5.42±0.65	1.19±0.38	0.00	0.00	0.50±0.50	1.75±0.53
Ti	0.08±0.09	0.09±0.09	0.27±0.27	0.00	0.00	0.22±0.22
Cr	0.00	0.00	0.00	0.00	0.44±0.34	0.35±0.35
Cu	0.00	0.00	0.00	0.00	0.00	0.15±0.15
Ca	0.00	0.00	0.00	0.00	0.34±0.34	0.75±0.42
Cl	1.80±1.35	1.23±0.15	1.05±1.04	1.06±1.06	0.00	0.53±0.52
K	1.10±0.82	0.11±0.38	0.56±0.55	7.28±0.42	0.92±0.77	7.40±0.40
O	17.63±3.54	63.03±5.79	19.79±5.62	51.57±2.40	24.99±9.49	47.11±8.25
Total	100.00	100.00	100.00	100.00	100.00	100.00

Gains and losses recalculated on an oxygen-free basis (from metal to oxide, in at.%):

Gains: Ir Ti Cl

Losses: Ru Os Pt Fe K

Gains: Ir Cl K

Losses: Ru Os Pt Ti

Gains: Ir Fe Ti Cr Cu Ca Cl K

Losses: Ru Os (Pt)

can sometimes contain oxygen in high concentrations (Table 1, columns 1, 3, 5); the stoichiometric proportions of *Me*/oxygen vary between 3/1 (Table 3, col. 5) and 1/3 (Table 1, col. 2). Optical microscopy is useful in distinguishing these.

Mineralogical identification

Whereas the analyses of primary species (alloys, sulphides, etc.) yield satisfactory metal ratios and stoichiometries, the impure, mixed or variable nature of the alteration materials do not yield reliable stoichiometric coefficients since these are mostly mineraloids and/or amorphous

compounds. However, crystalline alteration products, such as those displayed in Fig. 4d, gave more reliable determinations. It has been shown elsewhere that several *Me*/oxygen ratios coexist in the same materials (Augé and Legendre, 1994a,b; Legendre and Augé, 1993; MacDonald *et al.*, 1999a,b).

Results

Numerous defined species and undefined compounds were observed as free particles, inclusions, crusts, alterations, replacements, or entering into heterogenous agglomerates.

'IRITE' FROM THE URALS

TABLE 2. Electron microprobe analyses of altered chromite (Fig. 5c,d).

Wt.% <i>n</i> = 3	1 core	2 margin	At.% <i>n</i> = 3	1 core	2 margin
Ru	0.03±0.05	1.00±0.10	Ru	0.01±0.01	0.33±0.03
Os	0.14±0.14	0.21±0.18	Os	0.02±0.02	0.03±0.30
Ir	0.43±0.24	2.78±0.28	Ir	0.06±0.06	0.49±0.04
Pt	0.00	1.69±1.20	Pt	0.00	0.29±0.20
Fe	22.11±2.21	45.91±5.36	Fe	12.15±1.12	26.94±3.14
Cr	37.48±0.90	13.42±1.12	Cr	22.09±0.52	8.62±0.70
Mg	7.55±0.63	4.64±2.07	Mg	9.63±0.80	6.45±2.82
Al	4.36±0.04	3.27±0.04	Al	4.94±0.01	0.04±0.04
Ti	0.42±0.14	0.77±0.19	Ti	0.26±0.09	0.53±0.13
Cl	0.00	0.16±0.06	Cl	0.00	0.15±0.05
K	0.13±0.12	1.71±0.19	K	0.10±0.12	1.48±0.16
*	0.85-	0.40-	*	—	—
O	26.50±0.62	24.04±2.05	O	50.74±1.18	50.55±4.19
Total	100.00	100.00	Total	100.00	100.00

*Ni+Cu+Ca

Gains and losses recalculated on an oxygen-free basis (in at.%)

Gains (from core to margin): Ru Ir Pt Fe Ti Cl K

Losses (from core to margin): Cr Mg Al

Platinum group minerals

Native metals, intermetallics and alloys

Iridium and osmium occur together with rutheniridosmine, iridian-ruthenian osmium and osmian-

ruthenian iridium (Fig. 1a-f; Figs 3a, 4a,c,e,f; Table 1, columns 1, 3, 5). Platinum and iron are commonly present in small concentrations in iridium and osmium (Table 1, columns 1, 3, 5).

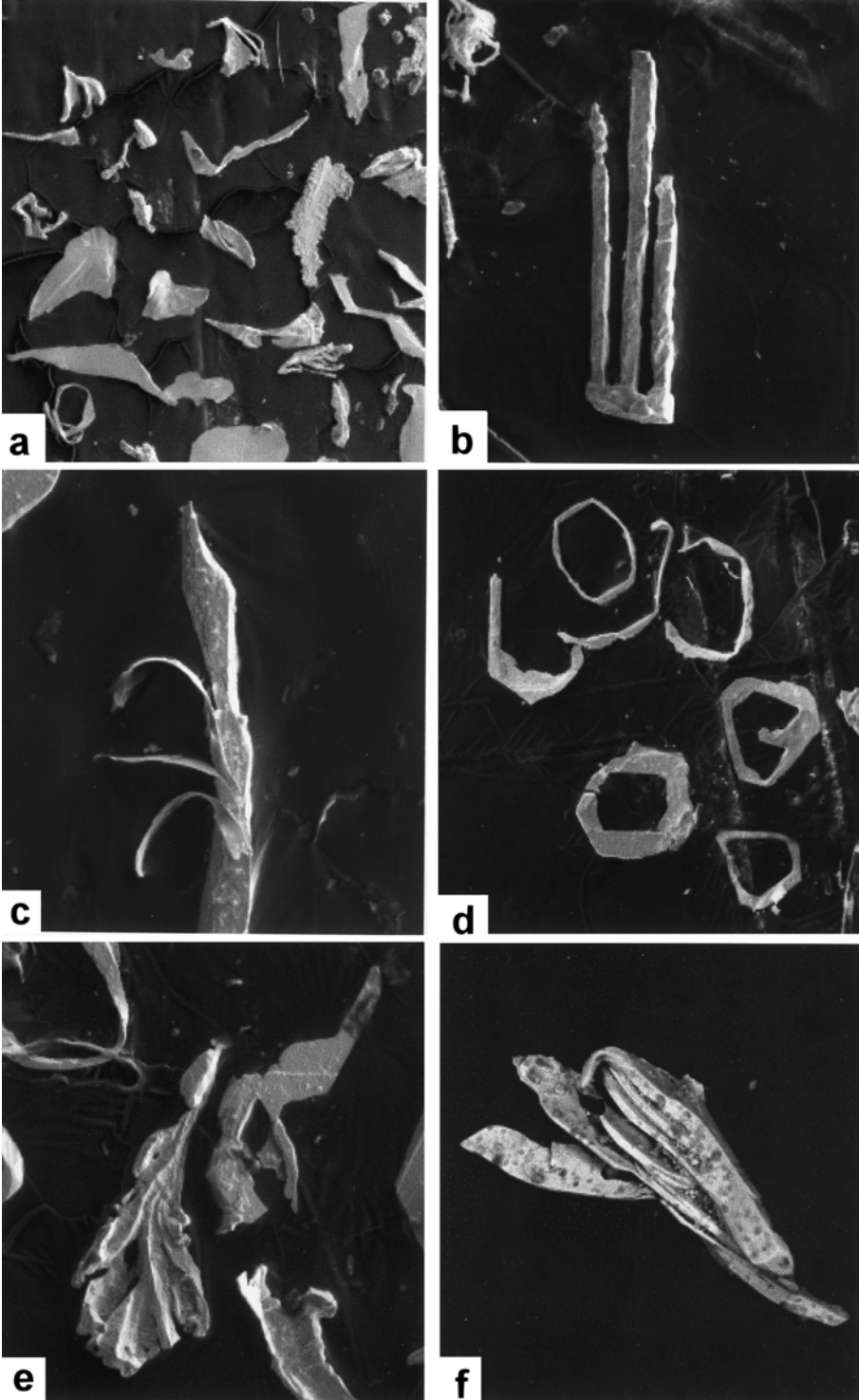
TABLE 3. Electron microprobe analyses of amorphous Ir-Os-Ru-Rh-Pt oxide (Fig. 6d).

Wt.%	1	2	3	1	2
	Native Ir incl. <i>n</i> = 2	Amorph. oxide <i>n</i> = 5	Rh inclusion <i>n</i> = 1	At.% Native Ir incl. <i>n</i> = 2	Amorph. oxide <i>n</i> = 5
Ru	6.57	6.49±1.54	1.49	9.59	7.13±1.34
Rh	0.76	3.46±0.80	43.36	1.09	3.36±0.78
Os	12.24	4.75±3.26	0.86	9.5	2.70±1.83
Ir	69.18	60.49±4.20	9.09	53.29	34.07±4.26
Pt	6.49	9.79±1.35	1.53	4.83	5.32±0.95
Fe	1.4	6.56±1.23	1.6	3.72	11.61±1.56
Ti	0.00	0.07±0.05	0	0	0.14±0.12
Cr	0.46	1.68±0.84	0.8	1.21	3.31±0.73
Cu	0.11	0.23±0.15	11.3	0	0.33±0.21
Sn	0.24	0.16 (1)	9.85	0.37	0.13 (1)
Sb	0.06	0.08 (1)	18.56	0	0.06 (1)
S	1.5	1.92 (1)	0.63	7.29	3.00 (1)
O	0.99	4.32±0.83	0.93	9.11	28.84±0.70
Total	100.00	100.00	100.00	100.00	100.00

Gains and losses recalculated on an oxygen-free basis (in at.%)

Gains (from native Ir to oxide): Rh Pt Fe Ti Cr Cu

Losses ("): Os Ir Sn S



The Ir/Os ratios of the alloys vary widely, as already stressed for Nizhnij Tagil by Cabri *et al.* (1996). Oxygen is present in all analyses, with very variable concentrations from 1 wt.% = 10 at.% (Table 3, col. 1), to 3 wt.% = 25 at.% (Table 1, col. 5).

Native iridium and osmium and their alloys occur with diverse habits and textures: (1) Micrometric spheres: either free, deposited on the surface of mineral grains or in their cavities, or dispersed in PGE-oxides. They are also present as unaltered residues in alteration oxide crusts (Fig. 4d). (2) Isolated lamellae with a large variety of baroque forms: blades (either straight, curved, crooked or twisted; isolated or stacked), leaves, twigs, threads, hollow hexagons, dendrites (Fig. 1a-f). They are also found included in chromite and in irarsite (cf. Borg, 1997). (3) Lamellae grouped in boxworks (skeletons) or in irregular lumps (Fig. 2a-f). These boxworks host 'irite' and microspherical iridium concentrations (Fig. 2b-c), and laurite (Fig. 2d,f). Identical boxworks were described by Cabri *et al.*, (1996, their Figs 27b and c) in untreated placers from Papua New Guinea. (4) Symplectite grains, in which one of the phases is selectively altered, revealing vermicular, kinked and parallel lamellae of less altered residues (Fig. 3a-b; Table 1, col. 1).

Such gradual alterations of eutectoids allow observation of the *in situ* formation of Ir oxides (Fig. 3c-d; Table 1, col. 2). The symplectite textures are interesting, since the kinked platelets revealed by the alteration can be compared to the baroque lamellar habits previously described.

Native ruthenium and rutheniridosmine occur as short crystals, lamellae and xenomorphic masses, commonly associated with iridium and osmium lamellae (Fig. 2f).

Platinum and ferroplatinum are definitely present, in spite of their solubility in aqua regia, but are relatively rare. Minor amounts of iridium were detected but palladium is very scarce, as observed by Cabri *et al.* (1996). Small crystals of platinum are commonly observed as dispersions in masses of otherwise very pure microcrystalline hematite.

Other species such as tulameenite and hongshiite (rare) (Fig. 4f) were observed, also an unusual alloy of Ru-Rh-Sn-Cu-Sb (Table 3, col. 3).

Other platinum group minerals

The following sulphides and sulpharsenides were observed: laurite (Figs 2d, 4e), irarsite, iridsite, prassoite, erlichmannite and hollingworthite. The first two are by far the most common. Xenomorphic laurite is common cementing iridium and osmium lamellae, whereas irarsite is found as crusts around other PGM.

Simple PGE-oxides

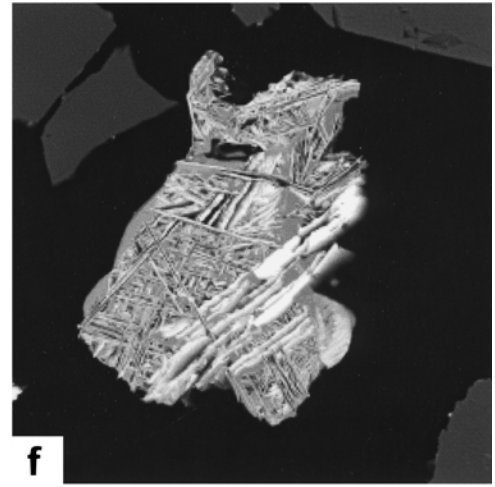
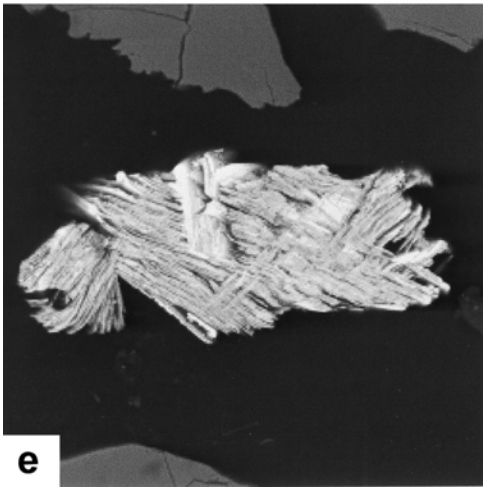
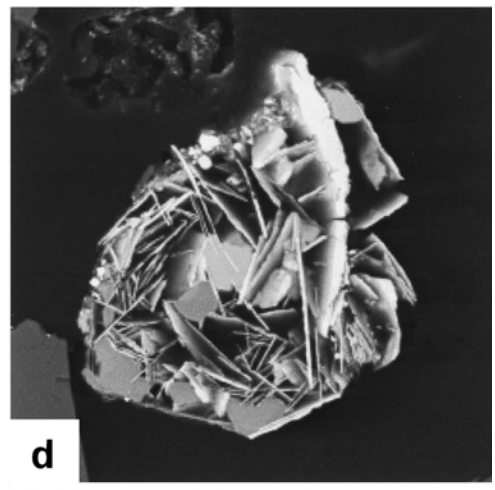
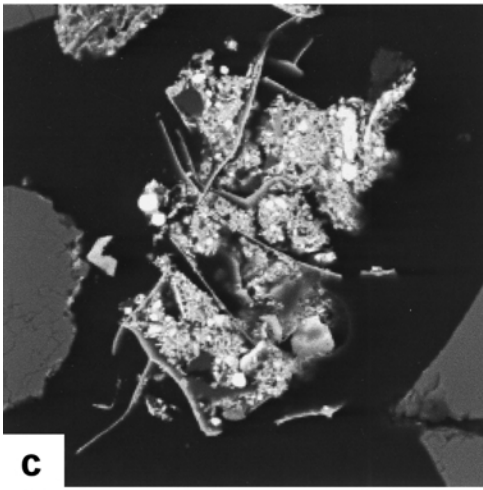
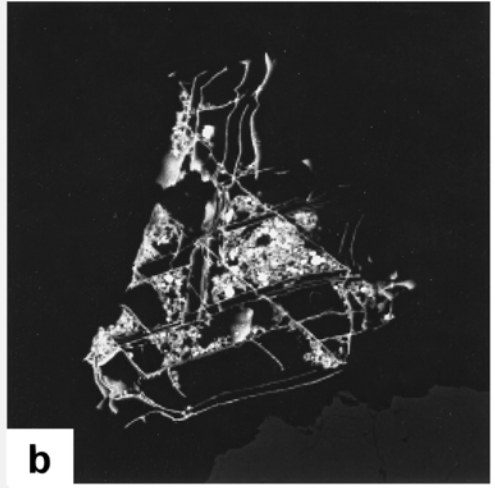
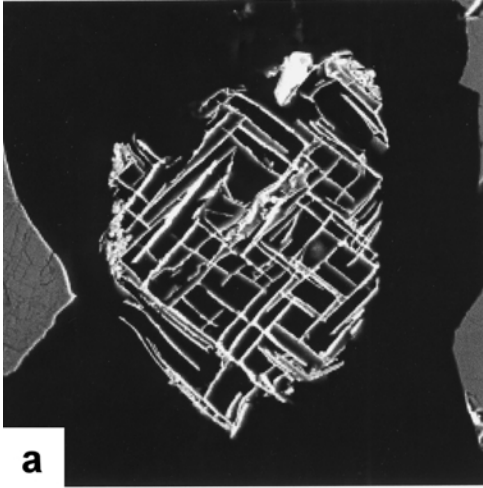
Smooth crystals of (Ru,Ti)O₂ and of (Os,Ir,Ru)O were observed included with clear-cut contacts in iridium and osmium blades. They are homogenous and take a good polish, contrary to the complex oxides. These are all of a brown/bronze colour. They are assumed to be of primary origin, as opposed to the oxidic alteration compounds. Several similar Ru- and Ir-Os-Ru oxides, with or without Fe, have already been described from several localities and with variable stoichiometries (Table 5 and references).

Complex PGE-oxides

Two broad groups can be distinguished. Topochemical alterations, formed at the expense of a precursor that is still preserved, at least partly. These alterations tend to yield crystal aggregates, or foliations. (Fig. 4a,d). The chemical analyses of these crystals allow for the elementary modifications provoked by the alteration of the native metals, notwithstanding adsorbed elements, like Cl and K (Table 1). When recalculated on an oxygen-free basis, Ru and Os show a clear tendency to decrease during oxide formation from the alloys, whereas Ir increases markedly. The trend for Fe is not so clear.

Another type of topochemical alteration is observed in chromite grains that have reacted along their borders to become enriched in non-

FIG. 1. (*facing page*) Isolated Ir and Os lamellae MNHN* [*See explanations of abbreviations on p. 394]. Hand mt. (a) General view of isolated iridium and osmium lamellae, threads and blades. SEM(SM). 1400 μ m. (b) Dendrite-like parallel stems of Os-Ru iridium. SEM(SM). 450 μ m. (c) Stem of Os-Pt-iridium with split-off lamellae. SEM(SM). 450 μ m. (d) Hollow Ir-Os foils with crystalline outlines. SEM(SM). 1200 μ m. (e) Leaf and blade of Ir-osmium. SEM(SM). 600 μ m. (f) Group of partly split-off, Ir-Ru-Os blades. The dirt particles on the surfaces are mixed Ir-, Os- and Pt-chlorocompounds. SEM(BS). 160 μ m.



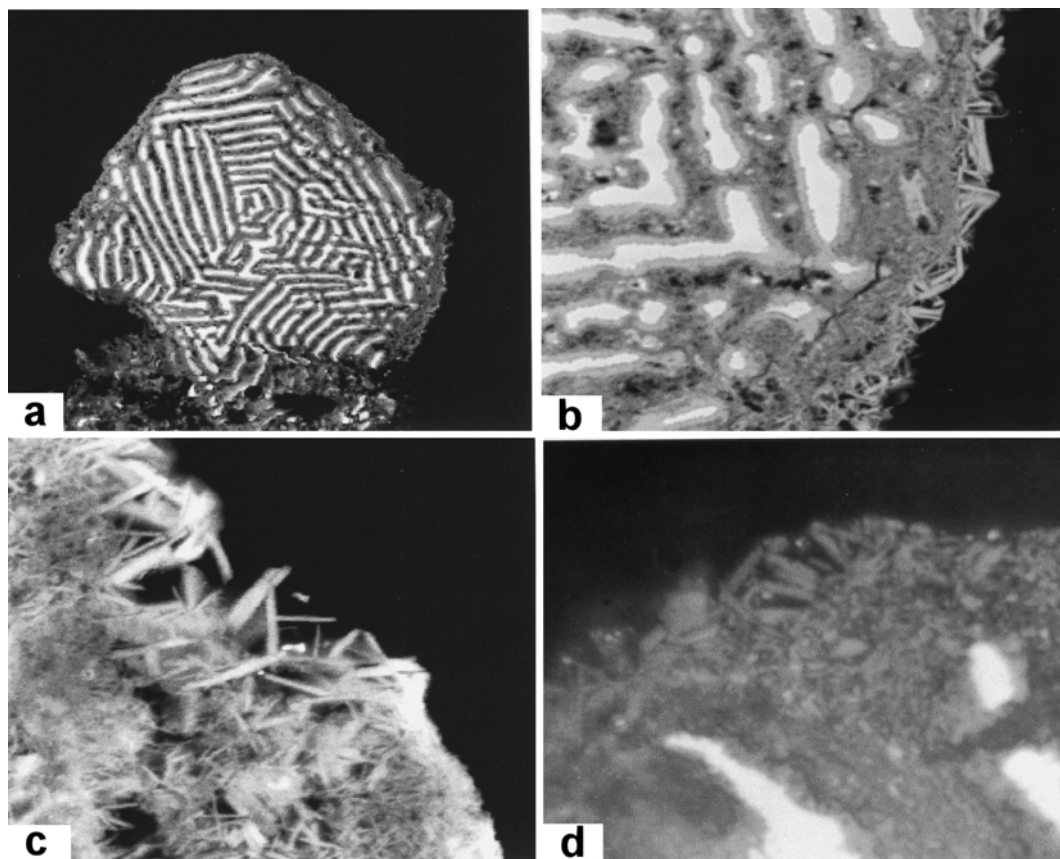
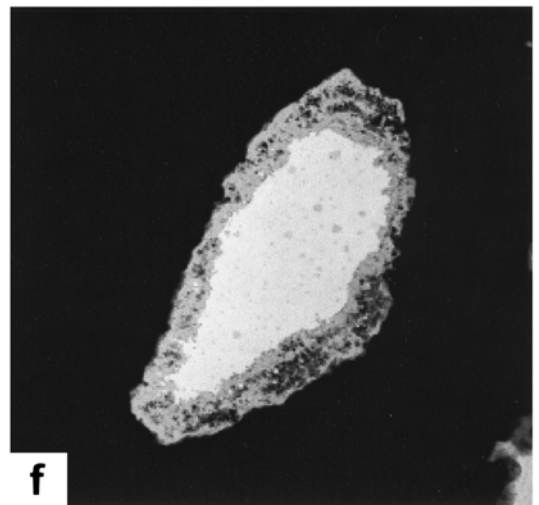
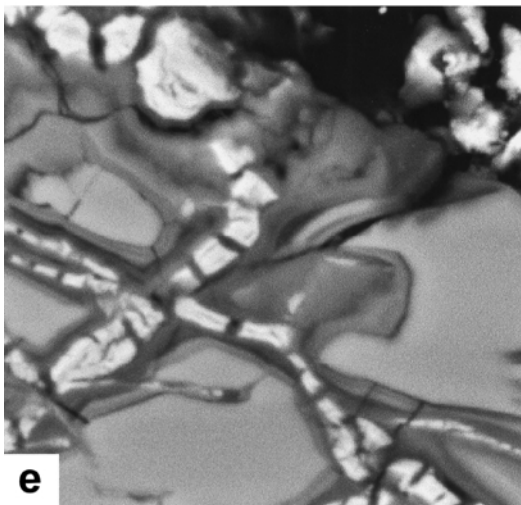
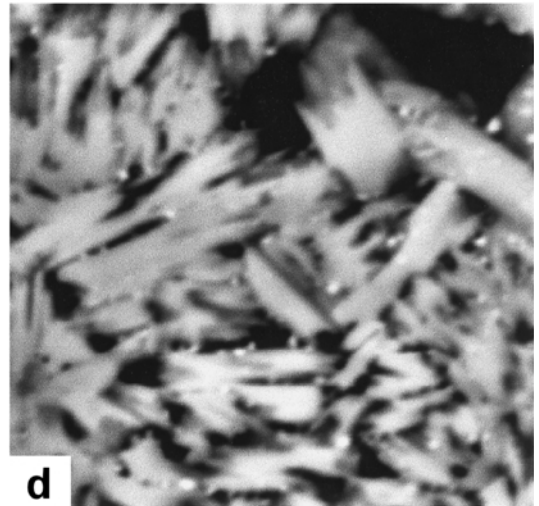
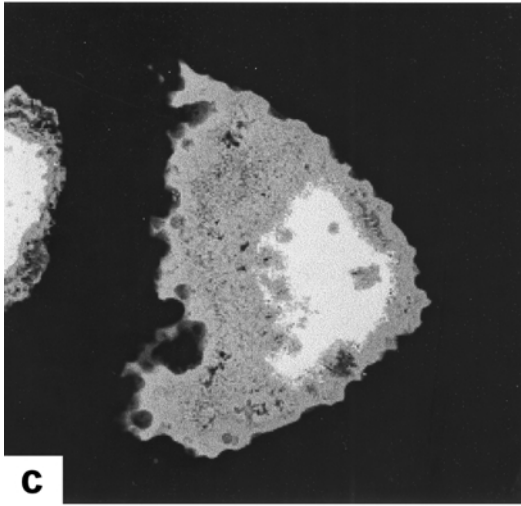
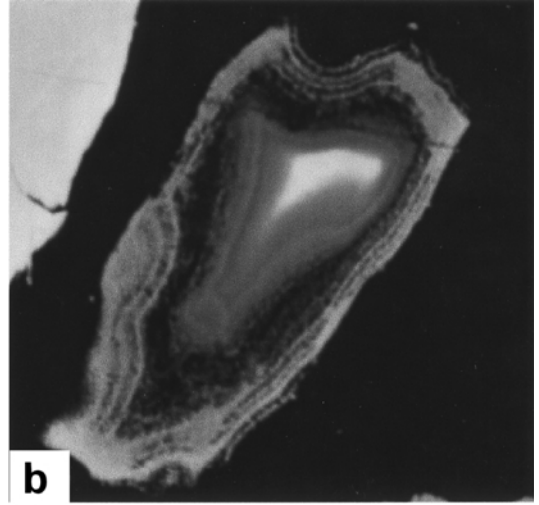
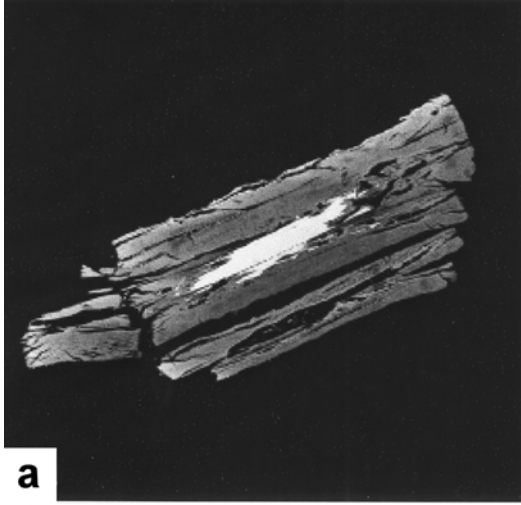


FIG. 3. Altered symplectic (eutectoid) grains ENSM. (a) Os-Pt-Ru iridium grain with eutectic texture. Metal residues (white) display parallel, curved and crooked lamellar shapes (Table 1, col. 1). Pol. sect. SEM(BS). 260 μm . (b) Border of the same grain, showing the residual metal (white), rimmed by incipient oxide (smooth grey), embedded in an oxidic matrix (fibrous grey), and a border of well-developed Ir-oxide crystals (light grey). The nearly complete disappearance of the metal in the border layer is notable. SEM(BS). 65 μm . (c) Border of the particle, showing the local development of larger fibrous/tabular Ir-oxide crystals. (Table 1, col. 2). SEM(BS). 10 μm . (d) Another field of the same border under RLM, showing the large difference in reflectance of the crystals and the metal. 12 μm .

particulate Ru, Ir, Pt, Ti, Fe, Cl, K, and depleted in Cr, Mg, Al. (Fig. 5c–d; Table 2). Inversion of the Fe/Cr+Al+Mg ratios between border and interior is noteworthy. One observes also in such chromites the internal formation of Ir-Fe oxides

along fissures. The composition of this reaction border shows clearly that chromite is indeed affected by the aqua regia treatment, and can thus be a source of the dissolved Cr found in the PGE oxides.

FIG. 2. (*facing page*) Grouped Ir and Os lamellae. (a). ENSM-6774. Hollow skeleton of Os-Ru-iridium lamellae. Pol. sect. SEM(BS). 325 μm . (b) ENSM-6774. Skeleton of iridium and osmium lamellae partly filled with 'irite'. Pol. sect. SEM(BS). 300 μm . (c) MNHN. Group of loose iridium lamellae filled with lumps of micrograined 'irite'. Pol. sect. SEM(SM). 140 μm . (d) ENSM-6774. Dense agglomerate of Ir-osmium lamellae, partly corrugated and bent. Pol. sect. SEM(BS). 260 μm . (e) MNHN. Disordered agglomerate of iridium and osmium lamellae (white straight lines) and of laurite (grey irregular masses). Partly pol. sect. SEM(SM). 140 μm . (f) MNHN. Compact grain composed of Ir-Ru-osmium (large diagonal and fine intercrossed lines), laurite (grey irregular masses) in a matrix of unresolved Ru-Os-Ir-Fe-oxide(s). Pol. sect. SEM(BS). 160 μm .



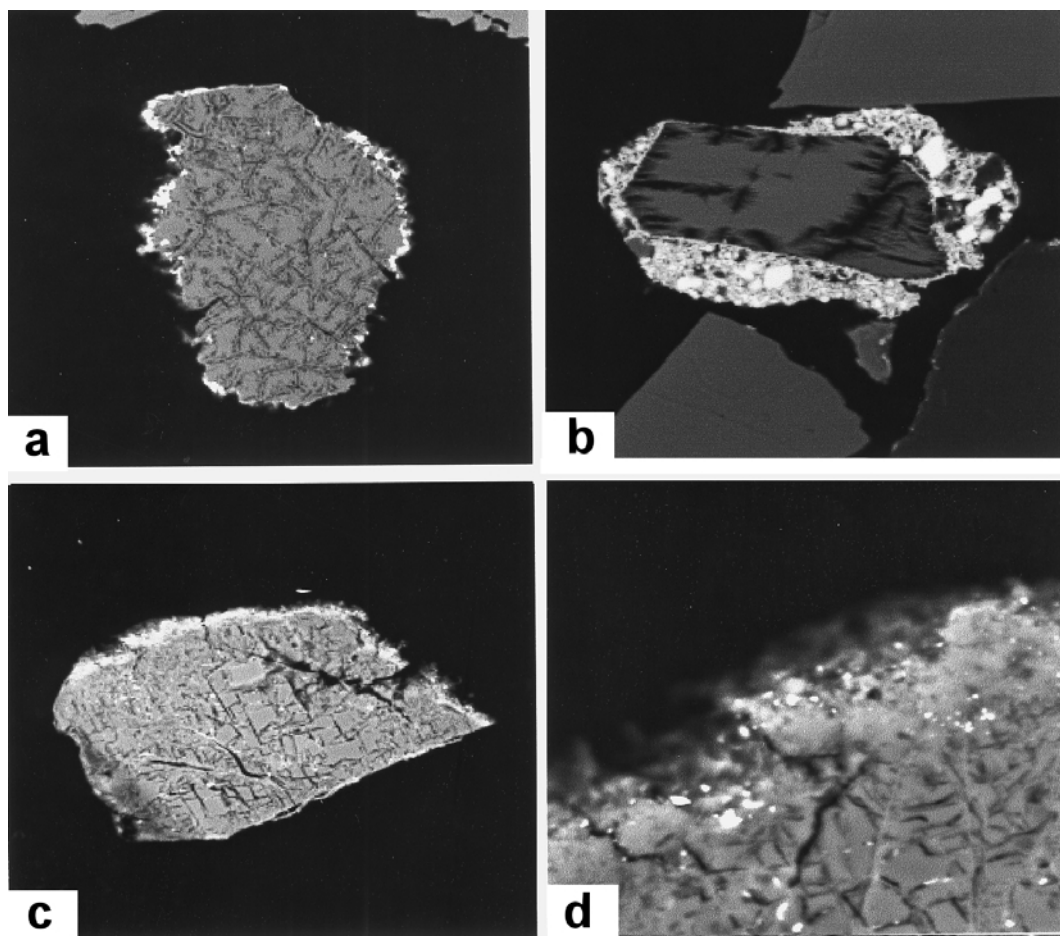


FIG. 5. Peripheral crusts and alterations of ilmenite and chromite. (a) ENSM-6774. Altered chromite (dark grey with convoluted cracks) bearing a fine layer of 'irite'. Pol. sect. SEM(BS). 260 μm . (b) MNHN. Altered ilmenite (various shades of dark grey) bearing a thick layer of 'irite' (spotted white). Pol. sect. SEM(BS). 140 μm . (c) ENSM. Chromite (dark grey with orthogonal cracks; Table 2, col. 1) rimmed with a lighter border. Pol. sect. SEM(BS). 160 μm . (d) ENSM. Enlargement of Fig. 5c, showing the lighter border as a diffuse reaction zone, enriched in unresolvable Fe-Ir-Os-Pt-Ru-Cl-K which are absent from the inner chromite (Table 2, col. 2), and in fine metallic inclusions. Pol. sect. SEM(VS). 50 μm .

FIG. 4. (*facing page*) Altered primary minerals. (a) ENSM-6774. Fibrous slab of alteration Ir-Ru-Pt-Os oxide (dark grey, bronze colour under reflected light; Table 1, col. 4) still containing residual rutheniridosmine (white; Table 1, col. 3). Pol. sect. SEM(BS). 160 μm . (b) NHML. Particle of Ir-osmium (inner white residue) surrounded by rhythmic layers of alteration Ir-Os-Ru-Fe-Ti-Cu oxides (various shades of grey). Pol. sect. SEM(BS). 125 μm . (c) ENSM-6774. Altered Ir-Ru-Pt osmium (white; Table 1, col. 5) with thick crust of alteration Ru-Os-Pt-Ir oxide(s) (spotted grey). Pol. sect. SEM(BS). 160 μm . (d) ENSM-6774. Enlargement of Fig. 4c showing fibrous microcrystals of Ir-Fe oxide, composing the crust and resulting from the alteration of the metal (Table 1, col. 6). SEM(BS). 10 μm . (e) ENSM-6774. Fragment of a large particle composed of laurite (light grey), rutheniridosmine (white, segmented) and Ru-Ir-Pt-Fe oxide (dark grey alterations of laurite). SEM(BS). 16 μm . (f) ENSM-6774. Particle of Os-Pt-Ru-iridium (white) containing hongshiite inclusions (grey), surrounded by a thick alteration crust of Ru-Os-Pt-Ir oxide(s) (spotted grey). Pol. sect. SEM(BS). 160 μm .

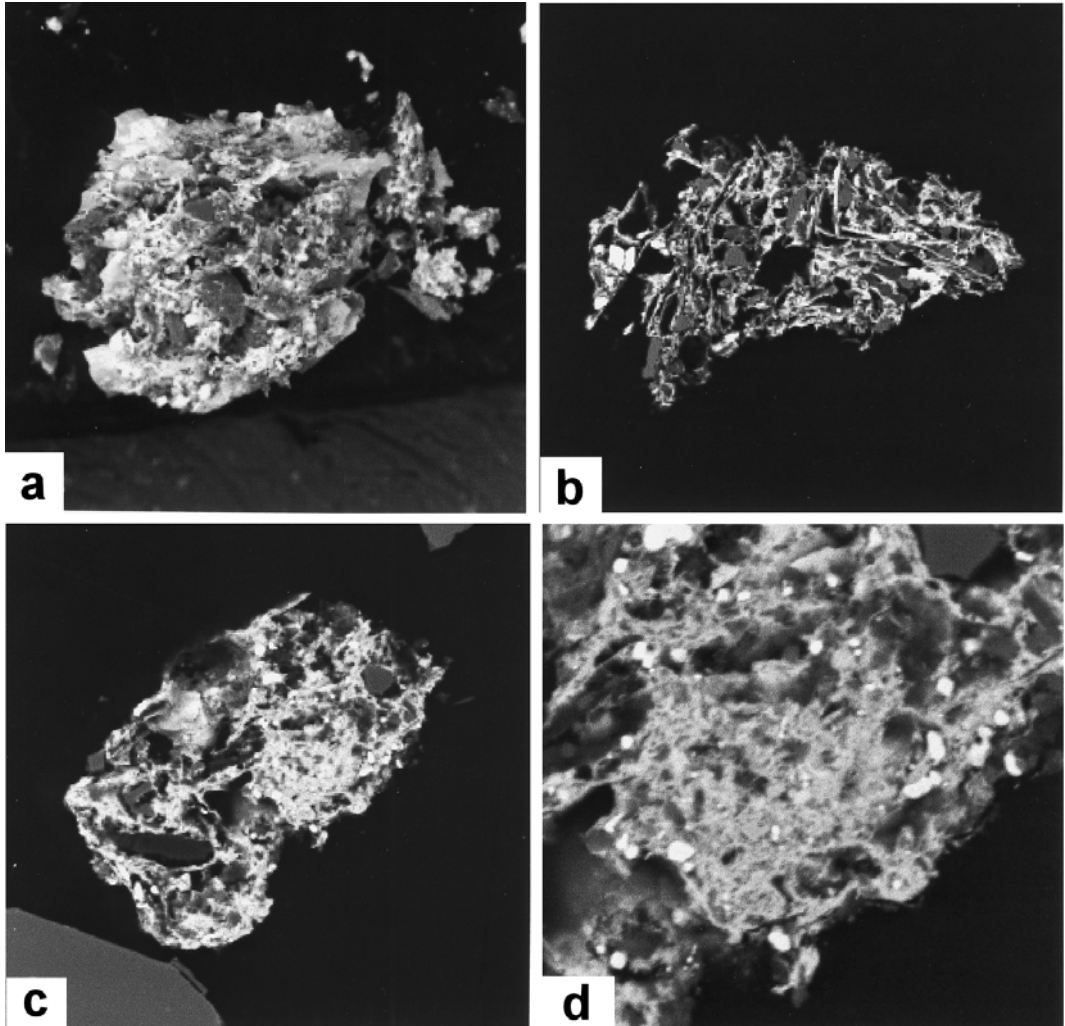


FIG. 6. Agglomerates of 'irite'. (a) NHMV. 'Irite' agglomerate composed of chromite and silica fragments (various shades of grey), iridium and osmium grains, and lamellae bound together by 'irite'. The smaller particles at the right of the main body were detached during mounting. Hand mt. SEM(SM). 550 μm . (b) NHMV. Fluffy 'irite' agglomerate composed of chromite, silica, Ir-Fe oxides and metal grains and lamellae. Pol. sect. SEM(BS). 700 μm . (c) ENSM-6774. Compact particle composed of 'irite' (large light grey spot to the right, and unresolved web), chromite and silica fragments (grey particles) and metals (white spots). Pol. sect. SEM(SM). 150 μm . (d) ENSM-6774. Blowup of the same particle, showing the mixed character of the 'irite' field (white metallic grains, dark grey silica and light grey 'irite'). This 'irite' displays a dark bronze colour under reflected light) 1300 μm .

No black shiny octahedra of pure Ir-Fe-Cr oxides were observed, as claimed by Hermann, and his successors (Dufrenoy, 1859). Likewise, complex Ir-Fe oxides with high Cr contents, claimed by Hermann, were not found.

Amorphous Ru-Os-Ir-Pt-Fe-Cr-Ti-Mn oxides and (oxy)hydroxides (?) occur with diverse

habits as layers on the surface of other mineral grains (Figs 4f, 5a-b), as fluffy webs including other mineral grains (Figs 6a-b, 7c), and as diffuse masses (Fig. 6c-d). Their colour under refelected light is a deep bronze, but the highest magnifications commonly disclose the presence of micrometric metallic remnants (Fig. 6d). Another

'IRITE' FROM THE URALS

TABLE 4. Electron microprobe data for Ir-Os-Pt-K-Cl-containing silica.

Wt.% <i>n</i> = 3	1 Fig. 7 <i>b</i> , thick dark layer	2 Fig. 7 <i>b</i> , thin bright layer	3 Fig. 7 <i>c</i> dark body	4 Fig. 7 <i>c</i> bright centre	5 Fig. 7 <i>d</i> , bind- ing medium	6 Figs 6 <i>b</i> , 7 <i>e,f</i> dark zones
SiO ₂	98.64±0.81	90.53±1.00	79.68±1.12	70.42±3.19	89.94±3.59	55.03±7.13
Os	0.00	0.00	0.00	0.00	0.51±0.72	1.54±0.09
Ir	0.00	2.41±0.27	3.82±0.74	3.98±1.43	0.30±0.42	17.92±6.67
Pt	0.44±0.45	2.56±0.26	8.58±0.44	15.84±1.88	1.98±1.70	14.39±4.22
Fe	0.35±0.17	2.78±0.54	4.17±0.47	4.04±0.47	1.17±0.67	2.32±1.43
K	0.04±0.03	0.22±0.01	0.39±0.14	0.29±0.05	1.13±0.34	0.39±0.46
Cl	0.30±0.14	1.10±0.06	1.92±0.24	3.76±0.63	1.55±0.77	3.81±0.81
*	0.23	0.40	1.44	1.67	3.42	4.60
Total	100.00	100.00	100.00	100.00	100.00	100.00

* Ca, Ti, Cr, Mn, Ni, Cu, Hg

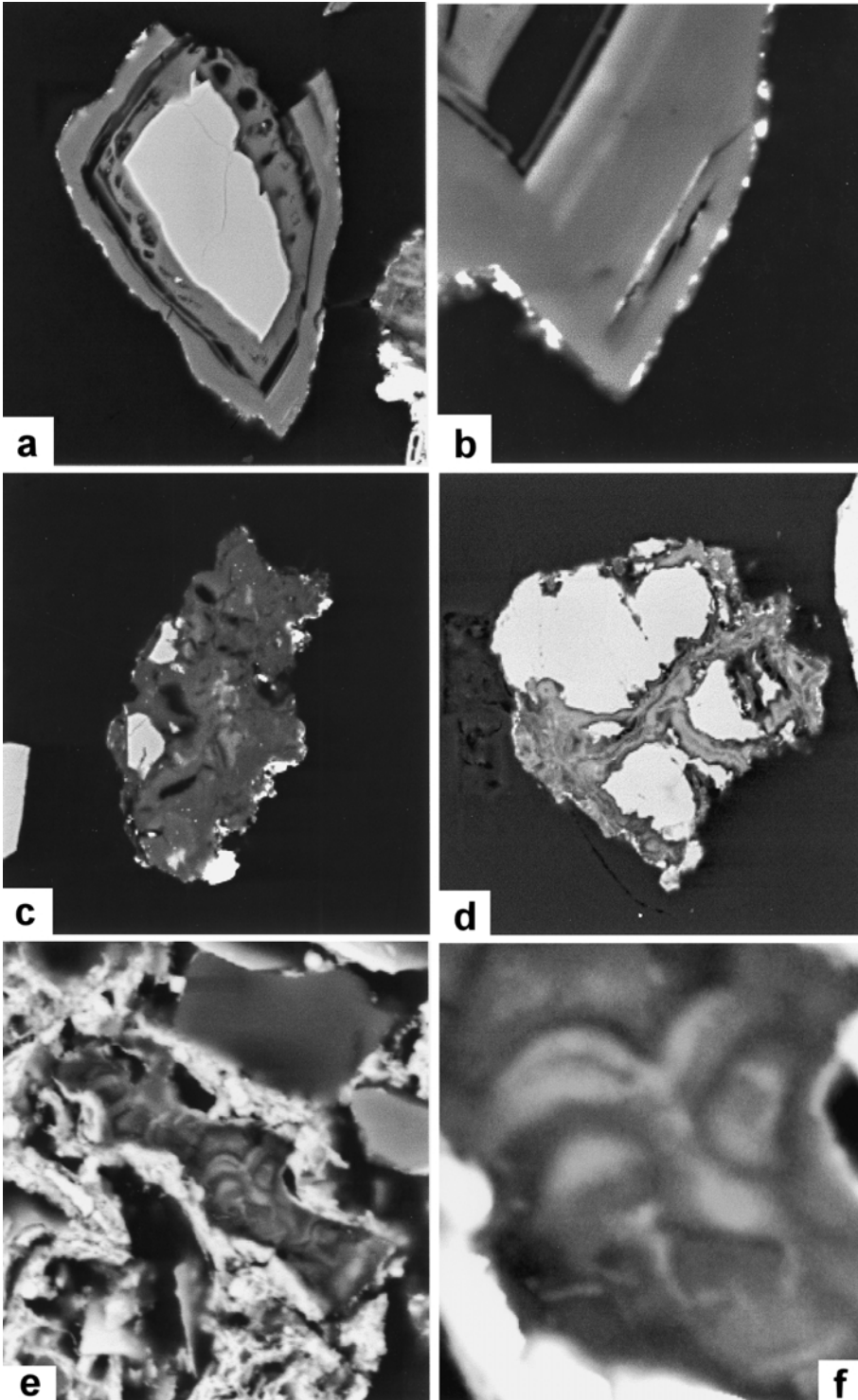
habit is of botryoidal aggregates filling cavities of chromite and boxworks of metallic lamellae (Fig. 2*b-c*).

The largest chemical differences observed between the native metals and these amorphous oxides are in the Ir content (increasing), and in a systematic decrease of Os (Table 3). These trends

are the same as for the crystalline oxides. These amorphous oxides contain several additional trace elements (Cl, K, Ca, Ti, Cr, Ni, Cu, Hg, S), probably adsorbed. Titanium is ubiquitous, and can sometimes equal the concentration of iron, indicating that it can be mobilized, possibly by the alteration of ilmenite (Fig. 5*b*). Some chemical

TABLE 5. Previous finds of Ru-Rh-Os-Ir-(Pt) oxides.

Compounds	Country	References
Ir-Pt-Ru-Rh-Fe-rich alter. product	Ethiopia	Cabri <i>et al.</i> (1981)
Ir-Fe oxide	USA	Rosenblum <i>et al.</i> (1986)
Ir-Rh-Pt-As-Fe oxide	USA	Rosenblum <i>et al.</i> (1986)
(Ir,Pt)O (with unaccounted Fe)	Colombia	Weiser (1992)
Ir oxide	Madagascar	Legendre and Augé (1993)
Ir-Rh-Fe oxides (<i>Me/O</i> = ±3)	N. Caledonia	Augé and Legendre (1994)
IrO ₂	Madagascar	Augé and Legendre, (1994)
Rh-Pt-Fe oxides	N. Caledonia	Augé and Legendre (1994)
RuMnO ₄	Ethiopia	Urashima (1994)
Ir-Fe oxide	USA	Tamana (1994)
Pt-Ir-Fe-Rh oxides	N. Caledonia	Augé and Maurizot (1995)
Ru-Mn-Fe hydroxide	N. Caledonia	Augé and Maurizot (1995)
Ir-Rh-Pt and Rh-Ir oxides	Colombia	Cabri <i>et al.</i> (1996)
Ir oxide or hydroxide	Russia	Cabri <i>et al.</i> (1996)
RuO ₄	Brazil	Milliotti and Stumpf (1996)
Ru-Os-Ir-Fe oxide	Greece	Garuti and Zaccarini (1997)
Ru-Os-Ir-Fe oxides	Russia	Garuti <i>et al.</i> (1997)
RuO ₂	Yugoslavia	Krstic and Tarkian (1997)
(Ru,Os ,Ir)O and (Ru,Os ,Ir)O ₂	Papua N. Guinea	Weiser and Bachmann (1999)
Ru-Rh-Mn oxide	South Africa	Hey (1999)
Ru-Ir-S oxide(s)	Zimbabwe	Evans and Spratt (2000)
Ru-Fe oxide	Brazil	Garuti <i>et al.</i> (2002)



elements are due to mostly destroyed precursors, such as the Rh-Sn-Sb-Cu alloy found as micrometric inclusions in an amorphous oxide (Table 3, col. 3). The latter still contains a minor amount of Sn.

Pt-Ir-Cl-K-containing silica (opal)

This occurs as rounded grains, shards, fragments, either free or included in agglomerates. Silicate grains may also be surrounded by zoned silica (Fig. 7a–b). These high-silica compounds present irregular textures, cracks, variable Si/O(OH?) ratios, and detectable concentrations of Pt, Ir, K and Cl, mostly as bright spots and bright interlayered zones, revealed by SEM(BS) (Fig. 7a–f; Table 4). Under reflected light, they are of a brownish colour and appear “dirty”, thus differing from plain quartz. They can include chromite grains and authigenic crystals (Fig. 7c). The brighter fields, disclosed by SEM(BS), are either irregular (Fig. 7c) or zoned (Fig. 7a–b), containing elevated amounts of Pt, Ir, K and Cl, with concentrations of Pt up to 20 wt.% (Table 4). It is remarkable that feldspars, quartz and silicates associated with the silica in the same aggregates are devoid of detectable Pt, Ir and Cl.

Pt-Ir-(Os)-K-Cl chlorocompounds

These are ubiquitous deposits on all mineral species. They occur as small amorphous particles, crystals or irregular masses (Fig. 8a–g). Variable proportions of Ir, Pt, K and Cl, show that several compounds may be present, and the inability to detect ammonium complicates matters. The PGE-chlorocompounds are best seen on flat surfaces of chromite crystals, where they occur as micrometric to submicrometric particles, sometimes forming euhedral crystals (Fig. 8d,g). The coverage is variable, with some chromites being densely covered (Fig. 8f), whereas others appear quite clean (Fig. 8c). The particles adhere firmly to the

surfaces, since they remain during SEM observation, unlike free dust particles. Chemical analyses of the most homogenous chlorocompounds (Fig. 8d,g) gave formulae near $Pt_1K_{1.5}Cl_{4.75}$ (oxygen not accounted for), close to potassium tetrachloroplatinate PtK_2Cl_4 . The trace amounts of Pt, Ir, K and Cl found in the analyses of nearly all particulates and reaction crusts, without particulate PGE-chlorocompounds being visible under the SEM(BS), are attributed to adsorption.

Minerals and compounds devoid of PGE

Native gold

Native gold occurs as small nuggets, partly covered with Fe-Mn hydroxides, in the ENSM sample. No PGM inclusions or PGE contents were found in gold or the Fe-Mn crusts.

Sulphides

Sulphides such as pyrite, chalcopyrite, pentlandite are present but rare.

Oxides

Chromite occurs as abundant octahedral crystals and fragments. Polished sections show various stages of alteration: some chromites seem completely unaffected, whereas others are altered along their border, or in-depth. In the latter case, convoluted fissures (Fig. 5a) are observed. Magnetite is rare. Hematite occurs as microcrystalline agglomerates of a blue colour, hosting dispersed platinum grains, but no other PGM. Rutile and ilmenite are rare, more or less altered (Fig. 5b). Fe-Mn-(oxy)hydroxides are rare. Some large particles have fragile botryoidal textures, and include native iridium and PGE chlorocompounds (Fig. 8a–b). The composition of these Fe-Mn oxyhydroxides is surprisingly pure. Cr-hydroxide(s): semi-transparent, altered fragments of Cr-hydroxide(s) could be abundant,

FIG. 7. (*facing page*) Pt-Ir-Cl-K-containing silica. (a) MNHN. Al-Si-Fe-Mg-Ca-O fragment (light grey) encrusted with zoned silica layers (dark grey; Table 4, col. 1). Pol. sect. SEM(BS). 160 μ m. (b) MNHM Enlargement of part of Fig. 7a. Zones of lighter grey shades correspond to increased concentrations of Pt, Ir and Fe (Table 4, col. 2). SEM(BS). 25 μ m. (c) MNHM. Silica grain (dark grey; Table 4, col. 3) showing lighter central spots (Table 4, col. 4), corresponding to increased concentrations of Pt. Light grey inclusions: chromite. Irite is concentrated along the right border (white). Pol. sect. SEM(BS). 140 μ m. (d) ENSM. Al-Fe- and Mg-Ca-silicate particles (smooth grey) cemented by fluidal Pt-Fe-Cl-K-containing silica (dark grey; Table 3, col. 5). Pol. sect. SEM(BS). 260 μ m. (e) Enlargement of the right hand side of Fig. 6b. Pt-Ir-containing silica. Pol. sect. SEM(BS). 50 μ m. (f) Enlargement of a portion of Fig. 7e showing concentric zones of Pt-Ir-enriched silica. SEM(BS). 12 μ m. (Table 3, cols 6 and 7).

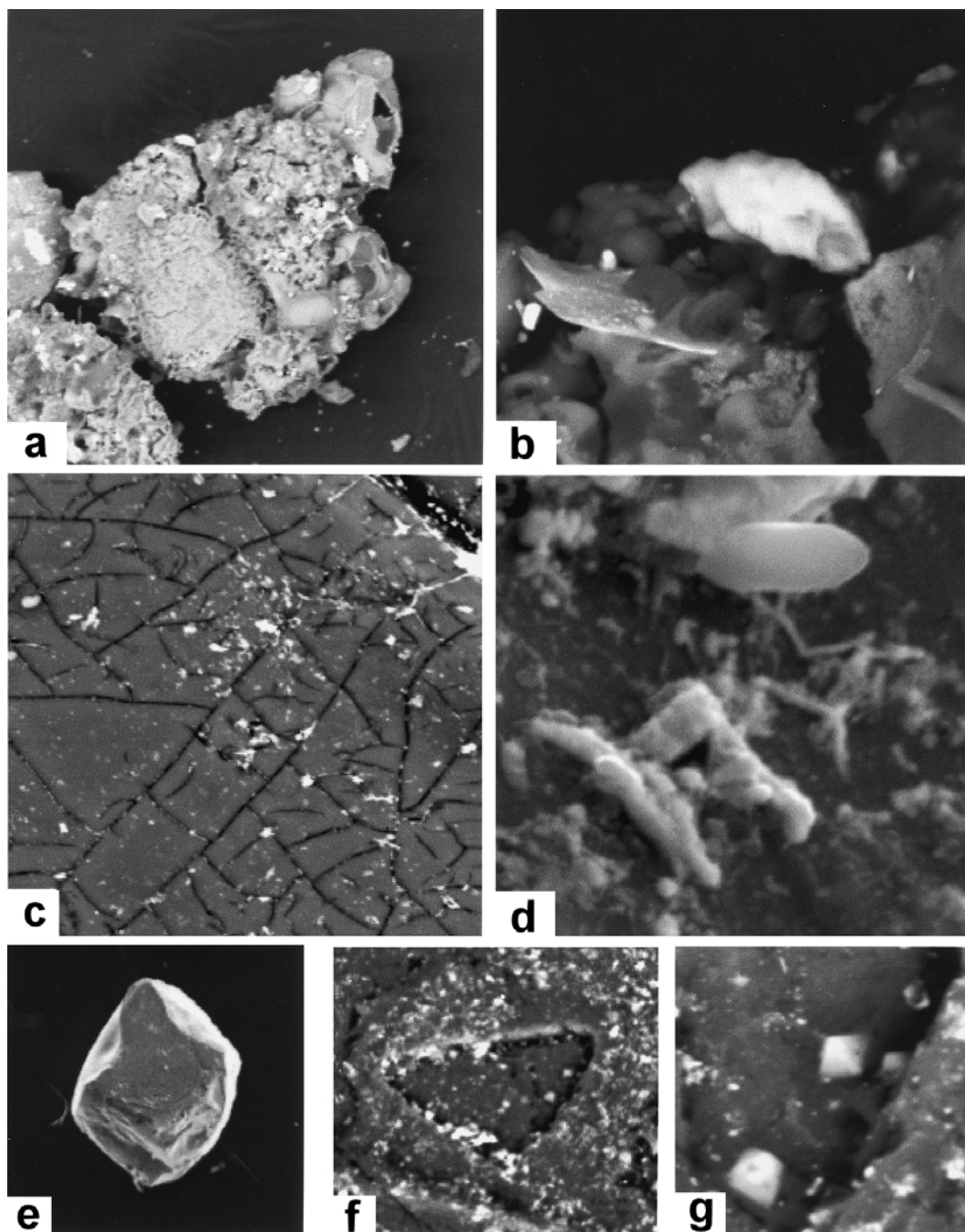


FIG. 8. Pt-Ir-(K)-chlorocompounds. (a) NHMV. Fe-hydroxide particle showing blistered parts to the right, and a metallic dusting (white). Hand mt. SEM(BS). 400 μm . (b) NHMV. Enlargement of Fig. 8a, showing a particle of Pt-K-Cl (white) and an incrustated lamella of iridium (left). Hand mt. SEM(BS). 35 μm . (c) NHMV. Surface of an altered chromite (dark grey), dusted with various chlorocompounds. SEM(BS). 130 μm . (d) NHMV. Enlargement of

but are difficult to recognize. They are devoid of Mg, Al and Fe, unlike fresh chromite.

Native Ir and Os morphologies (Figs 1 and 2)

Phosphate(s)

Monazite-Ce

Ca-carbonate and Ca-sulphate

These occur as very small crystals deposited with the PGE-chlorocompounds on the particulates (Fig. 8*d*). These two categories are devoid of PGE, in spite of their intimate association with the PGE-chlorocompounds.

Discussion

The three studied samples of 'irite' are obvious mixtures, and in this respect, Claus (1860) was correct. But this does not lessen interest in 'irite' as a material deserving careful study. In this respect, Hermann was also correct, and in particular, about the presence of PGE oxides which were rediscovered in the last decade (Ru-Rh-Os-Ir oxides in particular, cf. Table 5). However, 'irite' is a very challenging case of mixed, diverse products, among which it is difficult to distinguish the natural from artificial compounds. Whereas the Pt- and Ir-chlorocompounds are indisputable artifacts, Ru-Ir-Os alloys are among the least soluble compounds. In between, several compounds, either defined or undefined, show evidence of the harsh treatments given to the head-ores or which resulted from milder steps of the Berzelius process. Indeed, the latter combines the aqueous, acidic and oxygenated conditions favourable to the generation of oxides and hydroxides of every PGE (Westland, 1981), but criteria distinguishing natural from artificial products are lacking.

It has not been possible in the course of this work to solve the problems raised by the PGE-oxidic compounds and their precursors, and this remains a poorly explored area. A few outstanding observations will be discussed here and put in perspective.

The native metals and alloys with their baroque forms represent a concentrate of the most insoluble inclusions dispersed in the primary silicates and in the platinum nuggets. They represent intergranular deposits following the form of voids left between silicates, chromite and platinum grains, as observed by Borg (1997) in polished sections (hypidiomorphic textures). Borg also observed in polished sections of pristine materials from Nishnij Tagil the presence of threads and spliced-off lamellae as described here, included in chromite and in platinum, or sited at their boundaries.

The lamellar boxworks are the residues of nuggets composed of platinum (now dissolved away) and of iridium and osmium platelets. Actually, such lamellar forms and groups were separated by aqua regia, and observed by Berzelius (cf. Rose, 1842), Wyssotzky (1913; Exc. 9), and by Duparc and Tikonowitch (1920; Exc. 10), at a time when large nuggets were still accessible for experiments. However, the formation of boxworks does not necessarily demand an aqua regia dissolution. Exactly the same textures were described by Cabri *et al.* (1996) from placers in Papua New Guinea that had not been subjected to hydrometallurgical operations.

The high concentration of native iridium and osmium and of their alloys in the 'irite' samples draws attention to a placer sample from Nishnij Tagil studied by Cabri *et al.* (1996), and which has a composition that the authors suspected to be abnormally high in iridium and osmium (cf. Borg, 1997). It may be that the Cabri *et al.* sample was in fact 'irite' a hypothesis that could be checked by a search for associated Pt-Ir-K-Cl-chlorocompounds and PGE-containing silica.

Symplectite alloys (Fig 3)

These alloys display convoluted platelet forms, which are difficult to understand once they are liberated, but their similarity with the baroque forms observed as free objects is very suggestive.

Fig. 8*c*. showing a concentration of fibrous Ir-chlorocompounds (white, elongate), and one crystal of Ca carbonate (upper bipyramidal prism). SEM(BS). 12 µm. (e) NHMV. Chromite crystal. Hand mnt. SEM(SM). 650 µm. (f) NHMV. Enlargement of Fig. 8*e*, showing a triangular hollow in the chromite with 3–4 crystals of K-chloroplatinate (light grey), and a heavy dusting of the surface by various Ru-Os-Ir-Pt-K-containing particles (white). SEM(BS). 50 µm. (g) NHMV. Enlargement of Fig. 8*f*, showing two Pt-K-Cl crystals with bipyramidal habit. SEM(BS). 10 µm.

With regard to this discussion, an interesting picture credited to Quennessen is to be found in Duparc and Tikonowitch (1920; Exc. 11) showing a polished section of a large platinum nugget (dimensions not given) etched with aqua regia. This etching reveals a crown of unaffected vermicular Os-Ir alloy grains included in a xenomorphic phase of etched platinum.

PGE oxides

There is no doubt that these are abundantly represented in the samples, and that they formed by the alteration of precursors with which the oxides are often intimately mixed and chemically related. Similar or identical oxides have been observed in the last decade by several authors in PGE/PGM-containing placers, hard rocks, and laterites, from several countries, which have not been treated with aqua regia (cf. Table 5 and corresponding references). Figure 4*b* illustrates one from the Klamath Mountains, SW Oregon and Fig. 4*a* a Uralian 'irite' sample. Such a comparison does not prove that the Uralian oxide is natural, but the similarity suggests there is no need to invoke an artificial origin for all observed PGE oxides. The difficulty lies in the ability to distinguish the two. No doubt in the near future it will be possible to solve the crystallography of the microcrystalline oxides found as topochemical alterations of the alloys, and to investigate the conditions necessary for their formation. However, a large proportion of the oxides may be structurally amorphous and oxygen may be present in various stoichiometric proportions (Tables 1 and 3) and in several chemical states (oxide, hydroxide, oxyhydroxide, hydrate) (cf. Legendre and Augé, 1993; Augé and Legendre, 1994*a,b*; McDonald *et al.*, 1999*a,b*).

This raises a difficult problem. Where does the 'irite' that is present as a pervasive binding medium come from? It is ubiquitous; it is deposited as crusts on refractory minerals, and is mostly disconnected from visible precursors, features typical of a mobile phase. Is this phase a by-product of the aqua regia treatment, or of the later heating, neutralization and desiccation operations, or a natural alteration product? The presence of major Fe contents in these amorphous oxides (as well as other transition elements, like Ti and Cr) should also be accounted for, and could possibly be instrumental in the fixation of the PGE as solid oxides (Jedwab, 1995). It is not suggested that all the observed PGE-Fe-oxides in

'irite' are natural, but a part may be so. A careful study of 'pristine' Uralian placers is thus a necessary step towards a full understanding of their oxide mineralogy. It must also be stressed that the synthetic and theoretical chemistry of ternary compounds (PGE + O + Me) is still largely unexplored.

Primary minerals

In spite of the aqua regia dissolution, but also due to its concentrating action, the samples show the presence of rare primary minerals, which extend the field of the PG mineralogy towards new oxides: a Ru-Ti dioxide and Ru-Ir-Os oxide(s) were observed, which will be dealt with elsewhere. In this respect, these oxides and those presented in Table 5 (and in particular, a case of RuMnO₄ described by Urashima (1994) from Ethiopia), suggest that this group of primary compounds deserve to be examined more carefully. It is noteworthy that following Hermann's works, it was not until the introduction of the SEM/EMP that the possibility of PGE oxides was raised again.

Silica-containing Pt-Ir-Cl-K

This phase is an artifact beyond any doubt. But there are large variations in the types of Pt-Ir distribution (Fig. 7). Sometimes, the PGE seem to have been deposited as regular zones within the silica or around other silicates, whereas elsewhere they are deposited as irregular patches or rhythmic waves. Considering the adsorptive properties of silica (Hillebrand and Lundell, 1953), it is difficult to assign a precise moment for the adsorption of the PGE either when the silica was in a colloidal or gelatinous state, or during heating, or when it was already hard.

The interest in this silica lies in the fact that large quantities were produced and possibly released in various environments and at various times. Its rediscovery could be misleading, and give rise to hasty and erroneous conclusions about the 'natural' occurrence of PGE-chlorocompounds and PGE-silica. Also, in PGE prospecting, areas of high PGE concentrations could be found and might indicate old, overlooked dumps, instead of genuine geochemical anomalies (Borg, 1996, 1997). This could be especially important whenever the Urals are prospected for PGE. PGE silica could be the source of discrepancies between the amounts of PGE

found by complete chemical analysis and by ore dressing. In any case, this phase and its PGE contents need to be taken into account; it should not be regarded as just "sand".

Reactivity of the Ti oxides in aqua regia

The observation of major and minor titanium in some of the PGE-oxide analyses indicates some displacement of the element, perhaps from ilmenites which are clearly altered (Fig. 5*b*). The possible role of Ti in the formation of PGE-Ti-O ternary compounds was stressed by Jedwab (1995).

Reactivity of chromite in aqua regia

The observed formation of Fe-Ir-enriched borders on chromite is a noteworthy feature (Fig. 5*c-d*). Concomitant depletion of Cr, Mg and Al indicates that some Cr is displaced, and eventually reprecipitated elsewhere, perhaps as the observed particulate chromium hydroxide. If this is the case, the chromium hydroxide(s) should also be considered as an artifact. Platinum-chromium undefined oxides were observed by the author at Zabargad (Jedwab, 1995).

Pt-Ir-K chlorocompounds

Their abundance as particulates is rather surprising, but their weight equivalent is difficult to assess without complete chemical analyses. In any case they represent a loss of PGE, which should be considered. Duparc and Tikonowitch (1920; Exc.12) drew attention to losses of iridium and osmium in processing prior to the 20th century.

Ubiquitous presence of Cl and K (+Ir)

Minor amounts of these elements, found in nearly all mineral analyses, and especially on their surfaces, suggest some general adsorption mechanism. The chemical state of these adsorbates (nanoparticles? ionic compounds?) could not be established.

Some of Hermann's statements have not been supported by observations and analyses

It was not possible to confirm the presence of ammonium in the PGE-chlorocompounds.

No black, shiny octahedra of Ir-Fe-Cr oxides were observed, nor were Ir-Fe-Cr oxides with

high chromium contents, and Hermann's analysis should be considered as the mean composition of a mixture. The pristine black 'irite' powders observed by Hermann's 1841 paper in cavities of crude platinum nuggets are still problematic, but sampling was limited in this study. In that respect, the presence of abundant Pt-Ir-K-chlorocompounds in the MHMV sample (Fig. 8*c-g*) casts doubt on the alleged pristine origin.

Conclusions

The investigated samples have disclosed several features that confirm some of the observations made in the past by Hermann on crude Uralian placer platinum and on its hydrometallurgical residues. However, the origin of the Ru-Ir-Pt-Ti-Fe-Cr-oxides, confirmed by the present work, is still problematic. Some could be of natural origin, since similar PGE oxides have been found worldwide in pristine deposits and some could be artificial. Studies of unreacted Uralian placer samples are necessary to solve several of the problems raised by the crystalline and amorphous PGE oxides. PGE chlorocompounds and PGE-containing silica were detected and are considered as products of the hydrometallurgical operations to which the samples were subjected. Free particles of Ru-Os-Ir alloys with baroque forms, and boxworks of the same were observed, which have been found in pristine placers.

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Appendix

Excerpt 1. Hermann (1836), p. 215: "I owe to the kindness of my honourable friend, Mining Captain von Sobolewsky, a sample of the residue left after aqua-regia extraction of the platinum contained in the Uralian platiniferous sands, which are treated at the platinum plant which he commands. At the onset, I intended only to separate for my use the contained osmium-iridium. However, when I submitted that residue to the operations, I found that there was not only one osmium- and iridium-containing mineral, but three of them. Even the aspect of the residue showed that it is a mixture of different substances. In order to facilitate the separation of these different components, I sifted and decanted them. The sifting separated rough grains of the following minerals:

(1) Metallic alloys of osmium and iridium; (2) ilmenite [Titaneisen] in black rounded grains of greasy shine. These grains show frequently a crystal face, corresponding to the octahedron. Their spec. weight is 4.60 at 10°R. [4.6–4.8]; (3) chromite [Chromeisen] as shiny, blackish-green, crystalline fragments and as perfect octahedra. Spec. weight 4.60. [4.5–4.8]; (4) quartz grains. When agitating the residue in water, its components separate themselves into three layers: a lower one, composed of the metallic alloys of osmium and iridium; an intermediate one, mainly composed of ilmenite, chromite, quartz and hyacinth; and an upper one, composed of flakes of a black, graphite-like mineral. The latter attracted especially my attention. It was carefully decanted from all other components, which was not very difficult, since it remains in suspension in water thanks to its foliated structure. When dried, the mineral appears as a flaky, black, shiny, staining mass. It is attracted by the magnet. Its spec. weigh is 6.056. It is insoluble in acids and aqua-regia. It is slightly affected by concentrated potassium

hydroxide. But a mixture of potassium hydroxide and salpeter or potassium hydrochloride breaks up the mineral with evolution of osmium dioxide vapours. By the action of the named reagents on the dissolved mineral, one finds in the aqua-regia some iridium, even more iron oxide and chromic acid. Iridium sesquioxidel remains undissolved. When calcinated, the mineral loses nothing, except a trace of osmium. But when heated in a current of hydrogen gas, it loses oxygen with the formation of water. According to these preliminary tests, the mineral is thus composed of the following: oxides and oxyduls of iridium, osmium, iron and chromium.

It is thus a heretofore unknown mineral, and represents the first example of a natural occurrence of osmium and iridium in the oxidized state. I named that mineral irite with reference to its main component."

Excerpt 2. Hermann (1836), p. 229: "Triple salt of Iridium- and platinumchlorid with chlorammonium. This salt forms frequently in the St. Petersburg Platinum factory by evaporation of the solution from which Platinum has been separated with salmiac. It was considered until now as iridium chloride-chlorammonium. However, it contains in addition platinum chloride-chlorammonium and a small quantity of palladium."

Excerpt 3. Hermann (1841), p. 276: "I have described irite several years ago; but since the corresponding publication seems to have been ignored abroad, I allow myself to hark back to the subject. [...] Irite occurs in Urals together with platinum. It fills the spaces which frequently occur between the mineral grains forming the larger pieces of native platinum. The dark, iron-rich platinum varieties are especially enriched in irite. When Uralian platinum is dissolved in aqua-regia, irite remains undissolved, as well as

osmium-iridium, ilmenite, chromite, hyacinth, etc. From this residue of platinum dissolution, it is easy to separate irite by washing, since it remains suspended in water for a longer time than the other components, thanks to its low spec. weight and flaky habit. [...] Irite seems to have been observed often, but has always been overlooked until now, since it was considered by some as osmium-iridium, by others as iridium oxydul, and even as a mixture of osmium-iridium with chromite. But I must definitely disagree with these opinions."

Excerpt 4, Rose (1842), vol. 2: On the platinum ores of the Urals. 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."

Excerpt 5, Kenngott (1849), p. 61–62: "The Uralian mineral, which Hermann named irite with regard to its iridium content, has been examined in the collection of Herr Dr. Schneider. When observed under the naked eye, it appears as a fine black powder which sticks easily to the fingers, and in which isolated shiny particles sparkle, when changing the observation angle. At moderate magnification, one distinguishes three habits of particles forming the powder: flakes, irregular grains and small crystals. The latter form octahedra and are abundant, and may be considered either as regular octahedra, or as combinations of a rhomboheder with a hexagonal dyoheder[....]The colours are iron black and steel grey, and the lustre half-metallic to metallic. When finely ground, the powder is pure black and completely devoid of lustre."

Excerpt 6, Dana (1851), p. 232: "Irite.-Crystals of Irite in regular octahedrons have been observed by Kennigott (Min. Unters., i, 61).-They are much flattened parallel to one of the faces. The true formula of the species is probably included under R#R### [Berzelius notation], which embraces the spinels, magnetic iron and some other tesseral species".

Excerpt 7, Dufrenoy (1856–1859), p. 516: IRITE-This mineral occurs as regular, black octahedra, has a metallic shine, and looks like

oxydulated iron. Disseminated with the latter in platiniferous sands, it is regularly confused with it, but is not magnetic; Hermann (1) who brought it into notice, considers it as isomorphous with oxydulated iron, and he represents its composition by the formula (ir, os, Fe)(ir,os,cr)₂O₃ [sic] or more generally R# R### [Berzelius notation].

(1) Sur les combinaisons cristallisées d'osmium et d'iridium de l'Oural, par M. G. Rose (*Ann. de Poggendorff*, XXIX, p. 452.)"

[This latter paper was published under a German title in 1833, i. e. before Hermann's contributions and publications. In his 1842 book, Rose explicitly writes that this 1833-paper dealt with native Os and Ir, and neither 'irite'-like compounds or Hermann's works are alluded to in the book. We have not seen the 1833-paper. Dufrenoy probably mixed up his cards.]

Excerpt 8, Claus (1860), p. 285: "There is still a third platinum ore [in addition to Os-Ir-containing platinum and platinum], viz. "irite", defined by my Moscow friend Hermann, and which, according to his analysis, he considered as a combination of oxidized platinum metals with iron and chromium oxides. But I have reasons to doubt the existence of this mineral, not only because such a combination is already in itself unlikely ["unwarscheinlich"], but also because a pure mineral could not be separated by mere decantation from such a complicated mixture like the platinum residue. Indeed, when following my friend's method, I obtained a flaky pulverulent substance presenting all the properties that he ascribes to irite. But when examining it under high magnification, I recognized it as a heterogeneous mixture, the main mass of which being composed of fine flakes of osmiumiridium and chromite."

Excerpt 9, Wyssotzky (1913), p. 666–667: "Osmium varies between 0.18 and 14% in the raw platinum. It occurs as hexagonal scales, flattened grains and rods disposed according to the octahedron plane of the platinum crystal...."

By careful treatment of some platinum varieties with aqua regia, it is possible to get out of the platinum grain a crystalline skeleton, which is composed of hexagonal platelets of osmiridium and which form corresponds exactly to that of the platinum grain which has been treated with acid. In addition to the platelets, one finds also metallic threads, insoluble in aqua regia and apparently of the same composition, since they appear same-

wise under higher magnification as fine, elongate, parallel intergrown hexagonal platelets.”

Excerpt 10. Duparc and Tikonowitch (1920), p. 199–200: “Metallographic experiments on native platinum have been performed for the first time by R. Beck, and reproduced since then by others. (R. Beck: Ueber die Struktur des Uralischen Platins. Ber. Kön. sächs. Gesell. Wiss., 1907, LIX).

[...] We have already noted that native platinum includes nearly always iridium osmiure. When the polished nuggets are etched with aqua regia, the traces of welded osmiure crystals appear at first as fine hatchings, after what the surface shows off tabular porphyroblasts, distributed at random in the platinum mass. If the etching is protracted, a more or less voluminous residue is left, composed of hexagonal slabs or iridosmine grains, mostly very small, but sometimes rather large (Fig. 36). If one treats carefully some whole nuggets rich in osmiure directly with aqua regia, there remains sometimes a genuine crystallized skeleton, composed of the hexagonal platelets, skeleton which preserves the shape of the initial nugget. [Compare with Wysotzky!] This phenomenon occurs only for platinum nuggets very rich in osmiure; if the latter is less abundant, the skeleton decays and leaves a dust composed of fine hexagonal flakes of iridosmine, dispersed as a kind of colloidal solution which passes through the filters, but which may be centrifugated. The centrifugate is composed of finely divided osmiure which becomes an exceedingly fine dust [when dried?].”

Excerpt 11. Duparc and Tikonowitch (1920), pp. 199–200: “In some cases, the etching reveals that the nugget’s interior is composed of a kind of eutectic of osmiure and platinum, whereas the periphery appears as a well-crystallized intergrowth, reminiscent of that of pegmatites, as depicted by Fig. 37, which is borrowed from M. Quenessen.” [Caption of Fig. 37: “Metallographic section of a nugget after treat-

ment with aqua regia, disclosing the platinum/osmiure eutectic”.]

Excerpt 12, Duparc and Tikonowitch (1920), pp. 501–502: “At the onset, the aim was mainly to extract platinum only, and the other Platinum Group Metals were considered as of secondary importance. More than often, they were not even separated from the waste. But after years, this waste became sometimes a considerable, although unexpected, riches.”

Excerpt 13. Swjagintzeff (1932), p. 173: “Not to be forgotten is the work by Hermann (1836) [...] His irite is of black colour and is composed of osmium, iridium, chromium and iron with a sp. gravity of 6.056. Hermann gave for irite the formula $\text{Os}\#\text{Ir}\#\#\#\#\text{Fe}\#\text{Cr}\#\#\#3$ (according to Berzelius). But afterwards, the existence of this mineral became doubtful: according to all evidence, it is a mixture of osmiridium and ferrochromite [Eisenchromid, sic].”

Excerpt 14. Yushkin et al. (1986), p. 222: “Irite-Described by R. Hermann in 1836. According to Vernadsky, it is a mixture of osmian iridium, chromite and other minerals.”

Abbreviations used in Figures

NHML = Natural History Museum, London
 NHMV = Vienna Museum
 MNHN = Paris Museum
 ENSM-6774 = Ecole-des-Mines, Paris
 Pol. sect. = polished section
 Hand mt. = hand-mounted powder or separate particle(s)
 SEM = scanning electron microscope
 SEM(SM) = SEM(secondary mode)
 SEM(BS) = SEM(back scattered mode)
 RLM = reflected light microscope
 n μm = width in micrometers of a given picture
 Ir-osmium = iridian osmium
 Os-Ru-iridium = osmian ruthenian iridium, etc.