

THE COMPOSITION AND PROPERTIES OF SOME NATIVE PLATINUM CONCENTRATES FROM DIFFERENT LOCALITIES

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ABSTRACT

The mineralogy, microhardness, and reflectivity of Pt-Fe alloy concentrates from four localities are described. Microhardness does not give any useful indication of the chemical composition of Pt-Fe alloys, but the reflectivity is shown to increase strongly with the iridium content and decrease weakly with the other solid-solution elements. In the platinum-rich grains examined here, the mineralogical constitution depends critically on the ratio of iridium to osmium. This has been explained satisfactorily in terms of a pseudo-ternary phase diagram section, an important feature of which is a large three-phase field. This phase diagram, which may be generally applicable to all native-metal minerals composed of Pt, Ir, Os, Ru and Fe, shows the limits of the terminal solid solutions and predicts the compositions of contiguous phases.

The mineralogical studies indicate that sulfides of the platinoid metals other than platinum are formed in preference to cooperite, in agreement with previous work. Calculated free energies of formation are used to explain these observations. All the platinoid-metal sulfides apparently have formed at comparatively low temperatures.

SOMMAIRE

Les concentrés d'alliages Pt-Fe étudiés proviennent de quatre gisements. La microdureté n'indique rien d'utile sur la composition chimique de ces alliages; la réflectivité, par contre, augmente considérablement avec la teneur en iridium et diminue légèrement lorsqu'augmente la teneur des autres éléments dissous. La minéralogie des grains riches en platine, examinés ici, dépend du rapport iridium: osmium. Ce fait s'explique de façon satisfaisante par une section faite dans un diagramme de phases pseudo-ternaire, section remarquable par l'aire étendue d'un domaine à trois phases stables co-existantes. Ce diagramme de phases d'application générale à tous les minéraux natifs composés de Pt, Ir, Os, Ru et Fe, montre les limites des solutions solides partant des pôles et prédit la composition des phases contiguës. Les études minéralogiques, d'accord avec les travaux antérieurs, indiquent que les sulfures des métaux du groupe du platine, platine exclus, se forment plutôt que la cooperite. Le

calcul des énergies libres de formation explique ces observations: tous les sulfures des métaux en question ont dû se former à des températures relativement basses.

(Traduit par la Rédaction)

INTRODUCTION

Platinum-iron alloys are the best known members of the family of native platinoid metals. Despite this there is little information concerning the composition or the type and amounts of intergrown and associated minerals (Cabri 1972; Barrass 1974; Cabri & Feather 1975).

This study was undertaken to obtain information on the composition, hardness, and reflectivity of platinum and Pt-Fe alloys in a number of platinum concentrates, and to determine the mineralogy of the associated phases. Placer concentrates³ from Alaska, U.S.A.; Choco, Colombia; Urals, U.S.S.R.; and Yubdo, Ethiopia were examined, but the exact provenance of the concentrates within these localities is not known. In order that the reflectivity and hardness data might be used to characterize platinum grains according to their composition, similar data were obtained from a set of synthetic iron-platinum alloys of known composition.

The mineralogy of the platinum grains was used to deduce the condition under which the platinoid metals were originally formed.

METHODS OF INVESTIGATION

The concentrates were mounted in bakelite or a thermosetting plastic and hand polished by standard methods to a $\frac{1}{4}$ μ m diamond finish. Microhardness was determined using a Leitz microscope with a Vickers microhardness attachment. A 100 g load was used. Reflectivity was obtained using a Reichart Zetopan microscope. Reflectivity at one fixed wavelength (589 nm) was measured in air, using a NPL calibrated pyrite standard as a reference material.

Electron probe microanalysis was carried out with a Cambridge Instruments 'Microscan Five'

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³These were obtained from the geological collection of the University of Wales, Cardiff, U.K.

instrument. Specimens mounted in a non-conducting plastic were coated with a thin layer of carbon to prevent electrostatic charging. All measurements were obtained using a 15 kV beam potential to minimize penetration in the very small particles.

Analyses were carried out at four or five positions on each grain, a total of about 0.5×10^6 counts being accumulated. The statistical precision (2σ) of Pt would be $\pm 0.3\%$, and of Fe $\pm 0.1\%$. Elemental standards were used using the following X-ray lines for the metals detected $IrL\alpha_1$, $RuL\alpha_1$, $PtL\alpha_1$, $OsM\alpha_1$, $FeK\alpha_{1,2}$, $CuK\alpha_{1,2}$, $NiK\alpha_{1,2}$. CdS was used for sulfur using $K\alpha_{1,2}$. Corrections were applied for Cu enhancement of Ir. Where problems arose in finding the true background level on each side of the peak due to the presence of a contiguous

peak (e.g. for the L peaks of Os, Ir and Pt), the background was interpolated from a chart-trace obtained by a spectrometer scan. A computer correction program based on that of Duncomb & Jones (1969) was used to correct X-ray intensity data for absorption fluorescence and atomic number effects.

RESULTS

Natural platinum grains

Alaska. Under the polarizing optical microscope, the Pt-Fe alloy grains from Alaska are angular and typically 200-400 μm in diameter. They are creamy white in color and of high reflectance both in air and under oil. Most of the grains are isotropic.

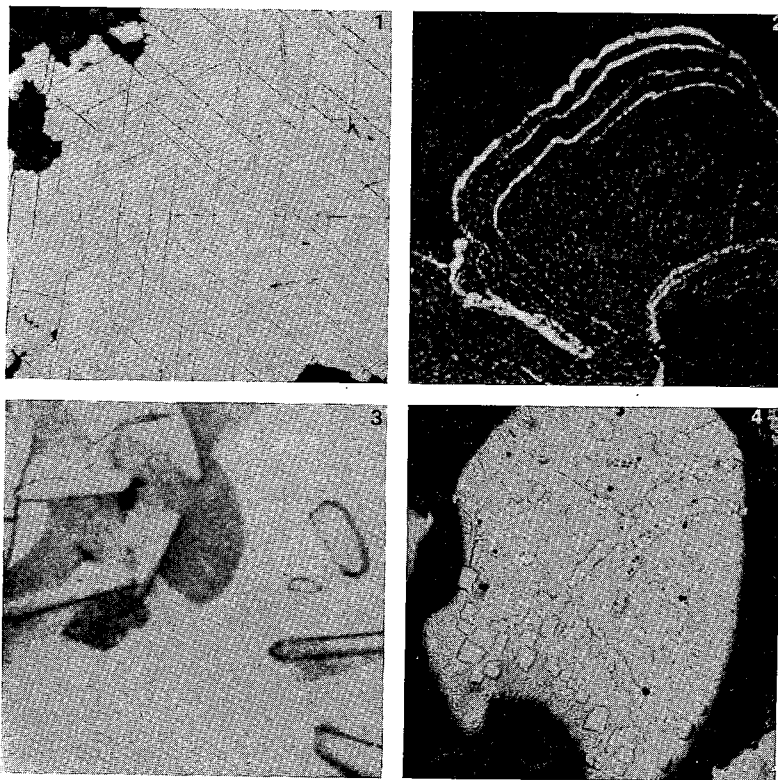


FIG. 1. Optical micrograph of Pt-Fe grain from Alaska, showing iridosmine plates in typical exsolution texture. (Approximately 335 \times).

FIG. 2. Osmium X-ray image showing iridosmine banding in Pt-Fe grain from Alaska. (Approximately 670 \times).

FIG. 3. Optical micrograph of Pt-Fe alloy grain from Yubdo, showing short rods or plates of iridosmine and darker grey complex sulfides of rhodium, iridium, iron and platinum. (Approximately 1070 \times).

FIG. 4. Optical micrograph of Urals Pt-Fe alloy with exsolution bodies of osmiridium. (Approximately 670 \times).

TABLE 1. COMPOSITION, REFLECTANCE AND MICROHARDNESS DATA FOR NATURAL AND SYNTHETIC PLATINUM-IRON ALLOY

Locality		Composition (wt.%)					Total	R% (589 nm)	VHN 100g
		Pt	Fe	Cu	Ir	Os			
Alaska, U.S.A.	1	89.5	7.7	0.6	1.6	0.6	100.0	66.9	314
	2	87.6	7.4	1.5	2.1	1.3	99.8	65.6	408
	3	88.2	7.7	0.8	1.9	0.7	99.3	66.1	330
	4	87.1	6.7	2.0	2.5	1.6	99.8	68.5	612
	5	90.4	8.1	0.5	0.2	0.8	99.9	66.2	314
	6	87.0	6.7	2.1	2.8	1.2	99.8	63.4	278
	7	91.3	5.2	0.6	2.3	0.4	99.8	65.8	
	8	85.1	13.6	0.6	0.1	0.4	99.8	63.1	670
average		88.3	7.9	1.1	1.7	0.9			
Choco, Colombia	1	91.6	6.8	0.6	0.5	0.8	100.3	63.2	398
	2	92.0	6.8	0.6	-	-	99.5	63.1	466
	3	94.8	4.8	0.5	-	-	100.0	63.1	487
	4	93.7	4.8	0.4	-	1.1	99.9	59.9	503
	5	94.9	4.7	0.4	-	-	100.0	63.3	415
average		93.3	5.6	0.5	0.1	0.4			
Yubdo, Ethiopia	1	88.8	8.0	0.9	1.1	1.1	99.9	54.6	334
	2	90.7	6.2	0.6	1.5	0.9	99.9	61.9	299
	average	89.8	7.1	0.7	1.3	1.0			
Urals, U.S.S.R.	1	89.6	6.9	0.5	1.7	1.4	100.0	67.0	292
	2	85.0	10.2	0.8	2.7	1.3	100.0	59.0	275
	3	90.9	6.4	0.8	1.1	1.1	100.3	67.4	238
	4	88.4	6.9	0.7	3.6	1.2	100.8	69.8	582
	5	88.7	6.4	0.9	1.8	1.9	99.6	66.3	284
	6	89.7	6.9	0.6	1.5	0.9	99.5	66.5	473
	7	92.1	4.3	0.5	1.3	1.7	99.8	67.3	137
	8	82.8	8.6	0.4	8.0	-	99.8	72.0	582
	9	79.9	9.8	2.5	8.0	-	100.2	72.0	625
	10	81.2	9.4	0.5	6.4	2.3	99.9	70.0	596
average		86.8	7.6	0.8	3.6	1.2			
Syn- thetic	1	90	10				66.0	417	
	2	80	20				60.5	563	
	3	70	30				56.7	574	
	4	50	50				54.0	412	

Minor phases found in the Pt-Fe alloy grains were identified as iridosmine and laurite by electron probe microanalysis. Some laurite inclusions have a considerable osmium content. Most iridosmine occurs as plates or lamellae (Fig. 1), often with a hexagonal shape, intergrown within the Pt-Fe alloy matrix. The plates were frequently very thin and had formed on well-defined matrix crystal planes. Some grains showed irregular concentric bands of hexagonal iridosmine (Fig. 2).

Eight Pt-Fe alloy grains were selected for quantitative analysis by electron probe. The results are tabulated together with the measured microhardness and reflectance in Table 1.

Colombia (Choco). The Pt-Fe grains from the Choco province of Colombia are creamy white, angular, and slightly smaller than the Alaskan grains.

Iridosmine and osmiridium were identified as precipitates or intergrowths within the grains, together with such sulfides as cooperite, braggite and laurite. Iridosmine was commonly enclosed within the Pt-Fe alloys and was irregular in shape or as coarse plates or lamellae. Osmiri-

dium was found as inclusions in the Pt-Fe grains. This cubic form, osmiridium, was less common than the hexagonal form, iridosmine. Braggite, cooperite, laurite and sperrylite were found as large irregular intergrowths. Gold was found among the associated minerals, which were predominantly magnetite with chromite and chalcopyrite.

Five grains of Pt-Fe alloy were selected for quantitative analysis. The results are shown together with the reflectance and microhardness in Table 1. Although sulfides of ruthenium and palladium were identified, the amounts of these elements in solid solution in the Pt-Fe are too small to measure.

Ethiopia (Yubdo). The eluvial Pt-Fe alloy nuggets from Ethiopia consist of a Pt-Fe matrix within which euhedral iridosmine particles are in a lamellar morphology (Fig. 3). The iridosmine is very high in osmium and could be readily identified by its strong brown-orange-red anisotropism.

Several different types of sulfide were detected. Laurite was often found as small anhedral particles, but a more massive unknown sulfide containing rhodium and iridium with iron or platinum is very plentiful. Some of these are visible as grey phases in Figure 3. The results of reflectance measurements, microhardness measurements, and probe analyses of two grains are given in Table 1.

U.S.S.R. (Urals). Pt-Fe grains from this source are angular to subrounded, and range from 300 to 500 μm in diameter. Some contain iridosmine in very large quantities. The plates generally contain more iridium and are thicker than those in the Alaskan or Choco samples, but have similar optical properties.

Osmiridium occurs as small angular particles which had exsolved both at the grain boundaries and within the Pt-Fe alloy grains. Typical structures are shown in Figure 4. A definite crystallographic orientation of these exsolution particles with respect to the matrix is strongly indicated by parallelism of the edges of the particles. Osmiridium is common in the Urals samples in contrast to those from the other localities.

Laurite, cooperite, braggite and sperrylite are intergrown with the Pt-Fe, mostly as small inclusions similar to those in the Choco samples. In addition, an unknown sulfide of iridium was identified by electron probe, but was not quantitatively analyzed. The associated minerals are magnetite, ilmenite-hematite, chromite, pyrite, chalcopyrite, cubanite, sphalerite, pyrrhotite and sperrylite. Chromite and the iron-rich minerals predominate.

The matrix parts of ten grains were analyzed by electron probe (Table 1).

Synthetic platinum-iron alloys

Iron is the principal alloying element in native platinum. In order to correlate reflectance and microhardness with composition, without interference from the variable amounts of other solid-solution elements, some binary platinum-iron alloys were purchased from Johnson, Matthey & Co. Ltd. These alloys had been prepared from pure elements and contained 10, 20, 30 and 50% wt. % iron.

After preparation by standard metallographic techniques, the alloys were analyzed by electron probe. A good consistency in the analytical results from different areas showed that the alloys were homogeneous. The reflectance and microhardness were also obtained under experimental conditions identical to those applied to the natural alloys. The results are shown in Table 1.

DISCUSSION

Elements in solid solution in native Pt-Fe

The results in Table 1 allow an estimate to be made of the amounts of different elements in solid solution in natural Pt-Fe grains. The data from Table 1 were used to produce the histograms for platinum, iridium, osmium, copper and iron (Fig. 5). Platinum varies considerably but is typically about 90%. Iron (~7%) is the most important "impurity". Iridium is scattered widely in the range up to 4%, but osmium is generally about 1% and copper is most commonly at levels below 1%.

When the mean analyses for the different regions are examined separately, it is seen that there are characteristic differences in the composition of the Pt-Fe. That from the Choco region is the purest at 92.5% Pt. This is due to the very low levels of all the "impurity" elements. The iron content averages less than 6%. The next purest is that from Ethiopia, but with only two analyses this observation is of little real significance. The Alaskan Pt-Fe is characterized by a significantly higher iron content than the others. The Urals material has an exceptionally large iridium content. The microscope work showed large amounts of native iridium exsolved in some of the Pt-Fe grains, so the average of 2.7% probably lies close to the equilibrium solubility of iridium in Pt-Fe of that composition. Ruthenium and other platinoids were in the form of sulfides and very little were detected in solid solution in the Pt-Fe grains.

Solute-dependence of reflectivity

Since iron is the most abundant solid-solution element in natural platinum, the reflectivity was plotted as a function of iron content. However, the resulting curve showed a very large scatter of the points. A somewhat better correlation was obtained by plotting the reflectivity

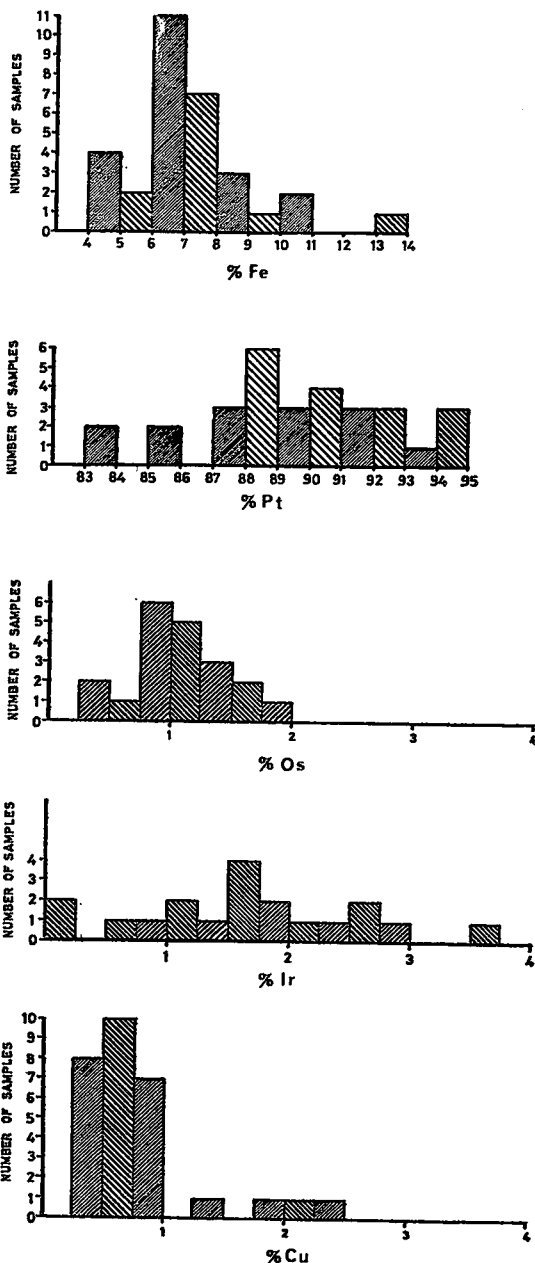


FIG. 5. Frequency distribution of platinum, iridium, osmium, copper and iron in natural Pt-Fe alloys.

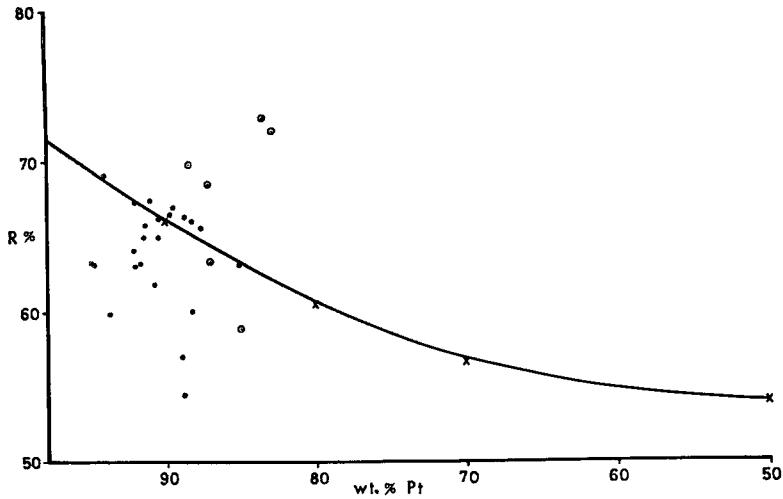


FIG. 6. Reflectivity at 589 nm as a function of platinum content.

tivities as a function of platinum content. The result is shown in Figure 6. The line joining the points marked with a cross represents the variation of reflectance with iron-content obtained from the measurements made on the pure, binary synthetic alloys. There is a reasonable grouping of the points from the natural alloys along this line. Those points which fall well below the line may be partly due to a badly prepared surface. The grains were very small and it was difficult to prepare a flat, scratch-free surface. Some of the grains, especially those from Choco, did not have a perfect surface and the reflectivity would be expected to be low.

Where the experimental points were significantly above the platinum-iron line, the alloys invariably contained a significant proportion of iridium. Points corresponding to Pt-Fe alloy grains with more than 2.5% iridium are marked with open circles in Figure 6. The deviation of the reflectance values from the platinum-iron curve was measured and plotted as a function of iridium content, for all grains containing an appreciable amount of this element. The result is shown in Figure 7. A strong, positive dependence of the reflectivity on the iridium content can be inferred from this curve. This result is in accordance with the observations of Stumpfl & Tarkian (1973), who noted that the reflectances of osmium, iridosmine and osmiridium all increase with increasing iridium content. The non-zero intercept of the difference curve with the ΔR axis means that there is a reflectivity difference of about 1% between large and small specimens of the same material, due to a slightly imperfect surface in the latter.

Comparison of the values shown in Figure 6 with those of Stumpfl & Tarkian (1973) shows that their reflectances are grouped about 2% higher than the platinum-iron alloy line. This may be due to use of different instruments and standards.

Solute-dependence of microhardness

There was no clear relationship between micro-indentation hardness and the iron content

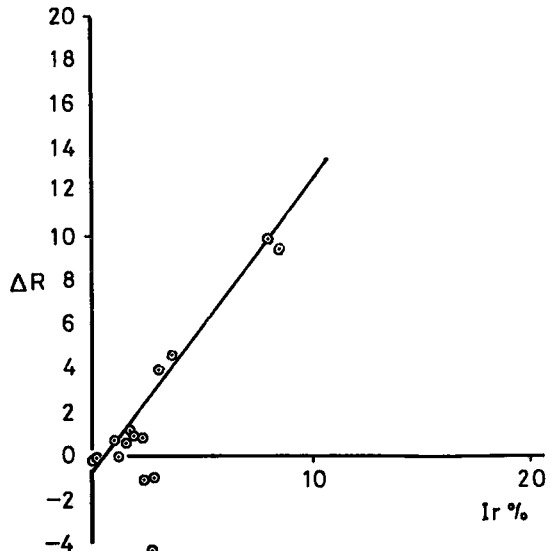


FIG. 7. Deviation of reflectivity from that of pure platinum-iron alloys, as a function of iridium content.

of natural Pt-Fe alloys, or indeed of any element alone or any combination of elements.

Of the elements present in natural Pt-Fe, iridium and osmium in solid solution would be expected to contribute little to the hardness. The Goldschmidt atomic radii of these elements differ by only about 3% from that of platinum (Hume-Rothery & Raynor 1956) so the size effect on hardness should be small. Osmium has a *cph* structure and could provide a minor hardness increment due to Suzuki locking. Neither element has a tendency to ordering.

Iron and copper, on the other hand, differ from platinum in atomic diameter by 8.3% and 7.9% respectively. A definite hardness increase due to size effect is thus possible. However, a much larger increase in hardness could result from ordering of the substitutional solute atoms. In the iron-platinum system, ordered phases based on FePt_3 , FePt and Fe_3Pt are known. Of these FePt_3 and Fe_3Pt are cubic but FePt is tetragonal since the iron and platinum atoms occupy alternate (001) planes of the *fcc* structure (Crangle & Shaw 1962).

According to Crangle & Shaw, FePt_3 extends over the range 21-40 at.% Fe. Vlasova & Sapozhkova (1970) reported that the FePt phase extends from 36-62% Fe. The overlap of the reported phase fields indicates a discrepancy in the structural investigations, but does suggest that the FePt_3 and FePt phase field is narrow. According to the above authors, FePt_3 extends

from 70 to 82 at.% Pt, and the $\text{FePt} + \text{FePt}_3$ phase field is small. The schematic phase diagram of Cabri & Feather (1975) is in broad agreement with this.

In such a system where the ordered phases have wide composition limits, only partial ordering is possible for compositions away from the stoichiometric ratio, hence the tendency to order must not be very strong. It is thus probable that the anti-phase boundary produced by a moving dislocation will have low energy. Pairing of dislocations is not expected to be favored energetically and the hardness of the alloy will be due to the formation of an anti-phase boundary behind moving single dislocations, as is the case for Fe_3Al (Flinn 1964).

The valency of iron and platinum is the same and the crystal structures are similar (*fcc*); hence Suzuki locking and the shear-modulus interaction would not be expected to contribute significantly to the hardness. The major effects which give rise to hardness change on alloying platinum with iron would be expected to be a small contribution due to size effect, and a moderate effect due to order-hardening.

The effect of copper on hardness should be similar to that of iron, although no true, ordered copper-platinum phase should exist at the low concentrations found in Pt-Fe. Copper does form a CuPt_3 phase (Miida & Watanabe 1974); its structure is slightly different from that of FePt_3 , and it is expected that the copper

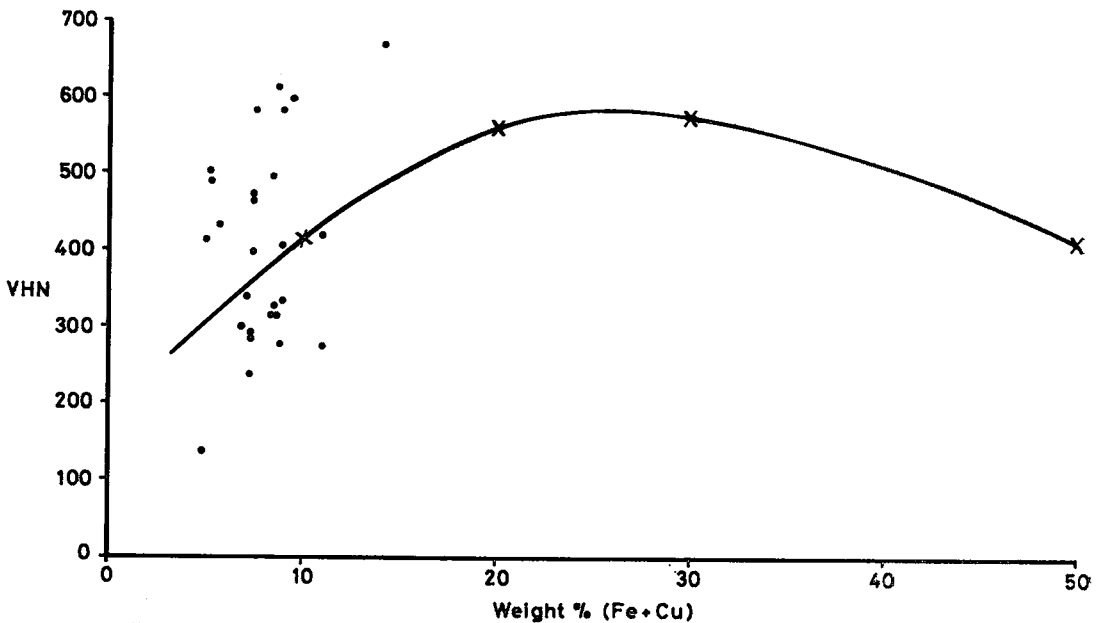


FIG. 8. Variation of microhardness with the sum of iron and copper contents.

would simply substitute for iron in FePt₃. Therefore, it is reasonable to suppose that a plot of microhardness versus the sum of the iron and copper contents would produce the best correlation of the experimental data. This is shown in Figure 8. The line joining the crosses is the microhardness data obtained from the binary, synthetic platinum-iron alloys. This line is a smooth curve which reaches a maximum at about the equi-atomic composition, which suggests that the FePt ordered phase is the one which contributes most to the hardness.

The data from the natural alloys do not correlate well. It is highly probable that this is because hardness is a very structure-sensitive property, depending not only on the composition but also on the thermal and mechanical history of the alloy. Other impurities, even in trace amounts, can have a significant effect on the mobility of grain boundaries and dislocations and can thus radically alter the hardness between apparently similar alloys. Ramdohr (1969) observed that Pt-Fe from placer deposits was significantly harder than commercially available platinum of identical composition. He ascribed this to 'cold-working' during transport in rivers, but this does not explain the anomalous softness of many of the natural grains, as seen in Figure 8. It is possible that much of the scatter can be attributed to the degree of order attained in the samples, since this is a complex function of the age and thermal/mechanical history of the samples as well as composition. For these reasons it is concluded that microhardness does not give any useful indication of the composition of Pt-Fe.

The magmatic origin of the platinoid metals

The platinoid-metal grains which have been studied here are of placer or eluvial origin, and have been subjected to weathering action and, except for the Yubdo material, transportation. However, each individual platinoid-metal grain represents a closed system, protected from the external environment by its own chemical inertness. The interiors of the grains thus preserve information concerning the formation of that grain from the magma. The possibility that the grains studied here have been appreciably altered during the degradation process can be discounted on the evidence of the intact structures indicative of cooling from high temperature. Thus the structures which are observed can give useful information on the local chemical conditions during the solidification and further cooling of the host magma. Presumably all the platinoid metals were in a very low concentration in the magma, so that when it cooled

the composition of the platinoid metal could be quite variable according to local conditions. Since the melting points of the platinoid metals are high compared with those of the ultrabasic rocks in which they are found, the first metal particles to form were almost certainly nucleated with a considerable degree of undercooling. A gradual increase in size would take place by diffusional growth while the particles were suspended in the melt.

In all the regions, except possibly the Urals, platinum is by far the most common platinoid metal (Mertie 1969). For this reason it is most probable that platinum grains would nucleate first and that the supersaturated iridium, osmium, and ruthenium would "dissolve" in the solid platinum directly from supersaturated solution in the magma. Iridium and platinum have the same crystal structure and solid solution is complete at high temperature so that, unless cooling is rapid, there is no means of knowing which formed first. Osmium and ruthenium have a *cph* structure and a miscibility gap exists in the osmium-platinum phase diagram. Separately nucleated osmium or ruthenium alloys would thus always be recognizable as such unless enough separate grains of platinum came into contact with a ruthenium grain for long enough to dissolve the latter. This possibility seems remote since the average separation distance between growing particles must be large.

Figure 2 shows evidence of cooling under supersaturated conditions. A grain of Pt-Fe alloy has encountered regions of high osmium and iridium during its period of suspension in the cooling magma. This must have occurred at temperatures where the miscibility gap exists, well below the melting point. The two phases coexist as separate bands which have formed by attachment of the condensing atoms onto the primary Pt-Fe alloy grain. The appearance of each band signifies a localized region richer in osmium or iridium rather than platinum.

We may then presume that, at high temperatures, the platinoid metals existed as small particles of platinum with lesser amounts of iridium, osmium, ruthenium, and iron in solid solution. Where there is a larger amount of osmium or ruthenium, separate intergrown particles or bands of iridosmine would also be present.

Below about 1000°C, a phase separation occurs between platinum and iridium (Rudman 1967). This results in the formation of exsolution laths and particles of iridium-rich alloy in the samples from Choco and especially from the Urals. In the latter a characteristic exsolution texture occurs.

The presence of banding, in natural grains which can be shown from exsolution bodies to have cooled from a high temperature, confirms the suggestion of Cabri & Harris (1975) that banding is a result of non-equilibrium cooling rather than elemental agglutination at low temperatures (Cousins 1973; Stumpfl 1974).

In many of the samples, for example those from Alaska and the Choco, the second phase which has formed from the Pt-Fe alloy solid solution is rich in osmium. Several analyses of these laths showed an osmium content of about 80% and a platinum content of about 5%. Such a large change in the composition of the exsolution bodies, coupled with the fact that miscibility gaps occur among each of the components of the Os, Ir, Pt ternary system at low temperatures, strongly indicate the presence of a large three-phase field in that system.

Analytical data for Pt-Fe alloy grains containing iridosmine and osmiridium were collected from our own analyses and from the literature (Cabri & Harris 1975; Stumpfl & Tarkian 1973). Our own data (Table 2) show the compositions of different minerals in single grains. Some Pt-Fe alloy grains contained both iridosmine and

osmiridium together, and these enabled the boundaries of the three-phase field to be determined. Data from alloys containing one each of the second phases gave additional information on the position of the tie-lines in the two-phase fields, and the limits of solid solution. All of the data were used to construct a low-temperature section through the pseudo-ternary phase diagram: Os(+Ru)-Ir-Pt(+Fe). Here, ruthenium is added to the osmium content since both have similar atomic radii and crystal structures. Iron is added to the platinum since they have an extensive mutual solid solution, and the iron content is always minor. The result is shown in the phase diagram of Figure 9. The triangular marks represent the boundaries of the three-phase fields. The filled circles represent grains with two phases, and tie-lines join their compositions. Phase boundaries are drawn with thicker lines.

Figure 9 is basically a phase diagram and all three terminal solid solutions are metallurgical entities. However, following the terminology of Harris & Cabri (1973) and Cabri & Feather (1975), the iridium-rich solid solution can be subdivided into iridium, osmiridium, and a high-platinum region for which there is as yet no approved name. The osmium-rich field comprises osmium and iridosmine. No attempt has been made to subdivide the solid solutions according to the mineralogical classification mainly because of the terminological difficulties which would ensue from the substitution of ruthenium for osmium, and because of the absence of an approved name for the high-platinum iridium alloy. Following crystallographic precedents, the iridium-rich, *fcc* phase field is denoted by α , and the *cph* osmium-rich field by ϵ . The platinum-rich field is unambiguously platinum-iron alloy.

Note in Figure 9 that although the solubility of platinum in pure iridium is approximately zero, the addition of osmium allows the solution of platinum up to a maximum of about 20 at. %. Also, small amounts of platinum greatly decrease the solubility of iridium in the epsilon phase. The comparatively large scatter in the analytical results collected by Harris & Cabri (1973) could be explained by this observation since the width of the two-phase field depends critically on the amount of iron and platinum in solid solution.

The Pt-Fe phase field is difficult to define. The scatter in the points is well beyond that due to experimental error and must be due to real compositional differences between alloys. It is possible that the description of a five-component system as a pseudo, three-component

TABLE 2. COMPOSITION OF MINERAL ASSEMBLAGES USED TO CONSTRUCT FIGURE 9

Locality	Mineral	Composition wt. %					
		Ir	Os	Ru	Pt	Fe	Cu
Alaska	Pt-Fe alloy	0.8	0.2	0.1	89.9	8.9	0.2
		48.1	21.5	8.8	20.9	0.1	0.6
		46.3	25.1	7.9	19.8	0.2	0.6
Alaska	Iridosmine	49.4	24.7	6.3	18.9	0.1	0.7
		25.0	67.2	4.9	2.6	0.1	0.3
		1.6	-	-	89.5	9.0	-
Alaska	Iridosmine	13.0	79.2	2.3	5.6	-	-
		1.7	0.2	0.1	88.7	9.3	-
Alaska	Iridosmine	17.2	69.9	7.8	4.7	0.4	-
		0.8	1.5	0.2	91.9	5.2	0.5
Alaska	Iridosmine	8.1	88.3	0.8	2.6	0.1	0.1
		1.0	-	0.3	89.2	9.5	-
Urals	Iridosmine	21.7	72.0	1.8	4.1	0.4	-
		58.0	23.1	6.9	11.7	0.4	-
Urals	Pt-Fe alloy	1.4	1.3	0.2	91.5	5.6	-
		11.5	83.3	1.2	3.8	0.2	-
Urals	Iridosmine	4.1	0.3	0.1	88.2	7.4	-
		51.2	29.9	1.8	16.8	0.3	-
Urals	Osmiridium	8.8	1.1	0.1	83.2	6.8	-
		58.6	25.5	2.0	13.7	0.2	-
Urals	Pt-Fe alloy	5.6	0.2	0.1	83.6	10.5	-
		56.6	26.0	2.0	14.9	0.5	-
Urals	Osmiridium	1.4	1.3	0.2	91.5	5.6	-
		11.2	83.8	1.2	3.6	0.2	-
Urals	Pt-Fe alloy	8.0	-	-	79.9	9.8	2.5
		80.6	8.7	-	9.3	1.4	-
Urals	Osmiridium	6.4	2.3	-	81.2	9.4	0.6
		65.2	19.6	-	13.1	1.2	1.0
Urals	Osmiridium	59.9	28.7	3.7	7.6	0.2	-
		39.2	55.2	4.4	1.1	0.2	-
Urals	Iridosmine	37.8	51.9	8.5	1.8	0.1	-
		36.1	52.8	9.2	1.8	0.1	-

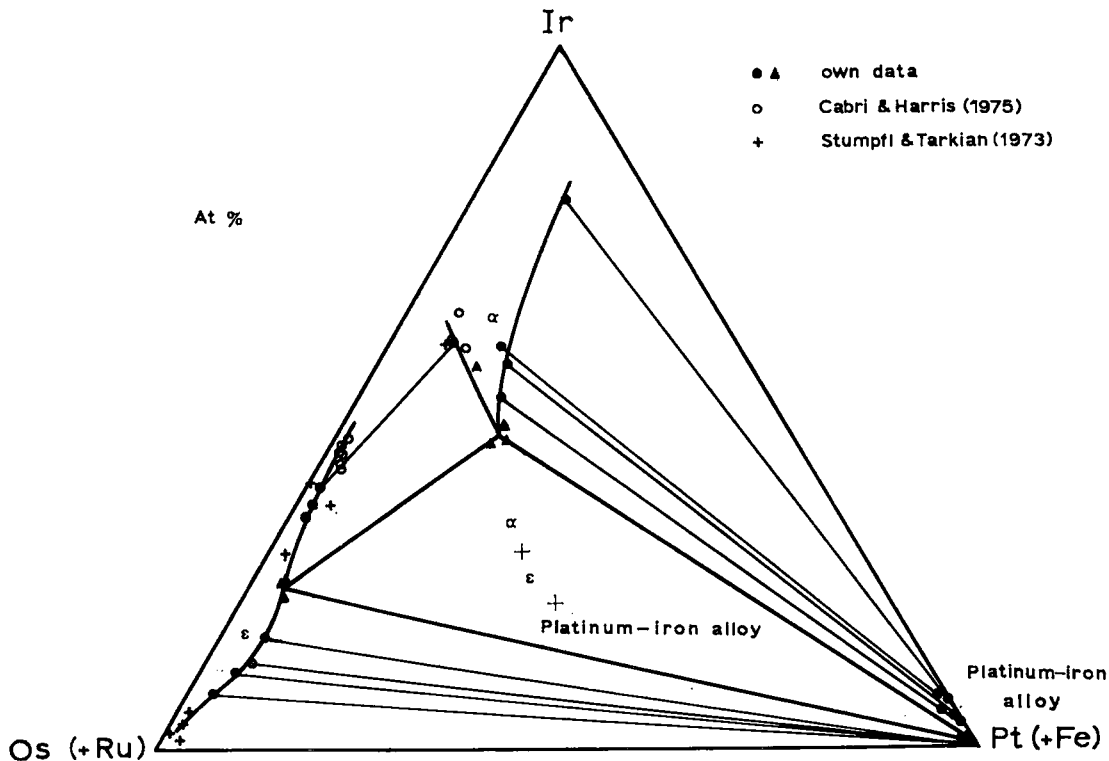


FIG. 9. Pseudo-ternary phase diagram of the system Os(+Ru) - Ir - Pt(+Fe).

system is not adequate to permit the proper delineation of the Pt-Fe alloy phase field. Alternatively, exsolution bodies too small to resolve with the optical microscope may be affecting the analyses. Despite this, it is clear that Pt-Fe alloy generally contains little osmium or ruthenium, but that large amounts of iridium can be present.

The phase in equilibrium with the Pt-Fe alloy will depend critically on the ratio of osmium to iridium. If more than one or two percent of both are present, then three phases will coexist. It is also apparent from this phase diagram that there is a very large miscibility gap in the platinum-osmium binary system.

The significance of the pseudo-ternary phase diagram, shown in Figure 9, is that all slowly cooled, natural alloys of osmium, ruthenium, iridium, platinum, and iron can be represented by points on this diagram. The only requirement is that equilibrium in composition must be attained, and under slow cooling conditions this is probably closely approached. To minimize the effects of non-equilibrium, our compositions were measured close to the interface between phases.

According to the ratio of the above-named components in the magma, any mineral assem-

blage of the native platinoid metals will consist of either a single solid solution, or a mixture of Pt-Fe alloy, α -phase, and ϵ -phase in the appropriate ratios. In the latter case the individual phases will have compositions lying on the boundaries of the single-phase fields and can be joined by tie-lines. This appears to be the case for most of the grains analyzed. In view of this, composition measurements on grains give limited information as to the mean platinoid-metal ratios in the magma, unless they are combined with an accurate assessment of the relative proportions of Pt-Fe alloy, and the α and ϵ phases.

Sulfide minerals

All of the platinoid metals are attacked strongly by sulfur and it is notable that native platinoid metals are found only in rocks with a low sulfur content (Mertie 1969). In some of the material studied here the presence of small sulfides formed in, or in association with, the Pt-Fe grains indicates that the magma contained small amounts of sulfur.

Despite the fact that the grains contain iron, osmium, iridium and ruthenium in addition to platinum, the sulfides are nearly always laurite, occasionally complex sulfides of iridium, os-

mium and ruthenium, and rarely braggite or cooperite.

As an aid to understanding the predominance of some platinoid-metal sulfides, especially laurite, the thermodynamic properties of the metals and sulfides were collected and the variation of free energy of formation (ΔG_f) with temperature was calculated. The sources of the thermodynamic properties were Kubachewski & Evans (1956), Hultgren *et al.* (1963) and Mills (1974). The temperature dependence of the heat capacities of the platinoid-metal sulfides is not known; estimates by Mills (1974) were used for the calculations. No great error is envisaged through the use of estimated heat capacities since a calculation made ignoring the heat-capacity terms altogether gives a very similar result. The greatest error is probably in the value of ΔH_{298} . The result is shown in Figure 10.

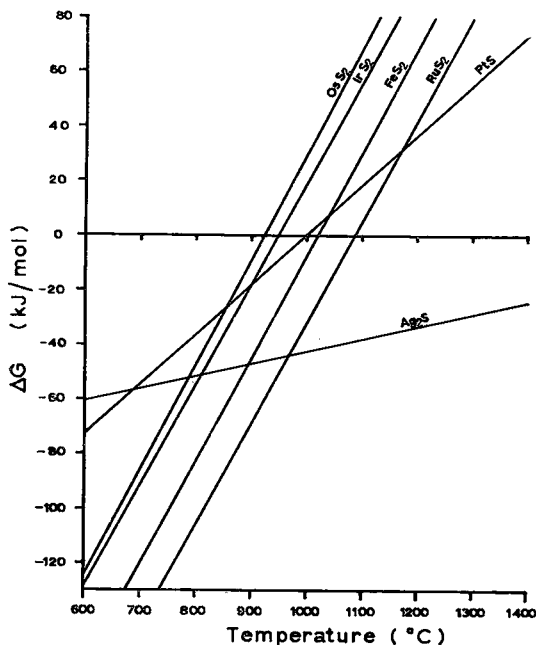


FIG. 10. Calculated Gibb's Free Energy of formation of sulfides of platinoid and other metals, as a function of temperature.

Keays & Crocket (1970) have produced a similar diagram although the free energies are expressed in a different way. The most important feature of Figure 10 is that the relative stabilities of Os₂S₅ and RuS₂ are transposed from Keays & Crocket's work, and accord better with the mineralogical data. The temperatures in Figure 10 are not exact, since the effect of pressure on ΔG is disregarded. Also, the sulfides

are assumed to be in equilibrium with S₂ vapor, although it is known that molecules up to S₈ can be formed. The proportion of higher molecular weight sulfur in a magma is not known. Both of these effects could raise the formation temperatures of the sulfides. The relative positions of the lines for the sulfides will be largely unaffected.

Whilst it is recognized that Figure 10 is only an approximation, several features of importance to the study may be noted. First, the sulfides decompose when $\Delta G=0$; hence, none of the platinoid-metal sulfides is stable at temperatures much above 1100°C. Indeed, only sulfides with small amounts of sulfur, such as Ag₂S, will be stable at high temperatures due to the large effect of the entropy of sulfur vapor. Because of this, the platinum-metal grains imbedded in the solidifying magma are free from sulfide minerals down to temperatures of that order. Secondly, ruthenium disulfide forms at higher temperatures than either FeS₂ or PtS, and remains thermodynamically more stable at low temperatures. This explains why laurite is so common among the minerals examined. Any sulfur vapor which came into contact with the platinoid metals would combine with dissolved ruthenium in preference to iron or platinum. Below 850°C all other platinoid-metal sulfides are more stable than PtS, but less stable than RuS₂. Thus, Figure 10 is in agreement with the experimental observation that Pt-Fe alloy grains associated with braggite or cooperite have a very low content of the other platinoid metals, and that laurite is the most common sulfide associated with the platinoid metals.

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