

THE ROLE OF COLLECTORS IN THE FORMATION OF THE PLATINUM DEPOSITS IN THE BUSHVELD COMPLEX

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ABSTRACT

We consider the formation of the platinum deposits in the Merensky and UG-2 Reefs in connection with the action of collectors settling under the influence of gravity. The sulfides in the UG-2 Reef, too small to have settled on their own, were carried down by larger chromite grains in piggy-back fashion. The sulfide droplets adhered to the chromite grains either because they could wet the chromite more readily than the silicates, or nucleation of sulfide liquid droplets could have taken place preferentially on the surfaces of chromite grains. An iron alloy, stable only under exceptionally low oxygen fugacity, could have acted as an efficient collector of platinum-group metals, which could have caused exceptional enrichment of some magma fractions. Some of the mineral intergrowths in the Merensky Reef may be relics of iron-platinum grains that reacted with sulfur, to form intergrowths of iron-platinum alloy with base metal sulfides that are pseudomorphous after the original crystals.

SOMMAIRE

On considère la formation des gisements de platine des bancs Merensky et UG-2 et le rôle d'agents collecteurs dans un champ gravifique. Les grains de sulfures du banc UG-2, trop petits pour pouvoir se déposer d'eux-mêmes, auraient été transportés "à cheval" sur des cristaux de chromite, plus gros. Les gouttelettes de sulfure auraient adhéré aux cristaux de chromite à cause soit d'une tendance à mouiller la chromite plutôt que les silicates, soit de la nucléation préférentielle de gouttelettes de sulfure liquide sur la surface des cristaux de chromite. Un alliage de fer, stable seulement sous fugacité d'oxygène exceptionnellement basse, aurait servi de collecteur pour les platinoides, enrichissant ainsi fortement certaines fractions du magma. Certaines intercroissances minérales du banc Merensky semblent être des reliques de cristaux d'un alliage fer-platine qui, par réaction avec le soufre, auraient donné une intercroissance d'un nouvel alliage fer-platine avec des sulfures de métaux vils, pseudomorphe des cristaux originels.

(Traduit par la Rédaction)

INTRODUCTION

Most of the sulfide occurrences of the Bushveld complex are associated with enrichments in platinum-group metals. However, there are only three known occurrences where the concentrations of these elements reach values of economic significance. These are the Merensky Reef (under which, for present purposes is included the Plat Reef), the Upper Chromitite Layer (or UG-2 Reef), and the three dunite pipes Driekop, Onverwacht and Mooihoek in the eastern Bushveld. In this paper, attention is given to one aspect of platinum deposits: the collection processes that gave rise to the concentration of the platinum-group metals.

GEOLOGICAL CONSIDERATIONS

As shown by von Gruenewaldt (1977) the occurrences of platinum-group metals of economic significance in the Bushveld complex, the Merensky Reef and the UG-2 Reef follow each other fairly closely. In the western Bushveld, the Merensky Reef is situated only about 150 m above the UG-2 layer (von Gruenewaldt 1977), but in the eastern Bushveld at the Atok mine, this distance is increased to 300 m (Schwellnus *et al.* 1976). Idealized sections through a portion of the Merensky suite of rocks are given in Figures 1 and 2. Cousins & Feringa (1964) provided sections through the UG-2 suite of rocks. Descriptions of the three dunite pipes can be found in Wagner (1973, pp. 50-92).

Most workers agree that the Bushveld complex was emplaced in the form of a magma from which the different rock units were formed by fractional crystallization and sedimentation of the crystals into cumulates (Willemsse 1969, Lombaard 1934, and many others). More than one heave of magma is postulated, but some workers (Coertze 1970, Schwellnus 1956) think that most different rock units are separate in-

trusions of magmas that underwent differentiation at depth.

The origin of the mafic magma is seen as the result of a process of differential melting of the upper mantle, but there was some degree of assimilation of the rocks that came into contact with the magma. In some instances, this assimilation could have played an important role in the formation of sulfide deposits (Coertze 1970, Liebenberg 1970, de Waal 1977, Naldrett & Cabri 1976). The upper mantle also must be considered to be the source of the platinum-group elements in mafic rocks.

CONCENTRATION AND DEPOSITION

There are two concepts of concentration and deposition that are of interest in the present paper: (1) crystal settling (Liebenberg 1970, Brynard *et al.* 1976), which suggests that platinum-group minerals settled out of a magma to become concentrated at the bottom of the magma chamber, and (2) concentration in a collector *e.g.*, sulfide which settled out of the magma, thus also concentrating the platinum-group elements. The rates of settling in both these instances must have been such that the platinum-group minerals or sulfide droplets settled at a rate different from that of the other crystals that formed in the magma at the same time; no concentration would have been effected by the settling process alone. The conditions under which particles or droplets can settle out of a magma have been discussed by Wadsworth (1973) among others. The grain sizes and densities measured by the author and his colleagues, or collected from the literature, are given in Table 1, and these were used, following Wadsworth (1973), for the calculation of the settling velocities for various mineral constituents (Table 2).

As only relative settling speeds are of interest here, the same density (2.58 g.cm^{-3}) and the same viscosity ($1000 P$) were used in all the calculations, although the estimates for these values given in the literature range from lower to higher values. Stokes' formula then simplifies to $V = 17169.4D(\rho_F - 2.58) \text{ m per year}$, where D is the particle diameter (cm) and ρ_F is the particle density (g.cm^{-3}).

Strictly, the densities should have been corrected for temperature, but in view of the larger influence exerted on settling velocity by grain sizes, it was decided that this correction would not have influenced the results unduly. A

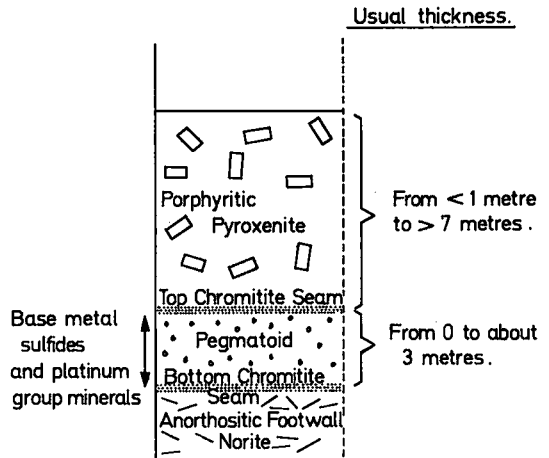


FIG. 1. Idealized section through the Merensky Reef in the western Bushveld complex.

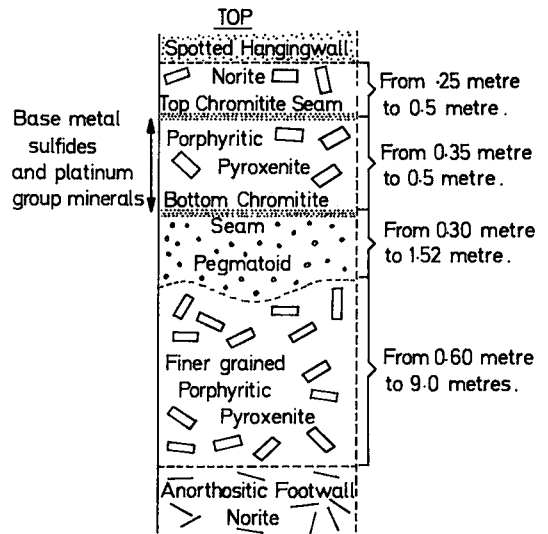


FIG. 2. Idealized section through the Merensky Reef in the eastern Bushveld.

further factor to be taken into account is that the crystals could have increased in size during settling and after deposition. As will be shown later, it is probable that many of the grains of platinum-group minerals attained their final sizes after having been deposited.

The size data reported in Table 1 were collected by different workers and are usually the sizes as seen in polished sections without any allowance for sectioning. The averages were calculated from a few tens to a few hundreds of grains and are usually close to the

TABLE 1. GRAIN SIZES OF SOME CONSTITUENTS IN THE MERENSKY REEF

Mineral	Rock unit/locality	Range	Average/Size
A. NE of Pilanesberg			
Chromite	Top layer	0.1-1.6mm	1.6mm
Chromite	Bottom layer		1.0mm
Pyroxene	Porphyritic pyroxenite	2 - 3 mm	1.5mm
Pt-Fe alloy	Pegmatoid		16 µm
B. South of Pilanesberg			
Chromite	Top layer	0.3- 2.5mm	1.0 mm
Braggite		3.5-47 µm	12.5 µm
Laurite		5.5-27 µm	13.25 µm
Sperrylite		6 -50 µm	20.0 µm
C. Near Rustenburg (1)			
Braggite	Silicate, area A	--	9.1µm
Braggite	Chromite, area A	--	6.1µm
Cooperite	Silicate, area A	--	11.1µm
Cooperite	Chromite, area A	--	8.1µm
Cooperite	Chromite, area B	--	4.9µm
Laurite	Silicate, area A	--	6.9µm
Laurite	Silicate, area B	--	7.4µm
Laurite	Chromite, area A	--	4.8µm
Laurite	Chromite, area B	--	6.1µm
D. Western Platinum Mine (2)			
Sperrylite	--	6-150µm	0-20µm
Braggite	--	37-300µm	
E. UG-2 Reef at various localities in the eastern and western Bushveld (3)			
Chromite	--	0.1- 4mm	0.5- 1.5mm
Cooperite/Braggite	--	0 - 20µm	1 - 3 µm
Sulfide aggregates	--	0 -200µm	20 -30 µm
F. Atok, northeastern Bushveld			
Chromite	--	0.07-0.7mm	0.5mm
Pyroxene	Porphyritic pyroxenite	1mm -1cm	3 mm
Braggite			12 µm
Laurite			15 µm
G. Some exceptional sizes			
Pt-Fe alloy	Northeast of Pilanesberg	--	115µm
Intergrowth of Pt-Fe alloy and pyrrhotite (1)	Rustenburg	--	190µm
Intergrowth of Pt-Fe alloy and pyrrhotite (1)	Rustenburg	--	132µm
Cooperite	Atok	--	100µm
Intergrowth of Pt-Fe alloy and pyrrhotite	Pilanesberg	--	112µm
Sperrylite (2)	Western Platinum Mine	--	150µm
Intergrowth of Pt-Fe alloy and sulfides (2)	Western Platinum Mine	--	100µm

- (1) Vermaak & Hendriks (1976) Figures C, G.
- (2) Brynard (1976) Figures D, G.
- (3) C. McLaren, personal communication - Figure E.

median size. The data from Vermaak & Hendriks (1976) listed in Table 1 were calculated as diameters from the volumes they reported. Table 1 also lists some maximum values observed in polished sections. A very minor proportion of the platinum-group minerals occurs as grains of such exceptional sizes.

The striking pattern emerging from Table 2 is that chromite could not easily have been separated from the other constituents in a crystallizing stagnant magma because, at the observed grain sizes, its settling velocity is similar to those of the silicate minerals. More significant, however, is the fact that the settling velocities of the platinum-group minerals seem so low that separation from the magma itself by a process of settling appears to be unlikely.

TABLE 2. SETTLING VELOCITIES FOR SOME MINERALS FROM THE MERENSKY REEF DENSITY OF MAGMA : 2.58 g.cm⁻³ VISCOSITY : 1000 P

Mineral	Density	Size, cm	Velocity, m per year
Pyroxene	3.35	2 (e.g. in pegmatoid)	52 882
		1 (e.g. in pegmatoid)	13 220
		0.3 (e.g. in porphyritic pyroxenite)	1 189
Chromite	4.5	0.1 (e.g. in porphyritic pyroxenite)	132
		0.3	2 967
		0.2	1 319
Braggite	8.9	0.1	62
		0.05	98
		0.0012 (av. Atok and S. of Pilanesberg)	0.16
Cooperite	10.2	0.01 (max. value Table 1)	13
		0.0008 (av. from near Rustenburg)	0.08
Sperrylite	10.59	0.015 (max. value Table 1)	31
		0.002 (av. S. of Pilanesberg)	0.55
Pt-Fe alloy	15	0.0115 (max. value Table 1)	28.20
		0.0016 (NE of Pilanesberg)	0.54
Sulfide droplets	4.5	0.05	82
		0.003 (UG-2 median)	0.30
Iron metal	7.8	0.03	82

The settling of platinum-group minerals from a crystallizing magma, on the assumption that they crystallized in the sizes in which they are encountered today, thus seems very unlikely.

If the density of a droplet of sulfide liquid is assumed to be 4.5, droplets with a diameter of about 0.5 mm (Table 3) will have a settling velocity of 82 m per year, the same as that of a chromite grain of 0.5 mm diameter. Many of the sulfide aggregates found in the Merensky Reef have diameters in excess of 0.5 mm. It is likely that these sulfide droplets could have accumulated in the Merensky Reef close to chromite grains by settling from the same magma. However, the sulfide aggregates found in the UG-2 Reef (Table 2) are considerably smaller, and have settling velocities much lower than those of the chromite with which they

TABLE 3. ESTIMATES OF CONCENTRATION OF Ni, Cu, Pt AND Pd IN ORIGINAL SULFIDE LIQUID

	Ni wt. %	Cu wt. %	Pt ppm	Pd ppm
Merensky Reef (1)	10.9	4.65	252	109
	10.9	4.65	258	102
Merensky Reef(2)	14.8(3)	7.81	325	133
Stillwater Sudbury(1)	4.5	4.0	160-550	600-2000
Noril'sk(1)			1.04	1.09
Picritic gabbro	9.0	10.8	18.0	47.8
Taxitic gabbro	7.6	10.9	15.2	42.1
Pachengo(1)	4.6	2.45	0.6	0.5
Marbridge(1)	6.5	0.38	0.36	0.92
Manbridge(1)	10.0	0.75	0.95	2.6
Shangani(1)	9.75	1.20	1.3	2.0
UG-2 Reef(4)	-	-	5835	3574

- (1) Naldrett & Cabri (1976)
- (2) Based on analyses by Steele et al. (1975) and listed in Table 4 of this paper.
- (3) This value, which is based on the total nickel content of the ore, is too high in that some nickel is accommodated in the ferromagnesian silicates.
- (4) Based on the values for the UG-2 Reef listed in Table 4.

occur, and therefore could not have settled as tiny separate droplets.

PEPA SETTLING

A chromite grain settling through a magma may encounter a tiny sulfide droplet on its way downward. If there were a mechanism that would cause the sulfide droplet to adhere to the chromite grain, it would be carried down and be deposited together with the chromite grain. If the chromite crystallized over a fairly lengthy time interval so that a fairly thick layer of chromite was eventually built up, the chromite grains would sweep the layer of magma quite efficiently of its sulfide droplets.

It is possible that sulfide droplets may have different wetting properties for chromite than for silicate particles, and if their affinity for chromite grains is greater, they will adhere to the chromite grains as soon as they touch them.

The author believes that there is textural evidence in the UG-2 Reef that sulfide droplets had a higher tendency to wet chromite and to adhere to it, than they had to do the same to silicate: (i) Between 80 and 98% of the sulfide grains in the UG-2 Reef occur at the grain boundaries of chromite (McLaren 1978). (ii) Where there is a narrowing space between chromite grains the point where this space is at its narrowest is often occupied by a sulfide grain or aggregate (Fig. 3). This is the position that would be occupied by a droplet with the higher wetting property towards chromite. (iii) Where two chromite grains touch each other in such a way that the thin acute triangular space between them is filled with silicate and sulfide material, the sulfide grain usually occurs at the apex (Fig. 4). Again, this is the position where the material with the higher wetting properties towards chromite would be expected to occur.

Alternatively, sulfide droplets could have been nucleated preferentially on the surface of chromite grains.

It is here proposed to call this settling mechanism *pepa settling*; *pepa* is southern Sotho for piggy-back carrying.

COLLECTION BY SULFIDES

Wagner (1973, p. 195) postulated that "... the small amounts of platinum contained in the magma were dissolved and concentrated in the

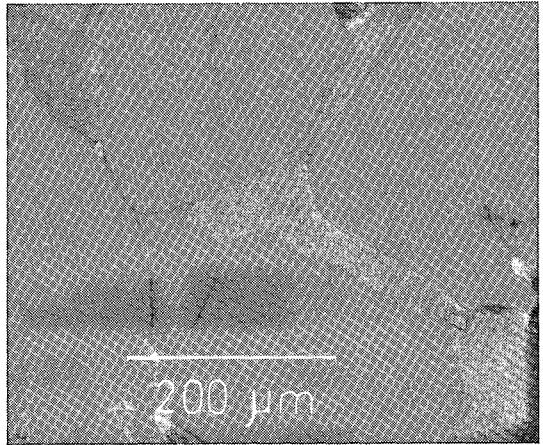


FIG. 3. A grain of pentlandite present at the narrowest point in a space between two chromite grains (right) and another at the apex of a triangular space (left).

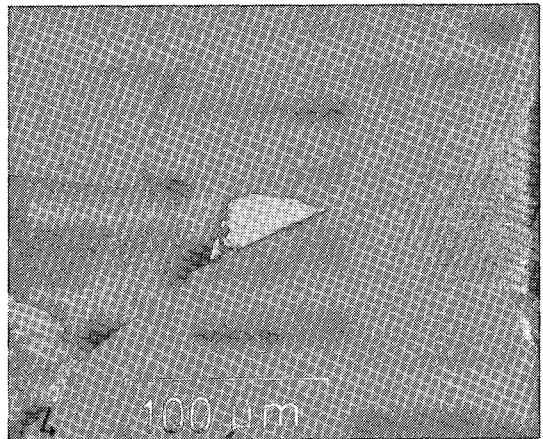


FIG. 4. A grain of pentlandite occupying the apex of an acute triangular space between chromite grains.

droplets of matte which the sulphur formed with the nickel, copper and iron that it extracted from the magma, the matte droplets being themselves concentrated in the magnesia-rich fraction that gave rise to the Merensky Horizon." Owing to the very pronounced preferred association of platinum-group minerals with sulfides, most workers agree that the collection of platinum-group metals by base-metal sulfides played an important role in the formation of the Merensky Reef and other deposits of platinum-group metals.

Naldrett & Cabri (1976) suggest a model

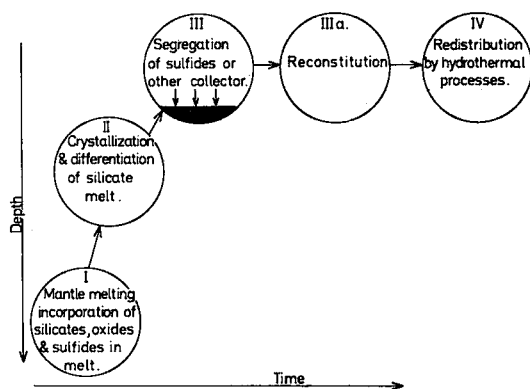


FIG. 5. Model (slightly modified from Naldrett & Cabri 1976) indicating four stages in the formation of platinum deposits.

for the formation of platinum-group-element concentrations. They recognize four important processes (Fig. 5): I. Mantle melting, during which platinum-group elements were incorporated in the melts. II. Crystallization and differentiation, during which the concentration of the platinum-group elements in the remaining melt and in the newly formed silicates and oxides are controlled by their partition coefficients. III. Tiny droplets of sulfides form, coalesce, collect platinum-group metals from their surroundings, and settle to form a sulfide-rich and platinum-rich zone. IV. During the cooling, crystallization, and phase transformation of the sulfides, the platinum-group metals exsolve, recrystallize and combine with other elements such as Te, Bi, Sb and As to form a series of platinum-group minerals.

Using data obtained from the literature, and assuming that all the platinum-group metals present in solid solution in sulfides and magnetite and as separate minerals were originally present in the sulfide liquid, Naldrett & Cabri calculated the contents of precious metals, nickel and copper in the sulfide liquid. From the results, they reason that "in sulfide melts giving rise to Ni-Cu ores, the 'normal' range of Pt is 0.36 to 1.6 ppm and Pd 0.5 to 2.6 ppm." Some of their results are included in Table 3, which also gives results calculated from other sources. These include results for the Merensky Reef from the analysis of a standard sample (Table 4) made up of material from four localities in the Bushveld complex (Steele *et al.* 1975), and results obtained from analyses of samples from the UG-2 Reef supplied by McLaren and described by him (1978).

TABLE 4. CHEMICAL COMPOSITION OF SAMPLES FROM THE MERENSKY REEF AND THE UG-2 REEF

Element	Merensky Reef % (1)	Element	Merensky Reef ppm (1)	UG-2 Reef ppm (2)
H ₂ O hygroscopic	0.15	V	60	
H ₂ O combined	0.77	Ba	50	
SiO ₂	51.8	Sr	50	
MgO	20.1	Co	36	
FeO	8.9	Pb	24	
Al ₂ O ₃	8.3	Zn	23	
CaO	5.4	Zr	10	
Fe ₂ O ₃	2.0	F	5	
Na ₂ O	0.8	S	4200.0	200.0
Cr ₂ O ₃	0.60	Y	5	
S	0.42	La	5	
CO ₂	0.23	Rb	4	
TiO ₂	0.21	Nb	1	
Mn ₃ O ₄	0.20	Pt	3.74	3.20
P ₂ O ₅	0.10	Pd	1.53	1.96
K ₂ O	0.11	Au	0.31	0.05
Cu (total)	0.09	Ag	0.42	0.05
Ni (total)	0.17	Rh	0.24	0.60
		Ru	0.43	1.06
		Ir	0.074	0.05
		Os	0.063	0.05

- (1) These are values obtained from the analysis of a composite standard sample made up of samples from four different localities in the Merensky Reef (Steele *et al.* 1975)
 (2) Average of analyses of samples from the UG-2 Reef in various localities around the Bushveld Complex, as obtained from C. McLaren (pers. commun.)

From the newer values given in this paper, one can see that the concentration of Pt and Pd in the Merensky Reef liquid would have contained 200 times the highest "normal" platinum level and 50 times the highest "normal" palladium level. For the UG-2 Reef these values are 2650 and 1375, respectively. A study of the available literature on the mineralogy of the Transvaal dunites (Mooihoek, Driekop and Onverwacht) indicate that they are very low in sulfides and, if there had been collection by sulfides, these would have contained abnormally high platinum and palladium values. Naldrett & Cabri point out that there is no known reason why the partition coefficients of precious metals between sulfide liquid and silicate magma should have been different in the Merensky Reef and other rich platinum deposits from those that operated in normal sulfide deposits such as Sudbury. It is clear then that some other mechanism operated uniquely in the cases of rich platinum deposits to effect either a much higher concentration of precious metal in the magma from which they formed, or to collect the precious metals from the magma much more efficiently than a sulfide liquid would under normal conditions.

In order to examine the sulfide-collection

hypothesis, Rajamani *et al.* (1977) followed a different approach to determine the degree of concentration of precious metals that can be brought about by sulfide collection. They determined partition coefficients:

$$D = \frac{\text{metal in sulfide liquid}}{\text{metal in basaltic melt}}$$

for Pd, Os, Ir, Pt and Au at 1255°C and found values of 118 for Pt and 156 for Pd. If there are 10 ppb of Pt and 20 ppb of Pd in the basaltic magma, the sulfide liquid could have concentrated these elements to levels of 1.18 ppm Pt and 3.16 ppm Pd. These values are fairly close to the "normal" values postulated for sulfide liquids by Naldrett & Cabri as quoted above. However, they are much lower than the values necessary to form deposits such as the Merensky Reef and the UG-2 Reef. Again, the indication is that sulfide collection from a normal magma could not have brought about the concentrations of precious metals listed in Table 3.

COLLECTION BY CHROMITE

There is a pronounced preferred association between chromite and platinum-group metals. This association is found not only in the Merensky Reef, where various authors reported high and significant correlation coefficients between platinum-group elements and chromite (Schwellnus *et al.* 1976, Cousins 1969, Newman 1973, Brynard *et al.* 1976) and the UG-2 Reef, where the platinum-group elements appear largely within a chromite reef, but also in many other deposits. Wagner (1973) reports that large chromite xenoliths in the Onverwacht dunite pipe "apparently acted like sponges so far as platinum was concerned." He reports values as high as 1872 g per tonne for ore in contact with the chromite, and states: "the richest ore was struck on it, and the abrupt falling off of values both above and below the level indicate, as previously stated, that the chromite acted like a great sponge, collecting the metal within itself, and in the dunite immediately adjacent to it."

Razin *et al.* (1965) as well as Naldrett & Cabri (1976) mention the possibility that the spinel structure could act as a collector for platinum-group elements at high temperatures.

Gijbels *et al.* (1974) found up to 0.68 ppm of ruthenium in chromite concentrates from the Bushveld complex, and concluded that

"high-temperature cumulus chromite concentrates these platinum metals very efficiently and then expels up to 25 per cent during subsequent cooling." The platinum-group metals determined by them included Ru, Os and Ir, but unfortunately not Pt and Pd.

In the UG-2 Reef, platinum-group minerals, particularly laurite, may occur included within chromite grains. Although only a minor proportion of the platinum-group minerals in the UG-2 Reef occurs in this manner (McLaren (1978) reports values of from 2.1 to 12.1%) it nevertheless demonstrates quite clearly that the chromite either grew around pre-existing laurite crystals, or that it exsolved the laurite during cooling.

Vermaak & Hendriks (1976) drew attention to the occurrence of sulfides within chromites, and doubted that determinations of platinum-group elements on mineral separates such as those reported by Gijbels *et al.* (1974) or Crockett *et al.* (1976) reflect the true concentration in chromite, because the sulfides may contain significant amounts of these. Cousins & Vermaak (1976) discussed the relation of platinum-group metals with chromite, and concluded that many of the data in the literature that indicate a significant degree of isomorphous substitution of these elements in chromite are questionable. There is no experimental evidence on the efficiency of chromite to act as a collector of platinum metals at high temperatures.

One major stumbling block in the theory that chromite could have collected the major amount of platinum-group metals found associated with it in deposits such as the Merensky Reef and the UG-2 Reef is the occurrence of many chromite layers that are not associated with such abnormal concentrations of platinum-group metals. The question arises as to why chromite could have acted as such a very efficient collector in some instances, while not doing so in the majority of cases.

The question of the collection of platinum-group metals by chromite is still very open, and experimental evidence on the partition of platinum-group elements into the spinel structure at high temperatures is necessary.

THE COLLECTION OF PLATINUM-GROUP ELEMENTS BY METALLIC ALLOYS OF IRON, NICKEL AND COPPER

The most pronounced geochemical property of platinum-group metals is their siderophile

character. As far as the author could determine, this property has not yet been proposed as a possible mechanism for the concentration of platinum-group metals in ore deposits. This can probably be ascribed to the fact that the occurrence of native iron in igneous rocks is rare, and the conditions under which this element can exist in the metallic form are seldom encountered. However, as worthwhile deposits of platinum-group metals are rare, they would be explained by a set of conditions that only rarely come into play. If this were not so, high-grade platinum deposits formed for instance by sulfide or chromite collection would have been common; if fractional crystallization of the magma could have concentrated these elements, such deposits would have been widespread.

Although the siderophile character of platinum-group metals has been utilized by chemists in the development of assay procedures (Plummer *et al.* 1959), and by metallurgists as a mechanism for separating platinum-group metals into a metallic phase from a sulfide matte, data on the partitioning into metal of platinum-group metals from silicates or sulfides, and the conditions that control this, are rare. The values listed in Table 5 show a maximum of 133.7 for the distribution ratio Pt in metal/Pt in silicate, and 336.5 for the distribution ratio

Pd in metal/Pd in silicate. Among the values listed, there are large variations. In some instances, Pt has the largest distribution ratio, and in others Pd. The partition coefficients under magmatic conditions may be in excess of the maximum values for distribution ratios listed in Table 5. The average Pt content of the metal phase is 9.4, about twice the value for Pd, 4.7.

Whatever the case, it is clear that if metallic iron can exist in a magma, it will be able to collect the platinum-group metals probably more efficiently than sulfide melt or chromite crystals, and if the iron in liquid or solid form can be concentrated by a process such as settling, the platinum-group elements will be concentrated with them.

OCURRENCE OF NATIVE BASE-METAL ALLOYS IN NATURE

Probably the best-known occurrences of native metal in igneous rocks are those that formed where the igneous rocks came into contact with some carbonaceous reducing agent, such as the occurrences at Bühl near Kassel, and at Ovifak on Disko Island in west Greenland (Ramdohr 1960, p. 337). At the latter locality,

TABLE 5. PLATINUM AND PALLADIUM IN PHASES OF METEORITES⁽¹⁾

Meteorite	Pd, ppm			Pt, ppm			$\frac{Pd_{met}}{Pd_{sil}}$	$\frac{Pd_{tr}}{Pd_{sil}}$	$\frac{Pt_{met}}{Pt_{sil}}$	$\frac{Pt_{tr}}{Pt_{sil}}$
	In metal	In troilite	In silicate	In metal	In troilite	In silicate				
Krymka	5.44	3.50	0.10	3.70	2.90	0.70	54.4	35.0	5.28	4.14
Serryukora	1.93	2.40	0.24	10.51	2.70	0.16	8.0	10.0	65.7	16.9
Sarator	3.85	0.80	0.02	13.37	2.80	0.10	192.5	40.0	133.7	28.0
Nikol'skoye	5.95	1.00	0.02	10.89	2.00	0.10	297.5	50.0	108.9	20.0
Yelenorka	6.37	0.80	0.02	11.65	1.60	0.10	336.5	45.0	116.5	16.0
Kyushu	3.0	0.3	0.05	17.65	5.00	0.26	60.0	6.0	67.7	19.2
Kunashak (light)	5.36		0.08	13.37		0.80	67		16.7	
Kunashak (dark)	4.92	4.60	0.044	6.85	5.30	0.10	111.8	104.5	68.5	53.0
Perromay (light)	5.77	1.20	0.05	12.47	2.40	0.10	115.4	24.0	124.7	24.0
Perromay (dark)	3.01	2.30	0.50	9.01	3.00	0.10	6.0	4.6	90.1	30.0
Dimmitte	5.2		1.0	4.8	6.0	0.4	5.2		12.0	15.0
Okhunsk	3.7	1.5	0.18	4.5-9.0	3.3	0.24	20.5	8.3	18.9-37.5	13.8
Pultusk	3.3	3.9	0.06	4.7	5.2	0.2	55.0	65.0	23.5	26.0
Zhortnevy	3.5	1.0	0.05	10.1	2.0	0.2	70.0	20.0	50.5	10.0
Doroninsk	9.0	3.6	0.2	5.2	4.8	0.16	45.0	18.0	32.5	30.0
Range							5.2-336		5.3-133	
Average	4.68			9.40			96.3		63.0	

(1) Data obtained from Vinogradov *et al.* 1972, 1973.

Goldschmidt & Peters (as quoted in Rankama & Sahama 1968, p. 690) reported 5 ppm of Pt and 1 ppm of Pd in the metal phase, demonstrating the effectiveness of iron as a collector.

A second mode of occurrence in nature is demonstrated by lunar rocks, in which iron is present in the troilite blebs, sometimes as small euhedral crystals, in a proportion of metal to sulfide of about 1:6, which is close to the Fe-FeS eutectic (Mason & Melson 1970, p. 43). A third mode of occurrence in nature is telluric iron, which may exist in the earth's core, and may contain the bulk of the earth's platinum-group metals. Its composition is probably similar to the metal phase in meteorites. According to the most modern theories on the origin of the earth, the metal phase of the primitive earth melted and coalesced when the temperature rose, and eventually intruded towards the centre of the earth (Mason 1966, p. 60). The question arises whether in the upper mantle all the available metal phase was removed, or whether in an inhomogeneous mantle some areas exist where metal phase is still present, which under suitable conditions would be incorporated in a newly formed magma.

In a recent discussion of the iron occurrences at Ovifak, Bird & Weathers (1977) proposed that this iron did not form from the reaction of lava with carbonaceous material as previously suggested, but that it represents telluric iron carried as xenoliths within erupting basalt. The main points of their arguments are that iron was found in dykes that had had no contact with carbonaceous sediments, that the cooling history as deduced from the textures did not agree with an *in situ* origin, and that cohenite, which may be indicative of high pressure, is present. Urey (1952, p. 78) discussed the iron from Disko Island, and reasons that its nickel content is much higher than expected for usual terrestrial iron sources; he mentioned that the oxygen isotopic composition in the Disko basalt indicates an origin from deep within the earth. He concludes: "These lines of evidence indicate that this iron phase at least partly comes from deep in the earth." He concluded also that the Kaersut iron is telluric.

A fourth mode of occurrence is that of native nickel-iron as the mineral awaruite at many localities in serpentinite bodies. The metal phase may be almost pure iron, nickel-iron, cobalt-iron or copper, as found in the Muskox intrusion by Chamberlain *et al.* (1965). Botto & Morrison (1976) provided a very thorough

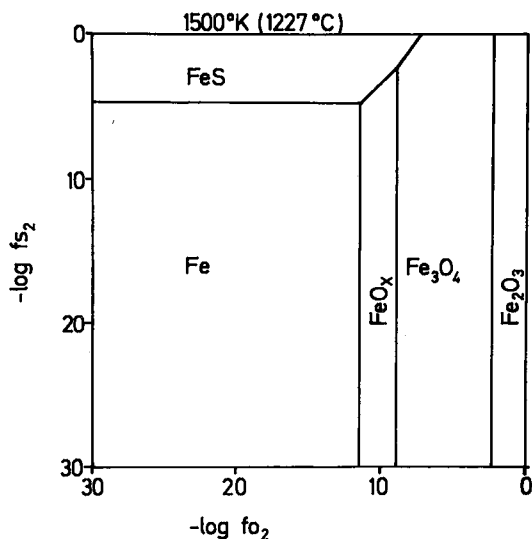


FIG. 6. Isothermal section at 1500°K through the $\log f(O_2)$ - $\log f(S_2)$ - T diagram for the Fe-O-S system (after Holland 1959) updated using thermochemical data from Stull & Prophet (1971).

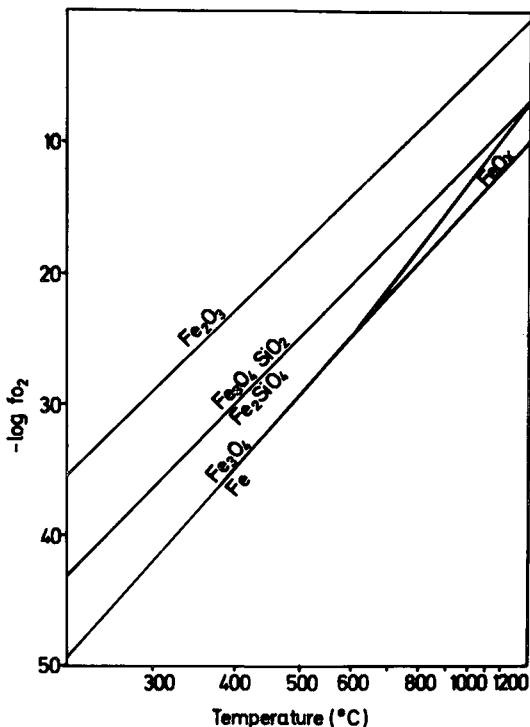


FIG. 7. The stability fields of iron and iron oxides in the Fe-O system (after Holland 1959) updated using data from Stull & Prophet (1971).

description of an occurrence of both awaruite and taenite in a rock they call josephinite from Josephine County, Oregon, and summarized the present state of knowledge about the environment in which these native metals can form. A fifth mode of occurrence is iron of meteoric origin, which in the present context may be of concern to those who believe that some large-scale layered complexes were formed as a result of meteorite impact.

CONDITIONS UNDER WHICH NATIVE METALLIC ALLOYS CAN EXIST IN MAGMAS

The dry conditions and very low oxygen pressure that exist on the moon and under which the troilite-iron assemblage mentioned above can form are very unlikely to occur at the earth's surface. Such conditions may occasionally have been possible at depth, particularly in the remote past of the earth's development.

At a temperature of 1500 K, an iron phase will be stable in the Fe-O-S system at an oxygen fugacity of $\log f(\text{O}_2)$ of about -12 and a sulfur fugacity of $\log f(\text{S}_2)$ of about -4, as shown in Figure 6. The stability field of the iron phase in this system will increase under the following conditions: with increasing temperature, as indicated in Figure 7 [updated from Holland (1959) using thermochemical data from Stull & Prophet (1971) and Robie & Waldbaum (1968)]. At 1200°C, iron is shown to exist at $f(\text{O}_2)$ below *ca.* 10^{-12} , $f(\text{S}_2)$ of *ca.* 10^{-6} , and a FeO above 0.1 (Shima & Naldrett 1975, Fig. 2). With increasing pressure, it is likely that the stability field of iron will increase because it has a higher density than the other phases in this system. With an increasing content of elements more electronegative than iron, *e.g.*, nickel, copper and the platinum-group elements, the field of stability of the iron-alloy field in an alloy-O-S system will increase. A portion of such a system is available in Figure 8, in which the composition of iron-platinum alloys in contact with iron oxide in equilibrium at various oxygen pressures is shown at a temperature of 1300°C. For the region where Nolan's data (1977) are available, the iron alloy in equilibrium with the tholeiitic melt is somewhat higher in platinum than the iron alloy in contact with the iron oxides.

It is interesting to note the following: (a) The composition of the iron alloy is dependent

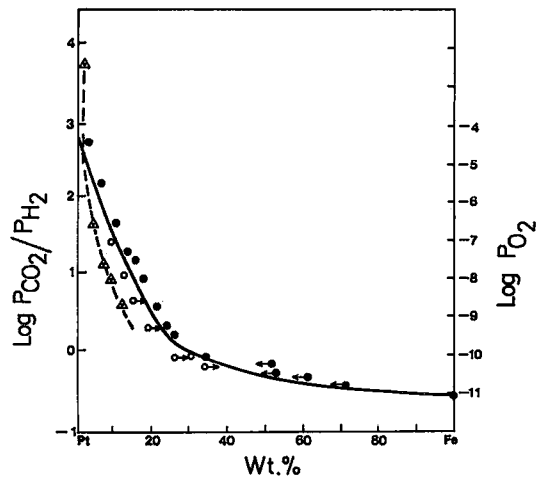


FIG. 8. Equilibrium iron content of Fe-Pt alloys in contact with iron oxide at 1300°C as a function of CO_2/H_2 ratios and oxygen pressures (in atm) after Taylor & Muan (1962). To this was added (broken line) the equilibrium iron contents of Fe-Pt alloy in tholeiitic melt as obtained from Nolan (1977).

on the oxygen fugacity of the system. The lower the oxygen fugacity, the richer will the alloy be in iron provided that the platinum content in the system remains constant. (b) If it is assumed that the alloy is present as a droplet or particle containing a constant weight of platinum, in a melt, then the size of this droplet or particle will also depend on the oxygen fugacity. The lower the oxygen fugacity, the larger the droplet or particle will be.

It is possible therefore that the very small grains of platinum-iron alloy rich in platinum could have existed as larger grains or droplets poorer in platinum in some previous stage of their history. This could have permitted settling velocities similar to those of the chromite or larger sulfide droplets.

It is likely that in the Pt-Fe-S system the composition of the Pt-Fe alloy in contact with pyrrhotite will be, in part, a function of the sulfur activity.

The unmixing of a complex of sulfide and platinum-group minerals from a magma may form larger composite droplets or grains, which may reach sizes sufficiently large for the required settling rates to be achieved more easily. However, the precipitation of such composites can take place only from a magma sufficiently enriched in platinum-group metals.

POSSIBLE MODELS FOR THE FORMATION
OF PLATINUM DEPOSITS BY COLLECTION
BY AN IRON-RICH ALLOY

As shown previously, the concentration of platinum-group metals in the original sulfide liquid in the Merensky Reef and UG-2 Reef are higher than the "normal" value by a factor of between 60 and 3650 times. The mechanism proposed here to effect such a concentration is the collection of these metals into iron alloys in the form of droplets and/or particles of sufficient size to move differentially with the magma and thus become concentrated. This process could have taken place at different stages: (1) During the melting of the mantle, particles of iron-nickel that are present in rare localities and that contain significant concentrations of platinum-group metals may lose some of their iron to the melt under conditions of increasing oxygen fugacity. This may continue until their sizes have diminished sufficiently for them to be carried along with the magma, thus forming an enriched-magma fraction that, after emplacement, sulfide exsolution, platinum collection within the sulfides, and co-precipitation with the sulfides, can give rise to platinum deposits richer than those formed from normal magma. (2) During or after emplacement of the magma, exceptional conditions may lead to a drop in the oxygen fugacity to such low levels that iron alloy may precipitate and form droplets or grains of such size that they can become concentrated. This would also concentrate the platinum-group elements collected within the iron alloy. After this concentration process, the oxygen fugacity may return to more normal values, and concomitantly the grains of iron alloy will decrease in size and lose their iron and platinum to the melt, the former eventually to form ferromagnesian minerals, and the latter to become concentrated with sulfides as in I above.

It is known that the Transvaal Supergroup in which the Bushveld complex was emplaced contain carbonaceous layers; these could have furnished reductants to lower the oxygen fugacity. However, other mechanisms could have been possible.

TEXTURES THAT MAY RESULT FROM
COLLECTION BY IRON ALLOYS

Once an enrichment has been effected in a magma according to one of the models suggested above, platinum-group minerals can be

expected to precipitate together with sulfides to form the textures so well known in the Merensky Reef, with the marked preferential association of platinum-group minerals with sulfide minerals. Some of the platinum will be collected by the sulfide liquid, but when it crystallizes, most of the platinum-group metals will exsolve and form further crystal growths on the platinum-group minerals. It is also possible that iron-platinum droplets or grains may survive in certain instances to become deposited together with the sulfide droplets. The question is whether there are any textures indicative of the previous existence of droplets or crystals of iron alloy rich in platinum of such sizes for settling in a magma to be a distinct possibility.

The two examples of eutectic-like intergrowths

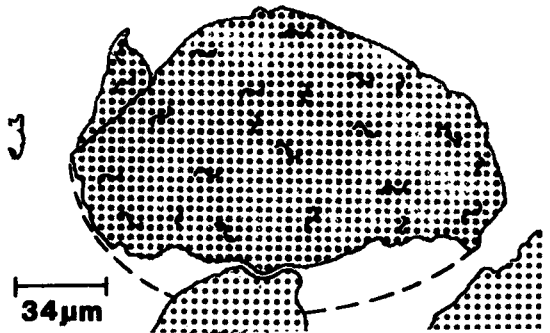


FIG. 9. Worm-like blebs of Pt-Fe alloy in pyrrhotite (after Vermaak & Hendriks 1976, Fig. 1E).

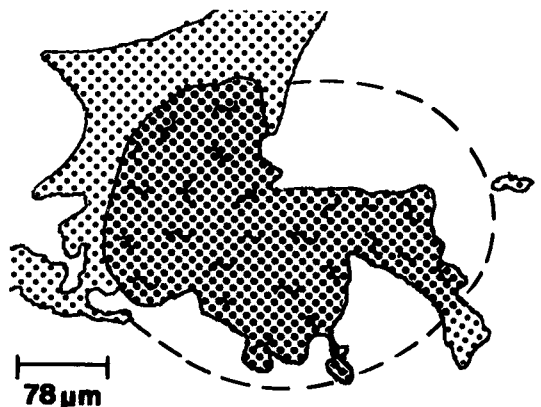


FIG. 10. Intergrowth of Pt-Fe alloy in pyrrhotite, attached to barren pyrrhotite (after Vermaak & Hendriks 1976, Fig. 1D).

of platinum and iron illustrated in Figures 9 and 10 can be visualised as portions of previous droplets (indicated by the broken line) that have been preserved only partially. Their sizes are such that they could have settled through a magma at sufficient speed for them to have been concentrated together with sulfides and chromite grains. The following arguments can be quoted against the idea that the types of grain they represent are eutectoids: (a) They are extremely variable in composition, with different proportions of sulfide to platinum-iron alloy. In a true eutectoid, this proportion should remain constant, provided that pressure, temperature and partial pressures remain constant. (b) Zonal intergrowths were encountered (Vermaak & Hendriks 1976) that are more iron-rich in the centre than at the outside. (c) Another example obtained from Brynard *et al.* (1976), shown here in Figure 11, has euhedral outlines, but consists of a eutectoid-like intergrowth of platinum-iron alloy with pyrrhotite, chalcocopyrite and a little pentlandite. Vermaak & Hendriks (1976) observed that "the shape of the Pt-Fe alloy-BMS aggregates may be as varied as the internal structure, but infrequently a rudely cubic or modified cubic outline is discernible". These aggregates are therefore pseudomorphous after some pre-existing mineral, and cannot be eutectoids.

The composite grain illustrated by Brynard *et al.* contained a significant amount of chalcocopyrite, and a small amount of pentlandite with the pyrrhotite, which together form the matrix in which the bodies of iron-platinum alloy occur.

These textures can be explained by considering that originally, these were droplets of iron-platinum alloy or crystals of a composition somewhere between Pt_3Fe and Fe (see Fig. 2). According to Figure 2 of Cabri & Feather (1975), a crystalline Pt-Fe alloy having compositions above 45% iron would have been tetragonal; compositions below 45% iron would have been cubic. It should be noted that these alloys could have contained nickel and copper in addition to iron and platinum-group metals. These grains now settled into a sulfide-rich area and, upon increase of the sulfur activity, acquired a composition somewhere within the triangular area bounded by Pt_3Fe , Fe and pyrrhotite (Fig. 12). For a constant Pt/Fe ratio, the composition should alter along a straight line joining the original composition on the Pt-Fe line with S. With sufficient sulfur added to the system, the line joining Pt_3Fe and pyrrho-

tite will eventually be reached. However, the proportions of Pt_3Fe to pyrrhotite will be different for different origins on the Pt_3Fe -Fe line. This explains the different ratios between iron-platinum alloy and pyrrhotite observed in different grains. If nickel had been present in the original alloy, some pentlandite could have formed, and if copper had been present, some chalcocopyrite. In this manner, a complex could have formed consisting of platinum-iron alloy in a matrix of pyrrhotite, chalcocopyrite and pentlandite. The platinum-iron alloy, being

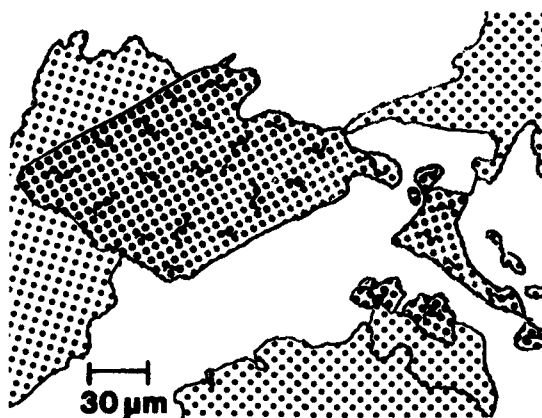


FIG. 11. Intergrowth of Pt-Fe alloy with pyrrhotite, attached to pentlandite (after Brynard *et al.* 1976, Fig. 8). It is postulated that the grains shown in Figures 9, 10 and 11 were alloys of iron and platinum, 9 and 10 as droplets, and 11 as a crystal. The aggregates now present formed as a result of reaction with S.

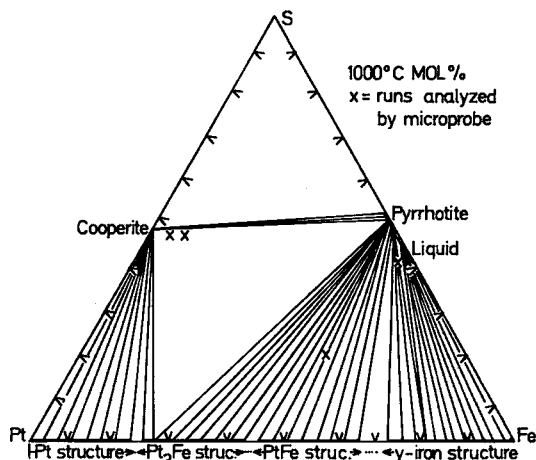


FIG. 12. The system Pt-Fe-S at 1000°C (after Skinner *et al.* 1976).

below its melting point, will retain the pseudomorphic form after tetragonal or isometric Pt-Fe as shown in Figure 11. If oxygen fugacity increased significantly during the reaction, iron may have been removed from the system, and the composition then would alter along a curve and not a straight line as postulated above. If the starting composition had been somewhere between Pt and Pt₃Fe (Fig. 12), the end result would have been an intergrowth of Pt-Fe alloy and cooperite such as that described by Vermaak & Hendriks (1976). The form and size of the original grain is determined roughly by the present distribution of the Pt-Fe intergrowth. Some of the newly formed pyrrhotite or other base metal sulfide overshoots the original grain boundary.

CONCLUSIONS

The grains of platinum-group minerals observed in the Merensky Reef and the UG-2 Reef are so small that they could not have settled sufficiently rapidly in their present form to become concentrated together with the grains of chromite, which are far larger. In the Merensky Reef, they could have settled in the form of composites of sulfide liquid and platinum-group minerals. However, in the UG-2 Reef, even the sulfide particles are far too small to settle at the same rate as the chromite grains. It is suggested that, possibly owing to a greater tendency for sulfide liquid droplets to wet chromite grains than to wet silicate, the sulfide grains adhered to settling chromite grains, and thus were carried down with them.

In both the Merensky and the UG-2 Reefs, the amount of sulfides present is far too small to explain the observed concentrations of platinum-group metals as resulting from their collection by liquid sulfides. Concentration as a result of collection by chromite is also considered to be insufficient for the concentrations observed. A mechanism that operates only under exceptional circumstances is considered necessary to explain the exceptional concentrations of platinum-group metals in the Merensky and UG-2 Reefs. It is suggested that the most pronounced chemical property of platinum-group minerals, their siderophile character, provides such a mechanism. Iron alloys then can act as collectors for platinum-group metals more efficiently than sulfide liquid.

Iron alloys can exist in magmas only under exceptional conditions, which can come into

play only rarely. The compositions of alloys of platinum and iron depend on oxygen and sulfur fugacities, and, if the alloys are present as droplets or grains, their sizes will change with changing oxygen and sulfur fugacities. In this way, particles or droplets may form that are of sufficient size to move differentially to the magma, and thus to become concentrated. When the oxygen pressure rises, most of the iron will disappear into ferromagnesian minerals. Iron could have been of telluric origin, or could have formed under reducing conditions.

Some of the mineral intergrowths observed in the Merensky Reef are considered to be modified grains or droplets of the original alloys that concentrated the platinum-group metals and afterwards reacted with sulfur to form complex mineral intergrowths, sometimes retaining a form pseudomorphous after the original crystals.

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