PLATINUM-GROUP ELEMENTS IN
MAFIC AND ULTRAMAFIC ROCKS:
A SURVEY

J. H. CROCKET

Department of Geology, McMaster University, Hamilton, Ontario L8S 4M1

ABSTRACT

A survey of platinum-group elements (PGE) in sulfur-poor ultrabasic and basic rocks shows that extrusive ultrabasic lavas, dunitic plutons of the Alpine and Alaska types and kimberlites have been most extensively analyzed. Data for basic rocks are restricted mainly to Pd and Ir in mid-ocean ridge and intraplate basalts, plateau-building and other continental basalts and diabases. Several studies on PGE in rocks and mineral separates from differentiated layered complexes are available. Higher PGE contents are usually found in the ultramafic class. Alaska-type complexes have higher PGE contents than Alpine-type dunites or ultrabasic extrusive rocks, and demonstrate a close association of PGE with chromite, magnetite and sulfides. Little is known of the relative importance of silicate minerals as PGE carriers, but some data indicate that olivine may concentrate iridium. Very low contents of palladium and iridium are found in sea-floor basalts (mid-ocean ridge) as compared to basalts from intraplate and off-ridge oceanic islands and continental environments. These differences may be related to a depleted source region for the mid-ocean-ridge basalts. In layered complex (Bushveld, Stillwater) the highest PGE concentrations are in sulfide-rich rocks. A second high concentration PGE association is with chromitites where the concentrators are mainly discrete PGE minerals and sulfides, the latter often occurring as inclusions in chromite. The association of some PGE with chromite extends to low PGE concentrations and is not readily explained by contamination. Initial magma PGE contents of layered complexes indicate that ore occurrences in these rocks are not related to PGE enrichment in the source rocks.

SOMMAIRE

Une étude bibliographique d'ensemble des éléments du groupe du platine (PGE) dans les roches ultrabasiques et basiques pauvres en soufre montre que les roches qui ont été le plus analysées sont surtout les laves ultrabasiques, dunites en plutons de type alpin et de type Alaska et kimberlites. Les données, pour les roches basiques, se limitent surtout au palladium et à l'iridium dans les basaltes des rides océaniques, des plateaux et autres basaltes et diabases continentaux. On dispose aussi de plusieurs travaux sur les PGE dans les roches et les concentrés minéraux de complexes stratiformes différenciés. Les plus fortes teneurs en PGE se trouvent d'ordinaire dans les roches ultramafiques. Les complexes du type Alaska contiennent plus de PGE que les dunites du type alpin et les roches extrusives ultrabasiques; de plus, ils révèlent que les PGE sont intimement associés à la chromite, la magnétite et les sulfures. On connaît peu l'importance relative des silicates comme porteurs de PGE; quelques données portent à croire que l'olivine concentre l'iridium. Les teneurs en Pd et Ir sont très basses dans les basaltes des rides océaniques, en comparaison des basaltes intra-plaques, ainsi que des basaltes des îles et des continents. Ces différences indiquent peut-être une région appauvrie comme source des basaltes des rides océaniques. Dans les complexes stratiformes (Bushveld, Stillwater), la plus haute concentration en PGE se trouve d'abord dans les roches riches en sulfures et ensuite dans les chromitites, où les agents concentrateurs sont surtout les minéraux des éléments du groupe du platine et les sulfures, ces derniers en inclusions dans la chromite. L'association de certains PGE à la chromite, qu'on observe même aux basses teneurs, s'expliquerait difficilement par contamination. La teneur en PGE du magma parental des complexes stratiformes montre que l'incidence du minerai dans ces complexes ne dépend pas d'un enrichissement en PGE à la source.

(Traduit par la Rédaction)

INTRODUCTION

Surveys of platinum-group elements (PGE) in terrestrial materials (Wright & Fleischer 1965, Yushko-Zakharova *et al.* 1967, Mertie 1969, Crocket 1969) emphasize the limited amount of data on sulfur-poor igneous rocks. Much of the early data on rocks and rock-forming minerals, consisting of determinations of Pt and Pd, are more than 50 years old. There is evidence that ppb-level determinations reported by the early techniques are in significant error.

The early work has established the major

features of PGE geochemistry, emphasizing the strongly siderophile character of the group, their common association with sulfides in ultramafic–mafic rocks and the very low concentrations associated with sulfur-poor silicate rocks and rock-forming minerals. However, much of the basic data required to model PGE concentration and ore formation could not be obtained by methods available to early workers. Thus mode of occurrence, concentration levels in potential

TABLE 1A. PLATINUM-GROUP ELEMENTS IN ULTRABASIC AND BASIC ROCKS AND ASSOCIATED MINERAL SEPARATES

Rock Type and Tectonic Setting	Method[1]	Refer-[2] ence	No. of[3] Samples	Ru	Rh	Pd	Os	Ir	Pt	$\frac{Pt}{Pt+Pd}$	$\frac{Pd}{Pd+Ir}$
						ULTRABASIC ROCKS					
Orogenic											
Synvolcanic Peridotitic komatiite, Pyke Hill, Munro Twp, Ont.	I	z	11	–	–	8	–	1.1	14	.64	.88
Komatiitic layered flow, Fred's flow, Munro Twp, Ont.	I	y	18	–	–	11	–	0.37	10	.48	.97
Tholeiitic layered flow, Theo's flow, Munro Twp, Ont.	I	y	11	–	–	11	–	0.39	15.5	.59	.97
Peridotitic komatiite, Mt. Clifford, Western Australia	I	r	19,21	–	–	8	–	2.4	–	–	.77
Dunite, Forrestannia, Western Australia[4]	I	s	25	–	–	4.7	–	7.7	–	–	.38
Average, ultramafic flows; unit weight assigned each occurrence omitting Forrestannia data				–	–	9.5	–	1.0	13	.58	.90
Alaska-type complexes USSR											
Dunite; Ray-Iz massif, Polar Urals	III	u	4	–	5	15	–	–	112	.88	–
Harzburgite; Ray-Iz massif, Polar Urals	III	u	4	–	2	4	–	–	26	.87	–
Dunite; Nizhniy Tagil, Kytlym, Khabarninskiy, Nuralinskiy, South Krak, Urals[5]	III	j	5	0.65	4	30	3.9	8.5	82	.73	.80
Alkalic ultramafic complex, mainly pyroxenites, Donbas-Azov region	?	v	11, 7	–	–	36	–	–	25	.41	–
Average, unit weight assigned each intrusion				0.65	3.8	28	3.9	8.5	72	.72	–
Alaska-type complexes, Alaska											
Peridotite-dunite and gabbro-hornblendite-pyroxenite complexes Duke Island, Union Bay, Blashke Islands, Eklutna, Salt Chuch, Mt. Fairweather, Klukwan	II	b	15,79, 70	–	29	107	–	–	54	.63	–
	omitting Salt Chuck		15,64, 73	–	29	32	–	–	54	.63	–
Alpine-Type											
Harzburgitic dunite; Mt. Albert pluton, Que. (ophiolite?)	I	d	13	–	–	9.5	6.7	2.2	–	–	.81
Peridotite, Burro Mtn. Calif.	II	x	18	–	<5	<4	–	–	<10	–	–
Dunite, peridotite; Red Mtn, Cypress Island, Twin Sisters, US	II	aa	4	–	<5	<4	–	–	<10	–	–
Non-Orogenic											
Kimberlites; southern Africa & India	I	ff	11	–	–	8.1	–	3.0	–	–	.13
Ultrabasic nodules, mainly garnet lherzolite from above kimberlite suite	I	ff	11	–	–	3.6	–	18	–	–	.17
Kimberlites; Yakutia, USSR	III	q	10	6.5	7.1	53	5	7.6	187	.78	.87
Ultrabasic nodules (garnet peridotite); Obnazhennaya pipe, Yakutia, USSR	III	q	2	–	12	80	–	18	35	.30	.82
Peridotite; Mid-Atlantic Ridge, Leg 37, Hole 334, DSDP	I	f	2	–	–	41	–	0.64	35	.46	.98
Others											
Pyroxenite in granulites, Kola peninsula, USSR	II	m	4	–	4	10	–	3	82	.89	.77
Eclogites, in close spatial association with above granulites, Kola peninsula	II	m	5	–	16	112	–	11	390	.78	.91

TABLE 1B. PLATINUM-GROUP ELEMENTS IN CHROMITES AND CHROMITE-BEARING ULTRABASIC ROCKS, MAINLY ALASKAN-TYPE

Sample Description		Method	Refer-ence	No. of Samples	Concentration, ppb							
					Ru	Rh	Pd	Os	Ir	Pt	Pt+Pd	Pd+Ir
Mt. Albert pluton, Quebec												
-accessory chrome spinel	Alpine	I	d	4	--	-	24	3.4	4.3	-	-	.85
-massive chromite shlieren		I	d	2	-	-	0.5	96	24	-	-	.02
Ray-Iz massif, Polar Urals; chromite ore		III	u	23	--	22	79	--	--	475	.86	-
Kempirsay massif, Urals; chromite ore		III	u	4	--	42	700	--	--	307	.34	-
Dunite massifs of the Urals including Nizhniy Tagil, Kytlym, Khabarninskiy, Nuralinskiy and South Krak; dunite samples containing chrome spinel schlieren or massive chromite ore		III	j	5	178	46	1120	112	95	8160	.88	.92
Nizhniy Tagil, Urals; chromite		IV	gg	8	240	-	--	520	-	-	--	--
Konder massif, Aldan; chromite		IV	gg	5	5320	-	-	1680	-	-	-	--
Inaglinsk massif, Aldan Shield												
-dunite with accessory and segregation chrome spinel		IV	gg	15	5.4	-	--	9.2	-	--	--	--
-dunite with accessory and segregation chrome spinel from the core of the massif		II	hh	11	4.7	170	73	7.7	226	446	.86	.24
-chromite		IV	gg	4	118	-	--	675	-	-	-	--

1. Key to analytical methods, Tables 1A and 1B: I neutron activation, II fire assay or chemical dissolution-emission spectroscopy or both, III fusion or acid dissolution-spectrophotometric or kinetic (or all three), IV fusion or acid dissolution-colorimetric or both, ? method unspecified. 2. Key to references: a) Baedecker *et al.* 1971, b) Clark & Greenwood 1972, c) Crocket, unpubl. data, d) Crocket & Chyi 1972, e) Crocket & Skippen 1966, f) Crocket & Teruta 1977, g) Crocket *et al.* 1967, h) Crocket *et al.* 1973, i) Das Sarma *et al.* 1966, j) Fominykh & Khvostova 1970, k) Gijbels *et al.* 1976, l) Gijbels *et al.* 1974, m) Golovnya & Khvostova 1974, n) Gottfried & Greenland 1972, o) Greenland 1971, p) Greenland *et al.* 1974, q) Kaminskiy *et al.* 1975, r) Keays, unpubl. data, s) Keays & Davison 1976, t) Keays & Scott 1976, u) Khvostova *et al.* 1976, v) Latysh & Buturlinov 1970, w) Laul *et al.* 1972, x) Loney *et al.* 1971, y) MacRae, unpubl. data, z) MacRae & Crocket 1977, aa) Page 1969, bb) Page *et al.* 1972, cc) Page *et al.* 1976, dd) Page *et al.* 1977, ee) Page *et al.* 1978, ff) Paul *et al.* 1977, gg) Razin & Khomenko 1969, hh) Razin *et al.* 1965, ii) Shaw *et al.* 1976, jj) Tolmachev *et al.* 1971, kk) Vincent & Smales 1956. 3. If there is more than one entry in this column, the first applies to the first element for which data are given, the second to the second element, and so on. 4. Forrestania data are scaled off Figures 4 to 8 of Keays & Davison (1976), and include ultramafic host rocks with <0.6 wt. % Ni. They are not included in the average for synvolcanic, orogenic ultramafic rocks because they probably represent a nickel sulfide ore environment in which sulfur saturation, with attendant scavenging of PGE, has occurred. 5. Averages were calculated from data in Tables 1 and 2 of Fominykh & Khvostova (1970) by assigning unit weight to each intrusion. Averages for individual intrusions are based on five samples from Nuralinskiy, three from Khabarninskiy and one each from the remaining three. 6. Excluding one sample in which chromite contamination of orthopyroxene is suspected. 7. Eleven composites representing 315 samples were analyzed.

mantle source-rocks and fractionation trends during igneous differentiation were poorly elucidated by early methods and remain obscure.

A recent issue of the journal *Economic Geology* (vol. 71, no. 7, 1976) was devoted to PGE. It is evident that much progress has been made in PGE mineralogy and in understanding the genesis of some ore deposits of the PGE and that more reliable data on PGE rock geochemistry are now available. With improved understanding of the genesis of ultramafic rocks more specific models for PGE concentration leading to ore formation have been developed. Nevertheless, some excellent attempts such as that of Naldrett & Cabri (1976) are obviously constrained by limited knowledge of PGE concentrations and modes of occurrence in potential source rocks.

Analytical developments have played an important role in the generation of a rock-geochemistry data base for PGE. Most data published by North American, European and Australian laboratories have been obtained by radiochemical neutron activation. Most studies from the USSR use fire assay, fusion or acid dissolution followed by spectrophotometric analysis. There is good evidence in the data compilation presented in Table 1 that these two classes of methods do not yield entirely consistent and coherent results. This is suggested by comparison of data on comparable rock types, *e.g.*, kimberlites. The advantages and disadvantages of the various methods should thus be appreciated when assessing data.

Briefly, the main advantages of the neutron-activation methods are high sensitivity, freedom from laboratory contamination and permissible use of nonquantitative procedure. The method is effective for the direct determination of Ru, Pd, Os, Ir and Pt in ultrabasic rocks in the 0.1 to 1 ppb range (0.01 for Ir), and for Pd, Os and Ir in basic rocks. No other methods have this capability. A potential interference on Ru determination arises from Ru produced by

uranium fission. This problem has been considered in detail by Gijbels & Zels (1977) who regard a Ru/U ratio of 0.1 as the minimum acceptable for direct activation analysis of Ru. Other limitations are that effective sample size for direct determination is limited to about 1 gram. In general, this leads to low values compared to a procedure where analysis of large samples is possible, if the sample material is characterized by highly dispersed concentrations of metals (sulfide or PGE minerals). Other disadvantages are that direct determination of Rh is precluded by short half-life, and fission-product interference effectively precludes determination of Ru in basic and more silicic rocks. The main advantages of the preconcentration spectrophotometric methods are: (1) they are comprehensive with respect to the PGE, yielding data for all six elements, and (2) they can be applied to samples of up to 30 grams. Their main disadvantages are: (1) use of large amounts of reagents requires careful blank control, (2) exacting quantitative chemical procedure is required, and (3) loss of Os and Ru can occur. The very serious problem of excluding contamination at the ppb level was recently discussed by Gijbels & Zels (1977) with respect to determination of ppb levels of Ru.

MINERAL AFFINITIES OF PGE

Before discussing the PGE abundance data (Table 1) it is useful to briefly note the main geochemical affinities of the group, particularly as related to the rock-forming minerals of basic and ultrabasic rocks. The prominent siderophilic and chalcophilic tendencies of the PGE are widely recognized. Siderophilic characteristics are exemplified by high concentrations (ppm levels) in iron meteorites, the high proportion of PGE carried by iron–nickel metal in chondrites, the strong partition of PGE in the metal phase in sulfide-bearing iron meteorites, the occurrences of many metallic alloys among the platinum-group minerals (PGM) and the high proportion of metallic bonding characteristic of many PGM. Chalcophile characteristics are manifest in the common occurrence of high, ppm-level PGE concentrations in association with Ni–Cu sulfide in mafic and ultramafic rocks and the occurrence of many sulfide minerals of the PGE. It is in silicate systems of relatively low $f(S_2)$ and high $f(O_2)$, in which major constituents are stable as silicate or oxide minerals (or both), that the geochemical affinities of the PGE are poorly understood. Such systems are important, however, in modeling PGE ore formation.

Chromite

Of the principal silicate and oxide minerals in mafic and ultramafic rocks, chrome spinel clearly is commonly associated with high PGE contents. Whether chromite concentrates PGE through a solid solution mechanism is uncertain, but in some instances, high PGE levels undoubtedly result from inclusions of PGM, PGE-rich sulfides and arsenides in chromite.

Higher PGE contents are observed in chromite-rich than chromite-poor rocks, e.g., dunites of the Alaska and Alpine types and rocks from layered complexes. For example, the study of Fominykh & Khvostova (1970) on Urals dunites shows that chromite-rich rocks are at least ten times richer in all PGE than rocks of normal chromite content, i.e., rocks containing accessory chromite only (see Fig. 3). In chromite separates from the Ray-Iz and Inaglinsk massifs, Khvostova et al. (1976), Razin et al. (1965) and Razin & Khomenko (1969) find PGE enrichments by factors of at least six relative to host dunites. In the Mt. Albert alpine intrusion Crocket & Chyi (1972) found that Ir and Os are enriched and Pd depleted in late massive chromite schlieren relative to accessory chrome spinel in dunite (Table 1B). The chromitite layers of the Stillwater complex are significantly enriched in Pt, Pd and Rh relative to the Peridotite and Bronzitite members of the Ultramafic zone, orthopyroxene cumulates of the Basal zone or gabbros of the Banded and Upper zones (Table 1A, this work; Page et al. 1976, 1972: Page 1969).

Studies on the mode of occurrence of PGE in chromite were carried out by Grimaldi & Schnepfe (1969), who compared the fraction of total Pt, Pd and Rh dissolved in Stillwater "A"-zone chromite with the fraction of total chromite decomposed by fusion with a deficiency of sodium peroxide. From this study, they inferred that nearly all Rh and about 70% of the Pt are present within the chromite, whereas practically none of the Pd is there. The physical state of the PGE in the chromite, whether in solid solution or as inclusions, was not directly indicated by the experiments. However, Grimaldi & Schnepfe (1969) noted the large scatter of the Pt data and suggested that some Pt within the chromite occurs as inclusions. They regard the Rh data as compatible with its occurrence as a solid solution or as uniformly distributed minute inclusions.

Page (1971) studied the G and H chromitite

zones of the Stillwater and found that sulfide and PGM occur as inclusions in cumulus olivine and chromite (and in other modes) in these rocks. This study strongly suggests that a high proportion of PGE associated with Stillwater chromite, particularly Pt and Pd, occur as inclusions. The occurrence of sulfide inclusion in the UG-2 chromitite seam of the Merensky footwall (Hiemstra 1979) and the observation of Hendriks & Peyerl (1971) that minute particles of PGM occur in chromite of the Critical Zone suggest that some fraction of the PGE complement of Bushveld chromite is represented by inclusions.

The role of chromite as a PGE concentrator was also found to be doubtful by Keays & Davison (1976) in a study of PGE in host rocks and nickel sulfide deposits of Western Australia. In ultrabasic host rocks of low nickel sulfide content from the Forrestania deposit no significant correlation of Ir or Pd with Cr was found. Keays & Davison (1976) interpreted this observation to imply that in the Forrestania environment, a nickel sulfide deposit of dunite association, chromite is not a major host for either Ir or Pd.

Whereas most of the studies discussed above suggest that high PGE levels in chromite are due to inclusions, a study by Gijbels et al. (1974) on the Os, Ru and Ir contents of mineral separates from the eastern Bushveld suggests that other processes cannot be dismissed. Gijbels et al. (1974) separated orthopyroxene, plagioclase and chromite from rocks taken mainly from the Critical Zone. On a basis on some 1000 polished-section observations they concluded that if mineral inclusions are present, they are submicroscopic (i.e., <0.25 μm). The highest contents of these three PGE were found in the chromites. For minerals at nearly the same stratigraphic level the concentrations of any one PGE followed the relationship orthopyroxene : plagioclase : chromite = 1:16:700. The relative proportions of Os, Ru and Ir in each of the minerals was Os:Ru:Ir = 1:7:1. Further, the PGE concentrations in a given mineral tend to decrease upward in the section. If these trends are to be explained on a basis of mineral inclusions, then all the inclusions, be they PGM, sulfides or arsenides, must have consistent Os:Ru:Ir proportions, and the inclusions must be incorporated into orthopyroxene, plagioclase and chromite in constant proportions. Clearly these considerations represent serious constraints for an inclusion origin for PGE in this particular instance.

The association of high PGE levels with chromite seems well established in certain types of mafic–ultramafic rocks such as Alaska-type intrusions and some layered complexes. This association may arise because chromite, immiscible sulfide and some PGM crystallize as early, high-temperature phases from mafic–ultramafic magma, or because processes that lead to saturation of such magma with respect to chromite also may cause saturation with respect to sulfur (e.g., Irvine 1975). The fate of PGE in a basic–ultrabasic magma saturated with respect to chromite only is less certain, but the Bushveld data of Gijbels et al. (1974) suggest that in layered complexes, where trace constituents may be affected both by initial separation of cumulus phases and their subsequent growth from intercumulus liquid, solid solution of some PGE (specifically Os, Ru and Ir) in chromite must be considered a realistic possibility.

Silicates

There are very few data bearing on the relative importance of the ferromagnesian silicates and plagioclase as concentrators of PGE. Abundance levels in basic and ultrabasic rocks, sulfides and chromites indicate that silicate minerals are very poor concentrators of these metals relative to sulfides and chromite. Nevertheless, most rocks contain only traces of the latter constituents whereas the silicates are major components.

Available data on mineral separates (Gijbels et al. 1974, 1976) pertain mainly to layered intrusions, where the role of postcumulus growth from interprecipitate liquid may be a complicating factor. The data on Rhum plagioclase, clinopyroxene and olivine (Gijbels et al. 1976) show that the highest Ir concentrations are in the olivine. However, a strong positive correlation of Ir with Cr in olivine complicates the interpretation, leading Gijbels et al. (1976) to suggest that chromite inclusions in olivine may be responsible for the high Ir contents. They contend that pure olivine probably contains 0.07 ppb Ir, similar to the averages of 0.06 and 0.075 found for plagioclase and clinopyroxene. Ross & Keays (1979) found 5.7 ppb Ir and 0.21 ppb Pd in olivine separated from the basal unit of the Victor shoot, Kambalda dome, Western Australia. These data are particularly significant because the low Pd content implies that the result does not reflect sulfide inclusions, which are well documented in Stillwater olivines (Page 1971).

Although the data base is clearly deficient, it seems possible that in sulfur-poor rocks olivine

may constitute a sink for Ir, and possibily for Os and Ru. The significance of possible olivine control on Ir abundance levels in low-sulfur host rocks of the Forrestania nickel sulfide deposit was discussed by Keays & Davison (1976).

COMPARISON OF AVERAGE PGE CONTENTS OF BASIC AND ULTRABASIC ROCKS

An overview of PGE levels in basic and ultra-basic rocks is presented in Figure 1. The comparison, essentially limited to Pd and Ir, shows that in general, sulfur-poor ultrabasic rocks are higher in these metals than are basic rocks. The differentiation of Ir between ultrabasic and basic rocks is more pronounced than that of Pd in that the Pd average for continental plateau basalts overlaps into the ultrabasic field. It is suggested that Os and Ru would show behavior similar to Ir and that Pt, like Pd, is probably less differentiated between mafic and ultramafic rocks. Adopting a general hypothesis that mafic magmas are partial melts of ultra-mafic rocks, the lower Ir contents of mafic rocks suggest preferential retention of the element in the more refractory phases of an ultra-mafic parent. Olivine may constitute such a sink for Ir.

PGE content of ultrabasic rocks

Abundance data for ultrabasic rocks are presented in Table 1A; histograms of average values for synvolcanic ultrabasic extrusive rocks, Alpine- and Alaska-type intrusive complexes and kimberlites plus associated ultrabasic nodules are presented in Figure 2. The following generalizations are drawn from these data: (1) For those classes of ultrabasic rocks where the requisite data are available, Pt and Pd are the dominant noble metals. Thus, the ultramafic flows, Urals dunitic plutons (Alaska-type) and USSR kimberlites are all characterized by more than 85% Pt and Pd with respect to total noble metals. In meteorites such as carbonaceous chondrites, commonly regarded as representatives of unfractionated material, $Pt + Pd/\Sigma PGE$ is approximately 39% (data from Table 1 with estimate for Rh). Apparently Pt and Pd are preferentially concentrated in melts originating from mantle sources. (2) The Alaska-type ultrabasic complexes are characterized by significantly higher PGE abundances than Alpine-type plutons or ultrabasic flows. Figure 2 includes data for only one Alpine-type pluton (Mt. Albert, Qué.). Data reported by Page (1969) and Loney et al. (1971) on other alpine dunites are at the sensitivity of the analytical methods employed (Pt 10 ppb, Pd 5 ppb, Rh 5 ppb) but confirm that
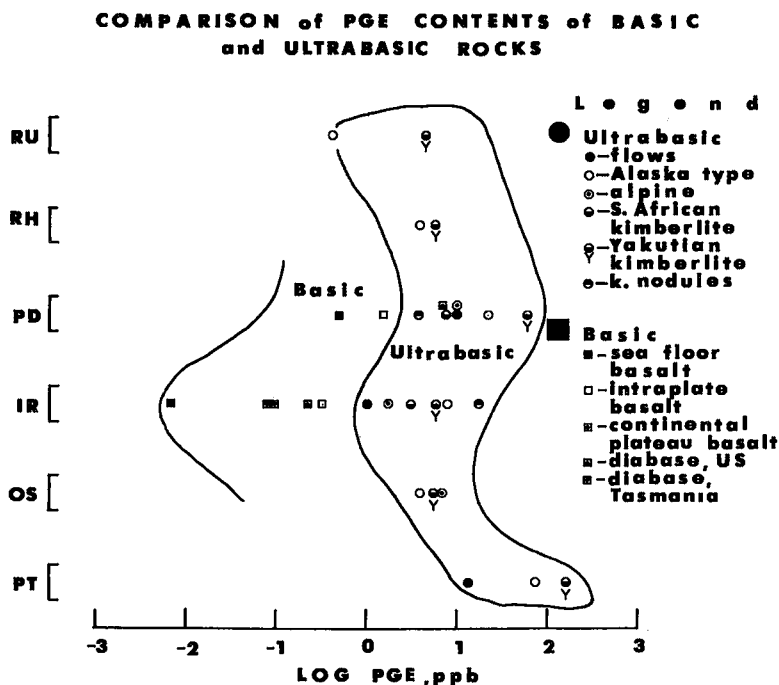

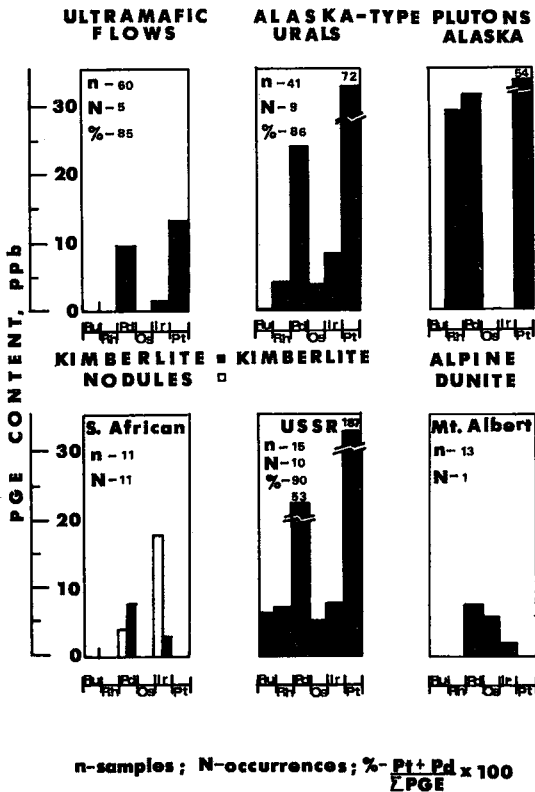FIG. 1. Comparison of PGE contents of basic and ultrabasic rocks.

FIG. 2. Average PGE contents of various classes of ultrabasic rocks.

low PGE levels characterize such rocks.

The Alaska-type complexes are zoned, differentiated bodies distinguished as a group by highly calcic clinopyroxene, lack of orthopyroxene and abundant hornblende, iron-rich chromite and magnetite. They may be of economic interest with regards to the PGE. In the Urals an association of high PGE levels with chromite is demonstrated by the data of Fominykh & Khvostova (1970). On the basis of petrographic studies and trace- and major-element correlations, Clark & Greenwood (1972) concluded that in occurrences in the Alaskan panhandle, the PGE are closely associated with the amounts of sulfide and oxide phases in the various rock types.

The ultrabasic lavas of the komatiite suite may host Ni–Cu sulfide mineralization and attendant high-PGE levels. The relatively low PGE abundances in the analyzed flows of low sulfur content indirectly attest to the key role of sulfur as a collector in the ore-forming process. Extrusive komatiitic peridotites prob-

ably provide as good estimates of average mantle PGE composition as any other class of rocks because they require a high degree of partial melting of mantle source-rock, 70% according to Green (1975). Some bias, however, is probably generated by preferential retention of PGE in refractory source-rock phases such as spinel.

In contrast to the ultramafic lavas and Alpine- and Alaska-type rocks, the kimberlites are products of magmatism in a nonorogenic environment. They are widely regarded as products of a low degree of partial melting of a garnet peridotite source-rock possibly represented by some of the ultramafic nodules carried in the kimberlite. Some of the garnet lherzolite nodules from the southern African kimberlite suite analyzed by Paul et al. (1977) suggest derivation from depths of 170 to 200 km. However, there is evidence that peridotite nodules from kimberlites may have suffered metasomatic alteration (Boettcher et al. 1977) and should not be considered as pristine, primitive mantle. The PGE data of Paul et al. (1977) indicate that the Pd and Ir contents of the kimberlites are similar to ultrabasic lavas and the Mt. Albert alpine dunite. The ultramafic nodule suite is characterized by very high Ir and low Pd contents in comparison with the kimberlites. If partial melting of such nodules produces kimberlite melts, then Pd seems to fractionate preferentially into the melt whereas Ir remains largely in the nodules. Paul et al. (1977) inferred from this observation that Pd and Ir are probably hosted by different phases in the nodules.

The study of Kaminskiy et al. (1975) presents data for all PGE in Yakutian kimberlites. In comparison with data of Paul et al. (1977), higher values are obtained for both Pd and Ir, although only the Pd data present a significant discrepancy. The Pd/Pd+Ir ratios in both sets of data are comparable with those of other ultrabasic rocks; in both investigations, garnet peridotite nodules are significantly higher in Ir than the kimberlites. Kaminskiy et al. (1975) analyzed only two nodules; comparison with the South African nodule suite is of little significance.

PGE in chromitites of Alaska-type ultrabasic rocks, USSR

The PGE content of chromite and chromite-bearing ultrabasic rocks of Alaskan-type is summarized in Table 1B. The data represent mainly the dunitic intrusions of the Urals and Polar Urals as well as intrusions from the Aldan
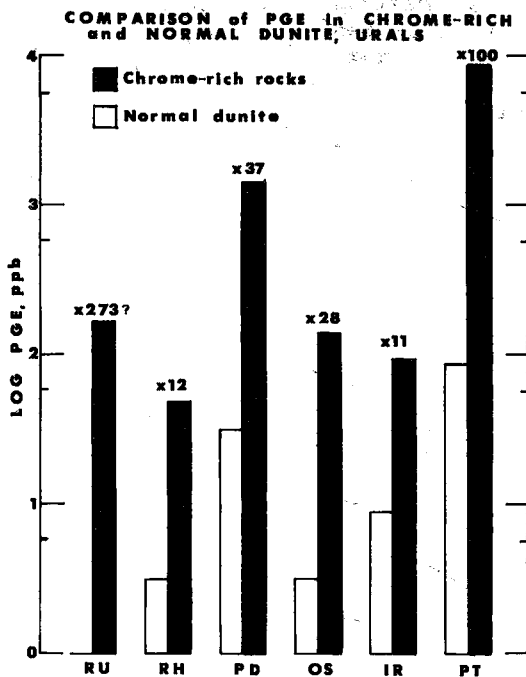
FIG. 3. Comparison of PGE in chrome-rich and normal dunite, Urals (after data of Fominykh & Khvostova 1970).

shield, south Yakutia and the Siberian platform north of the Aldan shield. Many Alaska-type plutons are characterized by marked enrichment of all PGE in chromite-rich schlieren and pods. The most comprehensive data are those of Fominykh & Khvostova (1970) for five dunite intrusions from the Urals. Overall averages for chromite-poor or chromite-free rocks are compared with averages for chrome-spinel schlieren and massive chromitite in Figure 3, and the following concentration factors (PGE in chromite-rich rock/PGE in chromite-free rock) obtained: Ru 275, Pt 100, Pd 40, Os 30, Rh 10 and Ir 10. The very high enrichment in Ru is possibly spurious, resulting from an anomalously low Ru value, 0.65 ppb, as the average for chromite-free rocks.

Fominykh & Khvostova (1970) do not discuss the question of the nature of the PGE–chromite association. However, Razin & Khomenko (1969), who studied PGE in the Nizhniy Tagil, Konder and Inaglinsk occurrences, contend that chrome spinel in dunites is a concentrator of traces of PGE. These probably replace chromium in the spinel lattice. On the other hand, the study of Clark & Greenwood

(1972) of occurrences in the Alaska panhandle presents evidence that sulfides may play an important role in the PGE–chromite association, at least in the Eklutna and Salt Chuck plutons.

It may be noted that in the alpine-type Mt. Albert harzburgitic dunite, PGE vary by factors of 2 to 3 in disseminated, accessory chromite relative to the whole rock. However, in massive chromitite schlieren of probable late deuteric origin both Os and Ir are enriched relative to the whole rock by factors of ten. In contrast, Pd is lower in the massive chromitite than in the whole rock.

PGE content of basic rocks

PGE data on basic rocks, presented in Table 1A, are mainly restricted to Pd and Ir. In general these rocks, represented mainly by basalt, are lower in Pd and Ir than the ultrabasic class. If the neutron-activation data are considered, basalts generally contain less than 10 ppb Pd and less than 0.5 ppb Ir. A comparison of ranges of values of PGE in basic rocks is shown in Figure 4.

Basalts representing oceanic crust are grouped according to tectonic setting and include those from active spreading ridges (sea-floor) and from intraplate or off-ridge oceanic islands. Most of the basalts from both groups are tholeiites. The sea-floor basalts include material obtained by drilling (Leg 37, DSDP at 36°N, Mid-Atlantic Ridge) and dredging, mainly from the Mid-Atlantic Ridge. The ocean-island basalt suite includes samples from Hawaii and Tahiti on which Ir was determined, and samples from Hawaii, Tahiti, Samoa, Galapagos, Reunion, Azores, St. Helena and Ascension on which Pd was determined. The sea-floor basalts are characterized by very low Pd and Ir contents and contrast with the higher PGE contents obtained for the intraplate basalts. In fact, the average Pd and Ir contents of sea-floor basalts are upper limits because for many of the samples, concentrations were below the analytical sensitivity (0.01 and 0.1 ppb for Ir and Pd, respectively). Gottfried & Greenland (1972) have commented on the differing Ir abundance levels in the ocean-ridge tholeiites and Hawaiian basalts. Noting that the ocean-ridge tholeiites generally have low $^{87}Sr/^{86}Sr$ ratios (0.702–0.704) and low LIL trace-element contents, whereas Hawaiian basalts are characterized by somewhat higher $^{87}Sr/^{86}Sr$ ratios indicative of a more primitive source area, they suggested that an inherently depleted source area is probably the cause of lower Ir contents of the mid-ocean-ridge basalts.
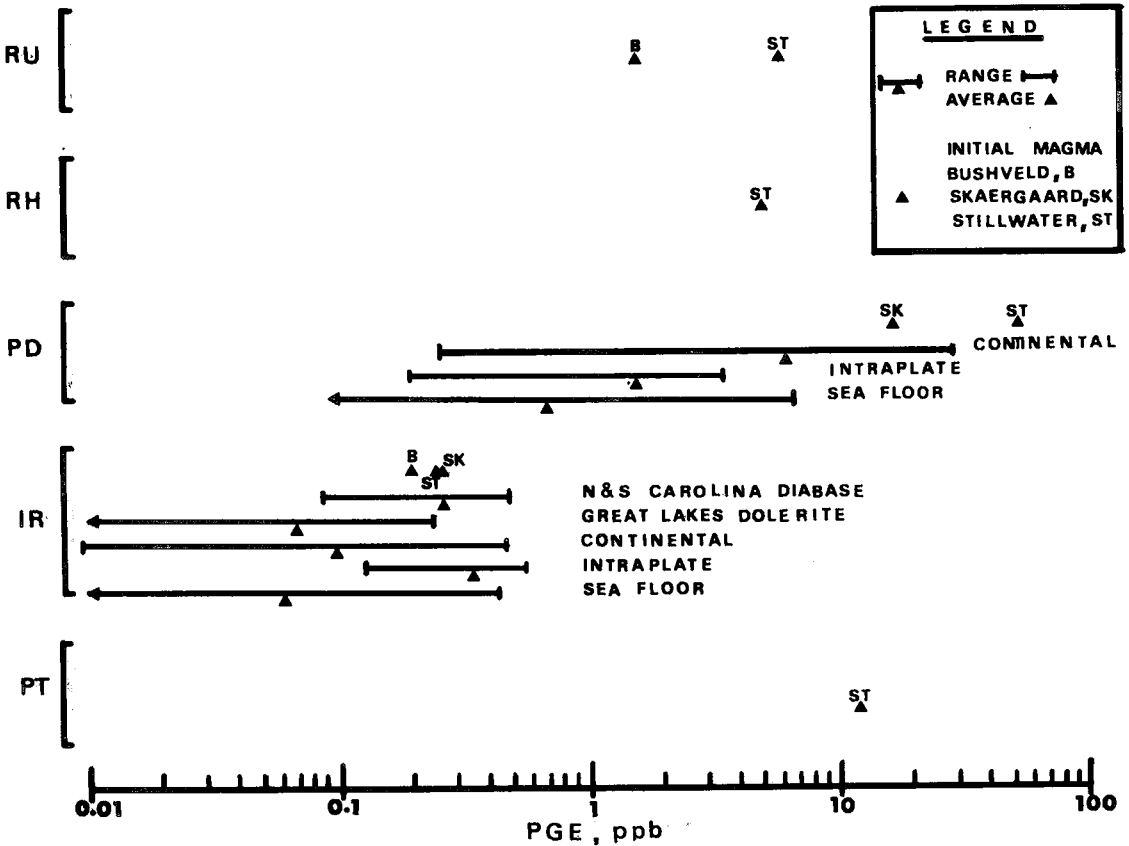
FIG. 4. Range and average values of PGE in basic rocks, including averages for initial magmas of various differentiated layered complexes.

The suite of continental plateau-building basalts, also mainly tholeiitic, represents samples from four provinces, although the majority of analyses pertain to Paraná Basin and Karroo samples. These rocks compare more closely with the intraplate basalts than the sea-floor tholeiites in terms of average Pd and Ir contents.

The Great Lake dolerite of Tasmania is a differentiated tholeiitic sheet whose Ir content was determined by Greenland (1971) over a stratigraphic interval of approximately 520 m. Ir decreases systematically from 0.25 ppb in basal mafic dolerites to 0.006 ppb in uppermost granophyre, implying a high crystal/liquid distribution coefficient. Greenland (1971) concluded from these data that the magmatic geochemistry of Ir is controlled by enrichment in early silicates or oxides (or both) in fractionally crystallized mafic magmas, with consequent depletion in silicic residual melts.

PGE content of layered ultrabasic–basic complexes

Some layered complexes (e.g., Bushveld, Stillwater) are hosts to economic concentrations of PGE. In the mineralized horizons the PGE occur largely as discrete PGM and in intimate association with Ni–Cu sulfides. The mineralization process is not well understood (Vermaak & Hendriks 1976, Vermaak 1976). With the exception of the Stillwater complex, PGE abundance data on layered complexes is very limited as indicated by the compilation in Table 1A.

One of the important uncertainties in modeling processes of PGE concentration in layered complexes is whether the parental magmas were unusually high in PGE. Although the definition of initial magma composition is complicated for some layered complexes, it is useful to examine estimates of PGE concentration in initial magmas. Available data are presented in Table 2.

TABLE 2. PGE CONTENT OF INITIAL MAGMAS OF SOME LAYERED COMPLEXES

Complex	PGE Concentration, ppb						Comment
	Ru	Rh	Pd	Os	Ir	Pt	
Skaergaard	-	-	17.5	-	0.26	-	Measurement on chilled gabbro of marginal facies
Bushveld	1.6	-	-	0.20	0.20	-	Calculated computer fit of abundance data. Average of 2 proposed initial magmas
Stillwater	6	<5	55	-	0.2-0.3	12	Initial magma represented by gabbros of the Basal Zone

The data are most complete for Ir, which averages 0.23 ppb for the three complexes. These Ir estimates are remarkably consistent and there is little difference between the Skaergaard, a layered complex lacking economic PGE concentration, and the Bushveld or Stillwater. The Ir average is comparable to averages for intraplate and continental basalts (Table 1A) although higher than the Ir average for sea-floor basalts. The latter, however, may well represent partial melts of depleted mantle, as suggested by isotopic and other trace-element evidence. In the case of Ir it does not appear that PGE-enriched basic magma is a major factor in the generation of ore deposits in layered complexes.

In addition to the major PGE concentrations in sulfur-rich rocks of layered complexes, chromite-rich strata may also show significant PGE enrichment. This is true of chromitites of the Peridotite Member of the Ultramafic Zone of the Stillwater and the UG-2 horizon of the Bushveld. In both cases discrete PGM and sulfides are important PGE hosts, occurring in part as inclusions in chromite.

Studies of mineral separates from layered complexes (Gijbels et al. 1974, 1976) have been carried out on Bushveld and Rhum rocks (Table 1A). The Bushveld data show a strong preferential association of Ru, Os and Ir with chromite. As discussed earlier it is by no means clear that these data (Gijbels et al. 1974) can be explained in terms of PGE-rich mineral inclusions. Plagioclases from Bushveld and Rhum rocks differ by approximately 100 in Ir content. This large variation has been discussed by Gijbels et al. (1976), but the cause of this difference remains uncertain. Bushveld mineral separates indicate decreasing Ru, Os and Ir contents stratigraphically upward from the Lower Zone to the Upper Critical Zone. This trend is analogous to that for Ir in the Great Lakes dolerite sheet (Greenland 1971), suggesting that in the ppb concentration range, partition of Ru, Os and Ir between silicate minerals and tholeiitic magma favors the solids.

Other data

PGE contents of more silicic rocks are very restricted, owing in part to the increasing analytical problems of sub-ppb-level determination of PGE. The Ir levels in rocks of intermediate to acid composition probably average about 0.025 ppb; Greenland et al. (1974) have shown that silicic plutonic rocks from the western U.S. may have Ir contents of <0.001 ppb.

Data on the PGE content of carbonaceous chondrites are included in Table 1A to provide an index to unfractionated or 'primitive' PGE ratios.

CONCLUSIONS

The main trends shown by the abundance data and conclusions drawn by various workers regarding PGE geochemistry in ultrabasic and basic rocks include the following:

1) There is a progressive decrease in average PGE content of sulfur-poor silicate rocks from ultrabasic, through basic to intermediate–acid compositions. These trends do not necessarily hold if silicate magma becomes saturated with respect to sulfur.

2) High PGE contents are commonly associated with chromite. Where levels of hundreds of ppb or a few ppm are involved, sulfides and discrete PGM generally accompany chromite and probably are the actual concentrator minerals. Whereas the same controls may be relevant at lower PGE levels, they have not been demonstrated; solid solution of PGE in chromite is argued or very strongly inferred by some investigators (e.g., Razin & Khomenko 1969, Gijbels et al. 1974).

3) PGE data on basic rocks are restricted largely to Pd and Ir. The sea-floor tholeiites from mid-ocean ridges are highly depleted in both Ir and Pd relative to other basalts. The PGE contents, in conjunction with other geochemical parameters, are suggestive of derivation of these rocks from a depleted source-region.

4) Fractional crystallization of basic magma leads to concentration of Ir, Ru and Os in early crystallizing fractions.

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