

Platinum Group Elements Geochemistry and Mineralogy

Subjects: [Mineralogy](#)

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Platinum (Pt), palladium (Pd), rhodium (Rh), iridium (Ir), ruthenium (Ru) and osmium (Os) are known as the platinum group elements (PGE). These metals are characterized by peculiar physical and chemical properties, such as high melting points, resistance to oxidation and corrosion, strong conductivity and ductility.

chromitite

ophiolite

platinum group elements

1. Introduction

Among the platinum group elements (PGE), platinum and palladium have gained a great economic importance due to their use in oil refining, electronics, jewelry, the glass industry, medical applications and in the catalytic converter of vehicles to reduce the pollutants of exhaust gases [\[1\]\[2\]\[3\]](#). Therefore, PGE and in particular platinum and palladium mine production have grown continuously since the second world war in response to the development of their modern applications.

Furthermore, considering the transformation towards a greener economy that started a few years ago and that PGE uses play an important role in reducing greenhouse gases, their price has increased rapidly [\[2\]](#). The PGE are among the less abundant elements in the Earth [\[2\]](#). However, local high PGE contents can be achieved through a combination of complex geochemical and geological processes that, in some cases, result in the formation of economic deposits [\[1\]\[4\]](#). Based on their geochemical behavior, the PGE have been divided in two subgroups: the Ir-subgroup (IPGE) consisting of Os, Ir and Ru and the Pd-subgroup (PPGE) consisting of Rh, Pt and Pd [\[5\]](#). The IPGE are more refractory and less chalcophile than the PPGE. Therefore, the IPGE are more concentrated in chromitite, while PPGE tend to follow the sulfides [\[4\]](#). For many decades, both the podiform and stratiform chromitites have been recognized as efficient collectors of the critical PGE. Chromitites start to precipitate at temperatures well above 1000 °C; therefore, most of them are enriched in the refractory IPGE, showing contents several orders of magnitude higher than their peridotites. Few chromitites contain economic amounts of the more valuable PPGE, such as the Upper Group 2 (UG2) stratiform chromitites of the Bushveld layered intrusion of South Africa, that still represent the only example of chromitite mined for the PGE recovery [\[1\]](#).

Additionally, the chromitites associated with the Ural–Alaskan concentrically zoned complexes are enriched in Pt and contain a great number of Pt-bearing minerals but, despite this enrichment, few of them are mined for the PGE recovery due to the small size of the mineralized bodies [\[6\]](#).

Two different types of chromitite have been reported within the ophiolites: (1) podiform chromitite that generally occurs in the mantle tectonite and (2) layered chromitite hosted at the base of supra-Moho cumulates, above the crustal sequence. About half a century ago, the podiform chromitites hosted in the mantle section of ophiolite complexes attracted the attention of economic geologists as a potential target for PGE recovery [7]. Several studies have shown that the majority of the ophiolitic chromitites are enriched in the refractory IPGE, and only a few of them show anomalous contents of the most economically significant PPGE.

It is generally agreed that the PGE enrichment in the podiform chromitites is due to the presence of the so-called platinum group minerals (PGM) that occur as tiny grains enclosed in the chromite crystals and, to a lesser extent, in the silicates of the chromitite matrix [8][9][10][11][12][13][14][15][16][17][18][19][20][21][22][23]. This observation has promoted investigation of the chromitites in order to verify the mineralogical nature, size, morphology and textural position of PGM, with the aim to understand their origin and to provide useful information for their beneficiation during mineral processing. Consistently with their geochemical signature, the most abundant PGM described in the podiform chromitites consist of IPGE-minerals (IPGM), such as sulfides of the laurite-erlichmanite series, alloys in the Os-Ir-Ru system and sulfarsenides of Ir, Ru and Os [8][9][10][11][12][13][14][15][16][17][18][19][20][21][22][23]. The few ophiolitic chromitites enriched in Rh, Pt and Pd were also proved to contain abundant and complex PPGE minerals (PPGM). The main target of this contribution is to provide an overview of unpublished and existing data from the few ophiolitic chromitites enriched in PPGE and PPGM, in order to evaluate their economic potential. Their PGE geochemical and mineralogical aspects are discussed and combined with the chromite composition of their host chromitites, with the aim to understand the processes that caused their anomalous enrichment in PPGE and PPGM.

2. The PPGE Enrichment in Ophiolitic Chromitites: How Was It Achieved

Although Pt and Pd can circulate through soils in aqueous solutions [24][25], under conditions of partial to complete serpentinization, the PGE are expected to behave inertly [5] and, eventually, to be remobilized only at a small scale [7][19]. Therefore, the effects of low-temperature metamorphism or alteration on the PGE distribution are considered negligible. Most of the overviewed chromitites have been affected by serpentinization to different extents, but their PGE contents have been broadly unaffected, as only redistributions may take place during alteration events, hence the overall PGE compositions represent high-temperature magmatic processes. According to the paper by Barnes et al. [26], the so-called “standard model” was proposed to summarize the hypothesis about the behavior the PGE in mafic and ultramafic melts formulated in the last years. The principles that have been widely accepted and summarized by Barnes et al. [26] are selected and listed in the following.

- (1).The predominant control of the distribution of PGE, being extremely chalcophile under almost all conditions, is the interaction of the magmas with magmatic sulfide liquids [26].
- (2).The partition coefficients of PGE from silicate into sulfide liquids are estimated to range from the order of thousands [26].

(3).The melting of magmatic sulfides hosted in the mantle source is a critical control of the PGE contents of the resulting melts. The presence of trace amounts of residual sulfide is enough to induce PGE depletion in mantle melts that are sulfide-saturated at source or, alternatively, the degree of partial melting is enough to remove all of the source sulfide and to dissolve it in the silicate melt [26].

(4).The refractory IPGE are retained in the mantle during partial melting, they decrease in residual melts during fractional crystallization and they are enriched in ultramafic magmatic rocks, independently from the presence of sulfides. On the contrary, the more chalcophile PPGE behave oppositely in the absence of a magmatic sulfide phase [5][26].

(5).The PGE, under the appropriate conditions, can be fractionated from one another during differentiation or partial melting of sulfide magmas [26]. Pd solubility in silicate melts is orders of magnitude higher than that of other PGE, which may be responsible for Pd depletion of the residual rocks [27][28][29].

Despite the many factors summarized above, the two main mechanisms controlling the behavior of the PGE during the crystallization of the host chromitite are the partial melting that the mantle source underwent and the crystal fractionation process. Ophiolite complexes represent different oceanic environments characterized by different degrees of partial melting, from low percentages of melting at some mid-ocean ridges (MOR) to higher values in supra-subduction zone (SSZ) complexes [30]. In order to extract all the PGE, including the most refractory, from their mantle source, in which they may occur as alloys and sulfides, high degrees of partial melting, up to 30%, are required [5]. Lower melting degrees between 20 and 25% will dissolve all the preexisting sulfides leading to PGE liberation, especially the PPGE, into the melts [31]. Most of the mantle-hosted ophiolitic chromitite formed because of the reactions between the residual mantle and percolating magma such as hydrous high-Mg boninitic melts in an SSZ geodynamic setting and the aluminous-rich melt formed in the MOR or in the back arc basin (BAB) environments of the ophiolites [30][32]. The composition of the chromites is related to the nature of the percolating melts, thus most of the Cr-rich chromitites precipitated in the mantle sections of an SSZ ophiolite, whereas Al-rich chromitites are typical of the MOR region. The degree of partial melting of the SSZ mantle is higher than those of the MOR mantle, suggesting that the Cr-rich and Al-rich chromitites should be IPGE- and PPGE-rich, respectively. However, on the basis of available data, this model was successfully applied only to the Bracco chromitite [33]. The PPGE enrichment over IPGE in the Al-rich chromitite of the Bracco ophiolite was explained with the low degree of partial melting of their mantle source. The low degree of partial melting was not high enough to remove all the PGE from the mantle, especially the refractory IPGE. The most incompatible elements, such as sulfur and the PPGE, were partially removed from the mantle, concentrated in the melt and subsequently incorporated in the Bracco chromite forming system [33]. According to **Table 1**, enrichments in PPGE have been reported in both Cr-rich and Al-rich chromitites; therefore, the model of the low degree of the mantle source as the main factor to control the unusual PGE distribution in the Bracco chromitites cannot be applied to all the overviewed chromitites in this contribution. Melts produced from partial melting of the mantle are either saturated or undersaturated in sulfur. In particular, magmas with boninitic affinity represent sulfur-undersaturated mafic melts, because they derived from a strongly depleted mantle that has lost most, if not all, of its original sulfide phase [31][32]. As a consequence, sulfur saturation is rarely achieved during the precipitation of Cr-rich chromitites hosted in the mantle section of SSZ ophiolite. Examples of these chromitites include those from Kraubath, Newfoundland, Loma Caribe, Veria, Leka,

Osthammeren, Ospa–Kitoi, Khara-Nur, Ulan-Sar'dag, Herbeira and Shetland. For this reason, Escayola et al. [34] proposed that sulfur saturation was achieved also in boninitic magma by reintroduction of sulfur into the residual mantle via metasomatic fluids. On the contrary, tholeiitic magma can be sulfur-saturated [32] and the reaction between this melt and mantle tectonites can be suitable for the precipitation of the chromitite enriched in the more chalcophile PPGE, after the formation of an immiscible sulfide liquid followed by a fractional crystallization process as reported for the Sebuku chromitite [35]. The chromitites from Bulqiza-Tropoja-Tropoja, Thetford Mine, Troodos, New Caledonia, Zambales, Al'Ays and some of Kraka occur in the cumulate sequence, above the petrographic Moho, of the host ophiolite, whereas those of Moa Baracoa, Nurali, Berit and very likely also those of Vourinos are located in the MTZ (Table 1 and references therein). The PPGE enrichment in most of these chromites, which are not hosted in the deep mantle, is probably due to the presence of an immiscible sulfide liquid formed from a differentiated melt that, during its migration from the mantle upwards to the MTZ and the cumulus zone, underwent extensive fractional crystallization processes. The original composition of the melt was initially boninitic or tholeiitic and reached the sulfur saturation during its strong differentiation or by assimilation of sulfur from an external source. According to Proenza et al. [36], the local enrichment in PPGE in the chromitite of Moa Baracoa was caused by their interaction with pegmatitic olivine-norite dikes that introduce the PPGE and sulfur to the chromitite originally only enriched in IPGE. The local enrichment of PPGE in the Cliff chromitite of Shetland ophiolite was attributed to a secondary alteration process that was able to upgrade the tenor of PGE [37].

Table 1. World-wide occurrences of PPGE-PPGM-rich ophiolitic chromitites (listed in alphabetical order according to the host country).

Country	Ophiolite	Name of the Deposit	Age	Type of Chromitite	Chromite Composition	PPGE Data *	PPGM Data	Ref.
Albania	Bulquiza-Tropoja		Jurassic	mantle-cumulate	n.a.	no	yes	[18]
Austria	Kraubath		Early Paleozoic	mantle	Cr-rich	yes	yes	[11] [38]
	Hochgrossen		Early Paleozoic	mantle	Cr-rich	yes	no	[11]
Canada	Newfoundland	Middle Arm Brook	Lower Ordovician	mantle	Cr-rich	yes	yes	[34]
	Thetford Mine		Lower Ordovician	cumulate	Cr-rich	yes	yes	[39] [40]
Cuba	Moa Baracoa	Potosi	Upper Jurassic-Lower Cretaceous	MTZ	Al-rich	yes	yes	[36] [41]
Cyprus	Troodos		Cretaceous	cumulate	Cr-rich	yes	no	[9]

Country	Ophiolite	Name of the Deposit	Age	Type of Chromitite	Chromite Composition	PPGE Data *	PPGM Data	Ref.
Dominican Republic	Loma Caribe	Loma Peguera	Jurassic-Cretaceous	mantle	Cr-rich	no	yes	[21] [42]
Greece	Pindos	Korydallos, Pefki	Middle-Upper Jurassic	mantle	Al-rich	yes	yes	[43] [44] [45] [46] [47] [48]
								[49]
								[45] [50]
Italy	Veria	Galaktos	Jurassic-Cretaceous	mantle	Cr-rich	yes	yes	[22] [23]
Indonesia	Sebuku Island	Pirogue	Cretaceous-Paleocene	cumulate	Al-rich	yes	yes	[12] [13]
Norway	Leka	Osthammeren	Lower Ordovician	mantle	n.a.	no	yes	[10]
Philippine	Zambales	Acoje	Eocene	cumulate	Cr-rich	yes	no	[53]

Country	Ophiolite	Name of the Deposit	Age	Type of Chromitite	Chromite Composition	PPGE Data *	PPGM Data	Ref.
Portugal	Braganca	Derruida	Paleozoic	n.a.	n.a.	yes	yes	[54]
Russia	Nurali	CHR II	Paleozoic	MTZ	Al-rich	yes	yes	[55]
								[56]
								[57]
	Ospa–Kitoi		Proterozoic	mantle	Cr-rich	yes	yes	[58]
								[59]
								[58]
	Khara-Nur		Proterozoic	mantle	Cr-rich	yes	yes	[59]
								[59]
								[60]
	Ulan-Sar'dag		Neoproterozoic	mantle	Cr-rich	yes	no	[60]
								[61]
								[61]
	Kraka	Wets Saksey, Loginovskoe, Babay	Paleozoic	cumulate	Cr-rich	yes	yes	[61]
								[61]
								[61]
		East Saksey, Laktybash, Khamitovskoe, Maly Apshak, Bol'shoy Apshak		mantle	Al-Cr-rich	yes	yes	[61]
								[61]
								[61]
Saudi Arabia	Al'Ays		n.a.	mantle-cumulate	Cr-rich	yes	yes	[30]
Spain	Herbeira		Paleozoic	mantle	Cr-rich	yes	yes	[62]
								[63]
Turkey	Berit		Cretaceous	MTZ	Al-rich	yes	yes	[64]
United Kingdom	Shetland	Harold's Grave	Early Paleozoic	mantle	Cr-rich	yes	yes	[65]
								[66]
		Cliff						[65]
								[66]
USA	Rattlesnake Creek	Pole Corral	n.a.	n.a.	n.a.	yes	no	[67]

Order of crystallization of the PGM associated with ophiolite chromitites was suggested: minerals in the Os-Ir-Ru alloys system, followed by sulfides of the laurite-erlichmanite series and part of the sulfarsenide irarsite and hollingworthite are the first to crystallize at temperatures above or around 1000 °C, prior or concomitantly with the host chromite. The precipitation of these PGM is mainly controlled by the sulfur $f(S_2)$ and arsenic $f(As)$ fugacities in the mantle [16][17][68]. In particular, the $f(S_2)$ during the precipitation of chromitites is expected to increase with decreasing temperature. Although at this stage the sulfur saturation is not achieved, minerals of the laurite-erlichmanite series start to precipitate [16][17][68][69][70]. The presence of abundant PPGM associated with magmatic Ni-Cu-Fe sulfides occurring in the silicate matrix of the host chromite in the PPGE-rich ophiolitic chromitites can be considered the witness of the presence of an immiscible sulfide liquid during their crystallization. When the magma reaches sulfur saturation, an immiscible sulfide liquid may segregate from the silicate melt, collecting the more

chalcophile PPGE available in the system. Therefore, the researchers can argue that the enrichment in PPGE in most of the overviewed ophiolitic chromitites was achieved thanks to the formation of an immiscible sulfide liquid becoming trapped interstitially to chromite crystals at a magmatic temperature, as a consequence of a crystal fractionation process. During the cooling of the PPGE-rich immiscible sulfide liquid, the PPGM start to precipitate together with Ni-Cu-Fe sulfides that may contain PPGE in solid solution as described for the Braganca chromitite [54]. The same model was previously applied to explain the PPGE enrichment in UG2 stratiform chromitites of the Bushveld layered intrusion of South Africa [4], and later also to the Korydallos [46], Al'Ays [30], Newfoundland [34], Nurali [55], Sebukú [35] and Zambales [53] ophiolitic chromitites overviewed in this contribution.

After their crystallization at the magmatic stage, the PPGM and their associated sulfides, being hosted in the silicate matrix of the host chromitite, are more vulnerable to secondary alteration processes [7]. During serpentinization, the magmatic PPGM and Ni-Cu-Fe sulfides underwent desulfurization, generating awaruite and alloys characterized by variable Pt-Pd-Rh-Cu-Ni-Fe assemblages. The occurrence of secondary PPGM containing Sb, As, Bi, Te, Sn, Hg, Pb and Au (**Table 2** and references therein) suggests that these elements were originally present in the differentiating magmatic sulfide liquid or, alternatively, they have been introduced by an external source transported by serpentinizing hydrothermal fluids that caused alteration of the host ophiolite [34][37]. Where alteration was most intense, magmatic PGM were transformed to PGE-bearing oxides, which reflects a further alteration stage in the sequence of low-temperature genesis of PGM, as documented in the chromitites from Pindos, New Caledonia, Sebukú, Nurali, Al'Ays, Herbeira and Berit [12][30][35][46][56][62][64]. Despite the evident mineralogical reworking and alteration of the PGM, the data summarized in this contribution suggest that the low-temperature secondary processes that affected the overviewed chromitites caused only a small scale redistribution of PPGE, without changing the whole-rock magmatic PGE contents.

Table 2. PPGM identified in the PPGE-enriched ophiolitic chromitites.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21
Rhodium																					
Approved minerals																					
Bowieite Rh ₂ S ₃	x	x		x								x									
Cuprorhodsite CuRh ₂ S ₄	x	x		x								x									
Kingstonite Rh ₃ S ₄	x																				
Hollingworthite RhAsS	x	x					x	x		x		x	x	x				x	x	x	x
Minakawaite RhSb																		x			

Zaccariniite RhNiAs		x				x				x	x						x		x				
Unnamed minerals																							
RhTe	x																						
Rh ₂ As	x																						
Rh ₂ S ₃		x																					
Rh ₅ S ₄												x											
Rh ₂ SnCu				x													x						
Unidentified minerals *																							
Rh-Pd-Sb			x																				
Rh-As																			x				
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21		
Platinum																							
Approved minerals																							
Braggite (Pt,Pd,Ni)S				x			x													x			
Cooperite (Pt,Pd,Ni)S	x			x				x				x			x		x						
Genkinite (Pt,Pd) ₄ Sb ₃																						x	
Geversite Pt(Sb,Bi) ₂																x			x				
Hongshiite PtCu																							x
Isoferroplatinum Pt ₃ Fe	x			x								x				x							
Malanite CuPt ₂ S ₄	x			x								x											
Platarsite PtAsS	x	x						x		x				x	x								
Platinum Pt	x																						

Sperrylite PtAs ₂	x			x			x					x	x			x		x	x	x	x
Tetraferroplatinum PtFe	x			x											x				x		
Tulameenite Pt ₂ FeCu	x											x									
Unnamed minerals																					
Pt(Ni,Fe) ₃							x	x													
Pt ₆ Cu																			x		
Unidentified minerals *																					
Pt-Cu	x			x												x					
Pt-Pd-Cu													x		x						
Pt-Pd-Au																				x	
Pt-Pd-Cu-Au																					x
Pt-Fe-Cu												x		x			x				
Pt-Pd-Cu-Ni-Fe			x	x											x		x	x			
Pt-Fe	x						x			x		x		x		x				x	
Pt-Ir													x								
Pt-Ir-Fe-Ni						x															
Pt-Ru-Rh												x									
Pt-Ir-Ru-Os																x					
Pt-Pd-S															x						
Pt-Pd-Rh																		x			
Pt-oxides												x			x			x	x		
Cu-Pt oxides																					x
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21
Palladium																					

Approved minerals									
Atheneite (Pd,Hg,Pt) ₃ As								x	
Cabriite Pd ₂ SnCu			x						
Froodite PdBi ₂								x	
Keithconnite Pd _{3-x} Te		x	x						
Mertierite II Pd ₈ (Sb,As) ₃			x						
Nielsenite PdCu ₃				x					
Paolovite Pd ₂ Sn				x					
Plumbopalladinite Pd ₃ Pb ₂								x	
Potarite PdHg		x	x				x	x	x
Skaergaardite PdCu				x					
Sobolevskite PdBi								x	
Stibiopalladinite Pd ₅ Sb ₂			x			x	x		x
Vincentite (Pd,Pt) ₃ (As,Sb,Te)									x
Zvyagintsevite Pd ₃ Pb				x				x	
Unnamed minerals									
Pd ₃ Fe			x						
Cu ₆ Pd								x	
PdAs ₂			x						
Unidentified minerals *									
Pd-Cu			x						

The PGE are listed among the rare, noble, critical and most valuable metals in nature. Presently, more than 90% of the PGE production comes from two countries, Russia and South Africa. Economically mineable PGE deposits are also found in the layered intrusions of the Great Dyke (Zimbabwe) and Stillwater Complex (USA) as well as in the Sudbury Basin in Canada [1][2]. PGE production in Russia is dominated by palladium, largely occurring in the Cu-Ni sulfide ore deposits of the Norilsk-Talnakh district, which belongs to the Siberian traps province [71]. The Bushveld layered intrusion in South Africa is known for its large platinum and palladium resources and, according to Cawthorn [1], there are enough PGE reserves to supply world demands for centuries using the current mining techniques. In the Bushveld, the PGE are recovered from three very different ore bodies, namely the Merensky

Pd-Cu-Sb				x			the entire
Pd-Rh-Sb	x						tites that
Pd-Pt-Fe-Cu-Ni				x			e PPGM
Pd-Pt-Cu-Sn-Pb		x					l in fresh
Pd-Sn				x		x	he PGE
Au-Pd		x					ophiolitic
Pd-Te					x		d (2) the
Pd-As					x		
Pd-As-S						x	
Cu-Pd-Au		x				x	
Pd-Pt-Au							Africa.
Pd oxides		x			x	x	

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1 = Bulquiza-Tropoja ^[18] (Albania); 2 = Kraubath ^[38] (Austria); 3 = Newfoundland ^[34], 4 = Thetford mine ^{[39][40]} (Canada); 5 = Moa Baracoa ^[41] (Cuba); 6 = Loma Peguera ^{[21][42]} (Dominican Republic); 7 = Pindos ^{[43][46][47]}, 8 = Othlydett, A. Skj. Vor ^[51] Gruenevald ^[23] (The association of PGE with chromitite in layered intrusions, 12 = New layered intrusions, 13 = and ophiolite complexes. *Econ. Geol.* 1989, 84, 180–187.

14 = Osmund ^[10] (Portugal); 15 = Morali ^{[55][56][57]}, 16 = Ospa–Kitoi, Khara-Nur ^{[58][59]}, 17 = Kraka ^[61] (Russia); 18 = Al'Ays ^[30] (Saudi Arabia); 19 = Herbeira ^[62] (Spain); 20 = Berit ^[64] (Turkey); 21 = Shetland ^{[65][66]} (UK). * = PGM without a precise stoichiometry.

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