

Conventional and unconventional ore deposits of Platinum-Group Elements (PGE)

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Abstract:

This contribution provides an overview of different types of ore deposits for platinum-group elements (PGE). Two main groups of PGE ore deposits are covered: (i) conventional PGE ore deposits, meaning ore deposits that currently play, or have played in the past, a major role in the global supply of PGE (i.e. magmatic ore deposits and placer deposits; respectively) and (ii) unconventional PGE ore deposits, meaning ore deposits that are not commonly considered for PGE mining but showing a certain degree of potential (i.e. hydrothermal; sedimentary and residual ore deposits). Today, the most important conventional PGE mines are situated in South Africa (*Bushveld Complex*, representing a layered mafic intrusion) and Russia (*Noril'sk-Talnakh*, representing a conduit type intrusion), which together control more than 80% of the current worldwide PGE supply. PGE-rich ores of conventional PGE ore deposit types are associated with magmatic sulfide mineralizations. Unconventional PGE ore deposits show evidence for PGE mobilization and re-precipitation down to ambient conditions. Manganese nodules and crusts on the seafloor (i.e. sedimentary ore deposit type) accumulate PGE via absorption while the enrichment of PGE in Ni-laterites (i.e. residual ore deposit type) is enhanced by biogenic-mediated processes resulting in the formation of micronuggets of PGE alloys.

Resumen:

Este trabajo hace una breve revisión de los diferentes recursos más importantes de elementos del grupo del platino (EGP), incluyendo: (i) depósitos convencionales de EGP -depósitos que son actualmente, o que han sido en el pasado, fuentes a nivel global de EGP- (i.e. depósitos magmáticos y placeres; respectivamente) y (ii) depósitos no convencionales de EGP, representados por depósitos que no han sido tradicionalmente considerados como fuentes primordiales de EGP, pero que muestran cierto potencial para ello (i.e. depósitos hidrotermales, sedimentarios y residuales). Actualmente, los depósitos convencionales (asociadas con mineralizaciones de sulfuros magmáticos) más importante se localizan en Suráfrica (*Bushveld*) y Rusia (*Noril'sk-Talnakh*), los cuales conjuntamente representan más del 80% del suministro global de EGP. En los depósitos no convencionales, las concentraciones significativas de EGP se asocian a procesos de movilización y re-precipitación de EGP en condiciones de baja temperatura. La acumulación de EGP en nódulos y concreciones de manganeso en el fondo del mar (i.e. depósitos sedimentarios) se asocia a procesos de absorción, mientras que en yacimientos de alteración meteórica como las lateritas de Ni (i.e. depósitos residuales) el enriquecimiento de EGP esta aumentado por procesos biogénicos, tales como los que han producido la formación de micropepitas de aleaciones de EGP.

Palabras Clave: Elementos del Grupo del Platino, Minerales del Grupo del Platino, Depósitos Magmáticos, Depósitos Supergénicos. | **Key Words:** Platinum-Group Elements, Platinum-Group Minerals, Magmatic Ore Deposits, Supergene Ore Deposits.

INTRODUCTION

What are PGE?

Platinum-group elements (PGE) are a group of six metals (i.e. Os, Ir, Ru, Rh, Pt and Pd) that are characterized by similar chemical and physical properties such as high resistance to corrosion and heat. In the periodic table of elements they occur as transition metals in the Groups VIII, IX and X of the Periodic Table in which the lighter PGE (i.e. Ru, Rh and Pd) appear in

period V and the heavier PGE (i.e. Os, Ir and Pt which are the densest known metals) in period VI (Fig. 1).

Platinum-Group Elements (PGE)		
44Ru hcp mp 2333°C	45Rh fcc mp 1963°C	46Pd fcc mp 1555°C
76Os hcp mp 3033°C	77Ir fcc mp 2446°C	78Pt fcc mp 1768°C

Fig 1. Platinum-group elements as listed in the periodic table of elements showing their atomic number, their crystal structure and their melting point (mp) in °C.

However, because of differences in their melting points, PGE are usually divided into IPGE (i.e. Ir group: Ir, Ru and Os; melting points 2446, 2333 and 3033 °C, respectively) and PPGE (i.e. Pd group: Pd, Pt and Rh; melting points 1555, 1768 and 1963 °C, respectively). Together with gold and silver PGE are also known as precious metals, hence highlighting their great economic value. Due to their unique properties, PGE are essential for a wide range of sophisticated technological applications and are therefore also considered critical elements for modern societies (Mudd *et al.*, 2018). Although already used by pre-Colombian South American natives for the production of artefacts, the discovery of the complete list of PGE as new elements is rather recent. The first scientific documentation of platinum goes back to the year 1748 by Antonio de Ulloa (Juan and Ulloa, 1748), when Spanish conquests found on their search for gold, Pt-Fe alloys in stream sediments in the today's area of Colombia/Ecuador. As the grains looked similar but different to silver the Spanish conquests named the grains "*platina*" meaning "*small silver*" (note that the Spanish word for silver is "*plata*"). Interestingly, the new material was considered as without use and hence worthless at that time. However, subsequent experiments with the material performed in Madrid lead to the purification of platinum in the year 1786. Os, Ir, Rh and Pd were discovered in 1803 and Ru in 1844.

Applications for PGE

Since the discovery of their unique properties in the 20th century, PGE have found applications in many fields. Today the most prominent use of PGE is that of catalytic converters for initializing oxidation and reduction reactions. In the automobile industry for example such PGE-based catalysts help to reduce emissions of e.g. carbon monoxide. Also, the chemical industry as well as the petrochemical industry rely on PGE-based catalysts where they play a major role in the production of intermediate and final products. In combination with other metals, PGE are used to achieve very hard alloys that can be used for durable coatings in industrial applications. The electronics industries use PGE for the production of e.g. liquid crystal displays, light-emitting diodes (LEDs) and computer hard discs. Due to their anticorrosive behavior, PGE are used for medical implants (e.g. dental implants) as well as for drugs against cancer. Jewelry is another prominent field for PGE usage. PGE (especially Pt, Pd and Rh) play also in the financial sector an important role where they are used for investments from simple coins/bars collection (physical) to more sophisticated financial assets (e.g. stocks and funds).

GLOBAL PGE PRODUCTION AND PRICE DEVELOPMENTS

According to the USGS 2016 Minerals Yearbook, the global PGE production by 2016 was 473 t (U.S.

Geological Survey, 2016). Approximately 23% was supplied by recycling of catalytic converters, jewelry and electronics.

However, half of the global primary (meaning from mining) PGE production was provided by South Africa, one third by Russia and the remaining by Canada, the USA and Zimbabwe. The dominance of only two countries (i.e. South Africa and Russia) accounting for >80% of the worldwide primary PGE supply, in combination with their high economic significance, has resulted that PGE are defined as "*critical materials for the EU*" by the European Commission (e.g., see European Commission, 2017). The market price for individual PGE is given in US \$ per troy ounce (\$/ozt) where 1 ozt equals 31.1 grams. Looking on the price developments of PGE (excluding Os that is locked at a price of 400 \$/ozt) for the last 5 years, a significant increase in value can be observed for Ir, Ru, Rh and Pd, whereas platinum shows a decrease (Fig. 2). The PGE with highest economic value is currently Rh with a market price of approx. 2800 US\$/ozt.

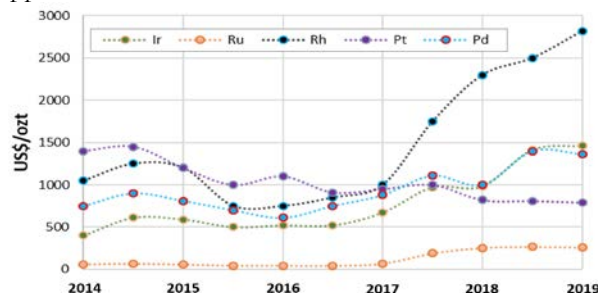


Fig. 2 Price developments for PGE except Os for the last 5 years: Ru (+350%), Ir (+265%), Rh (+170%), Pd (+82%) and Pt (-44%). Data was taken from infomine.com.

The current attractive market situation together with their status as critical metals motivates exploration projects for PGE, including the search of PGE in rather unconventional ore deposit types as explained below.

ORE DEPOSIT TYPES FOR PGE

Ore geologists differ in general between four main groups of ore deposits: (i) *magmatic*, meaning that the deposit formed upon the crystallization of magma, (ii) *hydrothermal*, meaning that hot water was involved in the formation of the deposit, (iii) *residual*, meaning that intense weathering of source rocks formed the deposit and (iv) *placer*, meaning that heavy ore minerals were physically concentrated due to water streams.

PGE can be found in varying concentrations in all of these four ore deposit types. However, today the vast majority of PGE are mined in different subtypes of the magmatic ore deposit type. These economically most important magmatic subtypes have in common that they are all associated with so-called large igneous provinces (LIPs) that are characterized with areal extents greater than 100 000 km² and occurring in intraplate tectonic settings.

CONVENTIONAL PGE RESOURCES

Conduit type intrusions

Noril'sk-Talnakh in Russia is an example of the conduit type (meaning that they occur in intrusions that are part of sill complexes and dike swarms; Fig. 3). The Ni-Cu-PGE ore deposits are associated with mafic magma that formed the so-called Siberian Traps, which is known as the largest continental flood basalt province on Earth (approximately 2.5 million km²).

From more than 300 intrusions mapped in the area, only about 10% have elevated sulfide concentrations. Platinum and Pd-rich sulfide mineralizations are believed to have formed via the fractionation of a sulfide melt generated by sulfur saturation of a mafic-ultramafic magma. Ore grades (Pt, Pd, Rh and Au) at Noril'sk-Talnakh are in the range of 7 g/t (Mudd *et al.*, 2018).

Reef-Type and Contact-Type Deposits

When a magma crystallizes in LIP intrusions, layering features occur, mainly due to differences in the specific weights of minerals (similar to sedimentary rocks). Within these so-called layered mafic intrusions ore mineralization can either occur as strata-bound (ore is confined to a stratigraphic unit) or stratiform (ore occurs in one or several layers).

Reef-type ("reef" is a mining term for a relatively flat-lying, tabular orebody) and contact-type (ore is found near the lower contact of mafic-ultramafic layered intrusions; Fig. 3) PGE ore deposits are strata-bound. They contain Cu-, Fe-, Ni-, and PGE-bearing minerals in form of disseminated magmatic sulfides within layers where silicates (e.g. pyroxene) and oxides (e.g. chromite) dominate. The dominance of South Africa with respect to the global PGE production mentioned above (50% of the global PGE supply) can be explained by the Bushveld Complex.

The Bushveld Complex is known as the largest known layered intrusion on Earth (on the surface it outcrops as so-called limbs in an area of ~66000 km²; i.e. eastern, western and northern limbs) that hosts the worldwide biggest PGE ore deposits (e.g. Merensky Reef, UG2 chromitite and Platreef). The average ore grade in the Bushveld complex ranges from 3 to 10 ppm total PGE (Thormann *et al.*, 2017). Other important examples of these types are the Great Dyke in Zimbabwe (ore grade ~4 ppm total PGE) and the Stillwater Complex in Montana (ore grade ~15 ppm total PGE).

Sudbury-type (impact-related)

This is currently a significant single-case type from Ontario (Canada), where the PGE mineralization is associated with the crystallization of a magma, that filled

a crater (the Sudbury basin) due to the impact of a meteorite ~1,8 million years ago.

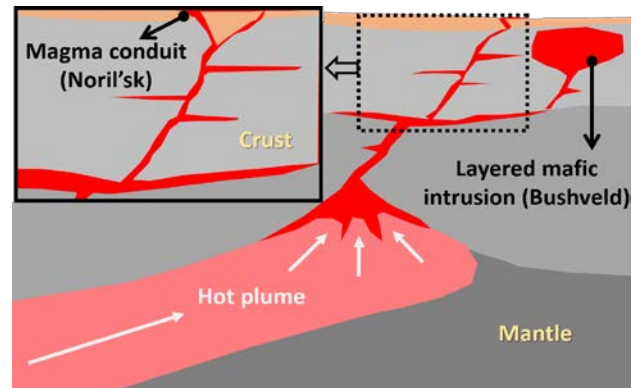


Fig 3. Simplified sketch showing the general geological setting for conventional PGE ore deposits (modified after Barnes *et al.*, 2016).

Placers

Because of their great historic importance (note that until the 1920s placers in Russia and Colombia have been the only source for PGE) placer ore deposits are accounted here to the conventional ore deposit types. Today they don't play an important role for the global PGE supply but in some developing countries artisanal (and often illegal) small-scaled mining activities occur (Fig. 4).

The formation of a PGE-bearing placer is explained by erosion processes of PGE-bearing source rocks (e.g. a magmatic intrusion) followed by the transportation of the sediments in a water stream. Due to the high specific weights of PGE-bearing minerals (e.g. "Pt-Fe nuggets"; Fig. 4) they are deposited as heavy minerals at specific locations (e.g. little basins or within the inner side of stream curves) where they can accumulate to ore grades. Placer deposits can be found in active water streams as well as in form of so-called "paleo-placers", meaning that they represent a remnant of a today inactive river or stream system.



Fig 4. Example of artisanal small-scale mining from placer sediments in South-America. Pt-bearing minerals ("Pt-Fe nuggets", labelled as "pt" in figure) and Au are concentrated via panning ("gold washing") together with other typical heavy minerals such as zircon (zr), magnetite (mgt), hematite (hem) and pyrite (py).

UNCONVENTIONAL PGE RESOURCES

Hydrothermal

Hydrothermal fluids (up to 300 °C) are good solvents. They can leach target metals from source rocks and transport them as complexes to where conditions are favorable for the crystallization of ore minerals. Typical hydrothermal ore deposits are for example porphyries, sedimentary exhalative (SEDEX) deposits or skarns and typical target metals from hydrothermal ore deposits are Cu, Mo, Au, Ag, Zn and Pb.

Experimental work has shown that also PGE can be mobilized in hydrothermal fluids (e.g. Colombo *et al.*, 2008). Under highly acidic and oxidizing conditions Pt and Pd can be dissolved into solutions as chloride complexes, whereas bisulfide complexes are believed to be dominant under more neutral and reduced conditions.

However, a world-class PGE ore deposit with a clear hydrothermal fingerprint for its genesis still has to be discovered. The maybe best field evidence supporting the existence of such hydrothermal PGE ore deposits are some Cu porphyries with elevated contents of PGE (especially Pt and Pd) where chloride complexes played an important role in their formation (e.g. Economou-Eliopoulos, 2005).

An example for the mobilization (and subsequent concentration) of PGE via bisulfide complexes are black shale ore deposits that also host important contents of Ni and Mo (e.g. Pasava *et al.*, 2013, 2017). Other potential hydrothermal PGE ore deposits include unconformity-related U-Au-PGE deposits, sediment-hosted strata-bound Cu deposits and ore deposits where serpentinization and metamorphism of ultramafic rocks occurred (e.g. ophiolites) (Wood, 2002).

Sedimentary

This type is rather new (a few decades) and describes the potential of marine manganese nodules and crusts to accumulate PGE during their formation. Manganese nodules and crusts form at the sides of seamounts where they can adsorb PGE (together with Ni, Co, Cu; hence they are also known as polymetallic nodules) from the seawater (Halbach *et al.*, 1989). Typical nodules have a size of a potato (up to 10 cm) and can contain PGE up to a few ppm (Hein *et al.*, 2000; Balaram *et al.*, 2006).

They occur widespread on the seafloors of our planet, which makes them attractive targets for mining activities (Fig. 5). However, as they can occur in depths down to 5-6 km such mining activities on the seafloor are currently facing significant technological and economical challenges (Glasby, 2002). Nevertheless, the potential of polymetallic nodules and seafloor crusts as future important resources for metals (including PGE) is

demonstrated by currently numerous exploration projects by different countries (licenses are provided through the International Seabed Authority) in the eastern Pacific Ocean.

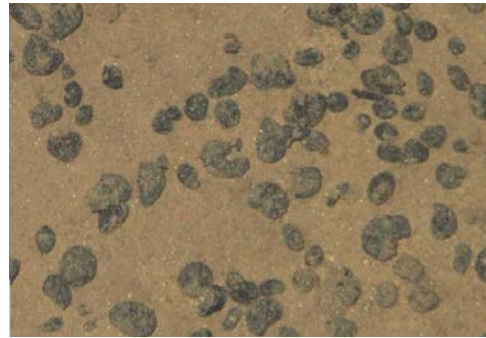


Fig 5. Polymetallic nodules in a compact arrangement on the seafloor making them attractive targets for mining. Shown area is approximately 0.8 m² (modified from Schoening *et al.*, 2017).

Residual

When ultramafic rocks are exposed to tropical weathering (meaning climate-related intense physical and chemical weathering) they form specific soils that are known as laterites. During the weathering process primary minerals such as olivine and pyroxene break down and secondary minerals form. These secondary minerals (e.g. different types of Mg-phyllsilicates that are often summarized under the term “garnierites” as well as different types of Fe-oxide(s) and clay minerals; see Villanova *et al.*, 2014) can contain economic values of Ni.

Currently, Ni-laterites are hosting about 70% of the global Ni resources and they supply about 40% of the worldwide Ni (Gleeson *et al.*, 2003; Mudd 2010). There are different types of Ni-laterites that all have a common, simplified structure from bottom to top: (serpentinized) protolith (e.g. harzburgites; hard rock) is followed by a layer of saprolite (containing secondary Mg-silicates; soft rock) and a final layer of limonite (dominated by Fe-oxide(s); soil) (Fig. 6). The transition from saprolite to limonite is marked by the so-called Mg-discontinuity.

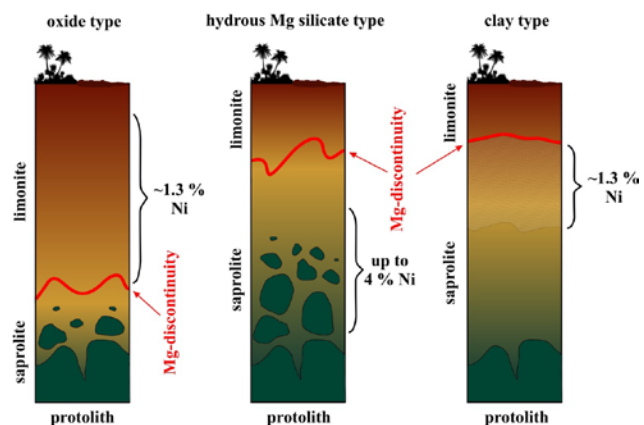


Fig 6. Subtypes of Ni laterites developed on serpentinized ultramafic protolith with indicated main Ni ore zones and grades (modified from Butt and Chuzel, 2013).

However, depending on the main ore mineralogy three types of Ni-laterites can be distinguished: (i) oxide-type, where the Ni is hosted by Fe-oxide(s) such as goethite, (ii) hydrous Mg-silicate type, where the Ni occurs mainly in before mentioned “*garnierites*”, and (iii) clay-type, where the Ni is concentrated in clay-rich layers (e.g. smectites) (Butt and Cluzel, 2013) (Fig. 6). Ni-laterites can contain other valuable metals in addition. Cobalt for example is often an important by-product in Ni-laterites of the oxide-type.

Due to the ultramafic nature of their source rocks, Ni-laterites have also a certain potential for PGE. Although little literature data is available, a few cases in the world highlight the potential of Ni-laterites as unconventional PGE resources. For example, up to 2 ppm Pt were reported from Ni-laterites from New Caledonia (Augé and Legendre, 1994).

On the other hand, processes responsible for the enrichment of PGE in the supergene environment are still matter of scientific discussion: whereas one group believes that PGE-bearing minerals found on the surface have exclusively a magmatic origin (the residual theory; meaning that PGE behave immobile), others opine that PGE can also be mobile under specific supergene conditions and form new minerals (the neoformation theory) (see Oberthür, 2018 and reference therein). A detailed investigation on the PGE geochemistry and PGE mineralogy on Ni-laterites from the Dominican Republic was led by the authors of this contribution (Aiglsperger *et al.*, 2015, 2016, 2017a, b). Different laterite profiles in the Falcondo mining area were investigated that showed highest PGE contents (up to 640 ppb compared to 50 ppb in the protolith) close to the surface.

With the aim to track down the mineralogical origin for the PGE anomaly, innovative hydrosorption techniques were applied. Hydrosorption (see www.hslab-barcelona.com for further information) simulates natural beach placers and is highly effective to concentrate heavy minerals with a grain size down to <30 µm. Hydrosorption led to the discovery of different platinum-group minerals (PGM) in all horizons of the lateritic profile that can be divided into three groups: (i) primary PGM (e.g. unaltered, euhedral laurite crystals), included in primary minerals such as chromite and believed to have formed under magmatic conditions, (ii) secondary PGM, occurring either included or as free grains with signs of alteration (e.g. altered laurite with porous textures and low S contents; believed to be a result of desulfurization processes during serpentinization) and (iii) neoformed PGM, occurring as accumulations of nanoparticles within a matrix of secondary Fe-oxide(s). Interestingly, different PGM can occur together in the form of so-called multistage grains, hence documenting the (trans-)formation processes of PGM in the studied Ni laterites (Aiglsperger *et al.*, 2017a; Fig. 7).

Following the approach by Cabral *et al.* (2011) trace amounts of iodine, which is known as a highly biophilic element, was detected in one neoformed PGM (Aiglsperger *et al.*, 2015). This points toward an involvement of biogenic processes (e.g. biofilms of microorganisms) that are likely to play a key role with respect to the mobilization and re-precipitation of PGE in Ni-laterites. Such processes may be responsible for the formation of biogenic-mediated PGM (“*growing of micro nuggets*”). These results show that a better understanding of the link between biology and mineralogy regarding PGE in the surface environment is needed, to evaluate the true potential of Ni-laterites (and other residual ore deposits). In addition, such an understanding could also help to develop innovative exploration strategies for future discoveries.

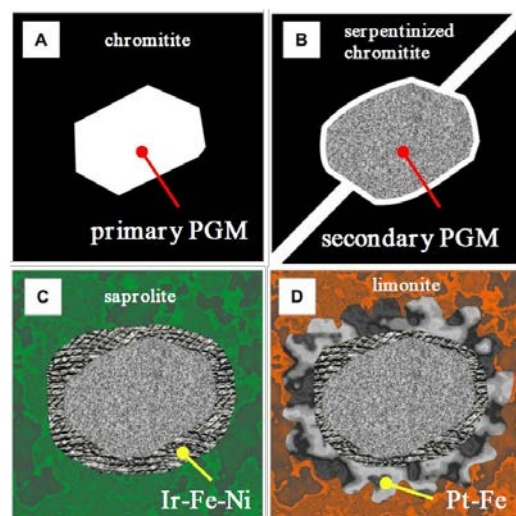


Fig 7. Cartoon showing the formation stages (A-D) of a multistage grain occurring in Ni-laterites from the Dominican Republic (see text for explanation; modified from Aiglsperger *et al.*, 2017a).

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