The Platinum-Group Elements: "Admirably Adapted" for Science and Industry

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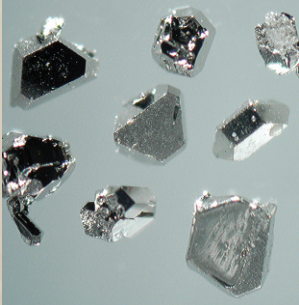
Synthetic crystals of platinum–rhodium alloy grown by high temperature vapor deposition (center crystal is ~1 mm in diameter)

The platinum-group elements (PGE) tend to exist in the metallic state or bond with sulfur or other Group Va and VIa ligands, and often occur as trace accessory minerals in rocks. Combined with three isotopic systems that contain the PGE, these elements afford a unique view of early solar system evolution, planet formation and differentiation, and biogeochemical cycling. Initial purification of the PGE was accomplished in the late 1700s, at which time their unique properties, including high melting point, chemical inertness, and ability to catalyze chemical reactions, became apparent. This led to enormous industrial demand, most notably for fuel production and engine emission control, which combined with scarcity in crustal rocks, has made the PGE a highly valued commodity.

KEYWORDS: platinum-group elements, siderophile, chalcophile, alloy, sulfide, catalysis

"Platinum is a most valuable metal; as it is not oxidisable, nor fusible under common circumstances, and only with difficulty combinable with sulphur, and not acted upon by common acids, it is admirably adapted for the uses of the philosophical chemist." *Elements of Chemical Philosophy*, BY HUMPHRY DAVY

INTRODUCTION

On 23 January 1817, Sir Humphry Davy delivered a lecture to the Royal Society of London describing the results of his recent experiments on the combustion of gas mixtures. Davy reported "the discovery of a new and curious series of phenomena," in which mixtures of highly explosive coal gas and air were found to cause a heated wire of platinum to "become ignited nearly to whiteness." Once the glowing of the wire was extinguished, it was found that the gas mixture was no longer inflammable. Davy reported that "I tried to produce these phenomena with various metals; but I have succeeded only with platinum and palladium; with copper, silver, iron, gold and zinc, the effect is not produced." What Davy had discovered was heterogeneous catalytic oxidation. Davy immediately recognized the practical application of his discovery and modified the safe-lamp he had designed for coal miners to include a Pt wire around the lamp flame (FIG. 1), thus limiting the amount of combustible gas available to the flame and reducing the chance of explosion.

Fast forward to the year 2007, and the impact of Davy's original discovery becomes apparent: ~9 million ounces of Pt and Pd (worth ~US$7 billion) were produced for the heterogeneous catalytic oxidation of automobile exhaust gas. This is in addition to the amounts produced for jewelry and other industrial processes (mostly catalysis related) involving one or more of the platinum-group metals (PGE: Os, Ir, Ru, Rh, Pt, Pd), totaling some 7 million ounces, worth ~US$10 billion[1]. How does an issue of *Elements* devoted to the PGE fit into

this picture? Most significantly, many of the chemical properties of the PGE that are of industrial interest also result in distinct geochemical behavior, affording a unique view of early solar system evolution and planet formation and differentiation. The PGE, along with rhenium and gold, are grouped together as the highly siderophile elements, which are defined by their extreme partitioning into the metallic, relative to the oxide, phase. The PGE are highly refractory, as gauged by their high melting and condensation temperatures (FIG. 2), and were therefore relatively concentrated in the feedstock for the terrestrial planets (Palme 2008 this issue). However, because of an aversion to bonding with oxygen, the PGE are now scarce in the crusts of differentiated planets and, instead, are concentrated in the core-forming Fe–Ni alloy. As discussed in the articles by Palme (2008) and Lorand et al. (2008 this issue), this tendency to exist in the metallic state (termed siderophile) or bond with sulfur and other Group Va and VIa ligands (termed chalcophile) has thus provided geochemists with a sensitive tracer of differentiation processes that involved metal or sulfide phases. As an invaluable bonus, three radioisotope decay systems include the PGE as parent (^{107}Pd–^{107}Ag), daughter (^{187}Re–^{187}Os), or both (^{190}Pt–^{186}Os). These systems have not only provided chronological information, but differences in parent–daughter fractionation have produced distinct isotopic tracers of a variety of geochemical processes (Carlson et al. 2008 this issue).

Owing to their scarcity, but enormous industrial demand, there is significant interest in understanding the rare occurrence of mineable PGE concentrations in the highly depleted crust. In this context, Mungall and Naldrett (2008 this issue) emphasize the chalcophile behavior of the PGE and the massive extraction capacity of magmatic sulfide liquids.

As a resident of London in the 1800s, Humphry Davy would have most certainly been subject to the poor air quality that typified this time. Today, it's not the burning of coal, but

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1 2007 PGE production statistics obtained from Johnson Matthey market data tables (www.platinum.matthey.com/publications/). Total PGE values are calculated from metal prices averaged for the 12-month period.

automobile exhaust that degrades the air quality of many urban centers. Autocatalysts have significantly reduced this problem (see below), but the PGE they contain (and those from other industrial sources) are released to the environment, and some of these PGE are bioavailable. As Rauch and Morrison (2008 this issue) describe, this is a matter of some concern, as the risks of PGE emissions to human health and the environment have not been accurately assessed. There is a clear call for more intense research in this area.
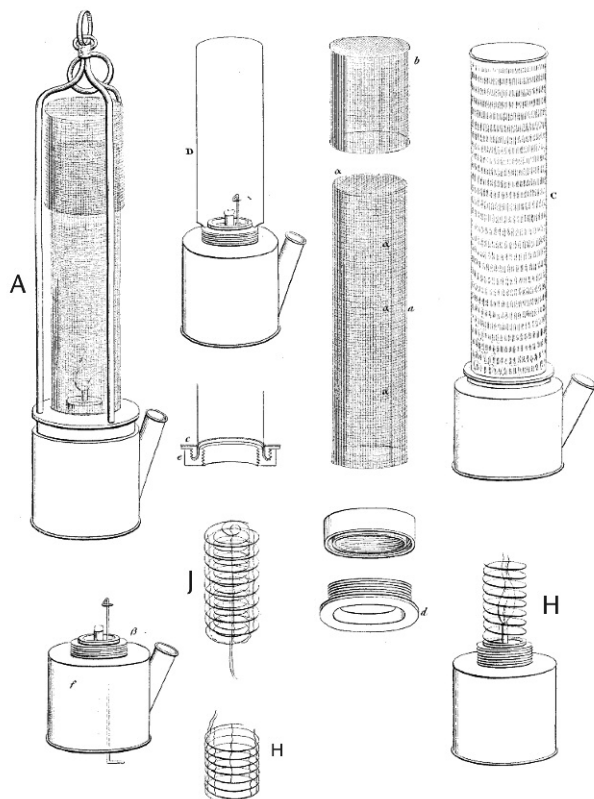
Platinum-Group Elements (PGE)

$_{44}$Ru	$_{45}$Rh	$_{46}$Pd
hcp mp 2607 K	fcc mp 2237 K	fcc mp 1828 K
$_{75}$Re hcp mp 3459 K	$_{76}$Os hcp mp 3306 K	$_{77}$Ir fcc mp 2739 K	$_{78}$Pt fcc mp 2041 K	$_{79}$Au fcc mp 1337 K

DISCOVERY AND PURIFICATION OF THE PGE

In 1741, the metallurgist Charles Wood returned to England with samples of platinum acquired in Jamaica but which likely came from the placer deposits of the Choco district of Colombia[2]. This material was given to Dr. William Brownrigg, whose description was read to the Royal Society of London by William Watson (Watson and Brownrigg 1750). In this description, the samples are referred to as "platina," which is derived from the Spanish for "little silver" and alludes to their appearance (FIG. 3). William Lewis performed an exhaustive battery of tests on this newly found material and concluded that "it follows, that platina is not, as some believe, gold naturally debased by the admixture of some other metallic body, but a metal of the peculiar kind, essentially different from all others" (Lewis 1757).

One important discovery made by Lewis is that platina is soluble in aqua regia, "excepting a little blackish matter" (Lewis 1754), which suggested the presence of impurities in the raw sample. Subsequent work on this residue led to the discoveries of iridium and osmium by Smithson Tennant, reported to the Royal Society of London on 21 June 1804. In the case of iridium, Tennant writes, "I should incline to call this metal *Iridium* [from *iris*, Greek for rainbow], from the striking variety of colours which it gives, while dissolving in marine acid [HCl]" (Tennant 1804). Tennant notes that during one of the osmium purification steps, "a pungent and peculiar smell is immediately perceived." He discovered that this smell "arises from the extrication of a very volatile metallic oxide," providing the basis for the name *Osmium*, which is derived from *osme*, Greek for smell. That smell, of course, originates from the highly toxic osmium tetroxide.

Three days later, Tennant's colleague William Wollaston reported the discovery of rhodium (Rh), which was purified from the solution remaining after precipitating platinum by treatment with sal ammoniac (NH_4Cl). He indicated that this new element should be "distinguished by the name *Rhodium* [from *rhodon*, Greek for rose], from the rose-colour of a dilute solution of the salts containing it" (Wollaston 1804). The following year, Wollaston (1805) reported the discovery of palladium, which was purified from the aqua regia solution used to dissolve raw platina. In his report to the Royal Society of London, Wollaston proposed the name palladium, "from the planet that had been discovered nearly at the same time by Dr. Olbers," referring to the discovery of the Pallas asteroid (originally considered to be a planet) by the German astronomer Heinrich Olbers on March 28, 1802. Records from his monetary accounts (Chaldecott 1979) reveal that Wollaston garnered significant income from a method he developed for platinum purification from raw platina, which he only made public in the Bakerian Lecture to the Royal Society (Wollaston 1829) shortly before his death in 1828. This income helped to furnish the endowment for the Wollaston Medal awarded by the Geological Society of London (FIG. 4). The medal was originally cast in gold, but from 1846 to 1860 it was cast in palladium extracted from Brazilian gold donated by noted assayer and metallurgist P. N. Johnson.

Ruthenium (Ru) was the last of the PGE to be discovered, and was isolated from the insoluble residue after aqua regia digestion of platinum ore from the Urals. The initial claim of discovery was by the German chemist Gottfried Osann in

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[2] The pre-Hispanic natives of this region had used material from the Choco deposits to produce exquisite jewelry and objects of practical use (fishing hooks, sewing needles, awls, tweezers). These people had remarkable metallurgical ability, making use of liquid-phase sintering of Au–Pt mixtures to produce malleable alloys which were fabricated into intricate objects (Scott and Bray 1980).

1827, although the definitive purification is attributed to the Russian chemist Karl Klaus, reported in 1844. Ruthenium is derived from *ruthenia*, Latin for Russia, named for Klaus's homeland, and in honor of Osann's original work (Griffith 1967).

INDUSTRIAL DEMAND FOR THE PGE

The most significant industrial demand for the PGE (see Figure 1 of Rauch and Morrison 2008) arises from their important role in the operation of modern automobiles, which is to catalyze key reactions involved in fuel production and engine emission control. The special role of the PGE in this context arises from two key properties. First, as a consequence of the very high oxygen potential defined by their metal-oxidation reactions, the platinum-group metals are stable in air even at relatively high temperature (see Figure 1 of Palme 2008). Second, the PGE have the remarkable ability to chemisorb simple gaseous molecules, like O_2 and CO, so as to result in significant coverage of the metal surface, but adherence is not so strong that surface reaction rates are retarded (Bond 1991). Consequently, the rates of certain chemical reactions are vastly accelerated by the presence of the PGE metal surface, although the metal itself is not a reactant or product, and reactions can be allowed to take place at higher temperatures without degradation of the metal surface. Optimal engine performance requires fuel that can be highly compressed before controlled ignition by the spark plug, and the measure of fuel performance in this regard is the octane rating. At petroleum refineries, the octane rating of fuel is improved by using Pt–Ir or Pt–Re catalysts in the reforming process to convert aliphatic hydrocarbons to aromatic hydrocarbons, such as in the dehydrogenation of n-heptane (octane rating = 0) to toluene (octane rating = 114). Octane ratings can also be enhanced using platinum catalysts for the isomerisation of C_4-C_6 alkanes (Parkins 1991). Combustion of fuel in car engines produces CO_2 and H_2O, as well as lesser amounts of CO, volatile organic compounds, and nitrogen oxides (NO and NO_2, together known as NOx). The latter three are considered harmful and can be reduced at the tailpipe using two important emission-control devices that incorporate the PGE as essential components. Just downstream from the fuel combustion chamber is an oxygen sensor, which consists of a ceramic solid electrolyte (usually impurity-doped ZrO_2) plated with platinum electrodes. This device monitors the oxygen content of the combustion gas and is part of a feedback loop to adjust the fuel/air ratio in the combustion chamber for peak performance and to optimize the conversion of unburnt fuel, CO, and NOx in the catalytic converter. The catalytic converter is located downstream from the oxygen sensor and consists of a honeycomb-structured ceramic core, coated with a porous "washcoat" of alumina, then the catalyst, which consists of some combination of Pt, Pd, and Rh (Bond 1991). The converter catalyzes three reactions that result in the production of harmless products:

(1) $\quad 2NOx = 1/2\ N_2 + xO_2$ (NOx reduction)

(2) $\quad 2CO + O_2 = 2CO_2$ (CO oxidation)

(3) $\quad 2C_xH_y + (2x+y/2)O_2 \rightarrow 2xCO_2 + yH_2O$
     (oxidation of unburned fuel)

A combination of physical and chemical degradation of the catalyst is thought to be responsible for the release of PGE aerosols to the roadside environment and beyond (see Figure 2 of Rauch and Morrison 2008).

FIGURE 3 Samples of "platina" recovered from the placer deposits in the Choco district of Colombia. Similar material was described by William Lewis to the Royal Society of London in 1754 and served as the feedstock for the first purification of Pt, Pd, Ir, and Os by Smithson Tennant and William Wollaston. The field of view is 5 cm wide (each nugget is about 3–5 mm in length). Sample is from the mineralogy collection of the Museum National d'Histoire Naturelle (#4.283; Picture D. Brabant, MNHN). PHOTO COURTESY OF JEAN-PIERRE LORAND

FIGURE 4 Front and back faces of the Wollaston Medal presented to Sir William Logan (first director of the Geological Survey of Canada) in 1856. The front of the medal depicts William Wollaston, the benefactor of the award. The medal is cast in palladium, which Wollaston discovered in 1805. The Wollaston Medal is the highest award bestowed by the Geological Society of London. NATURAL RESOURCES CANADA IMAGE NRCAN-4374, USED WITH PERMISSION OF NATURAL RESOURCES CANADA. HER MAJESTY THE QUEEN IN RIGHT OF CANADA

HEALTH AND WELL-BEING FROM THE PGE

From improving our smiles to curing life-threatening diseases, PGE are used in a number of therapies to enhance our health and well-being. For example, prosthetic teeth (bridges and crowns) are typically made of gold alloyed with Pt and/or Pd, which are added to improve strength and stiffness so as to endure the rigors of biting and chewing. Owing to their biocompatibility, high electrical conductance, and resistance to corrosion, Pt and Pt–Os alloy are essential components of implant devices used to treat irregular heartbeat and in the replacement of defective heart valves. Surgeons also make use of Pt as X-ray-opaque guidewires when performing angioplasty. Although osmium tetroxide is highly toxic to living tissue, biomedical researchers have long employed solutions of this compound to fix and stain fatty tissue for electron microscopy. Perhaps one of the most important PGE-based therapeutic materials is the anticancer drug cis-diamminedichoroplatinum(II) or cis-[Pt(NH$_3$)$_2$Cl$_2$],

also known as cisplatin. Although the cisplatin molecule had been known for some time, the discovery of its cancer-fighting properties was by chance. Barnett Rosenberg, a biophysicist at Michigan State University, had set out to examine the effects of electric fields on bacterial growth. Cultures of *E. coli* were immersed in a buffer solution containing ammonium chloride, and Pt was used as the electrode due to its perceived chemical inertness. The specific choice of AC electric field frequency and current were to eliminate electrolysis effects. As described in their original letter to the journal *Nature* (Rosenberg et al. 1965), it was subsequently realized that "both are mistaken ideas which led, via serendipity, to the effects described in this communication." Rosenberg and coworkers observed that the bacteria in cultures subject to the electric field exhibit filamentous growth (FIG. 5A), in contrast to their typical "sausage" shape (FIG. 5B). The effect was not due to growth, but rather to inhibition of cell division, and after further investigation, it was determined that the causative agent was not the electric field, but hydrolysis products of the platinum electrode. Subsequent work showed that several Pt(II) and Pt(IV) compounds exhibit antitumor activity, effectively inhibiting a type of sarcoma and leukemia in mice (Rosenberg et al. 1969). In 1971, cisplatin underwent clinical trials and was determined to be effective against tumors in human subjects, and in 1978, it was approved for treatment of ovarian and testicular cancers. A number of cisplatin analogs have since been developed that show less toxicity and equal or greater antitumor activity.
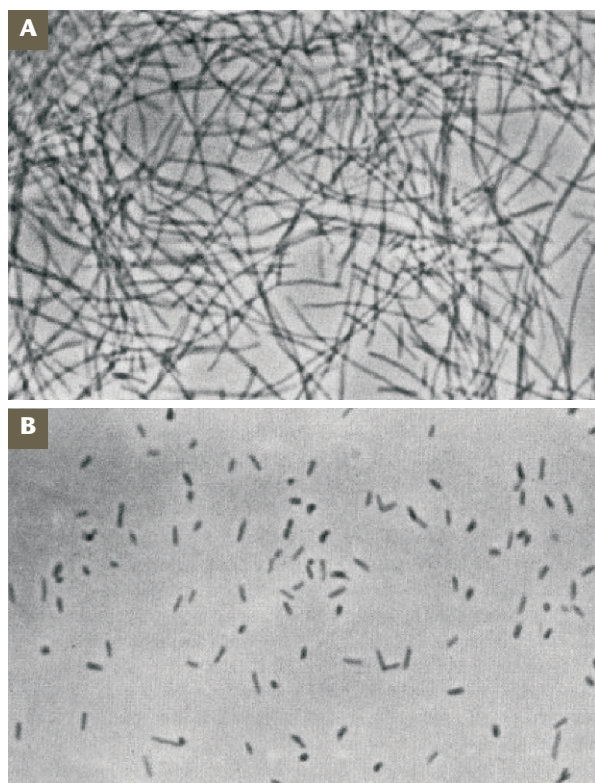
FIGURE 5 Phase contrast photomicrographs of *E. coli* cultured in growth medium containing (**A**) 8 ppm of platinum as the neutral species $[PtCl_4-(NH_3)_2]^0$ and (**B**) less than 6 ppm of platinum as the doubly negative species $[PtCl_6]^{2-}$. Magnified 600x. The image in (**A**) shows the development of filamentous forms, in contrast to the normal sausage shape shown in (**B**), indicating the inhibiting effect of $[PtCl_4-(NH_3)_2]^0$ on cell division, but not on growth. From Rosenberg et al. (1967). COPYRIGHT 1967 BY THE AMERICAN SOCIETY FOR BIOCHEMISTRY AND MOLECULAR BIOLOGY. USED WITH PERMISSION OF AMERICAN SOCIETY FOR BIOCHEMISTRY AND MOLECULAR BIOLOGY IN THE FORMAT MAGAZINE VIA COPYRIGHT CLEARANCE CENTER

THE IMPORTANCE OF PGE ACCESSORY MINERALS

One of the most fundamental, but perhaps least understood, aspects of PGE geochemistry is their distribution in rocks. Knowledge of this has an important bearing on the behavior of these elements during melting and solidification, in turn affecting PGE isotopic systems, as well as mineral beneficiation and ore recovery. Both experiments and studies of natural samples suggest that although trace quantities of Ir, Ru, and Rh can reside in the structures of silicate and oxide minerals (i.e. olivine and chromite), by far the dominant hosts for all the PGE are base-metal sulfides (pyrrhotite, chalcopyrite, and pentlandite) and PGE-bearing "accessory" minerals (PGM; Lorand et al. 2008). Although present in very low modal abundances, the PGM can dominate the whole-rock budget of the PGE they concentrate, especially in the case of refractory mantle samples. This is directly analogous to the role of zircon, apatite, monazite, etc., in controlling the behavior of trace lithophile elements in felsic igneous rocks. There are more than 100 distinct PGM species: some are comprised of PGE only, some occur in combination with Fe, Cu, or Ni, and some are bonded to Group Va and VIa ligands, such as S, As, Sb, and Te (Cabri 2002). Knowledge of intensive variables during PGM formation can be obtained with the appropriate phase-equilibrium and partitioning information, for which there is a growing literature (Makovicky 2002; Andrews and Brenan 2002; Bockrath et al. 2004). In sulfide-saturated igneous rocks, the PGM are likely to form either by exsolution from primary base-metal sulfides as a consequence of cooling, or by enrichment of PGM-forming components during the final stages of differentiation of magmatic sulfide liquid (e.g. Barnes et al. 2006). Although rare, spectacular, relatively large (centimeter-sized), euhedral crystals can be found in some differentiated massive-sulfide bodies (FIG. 6).

A common but somewhat enigmatic petrographic association for the PGM in sulfur-poor ultramafic igneous rocks is their occurrence as inclusions within chromite. Although a wide range of compositions have been documented for chromite-hosted inclusions (Legendre and Augé 1986), typical PGM
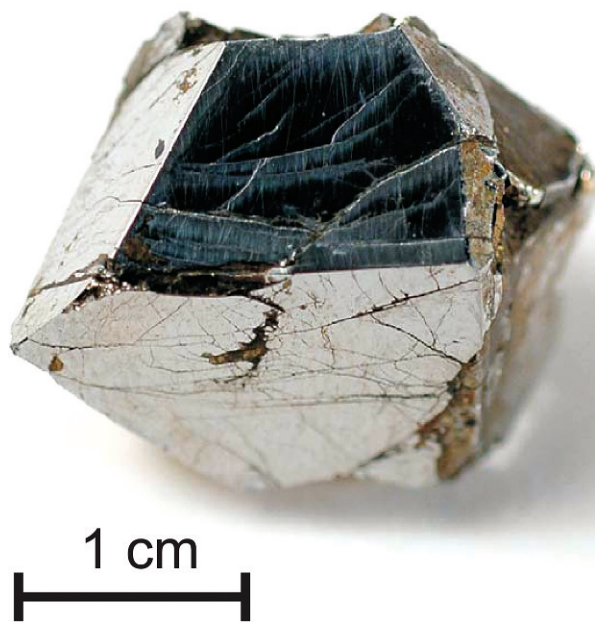
1 cm

FIGURE 6 Single crystal of the mineral sperrylite ($PtAs_2$) from Noril'sk (Russia). The sample is from the mineralogy collection of the Museum National d'Histoire Naturelle (#193.27; picture D. Brabant; MNHN). PHOTO COURTESY OF JEAN-PIERRE LORAND

are isoferroplatinum (Pt_3Fe), osmiridium (*hcp* Os–Ir alloy), and laurite–erlichmanite (RuS_2–OsS_2 solid solution; FIG. 7). Inclusions are generally submillimeter in size but may also occur at the nanometer scale, as inferred using in situ analysis by laser ablation ICP–MS (e.g. Ballhaus and Sylvester 2000). Although the process of PGM formation is not well understood, the presence of primary magmatic minerals included with some PGM suggests both phases formed at high temperature and were entrapped at the time of chromite crystallization. Alternatively, some chromite-hosted PGM could be the product of deposition from a PGE-laden hydromagmatic fluid or the result of desulfidation of pre-existing base-metal sulfides.

Weathering and erosion of PGM-bearing rocks produces PGM placers, which are dominated by alloys. Placer alloys are typically either Pt–Fe or Ru–Ir–Os–Pt; the latter exhibit a compositional gap consistent with the limits of miscibility known from phase-equilibrium experiments (FIG. 8; Cabri et al. 1996). Placer PGM have compositions similar to those found as inclusions in chromite, consistent with studies that have located placer sources in sulfur-poor ultramafic rocks (Hattori and Cabri 1992; Cabri et al. 1996). Of historical significance is that samples of platinum alloy from which the other PGE were originally purified were from placer deposits located in the Chocos district of Colombia and the Ural Mountains of Russia.

FUTURE PROSPECTS

Improved chemical separation and analytical techniques have provided the means to measure the elemental and isotopic composition of the PGE in laboratory and natural samples with unprecedented precision. The wealth of data acquired by these methods has expanded our knowledge of these elements and posed new questions regarding their behavior. As noted by Lorand et al. (2008), estimates of the primitive-mantle concentrations of the PGE are not in complete accord with levels in primitive meteorites, and our understanding of this discrepancy will require fuller knowledge of PGE fractionation processes during mantle differentiation. The distribution and stability of scarce platinum-group minerals may be critical to this assessment. In the context of core formation, Palme (2008) has emphasized that metal–silicate partitioning does not adequately account for the upper-mantle abundances of PGE, supporting a heterogeneous accretion model for Earth evolution. Complete assessment of this model awaits more experiments on the effect of high temperature on metal solubility, and agreement as to the interpretation of metal heterogeneity in experimental run-products. Although PGE ore deposits such as those in the Bushveld Complex in South Africa have been exploited for many years, the debate continues regarding the primary metal-concentration mechanisms. Whereas immiscible sulfide liquids have been shown to be important, both experiments and detailed field observations provide support for the role of hydrothermal solutions in dissolving and transporting the PGE (Mungall and Naldrett 2008). The PGE isotope systems have provided a wealth of insights regarding a range of geochemical processes. Uncertainties still exist, however, concerning the origin of Os isotope anomalies in oceanic basalts (Carlson et al. 2008), in terms of core input or the production of isotopically distinct reservoirs by low-pressure processes. As mentioned previously, the extraction and industrial use of the PGE have accelerated their dispersal in the natural environment. Rauch and Morrison (2008) emphasize that the ecological impact of the PGE is not well known, and there is clear need for further research in this area.
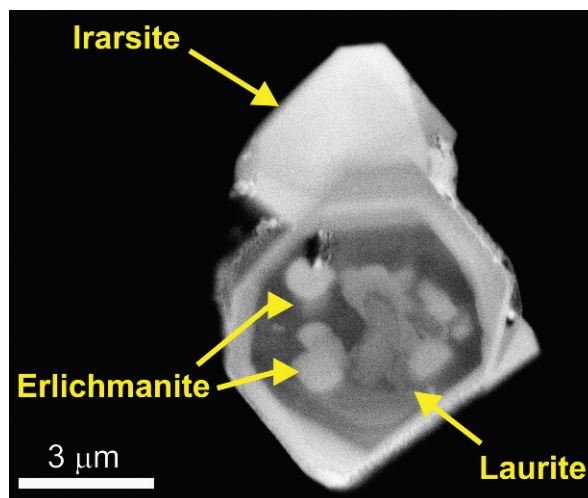
FIGURE 7 Backscattered-electron image depicting an aggregate of platinum-group minerals included in a chromite grain from the Mayarí-Baracoa ophiolite belt of eastern Cuba. The inclusion consists of distinct grains of irarsite (IrAsS) and laurite (RuS_2). The laurite contains a core of Ru-rich erlichmanite (OsS_2) surrounded by a layer of Os-poor laurite grading to Os-rich laurite at the rim. USED WITH PERMISSION FROM SPRINGER SCIENCE+BUSINESS MEDIA: GERVILLA ET AL. (2005; FIG. 4G)
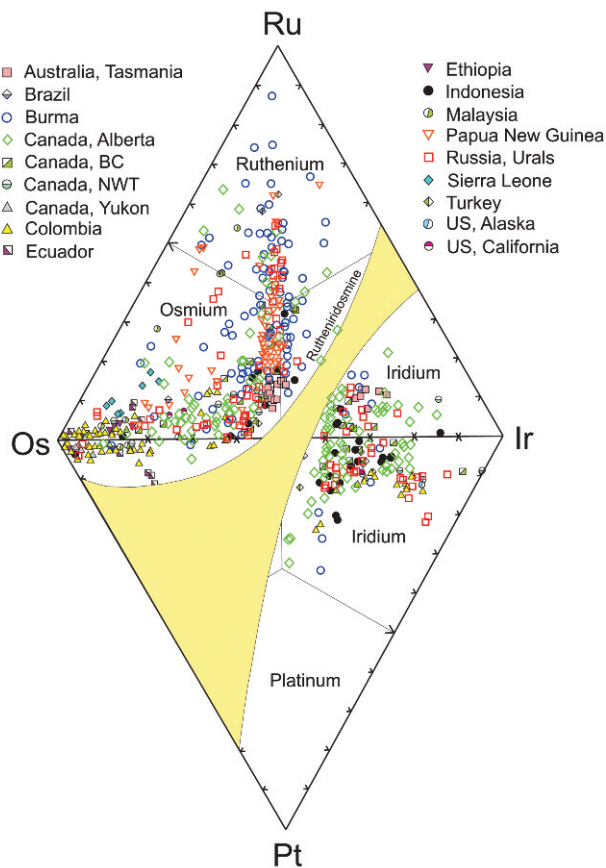
FIGURE 8 The quaternary system Ru–Os–Ir–Pt depicting the composition of platinum-group element alloys from worldwide placer deposits (after Cabri et al. 1996). The minerals in this system are either hexagonal (osmium, ruthenium, rutheniridosmine) or cubic (platinum, iridium). The majority of platinum-group minerals found in placer deposits are Ru–Ir–Os–Pt and Pt–Fe alloys. Rhodium and palladium are typically minor constituents of these phases. The yellow shaded region corresponds to the miscibility gap in the quaternary system, as defined empirically by the alloy compositions, and is consistent with experimental data in the Ru–Ir, Os–Ir and Os–Pt binary systems. Figure from *Exploration and Mining Geology*, volume 5, no. 2; REPRODUCED WITH PERMISSION OF THE CANADIAN INSTITUTE OF MINING, METALLURGY AND PETROLEUM

FOR MORE INFORMATION

The articles in this issue of *Elements* have been written with a specific focus on topics relevant to Earth scientists, but the scope of research related to the PGE is significantly broader. Useful texts that provide synopses of the chemical properties of the PGE are by Cotton (1997) and a compendium of papers edited by Hartley (1991). The reader is referred to *Platinum Metals Review*, published by Johnson Matthey Ltd., for a range of technical and historical information on the PGE. A detailed account of the history of the PGE, including important discoveries and scientific work, can be found in the book *History of Platinum and Its Allied Metals* by Donald McDonald and Leslie B. Hunt (1982). Enjoy!

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