

# Applications of PGE Radioisotope Systems in Geo- and Cosmochemistry



Photomicrograph of diamond with Fe-sulfide inclusion

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**The platinum-group elements contain three radioisotope systems that have been used in many and varied ways in geo- and cosmochemistry. Unique chronological applications include dating the formation of such diverse materials as sulfides, gold, organic-rich sediments, iron meteorites, and sulfide inclusions in diamonds. These systems also serve as isotope tracers for processes such as continental erosion, the deposition of extraterrestrial materials on Earth's surface, crust–mantle differentiation, recycling of subducted crust into the mantle, core–mantle exchange, and volatile-element depletion of planets and planetesimals. Although these systems have been in use for only a short time, the discoveries they have provided bode well for their incorporation as staples in the geochemical toolbox.**

KEYWORDS: isotopes, PGE, Re–Os, Pd–Ag, chronology, crust–mantle differentiation

## INTRODUCTION

The utility of the platinum-group elements (PGE) as geochemical tools is enhanced by the three radioisotope decay systems that they contain. Osmium is the daughter element in two decay systems, the very long-lived  $^{190}\text{Pt}$  to  $^{186}\text{Os}$  alpha-decay (half-life =  $4.5 \times 10^{11}$  y) and the more widely used beta-decay of  $^{187}\text{Re}$  to  $^{187}\text{Os}$  (half-life =  $4.16 \times 10^{10}$  y). In addition, the now-extinct isotope  $^{107}\text{Pd}$  decays to  $^{107}\text{Ag}$  (half-life =  $6.5 \times 10^6$  y) (TABLE 1). A key feature of these systems is that they track the unique chemical behavior of the PGE in the natural environment and thus provide information on natural processes to which the more commonly applied, lithophile-element-based radioisotope systems are not sensitive. All the elements involved show strong preference for metal and/or sulfide compared to silicate (Palme 2008 this issue; Lorand et al. 2008 this issue). Unlike any other element in a radioisotope system, osmium is a compatible element during melting in the mantle (stays in the residue). As a result, most magmas, and the crust formed from such magmas, have high Re/Os ratios compared to mantle rocks. With time, this results in distinctively radiogenic Os in the crust that serves both as a sensitive tracer of crust–mantle differentiation and the eventual transport of crustal materials into the marine environment through weathering and erosion.

Of these systems, Re–Os has seen the most use by far (Shirey and Walker 1998; Carlson 2005). Applications of Pt–Os decay are limited, but this system has been used to date Pt-rich ores and to address the fundamental question of

whether there is chemical exchange between Earth's mantle and core. The Pd–Ag system is being used to define the chronology of iron meteorite formation and to investigate the mechanism and timing of the volatile-element depletion that distinguishes Earth, and many meteorites, from the solar composition. The key to the explosion in applications of the PGE-based radioisotope systems is the improvement of chemical separation and mass spectrometric techniques (Reisberg and Meisel 2002). These techniques now provide sufficient sensitivity to analyze elements present at the  $10^{-9}$  to  $10^{-12}$  g/g range in many rock

types, and they are precise enough to resolve very small differences in  $^{186}\text{Os}$  and  $^{107}\text{Ag}$  created by Pt and Pd decay, respectively.

## PGE-BASED CHRONOMETRY

The most obvious use of radioisotope decay schemes is to tell geologic time. For this purpose, the remarkable success of PGE-based systems is based on their application to materials that cannot be dated using other systems.

### Ore Genesis

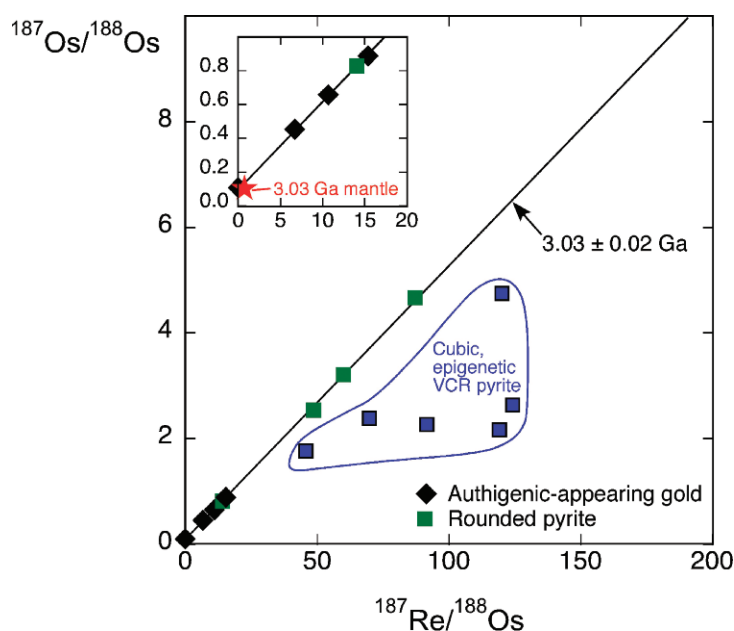
Unlike lithophile-element-based radioisotope systems (e.g. Rb–Sr, Sm–Nd), the PGE-based systems can be applied directly to study the origin of ore minerals rather than associated silicate phases. An early use of the Re–Os system was in dating molybdenite ( $\text{MoS}_2$ ) formation. Molybdenite is so Re rich and Os poor that Os in old molybdenite crystals consists almost exclusively of  $^{187}\text{Os}$ . Extensive recent development of this technique now allows excellent age precisions limited only by the rarity and paragenesis of molybdenite (Stein et al. 2001). At the other end of the range of Re/Os ratios, chromite has proven to be a particularly important mineral for Re–Os studies where its very low Re/Os ratio essentially “freezes in” the Os isotope composition of the magma from which it crystallizes, providing both a model age and petrogenetic information. This utility is enhanced by its resistance to alteration, high closure temperature, and generally high (many ppb) Os content.

Another ore-mineral group that has found extensive use in Re–Os dating is Fe( $\pm$ Ni $\pm$ Cu) sulfide. Sulfides have a high affinity for both Re and Os and can have high Re/Os ratios. Sulfides form the basis for numerous studies regarding the timing and petrogenesis of nickel, copper, gold, and lead ores in a variety of environments (e.g. magmatic, hydrothermal, and sedimentary; Walker et al. 1991; Morelli et al. 2004; Bierlein et al. 2006). One interesting application has

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been to reveal the source of gold in the world's largest gold deposit, the Witwatersrand basin of South Africa (Fig. 1). Models that suggest a detrital origin, precipitation from hydrothermal solution, or some combination of both have been debated for decades. Re–Os dating applied directly to gold from the Vaal Reef gold horizon produced an isochron age of  $3033 \pm 21$  Ma with an initial  $^{187}\text{Os}/^{188}\text{Os}$  ratio essentially identical to the mantle value at that time (Kirk et al. 2002). These results leave little doubt that the Os in these gold ores originated from the weathering of mantle-derived, mafic to ultramafic rocks in surrounding Mesoproterozoic terranes. The unusually high Os concentrations in the Vaal Reef gold, however, have been variably interpreted as supporting its derivation from high-degree melts of the mantle, such as komatiites, or indicating that hydrothermal gold grew around detrital PGE-rich alloy grains, weathered from the komatiites, that served only as nucleation centers for gold deposition. The definitive study to resolve these options has not yet been done.



**FIGURE 1** Re–Os isochron diagram for gold and pyrite from the 2.8–2.9 Ga Witwatersrand Supergroup, South Africa, redrawn from the data and information in the study by Kirk et al. (2002). Vaal Reef gold and rounded pyrite interpreted to be detrital produce an excellent  $3.03 \pm 0.02$  Ga isochron with an initial  $^{187}\text{Os}/^{188}\text{Os}$  ratio identical to the mantle value at this time (inset). Because both age constraints are older than the  $<2.9$  Ga age of the conglomerates, they confirm the detrital nature of the gold and suggest that the provenance of the conglomerate included magmatic rocks in a nearby 3 Ga greenstone belt. Epigenetic, cubic-morphology pyrite in the hydrothermally altered Ventersdorp Contact Reef (VCR) shows open-system behavior of the Re–Os system.

## Organic-Rich Sediments

A peculiar aspect of the PGE is their affinity for organic compounds in sediments such as black shales, coal, oil host rocks, and tar sands. Recent work has focused on leaching techniques that allow the isolation of the detrital versus hydrogenous components of Os found in the sediments. When the shales remain closed systems after deposition, such studies yield excellent Re–Os isochrons that provide both the age of sediment deposition and the Os isotope composition of the water mass from which they were deposited (e.g. Turgeon et al. 2007). This technique has been particularly useful for obtaining an absolute timescale for sediment stratigraphy, global glaciation events, and the rise of oxygen in the atmosphere (Bekker et al. 2004).

## Diamond Dating and Petrogenesis

The treasured gem properties of diamond stem from its crystal structure, but this structure effectively excludes radioactive isotopes suitable for direct dating of diamond formation. Diamonds, however, sometimes contain inclusions that provide both age and petrogenetic information. The high (ppm to ppb) Os concentrations in typical sulfide inclusions in diamond allow the Re–Os system to be applied to dating individual grains (e.g. Pearson et al. 1998; Fig. 2). The current “champion” among the oldest diamonds provided a  $3.52 \pm 0.17$  Ga isochron defined by 11 sulfides separated from 5 diamonds from the Panda kimberlite of the Slave Province, Canada (Fig. 2; Westerlund et al. 2006). The initial  $^{187}\text{Os}/^{188}\text{Os}$  ratio defined by this isochron is about 6% greater than expected for the mantle at that time. This likely implies diamond formation from fluids rising from an ancient subducting crustal plate into an overlying section of mantle. But not all diamonds are Archean in age. Indeed, there is good evidence from southern African diamond localities that the age and chemical properties of diamond correlate with the general physical features, for example, seismic velocities (Shirey et al. 2002) of the subcontinental mantle inherited during their Proterozoic crystallization. Re–Os examination of sulfide inclusions, particularly when combined with carbon and nitrogen isotope studies of the host diamond, offers a promising avenue to study the history of carbon-rich fluid migration at depths in excess of 150 km in the mantle.

## TRACERS OF EARTH EVOLUTION

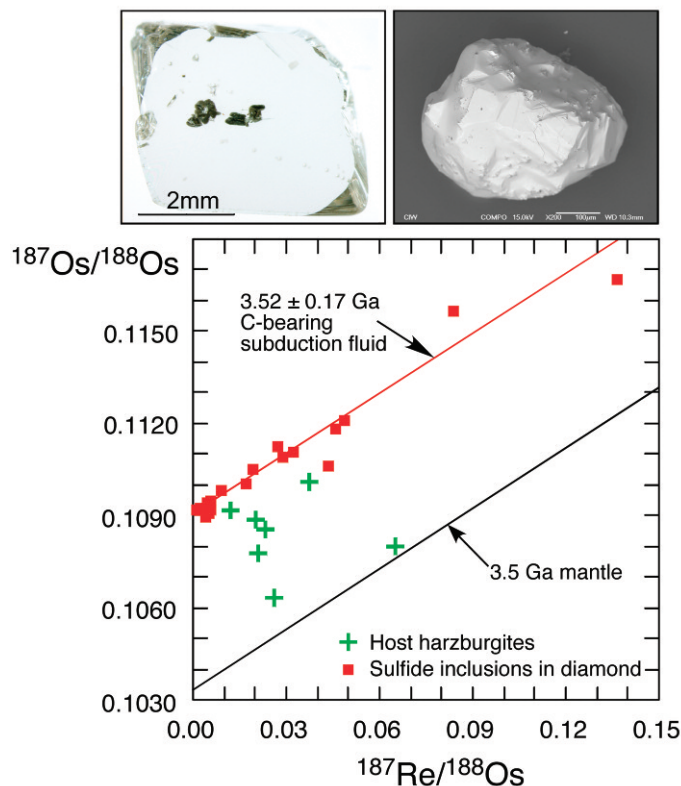
### The Marine Os Record

The Re–Os system has been used extensively to track the evolution of Earth's surface through the marine record of Os isotope variation (Pegram et al. 1992). Weathering of crustal rocks contributes Os with a very high  $^{187}\text{Os}/^{188}\text{Os}$  ratio to the oceans. Whereas most mantle-derived and extra-terrestrial rocks have  $^{187}\text{Os}/^{188}\text{Os}$  ratios near 0.13, modern ocean water has a  $^{187}\text{Os}/^{188}\text{Os}$  ratio closer to 1.0 (Levasseur et al. 1998). An important aspect of the marine record of Os

**TABLE 1** ISOTOPIC COMPOSITION OF PGE-BASED RADIOISOTOPE SYSTEMS

Isotope	Atomic %	Isotope	Atomic %	Isotope	Atomic %	Isotope	Atomic %	Isotope	Atomic %
$^{102}\text{Pd}$	1.02			$^{184}\text{Os}$	0.02				
$^{104}\text{Pd}$	11.1					$^{185}\text{Re}$	37.4		
$^{105}\text{Pd}$	22.3			$^{186}\text{Os}$	1.59			$^{190}\text{Pt}$	0.01
$^{106}\text{Pd}$	27.3			$^{187}\text{Os}$	1.51	$^{187}\text{Re}$	62.6	$^{192}\text{Pt}$	0.79
		$^{107}\text{Ag}$	51.8	$^{188}\text{Os}$	13.3			$^{194}\text{Pt}$	32.9
$^{108}\text{Pd}$	26.5			$^{189}\text{Os}$	16.2			$^{195}\text{Pt}$	33.8
		$^{109}\text{Ag}$	48.2	$^{190}\text{Os}$	26.4			$^{196}\text{Pt}$	25.3
$^{110}\text{Pd}$	11.7			$^{192}\text{Os}$	41.0			$^{198}\text{Pt}$	7.2

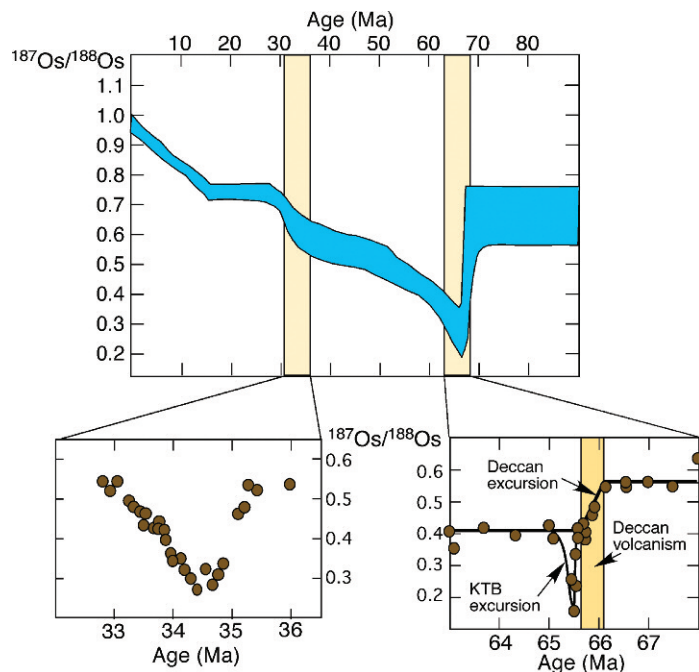
Data from Emsley (1992) except for Os from Shirey and Walker (1998)



**FIGURE 2** Re–Os isochron diagram for sulfide inclusions in diamonds and putative host harzburgites from the Panda kimberlite pipe, Slave craton, NWT, Canada (after Westerlund et al. 2006). The sulfide inclusions (red squares) regress to an age of  $3.52 \pm 0.17$  Ga (with 4 additional inclusions off scale) and have an elevated initial  $^{187}\text{Os}/^{188}\text{Os}$  isotope composition compared to a 3.5 Ga mantle (black line). With one exception, harzburgites that host the diamonds (green crosses) have  $^{187}\text{Os}/^{188}\text{Os}$  ratios above primitive mantle values, but less so than the diamonds. The upper left panel shows a polished Panda diamond plate with 4 inclusions in their “rosette” fracture system. Shown in the upper right is a typical scanning electron micrograph of a released inclusion prior to dissolution, chemical separation of the Re and Os, and mass spectrometry.

isotope variation is that the residence time of Os in seawater is short (35,000 years; Lévassieur et al. 1999); hence one can obtain high chronological resolution in the marine Os record contained in sediments to the point of being able to track glacial–interglacial variations in continental input to the oceans (Fig. 3; Oxburgh et al. 2007). Between about 15 Ma and the present and again from 40 to 25 Ma, the  $^{187}\text{Os}/^{188}\text{Os}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of seawater increased. These correlated variations presumably reflect periods of high weathering of the continental crust (Peucker-Ehrenbrink et al. 1995). The Sr and Os isotope compositions of seawater, however, do not always covary. Between 65 and 40 Ma, seawater Os became more radiogenic while the Sr isotope composition changed little. This likely reflects the fact that specific rock types involved in continental weathering can differentially influence the Os and Sr isotope compositions of continental runoff. For example, weathering of old organic-rich sediments can provide large quantities of highly radiogenic Os, but minimal Sr, to the oceans. In these situations, Os isotope variation in marine sediments could serve as an independent monitor of carbon recycling from the continents to the oceans (Pegram et al. 1992).

The Os isotope composition of the ocean shows a strong downward excursion at the Cretaceous–Tertiary boundary that is not accompanied by much variation in the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio. This strong swing is attributed to a combination of



**FIGURE 3** Os isotope data tracking the composition of seawater Os over the last 90 My. The upper figure shows the general increase in the  $^{187}\text{Os}/^{188}\text{Os}$  ratio following the steep decline near the Cretaceous–Tertiary boundary (Peucker-Ehrenbrink et al. 1995). The lower figures show high-resolution data for smaller time slices illustrating the ability of Os to record fine-scale variations in inputs into the ocean. Near the K–T boundary (KTB), this includes contributions of mantle Os attributed to eruption of the Deccan flood basalts and extraterrestrial Os added by the K–T impactor (Ravizza and Peucker-Ehrenbrink 2003). In the Oligocene (lower-left figure), the rapid rise in the  $^{187}\text{Os}/^{188}\text{Os}$  ratio is attributed to an increase in continental weathering after removal of glacial cover exposed fine-grained glacial sediments (Dalai et al. 2006).

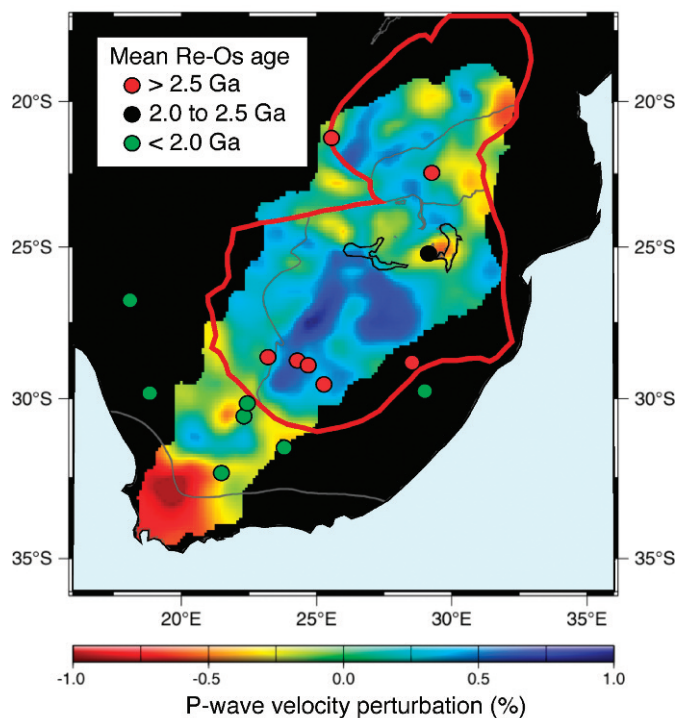
input of mantle Os from eruption of the Deccan flood basalts and input of extraterrestrial Os from the K–T impactor (Fig. 3). The big  $^{187}\text{Os}/^{188}\text{Os}$  excursion precisely at the K–T boundary reflects a nearly unique sensitivity of the PGE that allows detection of extraterrestrial contributions to the Earth. Most meteorites have PGE concentrations  $\sim 10^3$  times greater than those of mantle rocks and  $\sim 10^5$  times greater than those of most crustal rocks, but have PGE ratios and Os isotope compositions similar to those of Earth’s mantle (Palme 2008). Consequently, even small additions of extraterrestrial material will significantly reduce the  $^{187}\text{Os}/^{188}\text{Os}$  ratio and introduce concentration spikes in Ir in slowly accumulating sediments. This feature has been used to obtain constraints on the mass influx of extraterrestrial material to Earth and the variation in time of this influx (Dalai et al. 2006). It also been used to detect the contribution, and even the type (Koeberl and Shirey 1997) and size (Paquay et al. 2008), of meteorites involved in various terrestrial impacts.

### Dating the Age of Mantle Differentiation

Radiogenic isotope studies of mantle differentiation traditionally involve elements (Sr, Nd, Hf, Pb) that strongly prefer melt over residual solid. Therefore, mantle residues after melt extraction are difficult to study because they have very low concentrations of these elements. Furthermore, due to their low concentrations, these systems are extremely sensitive to overprinting should new melts migrate through older melt-depleted sections of the mantle. Although the Re–Os system is not completely insensitive to this type of metasomatic overprinting (e.g. Griffin et al. 2004), it has

proven uniquely suited to examining the history of melt extraction from the mantle (Walker et al. 1989). This is important because melt extraction changes the physical properties of mantle peridotite, lowering the residue's density by increasing its Mg to Fe ratio and reducing its Al concentration, and hence abundance of the dense aluminous phase garnet. Melt extraction also removes water and radioactive elements like U, Th, and K in the melt, leaving a residue that is of higher viscosity and that will grow colder than fertile mantle. Thus the ability to date the time of melt extraction from various portions of the mantle provides temporal information on a process that fundamentally alters the physical characteristics of Earth's mantle.

Perhaps the most definitive result from dating mantle differentiation with the Re–Os system has been to show that many sections of continental crust are underlain by mantle that suffered melt extraction at times approaching the age of the oldest overlying crust (Fig. 4). This result shows not only that continental crust formation is closely coupled to melt depletion of the underlying mantle, but also that the long-term survival of continental crust at Earth's surface may be due to the presence of this underlying thick layer of cold, rigid, buoyant mantle. Dating mantle samples using the Re–Os system has now been applied throughout the world to provide, in essence, a 3D map of continental ter-



**FIGURE 4** Overlay of P-wave seismic velocity variations at a depth of 150 km and average Re–Os model ages for mantle samples from kimberlites distributed across southern Africa. The points show kimberlites containing mantle samples from depths of up to 200 km. The points are color coded according to the average Re–Os age for all the mantle samples studied from each individual kimberlite. The red line outlines areas of Archean crust. Within the Archean crustal section, most mantle samples give Archean ages and most diamond-bearing kimberlites are confined to the blue areas of fastest seismic velocities. The fields outlined in black show the surface outcrop of the 2.05 Ga Bushveld and Molopo Farms igneous intrusions. The one kimberlite erupted near this area (Premier kimberlite, black dot) contains mantle samples that predominantly give Re–Os ages near 2 Ga. The correlation of younger mantle ages at Premier with slower seismic velocities suggests that the Bushveld event substantially modified the mantle under this part of the ancient southern African crust. Off the Archean craton, mantle samples give only Proterozoic ages, consistent with the age of the overlying crust. The light grey lines show boundaries between crustal terranes of different ages. Tomography is from Fouch et al. (2004), and Re–Os data are summarized in Carlson et al. (2005).

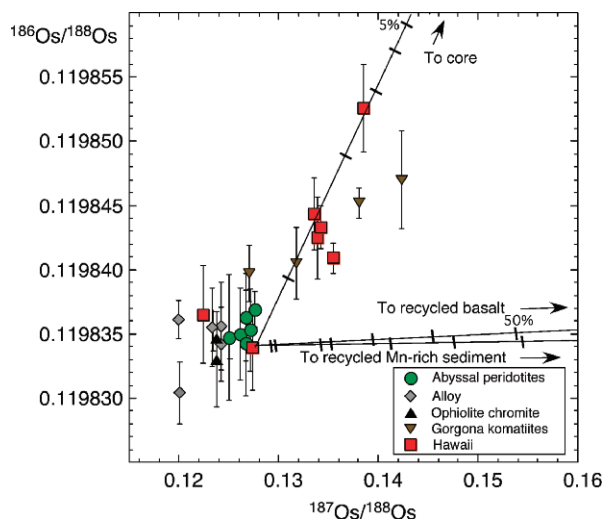
ranes showing where crust and mantle have similar ages, where young crust has been thrust over older mantle, and where old sections of mantle have detached from old crust, most likely as a result of major tectonic events (Carlson et al. 2005). The unique signatures of unradiogenic Os and Nd coupled with radiogenic Sr also have been used to show that old sections of melt-depleted subcontinental mantle are a particularly important source of the magmas that host igneous chromium and PGE deposits (e.g. Marques et al. 2003; Mungall and Naldrett 2008 this issue).

Widely dispersed, often intragranular, micron- to submicron-sized grains of PGE-rich minerals such as Fe–Ni sulfides, Ru–Os ± Ir sulfides, and Pt–Ir ± Os alloys contain the majority of the PGE in the mantle (Lorand et al. 2008). Although diffusion coefficients of the PGE through base-metal sulfides are quite high (Brenan et al. 2000), measurements of discrete PGE-rich phases in mantle rocks often show wide ranges in Os isotope composition (Meibom et al. 2002). While some of this isotopic variation may be due to precipitation from recent infiltrating melts, some of it must be long-lived. How can such isotopic heterogeneity survive for billions of years in the mantle when PGE diffusion is so fast? The likely answer is that the PGE are concentrated into discrete grains that are sufficiently separated from one another that diffusion over geologic timescales is ineffective in erasing the distinct differentiation history recorded by the discrete grains. As a result, sections of the mantle that were only recently removed from the actively convecting mantle can retain old melt-depletion ages (Parkinson et al. 1998). This result reflects an active Earth where any given portion of the convecting mantle may have passed through sites of differentiation (e.g. ocean ridges, intraplate hot spots, or the mantle wedge in convergent margins) several times over the history of the Earth. Indeed, recent Os isotope results for PGE-alloy grains from ophiolites of various ages suggest that the Os isotope composition of the mantle records “pulses” of mantle depletion attributable to discrete continental crust extraction events (Pearson et al. 2007).

### Crust–Mantle or Core–Mantle Exchange

Should some portion of Earth's crust be reintroduced into the mantle, for example by subduction, its presence will increase the  $^{187}\text{Os}/^{188}\text{Os}$  ratio of the mixture because of the crust's very high Re/Os and  $^{187}\text{Os}/^{188}\text{Os}$  ratios. Indeed, many intraplate ocean island basalts have more radiogenic Os than expected for mantle-derived melts, consistent with the contribution of recycled crustal components in the mantle sources of the lavas (e.g. Reisberg et al. 1993). Because of the long half-life and low natural abundance of  $^{190}\text{Pt}$ , the  $^{186}\text{Os}/^{188}\text{Os}$  ratio of this subducted crust will be only slightly higher than that of the mantle and hence will cause minimal change to the  $^{186}\text{Os}/^{188}\text{Os}$  ratio of the mantle (Fig. 5). Some hot-spot-related magmas, however, show a steep correlation between  $^{186}\text{Os}/^{188}\text{Os}$  and  $^{187}\text{Os}/^{188}\text{Os}$  (e.g. Brandon and Walker 2005). A suggested explanation for this correlation is that these magmas were derived from a section of mantle that had undergone chemical exchange with the core.

The PGE will be present in the iron metal of Earth's core at concentrations some thousand times higher than their abundance in the silicate Earth (Palme 2008). Models for core differentiation, based on iron meteorite analogs, suggest that the liquid of the outer core will evolve to high Re/Os and Pt/Os ratios. Although these ratios will be nowhere near as high as in crustal rocks, the high Os concentration in core metal will impose both the  $^{186}\text{Os}$  and  $^{187}\text{Os}$  characteristics of the core on a core–mantle mixture, even at very low percentages of core in the mixture (Fig. 5). A core–mantle interaction explanation for the  $^{186}\text{Os}$ – $^{187}\text{Os}$  correlation,



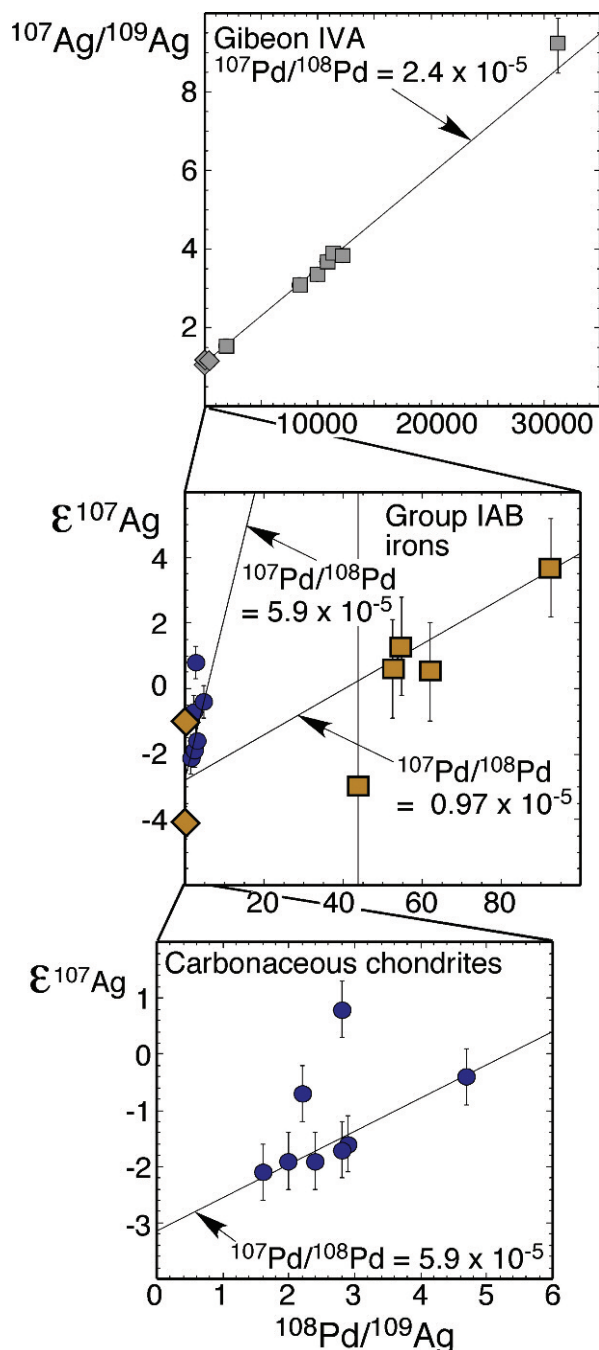
**FIGURE 5** Coupled  $^{186}\text{Os}$ – $^{187}\text{Os}$  isotope variation in direct samples of the mantle (abyssal peridotites and PGE-alloys and chromites from ophiolites) and volcanic rocks believed to originate by melting of plumes rising from the core–mantle boundary. Although crustal rocks (e.g. basalt) and various types of sediment have high Re/Os and Pt/Os ratios, their low Os concentrations coupled with only small ingrowth of  $^{186}\text{Os}$  due to  $^{190}\text{Pt}$  decay lead to nearly horizontal mixing lines with mantle peridotite on this diagram. In contrast, due to the very high concentrations of Os in the core, even a small addition of core material to the mantle will shift the Os isotope composition of the mixture towards the core component. The lines on the diagram show mixing trajectories expected for fertile mantle peridotite mixed with two types of crustal rocks (tick marks give 10% by mass increments of crustal rock in the mixture) and outer core (tick marks show 1% increments in core addition). The mixing lines were constructed using the end member parameters given in Carlson (2005), with data sources summarized in Carlson (2005) and Brandon and Walker (2005).

however, is not universally accepted. Alternatives include (1) the recycling of unusual, low-abundance sediment types that have enough Os to affect a sediment–mantle mixture (Scherstén et al. 2004); (2) the formation of discrete PGE-rich phases in the mantle that can effectively separate Pt and Re from Os; and (3) the recycling of eclogite with a sufficiently high Pt/Os ratio (Luguet et al. 2008) to produce the necessary isotopic differences. The controversy over the correct interpretation of the  $^{186}\text{Os}$ – $^{187}\text{Os}$  correlation is likely to remain for some time, but its resolution will help address the fundamental issue of whether there is chemical exchange between Earth’s core and mantle.

## METAL–SILICATE FRACTIONATION AND THE TIMING OF CORE FORMATION

### Core Formation and the Thermal History of Planetesimals

Due to the strongly siderophile nature of the PGE and Re, their radioisotope decay schemes provide one of the few avenues available for determining the timescale of formation of the various iron-metal-rich meteorites. Several excellent Re–Os isochrons suggest age differences in the range of tens of millions of years between the various groups of iron meteorites (Smoliar et al. 1996). Although the age range defined by Re–Os isochrons is robust, the absolute ages are dependent on the value used for the  $^{187}\text{Re}$  decay constant because the currently used decay constant was calculated from an extremely well-defined Re–Os isochron for the group IIIA iron meteorites, by assuming that this meteorite formed just shortly after the solar system, even though no other precise radiometric age for these meteorites exists (Smoliar et al. 1996).



**FIGURE 6** Pd–Ag isochrons from various classes of meteorites. For extinct radioisotope systems, isochrons give not the age of the sample, but the abundance ratio of the extinct isotope at the time the isochron relationship was established (e.g. the  $^{107}\text{Pd}/^{108}\text{Pd}$  ratio). The higher this ratio is, the older the sample, with the ratio decreasing by a factor of 2 every 6.5 My, the half-life of  $^{107}\text{Pd}$ . The top panel shows the results for the volatile-depleted Group IVA iron meteorite Gibeon (Chen and Wasserburg 1990). Here the very high Pd/Ag ratios (x-axis) have created a wide range in  $^{107}\text{Ag}/^{109}\text{Ag}$  ratios between metal (squares) and sulfides (diamonds). At much lower Pd/Ag ratios, and consequently much smaller variation in Ag isotope composition (now expressed as  $\epsilon^{107}\text{Ag}$ , i.e. the parts in 10,000 difference between  $^{107}\text{Ag}/^{109}\text{Ag}$  in the sample compared to that in a terrestrial Ag standard), the middle panel shows that the Group IAB iron meteorites Toluca and Canyon Diablo have correlated Pd/Ag ratios and Ag isotope compositions in metal (squares), but not in sulfides (diamonds). The middle panel also shows that MC–ICP–MS analyses are much more precise than the one thermal ionization analysis shown (Chen and Wasserburg 1990), whose error bars extend off the diagram. The lower panel shows that 6 out of 8 carbonaceous chondrites (also shown in the middle panel) lie on a Pd/Ag versus Ag isotope regression line with a slope of  $5.9 \times 10^{-5}$ , the highest value yet seen for any solar system material. Data sources include Chen and Wasserburg (1990) and Schönbachler et al. (2008) and references therein.

The Pd–Ag system also can be used to date iron meteorites, but its ability to do so is in part determined by the fact that Ag is a moderately volatile element while Pd, though among the more volatile of the PGE (Palme 2008), is more refractory than Ag. As a result, some groups of volatile-depleted iron meteorites have Pd/Ag ratios over 100,000, compared to a solar Pd/Ag ratio of about 3, leading to  $^{107}\text{Ag}/^{109}\text{Ag}$  ratios above 9, compared to a solar value of 1.079 (Chen and Wasserburg 1996). This huge range in Ag isotope compositions was critical in the discovery that  $^{107}\text{Pd}$  existed in the early solar system (e.g. Kelly and Wasserburg 1978) because the technique used for Ag isotope measurements (thermal ionization mass spectrometry) was limited in precision to a few per mil. Multicollector ICP analysis improves Ag isotope precision by a factor of ~20 (Fig. 6), which now allows this system to be applied even to meteorites with low Pd/Ag ratios. Even the most volatile-rich meteorites, the carbonaceous chondrites, provide enough variation in Pd/Ag and  $^{107}\text{Ag}/^{109}\text{Ag}$  ratios to define a correlation corresponding to an initial  $^{107}\text{Pd}/^{108}\text{Pd}$  value of  $5.9 \pm 2.2 \times 10^{-5}$  (Fig. 6; Schönbächler et al. 2008).

Given the initial abundance of  $^{107}\text{Pd}$  determined by the Pd–Ag isochron for carbonaceous chondrites, a variety of iron meteorites define Pd–Ag ages that range from 8.5 to 19.5 My after solar system formation (Schönbächler et al. 2008). These ages are much greater than the ca. 1 My metal–silicate separation ages inferred from Hf–W systematics of iron meteorites (Markowski et al. 2006), but they

date different events: Hf–W dates the time of metal–silicate separation on the parent planetesimal and Pd–Ag the time of crystallization of the planetesimal core.

## CONCLUSION

Over the last 20 years, the Re–Os system has made the transition from a novel technique undergoing development in only a few laboratories to an established tool of isotope geochemistry. Simplification of chemical separation and mass spectrometric procedures over this time period has opened the system to general use and to a much wider, and still expanding, range of applications. Pt–Os and Pd–Ag still require elaborate measurement procedures, but even the applications of these systems are expanding dramatically. These three radioisotope systems take advantage of the unique chemical characteristics of the PGE to open many new avenues of research that are not accessible in conventional isotopic studies. Given the youth of the application of these systems, the expectation is high for continued and expanded novel contributions to our understanding of a wide variety of fundamental problems in the Earth and planetary sciences.

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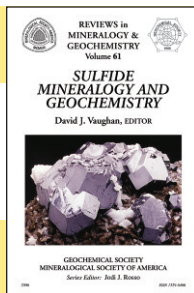
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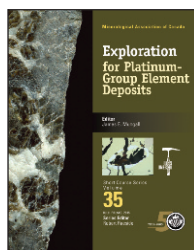


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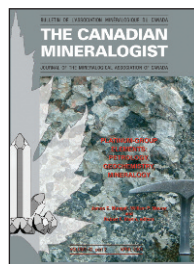
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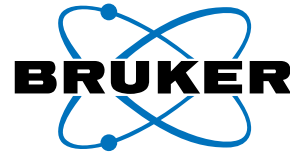
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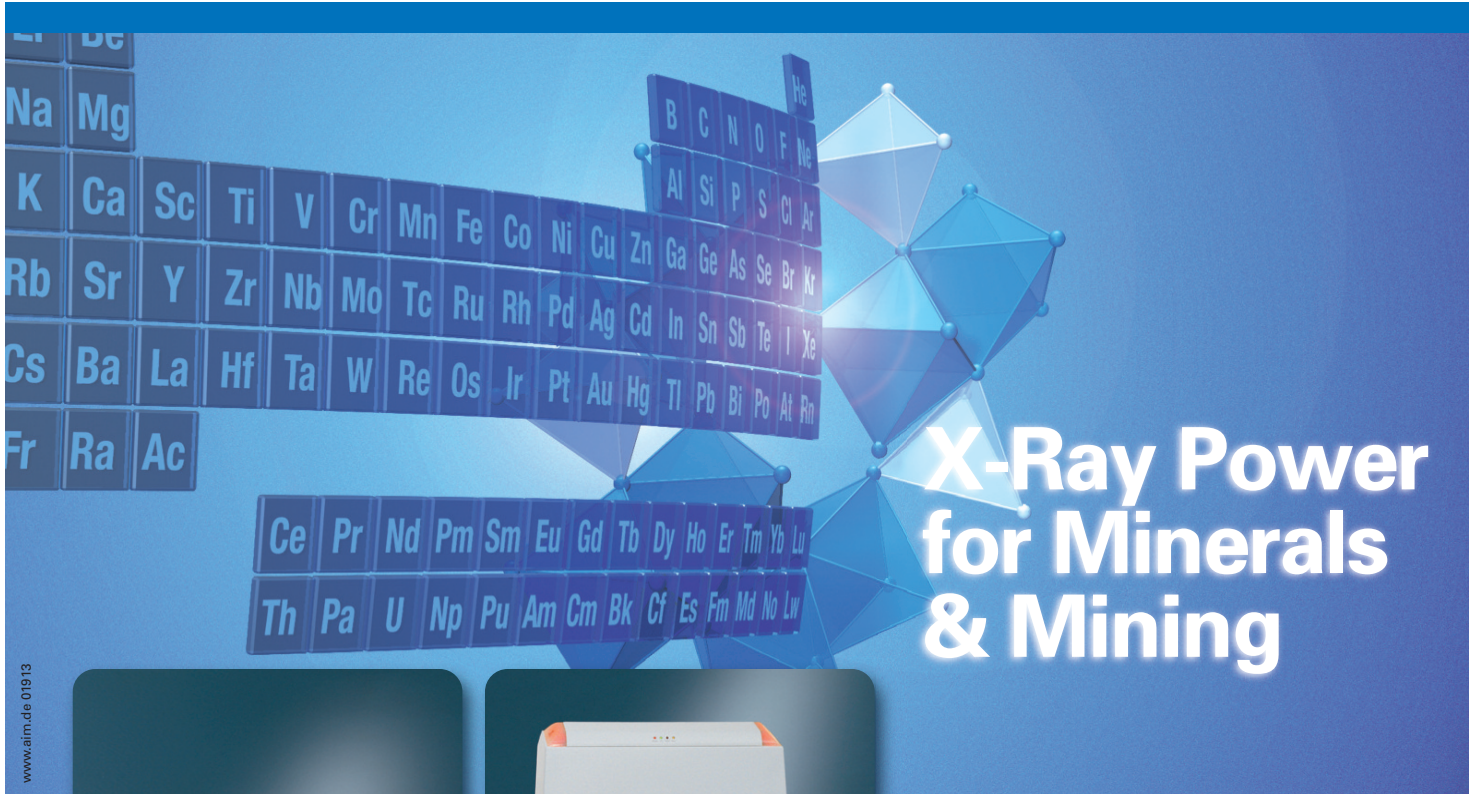
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