PLATINUM GROUP ELEMENTS AND THEIR ISOTOPES IN THE OCEAN

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doi:10.1006/rwos.2001.0286

Introduction

The platinum group elements (PGEs) include three second-series transition metals, ruthenium (Ru), rhodium (Rh) palladium (Pd), and three third-series transition metals, osmium (Os), iridium (Ir) and platinum (Pt). The marine chemistry of this group of elements is the least understood and most poorly documented among the many elements in the periodic table. During the 1970s and 1980s when the attention of the marine chemistry community was focused on characterizing the distribution of all the elements in the ocean, direct measurement of the PGEs in sea water was, for the most part, beyond the reach of available analytical methods. Indeed, the most important attribute that links the marine chemistry of all the PGEs is their very low concentration in sea water. This group of metals accounts for 6 of the 10 least abundant elements in sea water.

This article has three objectives. First, to explain how the dissolved inventories of PGEs in the ocean are maintained at such low concentrations relative to most other elements. Second, to review the current status of our knowledge regarding the vertical distribution of these metals in the oceanic water column. Third, to present a brief overview of areas of marine PGE research that are the focus present research activity, and are likely to motivate future investigation. These areas are (1) sea water Os isotope geochemistry; (2) Ir and the other PGEs as tracers of extraterrestrial material in marine sediments; and (3) anthropogenic release of PGEs to the marine environment.

The Apparent Rarity of the PGEs in Sea Water

The underlying reason for the very low concentrations of all the PGEs in sea water has little to do with the aqueous chemistry of these elements. Rather it is the chemical partitioning of these elements within the deep earth that explains their relative scarcity in the sea water (**Table 1**). Comparison of the PGE content of meteoritic material, believed to represent the primordial material that constituted the undifferentiated earth, to ultramafic rocks, believed to be representative of the deep silicate earth, reveals a nearly uniform 100-fold depletion of the PGEs in the deep silicate earth. This depletion indicates that roughly 99% of the whole earth PGE inventory is sequestered within the earth's metallic core. Further comparison of the PGE concentrations of ultramafic rocks to estimated PGE concentrations of upper crustal rocks shows an additional more variable depletion of the PGEs in rocks exposed at the earth's surface relative to the deep silicate earth. This concentration contrast results from the fact that the PGEs are retained in the solid residue when the deep earth is melted to form the earth's crust. The net effect of the strong affinity of the PGEs for phases that reside in the deep earth is a strong depletion of the PGEs in the rocks typically exposed at the earth's surface. In simplest terms the concentrations of the PGEs in sea water are low compared

Table 1 Representative PGE concentrations in important earth reservoirs and their ratios

	Ru	*Rh*	*Pd*	*Os*	*Ir*	*Pt*
Chondrites (ppb)^{a}	710	130	550	490	455	1010
Silicate earth (ppb)^{b}	5	0.9	3.9	3.4	3.2	7.1
Upper crust (ppb)^{b}	1.1	0.38	2	0.04	0.04	1.5
Sea water (pg kg^{-1})	2	100	60	10	0.1	50
Sea water (fmol kg^{-1})	20	100	550	50	0.5	260
Sea water/crust^{c}	2.00×10^{-6}	0.00026	3.00×10^{-5}	0.00025	3.00×10^{-6}	3.30×10^{-5}
Log (Seawater/crust)	−5.7	−3.5	−4.5	−3.6	−5.5	−4.5

^{a}Values from McDonough and Sun (1995) *Chem. Geol.* 120, p. 223.

^{b}Values from Schmidt *et al.* (1997) Geochim. *Cosmochim. Act.* 61, p. 2977.

^{c}Seawater/crust = (row 4)/(row 3) as a dimensionless ratio.

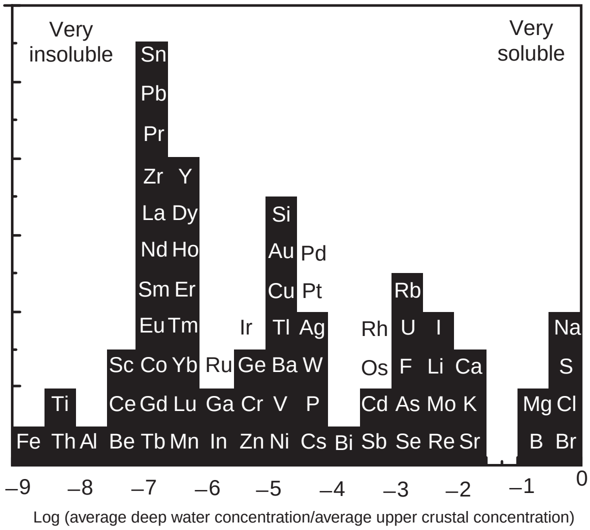

Figure 1 Histogram of seawater/upper crust partition coefficients. This parameter qualitatively represents gross patterns in elemental solubility across the periodic table. Note that the PGEs are neither particularly insoluble compared to other elements, nor particularly similar to one another. Data are derived from compilations by Taylor and McLennan (1985) *The continental crust, its composition and evolution.* Blackwell Scientific; Nozaki (1997) EOS v. 78, p. 221 and the PGE compilation in **Table 1**.

to other elements because there is a relatively smaller inventory of these elements in the earth's surficial environment.

In the context of the marine chemistry of the PGEs it is significant that the conceptual basis for considering these elements as a coherent group is more closely linked to their behavior in the deep earth than to their behavior in the ocean. Once the very low average crustal concentrations of the PGEs is taken into account it is clear that as a group these elements are not extremely insoluble in sea water (**Figure 1**). More importantly it also becomes apparent that there are obvious first order differences in the solubility of the PGEs. The striking contrast between the solid–solution partitioning of Os and Ir, two elements that exhibit very similar behavior in the deep earth, illustrates this clearly. The important general point here is that although the PGEs are often referred collectively, in a manner analogous to the rare earth elements, the PGEs do not exhibit systematic variations in charge or ionic radius that give rise to systematic similarities or differences in their marine chemistry.

Although the different PGEs do not share a coherent set of chemical affinities in the marine environment, the fact that all these elements occur in sea water at very low concentrations has two important implications that extend to all six elements in this group. The first and most obvious is that quantifying PGE distributions in sea water is analytically very challenging. Consequently, the cumulative set of published data constraining the water column distribution of these elements is quite small. Moreover, when different methodologies have been employed to measure the same element the results frequently disagree. The second implication of the low concentrations of the PGEs in sea water relates to understanding of the speciation of these metals in sea water. It is now generally accepted that many of the first series transition metals are strongly complexed in surface sea water by organic ligands that occur at nanomolar concentrations. Given that concentrations of the PGEs in sea water are 10^3–10^6 times lower than ligand concentrations it seems likely that the marine chemistry of the PGEs will also be strongly influenced by these ligands. Although this is largely a matter of speculation, the simple conceptual point is that a very complete description of all the more abundant species and their affinities for the various PGEs would be required to approach PGE speciation theoretically. Such a detailed description of sea water chemistry is unavailable, and as a result the true speciation of the PGEs in sea water is largely unconstrained. Finally it is noteworthy that the theoretical uncertainties regarding the speciation of the PGEs and the practical problems associated with the analysis of these elements in sea water are interrelated. A sound knowledge of the chemical form(s) of an element in sea water greatly facilitates the development of reliable methods for its separation and quantification.

Overview of Water Column PGE Data

Ruthenium (Ru)

There is little that can be said about the water column distribution of Ru because there are so few data available. The data that are available are limited to isolated analyses of surface sea water. The most recent work reports $20\,\mathrm{fmol\,kg^{-1}}$ for analysis of surface waters from the SIO (Scripps Institute of Oceanography) pier in southern California. Although this value seems reasonable given the relatively low concentration of Ru in upper crustal rocks (**Table 1**), there is no means of further evaluating the accuracy of this particular analysis, or of assessing how representative this single analysis is of the ocean in general. The likely valence of Ru in sea water is as Ru(IV) however, this assessment is based on very scant data for the stability constants for Ru in water. Ru enrichment in ferromanganese crusts has been interpreted as evidence that Ru is redox active in the marine environment; being subject to oxidation to an insoluble form that is coprecipitated with ferromanganese oxides. However, additional work is required to establish with any degree of certainty that this element is in fact redox active in the marine environment.

Rhodium (Rh)

The water column distribution of Rh has been investigated in only a single study. In analytical terms Rh is perhaps the most difficult of the PGEs to quantify because Rh has only one stable isotope, ^{103}Rh. Therefore, the efficiency of Rh preconcentration from sea water must be monitored using a short-lived radiotracer. This methodology was used to generate a full vertical profile from the eastern North Pacific (**Figure 2**). The significant features of this profile are the clear surface water depletion of Rh and the relatively large concentrations (approximately 100 fmol kg^{-1}) of Rh in deep waters. Distributions of this type are traditionally interpreted as the result of particulate scavenging in surface waters followed by remineralization at depth. Type of distribution contrasts strongly with that of Co, the first series transition metal which is located directly above Rh in the periodic table, illustrates that elements from the same group in the periodic table can exhibit very different chemical behavior. The contrasting behavior of Co and Rh is potentially related to the fact the Co has an active redox chemistry in the marine environment whereas Rh is believed to be stable only as Rh(III) complexes. It is unclear why the upper crustal partition coefficient calculated for Rh is so large (**Figure 1**); by analogy to other trivalent metals a much lower value would be expected.

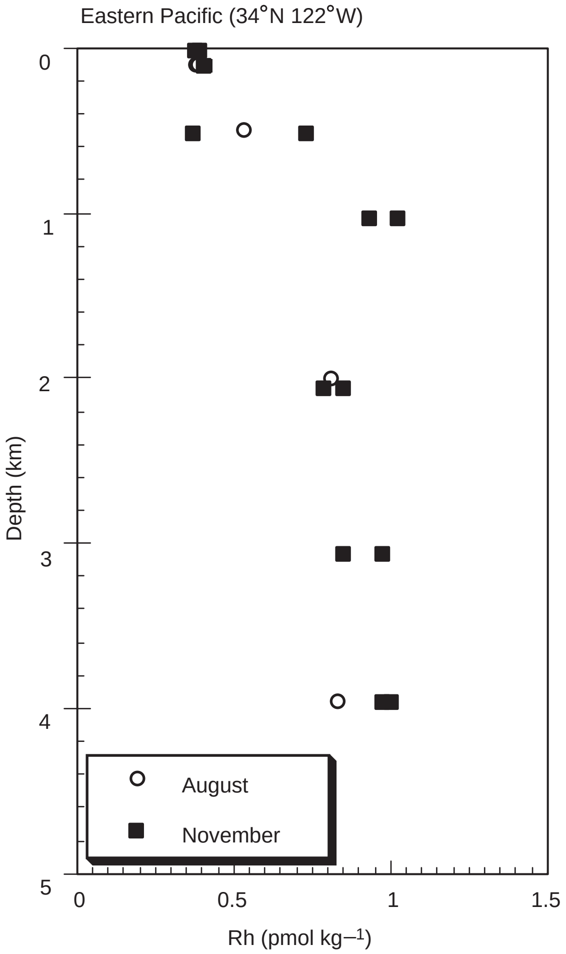

Figure 2 Profile of dissolved Rh in sea water. Data are from Bertine *et al.* (1993) *Marine Chemistry* 42: 199.

Palladium (Pd)

Our knowledge of the distribution of Pd in the water column is based on a study by Lee in 1983, the first to report a full vertical profile of any PGE in sea water. Vertical profiles of filtered and unfiltered samples from two different stations in the Pacific both show a systematic increase in concentration with increasing depth in the water column. The pattern of depth variation closely mimics that of Ni in the same samples. This similarity in the vertical distribution of these two metals and their similar upper crustal partition co-efficients (**Figure 1**) have been rationalized in terms of similar outer electron configuration. Both metals are believed to be stable in their divalent form in sea water. Subsequent more detailed study of the marine chemistry of Ni demonstrates that organic complexation plays an important role in Ni speciation, and laboratory experiments show the same can be true for Pd. Thus it seems likely that complexation by organic ligands plays an important role in Pd speciation in sea water.

Osmium (Os)

Until very recently there were no data available reporting the concentration of Os in sea water. Since 1996, however, there have been several independent studies that focused on this problem making Os the PGE whose marine chemistry has been most extensively studied. Although the recent studies agree that deep water Os concentration is roughly 50–60 fmol kg^{-1} (**Table 2**), the vertical distribution of Os in the water column is still open to debate (**Figure 3**). Results from analyses of samples from the Indian Ocean led to the conclusion that Os behaves conservatively in sea water. A separate study in the Eastern Tropical North Pacific reported a 30% depletion in Os concentration within the core of the oxygen minimum zone, and interpreted

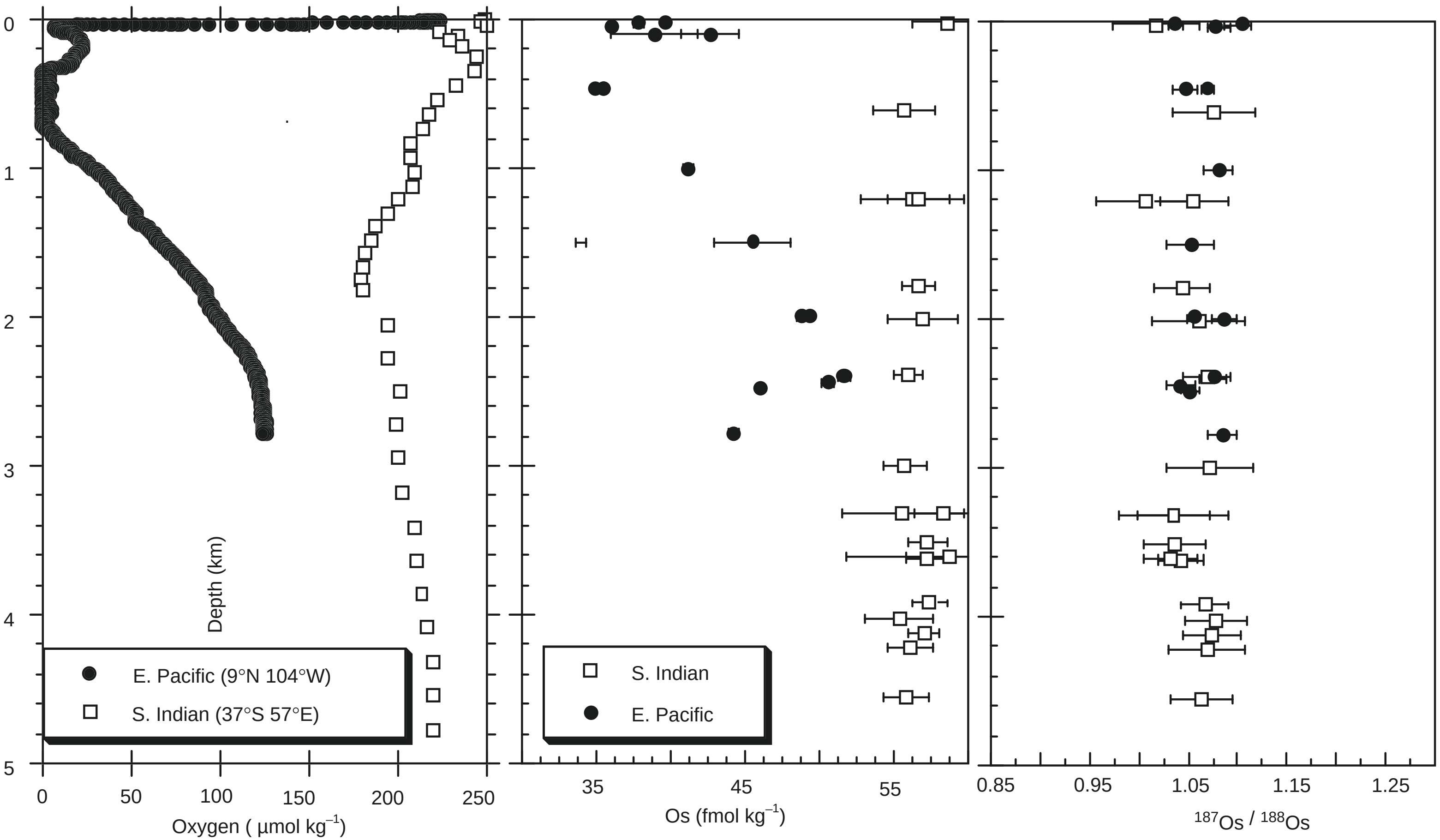

Figure 3 Vertical profiles of Os concentration and $^{187}Os/^{188}Os$ ratio in sea water from the Indian Ocean and the eastern tropical North Pacific. The Pacific data (Woodhouse *et al*. 1999 *EPSL* 173 : 223) include analyses of both filtered and unfiltered samples; no systematic difference between the two is apparent. Note that the low Os concentrations in the Pacific profile coincide with the core of a very strong oxygen minimum zone. Indian Ocean data (Levassuer *et al*. 1998 *Science* 282 : 272) indicate that Os behaves conservatively.

Table 2 Comparison of Os concentrations of fully oxic deep water from different studies

	Os (*fmol kg*$^{-1}$)
Indian Ocean[a]	55–59
Eastern Pacific[a]	44–52
North Pacific[b]	*53*–55

[a] See Figure 3.
[b] Sharma *et al.* (2000) *Earth Planet. Sci. Lett.* 179, p. 139.

this as evidence that Os was subject to removal from sea water under reducing conditions.

Although it is widely believed that Os is redox active is sea water, as first indicated by the strong enrichment of Os in anoxic marine sediments, detailed knowledge of Os speciation in sea water does not exist. Inorganic speciation calculations considering the major ions in sea water indicate that in fully oxic sea water Os should be stable in it highest valence, Os(VIII), and exist as an oxyanion. As mentioned above in the case of Ru, the paucity of data constraining the stability constants for potential Os ligands in sea water precludes any rigorous assessment of the likely redox state of Os in sea water. Some working on separation of Os from sea water have suggested that Os is strongly complexed by organic ligands in sea water. The fact that Os(VIII) is highly reactive toward many organic compounds, and is subject to reduction by them in the laboratory, lends some credibility to this inference.

Iridium (Ir)

Among the stable elements that have been measured in sea water Ir is the least abundant, with concentrations on the order of 1 fmol kg^{-1}. Although a full vertical profile from the open ocean is not available, a vertical profile from the Baltic Sea has been reported (**Figure 4**). These data provide compelling evidence that Ir, unlike Os, is not subject to enhanced removal from solution under reducing conditions. Rather, these data are suggestive of Ir scavenging in Baltic surface waters, likely by Fe- and Mn-oxyhydroxides, and subsequent release in deeper anoxic waters. Ir(III) is likely to be the stable valence of Ir in sea water. Given that Ir and Rh are believed to exist in the +3 valence, have a d^6 and electron configuration, and reside in the same group in the periodic table, it is surprising that the apparent crustal partition coefficients for these two elements differ so dramatically (**Table 1**). This inconsistency suggests either that this simplistic view of the speciation of these metals is incorrect, or that there is a large systematic error in the available concentration data for Rh or Ir. The former seems more likely than the later, and Ir removal from sea water via oxidation to an insoluble form of Ir(IV) has been proposed in previous discussions of the marine chemistry of Ir.

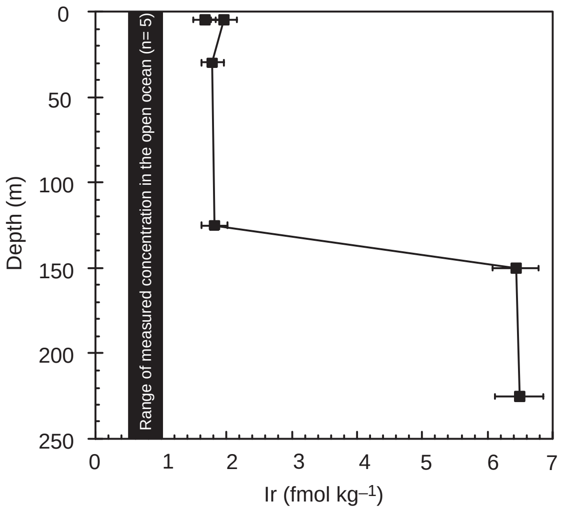

Figure 4 Dissolved Ir profile from the Baltic Sea plotted with the range of Ir concentrations reported for analyses of open ocean samples. Baltic Sea samples were filtered prior to acidification, open-ocean data were acidified and unfiltered. The abrupt increase in dissolved Ir at 150 m depth in the Baltic Sea profile coincides with complete depletion of dissolved oxygen. Anbar *et al.* (1996) *Science* 273: 1524.

Platinum (Pt)

Though relatively little work has been done on the water column distribution of Pt in recent years, several studies were conducted from the mid-1980s to the early 1990s. As is the case for Os, only a general consensus regarding deep-water concentrations was achieved, constraining values to fall between 1 and 0.3 pmol kg^{-1}. The depth variations reported in each of the three separate studies differed (**Figure 5**). Because each of these three studies employed different analytical methodologies, it is unclear to what extent the contrasting vertical profiles reflect true variability among the various ocean basins. Its seems unlikely that the strong near-surface Pt enrichment present in the Indian Ocean profile would be restricted to this ocean basin, or that deep water Pt concentrations would exhibit a four-fold difference between eastern and western Pacific. Though the differing vertical profiles suggest that some of the available sea water Pt data are subject to analytical artifact, it is uncertain which data are most reliable.

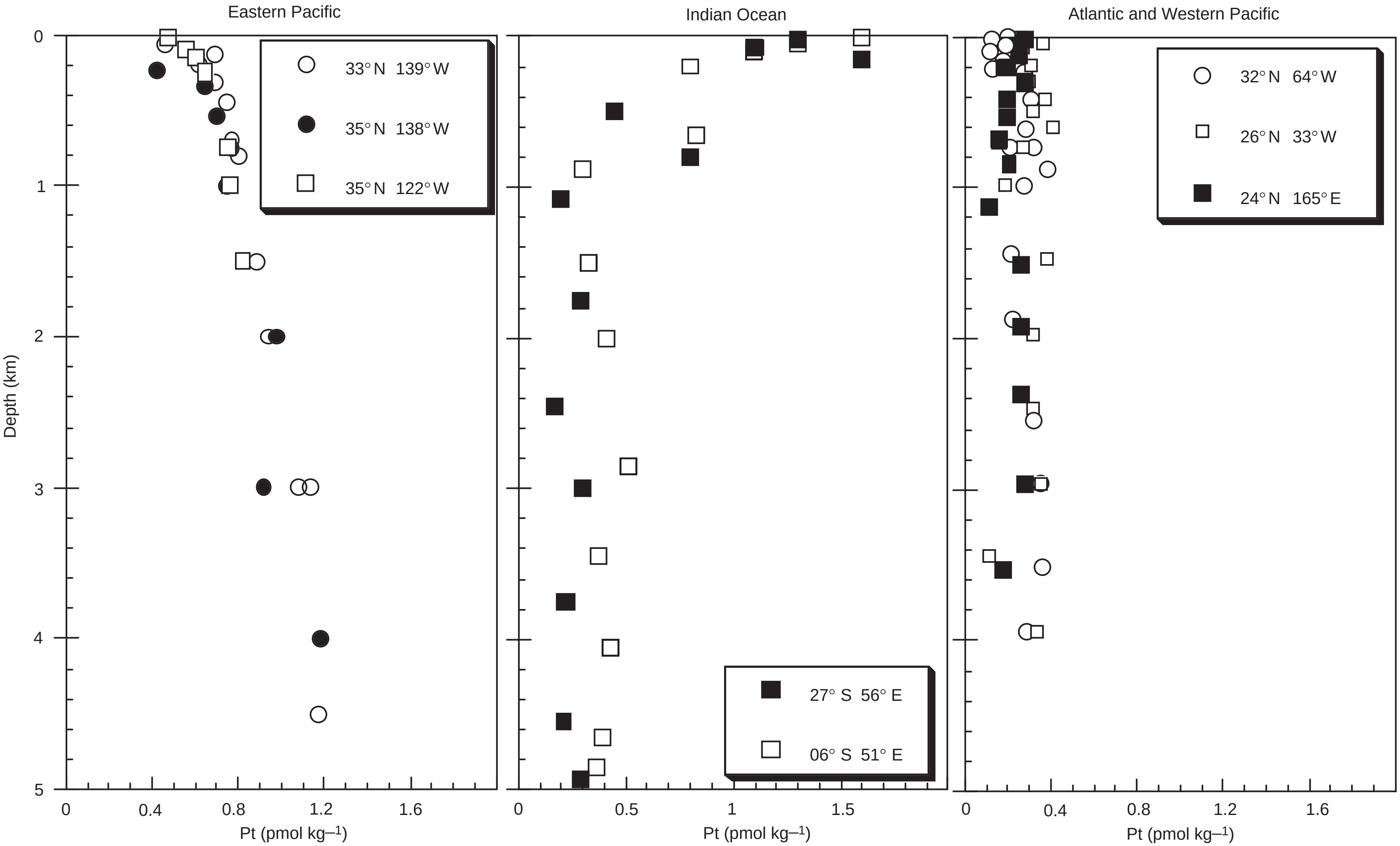

Figure 5 Dissolved Pt profiles from the Pacific, Indian and Atlantic Oceans. Although deep-water concentrations are similar to one another the vertical distribution of Pt differs dramatically among the various profiles. Data are from the following sources. Eastern Pacific: Hodge *et al.* (1986) *Analytical Chemistry* 58 p. 616; Indian: Jacinto and van den Berg (1992) *Nature* 338, p. 332; Atlantic and western Pacific: Colodner *et al.* (1993) *Analytical Chemistry* 65, p. 419 and Colodner (1991) The marine geochemistry of rhenium, platinum and iridium. Ph. D. thesis. MIT/WHOI Joint Program in Oceanography.

The uncertainties regarding the vertical distribution of Pt are mirrored in our understanding of the chemical form of Pt in sea water. There is agreement among different workers that the two relevant valances of Pt are Pt(II) and Pt(IV). Some workers argue that Pt(II), stabilized by strong chlorocomplexes, is the primary form of Pt in sea water, whereas others argue that Pt(II) is only significant in surface waters and that Pt(IV) dominates in oxic deep water. This author believes these types of inferences must be regarded as largely speculative because the relevant complexing ligands are unknown and consequently appropriate redox potentials cannot be prescribed. Moreover marine chemistry is replete with examples of persistent disequilibrium and the slow kinetics of ligand exchange are a persistent theme in discussions of the aqueous chemistry of Pt. Consequently even if the required thermodynamic data were available for Pt and the other PGEs, they would not necessarily inform us of the true speciation of these metals in sea water.

Topics of Special Interest in Marine PGE Research

Os Isotope Geochemistry

The isotopic composition of Os in natural materials varies as a result of the decay of two long-lived naturally occurring radionuclides. The decay of ^{187}Re produces ^{187}Os and the decay of ^{190}Pt produces ^{186}Os; changes in Os isotopic composition that arise from these decay schemes are commonly reported as variations in ^{187}Os/^{188}Os and ^{186}Os/^{188}Os, respectively (**Table 3**). The long half-life and low isotopic abundance of ^{190}Pt restricts the range of ^{186}Os/^{188}Os variations in most natural materials, making these isotopic analyses extremely challenging. Significant ^{186}Os/^{188}Os variability in marine deposits has yet to be documented. However, available Pt and Os concentration data from metalliferous sediments and marine manganese nodules demonstrate that these deposits have Pt/Os ratios among the highest measured in terrestrial materials. These data suggest that the Pt-Os decay scheme may be exploited in the future as a tool for dating these deposits, and provide the impetus for further investigating the geochemical processes that are responsible for producing the large Pt/Os ratio variation observed in marine deposits.

In contrast to the Pt-Os decay scheme, the Re-Os system gives rise to large variations in ^{187}Os/^{188}Os of marine deposits and is currently the subject of vigorous investigation. This work is motivated by two fundamentally important attributes of Os geochemistry; the relatively short marine residence time of Os, and the record of past variations in the ^{187}Os/^{188}Os of sea water preserved in marine sediments. Direct analyses of sea water do not yield evidence of any resolvable difference in the ^{187}Os/^{188}Os ratio between different ocean basins, but higher precision analyses of Mn crust surfaces do suggest that the ^{187}Os/^{188}Os of the Atlantic ocean may be slightly larger than in the Indian or Pacific basins. This isotopic contrast is extremely small compared to the large range in ^{187}Os/^{188}Os of sources of Os supplied to the ocean (**Table 4**). The nearly homogeneous character of modern sea water relative to oceanic inputs implies that the marine residence time of Os is poised close to the mixing time of the oceans. Spatial variations in ^{187}Os/^{188}Os of modern sea water are also small compared to the record of temporal variations in sea water ^{187}Os/^{188}Os preserved in marine sediments. Past variations in the ^{187}Os/^{188}Os of sea water provide a globally integrated record of Os input to ocean that can be exploited to make inferences about the geologic history of chemical weathering, and to identify extraterrestrial impacts in the sedimentary record. Detailed discussion of the marine Os isotope record is beyond the scope of this review.

Table 3 Radioactive decay schemes that influence the isotopic composition of naturally occurring Os

Parent	*Abundance*	*Half-life*	*Daughter*
^{187}Re	62.6%	42 billion years	^{187}Os
^{190}Pt	0.0124%	449 billion years	^{186}Os

Compiled from Walker *et al.* 1997 *Geochim. Cosmochim. Act.* 61, p. 4799.

Table 4 Comparison of ^{187}Os/^{188}Os ranges among ocean basins, sources of Os to sea water and Cenozoic sea water

	$^{187}Os/^{188}Os$
Atlantic Mn crust surfaces[a]	1.04–1.07
Indian Mn crust surfaces[a]	1.00–1.04
Pacific Mn crust surfaces[a]	1.00–1.04
Rivers[b]	0.64–2.94
Hydrothermal fluids[c]	0.11–0.39
Meteoritic material	0.12–0.14
Cenozoic sea water[d]	0.2–1.06

[a] Burton *et al.* (1999) *Earth Planet. Sci. Lett.* 171, p. 185.
[b] Levasseur *et al.* (1999) *Earth Planet. Sci. Lett.* 174, p. 7.
[c] Sharma *er al.* (2000) *Earth Planet. Sci. Lett.* 179, p. 139.
[d] Pegram and Turekian (1999) *Geochim Cosmochim. Act.* 63, p. 4053.

The PGEs as Tracers of Extraterrestrial Material in Marine Sediments

Very large concentrations of the PGEs in extraterrestrial material relative to the average upper crustal material (**Table 1**) make the PGEs valuable indicators of the presence of particulate extraterrestrial material in marine sediments. For example, addition of 0.1% by weight chondritic material to a sediment with average crustal Ir and Os concentrations would roughly double the concentrations of these elements in the mixture relative to that of the starting material. Ir is more widely exploited than Os as a tracer of particulate extraterrestrial material because methods for low level Ir analysis were established earlier and are more widely available. The global Ir enrichment at the Cretaceous–Tertiary boundary, and the subsequent identification of a major extraterrestrial impact crater, provide the best known example of this type of research. Ir data have been applied in a similar manner to study numerous other event horizons in the geologic record. Other PGE analyses can be integrated into these studies to provide additional constraints on PGE source. For example, the Pt/Ir ratios typical of upper crustal material are roughly 10 times larger than in chondrites (**Table 1**). This type of contrast in element ratios can be used to help evaluate whether elevated Ir concentrations are truly related to an extraterrestrial PGE source, or are the result of natural enrichment of PGEs from the ambient environment. Many studies motivated by the controversy surrounding the interpretation of the Ir anomaly at the Cretaceous–Tertiary Boundary have demonstrated that a wide variety of natural processing can give rise to PGE enrichments unrelated to any extraterrestrial input of these elements. Therefore, it is important to emphasize that the PGEs are only one of several possible lines of evidence used to test impact hypotheses in the geologic record.

PGEs in marine sediments are important not only in the context of identifying specific extraterrestrial impact events, but also in quantifying the background flux of cosmic dust to the earth's surface. This flux is critically important to determining what level of Ir enrichment is likely to constitute evidence of an extraterrestrial impact. Slowly accumulating pelagic clays from the abyssal North Pacific are the best available records of the average long-term flux of extraterrestrial material to the earth's surface. This is because of their very slow accumulation rates, on the order of a few millimeters per thousand years. These slow accumulation rates reflect the fact that this region of the ocean is far removed from terrestrial sources of particulate material. Thus a few meters of sediment can provide a nearly continuous record of accumulation that spans several million years and maximizes the contribution of the background flux of extraterrestrial Ir relative to total Ir burial flux. The best example of such a record is the red clay sequence from LL44-GPC3, a core recovered from the North Pacific (**Figure 6**). However in such sediment records the influence of Ir that is scavenged from sea water and is not directly associated with extraterrestrial particles complicates interpretations. In the case of LL44-GPC3, lower than chondritic Os/Ir ratios and $^{187}Os/^{188}Os$ ratios much higher than those that characterize meteoritic material indicate that more than 50% of the average total Ir flux is derived from sea water. Determining the proportion of the seawater-derived Ir that originated from dissolution of cosmic dust and that which originated from terrestrial sources is very

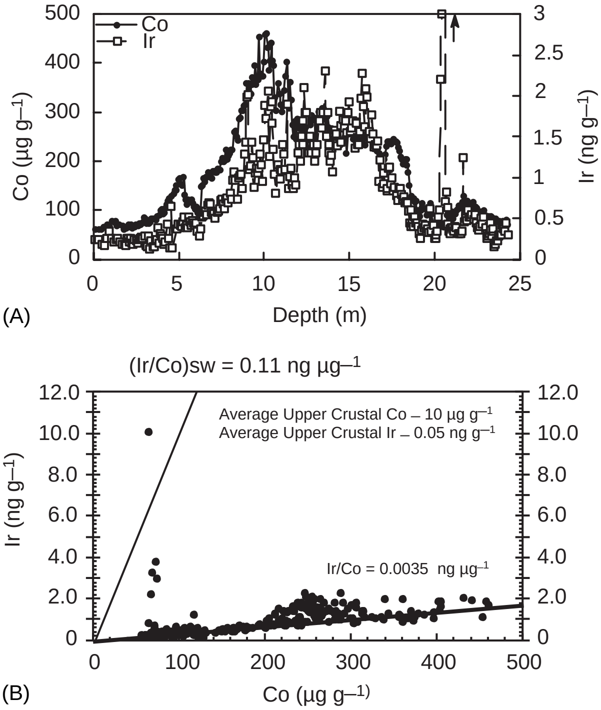

Figure 6 Concentration variations of Co and Ir vs. depth in LL44-GPC3 (A) and the same data plot as Ir vs. Co (B). The large Ir concentrations at 20 m depth (A) and 10 ng g^{-1} (B) correspond to the Cretaceous–Tertiary boundary Ir spike in this core. The slope of the Ir-Co trend represented by the bulk of the data is close to the Ir/Co ratio of average upper crust. This similarity suggests much of the Ir in this core may be derived from terrestrial rather than extraterrestrial sources. The steep line on the lower plot corresponds to the Ir/Co ratio of deepwater. In order for a significant fraction of the total Ir to occur as particulate extraterrestrial material Ir must be significantly more insoluble than Co, consistent with data from **Figure 1**. Data are from Kyte *et al.* (1993) *Geochimica et Cosmochimica Acta* 57: 1719.

difficult. Analyses of dissolved Ir in rivers that accompany recent analyses of dissolved Ir in sea water suggest that riverine supply of Ir may account for more than half of the seawater-derived Ir that accumulates in deep-sea sediments. Uncertainties associated with these types of interpretations ultimately limit the precision and accuracy of estimates of the long-term background flux of extraterrestrial Ir to the earth.

Anthropogenic Release of PGEs to the Marine Environment

Since the mid-1970s commercial demand for the PGEs, particularly Pt and Pd has been increasing rapidly (**Figure** 7). Although considerable effort is invested in recovering and recycling these metals, due in large part to their high cost, there is increasing evidence that release of these metals to the environment is giving rise to higher environmental concentrations in portions of the environment subject to anthropogenic perturbation. Among the many uses of PGEs, the utilization of Pt, Pd and more recently Rh, in automobile catalytic converters is the one pathway for anthropogenic PGE release to the environment that is best documented and most likely to lead to widespread dispersal of these metals. Although the most immediate impact of this mode of release is on land, anthropogenic PGEs also find their way to the marine environment. Direct release from storm sewers draining roadways, and indirect release from municipal sewage plants that treat road run-off with other wastewater streams are the two most likely modes of transport of autocatalyst PGEs to the marine environment. It is important to stress that the municipal waste streams may also carry PGEs associated with medical, dental, chemical and electronic applications.

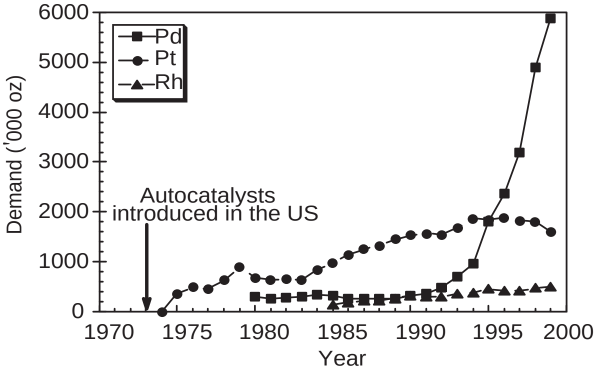

Figure 7 Representation of global demand for Pt, Pd and Rh by the automobile industry. Note that although no data are shown for Pd prior to 1980, Pd was used in some autocatalyst formulations prior to this time. These increasing demand trends suggest that PGEs release from autocatalysts is likely to become an increasingly important source of anthropogenic PGEs to the environment. Data are from the Johnson Matthey Platinum/2000 publication.

Although marine chemists have been aware of the potential importance of anthropogenic PGE release for many years, the same analytical challenges that limit the amount of PGE data from pristine marine environments are also responsible for the paucity of information constraining the distribution and behavior of anthropogenic PGEs in the marine environment. The long-standing interest of marine chemists in anthropogenic PGEs is clearly illustrated by the fact that the report of dissolved Pd profiles in sea water (see above) in the mid 1980s was accompanied by data demonstrating elevated Pd concentrations in contaminated sediments from Japan. Release from autocatalysts was suggested as a possible source. In the intervening years there have been very few studies that have addressed this matter. Recent work in contaminated sediments from Boston Harbor in the north-eastern part of the USA shows that human activity has resulted in greater than fivefold increases in bulk sediment Pt and Pd concentrations, relative to background levels of approximately $1\,\mathrm{ng\,g^{-1}}$ (**Figure** 8). However, as enrichment of these metals predated the introduction of catalytic converters, there must be important sources of these metals to the marine environment

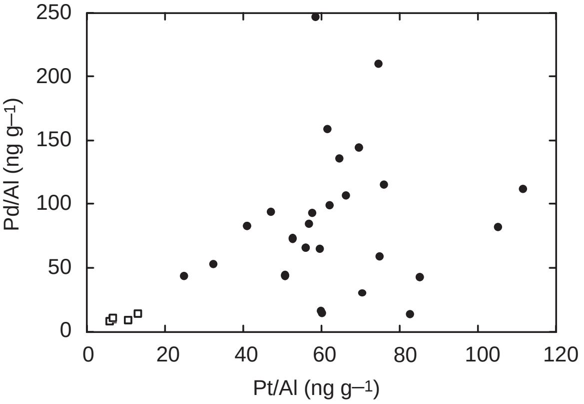

Figure 8 Plot of Pd/Al vs. Pt/Al in bulk sediment samples from Boston Harbor (●) and Massachusetts Bay (□) illustrating the influence of anthropogenic PGE release in this area. Pd and Pd concentrations are normalized to Al to eliminate grain size and dilution effects. All sediments from Massachusetts Bay are uninfluenced by human activity, based on depositional age estimates and Ag analyses. Contaminated sediments from Boston Harbor are enriched in Pt and Pd relative to pristine sediment. This is true for absolute Pt and Pd concentrations as well the Pt/Al and Pd/Al data shown above. Data are from Tuit *et al.* (2000) *Environmental Science Technology* 34: 927.

other than autocatalysts. Temporal trends in the data show that although the concentrations of Ag and Pb in Boston Harbor sediments are decreasing, likely due to the cessation of sewage release, concentrations of Pt and Pd are either stable or increasing with time. This trend is consistent with a significant input of these metals from nonpoint sources such as the release of untreated road run-off. The impact of human activity on levels of dissolved Pt and Pd in coastal waters is not well documented. Similarly, in the marine environment, the chemical form of anthropogenic PGEs, and the extent to which these metals are subject to biological uptake are also poorly known. These gaps in our knowledge of the marine chemistry of the PGEs will likely influence the future direction of marine PGE research.

Summary

The PGEs are among the least abundant elements in sea water. The low concentrations of these metals in sea water reflect their generally low concentration in earth surface material rather than uniformly low solubility. Although there is a general consensus regarding the approximate concentrations of these metals in sea water, their vertical distribution in the water column remains controversial and poorly documented. Improving our understanding of the marine chemistry of the PGEs both in the water column and in marine sediments is important to interpreting the marine Os isotope record, exploiting PGEs as tracers of extraterrestrial material in marine sediments, and understanding the consequences of anthropogenic release of PGEs to the marine environment.

See also

Glacial Crustal Rebound, Sea levels and Shorelines. Satellite Altimetry. Sea Level Variations Over Geologic Time.

Further Reading

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POLAR BEARS

See **MARINE MAMMAL OVERVIEW**

POLAR ECOSYSTEMS

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doi:10.1006/rwos.2001.0297

Introduction

The Arctic Ocean and the Southern Ocean together comprise a little under one-fifth of the world's oceans (the precise fraction depending on how these oceans are defined). The two polar oceans are similar in being cold, seasonal, productive, and heavily influenced by ice, and both have long been fished by man. They differ markedly, however, in geography, age, and many aspects of their biology.

In both polar oceans sea water temperatures are typically low, and in many areas are close to freezing ($-1.86°C$) for long periods. In areas of seasonal ice cover the surface waters undergo