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Determination of Rhenium and Platinum in Natural Waters and Sediments, and Iridium in Sediments by Flow Injection Isotope Dilution Inductively Coupled Plasma Mass Spectrometry

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Methods have been developed to measure Re, Ir, and Pt in natural waters and sediments by isotope dilution inductively coupled plasma mass spectrometry (ID-ICPMS). The techniques have been applied to determination of the three elements in sediments, Pt in seawater, and Re in seawater, sediment pore waters, and river waters. In each case, a stable isotope-enriched spike is added to the sample before processing. Sediments are dissolved in all-Teflon digestion vessels using a modified standard kitchen microwave oven. Anion exchange of the chloro complexes of Ir and Pt and of the perrhenate ion (ReO_4^-) is used to preconcentrate the elements and to separate them from concomitants which produce molecular ions in the argon plasma resulting in isobaric interferences. Samples are then introduced into the ICPMS in a small volume (300–600 μL) using flow injection. Overall recoveries were $90 \pm 10\%$ for all three elements, although the effects of variable recovery efficiency were minimized by the isotope dilution technique. The method has detection limits (3 times background) of approximately 5 pg of Re, 6 pg of Ir, and 14 pg of Pt.

INTRODUCTION

Rhenium, iridium, and platinum occur in trace concentrations in most earth-surface materials. The ability to determine these elements at natural levels is important for geochemical prospecting,¹ environmental monitoring,² and basic geochemical studies.^{3,4} The goals of this work (falling into the latter category) were to develop methods which would facilitate advances in our understanding of the behavior of Re, Ir, and Pt in the marine environment. Interest in the geochemistry of these elements has arisen from their use as sedimentary indicators of past meteorite impacts (Pt and Ir) or of anoxic environments (Re) as well as their economic importance. The decay of ^{187}Re (half-life 45 billion years) also offers a new method by which to date ancient sediments.⁵

Analytical methods for the determination of Re, Ir, and Pt in natural waters, sediments, and rocks include graphite furnace atomic absorption spectrometry (GFAAS for Re, Ir,

Table I. Comparison of Instrumental Detection Limits

method ^e	ref	detection limit, pg		
		Re	Ir	Pt
GFAAS	6, 7	750 ^a	30 ^a	20 ^a
SIMS	9	<40 ^b		
RIMS	8	200 ^c		
NTIMS	10	100 ^c	<40 ^b	
INAA	11		<0.02 ^b	
ACSV	13			0.1 ^d
FI-ID-ICPMS	f	5 ^a	6 ^a	14 ^a

^a Three times background. ^b Detection limit not stated; smallest sample measured. ^c Detection limited by filament background, quoted as 3 times background. ^d $3\sigma_{\text{sample}}$. ^e GFAAS, graphite furnace atomic absorption spectrophotometry; SIMS, secondary ion mass spectrometry; RIMS, resonance ion mass spectrometry; NTIMS, negative thermal ionization mass spectrometry; INAA, coincidence/anticoincidence instrumental neutron activation analysis; ACSV, adsorptive cathodic stripping voltammetry; FI-ID-ICPMS, flow injection isotope dilution inductively coupled plasma mass spectrometry. ^f This work.

and Pt),^{6,7} resonance ion mass spectrometry (RIMS for Re),⁸ secondary ion mass spectrometry (SIMS for Re),⁹ negative thermal ionization mass spectrometry (NTIMS for Re and Ir),¹⁰ instrumental and radiochemical neutron activation analysis (INAA and RNAA for Re, Ir),^{11,12} and adsorptive cathodic stripping voltammetry (ACSV for Pt).¹³ While the detection limits of these techniques (after preconcentration) are sufficient for analysis of natural samples (Table I), none of them allow simultaneous determination of all three elements. Additionally, GFAAS, RIMS, SIMS, and NTIMS require extensive purification of the elements in order to remove interferences and reduce matrix effects. The relative freedom of isotope dilution inductively coupled plasma mass spectrometry (ID-ICPMS) from interferences in variable matrices makes it possible to simplify these preconcentration procedures significantly.

Inductively coupled plasma mass spectrometry has become a preferred method of elemental analysis, with detection limits for most elements of less than 100 ng/L and rapid sample throughput.¹⁴ Previous work demonstrated the utility of

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ICPMS for determination of Re, Ir, and Pt in groundwaters and rocks;^{2,15-19} however, reported detection limits were not sufficient for detailed sediment sampling or surface water studies. Sen Gupta and Gregoire¹⁸ used acid digestion/sodium peroxide fusion/tellurium coprecipitation followed by isotope dilution ICPMS to determine iridium (and palladium and ruthenium) in silicate rock samples; however, their method calls for 5-g samples and they did not measure concentrations less than 0.1 ppb Ir. Jackson and co-workers¹⁹ also determined Ir and Pt by ICPMS following NiS fire assay/tellurium coprecipitation separation (in 15-g samples); however, NiS fire assay collection does not quantitatively separate Re from sediment fusions.²⁰ The limited sample sizes available from sediment cores, and low sedimentary Ir concentrations (<0.1 ppb), required that we minimize procedural blanks by simplifying digestion and purification of the samples. This was accomplished using a two-stage acid dissolution followed by a single anion-exchange column. Anion-exchange separation could also be applied with equal success to water samples. Minimum instrumental detection limits reported by Jackson et al. are 600 pg of Ir and 2000 pg of Pt, compared to 6 pg of Ir and 14 pg of Pt determined here.

McLaren and co-workers²¹ discussed the advantages of combining ICPMS with isotope dilution, where elemental concentrations are determined by the measurement of an isotope ratio rather than an absolute ion intensity. Whereas ion sensitivities may be enhanced or suppressed by nonspectroscopic interferences from concomitant elements,²² isotope ratio measurements are relatively impervious to these effects. (However, matrix-induced suppression of sensitivity will compromise limits of detection.) Furthermore, isotope ratios are less affected by instrumental drift than are ion sensitivities. Isotope ratios are influenced by isobaric interferences, however, and the oxides of the rare earth elements were found to create significant interferences for Re, Ir, and Pt in environmental samples. A single anion-exchange column was found to adequately reduce the levels of interfering molecular ions, taking advantage of the high affinity of ReO_4^- , IrCl_6^{2-} , PtCl_4^{2-} , and PtCl_6^{2-} for the resin.^{6,7} The sample eluted from the column contained the three elements, which could then be determined simultaneously by isotope dilution ICPMS.

EXPERIMENTAL SECTION

Apparatus. Sediment cores were collected aboard the RRS *Discovery* using a Kasten corer with a 2.3-m stainless steel barrel of 15 × 15 cm section. Samples were dissolved using 120-mL all-Teflon microwave digestion vessels, with pressure release valves (CEM Corp., Matthews, NC). The digestions were carried out in a standard kitchen microwave oven (Toshiba, Model ERS 8610B), modified to vent acid vapors to a fume hood. Re, Ir, and Pt determinations were performed on a VG Plasmaquad ICPMS (PQ1). A flow injection valve (Rheodyne, six port) was added to the sample introduction pathway, downstream from a peristaltic pump (Gilson Minipuls 2) and upstream of the nebulizer (concentric Meinhard, TR-30-A3, glass). The sample was introduced into the plasma via a water-cooled spray chamber (Scott double-bypass, borosilicate glass), and argon gas flows were controlled by mass flow controllers. Power for the ICP was

supplied by a Henry rf generator (Model 2000D). The detector used was a continuous dynode electron multiplier (Galileo Model 4870) in pulse counting mode, and the signal was processed by a VG MCA and IBM XT-286 computer.

Teflon labware was precleaned and cleaned between samples by soaking in aqua regia (a 3:1 mixture of 12 M HCl and 16 M HNO_3) for 1 day, followed by 50% HNO_3 for at least 1 day. Polypropylene and polyethylene labware was precleaned by soaking in 10% HCl + HNO_3 .

Reagents and Standards. Reagent-grade HNO_3 (16 M) and HCl (6 M) were triply distilled in a Vycor still. Reagent-grade HF (28.9 M) was singly or doubly distilled in a two-vessel Teflon still (Savillex Corp., MN) at subboiling temperatures and stored in HF-cleaned Teflon bottles, taking precautions to avoid the well-known hazards of HF. Sediment solutions were bubbled with Cl_2 (Mattheson, ultrahigh purity) in order to oxidize Ir before the ion-exchange step. Distilled deionized water (DDW) was used for all dilutions.

Re standards were prepared from Re metal by dissolution in concentrated HNO_3 . An Ir solution standard was purchased from SPEX Industries, as well as made by dissolving K_2IrCl_6 in 6 M HCl; these standards agreed to within 1%. A Pt atomic absorption spectrometry standard was purchased from Johnson-Matthey Aesar Corp. Stable isotope-enriched spikes for the elements were obtained from Oak Ridge National Laboratory. The isotope ratios used for isotope dilution calculations were $^{185}\text{Re}/^{187}\text{Re}$, $^{191}\text{Ir}/^{193}\text{Ir}$, and $^{192}\text{Pt}/^{194}\text{Pt}$, where the spike was enriched in the first isotope in each case. The spikes were supplied as metals and were dissolved as follows: the Ir spike was fused with Na_2O_2 in a zirconium crucible over a Bunsen burner and dissolved in 3 M HCl;²³ the Pt spike was dissolved in a 3:1 mixture of 6 M HCl and 16 M HNO_3 ; the Re spike was dissolved in 16 M HNO_3 . Spike solution concentrations were calibrated against standards by reversed isotope dilution ICPMS.

Sample Preparation. Sediment Dissolution. Sediment digestion was accomplished with acid dissolution aided by microwave heating. Samples were first dried at 110 °C overnight and disaggregated with a porcelain mortar and pestle. In order to oxidize organic matter, sediments were combusted overnight at 550–575 °C in covered porcelain crucibles. Although Re is volatile at these temperatures (as Re_2O_7), it was not measurably lost in this step, based on comparison of results from this method with previous work (see below). The major decomposition of the sample was performed using a mixture of HF and HNO_3 . However, the dissolution of carbonate-rich sediments resulted in the formation of a large amount of calcium fluoride precipitate. It was therefore preferable to treat the samples first with HCl in order to dissolve the carbonate, while keeping Ca in solution. This HCl solution was set aside while the remaining solids were digested with the HF/ HNO_3 mixture.

Between 0.5 and 1 g of sample was placed in a precleaned 50-mL polypropylene centrifuge tube, followed by the addition of 15 mL of 6 M HCl. The initial mixture was quite effervescent, and the samples were allowed to sit loosely capped overnight. The samples were then centrifuged for 10 min, and the HCl was decanted into polypropylene beakers and saved for later read-dition to the samples. Fifteen milliliters of a 5:1 mixture of concentrated HF and HNO_3 was added to the remaining solids, and this mixture was transferred quantitatively to a Teflon digestion vessel. The samples were allowed to sit loosely capped for at least 1 h as the reaction evolves heat, HF, and SiF_4 . The spike solutions were then pipetted into the sample vessels, and these were sealed with pressure release valves in place, using glass-reinforced polypropylene wrenches (Savillex Corp.). The samples were microwaved for 90 min at 20% power (153 W), as higher power levels resulted in venting through the pressure release valves and loss of sample. After being cooled to room temperature, the samples were transferred to Teflon beakers, rinsing the digestion vessels with 0.1 M HCl. The samples were taken to dryness at ~80 °C under infrared lamps in a Teflon vessel through which filtered air was passed.

The 6 M HCl solution, which had been set aside previously, was poured back into the sample beakers. The resulting slurry

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was transferred back to the digestion vessels for an additional 90 min of microwave heating (at 20% power) in order to promote the formation of Pt and Ir chloro complexes which could be subsequently separated by anion exchange. The samples were then returned to the Teflon beakers for evaporation ($\sim 80^\circ\text{C}$). Five milliliters 16 M HNO_3 was added to the empty digestion vessels, and these were microwaved at 40% power for 10 min to remove visible residue which had accumulated at the acid/vapor interface during the sample digestion. This acid was added to the samples and the evaporation continued to dryness. Samples were redissolved in 0.5 M HCl, using an ultrasonic bath to facilitate dissolution when necessary. The samples were filtered through 0.8- μm Nuclepore filters to remove any precipitate that had formed.

Water Sample Collection and Preparation. Seawater was collected for Pt and Re measurements in acid-cleaned 30- or 5-L Niskin bottles equipped with epoxy-coated internal springs and red silicone rubber o-rings, hung on a stainless steel hydrowire. Upon recovery on deck, samples were immediately drawn into acid-cleaned high-density polyethylene bottles. Samples were pressure filtered through 0.4- μm Nuclepore filters and compared to unfiltered samples, giving indistinguishable results. Seawater samples were acidified with triply distilled 6 M HCl (15 mL/L if Pt was to be determined or 4 mL/L for Re-only measurements). River water samples were collected from small boats using a plexiglass bottle holder at the end of a wooden plate. They were filtered through 0.4- μm Nuclepore filters and acidified with triply distilled 6 M HCl (4 mL/L) in the field. Sediments (both gravity cores and subcores of a box core) for pore water work were sectioned in N_2 -filled glovebag and pore waters separated by centrifugation. Pore waters were filtered through 0.2- μm acid-cleaned Gelman syringe disk filters and acidified with 0.1 mL of 16 M HNO_3 per 10-mL sample.

All samples were spiked with the ^{192}Pt and/or ^{185}Re tracers at least 24 h before passing through columns. Pt determinations were carried out on 2 L of seawater. Re measurements were performed on 10–20 mL of pore water, 50–200 mL of river water and 50 mL of seawater.

Column Preparation. Approximately 1.5 mL of the resin (Biorad AG1-X8, 100–200 mesh, Cl⁻ form) was added as a slurry to a 12-mL polyethylene column (Biorad, Polyprep). A porous polyethylene frit (cut with a no. 5 cork borer) was fitted into the column on top of the resin bed in order to prevent resuspension of the resin. The resin was then cleaned with 10 mL of 12 M HNO_3 initially at 90°C (no attempt was made to keep the acid hot after it was added to the column reservoir), 10 mL of 8 M HNO_3 , 20 mL of DDW, 10 mL of 6 M HCl, and 20 mL of 0.5 M HCl, sequentially. The resin was found to contain very high levels of Re (as high or higher than sample levels); however, this cleaning procedure reduced the Re blank introduced by the resin below detection limits.

Preconcentration. *Oxidation of Ir.* In order to ensure efficient retention of Ir on the resin, it was necessary to oxidize the element from Ir(III) to Ir(IV).⁶ A number of oxidants were tested, including $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ and H_5IO_6 , but these were unsatisfactory due to isobaric interferences (from CeClO) in the first case and insufficient oxidation in the second. Bubbling the sediment solutions with Cl_2 for 1.5 min⁶ oxidized the Ir and did not introduce blank problems. Care was taken to filter the gas to remove particles originating from corrosion of the gas delivery tube and valves.

Addition of Samples to Columns. Sediment solutions were poured into 100-mL polypropylene funnels which were fitted into the tops of columns and allowed to drip at the unregulated rate of ~ 1 mL/min. Small water samples were handled in the same manner. Seawater samples for Pt measurement were collected in 2-L bottles with tubulation at the base (Nalgene). A column was attached to the tubulation via a short length of corrugated Teflon tubing (Cole Parmer) and a pipet tip which fit into the column cap. The sample passed through the column at 1–2 mL/min.

Sample Elution. After the samples had passed through, the columns were rinsed with 50 mL of 0.1 M HCl and 50 mL of DDW to remove sea salts and loosely held metal ions. Because of the high affinity of Pt and Ir for the AG1-X8 resin, the elution of these elements was accomplished with 30 mL of 12 M HNO_3

Table II. ICPMS Operating Conditions

ICP rf power, W	1350
coolant Ar flow, L/min	13.7
auxiliary Ar flow, L/min	0.6
nebulizer Ar flow, L/min	0.7–0.8
peristaltic pump rate, mL/min	0.8
spray chamber coolant temp, $^\circ\text{C}$	8
interface configuration	standard sampling interface sampling cone orifice 1 mm skimmer cone orifice 0.7 mm
quadrupole detector	VG, Model 12-12S Galileo, Model 4870
run time per sample, s	20 or 40
run mode	peak jumping
points per peak	5
dwell time per point, μs	1280
sweeps per peak	600 for two isotopes (~ 20 -s run) 400 for six isotopes (~ 40 -s run)

at 90 – 100°C .⁶ Re could be eluted with 30 mL of 8 M HNO_3 at room temperature or with Pt and Ir. Eluted samples were collected in Teflon beakers and evaporated at $\sim 80^\circ\text{C}$ until their volume was reduced to less than 5 mL. They were then transferred to 5-mL conical Teflon vials and evaporated to ~ 100 μL . For simultaneous determination of all three elements, samples were diluted with 250 μL of 0.8 M HNO_3 plus 250 μL of 0.5 M HCl. (HNO_3 will keep Re oxidized, and HCl will keep Pt and Ir chloro complexed. In both cases, this will enhance the solubility of the elements.) Samples to be analyzed for Pt and Ir were diluted with 250 μL of 0.5 M HCl. For Re determinations alone, samples were diluted with 250 μL of 0.8 M HNO_3 .

Flow Injection ICPMS. Because this work was generally sample-limited and required measurements near the detection limit, it was beneficial to introduce the sample in a small volume in order to maximize sample signal relative to background. However, since at least two isotopes had to be determined for each sample, the sample volume had to be large enough so that many determinations of their ratio could be made. Additionally, the sample matrix became quite viscous if the evaporated column eluant was taken up in less than 250 μL of acid. On the basis of these considerations, samples were diluted either with 250 or 500 μL of acid, as above. The sample was introduced using a six-port flow injection valve downstream of a peristaltic pump, through approximately 30 cm of 0.5-mm i.d. Teflon tubing. This arrangement provided an all-Teflon introduction path and reduced diffusive broadening of the sample peak.²⁴ Data were acquired during the 20 or 40 s corresponding to maximum signal intensity from the 250- or 500- μL sample.

Typical operating parameters for the ICPMS are outlined in Table II. Background levels were generally 20 ± 5 counts/s. Isotope ratios were determined by peak jumping (switching between peak tops) on the isotopes of interest: some or all of the isotopes, ^{185}Re , ^{187}Re , ^{191}Ir , ^{192}Pt , ^{193}Ir , and ^{194}Pt . Five points were monitored across the top of each peak, with a dwell time of 1.28 ms/point. The integrated number of counts in each peak area (set of five points) was normalized for time and reported as counts per second. Procedural blanks were subtracted from each peak area prior to calculation of the ratios. Between 400 and 600 determinations of each ratio were made during the 20–40-s period of maximum intensity of the transient sample signal (400 for 250- μL samples and 600 for 500- μL samples). Typical counts measured for different sample types are reported in Table III.

Isotope Dilution Calculations. The precision of an isotope dilution calculation depends in part on the value of the ratio of spiked isotope to unspiked isotope (isotope A to isotope B). The optimal spiking ratio was established by compromise among a number of considerations. For samples with low concentrations compared to background, as was true for nearly all the samples analyzed in this study, $A/B = 1$ minimizes the effects of variable background count rates. However, in order to minimize the uncertainty introduced by propagation of errors through the isotope dilution equation, the ratio should be close to the

Table III. Typical Counts Collected for Individual Analyses

sample type	total counts ^a
0.75 g of sediment containing	
0.1 ng/g Re	1000 on ¹⁸⁷ Re
0.1 ng/g Ir	800 on ¹⁹³ Ir
1 ng/g Pt	4000 on ¹⁹⁴ Pt
50 mL of seawater containing	
8.4 ng/kg Re	13,000 on ¹⁸⁷ Re
2 L of seawater containing	
55 pg/kg Pt	1000 on ¹⁹⁴ Pt
sediment procedural blank	50–80 on ¹⁸⁷ Re
	50–80 on ¹⁹³ Ir
	50–80 on ¹⁹⁴ Pt
water procedural blank	20–50 on ¹⁸⁷ Re
	40–80 on ¹⁹⁴ Pt

^a Counts collected from preconcentrated samples on the unspiked isotope in each case. Counts collected on the spiked isotope were related to these counts by the target spiking ratios, as listed in the text. Count rates varied $\pm 30\%$ from these values based on instrumental sensitivity changes from day to day. Variations in results due to counting statistics may be calculated from the individual counting error on an isotope, uncertainties in the blank corrections, and error propagation through the isotope dilution equation.

geometric mean of the A/B ratios of the spike and sample.²⁵ Target spiking ratios were chosen to lie between 1 and the geometric mean value and were as follows $^{185}\text{Re}/^{187}\text{Re} = 2.5$, $^{191}\text{Ir}/^{193}\text{Ir} = 2$ and $^{192}\text{Pt}/^{194}\text{Pt} = 0.5$.

The number of moles of sample present in a solution spiked with an isotope-enriched tracer was calculated as follows:

$$S = T \frac{\% B_t R_m - R_t}{\% B_s R_s - R_m}$$

where there are at least two isotopes (A and B) and the spike is enriched in isotope A, S is the number of moles of sample, T is the number of moles of spike (or tracer) added, $\% B$ is the atomic abundance of isotope B, R is the ratio A/B, and the subscripts m , t , and s refer to mixture, tracer, and sample, respectively. R_t was taken to be the ratio measured by Oak Ridge National Laboratory, and R_s was calculated from the natural abundances of the isotopes.

The measured ratio of the mixture (R_m) was corrected for instrumental mass discrimination by comparing it to a "monitor" solution with a known isotopic ratio, consisting of a mixture of the tracer with a standard of natural isotopic composition. If the concentration and isotopic composition of the monitor are similar to those of the samples, multiple determinations of the monitor ratio provide an estimate of instrument uncertainty as well as bias.

Procedural blanks were run parallel to every five samples. Because it was difficult to calculate a meaningful blank concentration from spiked samples where the blank was small ($R_m \approx R_t$), the blanks were not spiked. Count rates on the blank solutions were subtracted from those of the samples before isotope dilution equations were applied.

RESULTS AND DISCUSSION

Recoveries. Chemical yields for all three elements were calculated by comparing the amount of spike in the final solution (as determined by comparison with Re, Ir, and Pt standards run on the same day) with the amount initially added to the samples. Recovery of the spikes was 80–100% for all three elements. The range in this value is due to the manner in which recoveries were calculated and difficulty in comparing samples and standards with very different matrices. Assuming isotopic equilibration between spike and sample solutions before any sample processing, isotope

dilution results are not affected by variable recoveries. For sediments, equilibration between sample (solid) and spike (in solution) is not possible before sample dissolution, and sufficient dissolution and equilibration must be inferred from results which are consistent with previous work, as in Table IV.

Recoveries for Re and Pt in seawater were also estimated by passing seawater through two columns in succession. The amount of Pt or Re eluted from the second column was indistinguishable from blank levels, suggesting recoveries by the first column of close to 100%.

Repeatability. For sediments, relative standard deviation of the method is based on duplicate processing of sample splits and is estimated to be 5% for Pt at the 1–10 ng/g level (12 duplicates), 20% for Ir at the 0.01–0.1 ng/g level (11 duplicates), and 15% for Re at the 0.01–0.1 ng/g level (5 duplicates). For seawater, the uncertainty in Pt measurements is estimated to be 15% at the 60 pg/kg level, based on quadruplicate analyses of two 8-L samples. The repeatability of Re measurements is estimated from six triplicate seawater analyses as 2% at the 8 pg/kg level. The precisions of sedimentary Ir and Re analyses at low (0.01–0.1 ng/g) levels and of seawater Pt determinations are limited counting statistics and uncertainties in the blank corrections.

Isobaric Interferences. There are a number of potential interferences on the Re, Ir, and Pt isotopes, including those from the oxides of Hf, Lu, Yb, and Tm; the chlorides of Tb, Gd, Sm, and Nd; and the hydrides of W, Os, Ir, and Pt. The chlorides and hydrides all presented negligible interference for the elements of interest. However, in the analysis of sediments, the oxides of the rare earth elements and Hf could potentially produce peaks of magnitudes similar to those of Re, Ir, and Pt. Although oxide levels for these elements were determined to be $<1\%$ of the elemental peak ($\text{MO}/\text{M} < 0.01$ in elemental standard solutions), their concentrations in typical sediments are up to 10^4 times those of Re, Ir, or Pt. After anion exchange, however, the concentrations of these isotopes in the sample were reduced to 1–10 times those of Re, Ir, or Pt, and the potential interference from these elements was reduced to $\leq 5\%$ of the total signal. For example, in sediment samples with between 1 and 4 $\mu\text{g/g}$ Hf initially, Hf was effectively reduced to less than 2 ng/g (recalculated as a sediment concentration). The separation efficiency varied among samples and runs and was treated as part of the total analytical uncertainty. Isobaric interferences were not a concern with water samples, as Hf, Lu, Yb, and Tm were not present in high concentrations relative to Re, Ir, and Pt.

Method Comparison. Because of the lack of standard sedimentary reference materials with known Re, Ir, or Pt contents, results from this method were compared to others in the literature for which samples were available. The concentrations found in this work are consistent with previous studies, within 10% of Ir concentrations determined by INAA and within 5% of Re concentrations determined by SIMS, as summarized in Table IV. Re seawater values agree quite well with the GFAAS technique,³ although the ICPMS technique yields higher precision by a factor of 30 and allows at least a 40-fold reduction in sample size. Sample throughput is relatively rapid compared to other available methods,^{6–12} requiring ~ 2 days for sediment dissolution, 1 day for column separations, and 1 min per individual analysis by ICPMS (including rinses between samples). ICPMS and flow injection valve setup and warmup time was generally 1–2 h.

The seawater Pt concentrations reported here fall at the lower end of the range of published values.^{4,26} Two previous studies of Pt in seawater disagree on the concentration and distribution of the element in the oceans. Goldberg et al.⁴

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Table IV. Interlaboratory/Intermethod Comparison

sample	this method (replicate no.)	literature data (method)	ref
pelagic sediment			
LL44-1 GPC3, 1440–1442 cm	2.1 ± 0.1 ng/g Ir (<i>n</i> = 3)	1.9 ng/g ^a Ir (RNAA)	36
LL44-1 GPC3, 1420–1422 cm	1.5 ± 0.1 ng/g Ir (<i>n</i> = 4)	1.5 ng/g ^a Ir (RNAA)	36
Black Sea			
recent sediments ^b	33.1 ng/g Re (<i>n</i> = 1)	31.8 ± 0.6 ng/g Re (SIMS)	20
Peru Shelf sediment			
phosphatic crust ^b	33.3 ng/g Re (<i>n</i> = 1)	34.6 ± 0.3 ng/g Re (SIMS)	20
black shale			
Bakken Shale ^b	287 ng/g Re (<i>n</i> = 1)	285 ± 11 ng/g Re (SIMS)	20
seawater			
deeper than 500 m	55 ± 14 pg/kg Pt	74 ± 35 pg/kg Pt (ACSV, Ind) ^c	26
		170 ± 31 pg/kg Pt (GFAAS, Pac)	4
whole water column	8.24 ± 0.07 ng/kg Re (<i>n</i> = 34, Atl + Pac)	9.1 ± 2.6 ng/kg Re (GFAAS, Pac)	7

^a Uncertainties not given. ^b These samples were splits of homogenized sediment or rock. ^c Atl, Atlantic; Pac, Pacific; Ind, Indian.

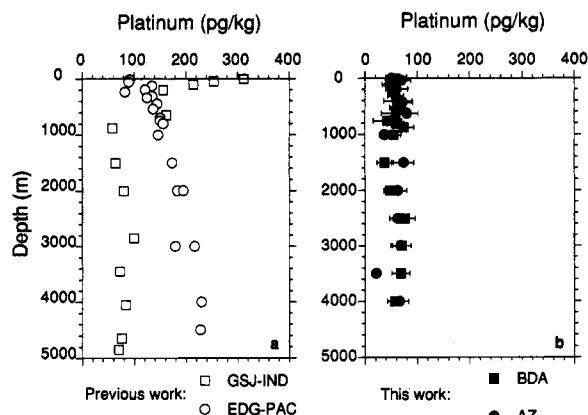


Figure 1. Platinum in seawater: (a) results from two previous studies in the Pacific and Indian Oceans;^{4,26} (b) results from this study from the Atlantic Ocean. Samples were collected in October 1989, aboard the *Atlantis II* at station BDA (near Bermuda, 32°10' E, 64°30' W) and station AZ (near the Azores, 26°20' N, 33°40' W). Error bars are 2σ.

showed depletion of the element in surface waters (using GFAAS), while Jacinto and Van den Berg²⁶ observed surface enrichment of the element (using ACSV, Figure 1a). In contrast, our results imply invariant seawater Pt concentrations (Figure 1b), with a featureless depth profile similar to that observed for gold.^{27,28} Our results might be artificially low for one of two reasons: Pt might be lost from the sample to container walls prior to addition of the ¹⁹²Pt tracer, or the tracer might not have equilibrated with the sample Pt. We do not believe either of these to be the case, as discussed below.

In order to minimize the possibilities for losses prior to spiking, samples were drawn from 30-L rather than 5-L Niskin bottles (lower surface area to volume ratio) and immediately pressure filtered. Samples were acidified and spiked within 1 h after filtration. Both of the previous studies utilized Teflon-lined Go-Flo sample collection bottles. As our sampling bottles were not Teflon lined, we cannot rule out the possibility that Pt was adsorbed by the PCV Niskin bottles. However, both of the previous studies show structure in the Pt water column profile (although opposite in shape); if either a fraction or a fixed amount of Pt was adsorbed by the bottles, we would expect to see structure as well. There is also no correlation between our results and the order in which the samples were drawn and filtered, which might be expected if significant adsorption was occurring over very short times.

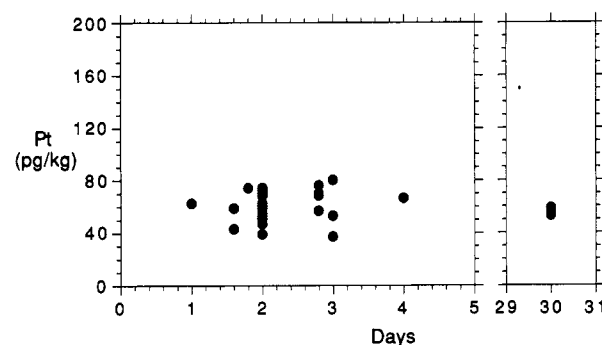


Figure 2. Pt concentrations vs spike/sample equilibration times. Calculated Pt concentrations do not correlate with the number of days between spiking and anion-exchange preconcentration.

The other possibility is that the Pt spike was not fully equilibrated with natural Pt in the sample and that recovery of the tracer from the preconcentration step was more efficient than recovery of natural Pt. This might have been the case if divalent Pt was more efficiently preconcentrated than quadrivalent Pt, since the sample is likely to contain mostly Pt(II) and the tracer (prepared by dissolving the metal in aqua regia) is probably quadrivalent.²⁹ However, experiments with solutions of PtCl₄²⁻ and PtCl₆²⁻ showed that both species were equally retained by the resin. Similar results were reported by Hodge et al.⁶ Thermodynamic calculations indicate that all the Pt in acidified seawater samples (at pH ~1) should be chloro complexed.³⁰ In addition, spiked samples were allowed to equilibrate from 1 to 30 days before the anionexchange step. No correlation between Pt results and equilibration times was observed (Figure 2), indicating that adequate mixing had occurred over 24 h.

The superior detection limits for Re offered by this technique make it possible to determine its concentration in samples for which only small volumes are available, such as sediment pore waters, or where concentrations are very low, such as some river waters. Representative results for pore and river waters are presented in Table V. Re concentrations in pore waters from Chesapeake Bay were observed to decrease with depth in the sediment. Re is removed from solution in this anoxic environment due to reduction of the highly soluble Re(VII)O₄⁻ ion. In river waters from the Amazon and Orinoco River basins, Re concentrations ranged from 0.2 to 48 ng/kg. The highest Re concentrations were found in Andean rivers, where drainage lithologies included black shale deposits. Like many other metals, Re is known to be enriched in black shales,

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Table V. Re in Sediment Pore Waters and River Waters

	Re concn, ^a ng/kg
Sediment Pore Waters	
Chesapeake Bay overlying water, cm	4.85
0-1	4.61
1-2	3.91
2-3	3.31
3-4	2.77
4-5	2.27
5-6	2.25
6-7	0.76
9-10	1.43
13-14	1.19
18-19	0.71
River Waters	
Amazon Basin rivers	
Guapay/Grande	8.56
Huallaga	3.70
Cana	3.01
Mamore	1.67
Maranon	0.65
Paranapura	0.65
Espiritu Santo	0.60
Shanusi	0.39
Amazon at mouth	0.20
Orinoco Basin rivers	
Acarigua	47.1, 47.0, 47.8
Apure at S. Fernando	7.3, 7.2, 7.0
Morador	4.1, 4.1
Tamanaco	1.5, 1.5
Apure at Portuguesa	1.5, 1.7
Canagua	0.41, 0.37
Orinoco at mouth	0.82

^a Relative standard deviation of Re analyses, 4% based on replicate analyses of Orinoco basin rivers. RSD, difference from the mean where number of analyses is 2. ^b Sampled July 1990, due east of Annapolis.

with levels up to 900 ng/g.^{5,31} The lowest Re concentrations were measured at the Amazon mouth.

Re, Ir, and Pt were determined in abyssal sediments from the northwest Atlantic Ocean. In a study of the redox behavior of the three elements, this technique was used to determine downcore variations in elemental concentrations at 1-cm intervals.^{32,33} Measurement of the three elements at this fine depth resolution (0.5–1-g sample) is made practical by the relative rapidity of the technique, as well as the favorable detection limits. Representative results for the three elements in a partially oxidized organic-rich turbidite unit are shown in Figure 3. Re has been removed from the oxidized (upper) section of the sediment, whereas Pt has been concentrated at the boundary. Ir concentrations are not significantly affected by the redox changes in these sediments.

As discussed above and illustrated in Figure 1, our results for Pt in seawater agree with neither of the previous studies in detail, although surface concentrations are similar to those reported by Goldberg et al.⁴ and deep concentrations agree with those of Jacinto and Van den Berg.²⁶ Although the three data sets were collected in three different ocean basins, it is highly unlikely that Pt would show such divergent oceanic behavior at the three sites. In order to test this hypothesis, we also measured Pt in two Pacific samples from the California Current region which had been preserved with 30 $\mu\text{mol/kg}$ KCN and stored at 6 months (CN^- strongly complexes Pt

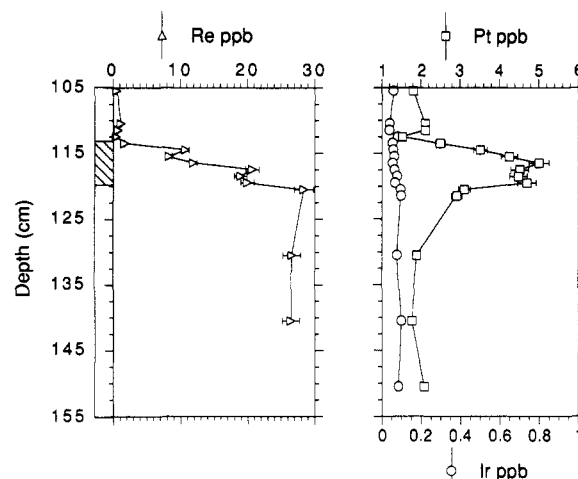


Figure 3. Re, Ir, and Pt concentrations in a partially oxidized organic-rich turbidite sediment from a basin in the foothills of the mid-Atlantic Ridge (25°39.8' N, 30°57.0' W). This Kasten core (11805) was raised from a depth of 6050 m, and a detailed geochemical description may be found in refs 33 and 37. The sediments are relatively organic-rich and are being progressively oxidized by the penetration of oxygen from bottom waters. The hatched region marks a gray-green transition zone between pale oxic sediments (above 114 cm) and green suboxic sediments (below 120 cm).

and has been shown to be an effective preservative for Au^{24}). The results (53 pg/kg Pt at 1400 m and 47 pg/kg Pt at 2000 m) fall within the range of values determined in the Atlantic Ocean (55 ± 14 pg/kg). Additionally, we measured Pt in 15 samples from a central North Pacific profile (14–6000-m depth), which had been acidified with HCl and stored for 5 years, and found no trend with depth and values (47 ± 8 pg/kg Pt) indistinguishable from the Atlantic profiles. The close agreement between stored samples and those processed at sea suggests that Pt was not significantly lost to the walls of the polyethylene bottles over these time periods and that the invariant profiles observed in the Atlantic Ocean are duplicated in the Pacific.

Jacinto and Van den Berg measured Pt by cathodic stripping voltammetry, in which a Pt-formazone complex is adsorbed on a hanging mercury drop electrode. The Pt-formazone complex catalyzes the production of hydrogen, and the reduction current associated with this reaction is said to be linearly related to the combined Pt(II) and Pt(IV) concentration. The different Pt concentrations observed in surface seawater by the ACSV and ICPMS techniques may be due to interference with the ACSV method by surface-active compounds,¹³ such as refractory organic matter present in surface seawater.

The preconcentration and purification methods used here are based on those developed by Goldberg et al., and so the two techniques are necessarily very similar; it is therefore surprising that they yield such different results. Goldberg et al. monitored recoveries (50–90%) using a radioactive Pt tracer and analyzed sample Pt using GFAAS. We corrected for variable recovery with a stable Pt tracer which was measured simultaneously with natural Pt by ICPMS. We do not have an explanation for the difference in results at this point, but note that our high recoveries (>80%) and evidence that sample and tracer Pt were adequately mixed (Figure 2) suggest that our technique was not missing a large fraction of the Pt in seawater. The featureless profiles observed in this study imply that Pt is fairly unreactive in seawater, consistent with the very slow kinetics of Pt ligand-exchange reactions.³⁴

Improvement of detection limits by at least a factor of 10 may be realized by increasing the efficiency of the sample

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introduction system, for example, with ultrasonic nebulization³⁵ or electrothermal vaporization.¹⁷ In either case, in order to retain the advantages of the isotope dilution method, it will be important to ensure adequate signal stability for measurement of an isotope ratio. Enhanced detection limits will enable the study of Ir behavior in seawater, for which previous determinations (on 100-L samples) have suggested a concentration of <2 pg/kg.¹⁶

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