

Direct Measurement of Femtomoles of Osmium and the $^{187}\text{Os}/^{186}\text{Os}$ Ratio in Seawater

Sylvain Levasseur,* Jean-Louis Birck, Claude J. Allège

Two depth profiles of the osmium concentration and the $^{187}\text{Os}/^{186}\text{Os}$ isotopic ratio in the Indian Ocean showed that the osmium concentration seems to be unaltered by chemical or biological processes occurring in seawater; accordingly, osmium is conservative. These data were obtained from an experimental method that eliminated the problems related to osmium preconcentration. This method led to a new evaluation of the concentration of osmium in seawater; the mean concentration of osmium and the $^{187}\text{Os}/^{186}\text{Os}$ ratio are equal to 10.86 ± 0.07 picograms per kilogram and 8.80 ± 0.07 , respectively. The results suggest the existence of an organocomplex that dominates the speciation of osmium in seawater.

The $^{187}\text{Os}/^{186}\text{Os}$ ratios in marine sediments are considered to indicate the relative variations of continental, mantle, and meteoritic input to seawater and to provide a record of continental weathering. However, to link the Os isotopic composition of seawater to geologic events, one must know the residence time of Os in the oceans. The residence time determines the response of the ocean to variations in the input of Os and, consequently, the shortest period and smallest amplitude of change that are resolvable by the present analytical precision of Os measurements (1). Until recently (2, 3), no direct measurement of the present-day composition of seawater Os could be made because of analytical difficulties. Here we present two depth profiles of the concentration and isotopic composition of Os that were measured in the Indian Ocean with an analytical technique (4) that had been adapted to water analysis.

Seawater samples were obtained in August 1997 at two different sites along the southwest Indian Ridge, during the EDUL cruise of the N/O *Marion Dufresne*. Seven samples were taken from the CTD4 site ($27^{\circ}52'S$, $63^{\circ}51'W$), and nine samples were taken from the CTD12 site ($34^{\circ}11'S$, $55^{\circ}37'W$) (5) (CTD, conductivity-temperature-depth). Our measurements, made on unfiltered samples, can be compared with measurements that were obtained earlier on unfiltered samples from the Atlantic and the Pacific Oceans (2).

The chemical separation method that we used was derived from the method described by Birck *et al.* (4, 6). Osmium isotopic ratios (7) and concentration measurements (Table

1) were constant within analytical uncertainty along each profile and from one site to another (the sites are separated by several hundred kilometers). Duplicate measurements were made on some samples to confirm the reproducibility of the results. The total procedural blank amounted to 4% of the sample total and remained constant within 15% throughout the duration of this study (8). The best statistical estimate of the mean of the $^{187}\text{Os}/^{186}\text{Os}$ ratios (Fig. 1A) over the two profiles is 8.80 ± 0.07 (2σ error). This ratio is in agreement with the ratios measured by Sharma *et al.* (2) (8.7 ± 0.2 for the North Atlantic Deep Water and 8.7 ± 0.3 for the central Pacific Ocean) but is higher than most of the ratios obtained from bulk or leached marine sediments (9), with the exception of the ratios obtained from some organic-rich sediments (10). This discrepancy is understandable because most of these sediments contain nonradiogenic Os in addition to their hydrogenous source. Although our profiles were on a ridge, we did not observe any decrease in the $^{187}\text{Os}/^{186}\text{Os}$ ratio with depth, contrary to the measurements from the Juan de Fuca ridge (2).

The best statistical estimate of the mean concentration of the samples is 10.86 ± 0.07 pg/kg (normalized to 35 per mil salinity) or 10.77 ± 0.07 pg/kg (unnormalized; 2σ error). This concentration is three times that previously measured in the Atlantic and the Pacific Oceans (2, 3). Because the range of the individual uncertainties (2 to 7%, except sample CTD12-7) of the Os concentration is similar to the whole variation over the two profiles, we cannot assess whether there is any correlation with salinity, but the constancy of the concentration profiles within 6% (Fig. 1B) strongly indicates that Os concentration is unaltered by chemical or biological processes that occur in seawater; hence, Os concentrations exhibit a conservative behavior.

It seems unlikely that the discrepancy between Os concentration data from this study and data from previous ones (2, 3) represents a real difference between the major oceans because the homogeneity of the $^{187}\text{Os}/^{186}\text{Os}$ ratio in the oceans [deduced from our data and the data in (2)] indicates that Os is reasonably well mixed. Thus, the observed difference probably results from differences in the analytical procedures.

It has been thought that some Os could be adsorbed to the walls of the storage vessel. With radioactive ^{185}Os as a hexachloroosmate (OsCl_6^{2-}), Koide *et al.* (3) estimated a loss of Os tracer in Pyrex bottles that was equal to 0.5% per day. Two of our samples, CTD4-9 and CTD12-11, were duplicated after 41 and 36 days, respectively. They should have lost 17 and 19% of their Os, respectively (3); instead, we observed no Os loss. Moreover, the same Os concentration was obtained for all our samples, even though we completed our analyses over a period of 3 months (which should imply a loss of 36% of Os between the first and last analyses). These results show that natural Os does not behave in the same way as the OsCl_6^{2-} tracer and that the recovery yield of Os that Koide *et al.* estimated is not indicative of the true yield.

To design a procedure that would enable the separation of Os from seawater, Sharma *et al.* (2) conducted experiments using seawater solutions that were doped with an Os standard, to which an Os tracer was added (both as OsCl_6^{2-}). They obtained nearly quantitative recovery yields and tracer sample equilibration. The lower Os concentrations that they measured suggest that their recovery of natural Os was not quantitative (even if reproducible) and, again, that Os is not in the OsCl_6^{2-} state in seawater.

Homogenizing tracer and sample Os before extraction is difficult. The critical period for the Os concentration measurement with our method occurs during the oxidation step, which permits the isotopic equilibration and the separation of Os from seawater into Br_2 . Duration tests were made on sample CTD4-6 to ensure that the oxidation step was long enough to oxidize all the Os contained in the sample (Fig. 2). It appears that 48 hours are required for a sample heated to 90°C in an oven to reach an Os concentration plateau (11). The long duration of the oxidation step in rather harsh conditions suggests that Os speciation is not, or is not dominantly, H_2OsO_5 or H_3OsO_6^- , in which species Os is already in the most oxidized state.

Hence, none of the species that were previously proposed on the basis of thermodynamic calculations seem to satisfy our observations (12). In these calculations, neither the presence of particles nor the presence of organic matter was considered, owing to a lack of thermodynamic data.

Laboratoire de Géochimie et Cosmochimie, Unité de Recherche Associée of CNRS 1758, Institut de Physique du Globe de Paris, Université Paris 7, 4 place Jussieu, 75252 Paris Cedex 05, France.

*To whom correspondence should be addressed.

The small mass of particulate matter in seawater (13) and the low Os concentration of continental material (14) show the contribution of terrigenous particles to be negligible. Meteoritic dust is also inadequate because of the discrepancy between the $^{187}\text{Os}/^{186}\text{Os}$ ratio of seawater (8.8) and that of meteorites (~ 1) (15).

However, our analytical procedure is able to oxidize scavenged metals and destroy oceanic organic matter (16), which did not occur in previous studies (2, 3). The difference in concentration between our data and the previous data could be interpreted as a result of organic trace metal speciation. A notable affinity of the platinum-group elements (to which Os belongs) for organic compounds

(17) strengthens this hypothesis. Particulate organic matter (POM) concentration declines rapidly through the thermocline and reaches a low level in deep seawater (13). This enrichment of the surface water is due to the biological activity that photosynthesizes and permanently recycles organic matter through the diverse trophic levels. Only a part of the POM escapes being recycled in the surface water and is oxidized below; it is unlikely that this phenomenon would induce the same

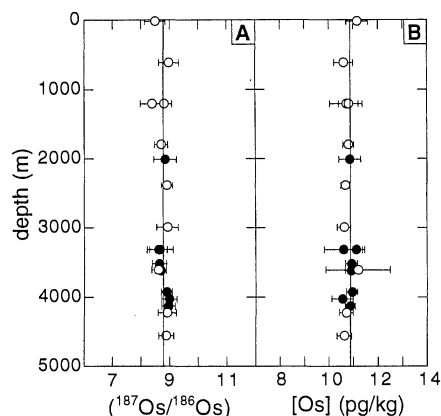


Fig. 1. Two depth profiles of (A) the $^{187}\text{Os}/^{186}\text{Os}$ ratio and (B) the normalized Os concentration (to 35 per mil salinity) in the Indian Ocean. Solid circles represent CTD4 sites, and open circles represent CTD12 sites. The vertical lines represent the average values. Error bars are 2 SD.

Table 1. Concentration and isotopic composition of Os in the Indian Ocean water. Concentrations and isotopic compositions are blank corrected. Precisions are expressed in 2σ . N , normalized to 35 per mil; σ , standard deviation; (1), first sample; (2), second sample.

Profile	Sample	Depth (m)	[Os] (pg/kg)	[Os] _N (pg/kg)	2σ ([Os])	$^{187}\text{Os}/^{186}\text{Os}$	2σ ($^{187}\text{Os}/^{186}\text{Os}$)	Salinity (per mil)
CTD4	CTD4-2	4129	10.84	10.93	0.20	8.95	0.24	34.7044
	CTD4-3	4027	10.52	10.61	0.44	8.98	0.26	34.7048
	CTD4-4	3924	10.92	11.06	0.23	8.89	0.20	34.7050
	CTD4-6	3619	10.88	10.97	0.26	8.69	0.19	34.7057
	CTD4-7	3518	10.89	10.98	0.25	8.64	0.26	34.7063
	CTD4-9 (1)	3317	10.57	10.65	0.78	8.63	0.46	34.7075
	CTD4-9 (2)	3317	11.08	11.18	0.36	8.63	0.31	34.7075
	CTD4-10	2010	10.82	10.92	0.45	8.84	0.39	34.6831
	CTD12-1	4560	10.61	10.70	0.29	8.87	0.26	34.7032
	CTD12-6	4225	10.67	10.76	0.28	8.91	0.32	34.7040
CTD12	CTD12-7	3609	11.16	11.25	1.32	8.60	0.23	34.7083
	CTD12-8	2995	10.59	10.68	0.28	8.93	0.37	34.7196
	CTD12-9	2389	10.64	10.73	0.18	8.91	0.20	34.7084
	CTD12-10	1797	10.77	10.89	0.22	8.70	0.23	34.5943
	CTD12-11 (1)	1205	10.69	10.88	0.66	8.40	0.42	34.3678
	CTD12-11 (2)	1205	10.78	10.98	0.40	8.80	0.29	34.3678
	CTD12-12	617	10.59	10.61	0.39	8.97	0.35	34.9418
	CTD12-13	22	11.14	10.96	0.45	8.48	0.36	35.5846

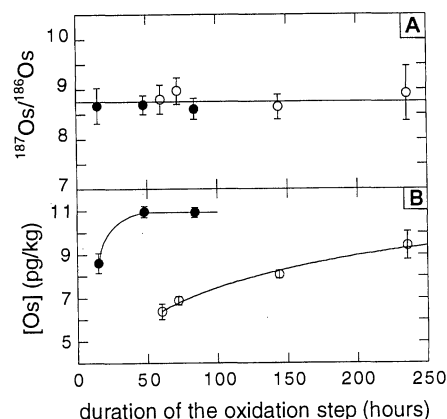


Fig. 2. (A) Plot of the $^{187}\text{Os}/^{186}\text{Os}$ ratio versus the duration of the oxidation step of the chemical separation procedure. The isotopic ratio is constant, and its mean is 8.72 ± 0.10 , in agreement with the mean of all samples. (B) Plot of Os concentration versus the duration of the oxidation step of the chemical separation procedure. On a heating plate, the duration is much longer because the heating conditions are much weaker; the vessel is only heated from below. Solid circles represent aliquots that were heated in an oven at 90°C , and open circles represent aliquots that were heated on a plate at 160°C . Error bars are 2 SD.

concentration of Os in the deep ocean as in the surface water. If Os comes from organic matter, the matter is certainly dissolved organic matter.

The residence time of Os (τ_{Os}) has been estimated indirectly with several different methods (1, 2, 10, 18, 19), all of which give estimates that are between 10^4 and 10^5 years. Knowing the Os concentration of seawater is a first step toward a direct calculation; to complete this calculation, we also need an evaluation of the input or output fluxes. Analyses of the Os concentration of some of the world's largest rivers (19) show that their Os concentration is similar to that in seawater. The precision is not yet sufficient to reduce the uncertainty by much, because the variation of the mean Os concentration of rivers could be estimated as being between one-half and twice the Os concentration in seawater. This results in the same residence time estimate [between 6.5×10^4 and 1.6×10^4 years (20)] as previous estimates.

References and Notes

- F. M. Richter and K. K. Turekian, *Earth Planet. Sci. Lett.* **119**, 121 (1993).
- M. Sharma, D. A. Papanastassiou, G. J. Wasserburg, *Geochim. Cosmochim. Acta* **61**, 3287 (1997).
- M. Koide, E. D. Goldberg, R. Walker, *Deep-Sea Res. Part II* **43**, 53 (1996).
- J. L. Birk, M. Roy Barman, F. Capmas, *Geostand. Newslett.* **20**, 19 (1997).
- All samples were collected with a rosette multisampler with polyvinyl chloride bottles. Conductivity, temperature, and pressure were monitored with a CTD probe. The depth and salinity were derived from the CTD data. After recovery, all the samples were stored in Pyrex bottles. Before being used, these bottles were degassed at 600° to 650°C . The characteristics of the glass of a degassed bottle are $^{187}\text{Os}/^{186}\text{Os} = 6.06 \pm 0.08$ and $[\text{Os}] = 0.22$ parts per trillion. To prevent bacterial growth or planktonic evolution, we added HgCl_2 to the seawater samples.
- A 50-ml fraction from each 500-ml sample was introduced into a 120- cm^3 Savillex perfluoralkoxy Teflon pressure vial with 2 cm^3 of Br_2 , 2 cm^3 of 50% H_2SO_4 , 2.5 cm^3 of 40% CrO_3 , and 10 ml of a ^{190}Os tracer solution. The vessel was then closed and heated to 90°C in an oven for 48 hours, and the Os was oxidized to OsO_4 and extracted from water into Br_2 . After cooling, the separation method was carried out as in step 3 of (4), but two extractions (each involving 1 cm^3 of Br_2) were made instead of one as in the original procedure. No modifications to the method were made beyond that step.
- Osmium isotopic ratios were normalized to $^{192}\text{Os}/^{188}\text{Os} = 3.08271$ and corrected with measured $^{18}\text{O}/^{16}\text{O}$ and $^{17}\text{O}/^{16}\text{O}$ ratios of 0.002047 and 0.00037, respectively [A. O. Nier, *Phys. Rev.* **52**, 885 (1937)]. The $^{187}\text{Os}/^{186}\text{Os}$ ratio was calculated from the measured $^{187}\text{Os}/^{188}\text{Os}$ with $^{186}\text{Os}/^{188}\text{Os} = 0.120343$ [J. M. Luck and K. K. Turekian, *Science* **222**, 613 (1983)]. We measured eight 0.5-pg standards, which had a mean value of 0.1748 ± 0.0010 and were undistinguishable within error from the measurements made on faraday cups on the larger standards in (4).
- The total procedural blank was 22 fg with a $^{187}\text{Os}/^{186}\text{Os}$ ratio of 3.9, including HgCl_2 . A variation of 50% on the concentration or composition of the blank would be necessary to induce a variation that is equivalent to the analytical uncertainty.
- B. K. Esser and K. K. Turekian, *Geochim. Cosmochim. Acta* **52**, 1383 (1988); W. J. Pegram, B. K. Esser, S. Krishnaswami, K. K. Turekian, *Earth Planet. Sci. Lett.* **113**, 569 (1992); G. Ravizza and G. M. McMurtry,

- Geochim. Cosmochim. Acta* **57**, 4301 (1993); G. Ravizza, *Earth Planet. Sci. Lett.* **118**, 335 (1993); B. Peucker-Ehrenbrink, G. Ravizza, A. W. Hoffmann, *ibid.* **130**, 155 (1994).
10. G. Ravizza and K. K. Turekian, *Earth Planet. Sci. Lett.* **110**, 1 (1992).
11. An increasing concentration over time could be interpreted as the result of a loss of tracer into the inner face of the Teflon vessel. In order to eliminate this possibility, 4 ml of CTD4-6 was analyzed with the procedure that was developed in (4), which is usually used for a wide variety of rock samples of small weight (without the dissolution step— H_2SO_4 was used instead of HNO_3). The measured [Os] was 10.2 ± 0.7 , and the $^{187}\text{Os}/^{186}\text{Os}$ ratio was 8.6 ± 0.5 (the values were corrected from the blank), implying that there was no measurable differential loss of tracer or sample.
12. D. G. Brookins, *Eh-pH Diagrams for Geochemistry* (Springer-Verlag, New York, 1988), pp. 92–93; F. G. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry* (Wiley, Chichester, UK, ed. 5, 1988).
13. W. M. Sackett, in *Chemical Oceanography*, J. P. Riley and R. Chester, Eds. (Academic Press, London, 1978), pp. 127–172.
14. B. K. Esser and K. K. Turekian, *Geochim. Cosmochim. Acta* **57**, 3093 (1993).
15. C. J. Allègre and J.-M. Luck, *Earth Planet. Sci. Lett.* **48**, 148 (1980).
16. A. Krogh and A. Keys, *Biol. Bull.* **67**, 132 (1934); J. H. Sharp, *Mar. Chem.* **56**, 265 (1997).
17. G. S. Jacinto and C. M. G. Van den Berg, *Nature* **338**, 332 (1989); A. D. Anbar, G. J. Wasserburg, D. A. Papanastassiou, P. S. Andersson, *Science* **273**, 1524 (1996) and references therein.
18. B. Peucker-Ehrenbrink and G. Ravizza, *Geology* **24**, 327 (1996); K. W. Burton et al., *J. Conf. Abstr.* **1**, 92 (1996).
19. A few results were obtained by M. Sharma and G. J. Wasserburg [*Geochim. Cosmochim. Acta* **61**, 5411 (1997)] with the same technique that was used to estimate the Os concentration in seawater. The data used here are our unpublished results from samples of several other major rivers, whose concentrations range from 5 to 25 pg/kg.
20. The residence time estimate is made with the assumption that the Os river input to the ocean is only 80% of the total input (2).
21. We thank the team of the EDUL mission, especially C. Mével, who agreed to sample seawater for us on an already scheduled mission, and A. Dappoigny, who performed the sampling. We also thank K. W. Burton for helpful discussions. This is Institut de Physique du Globe de Paris contribution 1565.

1 July 1998; accepted 4 September 1998

Experimental Demonstration of Guiding and Bending of Electromagnetic Waves in a Photonic Crystal

Shawn-Yu Lin,* Edmund Chow, Vince Hietala,
Pierre R. Villeneuve, J. D. Joannopoulos

The routing and interconnection of optical signals through narrow channels and around sharp corners are important for large-scale all-optical circuit applications. A recent computational result suggests that photonic crystals may offer a novel way of achieving this goal by providing a mechanism for guiding light that is fundamentally different from traditional index guiding. Waveguiding in a photonic crystal and near 100 percent transmission of electromagnetic waves around sharp 90 degree corners were observed experimentally. Bending radii were made smaller than one wavelength.

The efficient guiding and interconnection of light on a chip are important for telecommunication and optical computing applications (1, 2). Conventional dielectric waveguides can support guided modes along straight lines with high efficiency yet are restricted by radiation loss to a moderate bending radius (3). A recent theoretical investigation suggests that photonic crystals hold the key for overcoming this problem. It is predicted that a photonic crystal waveguide can guide light with great efficiency either along a straight path (4) or around a sharp corner (5–7). It is further suggested that light can be guided in air, minimizing guiding loss due to material absorption.

Photonic crystals, also known as photonic band gap (PBG) materials, are artificially engi-

neered dielectric materials that exhibit a frequency regime over which propagation of light is strictly forbidden (8). A linear defect in a photonic crystal can give rise to a band of defect states within the gap and act as a waveguide (see Fig. 1A). Light in the photonic crystal is confined to and guided along the one-dimensional (1D) channel because the gap forbids light from escaping into the bulk crystal. A waveguide bend (Fig. 1B) can then steer light around a sharp 90° corner. A simple scattering theory predicts the existence of reflection nodes where 100% transmission efficiency can be achieved through the bend (5). We now demonstrate waveguiding of electromagnetic (EM) waves by a PBG line defect and, more importantly, observe near perfect transmission of EM waves around a sharp corner in a photonic crystal.

The two-dimensional (2D) photonic crystal we used to construct straight waveguides and waveguide bends consisted of a square array of circular Alumina rods having a dielectric constant, ϵ , of 8.9 and a radius, r , of $0.20a$, where a is the lattice constant of the square array. In our experiment, the lattice constant was chosen

to be 1.27 mm. For such a 2D photonic crystal, a large photonic band gap exists for light polarized parallel to the rods that extends from a frequency of $0.32c/a$ (76 GHz) to $0.44c/a$ (105 GHz). Here, c is the speed of light.

A line defect is created inside the crystal by removing a row of rods. The line defect introduces an optical mode inside the crystal. Its localization strength depends on the specific modal frequency; at midgap, the guided mode extends less than one-half of a wavelength into the crystal (9). The translational symmetry along the line defect allows the guided mode to be described with two quantum numbers: frequency (f) and wave vector ($\mathbf{k}$). A f versus $\mathbf{k}$ dispersion relation uniquely characterizes the propagation of light in the waveguide. Computed results of such a dispersion relation along the high-symmetry crystal direction $\langle 10 \rangle$ are shown in Fig. 2, along with the extent of the PBG. The dispersion is strongly nonlinear near the cutoff at $\mathbf{k} = 0$. It becomes linear at higher frequencies and eventually intercepts the upper branch of the photonic band gap at $f = 0.44 c/a$. The bandwidth Δf of the guided mode is very large and extends over the entire width of the band gap. Had we chosen a lattice constant, a , of $0.59 \mu\text{m}$ (infrared regime) instead of 1.27 mm (millimeter-wave regime), the band gap would have been centered at a wavelength $\lambda = 1.55 \mu\text{m}$, and the guided-mode bandwidth $\Delta\lambda$ would have extended over a range of 430 nm.

To test the PBG waveguides, we used a HP8510C millimeter-wave source unit with a tunable frequency range from 75 to 110 GHz. The electric field of the emitted EM wave was polarized parallel to the dielectric rods and was coupled into the PBG waveguide with two metallic millimeter-wave waveguides, a transmitter and a receiver, placed next to the entrance and exit respectively, of the PBG waveguide. This scheme was used to optimize coupling into the PBG waveguide. It closely mirrors the setup used in the computational simulations (5). In the simulations, a point dipole, acting as a transmitter, was placed at the entrance of the PBG waveguide, and the field amplitude was monitored at a point located inside the guide

S.-Y. Lin, E. Chow, V. Hietala, Sandia National Laboratories, Post Office Box 5800, Albuquerque, NM 87185, USA. P. R. Villeneuve and J. D. Joannopoulos, Department of Physics, Massachusetts Institute of Technology, Cambridge, MA 02139, USA.

*To whom correspondence should be addressed. E-mail: slin@sandia.gov