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OSMIUM IN SEAWATER: ANALYSIS AND GEOCHEMISTRY

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ABSTRACT

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The marine geochemistry of osmium is not well understood. Osmium is one of the rarer elements in seawater and analytical difficulties have prevented the direct measurement of concentration and isotopic composition. A method for the direct analysis of seawater osmium has been developed and is described in this thesis. Low and constant blanks are obtained (0.12 pg osmium with $^{187}Os/^{186}Os = 2.6$) and spike-sample equilibration is achieved using this method.

A ^{191}Os radiotracer was used to develop the method. The storage of the seawater samples, and the distillation and microdistillation used for the isolation of the osmium, were examined using the radiotracer. It was demonstrated that seawater should be stored in either glass or Teflon bottles and acidified to pH2 using hydrochloric acid. It was shown that polyethylene bottles should not be used, as this material was found to rapidly adsorb the osmium from solution. The radiotracer experiments also showed that near quantitative yields are achieved from both the distillation and microdistillation.

Seawater was collected from the eastern Pacific Ocean, and osmium concentrations (6.6 to 9.8 pg/L) and isotopic ratios ($^{187}Os/^{186}Os = 8.89 \pm 0.09$ (2 sigma)) were measured using the method. The vertical profile shows that osmium concentration is not constant through the water column in this ocean region. A minimum at around 500 m depth, coinciding with a minimum of both dissolved oxygen and light transmission, can be explained by two processes: the horizontal advection of a water mass of low osmium concentration from the continental slope and the in-situ adsorption of osmium onto sinking particles. While the concentration and isotopic composition values are similar to those measured in the Indian Ocean, the data from the Pacific Ocean shows reduced concentrations under suboxic conditions. The seawater samples that were collected from close to the hydrothermal vents at 9°N of the East Pacific Rise, were not concentrated in osmium compared to deep seawater. Comparisons between filtered and unfiltered samples show that the majority of seawater osmium is in the dissolved phase.

The results suggest that osmium exists in several oxidation states and chemical speciations in seawater, and that suboxic conditions may reduce the osmium to a particle-reactive species. A calculation of the osmium oceanic residence time (33,000 years) indicates that osmium should be uniformly distributed throughout the oceans.

The samples were analysed by both negative thermal ionisation mass spectrometry (NTIMS) and inductively coupled plasma mass spectrometry (ICP-MS). An osmium standard solution was used to show that data obtained from both instruments are comparable. The memory or carryover effect that occurs when osmium is analysed by ICP-MS was investigated. This effect was overcome by flushing the instrument with 10% nitric acid between samples.

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CHAPTER 1: Introduction

1.1 Geochemistry of Osmium

1.1.1 Osmium Chemistry

Osmium (Os) is a hard brittle solid, grey/white in colour (Cotton and Wilkison, 1988). It is a trace element in group 8 of the periodic table, along with iron (Fe) and ruthenium (Ru). It is a platinum-group metal, the other five being ruthenium (Ru), rhodium (Rh), iridium (Ir), palladium (Pd) and platinum (Pt).

The chemistry of Os is similar to that of Ru, but very different from that of Fe. It has nine oxidation states and can form a wide range of compounds: oxo compounds, halides, osmates, ammines, phosphines, nitrido complexes, organometallic compounds and high-nuclearity carbonyl clusters (HNCC).

In seawater, Os has been predicted to form the +8 oxidation state, possibly as the tetraoxide OsO_4 (Whitfield and Turner, 1987) or as an oxyanion (Ravizza, 1995). Osmium tetraoxide is a yellowish/colourless crystalline solid. It is volatile and highly toxic (and so especially hazardous to the eyes), has a low melting point (40°C) and a characteristic penetrating ozone-like odour. It can be synthesised by simply burning Os in air, or oxidising an Os solution with nitric acid, peroxodisulphate in sulphuric acid or NaOCl. Osmium tetraoxide is used commercially in the cis-hydroxylation of alkenes. It is moderately soluble in water but extremely soluble in tetrachloro methane.

1.1.2 Osmium/Carbon Correlation

Osmium tetraoxide has a high affinity for organic matter (Ravizza and Turekian, 1989); concentrations of Os and organic carbon are strongly (positively) correlated in marine sediments (Ravizza, 1995; Ravizza et al., 1991). It has been suggested that Os dissolved in seawater may be actively removed from solution to be associated with organic matter and incorporated into underlying sediments (Ravizza et al., 1991). The high degree of Os enrichment measured by Ravizza et al. (1991) in Black Sea sediments has not been observed to such a high magnitude in oxic sediments, and it is therefore argued that euxinic conditions enhance removal of dissolved Os to sediments. The slope of the osmium-organic carbon trend is approximately 3 ng Os per gram organic carbon. If this osmium-organic carbon ratio is representative of the global sedimentary reservoir, roughly

5% of the continental crustal Os inventory is associated with buried organic carbon (Ravizza, 1995).

1.1.3 Osmium Sources

1.1.3.1 $^{187}Os/^{186}Os$ Isotopic Ratios and the Re-Os System

The $^{187}Os/^{186}Os$ isotopic ratio of a sample may be used as an indication of its source. The isotope ^{187}Re undergoes beta decay to form ^{187}Os, with decay constant $\lambda = 1.52\times10^{-11}$ yr^{-1} (Morgan, 1985; Palmer and Turekian, 1986). The $^{187}Os/^{186}Os$ ratio of a sample therefore depends on its $^{187}Re/^{186}Os$ ratio, its initial $^{187}Os/^{186}Os$ ratio and the age of the system.

The growth of ^{187}Os in a Re-bearing system is described by the following equation (Faure, 1986):

$$^{187}Os/^{186}Os = (^{187}Os/^{186}Os)_i + {}^{187}Re/^{186}Os\,(e^{\lambda t} - 1)$$

where

$^{187}Os/^{186}Os$ = ratio of these isotopes at the present time,

$(^{187}Os/^{186}Os)_i$ = initial ratio of these isotopes at the time the system became closed,

$^{187}Re/^{186}Os$ = ratio of these isotopes at the present time,

λ = decay constant of ^{187}Re (1.52×10^{-11} yr^{-1}),

t = time elapsed since the system became closed to Re and Os.

Iron meteorites generally have high Os and Re concentrations and a Re/Os ratio of around 0.08 (Faure, 1986). The isotope ^{186}Os is approximately equal in abundance to ^{187}Os in meteorites. Rocks composed of silicate minerals on the Earth and Moon are greatly depleted in Re and Os compared with metallic meteorites. These elements are siderophile and have thus been removed into the metallic core of the Earth. The Re/Os ratio of peridotites is similar to that of meteorites, whereas granites are highly depleted in Os and consequently have high Re/Os ranging from about 10 to more than 30. Rhenium is not strongly partitioned during partial melting and fractional crystallisation, and therefore ultramafic rocks, basalt and granite have similar Re concentrations. Osmium, on the other hand, is greatly depleted in basalt and granite compared with ultramafic rocks, and only a small fraction of the Os in the mantle has been transferred into the crust. The Re/Os ratio of the mantle has been stable throughout geologic time whereas the crust has elevated and highly variable Re/Os ratios. In general, the crust of the Earth has a much higher Re/Os ratio than the mantle and is thus significantly enriched in radiogenic ^{187}Os compared to Os in the mantle (Faure, 1986).

The table in Appendix II shows the ^{187}Os/^{186}Os values that are associated with various types of marine and geological material, and the literature reference from which these values have been obtained. Table 1.1. is a concise form of this table; values were obtained from a wide range of literature. A separate table has also compiled in the literature that shows typical Os concentrations and isotopic compositions found in various samples (Luck, 1990).

Table 1.1. Typical ^{187}Os/^{186}Os Ratios of Marine and Geological Material

^{187}Os/^{186}Os Ratio	Marine and Geological Material
≈ 1	meteorites and cosmic dust
≈ 1	mantle material
≈ 1	osmium used in industry, medicine and commerce (mined from ore deposits)
5.3-21.2	Mn nodules
8.6-8.8	seawater
>10	continental crust material

Osmium isotopic results are traditionally reported with respect to mass 186 (i.e. ^{187}Os/^{186}Os). It has been suggested (Beneteau and Richardson, 1992; Masuda et al., 1986) that ^{188}Os would be a better normalisation choice for several reasons. Firstly, ^{188}Os (13.27%) is more abundant than ^{186}Os (1.59%) and thus easier to measure precisely. Secondly, ^{186}Os has an isobaric overlap with an abundant W isotope (^{186}W, 28.64%). Finally, ^{190}Pt (0.0127%) decays to ^{186}Os with a half-life that is geologically meaningful ($t_{1/2}$ = 5.9x10^{11} yr); this addition will only be significant in Pt-rich minerals. To convert

$^{187}Os/^{186}Os$ to $^{187}Os/^{188}Os$, the former ratio must be multiplied by the $^{186}Os/^{188}Os$ ratio (0.12000), which is close to constant in nature.

Osmium isotopic ratios are reported in this thesis as $^{187}Os/^{186}Os$ as, despite the arguments noted above, this is still the convention used by the majority of the scientific community.

1.1.3.2 Anthropogenic Osmium Sources

Anthropogenic sources of Os to estuarine sediments have been examined at Long Island Sound, Connecticut (Esser and Turekian, 1993a). Surface sediments had $^{187}Os/^{186}Os$ values of 1.8-5.0 and Os concentrations of 64-774 pg/g, compared to preindustrial sediments that had $^{187}Os/^{186}Os$ values of 8.8 and Os concentrations of about 40 pg/g. The $^{187}Os/^{186}Os$ ratio in the samples is inversely correlated with Os concentrations, suggesting simple mixing between more radiogenic natural Os and less radiogenic anthropogenic Os. The primary source of anthropogenic Os is thought to be fixative solutions used to stain tissue for microscopy in medical laboratories. The Os isotopic composition of sediments may thus be used to track medical waste transport and burial in contaminated environments.

1.1.3.3 Extraterrestrial Osmium Sources: Meteorites and Cosmic Dust

Extraterrestrial material arrives on the earth's surface in the form of meteorites and cosmic dust (roughly 80 tons of it every day (Ravizza, 1992)). It has been shown that Os found in this material will have a $^{187}Os/^{186}Os$ ratio of around 1 (Martin et al., 1994). Modern pelagic carbonates have isotopic compositions in the range $^{187}Os/^{186}Os = 6.7$ to 8.3 (Oxburgh, 1996). These values are less radiogenic and show greater variation than those of osmium-rich modern sediments (Ravizza, 1991) and are interpreted to provide evidence that the dissolution of cosmic dust in the ocean's surface waters is a source of Os to seawater. When examining the importance of cosmic dust and other solid matter as a source of Os to seawater, it is essential to evaluate the fraction of the material that will dissolve into the seawater. Mass balance calculations have shown that 20% of cosmic dust dissolves in seawater (Esser and Turekian, 1988).

The $^{187}Os/^{186}Os$ ratios of samples from the Canyon Diablo meteorite and from the East Clearwater crater in Quebec have been measured (Fehn et al., 1986). These values were close to 1, typical of extraterrestrial material. In contrast, ratios in samples from the Ries crater in Germany were around 10, which is evidence of predominantly crustal Os in these rocks. Low $^{187}Os/^{186}Os$ values for samples from Stevns Klint, Denmark and Raton Basin, Colorado lead to the conclusion (Luck and Turekian, 1983) that these represent Os imprints of predominantly meteoritic origin. It has been calculated (Koeberl and Shirley, 1993) that tektites from the Ivory Coast incorporate about 0.6% of a meteoritic component.

The effects of meteoritic Os on the $^{187}Os/^{186}Os$ ratios measured in pelagic clays and Mn nodules have been examined (Esser and Turekian, 1988; Palmer et al., 1988). A simple model, in which the only sources of Os to the ocean are continental crust and extraterrestrial particles, results in a cosmic flux of Os to the sediment of 4.9 ng/cm^2/Myr, of which 20% is hydrogenous (Esser and Turekian, 1988).

1.1.3.4 Riverine Osmium Inputs

Due to difficulties in the analysis of the low concentrations of Os in river water, little has been published on the direct analysis of riverine Os. Osmium isotopic compositions ($^{187}Os/^{186}Os = 8.2$ to 10.9) and concentrations (15 to 120 pg/g) have been determined for deltaic and continental shelf sediments from major rivers (Esser and Turekian, 1993b). An isotopic composition value of $^{187}Os/^{186}Os = 10\text{-}11$ was determined as an average for currently eroding upper continental crust. It has been suggested (Pegram et al., 1994) however, that radiogenic Os is preferentially leached during mineral weathering, and thus the dissolved Os supplied by streams to the oceans may have an average $^{187}Os/^{186}Os$ distinctly more radiogenic (approximately 16) than average currently eroding continental crust $^{187}Os/^{186}Os$ (approximately 10.5). The isotopic compositions measured from the acidic hydrogen peroxide leaches of river sediments, were reported as $^{187}Os/^{186}Os = 1.4$ to 21.5 (Pegram et al., 1994).

The Os concentration and isotopic composition of river water have been determined in one central European and three North American rivers (Sharma and Wasserburg, 1997). The Fe-hydroxide precipitation procedure used in the analysis of river water was developed to concentrate Os from seawater (Sharma et al., 1997). It must be noted that this procedure measured Os concentration values that were 3-4 times lower than those measured in the eastern Pacific Ocean (see Chapter 5) and in the Indian Ocean (Levasseur et al., 1998). The Os concentration was about 8.6 pg/kg in the Vistula (Wisla) and the Mississippi Rivers, and about 2.7 and 2.9 pg/kg in the Connecticut and Columbia Rivers, respectively. The $^{187}Os/^{186}Os$ ratios were estimated as 8.8, 10.4, 10.7 and 14.4 for the Connecticut, the Mississippi, the Vistula and the Columbia Rivers, respectively. The isotopic composition for the Mississippi is identical to that of the loesses exposed in the upper Mississippi valley. This observation indicates congruent dissolution of the bedrock and little or no impact of anthropogenic sources on the Os isotopic composition of the dissolved load. Preliminary data from samples collected from several major rivers suggest that their Os concentration is in the range 5 to 25 pg/kg (Levasseur et al., 1998). The above examples of the direct analysis of river water represent early work on the subject,

A single sample of ambient seawater, collected from around the Juan de Fuca Ridge, gave a $^{187}Os/^{186}Os$ ratio of 6.9 ± 0.4 (Sharma et al., 1997). This result was used to calculate that ~80% of Os in the deep ocean is derived from the continents and the remainder from extraterrestrial and hydrothermal sources. However, plume samples from the eastern Pacific Ocean (this thesis, Chapter 5) show similar isotopic compositions to those of open-ocean deep seawater. Seawater from the Southwest Indian Ridge (Levasseur et al., 1998) showed no decrease in the $^{187}Os/^{186}Os$ ratio with depth. This suggests some analytical difficulty with the Juan de Fuca sample, rather than a reflection of local hydrothermal activity. The calculation of Os fluxes to the ocean is similar to earlier calculations (Pegram et al., 1994) based on results from the leaching of river sediments, which produced the same values. Both calculations rely on the assumption that the average Os input from the continental sources has a $^{187}Os/^{186}Os$ ratio of 10.5.

1.1.4 Seawater Osmium

1.1.4.1 Indirect Determination of the Osmium Isotopic Composition of Seawater

The extremely low concentration of Os in seawater prohibited the direct measurement, of both Os concentration and isotopic composition, for a long time. This hindered the calculation of both the Os marine fluxes and the Os oceanic residence time. Manganese nodules, metalliferous sediments, pelagic clays and, more recently, organic-rich mudrocks have all been analysed to indirectly determine the isotopic composition of Os in seawater. The Os concentration and isotopic composition of deep-sea sediments is controlled by the relative proportions of Os in a hydrogenous fraction, a detrital fraction and a particulate extraterrestrial fraction. Because the Os in each fraction has a different isotopic composition, it is important to determine the magnitude of each fraction.

During their formation, Mn nodules concentrate Os dissolved in the seawater and this makes them valuable recorders of the isotopic composition of seawater Os. The $^{187}Os/^{186}Os$ ratios of Mn nodules collected in the Atlantic, Pacific and Indian Oceans were measured as 6.0–8.4 (Luck and Turekian, 1983; Turekian and Luck, 1984). Further measurements of Mn nodules (Palmer and Turekian, 1986) found mean isotopic compositions in the three ocean basins that were indistinguishable. Considerable variability was observed within each ocean basin and this was attributed actual differences in the seawater composition. These variations in the $^{187}Os/^{186}Os$ of nodules were later interpreted (Palmer et al., 1988) to be controlled by the mixing of hydrogenous and very small particulate meteoritic or mantle Os.

Analyses of recent organic-rich sediments, rich in hydrogenous Os, from widely distributed localities suggest that the Os isotopic composition of seawater is nearly homogeneous with a $^{187}Os/^{186}Os$ ratio of approximately 8.6 (Ravizza and Turekian, 1992). Organic-rich marine sediments serve as natural preconcentrators of dissolved Os. They are relatively free of terrigenous material and their rapid accumulation makes the influence of cosmic Os negligible.

Temporal variations of seawater $^{187}Os/^{186}Os$ during the Cenozoic have been determined (Pegram et al., 1992) by analysing the hydrogenous Os released by acidic hydrogen peroxide leaching of layers in an abyssal North Pacific pelagic clay core. It was determined that seawater $^{187}Os/^{186}Os$ has increased from 3.2 at 58 Ma to the present-day value of approximately 8.6. It is suggested that the increase in the proportion of continental Os ($^{187}Os/^{186}Os \geq 10$) could be due to enhanced weathering rates of black shales associated with the uplift of the Himalayas.

Metalliferous carbonates deposited on the East Pacific Rise have been used (Ravizza, 1993) to infer variations of the $^{187}Os/^{186}Os$ ratio of seawater over the past 28 million years. There are several advantages in using metalliferous sediments as opposed to Mn nodules and pelagic clays for the indirect determination of seawater $^{187}Os/^{186}Os$. Firstly, metalliferous sediments contain predominately hydrogenous Os and can therefore be subject to bulk analysis. Manganese nodules and pelagic clays are strongly influenced by sources of Os other than seawater. Secondly, the presence of calcareous micro- and nannofossils in metalliferous carbonates provides better independent age control than can be obtained in pelagic clays. Finally, the abundance of carbonate material also allows isotopic analysis of both Os and Sr in the same sample powders. The data from metalliferous carbonates (Ravizza, 1993) are consistent with those previously published (Pegram et al., 1992). The research also shows that seawater Os and Sr isotope systems have been partially decoupled from one another over the past 28 million years, and it is suggested that accelerated weathering of ancient organic-rich sediments is a possible mechanism for this decoupling. The rapid increase in the $^{187}Os/^{186}Os$ ratio suggests that the seawater Os record can potentially be used as a stratigraphic tool in some Neogene marine deposits.

The marine $^{187}Os/^{186}Os$ record of the past 80 million years has been determined from the bulk and acid peroxide leach analysis of metalliferous sediments collected from the Pacific (Peucker-Ehrenbrink et al., 1995). The data shows a pronounced $^{187}Os/^{186}Os$ minimum of about 2 of seawater at the K-T boundary, probably reflecting the enormous input of cosmogenic material into the oceans by the K-T impactors. The $^{187}Os/^{186}Os$ ratio increases to about 3.5 at 63 Ma and is measured at 6 at 15 Ma. It is noted that seawater Os data obtained from pelagic clay leachates must be interpreted with great care, because of the likelihood that additional non-hydrogenous phases are attacked during leaching.

The Os isotopic composition of sediments spanning the past 200,000 years (two full glacial cycles) show there have been ocean-wide variations is seawater Os isotopic composition over this time (Oxburgh, 1998). While a relatively invariant $^{187}Os/^{186}Os$ ratio of 8.5-8.6 has been measured over much of this period, excursions to lower isotope compositions ($^{187}Os/^{186}Os$ of approx. 8.1) occur late in the last two glacial periods at 20 ka and 160 ka. It was inferred that these excursions to lower isotope compositions reflect reduced chemical weathering of the continents during times of extreme cold and aridity.

Metalliferous carbonates from the Atlantic and Pacific demonstrate that the Os isotopic composition of seawater was homogenous in the Atlantic and Pacific Oceans during the Middle Miocene (Reusch et al., 1998). The measurements confirm a long-term increase in marine $^{187}Os/^{186}Os$ ratios that began no later than 16 Ma. It was interpreted that this increase was most likely forced by weathering of radiogenic materials, either old sediments or sialic crust with a sedimentary protolith.

Organic-rich mudrocks from Jurassic coastal outcrops in England, have recently been analysed for Os and Re isotopic compositions and concentrations (Cohen et al., 1998). Most of the Os and Re in the samples was shown to be hydrogenous, and so the $^{187}Os/^{186}Os$ ratios of the samples reflect that of contemporaneous seawater, providing the first estimates of the Os isotope composition of Jurassic seawater.

1.1.4.2 The Direct Analysis of Osmium in Seawater

The direct measurement of Os concentrations and isotopic ratios in seawater has only very recently been achieved. The first technique to be published (Koide et al., 1996) involved anion exchange followed by the distillation of OsO_4. A total of 25 L of unfiltered seawater was passed through four parallel anion exchange resin columns. The resin was ignited at 400-450°C and then the Os was distilled from the ash as OsO_4 using ceric sulphate as the oxidant. An Os concentration of 1.7 pg/L with ^{187}Os / ^{186}Os = 6.3 was measured, both with an error of 50%. The biggest source of error was attributed to blanks contributed by the resin.

More recently, a Fe-hydroxide precipitation technique was developed and used to analyse seawater samples from the Pacific and Atlantic Oceans (Sharma et al., 1997). The variability in concentration was outside the uncertainty introduced because of blanks and indicated that sample and tracer Os had not fully equilibrated and/or that the complete removal of seawater Os was not achieved in the precipitation process. A reproducible value for the isotopic composition of the procedural blank could not be obtained. The unfiltered seawater samples (between 3.3 and 10.8 L) were stored in polyethylene bottles that were later shown to adsorb Os from solution.

The Os concentration of seawater was reported by Sharma et al. (1997) to between 15 and 19 fM. The $^{187}Os/^{186}Os$ ratio was found to be 8.7 for both North Atlantic deep ocean water (error of ± 0.2) and Central Pacific deep ocean water (error of ± 0.3). A distinctly lower isotopic ratio of 6.9 ± 0.4 was measured for a sample of ambient seawater collected from around the Juan de Fuca Ridge. This was attributed to reflect either local hydrothermal activity or analytical difficulty with the sample. The result was used to calculate that ~80% of Os in the deep ocean is derived from the continents and the remainder from extraterrestrial and hydrothermal sources, assuming that the average Os input from the continental sources has a $^{187}Os/^{186}Os$ ratio of 10.5 (Esser and Turekian, 1993b).

A modified bomb distillation technique (Levasseur et al., 1998) previously used for the extraction of Os from silicate samples (Birck et al., 1997), has recently been used to extract Os from seawater. The technique was used to analyse samples collected from two different sites along the Southwest Indian Ridge. A constant Os concentration (in the range 10.61 – 11.25 pg/kg with a mean of 10.86 ± 0.07 pg/kg) through the water column was measured, indicating conservative behaviour. Isotopic composition measurements (in the range 8.40 – 8.98 with a mean of 8.80 ± 0.07) were also found not to vary within analytical precision along the vertical profile. The measured Os concentration was 3-4 times higher than the Sharma et al. (1997) measurement, and this was attributed (Levasseur et al., 1998) to the differences in the extraction procedures of Os from seawater before analysis. Although the profiles were collected on a ridge, no decrease in the $^{187}Os/^{186}Os$ ratio was observed, contrary to the measurements from the Juan de Fuca Ridge (Sharma et al., 1997).

1.1.4.3 Osmium Oceanic Residence Time

If the size of a particular reservoir in the ocean remains constant over time, the combined input rate must equal the combined output rate. This condition is referred to as steady-state. The average amount of time a substance spends in a particular reservoir before it is removed through some transport process(es) is called its residence time (τ). If it is assumed that the oceans are at steady-state, the oceanic residence time of Os is given by the amount of Os in the ocean, divided by the total input or output of Os to the ocean (Brown et al., 1989). This is a mass balance approach to calculating the Os residence time.

τ_{Os} = total mass of Os in the oceans ÷ rate of supply (or removal) of Os to the ocean

The Os residence time may also be determined by observing a temporal variability in the Os oceanic isotopic composition. A change in the magnitude or in the isotopic composition of an input flux of Os to the oceans, results in a change in the seawater Os isotopic composition towards a new steady-state corresponding to the new flux balance (Oxburgh, 1998). The rate at which the steady-state composition is reached depends only on the Os residence time, as shown in the following equation:

$$\frac{\Delta R_t}{\Delta R_{st-st}} = 1 - \exp^{-\frac{t}{\tau}}$$

where:

ΔR_t = change in seawater isotopic composition at time t

ΔR_{st-st} = change in seawater isotopic composition at steady-state

t = time following the flux

τ = Os residence time

A third method of determining the Os residence time is by measuring a spatial heterogeneity in the Os isotopic composition within and between ocean basins. For example, an apparent homogeneity (or lack thereof) in the Os isotopic composition of sediments or Mn nodules may be used to place limits on the oceanic residence time of Os.

Before Os was directly analysed in seawater, estimates for the residence time of the metal in the oceans ranged between 100 yr (Palmer and Turekian, 1986), around 10,000 yr (Oxburgh, 1998; Oxburgh et al., 1995) and 32,000 yr (Peucker-Ehrenbrink and Ravizza, 1996). The strong differences in $^{187}Os/^{186}Os$ ratios within ocean basins, and in some cases between Mn nodules in close proximity, indicated a short mean Os oceanic residence time of 100 yr (Palmer and Turekian, 1986). These differences in isotopic composition were later interpreted (Palmer et al., 1988) as being due to the incorporation of varying amounts of cosmic dust during the nodule precipitation. This is confirmed by Mn crust data from the three ocean basins (Burton et al., 1996), which show considerably less variability in Os isotopic composition.

The measurement of considerably higher Os burial fluxes in marine carbonates than had previously be considered, indicated an Os oceanic residence time of 10,000 yr (Oxburgh et al., 1995). This estimate was calculated using output flux rather than input flux, which should be equal at steady-state. A seawater Os concentration of 1 pg/L was assumed for this calculation, but recent measurements show it is around 10.86 ± 0.07 (Levasseur et al., 1998) and this brings the residence time nearer to 100,000 yr. It was noted that this value was likely to be an overestimate, as it did not include the burial flux of Os in shelf sediments that are reducing but not anoxic. A box model, designed to stimulate the response of the oceans to an input flux that occurred at the onset of the Holocene, calculated an Os oceanic residence time of less than 12,000 years (Oxburgh, 1998). This determination of the residence time does not rely on knowing the seawater Os concentration. A study on the continental runoff of Os into the Baltic Sea suggested even higher values (Peucker-Ehrenbrink and Ravizza, 1996). The residence time of Os in seawater relative to continental runoff was calculated at about 32,000 yr.

The first calculation of the Os residence time based on results from the direct analysis of seawater was only recently made (Sharma et al., 1997). The Os concentrations and isotopic ratios were measured in seawater collected from the North Atlantic and Central Pacific Oceans, and the Juan de Fuca Ridge. The mean residence time of Os could not be derived directly from the data. However, using the Os/Ir ratio of seawater (≈22) and the Os/Ir ratio of continental rocks (≈1), and presuming chemically analogous behaviour of Os to Ir, a lower limit for the oceanic residence time of Os was estimated to be about 44,000 years.

The Os concentration of seawater samples collected from the Southwest Indian Ocean has recently been measured (Levasseur et al., 1998). These results were used, along with preliminary river water Os concentration data (mean Os concentration in large rivers = 8.2 pg/kg), to estimate an Os ocean residence time of 42,000 years. In chapter 5 of this thesis, seawater Os concentration data from the eastern Pacific Ocean are used to calculate a new oceanic residence time for Os. The Os concentrations are similar to those measured by Levasseur et al. (1998) in the Indian Ocean, indicating that there now exists accurate values for the Os concentration of seawater and hence, for the total mass of Os in the ocean. There is still uncertainty in the input and output fluxes of Os to the ocean, and this creates uncertainties in any residence times that are calculated by the mass balance approach.

1.1.4.4 The Speciation of Osmium in Seawater

The speciation of Os in seawater is not known. The pE-pH diagrams constructed for low Os concentrations (in the fM range) at pH = 8 and pE = 12 predict that $[H_3OsO_6]^-$ will be the dominant species (Palmer et al., 1988). Osmium has been predicted by thermodynamic calculations to form only the +8 oxidation state in seawater, possibly as the tetraoxide OsO_4 (Whitfield and Turner, 1987) or as an oxyanion (Ravizza, 1995).

However, an oxidation reaction has been suggested as being responsible for the enrichments of Os in ferromanganese minerals (Koide et al., 1991), in which case at least some of the dissolved seawater Os must be in an oxidizable state. This hypothesis suggests that Os in seawater cannot all be in the +8 state, as it is the highest Os oxidation state and thus cannot be oxidized any further.

A separate group (Levasseur et al., 1998) have observed that the oxidation step, used in a technique for the separation of Os from seawater, took a long time (48 hours) even under harsh conditions (acidic and oxidising conditions at 90°C). This lead to the suggestion that the Os speciation in seawater is not, or is not dominantly, H_2OsO_5 or $[H_3OsO_6]^-$, where Os is already in the most oxidized state. Osmium may even exist in more than one chemical speciation in seawater (Oxburgh, 1996). This is perhaps expected as Os has a variety of oxidation states.

1.2 Analysis of Osmium by ICP-MS

1.2.1 Introduction

Plasma spectrometry is one of the most popular and versatile techniques for the analysis of geological and environmental samples, including rocks and minerals, waters, dust, vegetation, soils, sewage sludges and sediments (Jarvis and Jarvis, 1992). The very high temperatures (up to 10,000K) in the ICP ensure far more efficient atomisation than for lower-temperature flames such as those used in atomic absorption spectrometry (AAS), and chemical interferences are consequently very small.

ICP-MS can theoretically be used to determine all elements in the periodic table with the exceptions of He, F and Ne. In practice this list also extends to H, C, N and O. The sensitivity of an element is controlled by its degree of ionisation in the ICP and the abundance of the isotope being measured. Detection limits are low: values better than 0.05 ng/mL for heavy elements such as the Rare Earth Elements (REE) and the Platinum Group Elements (PGE).

1.2.2 Sample Preparation

Samples are usually introduced into the spectrometer as a solution. Although slurry nebulisation, laser ablation and other methods are being developed, solid samples are still generally dissolved prior to routine analysis. It must be noted that sample preparation procedures (particularly sample dissolution) will ultimately limit the range of elements that can be accurately quantified.

Natural waters are close to neutral (pH of 6.5-8.0) and therefore carry only very low levels of dissolved transition metals. Pre-concentration procedures such as evaporation, chelation followed by solvent extraction, or ion-exchange chromatography are generally used. Botanical and other biological samples must be ashed (wet ashing or dry ashing) to ensure their complete decomposition. Digestion is regularly employed in the analysis of geological and environmental samples by plasma spectrometry.

1.2.3 Separation and Preconcentration Procedures of Precious Metals

The precious metals display only moderate sensitivity in plasma emission spectrometry but their high masses make them particularly well suited to determination by ICP-MS. Unfortunately, they occur in most natural materials at very low concentrations (Os at <1 ng/g) and are very heterogeneously distributed, so their determination almost invariably requires a separation and preconcentration step. Fire assay remains the most common sample preparation procedure for precious metal analysis. Nickel sulphide fire assay is generally preferred to classical lead fire assay for multi-element analysis because it provides efficient collection for most of the noble metals, although special techniques are necessary to avoid the loss of volatile Os compounds (e.g. OsO_4), particularly at the button dissolution stage.

1.2.4 Analysis of Osmium in Environmental Samples

The ability to measure the isotopic composition of nanogram or smaller quantities of Os is necessary for the development of the ^{187}Re-^{187}Os dating technique for geological samples. Osmium is found in similar abundance to Ir and serves almost equally well as an indicator of extraterrestrial (or mantle) material, but has a sensitivity approximately 30 times poorer than that of Ir, when determined by neutron activation.

A simple method for measuring Os isotopic abundances in clay material using ICP-MS has been reported (Lichte et al., 1986). The method involves fusing the sample with sodium peroxide, distillation of the Os as OsO_4 using perchloric acid, extraction into chloroform and then back-extraction into an aqueous phase. The use of a glass frit nebuliser increased the nebulisation efficiency to 90%, compared with 1-3% for conventional nebulisers. The instrument was calibrated using an Os standard dissolved in thiourea and sulphuric acid to match the sample solutions. The ^{187}Os/^{186}Os ratio was 1.12 ± 0.16, showing a typical non-crustal signature.

A comparison of Os analyses using two different types of mass spectrometers has been performed (Lindner et al., 1986): a laser microprobe mass analyser (LAMMA), which combines a pulsed-laser ablation ion source with a time-of-flight mass spectrometer, and an ICP-MS. The ICP-MS was somewhat less sensitive than LAMMA, even with the Os response strongly enhanced by introduction of the Os as the OsO_4 vapour into the argon torch. However, the combination of ion counting and mass scanning over a relatively stable Os ion beam, essentially free of isobaric interferences, resulted in mass spectra of better quality than those from LAMMA.

The OsO_4 vapour generator is a technique for introducing Os from an environmental sample into an ICP-MS instrument. The major advantage of this type of introduction technique is the high efficiency with which the Os is introduced into the spectrometer. A number of researchers have worked to develop the technique and their findings are reported in Chapter 3.

1.3 Objectives for this Study

Very little is known about the geochemistry of Os in seawater. The extremely low concentration of Os in seawater has prohibited the direct analysis for a long time. At the start of the research project, nothing had been published on the direct analysis of Os in seawater. All that was known about the marine geochemistry and cycling of Os was obtained from analyses of marine sediments. The opportunity arose to use a ^{191}Os radiotracer, and access to an NTIMS instrument was given, so it was decided that work should focus initially on the development of a method for the analysis of seawater Os. This would include developing techniques for the storage of seawater samples, for the separation and isolation of Os and for its analysis by both NTIMS and ICP-MS.

Seawater samples will then be collected, taken through the method developed using the radiotracer and analysed for Os concentrations and isotopic composition. The results will be used to obtain a better understanding of the geochemistry of Os. The vertical profile should be evaluated to gain information on the cycling of Os in seawater, and the concentration results used to calculate a new Os oceanic residence time.

CHAPTER 2: Development of a Method for the Separation and Preconcentration of Seawater Osmium

2.1 Introduction: Instrumentation, Radiotracer Preparation and Counting

2.1.1 Introduction

The three previous techniques for measuring Os directly in seawater have been examined in the introduction chapter. A technique that involves the use of anion exchange resins and the distillation of Os to OsO_4 was the first to be published (Koide et al., 1996). An Os concentration of 8.9 fM (1.7 pg/L) with $^{187}Os/^{186}Os = 6.3$ was measured. The technique resulted in large blank values of 101 pg and 110 pg and the error in the data was high at 50% for both the concentration and isotopic composition.

A very different technique was then reported (Sharma et al., 1997) that involves multiple steps including iron hydroxide precipitation, centrifuge separation, Carius tube oxidation, $CHCl_3$ extraction, $HCl-C_2H_5OH$ back-extraction, microdistillation and analysis by negative thermal ionization mass spectrometry (NTIMS). Osmium concentrations in seawater were reported to be between 15 and 19 fM (2.9 to 3.6 pg/L). The $^{187}Os/^{186}Os$ ratio was measured to be 8.7 for both North Atlantic deep ocean water (error of ± 0.2) and Central Pacific deep ocean water (error of ± 0.3). Spike-sample equilibration was not achieved. It is also thought that the complete removal of seawater Os was not achieved using the technique. An average procedural blank of 2.7 ± 0.9 fM with a variable isotopic composition (^{187}Os / ^{186}Os ratio of 1.3 ± 0.4) was measured. It was found that most of the reagent blank was introduced by the $CHCl_3$ used in the extraction and H_2SO_4 used in the dissolution. The SO_2 and NH_3 gases, used to reduce the seawater and then initiate the precipitation, may also have introduced a significant amount of Os contamination. The unfiltered seawater samples (between 3.3 and 10.8 L) were stored in polyethylene bottles.

A method using a modified bomb distillation technique (Levasseur et al., 1998) was being developed and had not been published at the start of this thesis. In this method, a 50 mL aliquot of seawater was introduced into a 120 mL Savillex perfluoralkoxy Teflon pressure vial with 2 mL of Br_2, 2 mL of 50% H_2SO_4, 2.5 mL 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 the water into the Br_2. After cooling, the liquid bromine was transferred by pipette into a 7 mL beaker containing 1 to 2 mL of cold water. Bromine (1 mL) was added to the aqueous phase remaining in the original Teflon vial, which was then closed and heated again. After chilling, this newly added Br_2 was transferred by pipette to the beaker. This bromine extraction step was repeated. The water in the beaker was discarded, 0.5 mL of distilled HBr was then added to the bromine and the whole solution was evaporated. The residue containing Os as $[OsBr_6]^{2-}$ was then purified by a microdistillation step (Birck et al., 1997).

A new technique needed to be developed for isolating and measuring Os in seawater. The technique would ideally be simple, with as few steps and reagents as possible to reduce any reagent blank. Any blank contamination needed to be low and reproducible so that the blank correction would introduce as little error as possible. If isotope dilution was to be used in the method, spike-sample equilibration would have to be achieved as this is a prerequisite to isotope dilution calculations. As well as sample preparation, a technique for the sampling and storage of seawater for Os analysis needed to be developed. Contamination and losses of Os would have to be minimised at every stage. Every step of the sampling, storage, preparation and analysis needed to be optimised as the final data would only be as good as the weakest link in the overall method.

2.1.2 Using a Radiotracer in Method Development

Using a radiotracer has many advantages over performing the same investigation by chemical analysis. Radiotracers are easy to detect and measure with high precision. The radioactivity is independent of pressure, temperature, and chemical or physical state. If the radiotracer is pure, no interference from other elements can occur, as is common in chemical analyses.

The primary assumption of radiotracer studies is that radioactive isotopes are chemically identical with stable isotopes of the same element, i.e. the substitution of ^{191}Os for the seven naturally occurring Os isotopes, does not change the type or strength of the chemical bonds, nor does it affect the physical properties of the compound (Choppin and Rydberg, 1980). Being a heavy element, these considerations can be neglected for Os. Another assumption is that the radioactive nature of the isotope does not change the chemical and physical properties. The level of radioactivity should be high enough to provide accurate data but not high enough to produce noticeable radiation effects.

2.1.3 Preparing the Osmium Radiotracer

For this work, two batches of ^{191}Os were produced by neutron activation of 96.93% isotopically enriched ^{190}Os metal from Oak Ridge National Laboratory. The metal was then fused and distilled into a HBr solution, a suitable form for the radiotracer experiments.

2.1.3.1 Producing ^{191}Os by the Neutron Activation of ^{190}Os

Four small quartz tubes (i.d. 1.5 mm, length approx. 6 cm) and four large quartz tubes (i.d. 8 mm, length approx. 10 cm) were sealed at one end using a blowtorch. The tubes were leached in 1:1 nitric acid : Milli-Q water for two days and then immersed for two days in Milli-Q water. The tubes were rinsed with acetone and left to dry. The smaller tubes were distinguished from each other by marking with a permanent marker pen. Approximately 1 mg of ^{190}Os metal was transferred into each small quartz tube from weighing paper. The small tubes were sealed and each was placed into a larger tube that was then sealed.

One of the tubes with 1.15 mg of Os metal was irradiated during May 1997. A second batch with 0.93 mg was irradiated during September 1997. The tubes were irradiated at the OSU TRIGA reactor in Corvallis, OR with a power of 1 MW for 34 hours. At the time of shipping, the contact activity was 0.087 mSv/hr.

Irradiation: $^{190}\text{Os} + {}^{1}\text{n} \rightarrow {}^{191m}\text{Os}$ m = metastable

Decay: $^{191m}\text{Os} \rightarrow {}^{191}\text{Os}$ half life = 13 hours
$^{191}\text{Os} \rightarrow {}^{191m}\text{Ir} + e^{-}$ half life = 15.4 days
$^{191m}\text{Ir} \rightarrow {}^{191}\text{Ir}$ half life = 49s

During the decay to ^{191}Ir, a combination of X-rays (65 KeV) and gamma rays (129 KeV) are emitted. With a half-life of only 15.4 days, the ^{191}Os radiotracer can be used for about two months before the activity becomes too low for precise measurement. Experiments must be carefully planned beforehand to make the most of the time available, as reactor time for the production of the radiotracer is expensive.

2.1.3.2 Fusion of the Radiotracer

Upon receipt in the laboratory, the radiotracer was carefully unpacked using tweezers whenever possible to reduce the operator's exposure. A Geiger counter was used to check that the packing material had not been contaminated. The large outer and small inner tubes were individually opened and the metal radiotracer was transferred to a Zr crucible. Sodium peroxide (0.196 g) was added to the crucible and the lid was placed on top. The crucible was heated to a dark red colour for one minute using a Bunsen burner and then left to cool. A greater amount of sodium peroxide (0.319 g) was used for the second batch in order to cover the solid totally.

2.1.3.3 Distillation of the Radiotracer

Upon cooling, the entire crucible and its fused contents were placed into a one litre distillation flask. For the first batch, the radiotracer was heated in a matrix of Milli-Q water (500 mL), sulphuric acid (14 mL) and 5.25% sodium hypochlorite NaOCl (4 mL). A total of 80 mL of hydrogen peroxide was used as the oxidizing agent for the second batch. The OSU distillation apparatus that was used is described later. The ^{191}Os radiotracer was oxidized to OsO_4 and was collected in four HBr fractions (each 10 mL). A fraction was considered full when 10 mL of water had been codistilled into the trap. The second batch of radiotracer was distilled at a much slower rate than the first batch. The first fraction was collected for 2h50 in the second batch distillation, but only 48 minutes in the first batch. Consequently, the majority of the Os distilled in the second batch was in the first fraction. In this second batch, the Os had enough time to be oxidized and distilled before the water codistilled and filled the trap. The latter fractions of the first batch contained considerable Os as water codistilled and filled the trap before the Os had been completely oxidized.

A Geiger counter was used to give a rough indication of the activity in each fraction. A more accurate assessment was made for the second batch by counting the activity of a 0.5 mL aliquot of each fraction in the NaI (Tl) well detector (see below). For the second batch of radiotracer, the first fraction contained 65.3% of the total radiotracer collected. Assuming a quantitative distillation, which was later shown to be the case for this type of distillation, the first fraction contained approximately 30.4 ng/mL of Os (both ^{191}Os and non-activated ^{190}Os) in a 4.5N HBr solution. It must be noted that this is a much higher concentration of Os than is found in seawater (approximately 3 pg/L (Sharma et al., 1997)). It wouldn't be possible to use a ^{191}Os radiotracer at the same concentration as is found in seawater, as the level of activity would be too low to measure with any accuracy.

This large difference in concentration may affect how the element behaves in a solution. This must be noted when utilising the radiotracer experiment results for real seawater analysis.

2.1.4 Cleaning the Glassware

The flask used in the distillation of the radiotracer was used to perform a qualitative test of the glassware cleaning procedure, used to clean glassware for both radiotracer experiments and real seawater distillations. The general cleaning procedure for the flasks and glass apparatus was to heat in refluxing 4.5N nitric acid for a minimum of 8 hours. The flask was filled with, and placed in a beaker containing, cold 4.5N nitric acid and the covered beaker was heated on a hotplate. Before cleaning, the flask showed an activity of 1600-1800 cpm using the Geiger counter. After just 90 minutes of heating, the flask was measured to be at background activity.

2.1.5 Shielding and Safety

As the radiotracer and any contaminated waste or utensils emit x-rays and gamma-rays, they must be shielded with a high atomic number material. A lead cage was constructed for storage of radioactive material. X-rays and gamma-rays are photons; they have no mass and no charge. They can travel from a few cm to very long distances in air. Personnel film and ring dosimeters were worn during experiments and counting. All experiments were performed in a fume hood. Routine surveys of the working area were performed and documented.

2.1.6 Counting the Activity of the Radiotracer

2.1.6.1 The NaI (Tl) Well Detector

The activity of the radiotracer was determined in a NaI (Tl) well detector. Thallium-activated sodium iodide is a very good scintillation material for gamma-ray spectrometry. It displays extremely good light yield and excellent linearity. A well crystal is a circular cylinder into which a well has been machined. A significant advantage of this geometry is the very high counting efficiency that can be achieved by placing the samples to be counted at the bottom of the well. Almost all of the gamma rays that are emitted from the source are intercepted and, for low-energy gamma rays like those emitted by the ^{191}Os radiotracer, the counting efficiency in this geometry can approach 100% (Knoll, 1979). A lead wall was built around the well detector to reduce the background effects due to cosmic rays and to gamma rays from surrounding material (Friedlander et al., 1966). The ambient background was also reduced due to the fact the counting well was in the basement of a building. Radiotracer solutions were counted in capped cylindrical glass vials (5 mL volume).

2.1.6.2 Software

The well detector was linked to a computer with Maestro II Software (model A64-BI, EGG Ortec). The software was used to display a disintegration energy spectrum emitted from the ^{191}Os radiotracer. The ambient background count (from cosmic and gamma rays) was subtracted from the measured spectra. This ambient background was generally found to be insignificant because of the shielding used around the well. The software was then used to calculate the Gross Area under the curve of the combined Os peaks at 65 and 129 KeV. This area under the curve is the integration of the counts in the Region of Interest (ROI). A Net Area was calculated by subtracting a spectral background due to Compton scattering. The chosen ROI was critical as the start of the slope of the 65 KeV peak was very close to the Compton continuum. The point where the slope of this peak and the continuum meet changes with instrumental drift, and so the ROI could not be fixed and had to be optimised for each counting run.

There is a certain amount of "Dead Time" during the counting time. During this Dead Time, the software is processing the data it has received and is not collecting the data coming from the well detector. The Dead Time is significantly higher when a sample with a high level of activity is counted. The software subtracts this Dead Time from the Count Time to give a Live Time. This represents the length of time the software was collecting data.

2.1.6.3 Decay Corrections

The ^{191}Os radiotracer has a short half-life (15.4 days) and a correction must be made for the decay when comparing activity counts measured at different times. An aliquot counted at the beginning of an experiment decayed a significant amount by the time it was counted at the end of the experiment. Activities were decay corrected to the activity at the start of the experiment using the equation:

$$R_0 = R_t \times \exp^{\frac{t \times \ln 2}{t_{1/2}}}$$

where:

R_0 = disintegration rates or Net Area when the radiotracer was distilled

R_t = disintegration rates or Net Area at the time of counting

t = time between radiotracer distillation and time of counting

$t_{1/2}$ = half-life = 15.4 days = 369.6 hours

2.1.6.4 Spreadsheet Computer Programme

A computer spreadsheet was developed to calculate the decay corrected disintegration rate. For the distillation and microdistillation experiments, the programme also compared the disintegration rate of the starting radiotracer with the radiotracer recovered after the experiment, giving the yield of each experiment. Corrections for differences between the starting and final radiotracer were made. These differences included the decay during the reaction, the "live" time the sample was counted for (samples with low activity had to be counted for longer to achieve acceptable accuracy and precision) and the dilution from pure radiotracer which the solutions represented.

2.1.7 Precision and Geometry Tests

2.1.7.1 Precision with Counting Time

The precision of counting and the positioning of the sample in the well were investigated using an array of radioactive sources. The first test was performed to investigate how precisely the activity of a sample could be measured using different lengths of time for the counting (live time). A ^{137}Cs source (84.6% emission at 661.2 KeV) was used as, from what was available at the time, this was the only source to have a high enough activity to produce reproducible disintegration rates. The source was placed at the bottom of the well and its activity was counted for different lengths of time. The results are shown in Figure 2.1. The graph shows a linear relationship between the length of time the sample is counted and the Net Area activity. The activity of the ^{137}Cs source can be measured to a precision of ± 0.25% for a Live Time between 107 and 655s. This precision was calculated by obtaining the activity for each data point (by dividing the Net

Area by the Live Time) and then determining the spread in these values. It must be noted that the peaks for Os are at a much lower energy (65 and 129 KeV) and the counting precision may therefore be different for an Os radiotracer.

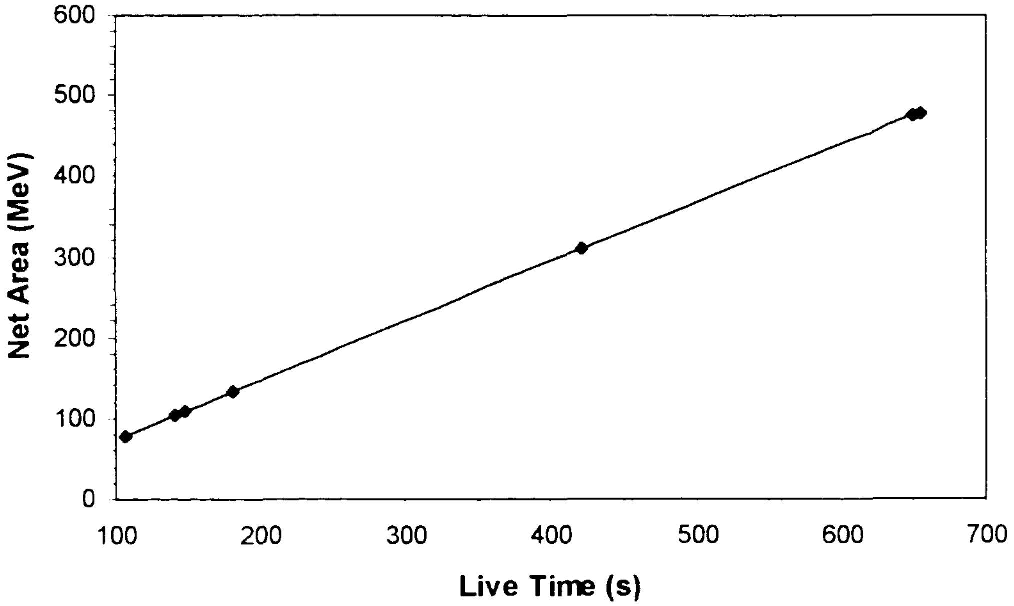


Figure 2.1. Live Time and Net Area

A ^{137}Cs source was counted for different lengths of time to investigate counting precision (the source was only counted once for each length of time and so the precision of each measurement is not known). The graph shows a linear relationship between the counting time (Live Time) and the activity (Net Area). The activity of this source may therefore be calculated to a precision of ± 0.25% (for a Live Time between 107 and 655s) by dividing the Net Area by the Live Time.

2.1.7.2 Geometry Calibration

Distributing radioactive material within a large volume of solution, as opposed to concentrating it in a smaller volume, will decrease the gamma ray intensity at the detector. With low energy gamma rays, an increase in the sample distance away from the detector window results in an increase in the number of gamma events which are attenuated by self absorption before being detected (Buesseler, 1986). This was investigated in order to determine the optimum volume for counting a radiotracer solution. It was also useful to determine to what extent the difference in volume affects the disintegration count. A 0.02 mL aliquot of ^{191}Os radiotracer was transferred to a glass counting vial and its activity was measured. Successive volumes (0.250 mL and then 0.500 mL) of Milli-Q water were added up to 5.000 mL, counting the activity of the solution three times and calculating the mean after each addition.

The graph of the results (Figure 2.2.) shows that the radiotracer may be counted in a solution of between 0 to 1.250 mL to give an activity with a precision of ± 1.9%. This was determined by calculating the standard deviation in the measured activity for this range in volume. As the solution volume increased over 1.250 mL, the activity recorded at the detector generally decreased. If a larger range in volume is taken into account, the precision of the measurement decreases. It was decided that as ± 1.9% was an acceptable counting statistic, the radiotracer would only be counted in volumes of between 0 and 1.250 mL. It should be noted that this is a counting statistic, and that when the radiotracer is used in distillations and microdistillations, the experimental reproducibility may not be as good.

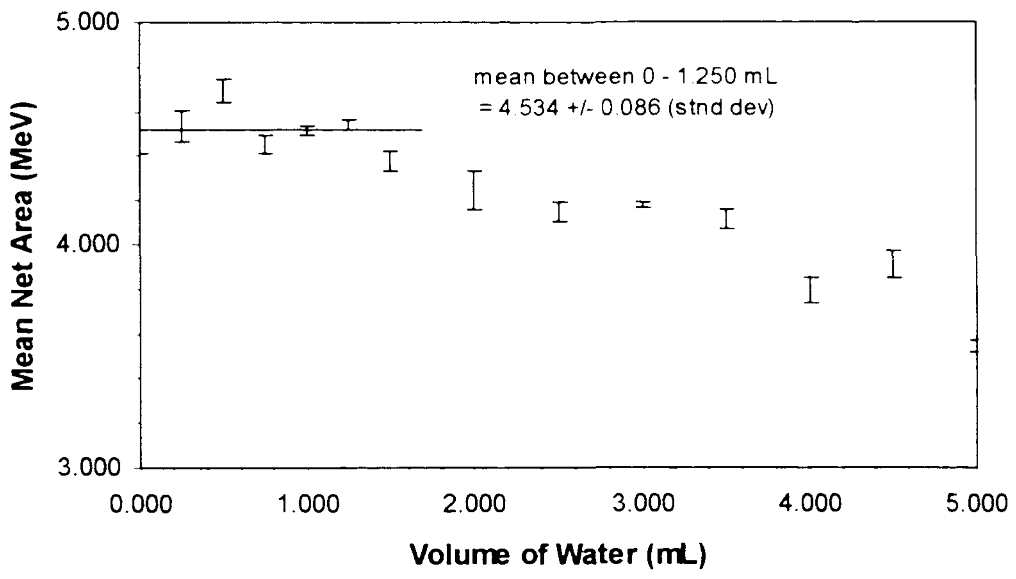


Figure 2.2. Geometry Calibration

The activity of an aliquot of ^{191}Os radiotracer was repeatedly measured (for the same length of time) after successive aliquots of water had been added to it. The results show that the activity of the radiotracer may be measured to a precision of ± 1.9% in a solution of volume between 0 and 1.250 mL.

2.1.8 Summary

The ^{191}Os radiotracer was prepared to develop a method for the analysis of seawater Os. The radiotracer was produced by the neutron bombardment of ^{190}Os metal. The metal was then fused with sodium peroxide, distilled and collected as in a 4.5N HBr solution. A NaI (Tl) detector was used in all counting of the radiotracer. The detector was linked to a computer with Maestro II software and a spreadsheet was used to assist in the calculating of the data. Precision and Geometry tests were performed on the well detector to ensure the validity of the data. The tests show a linear relationship between counting time and activity measured, and that a radiotracer should be counted as a solution of between 0 and 1.250 mL.

2.2 Storing Seawater Samples for Osmium Analysis

2.2.1 Introduction

Conditions required to retain Os in solution during sample storage were examined using the radiotracer. There is potential for the loss of Os in the seawater from both adsorption onto the inside surface of bottles and volatile losses. Osmium is known to be readily adsorbed onto surfaces, and this has been widely reported to cause memory effects during its analysis by ICP-MS (Dickin et al., 1988; Jarvis et al., 1992c; Richardson et al., 1989). Little has been published however on the adsorption and loss of Os to bottle surfaces.

Osmium is also known to be highly volatile as the tetraoxide form. The speciation of Os in seawater is not known; it has never been determined experimentally. However, pE-pH diagrams constructed for low Os concentrations (in the fM range) at pH = 8 and pE = 12 predict that $[H_3OsO_6]^-$ will be the dominant species (Palmer et al., 1988). Thermodynamic calculations predict that Os will form only the +8 oxidation state in seawater (Whitfield and Turner, 1987). Although non-volatile as an anion, the $[H_3OsO_6]^-$ species may be made volatile if acid is added to the seawater for storage. It is common practice to acidify seawater collected for trace metal analysis shortly after collection, as trace metal solutions are generally at their most stable under highly acidic conditions (Howard and Statham, 1993). Osmium standard solutions are normally sold as a 2.4N HCl solution.

Experiments performed (Koide et al., 1996) using a ^{185}Os radiotracer as the hexachloroosmate $[OsCl_6]^{2-}$, show a loss of radiotracer in the solution to the walls of polycarbonate and Pyrex bottles (0.5% loss per day) and polyethylene bottles (2.5% loss per day). Levasseur et al. (1998) however, observed no loss of Os from two seawater samples when they were stored in Pyrex bottles for a month longer than the majority of the other samples.

An understanding of these phenomena is essential for the study of Os in seawater. The seawater must be collected and stored prior to analysis, and steps must be taken to ensure that the metal is not lost through vaporisation or to the wall of the container during this time. A possible alternative is to distil the seawater immediately upon collection. This alternative method would be employed on seawater samples collected from the eastern Pacific Ocean.

2.2.2 Use of Radiotracers for Adsorption Investigations

The radiotracer is an ideal tool for such an investigation. In order to cover the glass surface of a one litre vessel with a monomolecular layer of a hydrated cation, only 10^{-7} to 10^{-8} moles are required. The amount of radionuclide that is adsorbed on the walls of the container in this investigation, will depend on the concentration, on the chemical state of the radionuclide and on the nature of the container material. Choppin et al. (Choppin and Rydberg, 1980) have used a thorium radiotracer to investigate the adsorption of thorium on the walls of glass and polyethylene containers, as a function of concentration and pH. Their results show that at $pH<2$, less than 10% of the thorium solution (2×10^{-8} M thorium perchlorate) adsorbed on the walls of both glass and polyethylene containers. This rapidly increased to over 80% adsorption at pH 4 for both materials. At pH between 6 and 12, the adsorption onto glass fell back down to <10% whereas it stayed at 90-100% for polyethylene.

2.2.3 Volatile Losses and Adsorption

Osmium in seawater is thought to be in the form of the oxyanion $[H_3OsO_6]^-$ (Palmer et al., 1988). This oxyanion is in equilibrium with the neutral molecules OsO_4 and H_4OsO_6 and the doubly charged anion $[H_2OsO_6]^{2-}$:

$$OsO_4 + 2H_2O \leftrightarrow H_4OsO_6$$
$$H_4OsO_6 \leftrightarrow H^+ + [H_3OsO_6]^-$$
$$[H_3OsO_6]^- \leftrightarrow H^+ + [H_2OsO_6]^{2-}$$

Little has been published on the physical process by which Os adsorbs to surfaces. Adsorption is the accumulation of molecules at a surface (Freemantle, 1987). Adsorption should not be confused with absorption, which is the diffusion of a substance through the bulk of another substance. Molecules and atoms can attach to surfaces in two ways (Atkins, 1990). Physical adsorption or physisorption occurs when molecules are bound to active sites on a solid surface by Van der Waals forces. The small amount of energy that is released when a particle is physisorbed is insufficient to lead to bond breaking, and so the molecule retains its identity, although it might be distorted by the presence of the surface. Chemical adsorption or chemisorption occurs when the molecules are held to the active sites on the surface by chemical bonds (usually covalent bonds). The enthalpy of chemisorption is very much greater than for physisorption, and the molecule may be torn apart.

It is possible that the anionic Os species adsorb at cationic sites on the bottle surface. The neutral species H_4OsO_6 may be adsorbed onto the surface by Van der Waals forces. Also, it is the hydrolysis product of OsO_4 and in this form may become reduced to the solid OsO_2 and deposit on the walls of the container. This reaction is promoted in the presence of olefins and is in fact how tissues are stained when OsO_4 is used in electron microscopy, since the black OsO_2 is deposited upon oxidation of the carbon double bond. It must be noted however that the transformation of OsO_4 to H_4OsO_6 is very slow (more than several days) (Bavay et al., 1967).

If the seawater is not acidified, equilibrium favours the singly charged anionic form (Palmer et al., 1988). In this ionic form osmium is non-volatile. If the seawater is acidified with H_2SO_4, the equilibrium is pushed towards the highly volatile OsO_4 form. If the seawater is acidified with HCl or HBr, a hexahalogen form may be produced. This however, requires the Os to be reduced from +8 to +4 state. It is unclear whether this will happen at pH2. If the Os is reduced at this acidity, the excess protons in the acidic solution will favour the neutral H_2OsX_6 species.

$$H_4OsO_6 \leftrightarrow H^+ + [H_3OsO_6]^- \xrightarrow{HX} H_2OsX_6$$

$$[OsX_6]^{2-} \xrightarrow{acidic} H_2OsX_6$$

The Os is now in the neutral H_2OsX_6 form which not volatile. It may however adsorb to surfaces through Van der Waals forces.

As a conclusion, there is potential for seawater Os to be adsorbed onto surfaces whether it is in the ionic or neutral form, but it is only volatile as the neutral OsO_4. This experiment will examine the combined losses through volatilisation and adsorption.

2.2.4 Adsorption Experiments

2.2.4.1 Experimental

Fourteen bottle experiments were set up to test the bottle material and the effect of acid addition to the solution (see Table 2.1.). The bottle materials tested were glass, polyethylene and Teflon. The bottles were chosen to be as similar to each other in size, shape and opacity of the bottle material as possible, so that only the material of the bottle was different. In this way, it is expected that losses to the different materials will be equivalent in the larger bottles used for storage.

The matrix used was sand-filtered seawater (250 mL), the organic content of which approximates open-ocean levels. Non-filtered coastal seawater will have a higher concentration of organic matter than open-ocean seawater. Osmium tetraoxide is known to have a high affinity for organic carbon (Ravizza and Turekian, 1989) and this high concentration of organic matter may affect the adsorption or volatilisation of the metal. In coastal waters, the speciation of elements with a high affinity for organic ligands may be affected by the higher concentrations of dissolved organic compounds present (Bruland, 1983). The seawater was acidified to pH 2 with hydrobromic acid (HBr), hydrochloric acid (HCl) and nitric acid (HNO_3) and a control with no added acid was included. The radiotracer (0.5 mL) was heated on a hotplate to evaporate excess solvent and quantitatively transferred to the seawater matrix. The approximate Os concentration (both ^{191}Os and non-activated ^{190}Os) of the solutions was 0.06 μg/mL. It must be noted that this is a much higher concentration of Os than is found in seawater (approximately 3 pg/L (Sharma et al., 1997)) and its speciation is unlikely to be the same. The HBr in glass bottle experiment was conducted in triplicate in order to check the reproducibility of the results.

After each solution had been mixed, an aliquot was immediately taken to obtain a "start" count. The solutions were left undisturbed, and an aliquot was taken after 3, 15, 21 and 28 days and counted in the well detector. As time passed, Os may have been lost to the walls of the bottles or to the air space inside the bottle. The concentration of radiotracer in the successive aliquots decreased with time and the well detector measured this.

Table 2.1. Number of Bottle Experiments with Each Acid and Bottle Material

Acid / Bottle Material	HBr	HCl	HNO_3	Control
Glass	3	1	1	1
Teflon	1	1	1	1
Polyethylene	1	1	1	1

2.2.4.2 Results

The results (Figures 2.3., 2.4. and 2.5.) clearly show that the radiotracer is retained in solution more effectively in glass and Teflon bottles than the polyethylene bottles. Even after 28 days, 99% and 95% of the radiotracer remained in the solutions that had been acidified and stored in the glass or Teflon bottles respectively. The solutions that had been stored in the glass and Teflon bottles but not acidified both had 80% of the radiotracer still in solution.

The polyethylene bottles performed very badly. After 15 days, the acidified solutions stored in polyethylene contained only 30% of the radiotracer added at the start of the experiment. After 28 days, this had decreased to 10%. The solution stored in polyethylene that had not been acidified performed even worse.

The results show that acidifying the solution to a pH of 2 does help to keep the ^{191}Os radiotracer in solution. It is not clear from the results which type of acid helps to keep Os in solution the best.

Some of the seawater samples that were acidified with HBr and stored in either glass or Teflon bottles showed an unexpected equilibration affect. The aliquots of the solutions that were taken immediately after mixing showed that the solutions contained only 5 and 12% of the Os added. The aliquots taken from the same solutions after 3 days contained 33 and 48% of the Os respectively. After 15 days, the solutions were measured to contained approximately the same concentration of Os as the solutions acidified with the other acids. The reason for this effect is not understood. A possible explanation is that the Os was adsorbed onto the wall of the container as soon as it was added to the matrix and then leached back into solution with time. It is not understood why this effect was not observed in the polyethylene bottles, or why it was only observed in one of the three solutions that had been acidified with HBr and stored in glass bottles. It was for this reason that HBr was not used to acidify real seawater samples.

2.2.4.3 Method to be used for Real Seawater Storage

It was decided that seawater should both be distilled on the ship and also collected and stored for distillation in the clean laboratory. This experiment shows that seawater should be collected in either glass or Teflon bottles, and acidified quickly after collection to pH2 using HCl. Even though Os remained in solution quantitatively under these conditions, the seawater should be analysed as quickly as possible as the stability of the Os in solution after 28 days was not examined.

Given the kinetics of losses, distilling the seawater on the ship immediately after collection may avoid the problem of Os losses. Sample storage problems can be avoided. A HBr distilled sample can be stored in a small Teflon vial, which is more practical for shipping and also reduces the risk of contamination during storage. It is however less practical to conduct distillations out at sea, and there may be a greater potential for contamination if the distillation is not conducted in a clean lab. Any contamination is not discovered until the samples are analysed after the cruise.

Distillation radiotracer experiments later showed that the Os collected in HBr after the distillation is relatively stable in solution. Isotope dilution helps to circumvent volatilisation problems. Spike and sample Os is equilibrated during the distillation (as shown later) and any loss in sample Os in the HBr results in an equal loss of spike Os. Thus concentrations and isotopic ratios are unaffected.

It was decided that the majority of the seawater samples collected in bottles for distillation in the laboratory should not be spiked upon collection. Osmium is thought to be present in different species in seawater ($[H_3OsO_6]^-$) and in the spike ($[OsCl_6]^{2-}$). It is assumed that spike-sample equilibration will not be achieved by simply adding the spike to the seawater. There is therefore potential for differential and irreversible loss of spike and sample to the bottle walls and to evaporation. The isotope dilution calculation may give an Os concentration that is either higher or lower than it should be depending on whether the spike or sample is preferentially lost. The spike should be added just before the distillation. In this case, any loss of Os before the distillation will only tend to produce a lower Os concentration by isotope dilution.

Samples collected from the Indian Ocean for Os analysis (Levasseur et al., 1998) were stored in Pyrex (borosilicate glass) bottles for 3 months during the period of analysis, and no Os loss was observed. This confirms the theory that glass is a suitable material for the storage of seawater for Os analysis.

On the following page: Figures 2.3., 2.4. and 2.5. show the percentage of ^{191}Os radiotracer, remaining in a seawater matrix acidified with different acids and stored in different bottle material, over the period of one month (G=glass, T=Teflon, P=polyethylene, B=HBr, C=HCl, N=HNO_3, Z=control). The results clearly show that the radiotracer is retained in solution more effectively in glass and Teflon bottles than the polyethylene bottles, and that acidifying the solution does help to prevent loss of Os. A problem with equilibration is observed with some of the HBr-acidified solutions.

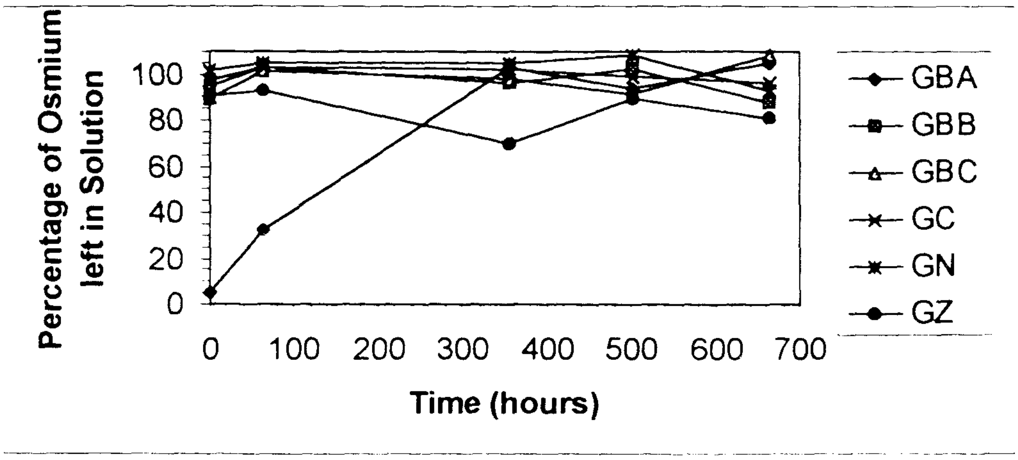


Figure 2.3. Adsorption Data for Glass Bottles
G=glass, T=Teflon, P=polyethylene, B=HBr, C=HCl, N=HNO_3, Z=control

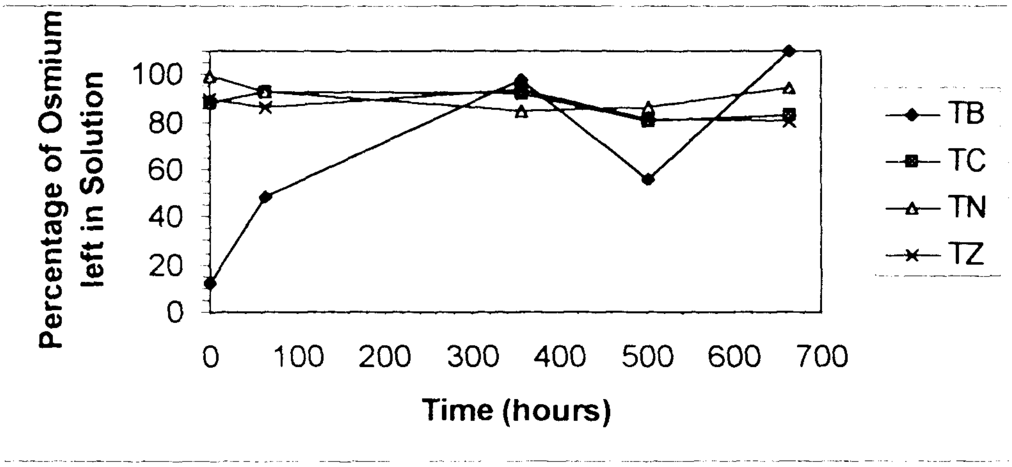


Figure 2.4. Adsorption Data for Teflon Bottles

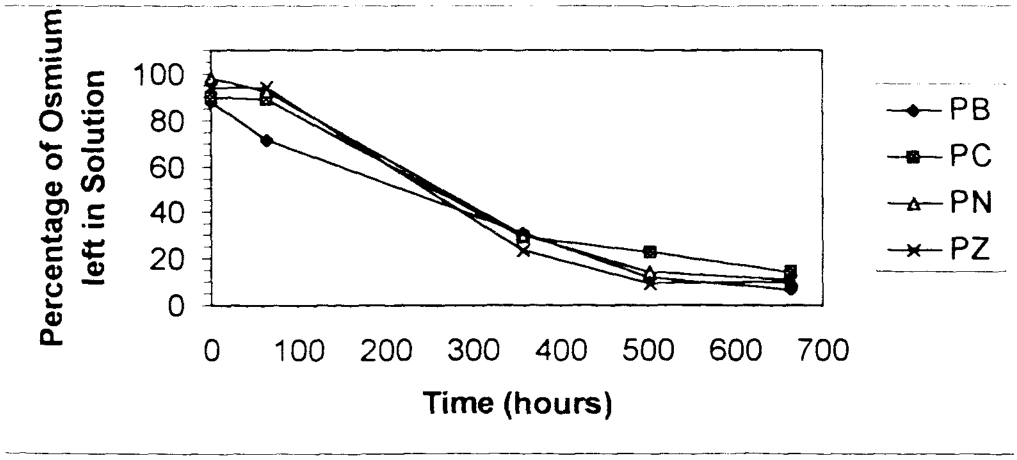


Figure 2.5. Adsorption Data for Polyethylene Bottles

2.3 Distillation of Osmium from Seawater

2.3.1 Introduction

The radiotracer was applied to investigate whether Os can be distilled directly from seawater. Similar distillations are used in the bulk and leach analysis of Os in sediment, after a fusion or leaching step (Hauri and Hart, 1993; Ravizza and Pyle, 1997). Sediments, however, have a much higher concentration of Os than seawater. Metalliferous sediments for example have Os concentrations of 60-600 pg/g (Ravizza and Pyle, 1997) compared to 10.86 ± 0.07 pg/kg for seawater (Levasseur et al., 1998). The few direct measurements of seawater Os have been close to the detection limit of the mass spectrometers, and so for a method to be viable, the Os must be quantitatively concentrated from the seawater.

The distillation was performed under a range of conditions in an attempt to optimise the yield and to gain information on exactly how the distillation proceeds. Different distillation apparatus, a variety of oxidizing agents and a number of solutions in the collecting tube were tested and the distillation was performed at different rates to develop a technique that isolated Os from seawater with a high and reproducible yield.

These experiments show that a direct distillation can be used in the isolation of Os from seawater. The seawater is acidified with sulphuric acid and hydrogen peroxide is used as the oxidizing agent. The OsO_4 produced is collected in HBr and about 10 mL of codistilled water is collected. If the distillation is performed at a slow and steady rate, taking 3h30 to 4h to fill the trap, a yield of over 90% is achieved. The experiments have also shown that spike-sample equilibration will be achieved using this method.

2.3.2 Equipment and General Procedure

2.3.2.1 Distillation Apparatus

Two sets of distillation apparatus or stills were employed, one from Oregon State University (OSU) and the other from the Woods Hole Oceanographic Institution (WHOI). The differences between the two sets of stills are described later in this section. Figure 2.6. shows the distillation apparatus and also the method developed from the radiotracer experiments and blank contamination measurements. This method was later used for the isolation of Os from eastern Pacific Ocean seawater.

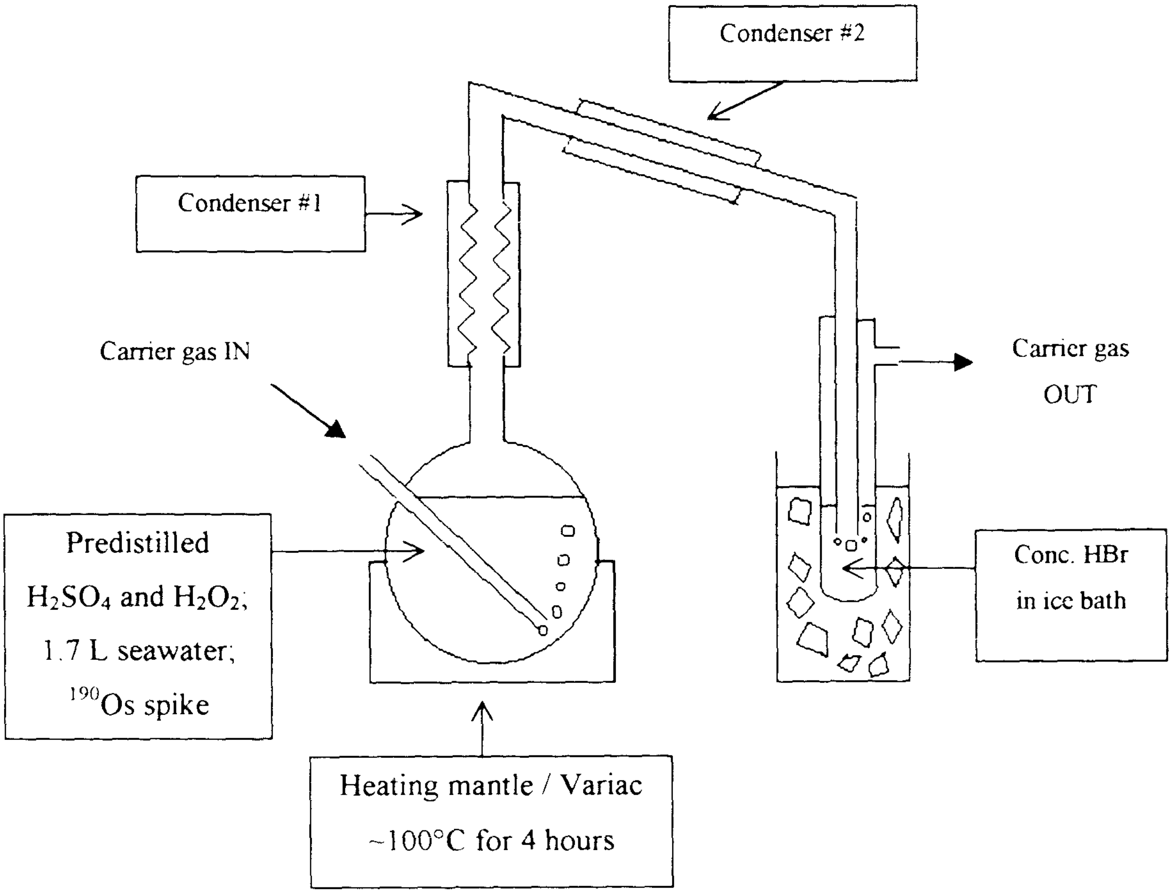


Figure 2.6. Distillation Apparatus

The distillation setup is used to separate Os from seawater. For samples distilled in the laboratory, the H_2SO_4 and H_2O_2 reagents were predistilled in the 2L flask to remove any Os contamination. The seawater (1.7 L) and ^{190}Os spike were then transferred to the flask. The solution was heated to approx. 100°C for 4 hours and the OsO_4 was collected in the conc. HBr cold trap. This HBr was then concentrated to 30 µL for the microdistillation to purify the Os. The total Os contamination for the whole procedure was measured as 0.12 pg. For samples distilled on the ship during the cruise, the method developed from the radiotracer experiments was used directly. In these distillations, the reagents were not predistilled and consequently, these analyses will have a higher Os contamination.

NOTE: Only the WHOI apparatus has two condensers. The OSU apparatus does not have condenser #1.

A comparatively larger distillation flask than is used for sediments is required for seawater analysis. Previous work has suggested that seawater has Os concentrations of between 1.7 pg/L (Koide et al., 1996), 3 pg/L (Sharma et al., 1997) and 10.86 pg/kg (Levasseur et al., 1998). Negative Thermal Ionization Mass Spectrometry (NTIMS) has a detection limit for Os of a few picograms (G. Ravizza and B. Peucker-Ehrenbrink, pers. comm., 1997). The NIMA-B NTIMS at WHOI is able to obtain 9.0 - 9.2 V intensity (with an electrometer current of 10^{-10} A) for 9 pg of ^{190}Os spike. It is known however that the same mass of Os isolated from sediment will give a much lower intensity. It is thought that impurities from the chemistry may interfere with the ionisation of the Os on the filament. In order to obtain concentration and isotopic ratio data, more than one litre of seawater must be distilled with a high efficiency. Two litre flasks were therefore employed for both distillation apparatus.

The flask was placed in a heating mantle with a variable heat control (or variac) and the distillation still was then put in place. This was performed before any reagents were added to ensure no Os was lost through oxidation before the trap was in place. The joints between the pieces of glassware were sealed with Teflon tape. Not only did this stop any leak of OsO_4 or water vapour, but it also served as a detector of leaks. Any water vapour leaking from the joint would condense on the tape and be seen as water droplets.

Two methods were used to determine whether Os was lost through the "exhaust' of the apparatus (i.e. not captured by the cold trap). A length of either Tygon or rubber tubing, known to adsorb Os, was attached to the trap outlet. After the distillation, the tubing was coiled and placed in a plastic bag for counting. In principle, the tubing also improves safety by diminishing the release of toxic, radioactive gases.

The other method for checking losses involved inserting a second HBr trap in parallel with the first one. Any OsO_4 not trapped by the first solution was directed through a second trapping solution. This solution could then be counted to give a measure of the non-captured Os.

Air was bubbled through the matrix as a carrier gas for the OsO_4. A filter was used on the tubing carrying the air to the flask to insure no particulate contamination was introduced.

2.3.2.2 The Matrix

The flasks can comfortably hold 1.5 to 1.7 L of seawater. The same sand-filtered seawater that was used in the bottle experiments was also used for the distillation experiments. Sulphuric acid was added to the seawater in the flask to increase the boiling point of solution, so that the reaction could be conducted at a higher temperature. Hydrogen peroxide in combination with concentrated H_2SO_4 forms the relatively stable H_2SO_5 (Gregoire, 1990).

The sulphuric acid also facilitates the volatilisation of the OsO_4 from the matrix. In seawater, the hydrolysed form of osmium tetraoxide H_4OsO_6 is likely to have mostly dissociated into its acid-base form (Palmer et al., 1988):

$$H_4OsO_6 \leftrightarrow H^+ + [H_3OsO_6]^-$$

Acidifying the seawater to approximately 1N favours the molecular form H_4OsO_6 and thus favours the production of OsO_4:

$$H^+ + [H_3OsO_6]^- \xrightarrow{H_2SO_4} H_4OsO_6 \leftrightarrow OsO_4 + 2H_2O$$

2.3.2.3 The Osmium Radiotracer

The radiotracer is transferred to the acidified matrix by pipette. The transfer of the radiotracer from the counting vial to the distillation flask was verified to be quantitative by counting the empty vial and pipette tip after the transfer. Quantitative transfer was achieved in each distillation.

The radiotracer was prepared in a 4.5N HBr solution. In this solution, Os will be in the form of a hexahalogen complex $[OsBr_6]^{2-}$. Osmium is not likely to be present in this form in seawater. In later experiments, distillations were conducted with radiotracer that had been collected in 30% hydrogen peroxide. It is thought that in this solution, Os is present as the same species $[H_3OsO_6]^-$ predicted to be dominant in seawater, and thus the distillation is more comparable to the distillation of real seawater Os. Enough radiotracer must be used in the distillation so that the collected fractions may be counted with precision. Two 20 mL batches of radiotracer had been prepared and either 0.5 mL or 1 mL aliquots of stock radiotracer was used for each distillation.

2.3.2.4 The Oxidizing Agent

Both 5.25% sodium hypochlorite (NaOCl) (bleach) and 30% hydrogen peroxide (H_2O_2) were tested as oxidising agents. Both of these oxidizing agents have the advantage that they do not contain any element that is not naturally found in seawater and may cause interferences during the analysis. Chromium trioxide, which is used as the oxidising agent in the microdistillation, was rejected as it is known to form a volatile Cr compound that hinders the task of concentrating of the sample ready for the microdistillation (G. Ravizza, pers. comm., 1997). This compound could be $CrCl_4$ which is formed as a vapour when the trihalide $CrCl_3$ is heated in an excess of chlorine (Cotton and Wilkison, 1988). Chromium trioxide is also highly poisonous. If Os occurs naturally in seawater in the +8 state, it is possible that an oxidizing agent is not actually needed. Acidifying the seawater favours the Os in seawater towards the OsO_4 speciation, as shown above.

2.3.2.5 Collection of the Distilled Osmium Radiotracer

The distilled radiotracer was collected in either ice-chilled concentrated HBr or 30% H_2O_2. Hydrogen peroxide was used in later reactions, both to test a double-distillation method and to produce a radiotracer in the H_4OsO_6 form. This is believed to be the dominant Os species in seawater, and so this solution can be used in a distillation that is more comparable to the distillation of real seawater Os.

The trap was placed in an ice bath. This is thought to greatly increase the efficiency as the gaseous OsO_4 is primarily trapped by condensing upon contact with the cold HBr (the boiling point of OsO_4 is 130°C). It is then converted to $[OsBr_6]^{2-}$.

2.3.2.6 Counting Activity with the Well Detector

Counting the Activity of the Trap Fractions

A 1 mL aliquot of each fraction (a HBr solution) collected was counted in the well detector and compared to the count of the original radiotracer added to the flask. The radioactivity of a solution can be attenuated by the solution itself. Hydrobromic acid was later found to attenuate more activity than water. This must be taken into account when comparing the radioactivity of the original radiotracer and the radiotracer collected in the trap. When using the OSU still, both solutions are 4.5 N HBr, and so the activity is directly comparable. In later reactions however, a greater volume (15 mL instead of 10 mL) of concentrated HBr was used in the trap, while the same amount of co-distilled water (10 mL) was collected. The resulting trap solution was therefore more concentrated in HBr (5.4 N) and thus the activity was attenuated to a greater degree than in the 4.5 N HBr solutions. When the WHOI still was used, 1 mL of a standard prepared from 1 mL radiotracer, 4 mL HBr and 10 mL water was counted and taken as the "start" activity. This was directly compared to the 1 mL aliquot of each fraction.

Counting the Activity of the Tubing on the Exhaust

The radioactivity of the tubing placed on the "exhaust" or outlet of the still was measured by counting it on top of the well detector. It was determined that count rates for the tubing counted on top of the well would have to be multiplied by 8.06 to be comparable with a source counted inside the well. This was done by comparing the count rates of 0.1 mL of radiotracer in a vial inside the well and 0.1 mL of radiotracer in a length of tubing on top of the well, and the measurements were repeated to verify the reproducibility.

Counting the Matrix

All distillations showed that it was not feasible to take an aliquot from the distillation matrix and count it directly. The signal to noise ratio was poor at this dilution. For the first three distillations for example, 0.5 mL of radiotracer was diluted over 3000 times when added to the 1500 mL seawater, 42 mL sulphuric acid and 25 mL or 10 mL oxidising solution. The count obtained therefore has to be multiplied by this multiplication factor in order to compare ^{191}Os concentrations. This multiplies the error by such an extent that the values are not useful.

2.3.2.7 Experimental Reproducibility for the Distillation Experiments

Precision and geometry tests have shown that the activity of the radiotracer may be counted to a precision of ± 1.9%. This is a counting statistic however, and the experimental reproducibility for the distillations should be determined so that the distillation experiments may be compared. Due to the relatively short half-life of the radiotracer, time constraints meant the experiments could not be repeated several times to evaluate the reproducibility of the results. The aim of using the radiotracer was to develop a method of isolating Os from seawater with a high yield. It was not essential that the yield of the distillation be highly reproducible, as an internal standard (^{190}Os spike) would be used to determine concentrations by isotope dilution. It was important that the same percentage of sample and spike Os be isolated from the matrix.

The experimental reproducibility must therefore be determined qualitatively, by comparing the yields of distillation experiments that were similar to each other. Distillations R2b and R2c for example, differ in two ways: the latter was performed at a slightly faster rate and 50% more HBr was present in the collection trap. The yields for the two distillations are 65.2% and 66.7%, respectively. These values are within 1.5% of each other. Distillations R4, R5 and R7 were conducted under similar conditions and produced yields 98.9%, 97.4% and 96.2% respectively. There is a difference of 3.7% in the yields obtained from the three experiments. These comparisons take into account both the experimental reproducibility of the distillation and the counting reproducibility of the radiotracer. They suggest that the reproducibility in the distillation and the counting is about 2%.

2.3.3 Results and Discussion

2.3.3.1 Preliminary Distillation (distillation R2a)

The feasibility of direct distillation of Os from seawater was tested first. The distillation was performed as is described above in the OSU still using NaOCl as the oxidizing agent and collecting in concentrated HBr. The matrix was heated quickly to a high temperature and the first 10 mL of condensed vapour was collected into the HBr after only one hour. Four fractions were collected in 1h20.

Problems with Sodium Hypochlorite as the Oxidizing Agent

It was noticed that the HBr in the first fraction darkened from a pale yellow to a lemon yellow colour, very quickly after the sodium hypochlorite (NaOCl) was added to the matrix, with the carrier gas passing through it but before the matrix was heated. This colour darkened further to an orange during the distillation and by the time the first fraction was full, it was a deep red colour. The following three HBr fractions were successively lighter orange in colour. A similar colour change had been observed when the radiotracer was prepared. The colour quickly turned back to the HBr pale yellow colour if the solution was heated on a hotplate.

Sodium hypochlorite was promoting the formation of chlorine gas, which was carried by the carrier gas to the trap as soon as the NaOCl was added to the matrix. This reacted with the HBr in the trap to produce Br_2, a red liquid:

$$2HBr + Cl_2 \rightarrow Br_2 \text{ (a red liquid)} + 2HCl$$

This may be a problem as it is not known how efficiently this new mixture will trap the OsO_4 bubbling through it. Also, this new solution may oxidize the Os in the solution when it is later concentrated. It was thought possible that the oxidising power of the NaOCl that remains in the flask decreases with time, and is no longer oxidizing any Os before it has all been oxidized. To test this, extra NaOCl was added to the matrix during the distillation just after the fourth trap fraction had been set in place. When this fraction was counted, it was found to contain less radiotracer than the third fraction. This shows that the NaOCl oxidant was not the limiting factor. These problems were investigated in further distillation experiments, but it is because of these concerns and separate worries about whether household bleach might contain impurities, that NaOCl was later rejected as the oxidising agent in favour of hydrogen peroxide.

Results

Fraction #1 contained only 29.8% of the original radiotracer. The total collected in four fractions contained only 46.7%. Over 50% of the radiotracer was unaccounted for. It is possible that the radiotracer had not been distilled and remained in the seawater matrix. It was not possible to count this solution directly due to the dilution of the radiotracer. It is also possible that OsO_4 was either never trapped or trapped and reoxidized out of the solution due to the presence of Cl_2/Br_2.

2.3.3.2 Reducing the Volume of Bleach Oxidizing Agent (distillation R2b)

The preliminary distillation showed that the direct distillation of Os from seawater was a viable concentration method, as long as the yield was increased. The main concern in the first experiment was that the excess of NaOCl hindered the trap efficiency. Therefore, this experiment was repeated under identical conditions, except a reduced volume of NaOCl (10 mL) was used.

The total yield for the reaction increased by nearly 20%. The first fraction, which was a rich orange colour, contained 37.7% of the original radiotracer and the total collected in four fractions was 65.2%. This still left 34.8% that had either remained in the flask unoxidized or had not been trapped in the cold HBr. This experiment suggested that the excess NaOCl was indeed hindering the efficiency of the cold trap, as this was the only variable that was changed from the preliminary distillation.

2.3.3.3 Increasing the Volume of Trap and Capturing Losses from "Exhaust" (distillation R2c)

Experimental

In an attempt to determine where the radiotracer losses had occurred, a third experiment was conducted. It was noticed that with only 10 mL HBr in the cold trap, the surface of the HBr was very close to the upper part of the frit of the gas dispersion tube. The OsO_4 bubbling through the trap may therefore not have be in contact with the solution for enough time to condense/convert it to the osmium hexahalogen form. The distillation was conducted with 15 mL of HBr in each trap fraction. To measure any loss of radiotracer through the exhaust of the still, a length of Tygon tubing was attached to it.

The reaction was unintentionally performed at a faster rate. The OSU still with no first condenser was used and it was thus more difficult to control the rate of reaction. Apart from the increased volume of HBr in the trap and Tygon tubing on the exhaust, this was the only difference with the last distillation.

Results

The results show that the rate at which the distillation is performed greatly affect the distribution of yields among the traps. Only 30.5% of the radiotracer was captured in the first fraction, yet the total in all four fractions was higher than the last distillation at 66.7%. A higher percentage of radiotracer was captured in the third and fourth fraction (9.4% and 8.3% respectively). This showed that the rate of the reaction had been too fast. Water was distilled from the flask before all of the Os had been oxidized to OsO_4.

After the fourth fraction was collected, the trap collecting tube was filled with water and left as the matrix solution in the flask cooled. Although the trapping efficiency of the room temperature water is thought to be less than that of cold HBr, when the activity of the water was counted in the well, it contained 3.3% of the radiotracer. This shows that OsO_4 was still being produced, or at least washed from the still, when the heat source was stopped.

2.3.3.4 Distilling Osmium as a Different Species (distillation R2d)

Experimental

Previous distillations have involved using the radiotracer in the hexahalogen speciation $[OsBr_6]^{2-}$. This is not likely to be the speciation of Os in seawater. In this distillation, the radiotracer was left to react with excess vinylacetic acid (1 mL) for 22 hours in the distillation flask, before the seawater matrix was added to it. The idea was that the ^{191}Os radiotracer would react with the alkene double bond of the acid, forming an intermediate cyclic compound and decompose to generate osmium dioxide OsO_2. The Os must be in the OsO_4 form to follow this reaction, which isn't thought to be the case when in a hydrobromic acid solution:

$$OsO_4 + CH_2{=}CH_2\text{-}CH_2COOH \rightarrow \text{5-ring} \rightarrow OsO_2 + HO\text{-}CH_2\text{-}CHOH\text{-}CH_2COOH$$

As an alternative attempt to capture any radiotracer lost through the exhaust, a second cold trap was installed in parallel with the first.

Results

During the reaction, extra NaOCl was added to the matrix as the solution was not observed to "fizz" and the HBr trap did not turn its usual orange colour. It was concluded that the NaOCl was oxidizing the excess vinylacetic acid and would not oxidize the Os.

The reaction progressed at a very fast rate, and yet, the yields were high. The first HBr fraction captured 44.3% of the radiotracer. Significant amounts of radiotracer were counted in the second and third fraction (16.2% and 11.7% respectively) which was expected for a fast distillation. The total recovery in the three fractions collected was 72.5%. It was not understood whether the generation of OsO_2 actually occurred because, when it is in a HBr solution, osmium is believed to be in the form $[OsBr_6]^{2-}$ and not as OsO_4. It was also not understood why the vinylacetic acid appeared to have improved the yield of the distillation.

Even though more NaOCl was used in this reaction, it seems it was consumed by the excess vinylacetic acid: the first fraction was a rich orange colour (not the deep red observed in the first distillation) and the yields suggest little OsO_4 was lost from Cl_2/Br_2 in the traps.

The second trap in parallel used to capture any OsO_4 leaking from the first trap only contained 0.3% of the original radiotracer, confirming that little OsO_4 escaped the trap of the OSU still.

The Second Radiotracer Batch

A second batch of radiotracer was used to perform six further distillations. In these experiments, the volume of seawater was increased to 1.7 litres. Hydrogen peroxide was used as the oxidizing agent. The seawater was acidified with 30 mL of sulphuric acid. All the distillations were performed at slow rates in order to maximize the total yield of the distillation and the amount of radiotracer collected in the first fraction. Any blank contamination associated with the HBr would thus be reduced if only one trap fraction was collected. Performing the distillation over a longer time also gives the sample and spike Os time to equilibrate, a prerequisite for isotope dilution measurements.

2.3.3.5 Efficiency of Distillation using OSU and WHOI Apparatus (distillations R4 and R5)

In these experiments, the radiotracer was used to determine the efficiency of distillation using two different sets of distillation apparatus or stills. The two stills came from Oregon State University (OSU) and the Woods Hole Oceanographic Institution (WHOI) and differed from each other in a number of important ways (as detailed below). This gave an ideal opportunity to investigate the way Os behaves during a distillation.

Experimental

The two experiments conducted in the stills were designed to be as similar to each other as possible, so that the only difference would be the difference in glassware. In both, a sand-filtered seawater matrix (1.7 L) was acidified with sulphuric acid and then the radiotracer and hydrogen peroxide were added. The solution was heated and the OsO_4 produced was collected in a cold HBr trap. Three or four fractions of distillate were collected from each distillation and counted. A length of rubber tubing as attached to the exhaust of each still to collect and measure any OsO_4 that was not trapped by the cold trap.

Results

The distillations proceeded differently in the two stills. Both stills were very efficient at distilling and collecting the radiotracer in the seawater solution. The OSU still was slightly more efficient, recovering a total of 97.0% in the four trap fractions; the WHOI still recovered 93.3%. However, the WHOI still was much more efficient at recovering the radiotracer in the first fraction. The first WHOI fraction contained 97% of the total recovered Os whereas the first OSU fraction contain only 66% of the total, significant fractions being recovered in each of the next three fractions. The slight difference in total yield was explained by the efficiency of the cold trap. The OSU trap was much more efficient than the WHOI trap. With the WHOI still, 5.6% of the radiotracer bypassed the trap and was captured by the rubber tubing attached to the exhaust. Only 0.4% of the radiotracer escaped the OSU trap (this value was reproduced in an earlier distillation).

The rubber tubing was determined to be efficient at capturing any escaping radiotracer. The length of tubing on the WHOI still exhaust was cut in half and the two halves were counted on top of the detector well individually. The majority of the activity (77%) was found to be in the first half of the tubing.

Discussion

The differences between the two stills were used to explain the difference in the results and to give a valuable insight into how Os acted during the distillation. The overall size and internal surface area of the OSU still was much greater than that of the WHOI still. This could be one explanation for why the OSU still was less efficient at recovering the radiotracer in the first HBr fraction. It had been observed that during the distillations, OsO_4 was produced and passed through the still into the cold trap before any water had been distilled over. This was detected using a Geiger counter held adjacent to the cold trap. Osmium adsorbs onto glass surfaces, especially under non-acidic conditions. It is possible that the OsO_4 produced in the flask adsorbed onto the wall of the still before it had a chance to reach the trap. It was then flushed into the trap as the water distilled through the still, and was thus found in significant concentrations in all four fractions. A similar OsO_4 adsorption effect is observed on the inside of the glassware of an OsO_4 vapour generator (Dickin et al., 1988; Jarvis et al., 1992c; Richardson et al., 1989).

There was no vertical first condenser on the OSU still and so distillations could not be conducted at temperatures above 100°C without quickly filling the collection tube with water. It may therefore have taken longer for the Os in the flask to be oxidized, another reason for the fact that the radiotracer was found in the later HBr fractions. As was shown in the first four distillations, this also made it harder to control the rate of the reaction. As mentioned above, the oxidized radiotracer passed through the still and was collected in the trap before any water was distilled over. It is not understood why the OsO_4 (mp, 40 °C; bp, 130 °C) is not condensed by the cold water (at approximately 5 °C) running through the vertical first condenser on the WHOI still. It is possible that this is due to kinetic factors and the high volatility of this gas.

A greater volume of HBr was used in the cold trap of the OSU still (as the collection tube was larger) and the dispersion tube that reached into it had a glass frit. Both of these facts explained the greater efficiency of the OSU cold trap. Both increased the area of contact between the cold HBr and the carrier bubbling through it, and gave the OsO_4 a greater chance of condensing, forming the osmium hexabromate complex and therefore being trapped.

2.3.3.6 Collecting the Osmium Tetraoxide in Hydrogen Peroxide (distillations R6 and R14)

Experimental

The radiotracer was required in a hydrogen peroxide solution for two experiments and was prepared in two distillations. In each distillation, the radiotracer was distilled from an acidified, sand-filtered seawater matrix and collected in a hydrogen peroxide cold trap. It is believed that OsO_4 bubbling through a 30% hydrogen peroxide cold trap either makes the Os take the form of a hydroxy anion or remains as OsO_4 trapped in solution.

Results and Discussion

The H_2O_2 trap was found to be much less efficient than the HBr trap. The Os recovered by the rubber tubing attached to the exhaust of the hydrogen peroxide trap was 35.5% and 20.2% for the two distillations (only 5.6% was recovered by the tubing on the HBr trap).

In both distillations, it was not possible to compare the activity of the radiotracer before and after the distillation as the radiotracer was in a different solution. The radiotracer was counted in 30% HBr at the start of the reaction and in 30% H_2O_2 at the end. As explained above, HBr is known to attenuate the activity of the radiotracer. The experiment showed that H_2O_2 attenuates less activity than HBr; both distillations gave about 120% yield if no adjustment was made for this attenuation factor.

The distillation was conducted under identical conditions as a previous experiment (distillation R4) apart from the difference in solution used in the trap. It was therefore assumed that the yield for this distillation was also quantitative. The activity of each fraction was thus adjusted to reflect the fact that the solvent was attenuating less activity.

With more radiotracer being lost through the exhaust of the still, the trap fractions contained less radiotracer than when HBr was used as the trapping solution. The percentage of radiotracer collected in the first trap was 61.9% for the first distillation and 76.5% for the second. For comparison, the recovery in the first trap when using a HBr trapping solution was 90.7%.

The only difference between the two distillations was the way in which the matrices were heated. Although the second distillation required one hour less to obtain the first 10 mL of condensate, it was heated at a much steadier pace than the first. To save time, the first distillation was heated at a faster pace at the start of the reaction. The heating mantle was then switched off completely for 15 minutes because of concerns that the reaction matrix was too hot. The Geiger counter held adjacent to the trap at this stage, showed no activity above background, i.e. all of the radiotracer was still present in the seawater matrix. The heating mantle was started again and the fraction was collected in only 1h35. This could have been showing the importance of heating the solutions at a steady pace. Alternatively, the differences in amount leaked through exhaust and percentage recovered in the first fraction, may be explained by the fact hydrogen peroxide is a poor trapping agent. In the longer distillation, the air carrier gas bubbled through the trap for an hour longer. This may have forced the OsO_4 out of the trap and into the rubber tubing.

2.3.3.7 Efficiency of Distillation with Osmium as a Seawater Species (distillation R7)

In previous reactions, the radiotracer was added to the flask in a HBr solution and so it is thought the Os was in the hexabromide form. Osmium is unlikely to have this speciation in seawater. Osmium is believed to be present in seawater as a hydroxy anion $[H_3OsO_4]^-$. The objective of this experiment was thus to investigate the efficiency of the distillation when the Os is present as the $[H_3OsO_4]^-$ species. It was thought that the ^{191}Os radiotracer collected in the hydrogen peroxide cold trap either takes the form of a hydroxy anion or remains as OsO_4 trapped in solution. The speciation of the Os is not known for sure. This distillation would however give a more accurate yield for a real seawater Os distillation.

Results

A total of 91.9% of the radiotracer was collected in the traps. The distillation was performed at a low rate and 90.1% of the radiotracer was collected in the first trap, with only 1.3% and 0.5% collected in the second and third traps respectively. Only 4.3% of the radiotracer was not captured by the traps. All of these values are remarkably similar to the distillation that was performed under the same conditions but with the radiotracer added in a HBr solution. This showed that under the conditions used in these distillations, the same percentage of Os was distilled, whether it was initially present as the perosmic acid or as the hexabromate. The important implications of this are discussed later.

2.3.3.8 Efficiency of Double Distillation Method (distillation R15)

In previous distillations, the OsO_4 has been collected in HBr. For a real seawater sample, the Os in this HBr requires further purification prior to instrumental analysis. One approach is to undertake a second distillation step. To examine this, the radiotracer was distilled from an acidified, sand-filtered seawater matrix and collected in a hydrogen peroxide cold trap (see distillation R14 above). A trap with HBr could not be used, as it would be difficult to perform a further distillation with the Os in this form. This hydrogen peroxide was then taken through a second distillation and the radiotracer collected in HBr. Conditions were similar to the previous distillation except the matrix was Milli-Q rather than seawater.

Results

A total of 78.0% of the original radiotracer was recovered in the traps, of which 75.8% was in the first trap. The rubber tubing on the outlet captured 10.2%. This is a low yield compared to the previous distillation in which a seawater matrix was used. This distillation was performed at a much faster rate; the first 10 mL of condensate was collected in only 2h20 in this reaction compared to 3h45 in the previous. This is thought to be the reason for the difference in yield and once again suggests the importance of performing the distillation at a slow rate.

2.3.4 Conclusions and Method for Separation of Osmium from Environmental Seawater Samples

The details about the reagents and the running conditions used in each of the distillation radiotracer experiments are included in Table 2.2.

It was decided that the WHOI still should be used for real seawater distillations. The experiments have shown that the OSU still is able to recover more of the radiotracer (97.0%) than the WHOI still (93.3%). This is essentially because the OSU trap is more efficient than the WHOI trap; only 0.4% of the radiotracer is lost through the OSU trap compared to 5.6% through the WHOI trap. However, the WHOI still has a smaller internal surface area and there is a first vertical condenser. These two factors mean that more of the radiotracer is recovered in the first trap fraction with the WHOI still (90.7%) than the OSU still (64.3%). This is a very important factor as in a real seawater distillation, only one fraction will be collected. This will reduce any Os contamination that may be found in the HBr and will also save time when concentrating the HBr. Three new sets of WHOI stills were used for actual seawater distillations. This was to avoid contaminating the seawater with ^{191}Os radiotracer not washed from the distillation flask and stills.

The radiotracer experiments show that the following is the optimum method for the distillation of Os from environmental seawater samples. The seawater (1.7 L) is acidified with 30 mL of sulphuric acid and 10 mL hydrogen peroxide is used as the oxidizing agent. The distillation is performed at a slow and steady pace, taking about 3h30 to 4h to fill the trap. About 10 mL of codistilled water is collected in the trap to enable any OsO_4, adsorbed onto the surface of the glass still, to be washed into the trap solution. It is however unclear how efficiently codistilled water will wash out Os adsorbed to the glassware.

Hydrobromic acid is used as the trapping solution. Hydrogen peroxide is a powerful oxidizing agent and it is thought that the Os is a lot less stable in this solution than when it is dissolved in HBr. The hydrogen peroxide solution containing the radiotracer was rapidly distilled during the double distillation procedure. This makes the double distillation method less appealing than the distillation-microdistillation method for isolation of Os from seawater.

The distillations have shown that under the above conditions, the same percentage of Os will be distilled, whether it is present in the seawater matrix as the hydroxy anion or as the hexabromate. This is a very important conclusion. The ^{190}Os spike to be added to the seawater for the isotope dilution is in a 6.2N HCl solution. The osmium will be present as the hexachloro ion $[OsCl_6]^{2-}$ in this solution. Although the distillation of this species has not been investigated, the fact the hydroxy anion and the hexabromate distil in the same proportions suggests that spike-sample equilibration will be achieved. The spike should be added to the seawater immediately before the distillation. Once the sample and spike Os has been collected in the HBr trap, any losses during the concentration, microdistillation or filament loading steps will not make any difference to the Os concentration and isotopic ratios calculated by isotope dilution.

Table 2.2A. Conditions Employed and Results for various Distillation Experiments

"OSU" is Oregon State University. "WHOI" is Woods Hole Oceanographic Institution. "Radiotracer" refers to the solution that the radiotracer was in at the start of the experiment.

Table 2.2A. Distillation Experiments

Distillation	R2a	R2b	R2c	R2d
Still, flask volume	OSU 2L	OSU 2L	OSU 2L	OSU 2L
Matrix, volume	sea water 1.5L	sea water 1.5L	sea water 1.5L	sea water 1.5L
Radiotracer	in HBr/H_2O	in HBr/H_2O	in HBr/H_2O	vinlyacetic acid
Oxidizing agent	NaOCl 25mL	NaOCl 10mL	NaOCl 10mL	NaOCl 37mL
Sulphuric acid	42mL	42mL	42mL	42mL
Trap solution	HBr 10mL	HBr 10mL	HBr 15mL	HBr 15mL
Time from starting the variac to fraction being "full"				
fraction #1	1h	1h	47min	50min
fraction #2	1h05	1h12	52min	58min
fraction #3	1h12	1h22	1h	1h05
fraction #4	1h20	1h31	1h15	not collected
Distillation time	fast	fast	very fast	very fast
Percent recovery of the radiotracer in successive fractions				
fraction #1	29.8%	37.7%	30.5%	44.3%
fraction #2	7.5%	15.9%	15.2%	16.2%
fraction #3	5.1%	7.9%	9.4%	11.7%
fraction #4	4.3%	3.7%	8.3%	not collected
fraction water			3.3%	
Total in traps	46.7%	65.2%	66.7%	72.2%
Exhaust capture	none	none	Tygon tubing	2nd trap
Exhaust recovery	n/a	n/a	0.0%	0.3%
Total Distilled	46.7%	65.2%	66.7%	72.5%

Table 2.2B. Conditions Employed and Results for various Distillation Experiments

Table 2.2B. Distillation Experiments

Distillation	R4	R5	R6	R7	R14	R15
Still, flask volume	WHOI 2L	OSU 2L	WHOI 2L	WHOI 2L	WHOI 2L	WHOI 2L
Matrix, volume	sea water 1.7L	sea water 1.7L	sea water 1.7L	sea water 1.7L	sea water 1.7L	Milli-pore 1.7L
Radiotracer	in HBr / H2O	in HBr / H2O	in HBr / H2O	in H2O2 / H2O	in HBr / H2O	in H2O2 / H2O
Oxidizing agent	H2O2 6mL	H2O2 6mL	H2O2 6mL	H2O2 6mL	H2O2 6mL	H2O2 6mL
	+6mL for #4	+6mL for #4	+6mL for #4	+13.331mL in radiotracer	only	+13.471mL in radiotracer
Sulphuric acid	30mL	30mL	30mL	30mL	30mL	30mL
Trap solution	HBr 5mL	HBr 15mL	H2O2 5mL	HBr 5mL	H2O2 5mL	HBr 5mL
Time from starting the variac to fraction being "full"						
fraction #1	4h15	3h75	4h30 (1h35)	3h45	3h30	2h20
fraction #2	4h25	4h15	4h48 (1h53)	3h58	3h45	2h37
fraction #3	4h45	4h35	5h05 (2h10)	4h20	4h05	2h58
fraction #4	5h05	4h55	5h30 (2h35)	not collected	not collected	not collected
Distillation time	very slow	very slow	very slow but	very slow	faster than R6	much faster than R7
			not steady			
Percent recovery of the radiotracer in successive fractions						
fraction #1	90.7%	64.3%	86.0%	90.1%	95.2%	75.8%
fraction #2	1.6%	18.7%	1.4%	1.3%	2.2%	1.7%
fraction #3	0.7%	10.0%	0.5%	0.5%	0.5%	0.5%
fraction #4	0.3%	4.0%	0.2%	not collected	not collected	not collected
fraction water						
Total in traps	93.3%	97.0%	88.1%	91.9%	97.9%	78.0%
Exhaust capture	Rubber tubing	Rubber tubing	Rubber tubing	Rubber tubing	Rubber tubing	Rubber tubing
Exhaust recovery	5.6%	0.4%	35.5%	4.3%	20.2%	10.2%
Total Distilled	98.9%	97.4%	123.6%*	96.2%	118.1%*	88.2%

* over 100% yield: HBr (start solution) was later shown to adsorb more activity than H_2O_2 (trap solution); explained sections 2.3.2.6 and 2.3.3.6

2.4 Efficiency of the Microdistillation

2.4.1 Introduction and Objective

A number of radiotracer experiments were performed to examine whether a microdistillation technique (Birck et al., 1997; Cohen and Waters, 1996; Roy-Barman, 1993; Roy-Barman and Allègre, 1995; Shen et al., 1996) could be used to purify the Os after the initial seawater distillation. The Os, present in HBr solution after the distillation, must be purified prior to instrumental analysis. Impurities can hinder the loading of the sample onto the Pt analysis filament. It may also suppress the ionization of Os on the filament and cause interferences at Os masses during the mass spectrometry.

Iron meteorite samples have been prepared using a microdistillation technique for Os concentration and isotopic ratio analysis (Birck et al., 1997). The Savillex vial microdistillation technique was reported to have yields of 65-80%. These samples had a much higher Os concentration (between 1-10 μg/g) than seawater (10.86 pg/kg (Levasseur et al., 1998)).

2.4.2 General Experiment Setup

2.4.2.1 Introduction

The microdistillation involves oxidizing the Os to OsO_4 inside a small inverted Teflon vial. The sample solution is placed as a small drop on the cap of the vial and the oxidized Os is collected in a drop of HBr in the tip of conical vial. Figure 2.7. shows the microdistillation setup that was developed using the radiotracer and used in the analysis of seawater Os from the eastern Pacific Ocean.

2.4.2.2 The Teflon Vial

In the following microdistillations, 5 mL conical Teflon vials from Savillex (#24) were used. Between experiments, the vials by rinsed with Milli-Q water, heated in a beaker containing refluxing 4.5N nitric acid overnight and then rinsed thoroughly with Milli-Q water.

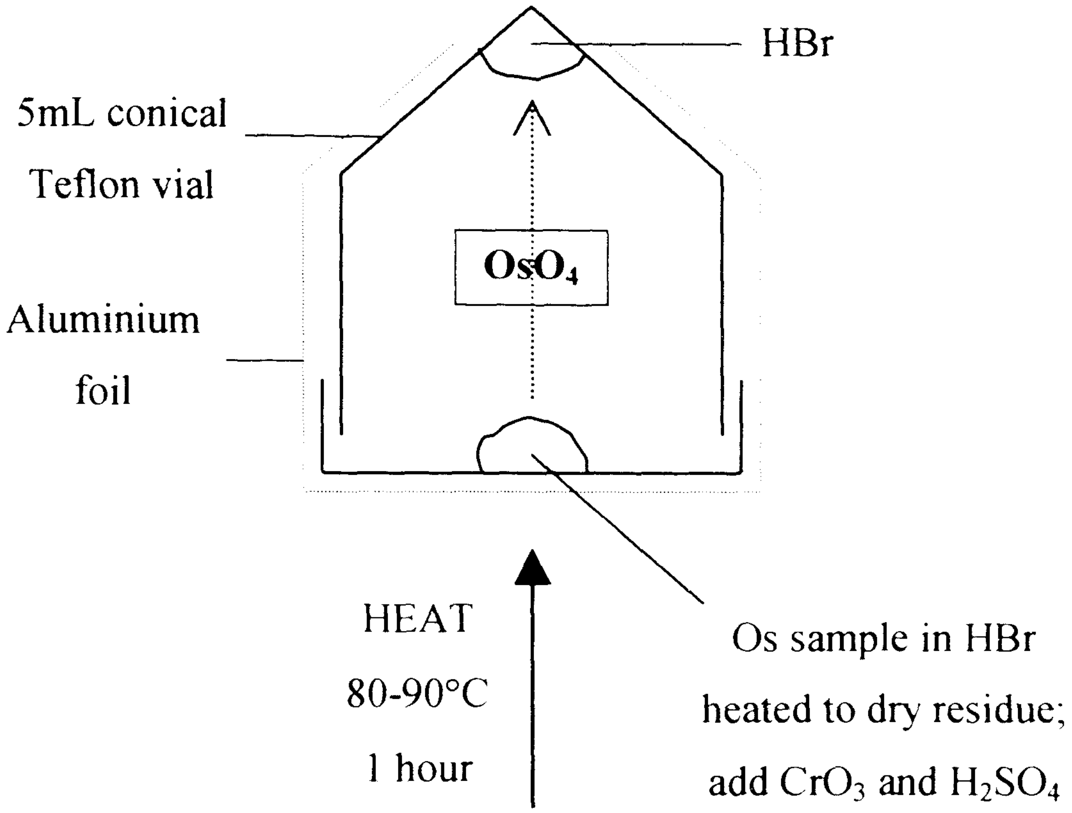


Figure 2.7. Microdistillation Setup

The Os sample in conc. HBr is placed on the inverted cap of the vial and heated to a dry residue. A drop of conc. HBr is transferred by pipette to the tip of the inverted conical base. The CrO_3 and H_2SO_4 solution is added to the dry residue, the base is quickly screwed onto the cap, the vial is wrapped in aluminium foil and heated on a hotplate at 80-90°C for 1 hour.

2.4.2.3 The Osmium Radiotracer

In some experiments, the radiotracer was used directly. The radiotracer had a high enough activity that 40 µL of it could be used directly in the microdistillation without need for concentrating. The aliquot was transferred by pipette onto the centre of an inverted Teflon cap and heated on a hotplate, generally to dryness. A separate 40 µL aliquot was always transferred by pipette into a counting vial, 1 mL of HBr was added and the solution was counted and taken as a "start" value.

In other experiments, radiotracer that had been distilled in a seawater distillation and collected in HBr was used. This was done in order to examine whether volatile or oxidized impurities from the seawater would interfere with the microdistillation. Because the 1 mL of radiotracer used in the distillation had been diluted to around 15 mL, the fraction had to be concentrated before it could be used. This was performed by heating 1 mL of the fraction in a small Teflon vial on a hotplate and concentrating it to 40 µL. The drop was then transferred by pipette onto the cap and heated to dryness.

2.4.2.4 Trapping the Osmium Tetraoxide

The OsO_4 was captured in two different ways. In the first, HBr was condensed as a lining around the base of the vial. This was done by heating the drop of radiotracer, placed on the cap of the vial, on a hotplate with the inverted base of the vial screwed on tightly. The HBr present in the radiotracer evaporated and condensed on the conical base. The idea behind this method was to increase the surface area of the trap in order to make it more efficient.

In the second method, a 20 µL drop of HBr was carefully transferred by pipette into the tip of the conical base. When the base was inverted, the drop was held in place by surface tension. When this second method was used, the vial was wrapped in aluminium foil during the reaction. This was to heat the walls of the vials to minimise the condensation of OsO_4 onto them. The aluminium foil was not wrapped near the HBr drop as the trap works more efficiently at low temperatures.

2.4.2.5 The Oxidizing Agent

With the radiotracer as a dry residue on the cap and the HBr either lining or as a drop in the conical base, a drop of oxidizing agent was added to the dry radiotracer. Both 5.25% sodium hypochlorite NaOCl (bleach) and CrO_3 were investigated as oxidizing agent. The

CrO_3 oxidizing solution was prepared by dissolving 1 g of CrO_3 in 0.4N sulphuric acid (approx. 100 mL). As in the distillations, the sulphuric acid is used to increase the boiling point of the reaction solution. In this way, the reaction can be carried out at a higher temperature. More importantly, the acidic conditions favour the formation of perosmic acid over its anionic form, and thus facilitate the production of OsO_4:

$$[OsBr_6]^{2-} + 2H^{+} \rightarrow H_2OsBr_6 \text{ --oxidant}\rightarrow OsO_4 + H_2O$$

At this acidity, the oxide CrO_3 is present as H_2CrO_4 (Cotton and Wilkison, 1988). The chromate ion is much less oxidizing in basic solution. It must be noted that Cr (VI) oxide is highly poisonous.

The conical base was screwed onto the cap quickly after adding the oxidizing agent to avoid losses of the radiotracer.

2.4.2.6 The Reaction and Counting

In the microdistillations where a drop of HBr was used as the trap, the vial was wrapped in aluminium foil. The vial was then placed onto a preheated hotplate at 80-90°C. The temperature of the hotplate was measured with a hotplate thermometer. The time required for the reaction was investigated by conducting the microdistillation for different lengths of time and observing the yield.

The vial was always left to cool before opening it to ensure that any OsO_4 still in the gaseous form would condense into the trap. When cool, the vial must be opened still inverted to avoid any left over residue on the cap of the vial falling into the conical base. The HBr drop was transferred to a counting vial, 1 mL of fresh HBr was used to wash the base and added to counting vial. The activity of the solution was counted in the well detector.

2.4.2.7 Experimental Reproducibility for the Microdistillation Experiments

As for the distillation experiments, the experimental reproducibility for the microdistillations should be determined. The aim of the microdistillation experiments was to achieve a high yield so that the method could be used to purify Os distilled from seawater. It was not essential that the yield of the microdistillation be highly reproducible, as equilibration between the internal standard (^{190}Os spike) and the sample Os, will have been achieved during the distillation. The interest in determining the experimental reproducibility for the microdistillations is so that the individual experiments may be compared.

Unlike the distillation, it was quite practical to perform up to four microdistillations simultaneously. The same experiment was performed a number of times under identical conditions, to obtain precision values for the yields. The experimental reproducibility can be determined by comparing the yields for experiments conducted under the same conditions. Microdistillations R8#2, R8#3 and R8#4 were conducted under identical conditions, and produced yields of 21.7%, 17.0% and 13.7%, respectively. The mean of these values is 17.5 ± 3.28% (standard deviation). Microdistillations R11#1 and R11#2, performed under the same conditions as each other, produced yields of 91.2% and 89.9%, and give a mean of 90.55 ± 0.65%. Microdistillations R10#1, R10#2 and R12#1 were performed under identical conditions, and one of them was performed on a different day to the other two. The yields were 91.7%, 93.0% and 94.9%, respectively. The mean is 93.2 ± 1.31%. For the first comparison (R8), the vials were only heated on the hotplate for 20 minutes. It was shown that a longer time was necessary to achieve acceptable yields for the microdistillation. The large difference in the yields for these experiments, may simply be caused by a temperature gradient on the hotplate. The experiments that were conducted for 3 hours (R10, R11 and R12) produced yields that were much more reproducible. They shows that the experimental reproducibility for the microdistillation, when conducted for 3 hours, is ± 1.9% (as shown by the counting statistic experiment), but only ±3.3% when conducted for 20 minutes.

2.4.3 The Radiotracer Experiments

2.4.3.1 Preliminary Microdistillation (Microdistillation R3a)

Experimental

In the first microdistillation experiment, the first batch of radiotracer was used. Because the first batch of radiotracer had a lower activity, it was concentrated before being used. One millilitre of solution was measured into a glass vial and its activity was counted. The aliquot was concentrated by heating on a hotplate (to 255 μL) and recounted to check for losses. As with other experiments, no radiotracer was lost during the evaporation. The liquid was then transferred in aliquots to the centre of an inverted cap of a Savillex conical vial. This cap heated on a hotplate to near dryness and then left to cool. Concentrated HBr

(10 µL) was deposited into the tip of the conical base of the vial, in preparation for the distillation. Sodium hypochlorite oxidizing agent (50 µL) was carefully transferred on top of the dried radiotracer and the inverted conical base was quickly screwed on tightly. The inverted Savillex vial was heated on a hotplate at 80°C for 20 minutes, and then left to cool. The vial was opened and the HBr in the tip was quantitatively transferred to a glass counting vial, made up to 1 mL with Milli-Q water and counted. The Savillex vial used for the microdistillation was also counted on top of the well.

Results and Discussion

The HBr in the tip of the vial contained only 5.27% of the original radiotracer. The count for the Savillex vial, multiplied by a conversion factor to take into account the fact the it was measured on top and not in the NaI well detector, gave 95.46%. This shows that the distillation, as performed, gives too low a yield to be used in the isolation of Os from seawater. However, the counts show that no radiotracer was lost during the experiment.

2.4.3.2 Seawater-Distilled Osmium Radiotracer and CrO_3 Oxidising Agent (Microdistillation R8)

Introduction

In this experiment, radiotracer predistilled from a seawater matrix and collected in HBr was used. As noted above, this radiotracer solution may contain volatile and oxidized impurities from the seawater distillation, and is therefore similar to the HBr fraction from a real seawater distillation.

In the previous microdistillation experiment, the HBr used to collect the radiotracer was deposited as a single drop in the tip of the conical base. In an attempt to improve the yield, the HBr was coated over the surface of the base in this experiment to increase its surface area.

Experimental

The following procedure was performed four times. Seawater-distilled radiotracer (1 mL) was concentrated to 30 µL and transferred to the upturned top of a 5 mL conical Teflon vial. The upturned base was screwed on tightly and the vial placed on a hotplate at 150°C. The HBr evaporated and coated the inside of the base of the vial, leaving the radiotracer as a dry residue on the top. The vial was opened and the Cr oxidizing solution (30 µL) was added to the dry residue. The base was quickly screwed on and the vial placed back onto the hotplate at 80-90°C for 20 minutes. During the heating, the Os was oxidized to the tetraoxide, evaporated and was trapped by the HBr lining the base. After the vial had been left to cool, the HBr was collected, 1 mL HBr was added and it was counted.

A correction in the count must be made as the starting and end fractions were counted as different solution. Both start and end solution volumes were 1 mL, but the aliquot counted at the start was in 3N HBr. The final solution was counted as 9N HBr. The hydrobromic acid has been determined to attenuate more radioactivity than water, and so the solution counted in 9N HBr will give a lower count.

Results

Three of the microdistillations gave yields in the range 13.7% to 21.7%. During the fourth microdistillation, radiotracer had spluttered onto the base of the vial, contaminating the HBr coating the vial base. These yields are an improvement on the last experiment, but are still much to low to be used for a real analysis.

2.4.3.3 Pure Osmium Radiotracer and Partial Radiotracer Concentration (Microdistillation R9)

To test whether the seawater impurities had hindered the oxidation of the radiotracer in the last experiment, the microdistillation was repeated using pure radiotracer that had not been distilled in a seawater matrix. The importance of how far the radiotracer should be concentrated was also investigated. One fraction of radiotracer was concentrated to about 5 μL and a second to a dry residue.

Results

During the oxidation, the HBr lining in the first vial turned a lemon yellow colour whereas the lining in the second vial stayed colourless. The first gave a yield of only 0.1% and the second of 35.9%. This shows that it is important to concentrate the radiotracer to dryness before distilling it. The radiotracer that was only concentrated to 5 μL gave a yield of only 0.1%. It seems that not concentrating the radiotracer to dryness interfered with the oxidation of the Os, probably caused by the reductive nature of HBr. All of the radiotracer was counted to be still in the vial, and this shows that the poor yield was due to the radiotracer not being oxidised, rather than leakage from the vial. The 35.9% yield was a great improvement on the last experiment. The difference in the form of the radiotracer was the only difference between the two reactions. This suggests that volatile and oxidized impurities from the seawater may hinder the oxidation of the radiotracer. These impurities will always be codistilled during the distillation of Os from seawater and a method for the microdistillation that overcomes this problem must be found. The yield must also be improved for the technique to be useful for preparing a real seawater sample.

2.4.3.4 Aluminium Foil and Pure Osmium Radiotracer (Microdistillation R10)

A technique for the microdistillation which gives yields of 65-80% has been reported (Birck et al., 1997). A single drop of HBr is placed into the tip of the base and the vial is wrapped in aluminium foil before it is heated on the hotplate. The idea is to heat the walls of the vial to prevent the OsO_4 from condensing onto them. The technique also uses a much longer distillation time of 3 hours.

This technique was investigated using four vials set up in parallel: Three were distilled for 3 hours and the other for 1h40 in order to investigate the time needed for the microdistillation. One of the vials that was distilled for 3 hours was not wrapped in aluminium foil as a control. Pure radiotracer that contains no seawater impurities was used.

Results and Discussion

The yields were a marked improvement on earlier experiments. The two vials that were wrapped in aluminium foil and heated for 3 hours had yields of 91.7% and 93.0%. The vial that was wrapped in foil but only heated for 1h40 gave a yield of 88.9%, suggesting that the longer reaction time is necessary for a higher yield. The vial that was not wrapped in foil and heated for 3 hours gave a yield of 54.7%, low compared to the vials that had been wrapped in foil but higher than the earlier experiments which were only heated for 20 minutes.

The higher yields suggested that the technique could be used in the isolation of Os from seawater. The next step was to test whether the impurities found in seawater would hinder the oxidation of Os during this microdistillation. It must also be kept in mind that the radiotracer experiment can only determine the yield of the microdistillation. The effectiveness of the purification cannot be tested.

The aluminium foil used to wrap the first vial was rolled into a ball and its activity was counted. It was counted to have 0.6% of the original radiotracer. This shows that some of the radiotracer, probably as OsO_4, is leaking out of the vial during the distillation. It is likely that more than this actually leaks out of the vial as aluminium foil is not believed to be efficient at capturing OsO_4. An estimate of the amount that has leaked was determined from the Os that cannot be accounted for. When the vial was counted on the well after the reaction, it was found to contain 6.0% of the original radiotracer. The trap contained 91.7% so this still leaves 2.3% which is unaccounted for and must have leaked from the vial.

2.4.3.5 Aluminium Foil and Seawater-Distilled Osmium Radiotracer (Microdistillation R11)

The previous experiment was repeated using radiotracer that had been distilled from a seawater matrix. This would be a test as to how the technique would perform if Os was isolated from real seawater. Performed in duplicate, 1 mL of distilled radiotracer was concentrated to 30 μL and taken through the same microdistillation as in the previous experiment.

Results and Discussion

The yields for the two distilled vials were 91.2% and 89.9%. These yield are very close to the yields obtained in the previous experiment and show that the technique produces a high yield, even when the Os has been distilled in a seawater matrix.

2.4.3.6 Microdistillation Time with Aluminium Foil and Pure Osmium Radiotracer (Microdistillation R12)

The previous experiments have shown that the microdistillation produces an excellent yield for the technique to be used in the purification of Os, after it has been distilled from seawater and collected in cold HBr. The effectiveness of the microdistillation as a cleanup step has not been tested with these radiotracer experiments. The objective of the following experiment was to investigate how the yield varies with the length of time of the microdistillation. Pure radiotracer was used in this experiment. Three vials were prepared as in microdistillation R10, wrapped in aluminium foil. The three vials were placed on a hotplate at 80°C and left for 1h10, 2h and 3h.

Results and Discussion

Yields for the three vials heated for 1h10, 2h and 3h were 84.3%, 90.7% and 94.9% and respectively. This shows that the yield increases with time of microdistillation. As noted above, the experiment gives no information on how well the Os is being isolated from impurities that could cause an interference during the analysis of the sample. It is possible, for example, that although running the microdistillation for a longer time increases the yield of recovery of Os, more volatile and oxidized impurities are transferred to the HBr in the tip of the vial. As it is not possible to analyse the radioactive HBr solution for any impurities it may contain, this question must be investigated when real samples are prepared and analysed.

2.4.4 Conclusions and Method to be used for Environmental Seawater Microdistillations

2.4.4.1 Losses through Leaking

The amount of radiotracer that had been lost through leaking out of the vial during the heating was determined. After the microdistillation the used vial, emptied and rinsed of the trapping HBr, was counted on top of the well detector. To be comparable to radiotracer counted in the well, this had to be corrected for counting geometry. The percentage of radiotracer that had leaked was calculated as being the radiotracer that could not be accounted for:

Leak = Original Radiotracer - (Radiotracer recovered + Radiotracer left in vial)

A plot of the percentage yield of the reaction vs the percentage of leak (Figure 2.8.) shows that the two values are negatively correlated. This shows that it is important to trap the gaseous OsO_4 in the HBr as quickly as possible. The aluminium foil facilitates this greatly. Indeed, experiments that were conducted without the foil show a lower total yield. They also show that Os not recovered has both been lost by condensing around the walls of the vial and lost through leaking. Microdistillation R12 demonstrates this point well. Three microdistillations were performed under identical conditions, but for different lengths of time. At the shorter reaction times, not only does the total yield decrease but also both the percentage left in the vial and the percentage that has leaked out increase.

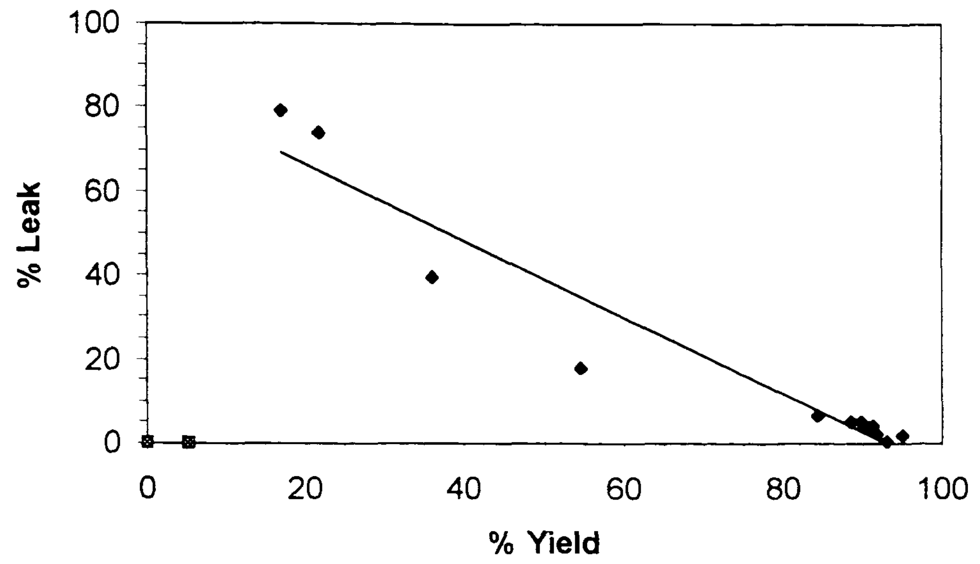


Figure 2.8. Microdistillation: Percentage Yield vs Percentage Leak

Results from the microdistillation experiments show that the yields of the reactions are negatively correlated to the amount of radiotracer that leaks from the Teflon vial. The two square data points indicate experiments where the radiotracer had not been oxidized at all.

Two exceptions to this are the radiotracer that was oxidized using NaOCl and the radiotracer that was not concentrated to dryness before the microdistillation. Figure 2.8. shows that these two results (the two squares) fall outside the negatively correlation line. This shows that the low yields for these two experiments resulted not from the fact that the OsO_4 had leaked out, but because the radiotracer had not been oxidized at all. It is possible that the leaking can be minimised by wrapping Teflon tape around the screw thread of the vial before screwing on the lid.

2.4.4.2 Microdistillation Procedure for Seawater Concentrates

The reagents and experiment conditions used in each of the microdistillation experiments are shown in Table 2.3. The radiotracer experiments have shown that Os can be recovered from the microdistillation with a high enough yield to be used for real seawater analysis. It must be noted that these experiments have only given information on the yield of the microdistillation. No information about the effectiveness of the purification of Os can be concluded from radiotracer experiments. Quantitative recovery is not essential for the microdistillation as the spike is added immediately before the distillation. A higher yield will however facilitate the analysis and give higher precision in the data.

The following microdistillation technique will be used for seawater analysis:

1. After the distillation, the sample in HBr solution is concentrated from 15 mL to approx. 30 µL on a hotplate at 130-140°C.
2. The 30 µL sample is transferred by pipette onto the centre of the upturned lid of the Teflon vial.
3. The sample is heated on a hotplate at 130-140°C until a dry residue is left.
4. The dried sample is left to cool while 20 µL conc. HBr is transferred by pipette into the tip of the conical base of the vial. This drop is held in place by surface tension.
5. The oxidant, 20 µL of CrO_3 in sulphuric acid solution, is transferred by pipette onto the dry sample and the inverted base is quickly screwed on tightly. Teflon tape may be used in the threads of the vial to reduce losses of OsO_4.
6. The inverted vial is carefully wrapped in a small square piece of aluminium foil. The underside and walls of the vial should be covered in aluminium foil, but the area around the HBr drop should left clear so it is not heated.
7. The vial is placed on a preheated hotplate at 80-90°C and heated for one hour. Radiotracer experiments have shown that slightly more Os (only 3.1% more) may be recovered if the vial is heated for three hours. However, it is though that the efficiency of purification decreases when the microdistillation is performed for longer.
8. After one hour, the vial is taken off the hotplate and left to cool.
9. The aluminium foil is carefully removed and the still holding the vial inverted, it is opened.
10. The sample, now in about 40 µL HBr (the additional volume is from the 20 µL of oxidant), is concentrated to 1-2 µL for loading onto the Pt filament.

Table 2.3. Conditions Employed and Results for various Microdistillation Experiments

Table 2.3. Microdistillation Experiment

Microdistillation	R3a	R8	R8	R8	R8	R9	R9	R10	R10	R10	R10	R11	R11	R12	R12	R12
vial number	#1	#1	#2	#3	#4	#1	#2	#1	#2	#3	#4	#1	#2	#1	#2	#3
Radiotracer used:																
sea water distilled 1mL	yes	yes	yes	yes	yes							yes	yes			
pure 40 μL						yes	yes	yes	yes	yes	yes			yes	yes	yes
Radiotracer heated:	almost dry	dry	dry	dry	dry	to 5uL	dry	dry	dry	dry	dry	dry	dry	dry	dry	dry
Oxidising Agent used:																
CrO_3 (μL)		30	30	30	30	30	30	20	20	20	20	20	20	20	20	20
NaOCl (μL)	50															
HBr trap in conical:	tip	lining	lining	lining	lining	lining	lining	tip	tip	tip	lining	tip	tip	tip	tip	tip
HBr trap volume (μL)	10	30	30	30	30	30	30	20	20	20	20	20	20	20	20	20
Aluminium Foil?	no	no	no	no	no	no	no	yes	yes	yes	no	yes	yes	yes	yes	yes
Temperature	all microdistillations were performed on a hotplate heated to 80-90°															
Time (hours)	0h22	0h20	0h20	0h20	0h20	0h20	0h20	3h	3h	1h40	3h	3h	3h	3h	2h	1h10
% Left in Vial	95.0	7.2	4.1	3.8	na	100.0	24.6	6.0	6.3	6.3	27.5	4.6	4.9	3.1	5.6	9.1
% Leaked Out	0.0	5.4	74.2	79.2	na	0.0	39.5	2.3	0.7	5.1	17.8	4.2	5.3	2.0	3.7	6.6
% Yield	5.3	87.4*	21.7	17.0	13.7	0.1	35.9	91.7	93.0	88.6	54.7	91.2	89.8	94.9	90.7	84.3
		*R8#1 was contaminated														

CHAPTER 3: Analysis of Osmium by ICP-MS and NTIMS

In this chapter, a standard solution is used to investigate the analysis of Os by ICP-MS. In the first part, the isotopic composition of the solution is measured by ICP-MS and the results are compared with values obtained by NTIMS. In the second part memory effects, which can be the largest source of blank contamination during Re/Os analysis by ICP-MS, are investigated. In the third part, the use of the osmium tetraoxide vapour generator for the analysis of Os by ICP-MS, is examined. Both ICP-MS and NTIMS were later used to measure Os concentrations and isotopic compositions of seawater and the results presented in this chapter were invaluable.

3.1 Using the ^{187}Os/^{186}Os Isotopic Ratio of a Sample as an Indication of its Source

3.1.1 The Osmium Standard Solution

In order to investigate the analysis of Os concentrations and isotopic ratios in marine samples using ICP-MS, a 1000 μg/mL osmium ICP/DCP standard solution in 20% HCl was obtained from Johnson Matthey. A certificate of analysis was included with the solution, showing the concentrations of 70 elements in the solution; of course, only Os showed a significant concentration. The certificate did not however show the abundance of each Os isotope in the solution. It was assumed that the Os would have the naturally occurring isotope abundances shown in Table 3.1.

Table 3.1. Relative Abundance of Naturally Occurring Isotopes
(De Bièvre and Barnes, 1985):

Mass	Relative Abundance (%)
184	0.02
186	1.6
187	1.6
188	13.3
189	16.1
190	26.4
192	41.0

3.1.2 ICP-MS Experiments

The Os standard solution was diluted to 1 ng/mL using Milli-Q water and analysed by ICP-MS. It was immediately noted that the count for the ^{187}Os was higher than the count for ^{186}Os. The naturally occurring abundance of these two isotopes in unradiogenic samples is equal; both make up 1.6% of Os. This solution was measured to have a ^{187}Os/^{186}Os ratio of 2.73 ± 0.048. A freshly diluted solution was analysed a month later on a different ICP-MS instrument, and the measured ^{187}Os/^{186}Os ratio was 2.75 ± 0.056. A different aliquot of Os standard solution from Johnson Matthey was diluted, analysed by ICP-MS and again produced a ^{187}Os/^{186}Os ratio of 2.75 ± 0.047. This showed that it was not just the recently ordered standard solution that displayed a radiogenic Os measurement. The other isotopes of Os were measured with the same ratios as shown in Table 3.1.

3.1.3 Isobaric Interferences

There are two explanations for the result. Either the solution does in fact contain a higher proportion of ^{187}Os relative to ^{186}Os (the solution is radiogenic), or an isobaric interference is causing a high ^{187}Os count.

A possible isobaric interference could have come from ^{187}Re in the solution. The certificate of analysis however, shows that the solution only contains <0.1 µg/mL rhenium. Also, the count analysed for ^{185}Re (which makes up 37.4% of natural rhenium compared to 62.6% for ^{187}Re) is no higher than background values, confirming that there is not a significant concentration of Re. Another interference could have come from $^{39}K_3{}^{35}Cl_2^-$ (mass 187), as has been noted in the literature (Leich et al., 1985). The chloride is present in the solution as HCl, but there is no source of potassium, so interference from this ion seems unlikely. The $^{186}OsH^-$ ion also has a mass of 187 and hydrogen is present in the solution in water and HCl. This cation may be formed after the plasma stage of the instrument before the ion detector, or may even survive passage through the plasma if it travels along the cooler periphery of the torch. However, ^{186}Os makes up only a small percentage of the total Os, and it is not thought that this cation would significantly increase the ^{187}Os count. This is shown in the fact that the other Os isotopic ratios are measured at their expected values (for example, $^{189}OsH^-$ does not have a significant effect on the ^{190}Os count etc.).

Johnson Matthey were contacted to enquire whether the isotopic abundance of their standard solutions was measured. They replied that they had no facility to do this, but that the solution probably came from a natural source.

3.1.4 NTIMS Experiments

In order to check that the solution really was radiogenic, the sample was analysed using Negative Thermal Ionisation Mass Spectrometry (NTIMS) at the Open University. NTIMS is not affected by isobaric interferences and is thus ideal for checking the result.

Two separate 1 ng aliquots were analysed and gave the following isotopic compositions:

$^{187}Os/^{186}Os = 2.73906 \pm 0.000889$ (1 sigma)

$^{187}Os/^{186}Os = 2.73780 \pm 0.000773$ (1 sigma)

3.1.5 Conclusions

The $^{187}Os/^{186}Os$ ratio values obtained by NTIMS (2.74) are very close to the values obtained by ICP-MS (2.73 and 2.75), and therefore confirm that the Os standard solution provided by Johnson Matthey is radiogenic.

The $^{187}Os/^{186}Os$ ratio of a sample is an indication of its source, due to the fact that ^{187}Re decays to form ^{187}Os ($\lambda = 1.52\times10^{-11}$ yr^{-1} (Morgan, 1985; Palmer and Turekian, 1986)) and that geological samples have different Re/Os ratios. A large table of $^{187}Os/^{186}Os$ isotopic ratios and the source of the material that is associated with the values has been compiled (see the table in Appendix II).

With a $^{187}Os/^{186}Os$ ratio of 2.74, the source of the Os in the standard solution is not obvious. The table in Appendix II shows many Os isotopic ratios between 0.90 and 1.30 (for meteorites, mantle-derived material and basalts), and between 5.20 and 8.80 (marine Mn nodules and terrigenous sediments), but no intermediate values. It has been suggested that this Os could originate from Sudbury nickel ores, Ontario, Canada (Anthony Cohen, pers. comm., 1996). However, the published isotopic ratios for this material (Dickin et al., 1992) are more radiogenic than the measured 2.74, clustering at around 4.99. A mixture of radiogenic and unradiogenic Os would account for the measured isotopic composition.

The analyses of the solution have shown the isotopic composition values measured by ICP-MS and NTIMS are within error of each other. This is an important observation as both ICP-MS and NTIMS were later used to measure Os concentrations and isotopic compositions of seawater. It must be noted that the solutions used in these experiments are many orders of magnitude more concentrated than for seawater sample solutions. The precision of measurements is likely to be reduced when solutions of lower concentration are measured. The experiments using the Os standard solution were performed to measure the isotopic composition and to test the memory effect. Solutions of high Os concentration were used to maximise the accuracy and precision of the measurements. This work was conducted before the research on Os in seawater had been commenced, and unfortunately, solutions of low concentration were not used to test the accuracy and precision of NTIMS and ICP-MS measurements.

3.2 The Memory Effect when Analysing Osmium by ICP-MS

3.2.1 Introduction

When an Os solution is analysed by ICP-MS, it is adsorbed and retained by the sample introduction assembly (sampling tube, nebuliser and torch). If more samples are analysed, this absorbed Os is released and contaminates the later solutions. The instrument therefore measures a higher concentration of Os than is actually present in that solution. This memory or carryover effect is more readily observed with Os than with other elements. Lithium for example, is also known to have a high affinity for glass and plastic surfaces, and therefore memory effects are also an important consideration when analysing lithium using ICP-MS (Jarvis et al., 1992b). These memory effects can cause systematic errors in the analysis of these elements.

The mechanism by which Os is adsorbed onto surfaces is not known. It is possible that Os may accumulate in tiny scratches and defects on surfaces inside the instrument. It is also possible that no such imperfections are needed, and that the Os species bond to the surface by Van der Waals interactions or ionic bonds.

A variety of approaches have been taken to eliminate the memory effect. The significant memory or carryover effect between samples of Os can be eliminated by the nebulisation of 2 mL of a solution containing 500 ppm Sn (tin) as stannous chloride (Gregoire, 1990). A tin solution was therefore tested as a washout for this experiment, but at a much lower concentration.

Instrumental memory effects can be the largest source of potential blank during Re/Os analysis by ICP-MS (Dickin et al., 1992). To avoid these problems while analysing Os in nickel ores, Dickin et al. changed the complete analytical system (distillation apparatus, tubing and torch) in between each run. A blank (reagent only) was always made before each analysis to test the success of these measures. This is a time-consuming procedure to follow.

The design of the nebuliser can critically affect washout times. A comparison of the washout times for a Meinhard and a de Galan nebuliser has been published (Jarvis et al., 1992a). A solution of 100 ng/mL indium in 1% HNO_3 was passed through the instrument and 2% HNO_3 was used as the washing solution. The Meinhard nebuliser required about 1 minute for the signal to return to background levels. The washout time for the de Galan V-groove nebuliser was much longer, taking 165 s to reach 1% of the original signal. This is probably because liquid is retained on the face of the nebuliser and drawn back into the groove.

An effective washout solution has been suggested (Jarvis et al., 1992c) when using an OsO_4 vapour generator. The team suggests flushing the system using deionised water and 5 M HNO_3, and increasing the Ar carrier gas flow. This technique physically flushes out the sample and oxidises or ionises any Os that remains in the sample chamber, sampling tube or torch. It is also suggested that the entire sampling assembly should be changed between groups of 6-12 analyses of the same sample, or between each different sample. The whole assembly should be cleaned in an aqua regia bath overnight.

3.2.2 Initial Experiments

3.2.2.1 Experimental

During the two days that were spent at CARE, Silwood Park, the Os memory effect during ICP-MS analysis was examined. A solution of Os was run through the instrument and different washout solutions were tested for their flushing effect. The instrument was a Fisons Instruments VG Plasma Quad 2STE. A strong alkaline solution called Tamapure Super Clean (TMSC) and different concentrations of HNO_3 were tested as washout solutions. Running an ammoniacal solution of Os (instead of the usual acidic solution) with an ammonia washout solution, was also tried. In a different experiment, the Os was chelated using sodium diethyldithiocarbamate. Sodium acetate trihydrate was used to buffer the solution to pH 7.5. The idea behind using a chelating agent was to form an organic shell around the Os, which would pass through the sampling tube and nebuliser without being adsorbed, and would then dissociate in the high temperature plasma.

3.2.2.2 Results

The main objective of the time spent at Silwood Park was familiarisation with the instrument. Experiments were not performed as methodically as the later experiments at Southampton. The following results were therefore useful in the further work, but they have not been expanded upon.

When using 3% HNO_3 to washout a solution of 10 ng/mL Os in 2% HNO_3, the signal decayed to about 1% of the original rate after 3 minutes. The TMSC washout solution did no better than this. When using alkaline solutions (1% ammonia to washout a solution of 10 ng/mL Os in 0.5% ammonia), the observed memory effect was much smaller, taking less than 3 minutes for the signal to decay to background. The results from the chelated Os solution did not look promising. Firstly, the presence of the buffer and chelate had the effect of halving the instrument count rate. This was probably due to the sodium in the chelate absorbing the plasma's energy, thus the sample was not as effectively dissociated and ionised. Secondly, the 3% HNO_3 washout solution did not reduce the memory effect any more efficiently than when the Os was not chelated.

3.2.3 Further Experiments

3.2.3.1 ICP-MS Operating Conditions

The ICP-MS instrument at the University of Southampton showed much higher sensitivity than the instrument at Silwood Park; the count rates were over 30 times higher for the same solution. The instrument at Southampton is thought to have a higher sensitivity due to well-matched components and a good RF (radio frequency) generator (Andy Milton, pers. comm., 1996). The operating conditions that were used are shown in Table 3.2.

Table 3.2. ICP-MS Operating Conditions

ICP RF power, W	1350
Coolant Ar flow, L/min.	13.5
Auxiliary Ar flow, L/min.	1.11
Nebuliser Ar flow, L/min.	0.98
Peristaltic pump rate, mL/min.	0.6
Spray chamber coolant temp., °C	0
Interface configuration	Standard sampling interface Sampling cone orifice 1 mm Skimmer cone orifice 0.7 mm
Quadrupole	VG PQ2+
Detector	Galileo
Run time per sample, s	30
Run mode	Peak jumping
Points per peak	3
Dwell time per point, μs	10.24

3.2.3.2 Osmium Solutions

A 1 ng/mL Os in 2% nitric acid solution was made up in three steps as follows. One millilitre of Os solution (1000 µg/mL) was transferred by pipette to a 100 mL volumetric flask and made up to the mark using Milli-Q water. One millilitre of the resulting solution was again diluted 100 fold with Milli-Q water. One millilitre of this solution was transferred into a 100 mL volumetric flask, 2 mL of nitric acid was added and the flask was made up to the mark using Milli-Q water.

A 1 µg/mL Os in 0.5% ammonia solution was made up as above, 0.5 mL of ammonia solution being added in the final step instead of nitric acid. The ammoniacal washout solution was made up by transferring 0.5 mL of ammonia solution into a 100 mL volumetric flask and making it up to the mark using Milli-Q water.

A 100 µg/mL tin solution was made up in three steps by diluting a 1000 ppb tin solution using Milli-Q water. The solutions of TMSC, 2-5% nitric acid, 10% nitric acid and 0.5% perchloric acid with 0.5% nitric acid were already available, having previously been made up.

3.2.3.3 General Procedure

1. The instrument was set to peak jump within the mass range 184-192 (excluding 191); thus the count rate for all the isotopes of Os and Re were measured. The count rate at mass 185 was used to confirm that no Re was present in the sample, and thus no isobaric interference occurred at mass 187 (Re has two isotopes: ^{185}Re and ^{187}Re).
2. The instrument was flushed in between runs using 2-5% nitric acid.
3. The sampling tube was placed into the Os solution and the stopwatch and computer run were started (It took some time (approx. 15-20 s) before the Os reached the detector).
4. Counts were collected for 30 s time slots (although the time in between slots was 35.8 s as the instrument did not record data for a period of about 6 s while the data was calculated and printed).
5. Throughout the experiment, the time on the stopwatch (indicating the time passed since the probe had been placed into the Os solution) was noted on the printout.
6. The Os solution was passed through the instrument for 10 minutes (only 5 minutes for Run A), the probe was removed and wiped with a tissue and placed into the washout solution. The washout solution was normally passed through the instrument for 30 minutes to observe the decaying count.

3.2.3.4 Experiment Runs

- Run A: 1 µg/mL Os in 2% nitric acid using 2-5% nitric acid as the washout.
- Run B: 1 µg/mL Os in 2% nitric acid using 10% nitric acid as the washout.
- Run C: 1 µg/mL Os in 2% nitric acid using a mixture of 0.5% perchloric acid and 5% nitric acid as the washout.
- Run D: 1 µg/mL Os in 2% nitric acid using Tamapure Super Clean (TMSC) (for 5 min.), 10% nitric acid (for 5 min.) and 2-5% nitric acid (for 10 min.) as the washout.
- Run E: 1 µg/mL Os in 2% nitric acid using 100 ppb Sn solution (for 5 min.), 10% nitric acid (for 5 min.) and 2-5% nitric acid (for 10 min.) as the washout.
- Run F: 1 µg/mL Os in 0.5% ammonia solution using 0.5% ammonia solution as the washout.

3.2.3.5 Results

The results are illustrated in Figures 3.1., 3.2. and 3.3. The instrument became less sensitive during the day, and so the count rate measured for the same Os solution decreased from Run A to Run E (Run F was 1 µg/mL Os in ammonia solution instead of nitric acid and the count rate was shown not to be comparable). The data therefore had to be normalised in order to compare the various runs. The data was normalised to Run C at time t = 608.6 s; this was the first measured value after the sampling tube had been removed from the Os solution and placed into the washout solution. In this way, the count for each run was identical when the decay began and so the memory effects could be directly compared. Data for Run F, which gives much lower count rates than the other runs, was not normalised as this solution is ammoniacal instead of acidic.

Run A is illustrated in Figure 3.1. and shows the count rate for the different Os and Re isotopes with time. The instrument ion detector was switched off between 1800-2400 s and again between 2450-2800 s, which is why data appears to be missing. The washout solution was still running through the instrument during these times, and so the experiment was still proceeding.

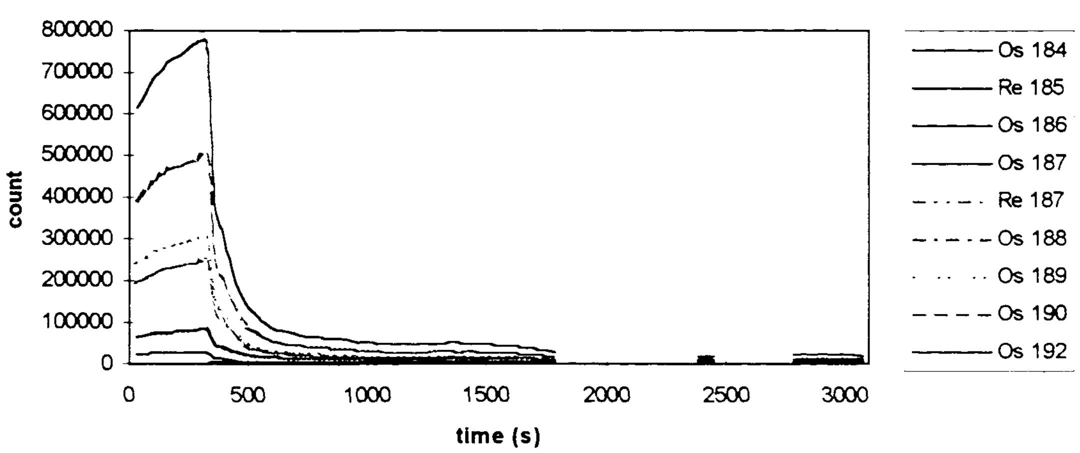


Figure 3.1. The ICP-MS Memory Effect of Osmium (2-5% Nitric Acid Washout Solution)

Figures 3.2. and 3.3. show the results for the isotope ^{192}Os for all the runs (Runs A to F); Figure 3.2. shows the whole run whereas Figure 3.3. shows the decaying counts and memory effect after the sampling tube has been removed from the Os solution. It is possible to identify from Figure 3.3. the washout solutions that are the most efficient.

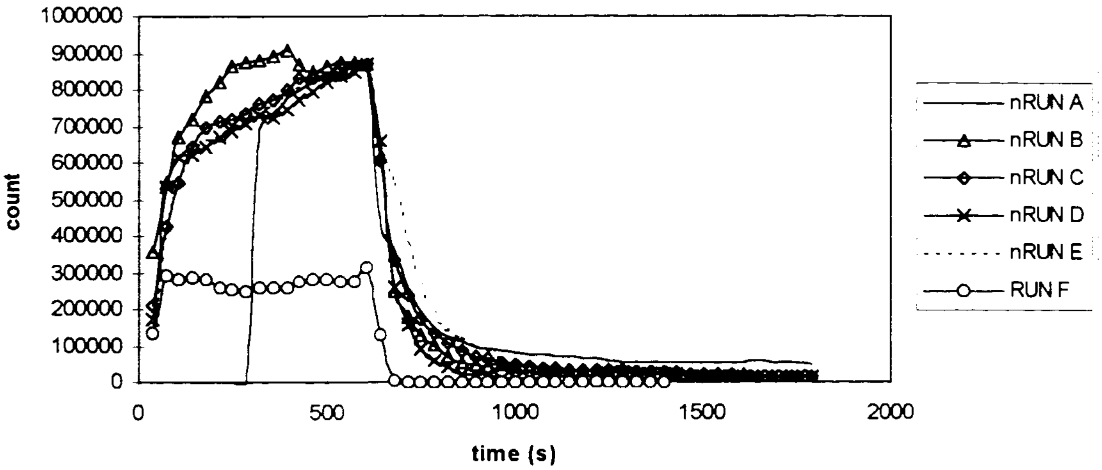


Figure 3.2. The Memory Effect of ^{192}Os with Different Washout Solutions

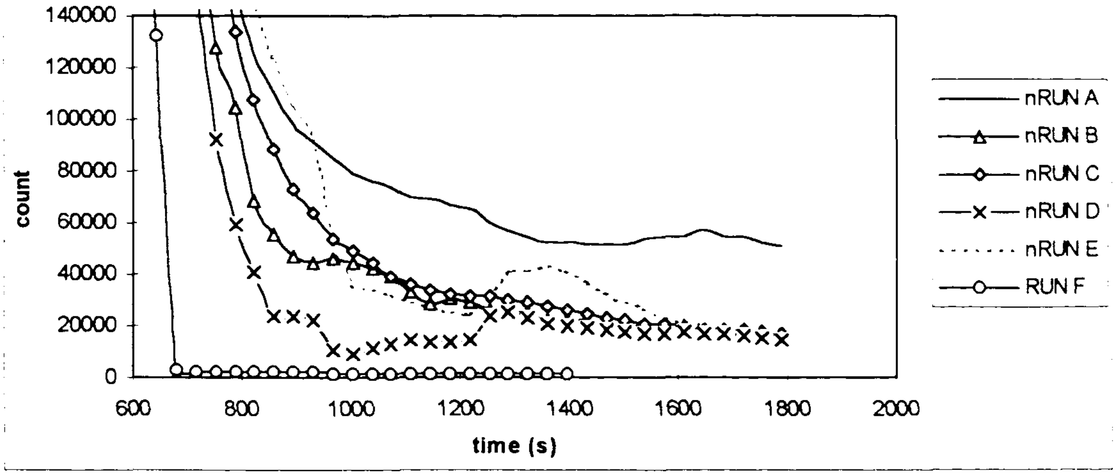


Figure 3.3. The Memory Effect of ^{192}Os with Different Washout Solutions (Enlarged)

- Run A: 1 µg/mL Os in 2% nitric acid using 2-5% nitric acid as the washout.
- Run B: 1 µg/mL Os in 2% nitric acid using 10% nitric acid as the washout.
- Run C: 1 µg/mL Os in 2% nitric acid using a mixture of 0.5% perchloric acid and 5% nitric acid as the washout.
- Run D: 1 µg/mL Os in 2% nitric acid using Tamapure Super Clean (TMSC) (for 5 min.), 10% nitric acid (for 5 min.) and 2-5% nitric acid (for 10 min.) as the washout.
- Run E: 1 µg/mL Os in 2% nitric acid using 100 ppb Sn solution (for 5 min.), 10% nitric acid (for 5 min.) and 2-5% nitric acid (for 10 min.) as the washout.
- Run F: 1 µg/mL Os in 0.5% ammonia solution using 0.5% ammonia solution as the washout.

3.2.3.6 Discussion

Figures 3.1. and 3.2. show that even when the acidic Os solution has been passing through the instrument for 10 minutes, the count rate has not stabilised and is still rising. This is probably due to the memory effect: the signal at the start is lower as some Os is being adsorbed before it reaches the detector. As more solution is introduced, sights for Os to adhere to (tiny scratches and defects) are taken up and some of the adsorbed Os is washed through, thus the signal increases. Figure 3.1. shows that the Os solution is radiogenic. The count rate for ^{187}Os is 2.6-2.7 times larger than the ^{186}Os.

The ammoniacal Os solution does reach a stable count rate quickly. However, the count rate for this solution is only one third of the count rate for the acidic solution, even though the two solutions are of the same Os concentrations. This is contrary to what was observed during the experiments at Silwood Park where the count rates were the same for both acidic and basic solutions.

Figure 3.3. shows that 2-5% nitric acid (Run A) is the least efficient washout solutions that was used in this experiment. Using a higher concentration of this acid (10% nitric acid, Run B) or adding 0.5% perchloric acid (Run C) significantly improve the flushing out of the adsorbed Os. Using a tin solution at the concentration used (Run E) does not improve the washout rate. For the 5 minutes during which time this solution has been running through the instrument, the count rate is actually higher than for the 2-5% nitric acid run. The count rate is only significantly reduced when the sampling tube is placed into the 10% nitric acid. The tin washout solution indicated in the literature was of a much higher concentration, and it may be worth trying a higher concentration. The TMSC followed by nitric acid (Run D) performs very well in displacing the adsorbed Os.

The memory effect is almost eliminated when conditions are ammoniacal instead of acidic (Run F). The count rate decayed to background just 1.5 minutes after the 0.5% ammonia solution had passed through the instrument. However, as mentioned above, the count rate for the Os in ammonia solution is much lower than the count rate of the Os in nitric acid solution, and more work is needed to verify this unexpected effect. There is also the fact that acid is added to solutions in order to keep the metal in solution (the Os solution is sold in 20% HCl). Ammonia may not hold the metal in solution in the same way that the acid does. The memory effect is suppressed when the solution is made ammoniacal (Russ III et al., 1987). It is suggested that this may not prevent contamination from accumulation on the torch, rather it suppresses its remobilisation.

3.3 Osmium Tetraoxide Vapour Generator

3.3.1 Introduction

The OsO_4 vapour generator is a technique for introducing Os from an environmental sample into an ICP-MS instrument. The major advantage of this type of introduction technique is the high efficiency with which the Os is introduced into the spectrometer. In ICP-MS, samples usually introduced into the plasma by means of a nebuliser and spray chamber with an efficiency of only 1%. By using an OsO_4 vapour generator rather than a nebuliser, the sensitivity is enhanced by a factor of about 100 (Russ III et al., 1987). Part of the improvement may also be related to the use of a dry plasma as the solvent cooling of the plasma is minimised.

The Os in the sample must be preconcentrated before the vapour generator step; for example, sediments are taken through a NiS fire assay. The sample is then transferred to the reaction vessel of the OsO_4 vapour generator. An oxidising agent is added to the sample, the acidity of the reaction may be altered and the reaction vessel is heated. The Os is oxidised and introduced into the mass spectrometer as OsO_4. A condenser may be included in the design of the apparatus to reduce the water content of the vapour entering the plasma. The Os can be introduced and measured over a length of time or passed into the mass spectrometer in a pulse. Most researchers report memory effects between samples and have taken a number of steps to eliminate or reduce this problem.

A number of researchers have worked to develop the technique and their findings are reported below. A number of different reaction vessels, oxidising agents, heating methods, condensers, traps and ICP-MS operating conditions were used in an attempt to optimise the technique. Different methods for eliminating the memory effect were also employed. The results were used to construct an OsO_4 vapour generator. The results were also useful for developing the distillation of seawater technique, which is discussed later.

3.3.2 Reaction Vessel

All glass reaction vessels in the literature have a glass frit near the bottom of the vessel for the sample and oxidant to rest upon. Gregoire (1990) used a 250 mL reaction vessel which was insulated with a layer of glass wool. The temperature of the reaction has been measured using a thermometer (Tao et al., 1988) and a thermocouple placed between the heating coil and the wall of the reaction vessel (Bazan, 1987).

The sample and oxidising reagents are introduced into the reaction vessel via an inlet tube with a stopcock or a self-sealing membrane. Bazan (1987) loaded 1 mL of the oxidant solution and 1 mL of the Os solution into the vessel. The oxygen in the vessel was then eliminated before heating by flushing with argon. This helped to avoid problems with plasma instability when the generator was opened to the torch. Dickin et al. (1988) used a self-sealing membrane made of virgin Neoprene, coated on the inside with silicone grease. Solutions were injected through this with a syringe.

3.3.3 Oxidising Agents

A variety of oxidising agents or oxidants have been used to oxidise the Os in the sample to the tetraoxide. Richardson et al. (1989) have found that the choice of reactant significantly influences the Os count rate. Orthoperiodic acid (H_5IO_6), nitric acid (HNO_3) and hydrogen peroxide (H_2O_2) were used individually. Hydrogen peroxide produces a vigorous reaction. Orthoperiodic acid is a stronger oxidising agent than HNO_3 and releases more OsO_4. The reaction between a chilled 5% H_5IO_6 solution and a chilled Os bearing sample was determined to be the technique that gave the most reproducible results. Beneteau et al. (1992) used a 10% H_5IO_6 solution.

Bazan (1987) used a continuous-flow OsO_4 vapour generator to investigate different oxidising agents at different concentrations, including H_2IO_6, H_5IO_6, $KMnO_4$, $K_2Cr_2O_7$, H_2O_2 and HNO_3. Varying the oxidising agents resulted in intensities (ICP-AES) that were comparable. Varying the Os solution matrix, i.e., molarity, acid, or base, but maintaining the same oxidising agent resulted in distinctly different maximum signal intensities for the OsO_4 produced. Orthoperiodic acid (H_5IO_6) was chosen for the following reasons: (1) ease of handling, (2) long shelf life, (3) high and equal signal intensities for the three concentrations of oxidant used, and (4) least number of foreign elements introduced into the effluent if further analysis was required.

Russ et al. (1987) used 2.5% periodic acid (HIO_4) as the oxidising agent. Using 10% HIO_4 resulted in white crystals forming on the frit at the bottom of the reaction flask, preventing the flow of the sparging gas. Dickin et al. (1988) also used HIO_4 and noted the possible problem of isobaric interferences on Os by molecular ions (e.g. HIO_4 = mass ^{192}Os). However, no evidence of any interfering species of this nature was found.

Tao et al. (1988) have examined the use of $K_2Cr_2O_7$, $KMnO_4$, $Ce(SO_4)_2$ and H_2O_2 as oxidising agents and selected 0.4 M $K_2Cr_2O_7$ for their work. All gave the same emission profile except H_2O_2, which gave a lower emission intensity. The $KMnO_4$ solution was not appropriate because it generated MnO_2, which was not removed from the wall of the reaction vessel.

Gregoire (1990) found that both HIO_4 and a 1:1 mixture of concentrated H_2SO_4 and 30% H_2O_2 gave an Os count rate four times greater than obtained with 10% H_5IO_6. Although H_2O_2 has a short shelf-life, in combination with concentrated H_2SO_4 the relatively stable H_2SO_5 is formed. The thermal stability of this reagent was demonstrated when it was used for the oxidation of a second aliquot of Os solution after being heated at 140 °C for a period of 10 min. This mixture was selected by the group because of the high boiling point of H_2SO_4 (338 °C at 98%) compared to that of HIO_4 (200 °C) and because the carrier argon gas reaching the plasma contained only OsO_4, water and liberated oxygen. When aqua regia is used, very corrosive gases may reach the plasma.

3.3.4 Other Reagents

Bazan (1987) has argued that the acidity or alkalinity of the reactants has a very marked effect on Os count rates. Before samples were analysed, they were left overnight, after being made basic with a 0.1 N ammoniacal solution. While Dickin et al. (1988) observed different emission characteristics for samples of different pH (i.e. emission may occur at different temperatures), they found that the total Os counts that can be yielded from a sample are not dependent on pH.

3.3.5 Heating Coil, Condenser and Water Trap

The kinetics of the conversion of Os to OsO_4 is relatively slow and the rate is considerably dependent on temperature. Heating coil or tape is therefore used to heat the flask and contents, and therefore increase the rate of the reaction. These elevated temperatures however, generate a large amount of water vapour. This cools the plasma, greatly reducing its efficiency. A condenser and a water trap may be used to remove the water vapour from the gases before they reach the plasma. Hutton and Eaton (1987) found that the advantages of operating the ICP ion source with constant and low or dry aerosol water loading are many fold. It was found that reduction of the "water loading" of the plasma by chilling the sample stream decreases the background spectrum, the formation of oxides or polyatomic species and the ion kinetic energy. The behaviour of the plasma is thus more predictable. It is not understood why the OsO_4 (mp, 40 °C; bp, 130 °C) is not condensed by the cold water condenser. It is possible that this is due to kinetic factors and the high volatility of this gas.

Tao et al. (1988) tried to remove all the water vapour in their experiments. The temperature of the reaction vessel is set to 90 °C. The solution was heated to 90 °C in about 5 minutes and then the OsO_4 was purged from the solution with argon gas for 7 minutes. Although the rate of evolution was faster at 95 °C, this produced more water vapour. A water condenser removed the bulk of the water and a water trap captured the rest. For the water trap, magnesium perchlorate $Mg(ClO_4)_2$, calcium sulphate $CaSO_4$, calcium chloride $CaCl_2$ and sodium hydroxide NaOH were examined. Osmium tetraoxide reacted with NaOH and was absorbed by $CaSO_4$. $CaCl_2$ did not react with the OsO_4, but its efficiency at trapping the water was inferior. $Mg(ClO_4)_2$ neither reacted with OsO_4 nor absorbed it, and was used for further experiments.

Richardson et al. (1989) argue that removing all of the water vapour may create a problem. An infrared phototransistor aimed at the plasma was used to observe the IR emission that occurs with water flow-through and dry ice cooling of the condenser. Lower water temperatures in the condenser yield hotter, more dehydrated plasmas that show a higher apparent radio frequency power. However, when using dry ice, variations in the coolant temperature and thus the humidity of the plasma are unavoidable. When the OsO_4 and carrier gas stream are cooled by a continuous flow of cold water, the plasma is more stable because the sample stream is dehydrated in a consistent manner. A cold water spiral condenser with no water trap was therefore used.

Bazan (1987) used a cold water condenser and heated the vessel to 135 °C. Dickin et al. (1988) used a spiral condenser to lengthen the cooling path and a water jacket cooled by dry ice. Gregoire (1990) selected a temperature of 140 °C as a balance between sufficiently rapid reaction kinetics and the unwanted volatilization of oxidizing agent and water to the argon plasma. It was noted that high acid vapour content of the carrier gas caused the premature corrosion of sampler and skimmer orifices.

Gregoire (1990) reported that the OsO_4 generator produces a long transient signal lasting approximately 15 min. Richardson et al. (1989) have shown that the count rate reaches a peak in less than one minute and then drops exponentially. Some (Dickin et al., 1988; Jarvis et al., 1992c; Richardson et al., 1989) have found it desirable to achieve an Os count rate which is constant for the duration of the sample analysis. This can be achieved by initially chilling the vessel to about 0 °C to retard OsO_4 vapour generation. Heat is applied later on in the run to sustain the Os signal plateau. Sulphuric acid may be added to the reaction mixture to drive off the last of the Os from the sample. The boiling point is raised by several degrees, thus allowing a higher reaction temperature. This solves the problem of the heating becoming ineffective at the end of the run, due to the boiling point of the reactant mixture being reached before all the Os has been driven off. However, this also produces more OsO_4 at the start of the reaction which is disadvantageous (Richardson et al., 1989).

3.3.6 Argon Gas-flow Rate

The carrier gas flow generally needs to be higher for the OsO_4 vapour generator than for a nebuliser. The count rates generally increase with increasing carrier has flow-rates. Gas flow rates of 500 mL/min (Tao et al., 1988), 720 mL/min (Bazan, 1987), 1000 mL/min (Gregoire, 1990), 1600 mL/min (using a long torch) (Beneteau and Richardson, 1992) and 1800 mL/min (using a long torch) (Richardson et al., 1989) have been used.

3.3.7 Osmium Tetraoxide Trap

Osmium concentrations in marine samples are low when compared to other trace metals (Esser and Turekian, 1993a; Koide et al., 1991; Ravizza and Turekian, 1992). The Os may be preconcentrated using the OsO_4 vapour generator, but however, the Os concentration may still too low to be measured directly by ICP-MS. One solution is to trap the OsO_4 (mp, 40 °C; bp, 130 °C) as it is being produced by condensing it in a cold trap and then introducing it into the plasma as a pulse by heating the trap.

Tao et al. (1988) have employed this technique to measure Os by ICP-AES. For the condensation of OsO_4, liquid nitrogen and dry ice-ethanol baths were examined. With a liquid nitrogen trap (bp, -196 °C) is used, helium gas (bp, -269 °C) must be used instead of argon gas (bp, -186 °C) for purging the volatile oxides, otherwise the carrier gas will condense in the trap. At such a low temperature, carbon dioxide (bp, -79 °C) is also trapped and can create interferences during analysis. With a dry ice-ethanol trap, which has a temperature of -72 °C, carbon dioxide is not condensed but OsO_4 is liable to elute from the trap. The efficiencies of trapping and vaporising the oxide must be enhanced by increasing the surface area of the trap. Packing the trap with quartz wool gave a signal peak 3 times larger than that with glass beads, and was more effective in stopping the oxide eluting. The group decided to use a long, thin trap (4.5 mm internal diameter; 45 cm length) packed with fine grade (1-6μm) quartz wool, in a dry ice-ethanol bath. After the oxide was thoroughly trapped, the dry ice-ethanol bath was removed and the trap was heated with a Nichrome heater while argon gas was passed through the trap. Condensed OsO_4 was vaporised in the first 5 seconds.

3.3.8 Argon Bypass

Since the plasma torch of the ICP requires a constant flow of gas to maintain its integrity, a bypass must be included in the design of the vapour generator. Argon gas can then be fed to the plasma while the sample and oxidizing agent is introduced into the vessel and, if an oxide trap is being used, while the oxide is being produced and trapped.

3.3.9 Capillary Tubing

The size of the capillary tubing connecting the generator to the torch is a critical feature of the OsO_4 vapour generator. Dickin et al. (1988) determined the optimal internal diameter of the polyethylene tubing for their experiments to be 1 mm. The frit in the reaction vessel of the generator produces a lower back-pressure on the Ar supply than when a nebuliser is used. This alters the optimum gas flow conditions. The use of a fine capillary to connect the generator and torch increases the back-pressure, thus bringing optimum running conditions for the generator back near to those with the nebuliser.

Bazan (1987) used a flexible connecting tubing made of Teflon, since it does not react with OsO_4. This was confirmed by Tao et al. (1988) who noted that OsO_4 was easily reduced with polyethylene or polypropylene (polyethylene tubing was used by Dickin et al.). The group used glass ball joints and Teflon tubing for all connections. The Teflon tubing connecting the generator to the plasma had an internal diameter of 1.5 mm and a length of 1 m. Tygon or Pyrex glass tubing (5 mm internal diameter, 0.5 m length) was used by Gregoire (1990) to transport the argon gas from the condenser to the torch.

3.3.10 Memory Effects

When Os is in contact with a surface, either in a solution or in a gaseous form, it may be retained by that surface. The surface can be the inside of the glass reaction vessel or condensers/traps of the vapour generator, the capillary tubing connecting the generator to the torch or the torch of the ICP-MS. As the generator setup is used to analyse further samples, the absorbed Os is released and contaminates the sample being analysed. The ICP-MS therefore measures a higher concentration of Os than is actually present in that sample. In order to avoid this memory effect, a thorough cleaning process must be performed on all parts of the generator and the torch in between each sample.

Richardson et al. (1989) have noted that memory effects are one of the most serious sources of systematic error in the analysis of Os, even after the generator was cleaned. The group alleviated the problem by replacing the entire sampling assembly regularly (daily, between groups of the same sample or between different samples) and cleaning the torches and generators in an aqua regia bath overnight. Sampling tubes were stored in 5 M nitric acid when not in use. The following technique was developed to physically flush out the sample and oxidise or ionise any Os remaining in the sample chamber, sampling tube or torch. Firstly, the sample was flushed into the waste tube. The vessel was then rinsed and flushed out, with cold distilled water and then with cold 5 M nitric acid. The sampling tube and torch were purged of the sample by injection 3 mL of 5 M nitric acid into the sample chamber and routing the Ar carrier gas flow through the generator, until the count rate returned to near background. A final rinse with distilled water removed the nitric acid before the next run. The same strategy for reducing memory effects was taken by Jarvis et al. (1992c).

Russ et al. (1987) have also observed the memory effect. However, contrary to other researchers, they suggest that the problem resulted from previous work done with the same torch at much higher Os concentrations rather than accumulation of material from the immediately preceding analyses. They propose that if proper care is exercised, it is unlikely that such memory effects are significant.

Dickin et al. (1988) were unable to develop a technique which they felt adequately suppressed the memory effects. They noted that after cleaning the generator apparatus, reagent blanks yielded comparatively low count rates. However, in subsequent samples the memory effect built up during the run, while at the same time the signal from the sample being analysed tailed off. Osmium absorbed onto surfaces of the generator was being remobilized by oxidising species carried over from the generator. It is important that measurements of blanks made between analyses be performed with oxidising washout solutions. As the contaminant Os is evolved slower than the sample, they should also be continued long enough to detect the contamination; i.e. at least 20 minutes.

3.3.11 Ventilation

Although only a small quantity of OsO_4 will be produced, the compound is highly toxic and so careful ventilation of the generator must be made. Tao et al. (1988) have also noted that Cl_2, a toxic gas, may be produced in the HCl solutions.

3.3.12 ICP-MS Operating Conditions

Jarvis et al. (1992c) have noted that the plasma operating conditions used with the generator are the same as those used with a conventional nebuliser, with the exception of the carrier gas flow which in general needs to be higher. However, Tao et al. (1988), who tried to remove all of the water vapour from the carrier gas by using a water trap, found that the optimum operating conditions of the plasma were considerably different from those for a sample containing water vapour. The group found that when the gaseous sample was introduced, a better signal to background ratio was obtained at lower output power of the ICP-AES (0.7-1.5 kW) than for wet sample introduction. This is because the gaseous sample did not consume the energy necessary for vaporisation, atomisation and excitation of large amounts of water. In order to obtain reproducible Os isotopic composition and concentration analyses from small samples, Richardson et al. (1989) optimised the techniques by investigating the effects of various ICP-MS parameters such as torch length, Ar flow-rate and power. "Torch length" refers to the distance from the sampling cone tip to the torch. The use of the long (19 mm) versus the short torch did not appear to have a noticeable effect on the results, and the long torch was used in the study. The use of a long torch requires a high flow-rate of Ar in order to sample the hottest part of the flame. Russ et al. (1987) operated the mass spectrometer in a single region in scanning mode, which scanned the selected mass region once per second. Scans typically covered the range of m/z 184-194. Successive sweeps were summed for periods of 5 minutes. Typically four accumulations (20 minutes total) were made per sample.

3.3.13 Conclusions

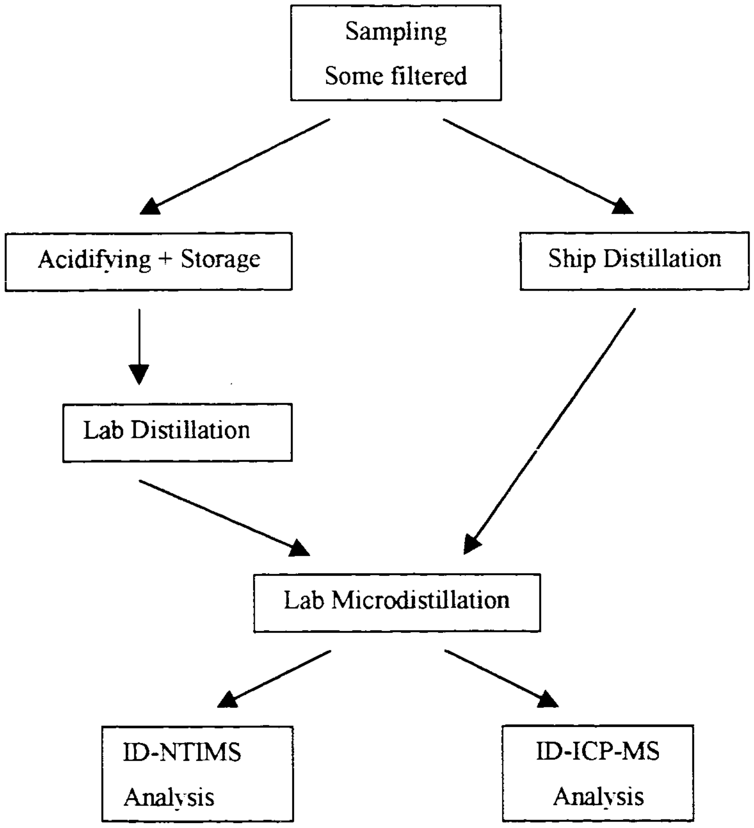
The OsO_4 vapour generator technique can greatly increase the sensitivity of Os analysis by ICP-MS. The review information was used to assemble the apparatus needed for the technique. Due to a shift in the focus of the research however, the OsO_4 vapour generator was never used for Os analysis. Published data suggested that NTIMS is 10^3 to 10^4 times more sensitive when analysing Os and Re than ICP-MS (Hirata and Masuda, 1992) and that isotope dilution NTIMS is the technique of choice for high precision Re-Os analysis. The review information did prove useful when the technique for the isolation of Os from seawater was developed.

CHAPTER 4: Collection of Seawater from the Eastern Pacific Ocean and Analysis for Osmium

4.1 Introduction

Chapter 2 described how a ^{191}Os radiotracer was used to develop a method for the storage of seawater, and for the extraction and isolation of the seawater Os through distillation and microdistillation. This chapter investigates other analytical procedures. The sampling of open-ocean seawater and seawater collected near hydrothermal vents is described. Some of the samples collected were stored for distillation in the laboratory while others were distilled on the ship, and the differences between the two are discussed. The measurement of procedural and reagent Os blanks for the analytical method is then explained. The difficulty in calibrating the ^{190}Os spike used for isotope dilution concentration measurement is investigated. Finally, the determination of Os concentration and isotopic composition by NTIMS and ICP-MS, how the measurements compare, and how the data obtained is treated are discussed. The complete analytical procedure used for the analysis of Os in seawater and vent-influenced samples is shown in Figure 4.1.

Figure 4.1. Analytical Procedure



4.2 Sampling and Storage

Seawater and vent-influenced samples were obtained on Atlantis cruise A3-11 to 9° North of the East Pacific Rise (EPR) during November-December 1997. Figure 4.2. shows that the seawater was collected at two stations east and west of the EPR ridge axis (round dots). The map also shows the location of the hydrothermal vent (rectangular box). The samples were collected using six PVC Niskin bottles (10 L) with Si o-rings and Si tubing in place of the springs. The Niskin bottles were secured to a rosette package equipped with a CTD and a transmissometer. Sampling was performed over a series of nights and generally two casts were performed per night. The Niskin bottles were cleaned before the cruise by leaching the internal walls of the bottles with 4.5N HNO_3 for two weeks.

The Niskin bottles were prepared for collection just before the cast to minimise their contamination. The rosette was lowered into the sea to the deepest depth required, and the Niskin bottles were closed while the package was brought to the surface. The bottles were closed electronically at the required depths. The depth of the rosette package was displayed in real time on the ship, as well as other parameters including salinity, temperature, dissolved O_2 and light transmission. These parameters were recorded.

Seawater samples influenced by the hydrothermal vents were also collected using the rosette package. The package was lowered to about 30 m above the sea floor and the hydrothermal plume was located using a "tow-yow" technique. The package was raised and lowered through approximately 200 m of water column while the ship travelled slowly, perpendicular to the vent axis. The plume was located by observing a decrease in the light transmission recorded in real time on the ship. The bottles were closed at the minimum transmission as is shown in Figure 4.3. These samples are not pure hydrothermal vent fluids and will have been diluted with the surrounding seawater.

The samples destined for laboratory distillation, were stored in glass (2.5 L) and Teflon (2 L) bottles. The glass bottles were cleaned before the cruise by filling each bottle with refluxing 4.5N HNO_3 and leaving overnight with the cap resting on top of the bottle. The Teflon bottles were cleaned by heating for two hours in 5 L covered beakers containing refluxing 4.5N HNO_3. Both types of bottles were thoroughly rinsed with Milli-Q water after cleaning.

Figure 4.2. Sampling Map

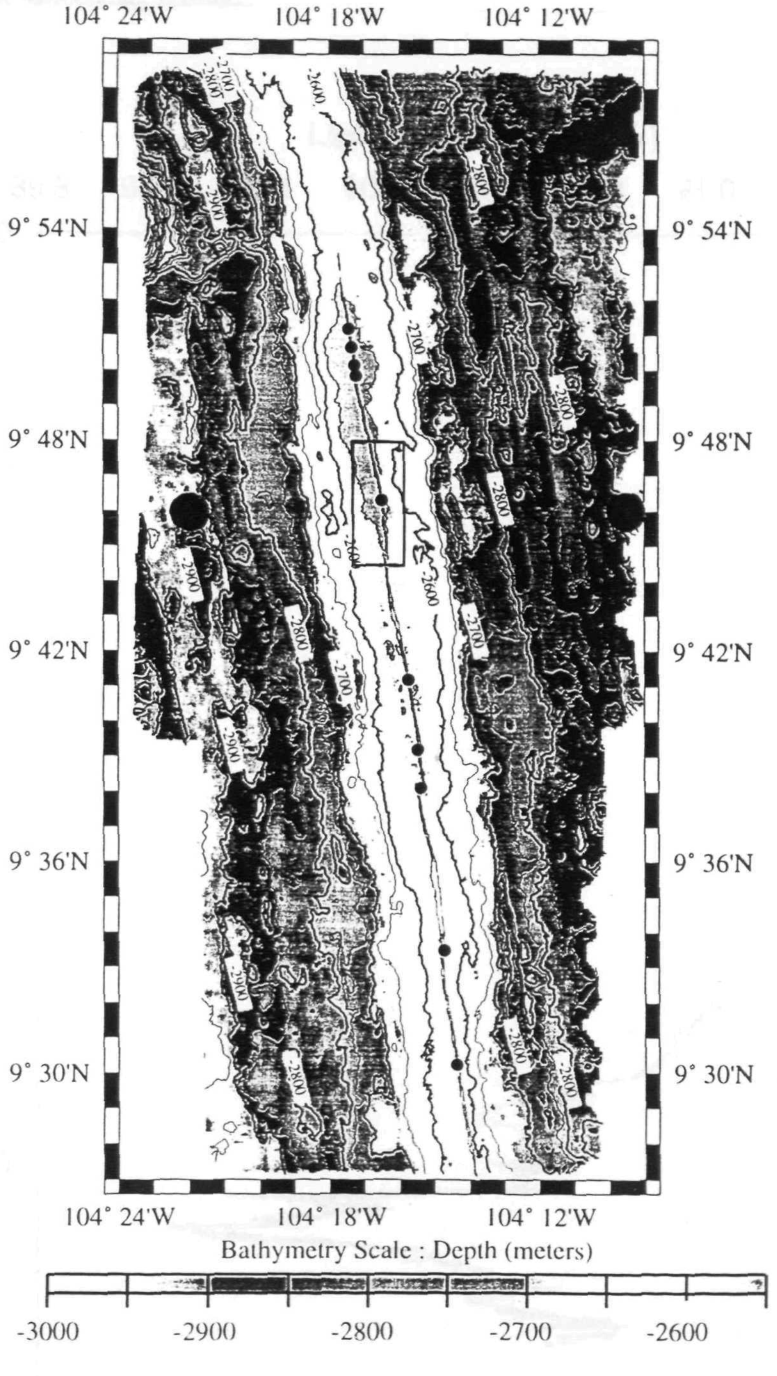
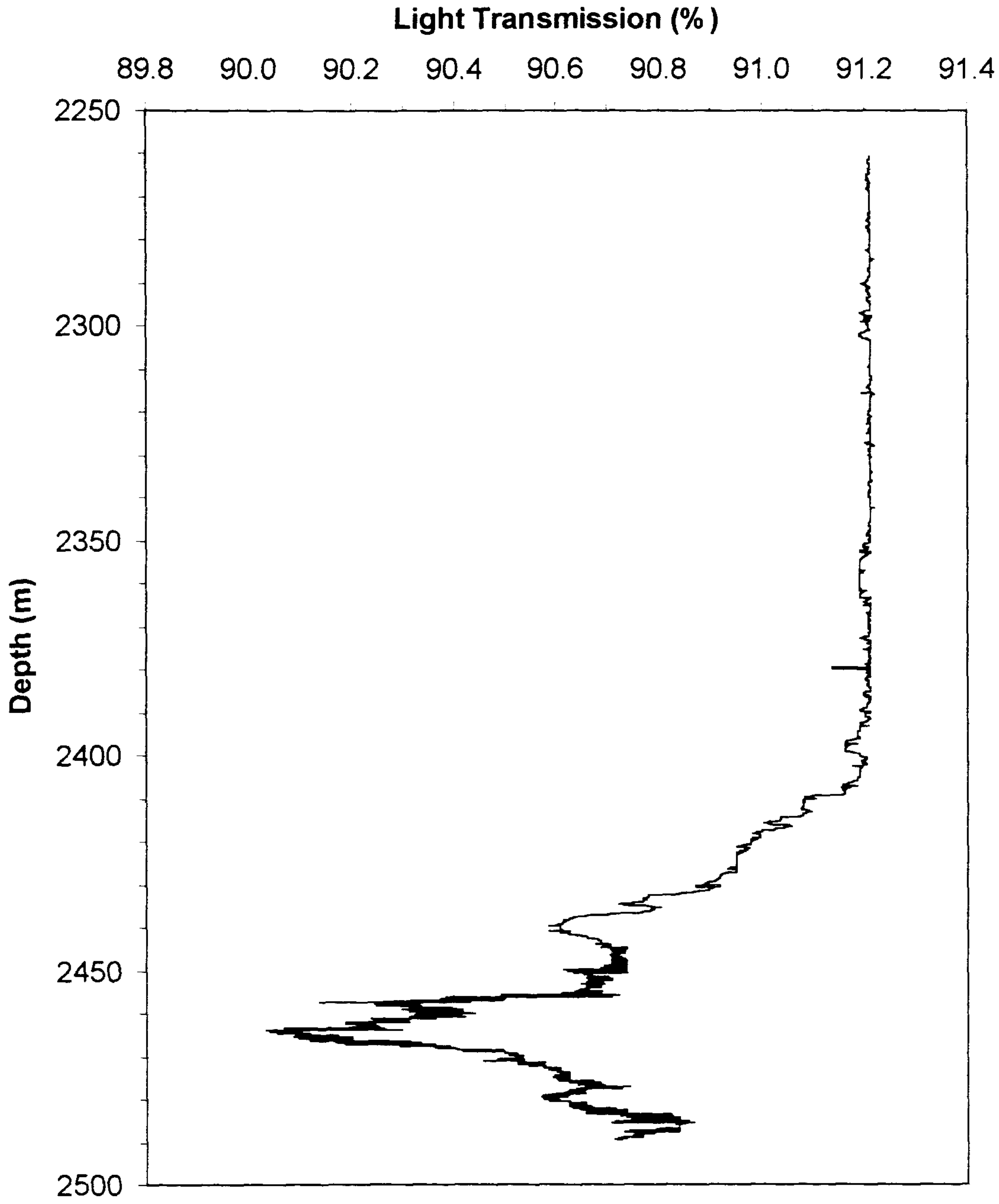


Figure 4.3. Light Transmission Minimum for Sampling Hydrothermal Vent Fluids

The hydrothermal vent plume was located by observing a decrease in the light transmission. The Niskin bottles were closed electronically. These samples are not pure hydrothermal vent fluid and will have been diluted with the surrounding seawater.



The samples were quickly transferred from the Niskin bottles directly to the labelled glass and Teflon storage bottles. The bottles and caps were rinsed three times with sample seawater before collection. The samples were acidified with 6N HCl (4 mL in the 2 L glass bottles and 5 mL in the 2.5 L Teflon bottles) within two hours of collection, and the bottles were sealed with Parafilm and enclosed in plastic bags.

The majority of the samples collected were not filtered before analysis. A comparison between filtered/unfiltered sample was made with two seawater and two vent-influenced samples. In the four comparisons, the filtered and unfiltered samples were collected from the same Niskin bottle as follows. The sample was firstly collected directly from the Niskin bottle into a storage bottle. A filter was then attached to the Niskin outlet tap and the Niskin was pressurised to approximately 2 atm using nitrogen gas. The two Niskin stopcocks were fixed shut so as not to open when the bottle was pressurised. The filtered sample was collected into a storage bottle from the filter setup. The filters used were 0.4μm polycarbonate membrane filters from Nucleopore. They had been washed and soaked in lightly acidified (nitric) Milli-Q water, and were only handled with Teflon forceps.

Samples were also collected for distillation on the ship. The samples were transferred from the Niskin bottles to a measuring cylinder (2 L) (that had been rinsed three times with sample) and 1.7 L of the sample was transferred directly to the distillation flask.

4.3 Procedural and Reagent Osmium Blank Analysis

4.3.1 Introduction

Blank contamination can be a difficult problem when analysing very low concentrations such as Os in seawater (10.86 ± 0.07 pg/kg measured in Indian Ocean seawater (Levasseur et al., 1998)). A strategy for reducing contamination at each step of the sample preparation must be developed, as the procedural blank will only be as low as the weakest link permits. Blank contamination should ideally be low and constant.

The radiotracer experiments only determined the yields of the distillation and microdistillation techniques, and not the blank contamination that is introduced with the techniques. Osmium blank contamination was measured in two ways. The first was to analyse an osmium-free solution using the whole sample preparation procedure. This would determine a value for the Os contamination added to a sample during its preparation. As long as this value was low compared to Os in the sample, and that it was shown to be constant, it could be subtracted from the measured Os concentration to obtain the concentration of Os in the sample. The second method was to analyse the Os blank in the reagents used during the procedure, including HBr, reagent grade H_2O_2, laboratory-distilled H_2SO_4, ship-distilled H_2SO_4 and the microdistillation step. This would be useful in isolating large inputs of Os contamination from a particular reagent or preparation step.

4.3.2 Early Procedural Blank

The Os contamination for the whole sample preparation procedure was measured using an osmium-free solution. The osmium-free solution was prepared by heating Milli-Q water (1.7 L) in an open flask with H_2SO_4 (10 mL) and H_2O_2 (3 mL) for two hours to oxidise and remove any Os in the solution. Milli-Q water was not used directly as it may contain Os. The osmium-free solution was covered and left to cool. This matrix was taken through the Os separation method developed using the radiotracer and treated as a seawater sample being prepared for analysis. Conc. HCl (3.4 mL) was added to the matrix in the same way that the seawater samples were acidified upon collection. Then H_2SO_4 (30 mL), ^{190}Os spike (51.7 mg) and H_2O_2 (5 mL) were added to the matrix and it was distilled, collecting any OsO_4 contamination present and some codistilled water in conc. HBr. The HBr/water solution was concentrated, taken through the microdistillation procedure and analysed by isotope dilution NTIMS.

It was later discovered that the measured value for the Os contamination (5.3 pg) was inaccurate as the NTIMS measurement had been performed on a new batch of Pt filament contaminated with Os. The result of the filament contamination was that the measured value for the Os concentration of a sample was too high and actually varied throughout the analysis. The molecular ratio measured by the instrument, which should remain constant, varied throughout the analysis as the sample-spike Os was used up and the filament contaminant Os became more important.

4.3.3 Reagent Blanks and Microdistillation

A strategy for measuring the Os blank in each reagent was developed. A total Os blank of only 1 pg would be significant, and so many of the reagents had to be preconcentrated before their analysis, so that even very low levels of Os contamination could be measured.

Because of the low Os concentrations of the blanks, the measurements were close to the background and to the detection limits of the ICP-MS instrument and it was difficult to obtain highly precise measurements. For this reason, the following blank values stated are maximum values, where the extreme error value was taken through the isotope dilution calculations. Each reagent blank was determined as follows:

Conc. HBr (3.5 mL) used in OsO_4 trap and microdistillation: Conc. HBr (17.4776 g) and ^{190}Os spike (0.0537 g) were concentrated on a hotplate at 140°C to ~10 μL. Milli-Q water (200 μL) was added (to dilute the solution to a ~0.5N HBr matrix) and the solution was analysed by isotope dilution ICP-MS. A maximum Os concentration of 2.6 fg/g was measured (determined by using the extreme error value from the ICP-MS data). A total of 5.27 g HBr is used in the OsO_4 trap and microdistillation, and so the HBr used in the whole procedure provides a maximum of 13.8 fg Os blank.

Reagent grade H_2O_2, laboratory-distilled H_2SO_4 and ship-distilled H_2SO_4 used in the distillation: The sulphuric acid batches (that were cleaned of Os by distilling on the ship and in the laboratory) could not be analysed directly by ICP-MS as it is a non-volatile acid. Also, they needed to be concentrated so that even very low concentrations of Os contamination could be measured. The three reagents were individually distilled from an osmium-free solution, any OsO_4 was collected in conc. HBr and analysis was by isotope dilution ICP-MS. The H_2O_2 was distilled in the osmium-free solution with no acid added to the matrix. An oxidising agent was needed to distil the H_2SO_4 batches and so H_2O_2 (10 mL) was used. The H_2O_2 (10 mL used in the distillation) contributed a maximum total Os blank of 810 fg, laboratory-distilled H_2SO_4 (30 mL) a maximum total blank of 600 fg and the ship-distilled H_2SO_4 (30 mL) a maximum total blank of 670 fg. The reagent grade H_2O_2 had a maximum Os blank of 81 fg/mL and was therefore a significant contaminant. The H_2SO_4 batches were distilled with H_2O_2, which had a significant Os blank and was the reason for the maximum blank values of 600 fg and 670 fg measured in these two analyses. Both batches of H_2SO_4 actually contained an insignificant amount of Os blank.

Osmium blank from the microdistillation: A single drop of ^{190}Os spike solution (33.2 mg) was taken through a microdistillation to measure the Os blank contribution from all the reagents used in the microdistillation step. The product was analysed as a 5% HBr solution by isotope dilution ICP-MS. The maximum Os blank was 79 fg for the whole microdistillation procedure.

In conclusion, the HBr, the H_2SO_4 batches and the microdistillation step contributed an insignificant amount of Os contamination. The reagent grade H_2O_2 however, had a maximum Os blank of 81 fg/mL (a maximum total Os contamination of 0.81 pg when 10 mL of H_2O_2 is used) and was therefore a significant contaminant. These values show that the first procedural blank (5.3 pg), measured by NTIMS using the contaminated filament, is too high. The sum of the blank for the H_2O_2 (maximum of 0.810 pg), the HBr (maximum of 0.014 pg) and the microdistillation (maximum of 0.079 pg) gives a total procedural blank of only 0.90 pg. This shows that filament Os contamination was contributing to the measured concentration.

4.3.4 Distilled Reagents Blank

In an effort to reduce the Os blank, a new strategy was taken. The distillation technique developed using the radiotracer was modified to reduce the Os blank associated with the technique. The H_2SO_4 and H_2O_2 reagents were predistilled immediately before the distillation, to remove any Os blank in them. Also, higher grade 30% H_2O_2 (Ultrex grade from VWR Scientific) and conc. H_2SO_4 (Optima grade from Fischer Scientific) were used. The Ultrex grade H_2O_2 for example, contains no stabiliser and is double distilled, so possibly contains less Os blank than the reagent grade H_2O_2.

The new blank was measured as follows: Milli-Q water (approx. 1.7 L) was transferred to the flask. Optima grade H_2SO_4 (30 mL) and Ultrex grade H_2O_2 (10 mL) were added. The flask was covered with a Teflon watch "glass", air was bubbled through the matrix and it was heated to ~90°C. After one hour, the watch glass was removed and the flask was heated for one more hour. The matrix was then covered and left to cool. Spike (10 μL) was carefully measured into the flask, the distillation apparatus was assembled (including carrier gas, condensers, joints were sealed with Teflon tape, conc. HBr in the trap and ice bath around the trap) and the matrix was distilled for 3h45. The HBr/codistilled water solution was concentrated by heating on a hotplate and taken through the microdistillation step. It was then analysed by isotope dilution NTIMS on Pt filament that was known to be free of Os contamination.

The two measurements of the Os blank gave values of 0.125 ± 0.004 pg with $^{187}Os/^{186}Os = 2.51 \pm 0.51$ and 0.111 ± 0.003 pg with $^{187}Os/^{186}Os = 2.60 \pm 0.62$. The average measured Os blank value was 0.12 pg ± 0.01 pg total for the whole sample preparation procedure. The $^{187}Os/^{186}Os$ ratio of the blank was 2.56 ± 0.80. The error on the concentration is 8.6%, but as the contaminant Os (0.12 pg) is less than 1% of the sample Os (~13 pg in 1.5 L seawater), the error in the measured sample Os concentration will be less than 0.86%.

4.3.5 Ship Distillation Procedural Blanks

Osmium contamination for ship-distilled samples was different to that for laboratory-distilled samples. The distillations performed on the ship were conducted in a wet laboratory that was not designed for trace metal analysis (there were many metal surfaces and the air was not filtered). The distillation stills were cleaned overnight in cold HNO_3 and the efficiency of this cleaning technique has never been measured directly. Also, reagent grade reagents were used for the distillation and they were not predistilled immediately before the distillation. The Os blank contamination for ship-distilled samples was measured twice by performing the following in duplicate: Osmium-free solutions were prepared by distilling Milli-Q water. These solutions were then distilled with the H_2O_2 and H_2SO_4 reagents, in the same way that the seawater samples were distilled. The HBr/water solutions were then concentrated and purified by microdistillation. One of solutions was analysed by NTIMS, while the other by ICP-MS.

As for the earlier laboratory-distilled blank evaluation, the measured Os contamination value for the NTIMS measurement (6.6 pg) was inaccurate as the analysis had been performed on Os-contaminated Pt filament. This value may appear to be slightly greater than the value measured for the laboratory-distilled blank (5.3 pg), but this may just be reflecting a greater Os contamination from the filament.

The solution analysed by ICP-MS produced a value of 0.17 ± 0.08 pg with a $^{187}Os/^{186}Os$ ratio of -23.8 (negative). When the data was examined more carefully, it was noted that over-correction for Re interference at ^{187}Os had produced a negative average ^{187}Os value, and hence a negative isotopic composition value. This also affected the concentration calculation, as the isotope dilution calculation takes into account the isotopic composition of the sample. The calculations were repeated, this time ignoring the Re interference, which was very low in any case. The new value was 0.33 ± 0.09 pg (counting precision only) with a $^{187}Os/^{186}Os$ ratio of 4.08 ± 1.31. However, too much spike had been added to the Milli-Q water just before the distillation (the solution had been "over-spiked"). The measured $^{190}Os/^{192}Os$ ratios for the samples were all between 4 and 6, while it was 37.6 for the blank determination. At this $^{190}Os/^{192}Os$ ratio, the error magnification introduced by error propagation through the isotope dilution equation is a factor of ~4 (G. Ravizza, pers. comm., 1998). The actual value for the blank is actually between 0.08 and 1.32 pg. It must be noted that this is only a single determination of the ship-distilled samples blank, and the validity of the value has not been tested.

In conclusion, an accurate value of the Os blank contamination for ship-distilled samples was never obtained. During the direct measurement of the ship-distilled blank, too much ^{190}Os spike was added to the distillation solution, with the result that the value obtained had a large error magnification. The sum of the Os contamination from the non-distilled H_2O_2, the HBr and microdistillation alone, show that the ship-distillation blank is in the order of 0.90 pg.

4.3.6 Conclusion

The distillation procedure developed using the radiotracer was modified after a significant Os blank was measured. Reagent grade H_2O_2 was measured to have a significant Os blank (maximum 81 fg/mL), whereas conc. HBr (maximum 2.6 fg/g), both H_2SO_4 batches and the whole microdistillation step (maximum 79 fg total) had low or zero Os blanks. Higher-grade reagents H_2O_2 and H_2SO_4 were used and predistilled before the seawater was added to the flask, to oxidise and remove the Os contamination. A low and reproducible total Os blank of 0.12 pg ± 0.01 pg with ^{187}Os/^{186}Os = 2.56 ± 0.80 was measured for the whole procedure for laboratory-distilled samples. An accurate value for the Os blank for ship-distilled samples was never obtained, but measurements of reagent and microdistillation blanks indicate it is at least 0.90 pg.

4.4 Analytical Techniques

4.4.1 Samples Distilled in the Clean Laboratory

All the samples that were stored for later distillation were prepared in a clean laboratory. The distillation technique used to prepare samples in the laboratory (shown below) differs from the original one developed using the radiotracer, as a significant Os blank contribution was measured. The new technique, in which the reagents are predistilled, has a low and reproducible Os blank of 0.12 ± 0.01 pg.

4.4.1.1 Distillation

1. The 4.5N HNO_3 used to clean the flask is emptied and the flask is rinsed thoroughly with Milli-Q water.
2. The reagents are predistilled to remove Os blank before the distillation. Milli-Q water (approx. 250 mL) is transferred to the flask. Concentrated Optima grade H_2SO_4 (30 mL) and 30% Ultrex grade H_2O_2 (10 mL) are measured into the flask.

3. The flask is heated in a heating mantle (variac setting 50 (on the variac scale of 0-120 with no units)) with carrier gas bubbling through the solution and with a Teflon watch "glass" covering the flask.
4. After one hour, the watch glass is removed and the variac is reduced to setting 45.
5. After one hour, the flask is covered with the watch glass and the heating mantled is turned off. The solution is left to cool for one hour.
6. The distillation apparatus is removed from the cleaning beaker (containing 4.5N HNO_3), rinsed thoroughly with Milli-Q water and assembled around the flask.
7. Concentrated HBr (3.5 mL) is measured into the trap.
8. The sample (approx. 1.5 L weighed accurately) is carefully transferred into the flask.
9. One drop of ^{190}Os-enriched spike solution (which is approx. 30 mg) is very carefully added to the flask. The exact quantity of spike added is determined by weighing the difference in mass of the spike bottle.
10. An ice/water bath is placed around the trap, water is passed through the condensers and the joints between the pieces of distillation apparatus are sealed using Teflon tape.
11. The flask is heated with the heating mantle (variac setting between 45 and 52).
12. After about 3h30, the first condenser is stopped and approx. 10 mL of codistilled water is collected over a period of 10-15 minutes.
13. The HBr/water solution collected is immediately transferred to a Teflon vial (12 mL) and sealed tightly, the heating mantle is stopped and the matrix is left to cool.
14. The sealed vial is placed on a heating plate at ~80°C for one hour to ensure the OsO_4 collected is converted to $[OsBr_6]^{2-}$.

4.4.1.2 Microdistillation

1. After the distillation, the sample in HBr solution is concentrated from 15 mL to approx. 30 μL on a hotplate at 130-140°C.
2. The 30 μL sample is transferred by pipette onto the centre of the upturned lid of the Teflon vial.
3. The sample is heated on a hotplate at 130-140°C until a dry residue is left.
4. The dried sample is left to cool while 20 μL conc. HBr is transferred by pipette into the tip of the conical base of the vial. This drop is held in place by surface tension.
5. The oxidant, 20 μL of CrO_3 in sulphuric acid solution, is transferred by pipette onto the dry sample and the inverted base is quickly screwed on tightly. Teflon tape is used in the threads of the vial to reduce losses of OsO_4.

6. The inverted vial is carefully wrapped in a small square of aluminium foil. The underside and walls of the vial should be covered in aluminium foil, but the area around the HBr drop should be left clear so as not to be heated.
7. The vial is placed on a preheated hotplate at 80-90°C and heated for one hour. Radiotracer experiments have shown that slightly more Os (only 3.1% more) may be recovered if the vial is heated for three hours. However, it is though that the efficiency of purification decreases when the microdistillation is performed for longer.
8. After one hour, the vial is taken off the hotplate and left to cool.
9. The aluminium foil is carefully removed and the vial is opened, keeping it inverted.
10. The sample, now in about 40 µL HBr in the conical tip of the vial (the additional volume is from the 20 µL of oxidant), is concentrated to 1-2 µL for loading onto the Pt filament.

4.4.2 Samples Distilled on the Ship

Ship-distilled samples were prepared using the technique developed using the radiotracer. It differs from the laboratory distillation technique in that the reagents are not predistilled before the distillation. The Os blank in the reagent grade H_2O_2 was only discovered after the cruise. Two distillations were performed in parallel on the ship. The heating mantles and the distillation apparatus were secured using Velcro and elastics. The glassware cleaning procedure was modified, as beakers of boiling acid were considered to be too hazardous on the ship. The distillation apparatus was disassembled between experiments, rinsed with Milli-Q and left to leach overnight in a 5 L plastic tray containing room temperature (~30°C) 4.5N HNO_3. The apparatus was then transferred to a plastic tray containing fresh 4.5N HNO_3 and left for a few hours, before being thoroughly rinsed with Milli-Q water. The efficiency of this cleaning technique has never been measured directly. The distillation flasks were filled with 4.5N HNO_3, partially covered using a stopper and heated in a fume hood (with air bubbling through the solution) to the refluxing point of the solution for ~3 hours. The flasks were emptied and thoroughly rinsed with Milli-Q water, immediately before being used for the next seawater sample.

4.5 Spike Solution Preparation and Calibration

A ^{190}Os spike solution was prepared by diluting a spike solution normally used to analyse Os in sediments by isotope dilution. This spike solution was originally prepared by fusing 96.93% isotopically enriched ^{190}Os metal (from Oak Ridge National Laboratory) with sodium peroxide and then distilling into HCl. A similar method was used in the preparation of the ^{191}Os radiotracer solution. The isotopic composition of the spike solution (G. Ravizza, pers. comm., 1998), which will remain the same when the solution is diluted, is shown in Table 4.1. The atomic weight of the spike is 189.965.

Table 4.1. Isotopic Composition of the ^{190}Os Spike Solution

Atomic Weight	Abundance (%)	Error in Abundance (%)
185.95388	0.021	0.001
186.95579	0.025	0.001
187.95588	0.517	0.002
188.95818	0.962	0.005
189.95848	96.57	0.28
191.96151	1.90	0.01

The ^{190}Os spike solution (0.5091g) was diluted (to 51.9364g) using 6.2N HCl. The concentration of this new spike was calibrated using an Os standard solution (in 6.2N HCl) of known concentration. In the first attempt to calibrate the spike, five spike-standard solutions were prepared. Osmium standard solution in 6.2N HCl (0.500 g) was transferred to a vial and ^{190}Os spike solution also in 6.2N HCl (0.500 g) was added to this. The five solutions were diluted with Milli-Q water and analysed by ICP-MS. A large range in spike concentration was measured, and lower values were obtained when the solutions were reanalysed 15 days later. It was clear that the standard and spike solutions had not equilibrated, even though the matrix of both solutions (6.2N HCl) was the same.

In the second attempt, five more solutions of Os standard solution in 6.2N HCl (1.0 g) and ^{190}Os spike solution in 6.2N HCl (1.0 g) were prepared. These solutions were concentrated to a volume of 30 μL, by heating on a hotplate at 120°C for approximately 5 hours. This was done in an attempt to equilibrate the two solutions and to increase the Os concentrations of the solutions for greater precision during analysis. The solutions were diluted with Milli-Q water and analysed by ICP-MS, and again a large range in spike concentrations was measured. When one of the solutions was analysed a few hours later, the measured proportion of spike to standard Os had changed. It seemed that even after heating, the two solutions had not equilibrated.

In the third attempt, three spike-standard Os solutions were prepared and distilled in order to assure equilibration. A solution of Milli-Q water (164 mL), H_2SO_4 (18 mL), CrO_3 (1mL), ^{190}Os spike solution (1 g) and Os standard solution (1 g) was heated for 4 hours and the OsO_4 was collected in HBr (4mL). The HBr solution was concentrated to 40 μL by heating on a hotplate, then diluted with Milli-Q water (1mL) and analysed by ICP-MS. Much better precision between the three solutions was achieved and when the solutions were analysed a few hours later, the measurement showed that no change in spike concentration.

The concentration of the spike solution was measured to be 299.40 ± 22.5 pg/g (326.35 pg/mL).

4.6 Mass Spectrometry

4.6.1 Negative Thermal Ionization Mass Spectrometry (NTIMS)

The Os was measured on the hand-built NIMA-B NTIMS instrument at the Woods Hole Oceanographic Institution (WHOI). The details of mass spectrometry on this instrument have been published (Hauri and Hart, 1993). After the microdistillation, the sample (in a 9N HBr solution) was concentrated on a hotplate to <1 μL. It was then carefully loaded onto the centre of a Pt filament and dried down gently by passing a current (0.8 A) through the filament. The loading was performed using a piece of Teflon tubing (id 1 mm, length 4-6 cm) attached to a 2 μL syringe. The pieces of Teflon tubing were leached in advance in 6.2N HCl at 80°C overnight and then rinsed thoroughly with Milli-Q water. Filaments for mass spectrometry consist of 0.025 mm x 0.508 mm zone refined 99.95% Pt ribbon.

After loading and drying, the sample was then conditioned for 4-12 hours at ~600°C by passing a current (1.0-1.3 A) through the filament under vacuum ($<1\times10^{-7}$ Torr). The purpose of this step was to reduce the Os on the filament to the metallic form (which ionises more easily then the +4 oxidation state) and to drive off any volatile organic contaminants.

A solution of 5% $Ba(NO_3)_2$ (approx. 20 nL) was loaded directly onto the sample just before analysis and dried (using a 0.8 A current), in order to supply electrons for negative ion formation. The sample was heated slowly (over a period of 1 hour) to a running temperature of 600-800°C, under a vacuum ($\sim3\times10^{-7}$ Torr). Oxygen was then bled into the source at a rate to yield an overall pressure of $\sim6\times10^{-7}$ Torr. In the presence of oxygen, Os ionises efficiently to the negatively charged trioxide $[OsO_3]^-$. The peaks at masses 240, 238, 237, 236, 235 and 233.5 were measured, which correspond to the trioxides $^{192}Os^{16}O_3$, $^{190}Os^{16}O_3$, $^{189}Os^{16}O_3$, $^{188}Os^{16}O_3$, $^{187}Os^{16}O_3$ and a background measurement respectively. The background measurement was subtracted from the Os peaks. Mass 233, which corresponds to the trioxide $^{185}Re^{16}O_3$, was monitored for Re interference. Although the majority of contaminant Re ionises as the tetraoxide at mass 249 and 251, Re interference can cause a problem as the trioxide $^{187}Re^{16}O_3$ interferes with $^{187}Os^{16}O_3$ at mass 235. There is no Os peak at mass 233 and so an absence of counts at that mass indicates that Re interference is not a problem.

The external reproducibility for the NIMA-B NTIMS instrument is 0.3% for Os standards of 100 pg (G. Ravizza, pers. comm., 1998). Little data exists on the reproducibility for lower concentrations of standard. It is shown later that two sets of duplicate seawater samples, collected from the same depth and distilled independently, produced Os concentration measurements by NTIMS that were within 1.3% and 1.6% of each other. These values take into account both the experimental and the analytical reproducibility.

4.6.2 Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

Analyses were performed on the Finnigan “Element” ICP-MS at WHOI. All of the ship-distilled samples and three of the laboratory-distilled samples were analysed by ICP-MS. The instrument is less sensitive for Os measurement than is NTIMS, leading to larger error bars for each data point in the profile, but analyses can be performed at a much faster rate than on the NIMA-B NTIMS.

Chapter 3 explains how an Os standard solution was used to investigate the analysis of Os by ICP-MS. Conclusions from these experiments were used for the analysis of Os in marine samples, including the washout solution which should be used between samples. Samples were analysed using a free aspiration technique to minimise memory or carryover effects. Instead of using a rotary pump to inject the sample into the instrument, the sample was aspirated through the capillary tubing by the reduced pressure caused by the flow of argon gas. A clean torch and a clean cone were installed at the start of the day and the instrument was tuned to indium using a multiple element tuning solution, to optimise the signal intensity (generally to around $1.5x10^6$ cps). The aspiration rate (0.11 – 0.13 g/min) and analysis time (3 minutes) were determined in order to calculate the exact volume of sample aspirated per analysis. The samples were then diluted to a little more than this volume, so that the entire sample was used in a single analysis. This was done to maximise the total amount of Os measured during the analysis and thus increase the count rate and precision of the measurement. The following masses were measured and recorded: 185 (to monitor ^{187}Re interferences on ^{187}Os), 187 and 188 (for isotopic composition data), 190 and 192 (for isotope dilution concentration data) and 194 (to monitor Pt interferences on ^{190}Os and ^{192}Os). The instrument analysis method comprised of 50 runs of 20 passes for each peak, recording at 10 locations on each peak.

After the microdistillation, the sample Os is in a 40 μL HBr solution. For analysis by ICP-MS, this solution was typically concentrated to 20 μL by heating on a hotplate and diluted with Milli-Q water (370 μL). Samples were analysed as ~0.5N HBr solutions. The instrument was flushed with 0.5 N HNO_3 in between samples while the Os count was monitored, to ensure there was no carryover between samples.

4.6.3 Comparison of NTIMS and ICP-MS

Both negative thermal ionization mass spectrometry (NTIMS) and inductively coupled plasma-mass spectrometry (ICP-MS) were used for the analysis of seawater and vent-influenced samples. Published data suggests that NTIMS is 10^3 to 10^4 times more sensitive for Os and Re analysis than ICP-MS (Hirata and Masuda, 1992) and that isotope dilution NTIMS is the technique of choice for high precision Re-Os analysis. However, 30-40 samples can be analysed on most ICP-MS instruments per day, compared to a maximum of two per day on the NIMA-B NTIMS instrument. Samples may be analysed by ICP-MS as a 5% HBr solution, whereas samples analysed by NTIMS must be concentrated to 1-2 μL, carefully loaded onto a Pt filament and then conditioned. The high sensitivity of NTIMS was required to obtain Os isotopic composition data, and so the majority of the samples prepared in the laboratory were analysed by NTIMS. All of the samples distilled on the ship were analysed by ICP-MS. Three laboratory-distilled samples were analysed by ICP-MS. Prepared samples did not contain a sufficient amount of Os to be split and measured by both NTIMS and ICP-MS.

4.7 Data Reduction

4.7.1 NTIMS Data Reduction

Data was obtained from the NTIMS instrument in the form of the osmium trioxide molecular ratios 235/236, 237/236, 238/236 and 240/236. These osmium trioxide molecular ratios were converted to Os atomic ratios by performing an oxide correction on the data. Oxygen isotope abundances (^{16}O = 99.759%, ^{17}O = 0.0374% and ^{18}O = 0.2039%) (Nier, 1950) were used to calculate the following trioxide probabilities: P^{48} = 99.2787%, P^{49} = 0.11166% and P^{50} = 0.60876% where P^{48} is the probability that the trioxide formed has a mass of 48 ($^{16}O^{16}O^{16}O$). The average ratios $^{187}Os/^{188}Os$, $^{189}Os/^{188}Os$, $^{190}Os/^{188}Os$ and $^{192}Os/^{188}Os$ of the sample-spike mixture were thus calculated.

The sample (not blank corrected) Os concentration and isotopic composition were then calculated by performing the isotope dilution calculation (Heumann, 1988). Finally, the Os blank contamination was subtracted to obtain the true Os concentration and isotopic composition of the seawater sample.

4.7.2 ICP-MS Data Reduction

Data obtained from the ICP-MS instrument was in the form of counts per second (cps) at the ten locations on each peak, recorded over the 50 runs. The average count at the ten locations on each peak was taken to obtain the average peak count for that run. The Os count for each mass was then calculated by subtracting any interference from each peak. For example, the count for ^{187}Os was calculated by subtracting the rhenium (^{187}Re) interference from the total count at mass 187. The average count for each Os isotope over the 50 runs was calculated and the Os ratios required for the isotope dilution calculation was obtained from these values (the ratio of averages method). An alternative method was to calculate the ratios for each of the 50 runs, and then take the average of those ratios (the average of ratios method). In general, the two methods for obtaining the Os isotopic ratios produced similar values. The isotope dilution calculation was made to obtain the sample Os concentration and isotopic composition. A value for the Os contamination of samples distilled on the ship could not be obtained and so no blank contamination correction was made for these samples. The Os contamination for the samples distilled in the laboratory however, was measured and so this value was subtracted from the three samples distilled in the laboratory and analysed by ICP-MS.

4.7.3 Isotope Dilution Equations

The isotope dilution equation for Os, when normalising to the isotope ^{188}Os, can be written as:

$$C_S = \frac{AW_S}{AW_{SP}} \times \frac{M_{SP}}{M_S} \times \frac{C_{SP}}{A_S^{188}} \times \frac{A_{SP}^{190} - R_M^{\frac{190}{188}} A_{SP}^{188}}{R_M^{\frac{190}{188}} - R_S^{\frac{190}{188}}}$$

where:
C = concentration of...
AW = atomic weight of...
M = mass of...
A^x = abundance of the isotope x in...
$R^{x/y}$ = ratio x/y in...
S = sample
SP = spike
M = mixture (spike-sample)

For highly accurate measurements, the isotopic composition (^{187}Os/^{188}Os ratio) of the sample ($R_S^{187/188}$) must be known in order to calculate the atomic weight of the Os in that sample (AW_S). The atomic weight of Os in a sample is generally around 190.2, but the exact value will vary with the isotopic composition of that sample. When normalising to the isotope ^{188}Os and using the ^{190}Os spike with isotopic abundances shown in Table 4.1., the equation is:

$$C_S = \frac{(1409.571027 + 186.95579 \times R_S^{\frac{187}{188}})}{189.9654717} \times \frac{M_{SP} \times C_{SP}}{M_S} \times \frac{(0.9657 - R_M^{\frac{190}{188}} \times 0.00517)}{(R_M^{\frac{190}{188}} - 1.98379)}$$

(A_S^{188} cancelled-out with another factor during the calculation)

. When normalising to the isotope ^{192}Os and using the ^{190}Os spike with isotopic abundances shown in Table 4.1., the equation is:

$$C_S = \frac{(457.2650938 + 186.95579 \times R_S^{\frac{187}{192}})}{189.9654717} \times \frac{M_{SP} \times C_{SP}}{M_S} \times \frac{(0.9657 - R_M^{\frac{190}{192}} \times 0.019)}{(R_M^{\frac{190}{192}} - 0.64354)}$$

4.8 Summary

Samples were collected for Os analysis during a cruise to 9°N of the East Pacific Rise. A seawater vertical profile was obtained using Niskin bottles attached to a rosette and CTD package. The hydrothermal vent plume was located and sampled using a "tow-yow" technique. Samples were stored for later analysis and also distilled on the ship.

A significant Os blank contamination (5.3 pg) was measured for the whole analytical procedure, although this value was later discovered to be inaccurate as the NTIMS measurement had been performed on contaminated Pt filament. A number of experiments were performed in an effort to pinpoint and eliminate blank contamination. Low Os blanks were measured in the HBr, the H_2SO_4 and the whole microdistillation step, but a significant blank was found in the reagent grade H_2O_2 oxidising agent used in the distillation. A new technique for the distillation was developed, in which higher-grade H_2O_2 and H_2SO_4 reagents were used and predistilled to remove Os before the seawater distillation. A low and reproducible total Os blank of 0.12 ± 0.01 pg with $^{187}Os/^{186}Os = 2.56 \pm 0.80$ was measured for the whole sample preparation laboratory procedure. An accurate value for the Os blank for ship-distilled samples was never obtained, but measurements of reagent and microdistillation blanks indicate it is at least 0.90 pg.

The calibration of the spike had to be repeated a number of times, due to an apparent lack of equilibration between the spike and standard solutions. The concentration of the spike solution was determined using a backwards isotope dilution method (with an Os standard solution of known concentration) and measured to be 299.40 ± 22.5 pg/g (326.35 pg/mL).

Samples were analysed by both NTIMS and ICP-MS. Although ICP-MS is less sensitive for Os analysis than is NTIMS, less sample preparation is required and the analysis is much faster.

CHAPTER 5: Results and Discussion

5.1 Introduction

In this chapter, the data from samples collected in the eastern Pacific Ocean are presented and discussed. Firstly, the Os concentration and isotopic composition vertical profiles are introduced. The differences between the two sets of data are discussed and the results are compared with other seawater Os data from the Indian, Atlantic and Pacific Oceans. A correlation between dissolved oxygen and Os concentration is noted, the validity of the data set is discussed and hypotheses are proposed to explain the shape of the profile. The marine geochemistry of Os is then compared with other metals. The results from filtered and unfiltered, plume and near sea floor samples are presented. Finally, the data are used to calculate Os oceanic residence times, and the implications of the data for the speciation of Os in seawater are discussed. Ideas for future work that should be conducted are presented.

5.2 Osmium Concentration Vertical Profile Results

The data (Tables 5.1. and 5.2.) and vertical profiles (Figures 5.1. and 5.2.) show that the Os concentration of unfiltered seawater is not constant throughout the water column in this area of the eastern Pacific Ocean. Elevated concentrations (7.19 and 7.54 pg/L at 25 m for laboratory-distilled samples) are found in surface waters, a small but distinct minimum (6.64 and 6.75 pg/L) is observed at 460 m and the concentration increases with depth below this (to 9.82 pg/L at 2401 m). While clear, the exact features of the Os minimum are poorly defined between 100 and 1000 m, as only two laboratory-distilled samples were analysed in this section of the water column (at 459 and 462 m).

5.3 Osmium Isotopic Composition Vertical Profile Results

Figure 5.3. shows that the $^{187}Os/^{186}Os$ ratios for the seawater (for laboratory-distilled samples analysed by NTIMS, with blank correction) lie in the range 8.7 to 9.2, with a mean of 8.89 ± 0.09 (2σ). The profile shows that the $^{187}Os/^{186}Os$ ratio of seawater is constant through the water column. Samples distilled on the ship and analysed by ICP-MS have $^{187}Os/^{186}Os$ ratios in the range 7.0 to 8.2 (not blank corrected), with a mean of 7.50 ± 0.39 (standard deviation).

Sample	Note	Analysis	Depth (m)	[Os] (pg/L)	± [Os] (pg/L)	$^{187}Os/^{186}Os$	± $^{187}Os/^{186}Os$
3-8T		NTIMS	25	7.19	0.07	9.17	0.11
3-8G		NTIMS	25	7.54	0.03	8.65	0.06
3-7T		NTIMS	44	6.86	0.04	9.01	0.09
8-6UG		ICP-MS	100	8.11	0.36	7.54	0.65
8-6FG	filtered	ICP-MS	100	7.40	0.55	6.90	0.87
12-7G		NTIMS	459	6.75	0.03	8.91	0.06
5-6T		NTIMS	462	6.64	0.04	8.72	0.11
5-5T		NTIMS	1000	7.83	0.06	9.00	0.12
8-4G		ICP-MS	1496	8.66	0.49	6.43	0.73
3-3T		NTIMS	1500	6.47	0.06	8.76	0.20
12-6G		NTIMS	1997	9.27	0.05	9.06	0.11
5-4T		NTIMS	1998	9.39	0.04	8.79	0.05
3-4T		NTIMS	2401	9.82	0.08	8.96	0.11
15-7G	vent-influenced	NTIMS	2440	9.62	0.08	8.69	0.12
22-5UG	vent-influenced	NTIMS	2480	8.74	0.05	8.77	0.08
12-4G	30m above sea floor	NTIMS	2778	8.41	0.08	9.04	0.13

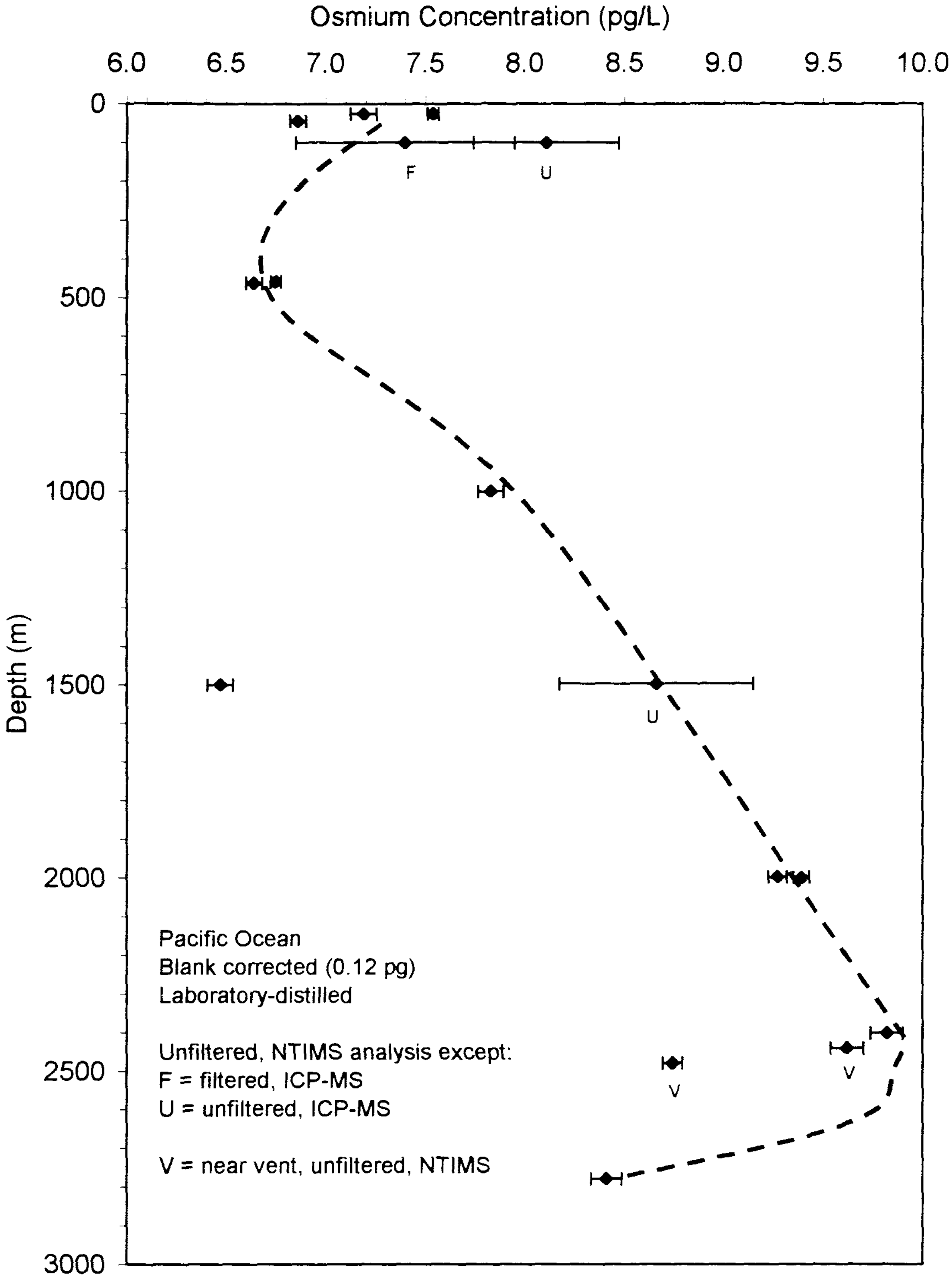
Table 5.1. Laboratory-Distilled Samples Data

The ± errors are two-times standard error of the instrument counts; G, T and D in the sample label signify the samples were stored in Glass or Teflon bottles, or ship-Distilled, respectively. All samples unfiltered except where indicated U or F – unfiltered / filtered comparison.

Sample	Note	Analysis	Depth (m)	[Os] (pg/L)	± [Os] (pg/L)	$^{187}Os/^{186}Os$	± $^{187}Os/^{186}Os$
5-8D		ICP-MS	14	8.97	0.71	7.06	0.71
3-8D		ICP-MS	25	10.12	0.67	7.37	0.68
12-7D		ICP-MS	459	8.08	0.61	7.35	0.74
25-4UD		ICP-MS	460	9.54	1.80	7.01	1.34
25-4FD	filtered	ICP-MS	460	9.07	0.52	7.65	0.54
12-6D		ICP-MS	1997	10.15	0.28	7.37	0.36
5-4D		ICP-MS	1998	11.77	0.46	8.22	0.48
26-6UD	vent-influenced	ICP-MS	2436	12.24	0.51	7.02	0.60
26-6FD	vent-influenced+filtered	ICP-MS	2436	11.79	0.64	7.19	0.52
17-7D	vent-influenced	ICP-MS	2447	10.02	0.52	7.96	0.62
17-4D	vent-influenced	ICP-MS	2453	11.40	0.78	7.80	0.73
22-7UD	vent-influenced	ICP-MS	2480	11.91	0.79	7.86	0.62
22-7FD	vent-influenced+filtered	ICP-MS	2480	11.68	0.67	7.65	0.51

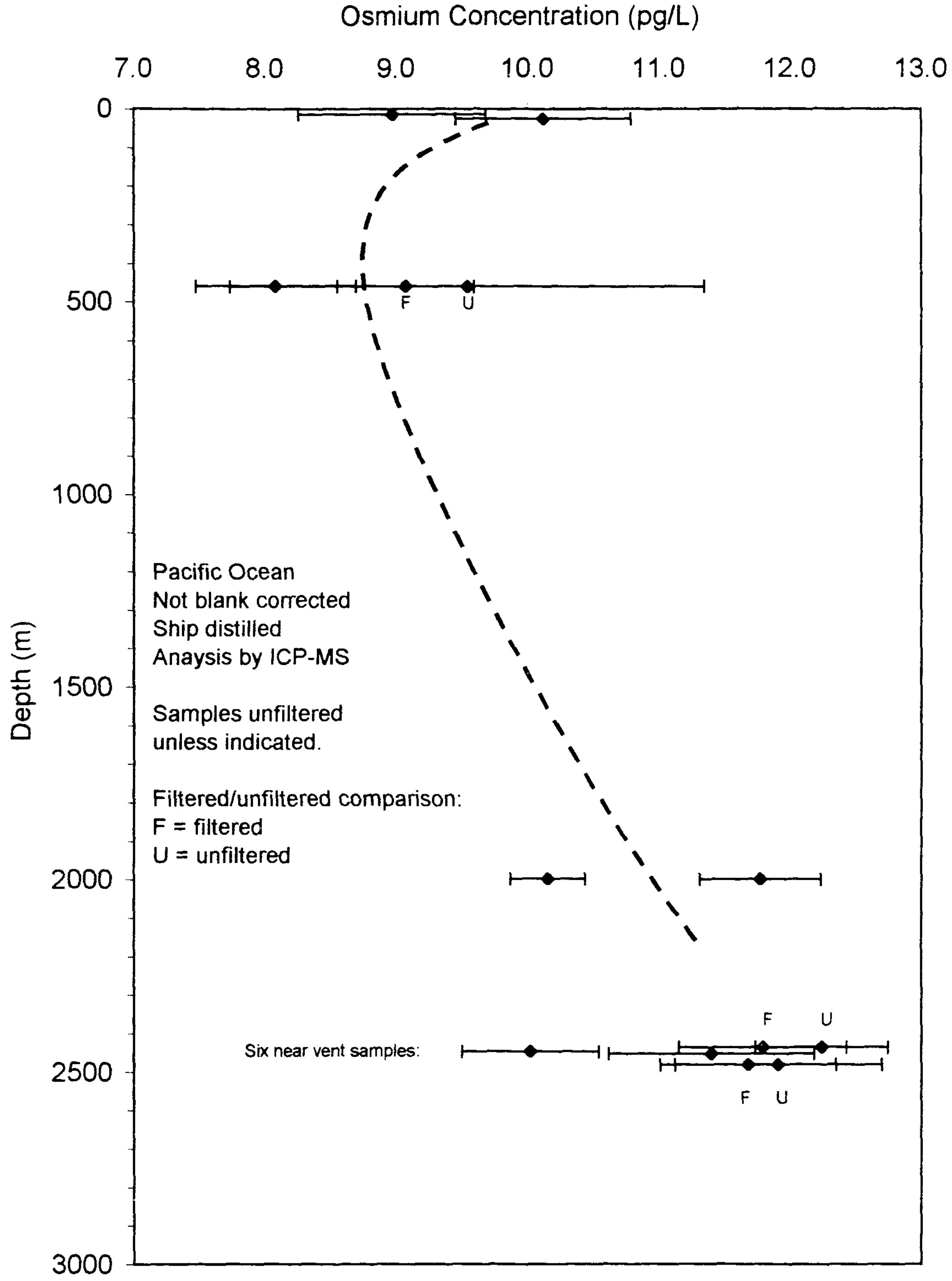
Table 5.2. Ship-Distilled Samples Data

Figure 5.1. Osmium Concentration Vertical Profile and Vent-Influenced Samples (Laboratory-Distilled Samples)



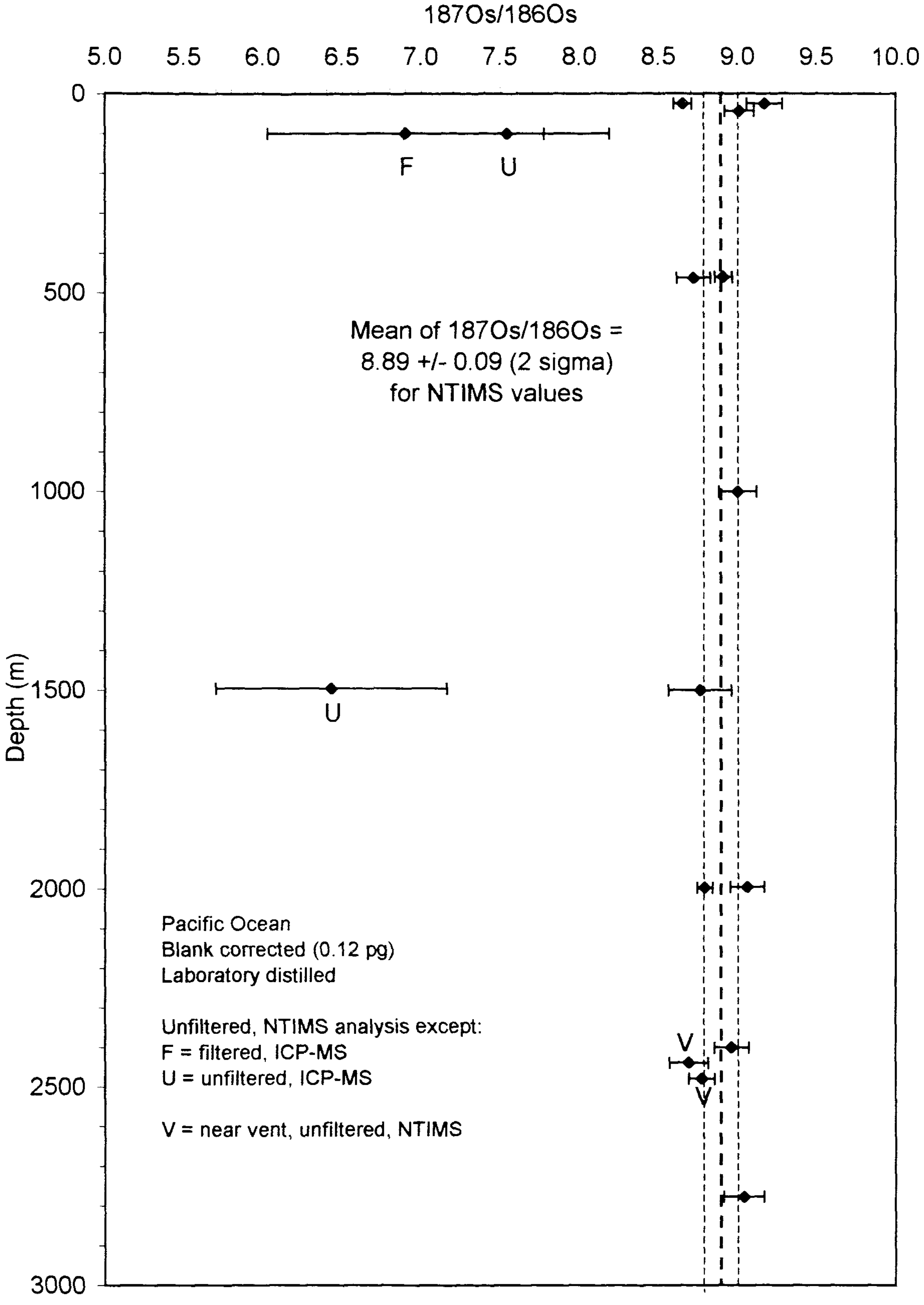
Best-fit line of open-ocean sample (i.e. not including near vent samples); not including 1500 m "flier".

Figure 5.2. Osmium Concentration Vertical Profile and Vent-Influenced Samples (Ship-Distilled Samples)



Profile line showing Os concentration minimum at 500 m.

Figure 5.3. Osmium ^{187}Os/^{186}Os Vertical Profile and Vent-Influenced Samples (Laboratory-Distilled Samples)



5.4 Comparison between Laboratory-Distilled and Ship-Distilled Samples, and NTIMS and ICP-MS Measurements

5.4.1 Introduction

The samples from the eastern Pacific Ocean were distilled either in the laboratory or on the ship during the cruise. The Os from every sample was purified by microdistillation in the laboratory, and then analysed by either NTIMS or ICP-MS. The first set of samples (shown in Table 5.1. and Figure 5.1.) was distilled in the laboratory and most of the samples were analysed by NTIMS (three of these samples were analysed by ICP-MS). The second set (shown in Table 5.2. and Figure 5.2.) was distilled on the ship and all the samples were analysed by ICP-MS. A low and reproducible Os blank of 0.12 ± 0.01 pg with $^{187}Os/^{186}Os = 2.56 \pm 0.80$ was measured for the whole preparation procedure for laboratory-distilled samples. An accurate value for the Os blank for ship-distilled samples was never obtained, but measurements of reagent and microdistillation blanks indicate it is at least 0.90 pg total (irrespective of the amount of seawater analysed).

While the concentration profiles generated for the two sets of samples show the same shape (an elevated concentration at the surface with a minimum at around 500 m and a gradual increase below this depth), both the Os concentration and isotopic composition values are slightly different. All samples analysed by ICP-MS show significantly lower $^{187}Os/^{186}Os$ ratios than those analysed by NTIMS. The samples prepared on the ship, which were all analysed by ICP-MS, show approximately 2 pg/L higher Os concentrations than the laboratory-distilled samples (analysed by NTIMS or ICP-MS).

There are a number of explanations for the difference in the values obtained for the two sets of samples, and each explanation is explored below. The first explanation is that one of the mass spectrometers is producing inaccurate measurements. The second is that the samples prepared in the laboratory have undergone loss of Os by adsorption to the bottles during storage. The third explanation is that the samples distilled on the ship have a higher Os blank contamination than the samples distilled in the laboratory, or that a difference in analytical procedure (in the addition of the ^{190}Os spike solution for example) caused the difference in measured concentration.

5.4.2 Mass Spectrometry Explanation

There appears to be a significant difference in the isotopic composition data obtained by NTIMS and ICP-MS. All the laboratory-distilled samples were stored and prepared for analysis under the same conditions, and while the majority of them were analysed by NTIMS, three of the samples were analysed by ICP-MS. The three laboratory-distilled-ICP-MS samples show distinctively lower isotopic compositions (^{187}Os/^{186}Os = 6.4 – 7.5) than the laboratory-distilled-NTIMS samples (^{187}Os/^{186}Os = 8.7 - 9.2). As all the samples were stored and distilled under the same conditions, it seems unlikely that adsorption or contamination is responsible for the difference. The Os concentrations measured for these three samples plot relatively well with those analysed by NTIMS.

It appears that the ICP-MS instrument is producing slightly lower isotopic composition values than NTIMS. The ^{187}Os/^{186}Os values measured by NTIMS (mean of 8.89 ± 0.09 (2σ)) are much closer to those previously measured for seawater Os, than the ICP-MS values (mean of 7.50 ± 0.39). For example, ^{187}Os/^{186}Os values of 8.80 ± 0.07 for Indian Ocean seawater (Levasseur et al., 1998) and 8.7 ± 0.3 for North Atlantic and Central Pacific seawater (Sharma et al., 1997) have been obtained. It must be noted that at present, ICP-MS is not as sensitive as NTIMS for very low Os concentration measurements (Hirata and Masuda, 1992). The ICP-MS instrument count rates for the ^{187}Os and ^{188}Os peaks were low (approximately 200-300 counts average per run, for both peak) and show that these analyses are close to the detection limit of the instrument. The background count for the "Element" ICP-MS instrument is around zero, and so no background correction is made. The counting statistics for the ICP-MS isotopic composition measurements, are not as precise (they have larger error values) than those for the NTIMS isotopic composition measurements (shown in Tables 5.1. and 5.2.). Also, correction for Re interference on ^{187}Os had to be taken into account for the ICP-MS analyses, which was not the case for NTIMS analyses. The count rates for ^{185}Re were also low (approximately 5-20 counts average per run) and so uncertainty in the correction that has to be made at mass 187, creates errors in the calculated ^{187}Os/^{186}Os value. It is for the reasons above that the isotopic composition data produced by NTIMS, is likely to be more accurate than those produced by ICP-MS.

5.4.3 Adsorption Explanation

The second explanation for the difference in the values obtained for the two sets of samples concerns adsorption. Osmium is known to be readily adsorbed onto surfaces, and there is potential for the loss of Os in the seawater by adsorption onto the inside surface of the storage bottles. The radiotracer was used to investigate adsorption and volatile loss effects and it was shown that the seawater should be stored in either glass or Teflon bottles and acidified quickly after collection to pH2 using HCl. Despite these precautions, it is possible that Os adsorption to the storage bottle is responsible for the ~2 pg/L difference in Os concentration between the two data sets.

However, the laboratory-distilled samples were prepared in a random order over 2 months, and the smooth Os concentration profile shown in Figure 5.1. would not have been produced had ongoing adsorption or volatile losses taken place during this period. Two sets of duplicate samples, collected from approximately the same depths and then distilled nearly a month apart, produced concentration values that were within 1.6% and 1.3% each other. Two samples (5-6T and 5-4T) that had been collected from 462 m and 1998 m and stored in Teflon bottles, were distilled and measured to have Os concentrations of 6.64 and 9.39 pg/L, respectively. The duplicate samples (12-7G and 12-6G), collected from 459 m and 1997 m and stored in glass bottles, were distilled nearly one month later and their analysis produced Os concentrations of 6.75 and 9.27 pg/L (within 1.6% and 1.3% of the earlier measurements) respectively. A different sample collected from 25 m, was split and stored in both a Teflon and a glass bottle (samples 3-8T and 3-8G originated from the same 10 L water mass, collected in a single Niskin bottle). The two fractions were distilled at the same time in parallel, and the measured Os concentrations (7.19 and 7.54 pg/L) are within 4.6% of each other. The above comparisons shows that the samples have not lost Os between the time it took to distil them. They also show that there is no or little difference between the adsorption characteristics of Teflon and glass bottles.

Levasseur et al. (1998) observed no loss of Os from two seawater samples when they were stored in Pyrex bottles for a month longer than the majority of the other samples. Samples collected from the Indian Ocean for Os analysis (Levasseur et al., 1998) were stored in Pyrex (borosilicate glass) bottles for 3 months during the period of analysis, and no Os loss was observed. This confirms the theory that glass is a suitable material for the storage of seawater for Os analysis.

5.4.4 Blank Contamination Explanation

The third explanation for the difference between the two data sets is that the ship-distilled samples are reflecting a greater Os contamination than laboratory-distilled samples. A low and reproducible Os blank of 0.12 ± 0.01 pg with $^{187}Os/^{186}Os = 2.56 \pm 0.80$ was measured for the whole preparation procedure for laboratory-distilled samples. An accurate value for the Os blank could not be obtained for ship-distilled samples. The sum of the blank contamination from the H_2O_2 (maximum of 0.810 pg), the HBr (maximum of 0.014 pg) and the microdistillation (maximum of 0.079 pg) gives a total procedural blank of 0.90 pg total (irrespective of the amount of seawater analysed). This gives an indication that the contamination blank for ship-distilled samples must be at least 0.90 pg and is direct support for a higher blank for the ship-distillation procedure. This value only accounts for contamination introduced by the H_2O_2 and HBr reagents and through the microdistillation, and does not take into account any possible contamination from the working conditions on the ship or the fact the distillation glassware was only cleaned in cold HNO_3 on the ship.

There is evidence to support the blank contamination explanation from the data. The ship-distilled samples (8.08-11.77 pg/L, not including plume samples) show ~2 pg/L higher Os concentration at all depths than laboratory-distilled samples (6.47-9.82 pg/L). The isotopic ratio values are lower for the ship-distilled samples (mean $^{187}Os/^{186}Os = 7.50 \pm 0.39$) than for laboratory-distilled samples (mean $^{187}Os/^{186}Os = 8.89 \pm 0.09$ (2σ) for samples analysed by NTIMS). Osmium contamination in environmental analysis has a low $^{187}Os/^{186}Os$ ratio (as the measurement of the laboratory-distilled blank shows), and so when relatively radiogenic samples are being prepared (such as seawater), any contamination has the effect of increasing the measured Os concentration and decreasing the measured isotopic ratio.

The difference in the Os concentration measured for the two sets of samples, may be as a result of differences in the analytical procedure between laboratory and ship distillations. The difference in the method used to distil the seawater has already been noted (section 4.4). The addition of the ^{190}Os spike solution, which is critical to the measurement of the Os concentration, was performed by different methods for laboratory and ship distillations. The amount of spike added to the seawater was determined by the difference in mass of the spike bottle for laboratory-distilled samples. This was not possible on the ship, and so the spike was added to the seawater by pipette for ship-distilled samples. This method is likely to be less accurate and less precise than the weighing method. It is possible that an unknown, systematic error in the addition of the spike between the two sample sets, resulted in the ~2 pg/L difference in measured Os concentration.

5.4.5 Summary

All the samples analysed by ICP-MS show lower isotopic compositions than those analysed by NTIMS. The comparison to previously published data, the higher instrument count rates and better precision in the measured values, all suggest that the isotopic composition values obtained by NTIMS are more accurate then those obtained by ICP-MS. The data suggests that the samples have not lost Os between the time it took to distil them, and that there is no or little difference between the adsorption characteristics of Teflon and glass bottles. The difference in Os concentration between eastern Pacific seawater (this thesis) and Indian Ocean seawater (Levasseur et al., 1998) cannot be explained by adsorption, as glass bottles were used in both sets of samples. There is direct evidence that ship-distilled samples have higher blank contamination than laboratory-distilled samples, as blank contamination introduced by the reagents and the microdistillation alone account for 0.90 pg of Os blank.

5.5 Seawater from the Pacific, Indian and Atlantic Oceans

5.5.1 Osmium Concentration in the Oceans

The Os concentration vertical profiles of eastern Pacific Ocean seawater (this thesis) and Indian Ocean seawater (Levasseur et al., 1998) are shown in Figures 5.4. and 5.5. The shape of the profiles is different. In the eastern Pacific Ocean, elevated Os concentration were measured at the surface, with a minimum at around 500 m and a gradual increase below this depth. A constant Os concentration was measured at all depths in the Indian Ocean (with a mean of 10.86 ± 0.07 pg/kg with 2σ error). However, only two measurements were made above 1200 m in the Indian Ocean, and it is possible any structure in the vertical profile in this section of the vertical profile was missed. The difference in the shapes of the profiles is explained (in section 5.7.) by the difference in the dissolved oxygen profiles between the two sampling sites. Dissolved oxygen measurements were not made when the samples were collected in the Indian Ocean, but Figure 5.11. (presented later) shows the oxygen profile for Geosecs station 37°45 S, 57°37 E, which is very close to one of the Indian Ocean sampling sites. It shows there are no suboxic conditions in the water column in this region, as are found in the eastern Pacific Ocean sampling sites. The importance of this is discussed in section 5.7.

The Os concentration measured for deep eastern Pacific Ocean seawater (9.82 pg/L) is 10% lower than the mean measured in the Indian Ocean (10.86 ± 0.07 pg/kg) (Levasseur et al., 1998). This difference cannot be explained by loss of Os through adsorption to the storage bottle, as glass bottles were used in both sets of samples.

The Pacific concentrations are 2 - 3 times larger than previously measured Os concentrations in the Atlantic and Pacific Oceans (Sharma et al., 1997). These samples were collected and stored in polyethylene bottles, which were shown in the radiotracer experiments to adsorb Os. A very different technique (precipitation) was used to extract the Os from the seawater before analysis, and it is possible that this technique does not extract all of the Os from the seawater.

5.5.2 Osmium Isotopic Composition in the Oceans

The mean $^{187}Os/^{186}Os$ ratio of 8.89 ± 0.09 (2σ error) (standard deviation) for eastern Pacific Ocean seawater is in agreement with the value of 8.80 ± 0.07 (2σ error) measured in the Indian Ocean (Levasseur et al., 1998). This suggests there are no or little differences in isotopic composition between these two ocean basins. Figures 5.6. and 5.7. show a comparison between the $^{187}Os/^{186}Os$ vertical profiles in the Pacific and Indian Oceans. The Os isotopic composition of seawater was found not to vary within analytical precision, along the profiles in both ocean basins.

The $^{187}Os/^{186}Os$ measured in the eastern Pacific Ocean (8.89 ± 0.09 (2σ)) is slightly higher than has been measured (Sharma et al., 1997) in North Atlantic (8.7 ± 0.2) and Central Pacific (8.7 ± 0.3) seawater. It is also slightly higher than the value (8.6) determined by the analysis of organic-rich sediments (Ravizza and Turekian, 1992) and pelagic clays (Pegram et al., 1992).

Figure 5.4. Pacific Ocean- Osmium Concentration Vertical Profile (this study)

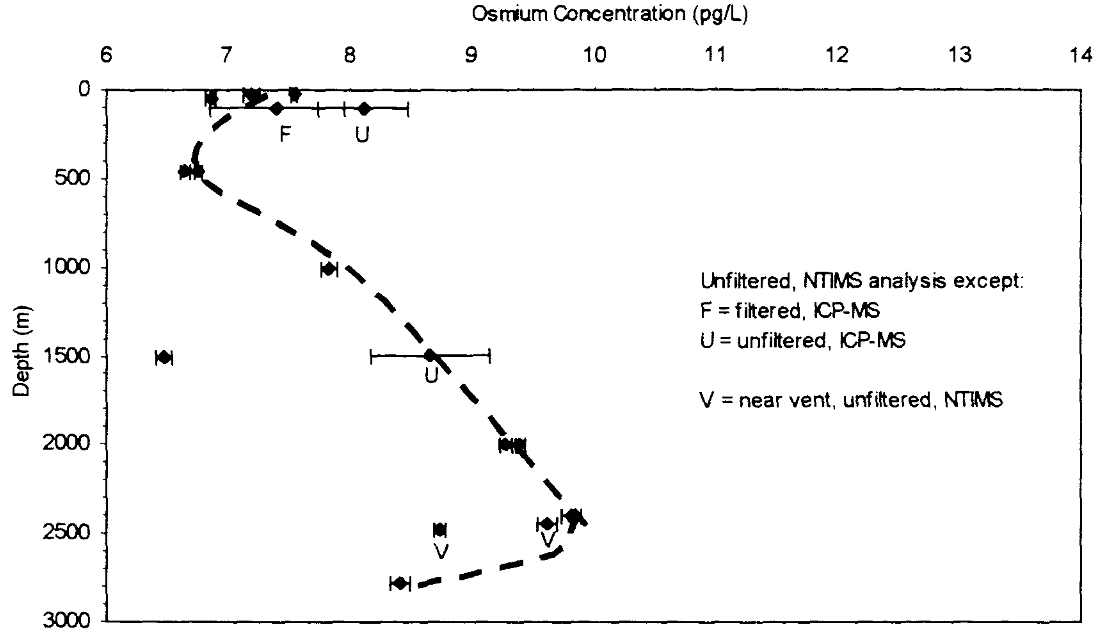


Figure 5.5. Indian Ocean- Osmium Concentration Vertical Profile (Levasseur et al., 1998)

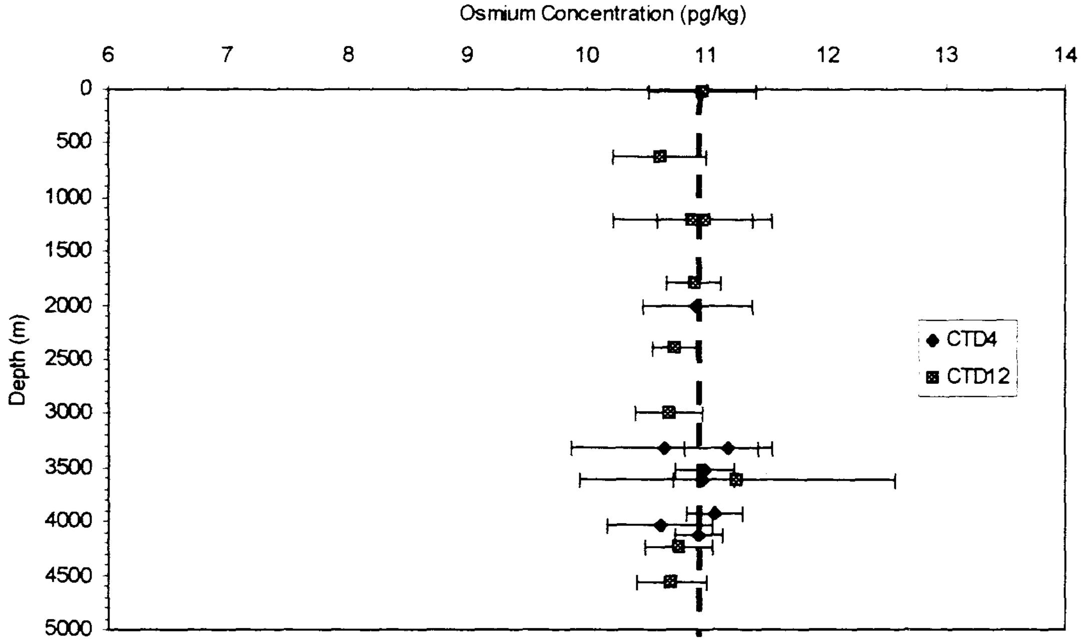


Figure 5.6. Pacific Ocean- $^{187}Os/^{186}Os$ Vertical Profile (this study)

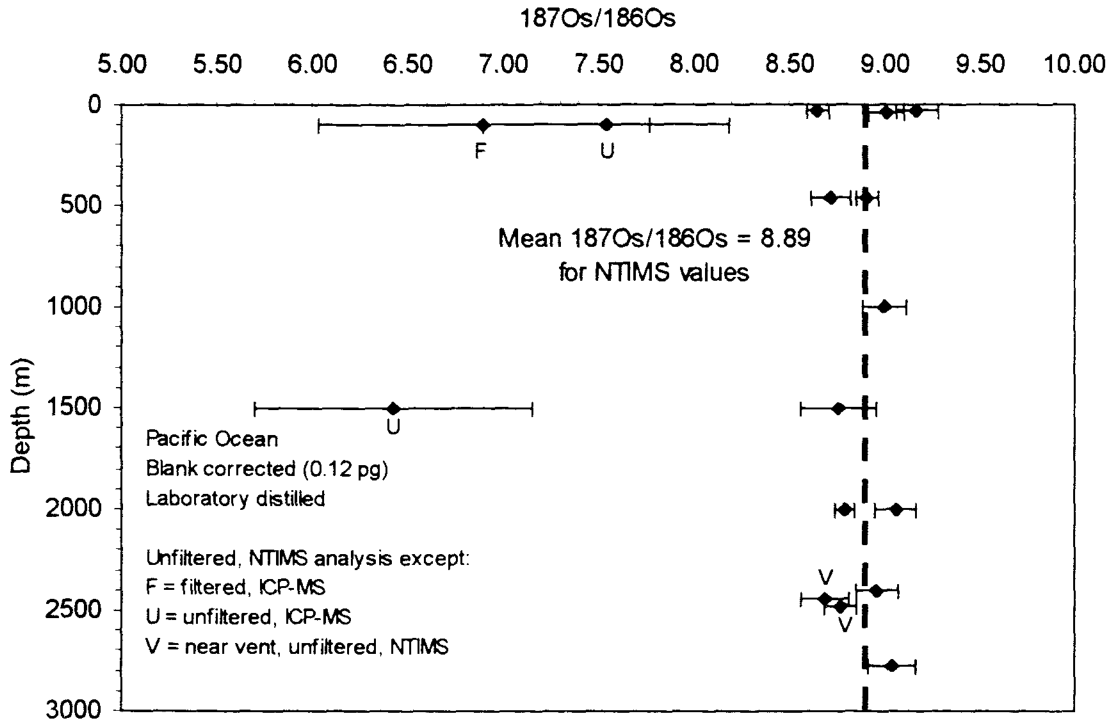
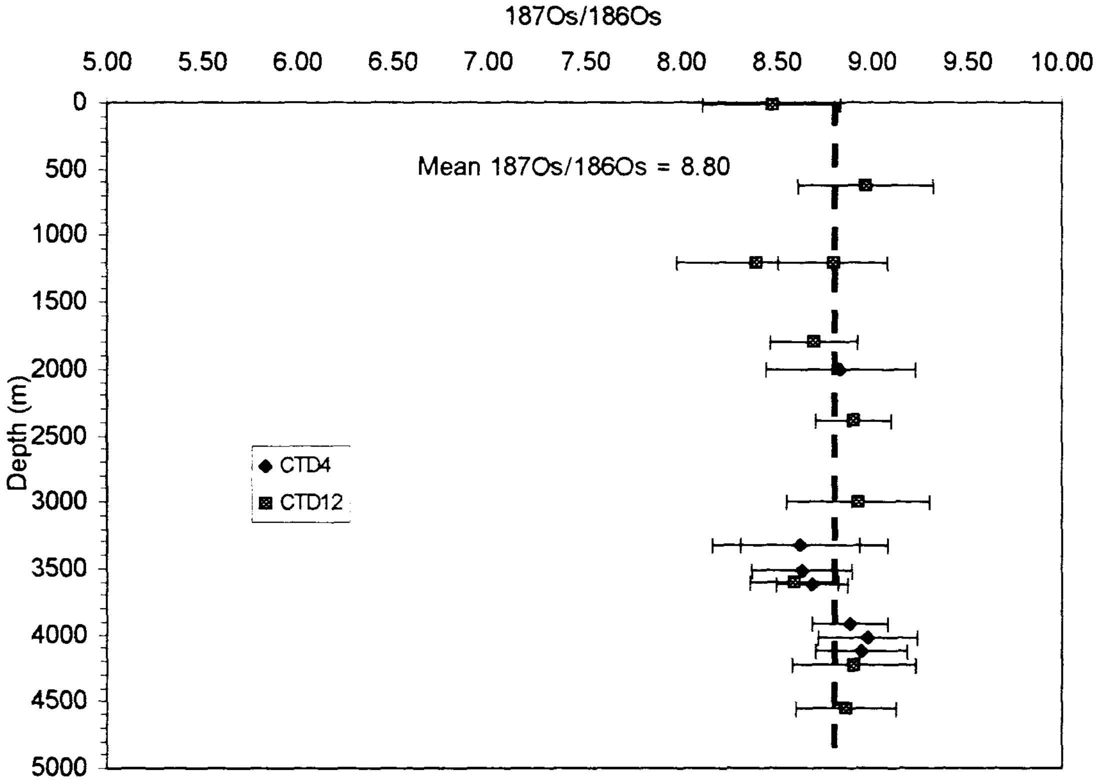


Figure 5.7. Indian Ocean- $^{187}Os/^{186}Os$ Vertical Profile (Levasseur et al., 1998)



5.6 The Osmium Concentration / Dissolved Oxygen Correlation and the Minimum at ~500 m Depth

The Os concentration vertical profiles from the eastern Pacific Ocean show elevated concentrations are found in surface waters, a small but distinct minimum is observed at around 500 m and the concentration increases with depth below this. The Os minimum coincides with a minimum of both dissolved oxygen and light transmission at around 500 m, as measured by the CTD (see Figures 5.8. and 5.9. for the CTD vertical profiles). A separate dissolved oxygen profile (Figure 5.10.), obtained at a station nearby for the WOCE Hydrographic Programme (Station 167 at 9.5°N, 110°W along P18 conducted in 1994), shows the same shape as the profile obtained in this study with suboxic conditions at 500 m (WOCE, 1994). Levasseur et al. (1998) collected seawater samples for Os analysis, from two different sites in the Indian Ocean (34°11'S, 55°37'W and 27°52'S, 63°51'W), but did not make dissolved oxygen measurements. Figure 5.11. shows a dissolved oxygen vertical profile from Geosecs station 37°45 S, 57°37 E, which is very close to one of the Indian Ocean sampling sites. There are no suboxic zones in the water column in this region of the Indian Ocean.

The shape of the Os concentration vertical profiles is very similar to that of the dissolved oxygen vertical profile. The validity of the Os concentration profile is supported by the fact the two vertical profiles show the same structure. Duplicate seawater samples were collected in the suboxic region at around 500 m (from the same depth on different days), distilled in the laboratory and analysed by NTIMS. There is excellent agreement between these two measurements that show the location of the Os-minimum (6.64 pg/L at 462 m and 6.75 pg/L at 459 m; within 1.6% of each other). The three ship-distilled samples that show the Os-minimum in the other profile are all within error of each other.

The correlation between the dissolved oxygen and the Os concentration in the eastern Pacific Ocean (measured in laboratory-distilled samples) is shown in Figure 5.12. The data points for plume and near-sea floor samples have not been included in the graph, as the osmium concentration of these samples may have been altered by factors other than the dissolved oxygen content of the water. The two samples collected from 25 m depth have the highest dissolved oxygen concentration (3.020 mL/L) and clearly fall outside the correlation. It is likely that this is an error introduced by the rapid change in dissolved oxygen with depth in the surface waters. The sample from 1500 m, which did not fit in the concentration profile line, also falls outside the correlation.

Figure 5.8. CTD Oxygen and Light Transmission Profile

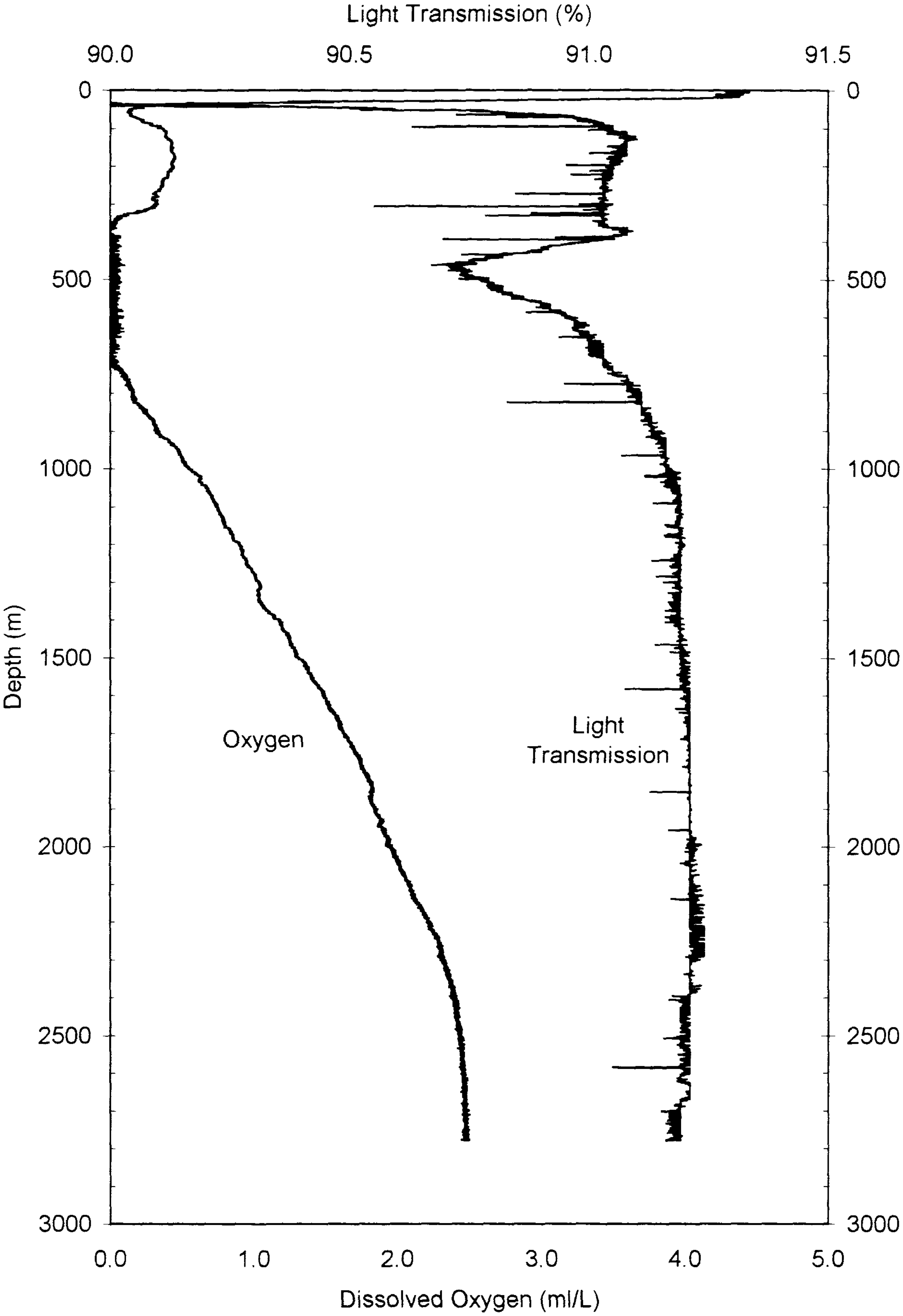


Figure 5.9. CTD Temperature and Salinity Profile

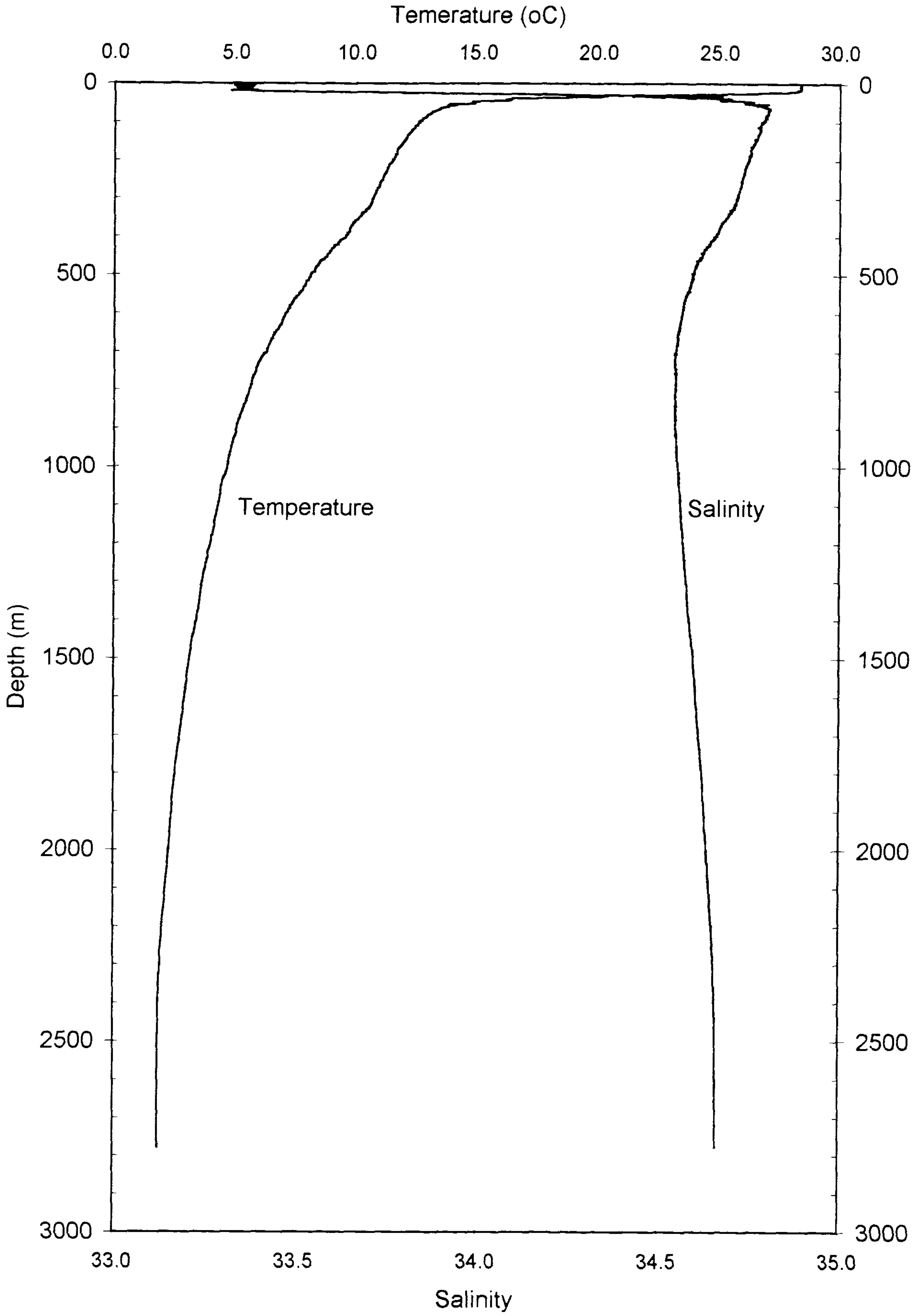


Figure 5.10. Dissolved Oxygen Profile for the eastern Pacific Ocean (WOCE P18 St167 9.5N 110W 1994)

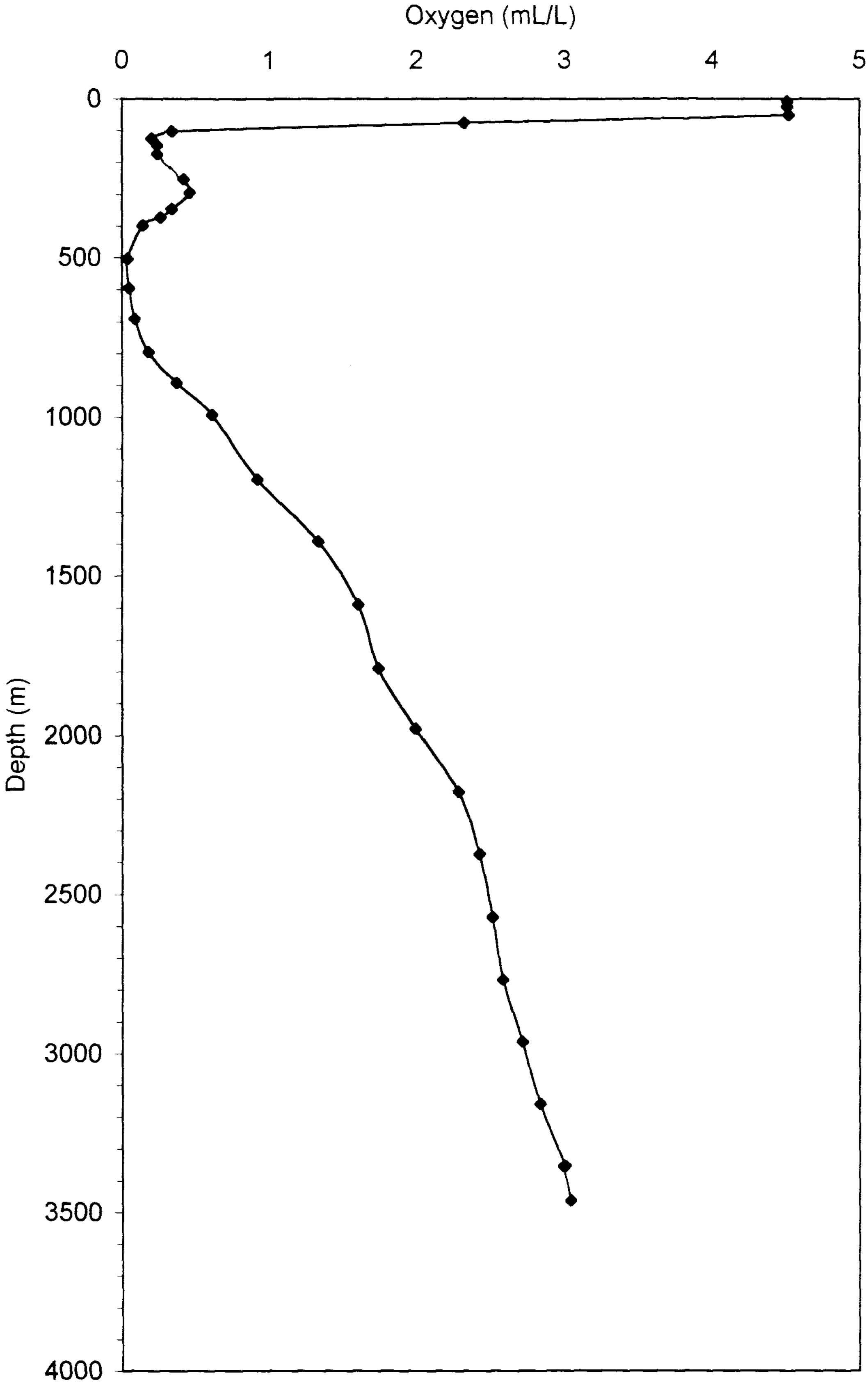


Figure 5.11. Dissolved Oxygen Profile for the southwestern Indian Ocean (Geosecs station 37°45 S, 57°37 E)

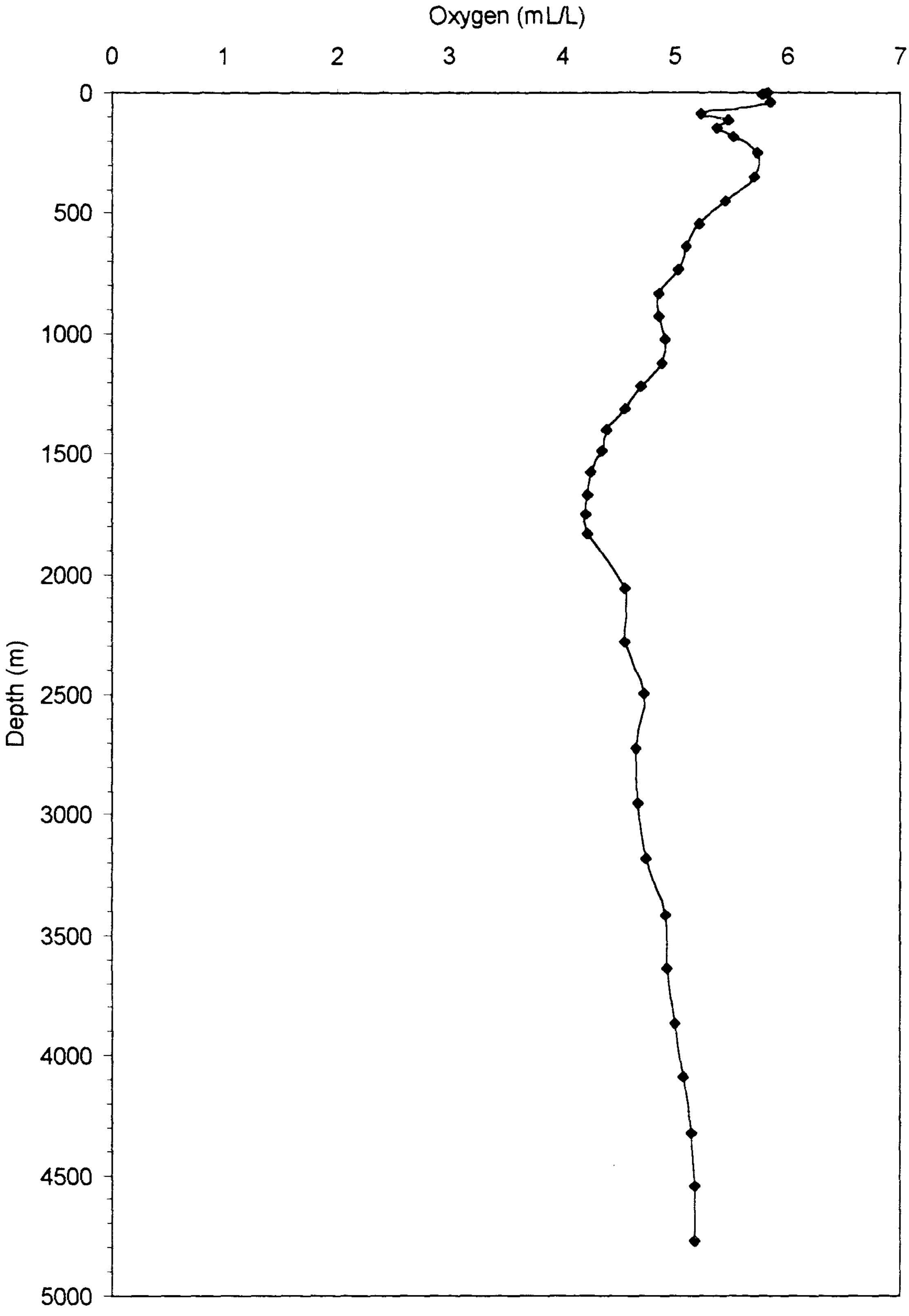
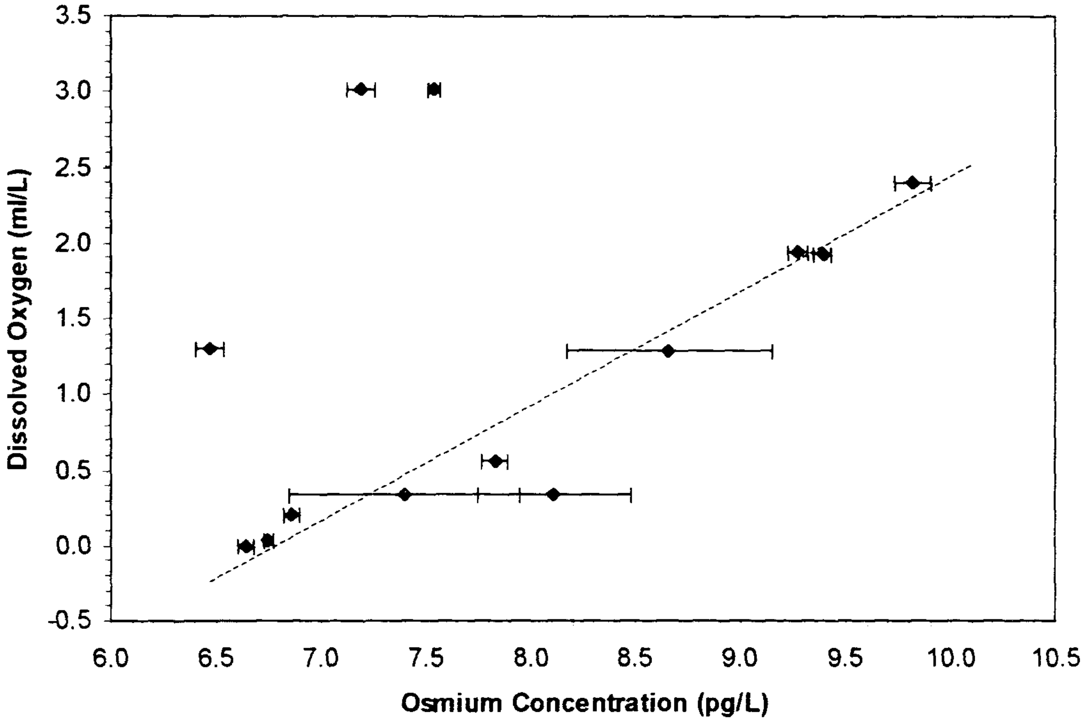


Figure 5.12. Correlation between Dissolved Oxygen and Osmium Concentration observed in the Eastern Pacific Ocean

Sample	Depth (m)	[Os] (pg/L)	^{187}Os/^{186}Os	Dissolved O$_2$ (mL/L)
3-8T	25	7.19	9.17	3.020
3-8G	25	7.54	8.65	3.020
3-7T	44	6.86	9.01	0.205
8-6UG	100	8.11	7.54	0.337
8-6FG	100	7.40	6.90	0.337
12-7G	459	6.75	8.91	0.033
5-6T	462	6.64	8.72	0.000
5-5T	1000	7.83	9.00	0.559
8-4G	1496	8.66	6.43	1.286
3-3T	1500	6.47	8.76	1.307
12-6G	1997	9.27	9.06	1.938
5-4T	1998	9.39	8.79	1.928
3-4T	2401	9.82	8.96	2.403
15-7G	2440 plume	9.62	8.69	2.414
22-5UG	2480 plume	8.74	8.77	2.420
12-4G	2778 seafloor	8.41	9.04	2.473



5.7 Hypotheses to Explain the Osmium Concentration Vertical Profile

5.7.1 Introduction

There are several hypotheses that could explain the shape of the Os concentration profile and the differences to the Indian Ocean data. The first is that the variation with depth is reflecting a sampling or analytical effect, rather than the actual Os concentration. The second hypothesis is that the variation in Os concentration with depth is due to the chemical and biological activity of the element and vertical transport. This would show that Os is a non-conservative element, which is the case for most of the minor and trace constituents of seawater. The third hypothesis is that horizontal currents of water exist in the water column and the variation with depth is explained by mixing of water masses that have different Os concentrations. The vertical profile could also be a result of a combination of the above processes. Each hypothesis is discussed below.

5.7.2 Data Reliability

The reliability of the data must be examined before any conclusions about the marine geochemistry of Os can be drawn from the results. It must be shown that the profiles represent the actual variation in concentration with depth and that this variation has not been introduced by the analytical procedure.

There are a number of arguments that show that the data is reliable. Firstly, the vertical profiles consist of many data points (fourteen seawater samples for the laboratory distillation profile). A relatively smooth best-fit line can be drawn that passes through the majority of the points. One measurement at 1500 m is clearly outside of this line. A different sample collected from the same depth was analysed and this new measurement plots well along the best-fit line.

Seawater samples from both 460 and 1998 m depth were collected in duplicate (from the same depth on different days), and then distilled and analysed separately. There is good agreement in both duplicate measurements (1.6% and 1.3% difference in the measured Os concentration, respectively). There is also good agreement when a sample (from 25 m) from the same Niskin bottle was split and stored in both glass and Teflon bottles, and then distilled and analysed separately (4.6% difference in the measured concentrations). It is very improbable that such good agreement between replicates would have been measured, if spike-sample equilibration had not occurred during the distillation.

The Os concentration of laboratory-distilled samples was measured using two types of mass spectrometers (NTIMS and ICP-MS) and the results plotted on the same graph. The Os concentrations of three samples analysed by ICP-MS fit relatively well on the NTIMS best-fit line. Samples analysed by NTIMS have small error bars due to the high precision of this instrument for Os analysis, increasing the confidence with which a best-fit line can be drawn. Samples were collected, prepared and analysed in a random order. This negates the possibility that the variation of concentration observed was due to a build up of Os contamination or drift in the instrument as successive samples were analysed. A low and constant Os blank value of 0.12 pg was measured for the whole analytical technique for laboratory-distilled samples, which reduces the possibility that error was introduced through blank-correction of the data.

It is unclear why the first Os concentration measurement at 1500 m (6.47 pg/L) was significantly lower than the second measurement at the same depth (8.66 pg/L). The second measurement plots well along the best-fit line of the vertical profile. The collection depth for each sample was recorded by the CTD and it was not verified by a second method. It is possible that during the collection of the first sample, the Niskin bottle did not close, or only partially closed, at 1500 m and that the sample was actually collected from a different depth. The Os concentration for that sample (6.47 pg/L) is close to the measurements made for two samples collected at around 460 m (6.64 pg/L and 6.75 pg/L) and so it is possible that the collection bottle actually closed at 460 m. It is also possible that a leak in the apparatus during the distillation caused the sample Os to be lost preferentially to the spike Os (as sample and spike Os are not necessarily distilled at precisely the same time) or that an error was made in the transfer of the ^{190}Os spike solution to the seawater.

5.7.3 Particle Adsorption Hypothesis

One hypothesis is that the chemical and biological activity of Os causes the variation in concentration through the water column. The shape of the Os concentration vertical profile is very similar to that of the dissolved oxygen vertical profile. Both profiles show a minimum at around 500 m and then an increase with depth below this. A separate dissolved oxygen profile also collected in the eastern Pacific Ocean (Figure 5.10.) confirms the same shape of the profile and the suboxic conditions at 500 m. Figure 5.12. shows a tight correlation between dissolved oxygen and Os concentration.

It is possible that the concentration of dissolved oxygen in the seawater directly affects the biogeochemical activity, and thus the Os concentration, of that seawater. For example, it is possible that the variation in the level of dissolved oxygen changes the speciation, and even the oxidation state, of the Os. The speciation of Os in seawater has never been measured. An oxidation reaction for the enrichment of Os in ferromanganese minerals has been suggested (Koide et al., 1991) and this provides evidence that at least some of the dissolved seawater Os must be in an oxidizable state (i.e. all of the Os cannot be in the +8 oxidation state as this is the highest oxidation state for Os). It is proposed that at medium to high dissolved oxygen concentrations, Os exists in a non-particle reactive, fully oxidised form (possibly in the +8 oxidation state). The majority of the Os is therefore in the dissolved phase. In suboxic conditions, more of the Os is in a particle reactive, reduced form (the results do not give an indication as to the oxidation state of this species). This results in Os being removed from a suboxic section of the water column as the particles sink through the water, effectively an Os sink at 500 m. Osmium is then released back into the dissolved phase as the particles sink to waters with higher dissolved oxygen concentrations. This would explain the increase in Os concentration down the water column as the dissolved oxygen concentration increases. If the Os is adsorbed onto the particles by physical adsorption (through Van der Waals bonds for example) rather than chemical adsorption, the kinetics of the adsorption and desorption would be rapid enough to account for the observed variation in Os concentration through the water column.

A comparison between filtered and unfiltered seawater was made in the osmium/oxygen minimum at 460 m. The analysis showed that there was very little difference between the Os concentration of filtered and unfiltered seawater, suggesting that little of the Os is in the particulate phase. It is still possible however, that the particles are acting as an Os sink at this depth. If the rate of sinking is high enough, a small amount of Os attached to many particles may efficiently remove Os from that depth. It has been shown that even though Mn is only very weakly associated with particles, the amounts of Mn involved with sinking biogenic particles is high (Martin and Knauer, 1984). The efficiency with which Os is extracted from particulate matter was not tested in the radiotracer experiments. It is possible that Os is in fact adsorbed onto the particles, but that the distillation is not extracting that Os.

5.7.4 Advection Hypothesis

A different hypothesis is that Os is actually a conservative element in the oceanic water column, and that the structure of the vertical profile is produced by the mixing of water masses that have different Os concentrations. The Os concentration minimum observed is thus caused by a water mass of low Os concentration, advected along the isopycnal at around 500 m, mixing with water of a higher Os concentration above and below it (Figure 5.13.).

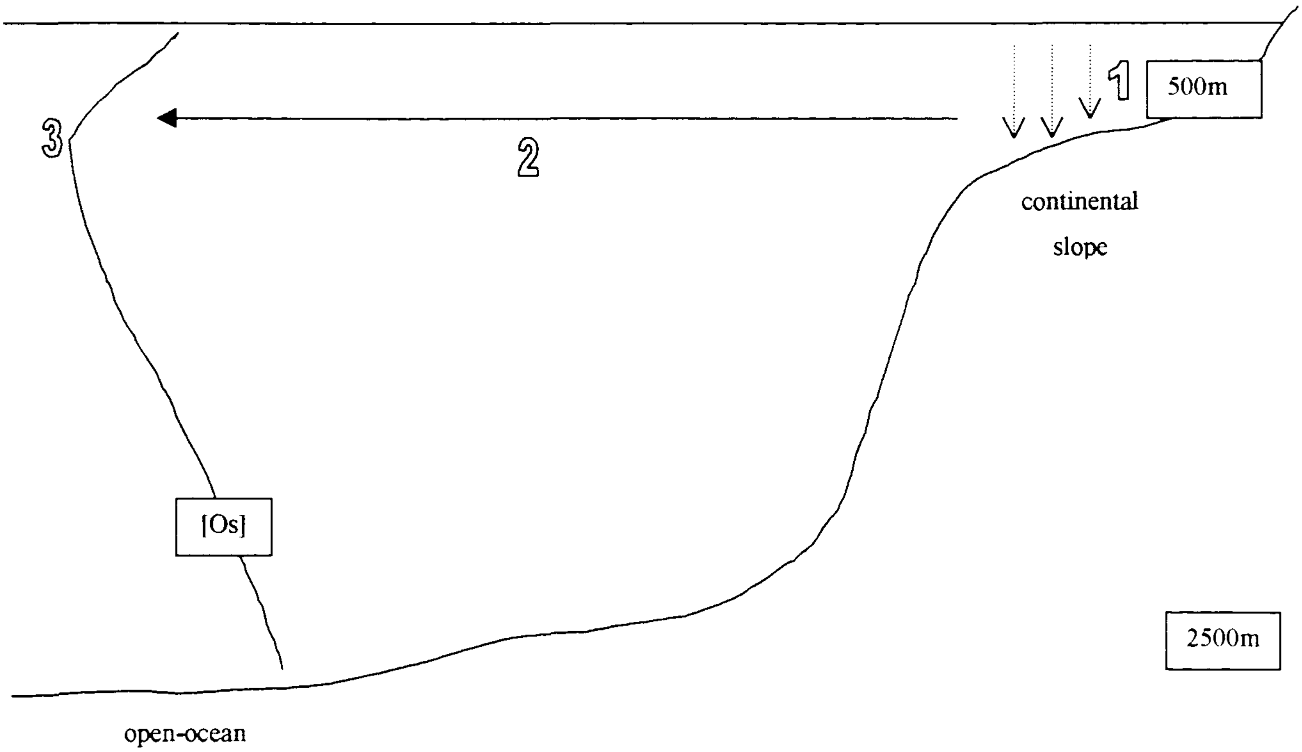


Figure 5.13. Advection Hypothesis

1. High productivity on the continental shelf creates suboxic waters and reducing conditions, and thus there is enhanced removal of Os to high organic carbon concentration sediments. A water mass of low Os concentration is formed.
2. The water mass is advected (west at 500 m depth) along the isopycnal. Mixing occurs with open-ocean seawater that has a higher Os concentration.
3. The resulting vertical profile has an Os concentration minimum at 500m.

It is thought that the water mass originates from the continental slope region along the coast of Central America (Reid, 1997). Upwelling and high productivity occurs in this area. The high productivity produces anoxic or suboxic waters and reducing sediment conditions associated with the high carbon flux to the sediment. Anoxic conditions are known to enhance the removal of dissolved Os to underlying sediments (Ravizza, 1995; Ravizza et al., 1991). Anoxic coastal sediments off Peru and in the Baltic Sea form under highly reducing conditions and have high organic contents (Koide et al., 1991). It is proposed that the removal of Os from the dissolved phase to the sediment will create a water mass with low Os concentration along the coast of the East Pacific. This water mass will travel west at a depth of around 500 m along the isopycnal, forming a tongue of suboxic, osmium-depleted water extending west from the continental slope. The water mass will mix with open-ocean seawater that has higher Os and dissolved oxygen concentrations. The mixing of these two water masses will create both the Os and dissolved oxygen vertical profiles that have been measured.

A fall in the light transmission was measured at 460 m depth on every cast performed during the cruise. It is thought that particulate matter, originating from the continental shelf, is being advected with the water mass to the open ocean.

5.7.5 Other Trace Elements

A similar phenomenon has been observed in the eastern Pacific Ocean with dissolved Mn in suboxic conditions (Burton and Statham, 1988). A significant increase in the concentration of dissolved Mn was reported in regions of low oxygen concentrations (below 100 μmol/L). A core of water was measured with enhanced concentrations of dissolved Mn (0.5 - 1.4 nmol/L) centred on about 600-700 m, with decreasing concentrations in the offshore direction. Two processes, similar to the ones used to explain the Os minimum above, were proposed to explain the increase in dissolved Mn in the dissolved oxygen minimum: the diffusion and advection of Mn from the continental slope region, and the release of Mn from particles sinking from the surface waters. For the former process, it was suggested that Mn would diffuse across the sediment-water interface at the continental slope, and that this water was advected and supplied dissolved Mn to the water column. For the process of Mn release from particles, it was proposed that this release was either caused by the dissolution of an oxidized phase under the conditions of lowered pE or by the decomposition of organic material, or a combination of these processes.

The dominant factor influencing the aquatic geochemistries of Mn and Cr is the change of oxidation state of the elements between reducing and oxidizing environments, coupled with the marked difference between the oxidation states in terms of their forms and reactivity (Burton and Statham, 1988). Manganese and chromium form a contrasting pair with opposite tendencies (Murray et al., 1983). Under oxidizing conditions Mn (IV) is scavenged as MnO_2 while Cr (VI) is soluble as CrO_4^{2-}. Under reducing conditions Mn (II) is soluble as Mn^{2+} while Cr (III) is removed as $Cr(OH)_3$.

Combined water column and particle trap data clearly indicate that Mn is released from particles as they sink through the oxygen minimum (Martin and Knauer, 1984). Mass-balance calculations indicated that in the suboxic region, the net release from particles was inadequate to sustain the observed concentrations of dissolved Mn and that it was necessary to invoke a balancing flux due to horizontal diffusion and advection. The data showed that only 30% of the dissolved Mn in the oxygen minimum was from sinking particulate regeneration, and that the other 70% probably resulted from continental slope release and horizontal transport processes. It was also shown that Mn is only very weakly associated with particles, but that nevertheless, the amounts of Mn involved with sinking biogenic particles is high. This gives evidence to the fact that the adsorption of Os onto particles may create an effective sink at the oxygen minimum, even if Os is not highly particle reactive.

Additional evidence indicating the importance of advective processes is provided by other trace element data (Martin et al., 1983). Dissolved Ag and Cu concentration minima were found in waters of maximum Mn concentration. Because no evidence of in-situ Ag and Cu removal was found with particle trap flux data, it was proposed that these were removed in continental slope sediments via sulfide precipitation, and that these waters were advected horizontally to the study area 400 km offshore.

A depth profile of the concentration of Re in the Pacific Ocean (22°N, 158°W) (Anbar et al., 1992) has been obtained using isotope dilution negative thermal ionisation mass spectrometry (ID-NTIMS). A narrow range for Re concentration (7.20 – 7.38 ng/kg) for depths between 45 and 4700 m, demonstrates that Re is relatively well mixed throughout the water column and is a conservative element. A minor level of Re scavenging in near surface waters and an input of Re to the ocean surface are observed.

Both Re and Mo behave conservatively in seawater yet are strongly enriched in reducing sediments (Crusius et al., 1996). The absence of Re and Mo enrichments in sediment trap samples from sulfide-bearing basins, suggests the metals are removed from the seawater to the sediments at or below the sediment-water interface. The results in this thesis suggest that both the adsorption of Os onto particles sinking to the sea floor, and the removal of dissolved Os at the seawater-sediment boundary, contribute to the flux of Os from seawater to the sediments.

5.8 Filtered/Unfiltered Sample Comparison

A comparison between filtered and unfiltered samples was made with two seawater and two vent-influenced samples. In the four comparisons, the filtered and unfiltered samples were collected from the same Niskin bottle. The data suggests that the majority of the Os in both seawater and vent-influenced samples is in the dissolved phase. In all four comparisons, the concentration obtained from the unfiltered sample was slightly higher than the concentration from the filtered sample. At 100 m depth, 91% of Os is in the dissolved phase and this increases to 95% at 460 m. The vent-influenced samples show that between 96% and 98% of vent sample Os is in the dissolved phase. This data is however not as reliable as the vertical profile data, as all eight samples were analysed by the less sensitive ICP-MS, resulting in larger error bars (shown in Figure 5.2.).

The radiotracer experiments did not examine how efficiently Os is extracted from particles during the distillation. It is also possible that the method is simply not separating any Os found on the particles, which would explain the similarity between the Os concentration measured in filtered and unfiltered samples. However, the particle adsorption hypothesis used to explain the vertical profile suggests rapid equilibration between dissolved and adsorbed Os, and it is thus unlikely that the distillation is unable to remove the Os from the particles.

5.9 Samples Influenced by the Hydrothermal Vents

A total of eight samples collected from close to the hydrothermal vents were analysed. Two of the samples were prepared in the clean laboratory and analysed by NTIMS, while the other six were prepared on the ship and analysed by ICP-MS. Osmium concentrations in the vent-influenced samples (8.86 and 9.74 pg/L at 2480 m and 2440 m respectively; collected on different days) are actually lower than concentrations of open-ocean deep-seawater samples (9.82 pg/L at 2401 m). This suggests that Os may be scavenged from seawater by hydrothermal vent plumes.

The results show that either hydrothermal vent fluid is not highly enriched in Os relative to seawater, or that the Os is quickly diluted or removed from the vent fluid. The samples were collected when a decrease in the light transmission in the water column was noted, and not directly at the black smoker vent, so the vent fluid will have been diluted with the surrounding seawater before it is collected. If hydrothermal vent fluid is enriched in Os relative to seawater, it is possible that the higher concentration has been diluted to background before collection. Sampling directly inside the black smoker vent, with a titanium sampler for example, could produce a better measurement of the Os concentration of vent fluid.

An isotopic composition (^{187}Os/^{186}Os = 6.9 ± 0.4) distinctly lower than that of deep-seawater has been measured in a sample of ambient seawater collected around the Juan de Fuca Ridge (Sharma et al., 1997). The measured Os concentrations for this sample (2.6 and 2.9 pg/L for the same sample) were slightly lower than the concentrations of the deep seawater samples (2.8 – 3.6 pg/L). It was suggested that these results may be reflecting local hydrothermal activity, or alternatively some analytical difficulty with the sample. The reduced Os concentrations measured in these samples support the idea that Os may be scavenged from seawater by hydrothermal vent plumes. Samples collected along the Southwest Indian Ridge (Levasseur et al., 1998) show no difference in either the measured ^{187}Os/^{186}Os ratio or Os concentration when compared to deep seawater. Ridge-crest sediments have been analysed and were found to be enriched in Os (Ravizza et al., 1996). This suggests that mid ocean ridges may actually be a sink of Os rather than a source.

5.10 Near Sea Floor Sample

One sample in the vertical profile was collected from a depth of 2778 m, only 30 m above the sea floor. This was performed using a pinger attached to the rosette and CTD package. The Os concentration in this sample is significantly lower (8.41 pg/L) than other deep-sea samples (a sample collected from 2401 m was measured to have an Os concentration of 9.82 pg/L). The ^{187}Os/^{186}Os ratio for this sample is 9.0, which is within error of the mean (8.89 ± 0.09 (2σ)) measured throughout the water column.

As only this one sample was collected and analysed from sea floor, caution must be taken against drawing too many conclusions from the result, as it may simply be an outlier. However, if this data point is correct, it is showing that the Os concentration of seawater at the sea floor is less than that of deep seawater. This could be explained by a flux of Os from the seawater to the sediment at their interface on the ocean floor.

5.11 Calculating Osmium Oceanic Residence Time

5.11.1 Introduction

If the size of a particular reservoir in the ocean remains constant over time, the combined input rate must equal the combined output rate. This condition is referred to as a steady-state. The average amount of time a substance spends in a particular reservoir before it is removed through some transport process(es) is called its residence time (τ). For example, the oceanic residence time of an element is given by the amount of element in the ocean, divided by the total input or output of that element to the ocean. This mass balance approach to calculating the oceanic residence time is only valid if the modern oceans are in steady-state. There is evidence to suggest that the oceans are not currently at steady-state, based on an increase in the Os isotopic composition of seawater over the past 10,000 years (Oxburgh, 1998).

The seawater Os concentration data from the eastern Pacific Ocean may be used to calculate an oceanic residence time for Os. The deep-ocean Os concentrations are similar to those measured by Levasseur et al. (1998) in the Indian Ocean, indicating that there now exists accurate values for the Os concentration of seawater and hence, for the total mass of Os in the ocean. The total volume of the oceans (including adjacent seas) is 1.37×10^9 km^3 or 1.37×10^{21} L (Libes, 1992). It may be assumed that the deep-sea Os concentration (9.8 pg/L at 2401 m depth) is a representative value for the ocean, as the concentrations for depths above this have been reduced, either because of advection and mixing of different water masses or because of adsorption onto sinking particles. It is assumed that reduced Os concentrations caused by suboxic conditions, do not make a significant difference to the total mass of Os in the ocean. The total mass of Os in seawater in the ocean is thus 13,400 tons (1.34×10^{10} g). There is still uncertainty in the input and output fluxes of Os to the ocean, and this creates uncertainties in any residence times that are calculated by the mass balance approach.

5.11.2 From Extraterrestrial Material Input

The total input flux of Os to the ocean may be determined from the input flux of Os from extraterrestrial material. Preliminary calculations of the Os ocean budget suggest that ~80% of Os is derived from the continents and the rest (~20%) from extraterrestrial and hydrothermal sources (Pegram et al., 1994). It must be noted that this budget calculation assumes that the average Os input from the continental sources has a ^{187}Os/^{186}Os ratio of

10.5 (Esser and Turekian, 1993b). The hydrothermal vent data in this thesis suggest that hydrothermal vents are not significant source of Os to the ocean, as the Os concentration and isotopic composition values are similar to the non-plume deep-sea values. Thus the Os extraterrestrial input represents ~20 % of the total Os input to the ocean.

The extraterrestrial input is thus only a minor component of the total Os input and the value must be multiplied by five in order to obtain the total Os input to the ocean. This value of ~20 % for the extraterrestrial input component is only an approximate calculation, and also the amount of extraterrestrial material that dissolves into the seawater is not well understood. These lead to inaccuracies in the calculation of the Os residence time from the extraterrestrial input and so in the following section, the total Os input flux to the ocean is determined using the riverine Os input flux, which is a major component.

5.11.3 From Riverine Input

Some 3.75 x 10^{16} kg of water are supplied annually to the oceans by rivers (Brown et al., 1989). The mean Os concentration of river water is assumed to be similar to that of the Mississippi River at 8.6 pg/L (45.1 ± 0.8 fM/kg was given as the most reliable value of the concentration of Os in river water) (Sharma and Wasserburg, 1997), which is very close to the value of 8.2 pg/L obtained by Levasseur et al. (pers. comm., 1998). This produces a mean flux of Os to the oceans from rivers of 3.23 x 10^{17} pg/yr (323 kg/yr). Preliminary calculations suggest that ~80% of Os is derived from the continents (Pegram et al., 1994) and so the total Os input to the ocean is 403 kg/yr. If the total mass of Os in seawater in the ocean is 13,400 tons (1.34 x 10^{7} kg) as calculated above, then the Os oceanic residence time is ~33,000 years. It must be noted that there is still uncertainty in the Os concentration of river water and this creates uncertainty in the subsequent residence time calculation.

5.11.4 Conclusions

The calculation for the Os oceanic residence time of ~33,000 years is long compared to the average oceanic mixing time of 500 to 1000 years (Brown et al., 1989). This suggests that Os should be uniformly distributed throughout the oceans and that perturbations due to a sudden input of Os to the ocean (for example a meteoritic impact or large volcanic eruption) will take a substantial time to damp out.

The value of ~33,000 years compares well with previous determinations in the literature calculated by mass balance approach. The Os concentration data of seawater samples collected from the Southwest Indian Ocean have recently been used, along with preliminary river water Os concentration data (research conducted independently from Sharma and Wasserburg; mean Os concentration from Amazon, Changjiang, Mekong, St Lawrence, MacKenzie and Niger Rivers = 8.2 pg/kg), to estimate an Os ocean residence time of 42,000 years (Levasseur et al., pers. comm., 1998). A calculation of the Os residence time based on results from the direct analysis of seawater, the Os/Ir ratio of seawater ($\approx$22) and the Os/Ir ratio of continental rocks ($\approx$1), and presuming chemically analogous behaviour of Os to Ir, gives a lower limit of about 44,000 years (Sharma et al., 1997).

A value for the Os oceanic residence time of less than 12,000 years has been obtained from a box model, designed to stimulate the response of the oceans to an input flux that occurred at the onset of the Holocene (Oxburgh, 1998). This value does not rely on an accurate value for the concentration of Os in seawater and opposes the theory that the ocean is at steady-state. It does however rely on other assumptions, including that the residence time of Os does not change significantly over the interval of interest (i.e. the ratio of input flux to seawater Os concentration does not vary greatly). The value provides an average glacial-interglacial estimate value that infers a much shorter residence time in the glacial to give this averaged short residence time. Differences in the Os isotopic composition of Mn crust has be measured between different ocean basins (Burton et al., 1996), which indicate a short residence time. There is still a wide range in values for the Os oceanic residence time in the literature and more research is needed.

5.12 Implications of the Pacific Data for the Speciation of Osmium in Seawater

The conclusions from pE-pH diagrams (Palmer et al., 1988) and past results from the direct analysis of seawater Os (Koide et al., 1996; Levasseur et al., 1998; Sharma et al., 1997) have not conclusively resolved the question of the speciation of Os in seawater. The radiotracer experiments and the Pacific Ocean seawater results in this thesis, provide new evidence on the subject.

Osmium exhibits a complex marine chemistry and may exist in more than one oxidation state in seawater (Koide et al., 1991). One of the hypotheses used to explain the shape of the Os concentration vertical profile from the Pacific Ocean, is the in-situ adsorption of Os onto fast sinking particles. The Os concentration minimum at 500 m coincides with a suboxic region in the water column. The suboxic conditions may be forcing the Os to change oxidation state. At medium to high dissolved oxygen concentrations, Os may exist in a non-particle reactive, oxidised form (possibly in the +8 oxidation state) and therefore, the majority of the Os is in the dissolved phase. In suboxic conditions the Os, or at least a certain fraction of the Os, is reduced and made particle reactive. The Os is then adsorbed onto fast sinking particles, and there is effectively a sink of Os in this section of the water column. This behaviour is analogous in some respects to the aquatic geochemistries of Mn and Cr (discussed in section 5.3.5).

If this hypothesis is correct, it shows that Os must exist in seawater as a species that can be readily reduced by suboxic conditions. The mechanism for the adsorption of Os onto particles is not understood. In the hypothesis above, the speciation of the oxidised and reduced forms of Os may be similar (both as oxyanions for example) or different (an oxyanion and an organic complex). In either case, the hypothesis requires that the forms behave differently towards particles in the seawater.

Research conducted on modern marine carbonates (Oxburgh, 1996) confirms the theory that osmium may exist in several oxidation states and chemical species in seawater. The isotopic compositions of these carbonates were generally less radiogenic and showed more variation than osmium-rich sediments (Ravizza, 1991). This indicates that the carbonates tap into a reservoir of Os that is less radiogenic that the oceanic mean. It was suggested that cosmic material dissolves in the ocean surface waters. This releases Os into the ocean that is of different oxidation state and chemical speciation from mean oceanic Os. This Os is kinetically stable and is readily scavenged by sinking biogenic material, before it can equilibrate with the oceanic conditions. However, this hypothesis relies on a long equilibration time (approx. 50 years) between the different forms of Os. The particle adsorption in this thesis suggests a rapid equilibration for the Os redox reactions.

The fact that Os may exist in more than one oxidation state in seawater creates a potential problem for its analysis. A particular technique used for the separation of Os from seawater may only isolate the Os that is present in a particular oxidation state or as a particular species. If Os exists in a species that is extremely resistant, for example Os locked up in highly refractive organic material, the technique may not separate all the osmium from the seawater. The radiotracer experiments show that the distillation used in this study will separate from a seawater matrix, Os that is present as both the oxyanion and the hexabromate, with equal and near-quantitative yields. The Os separation method used in this study, and the one employed in an Indian Ocean study (Levasseur et al., 1998), involve the oxidation of Os to OsO_4 as the first step. The two techniques produce comparable values for deep-water Os concentrations. It must be noted that it has not been determined whether these oxidation techniques separate every species of Os present in seawater. Levasseur et al. (1998) have suggested that the analytical procedure used to study Indian Ocean samples, is able to oxidize scavenged metals and destroy oceanic organic matter.

The analysis of Atlantic and Pacific seawater using a very different technique (Sharma et al., 1997) produced Os concentrations that were 2-4 times less than those measured with the two oxidation techniques (this thesis and Levasseur et al. (1998)). The first step of the Sharma et al. (1997) method involved adding $FeCl_3$ to the seawater, reducing the seawater using SO_2 gas and then initiating an iron hydroxide precipitation using NH_3 gas. Based on the homogeneity of the $^{187}Os/^{186}Os$ ratio, it appears that Os is reasonably well mixed in the oceans. The differences in Os concentration and vertical profile, measured in the eastern Pacific Ocean (this thesis) and in the Indian Ocean (Levasseur et al. (1998)), is attributed to the difference in dissolved oxygen concentration, rather than a difference between the ocean basins. It is thought that the discrepancy in the measured Os concentration between this thesis (and Levasseur et al. (1998)) and Sharma et al. (1997) does not represent a real difference in Os concentrations between the oceans, but rather a difference in the analytical method employed. The method of reduction and precipitation may only separate Os that is present in a particular species or oxidation state, and therefore only a fraction of the Os present in the seawater, explaining the discrepancy of the Os concentration values. Also, the samples were collected and stored in polyethylene bottles and these were shown in the radiotracer experiments to adsorb Os from solution. This loss of Os to the storage bottle may also be responsible for the difference in measured concentration.

The suboxic conditions at around 500 m in the eastern Pacific Ocean appear to be responsible for a 30% decrease in Os concentration at this depth, compared to deep-seawater. If the particle adsorption hypothesis is correct, it is possible that as particles sink into this suboxic zone, they only adsorb Os which is in a particular oxidation state or species (30% of the total Os) and that the remainder (70%) is left in solution. Osmium may be exist in more than one oxidation state throughout the water column, and may only be particle reactive under suboxic conditions that cause a change in its oxidation state or speciation.

5.13 Future Work

One of the hypotheses for the Os concentration minimum at 500 m in the open-ocean water column, is that a water mass of low Os concentration is created at the continental slope by the removal of dissolved Os to organic-rich sediments. This water mass is then advected and mixes with the open-ocean water. This hypothesis should be investigated further by collecting and analysing seawater from the continental shelf of the eastern Pacific Ocean. If the hypothesis is correct, a lower Os concentration will be measured in these samples than is found in open-ocean seawater, as the Os will have been removed to the sediments. Sediments could also be collected from the eastern Pacific continental shelf and analysed to determine whether they have been highly enriched in Os.

The process by which Os is removed from seawater to organic rich sediments under reducing conditions is unknown. The results of this study suggest that both the adsorption of Os onto particles sinking to the sea floor (as shown by the Os concentration minimum in the suboxic region), and the removal of dissolved Os at the seawater-sediment boundary (as shown by the low Os concentration measured in the seawater collected from 30 m above the sea floor), could contribute to the flux of Os from seawater to the sediments. This should be further evaluated by collecting sediment trap samples at the continental shelf of the eastern Pacific Ocean, at several depths through the water column, and analysing for Os. An increasing Os concentration down through the water column in the suboxic zone, would show that Os is being adsorbed onto the sinking particles from the seawater. The rate of flux of sinking particles, as well as their Os concentration, should be determined to calculate the rate of removal of Os from the dissolved phase. If zero concentrations of Os were measured on the sediment trap material, this would suggest that the major process for the removal of the metal to the sediments occurs at the water-sediment boundary.

The second hypothesis for the Os concentration minimum, is the in-situ adsorption of Os onto fast sinking particles in the suboxic section of the water column. It is suggested that the adsorbed Os is then dissolved back into the seawater as the particles sink to oxic waters. This hypothesis could be investigated by collecting sediment trap samples in the open eastern Pacific Ocean. Sediment trap samples collected in the suboxic region should have a much higher Os concentration that the samples collected in the oxic regions. The sediment trap samples could then be prepared using a method that is known to separate the

Os (NiS fire assay for example), rather than a seawater distillation. The efficiency of the distillation at separating Os associated with particles should also be determined.

The comparisons between filtered and unfiltered seawater in this study suggested that little Os is associated with particles. This was true throughout the water column, including in the suboxic region where one of the hypotheses suggest that Os is being adsorbed onto the particles. Combined water column and particle trap data for dissolved Mn in the eastern Pacific Ocean (Burton and Statham, 1988) show that Mn is only very weakly associated with particles, but that nevertheless, the amounts of Mn involved with sinking biogenic particles is high. If the flux of particles falling through the water column is high, even a small amount of element being adsorbed onto the particles will result in a significant sink of that element. The collection of sediment trap samples could show if the flux of falling particles is sufficient to explain the Os minimum.

One sample in this study was collected from a depth of 2778 m, only 30 m above the sea floor. The Os concentration of this sample is significantly lower (14% lower) than that of other deep-sea samples. It suggests that Os is removed from the dissolved phase at the seawater-sediment boundary. There appears to be a flux of Os from the seawater to the sediment, and that the Os concentration of seawater near the sea floor is less than that of deep seawater. Only one sample was collected and analysed from so close to the sea floor. The validity of this result could be verified by collecting and analysing further seawater samples from close to the sea floor. This would provide a valuable insight into the cycling of Os in the ocean, and its removal from seawater.

Seawater collected in the Indian Ocean and analysed using a different method (Levasseur et al., 1998) showed a very similar Os concentration and isotopic composition to that measured in seawater from the eastern Pacific Ocean in this study. While this is very encouraging, a constant Os concentration at all depths was measured in the Indian Ocean, indicating a conservative behaviour for Os. Dissolved oxygen measurements were not made in the Indian Ocean, but it is thought that that there are no suboxic conditions in the water column where these samples were taken, as there are in the eastern Pacific Ocean sampling sites. The Os concentration minimum measured in the Pacific Ocean is thought to be associated with the low oxygen concentration at 500 m depth. Also, only two measurements were made above 1200 m depth in the Indian Ocean, and it is possible any structure in the vertical profile at this depth was missed. The two data sets are therefore compatible with each other. It would useful however to collect seawater from other locations in the Pacific Ocean and other oceans where there are no suboxic regions to verify the arguments in this study.

The method developed in this study to separate, isolate and then measure the Os in seawater could equally be used to measure Os in other environmental samples, including river waters. Due to difficulties in the analysis of the low concentrations of Os in river water, little has been published on the riverine input of Os to the ocean. Results from the analysis of Os in seawater, have recently been used to calculate that ~80% of Os in the deep ocean is derived from the continents and the remainder from extraterrestrial and hydrothermal sources (Sharma et al., 1997). These are very early calculations however and the possibility of measuring Os in river water directly, would help to more accurately determine the total input of Os to the ocean and the contribution from each source. This would greatly advance the understanding of the marine geochemistry and cycling of Os, and a more accurate calculation of the Os oceanic residence time could be made.

High Os concentrations and low ^{187}Os/^{186}Os ratios measured in estuarine sediments, have been used to track sewage sludge discharged into a harbour (Esser and Turekian, 1993a). It is possible that the outflow of a large river into the sea may be examined in a similar way, by analysing the sediments near the river outflow for Os. River water is expected to have high ^{187}Os/^{186}Os ratios due to the radiogenic Os found in continental crust (Peucker-Ehrenbrink and Ravizza, 1996) and possibly high Os concentrations. The ^{187}Os/^{186}Os values for river sediment leaches from the eastern and central U.S., the Ganges River, and the Rio Maipo range from 10.1 to 21.5 (Pegram et al., 1994), suggesting that the ^{187}Os/^{186}Os of the soluble river load delivered from the major continental areas to the oceans is more radiogenic than average currently eroding continental crust (^{187}Os/^{186}Os = 10.5 (Esser and Turekian, 1993b)). This radiogenic osmium may imprint on the sediment near the river outflow.

The Os concentrations of the samples collected near the hydrothermal vents in this study, are very close to those of deep-seawater. The samples were collected when a decrease in the light transmission in the water column was recorded, and not directly at the black smoker vent. The results suggest that either vent fluid is not highly enriched in Os relative to seawater, or that the Os was removed or diluted to background levels with the surrounding seawater before the samples were collected. The Os input to the ocean from hydrothermal activity, could be determined by sampling directly inside the black smoker vent, with a titanium sampler for example.

The method development experiments showed that the Os radiotracer was quickly removed from a seawater matrix when it was stored in a polyethylene bottle, even if the matrix was acidified. It is unclear however if the speciation of the ^{191}Os radiotracer was the same as the speciation of Os in seawater. The adsorption of Os to bottle surfaces could be determined directly, by comparing the Os concentration of a sample that had been stored in a polyethylene bottles for a few months, with that of a sample analysed immediately upon collection. From the radiotracer experiment results, it is expected that the Os concentration of the stored sample will be much lower, due to its adsorption onto the wall of the storage bottle. Samples collected from the Indian Ocean for Os analysis (Levasseur et al., 1998) were stored in Pyrex (borosilicate glass) bottles for 3 months during the period of analysis, and no Os loss was observed. This confirms the theory that glass is a suitable material for the storage of seawater for Os analysis.

5.14 Summary

The Os concentration of a vertical profile collected in the eastern Pacific Ocean is not constant with depth. A small but distinct minimum (approximately 30% reduction) occurs at around 500 m, which coincides with a minimum of both dissolved oxygen and light transmission. The ^{187}Os/^{186}Os ratio of eastern Pacific Ocean seawater is 8.89 ± 0.09 (2σ), constant throughout the water column. This is in good agreement with the value ^{187}Os/^{186}Os $= 8.80 \pm 0.07$ measured for seawater collected from the Indian Ocean (Levasseur et al., 1998) and this suggests that Os is well mixed in the oceans.

All the samples analysed by ICP-MS show lower isotopic compositions than those analysed by NTIMS. The comparison to previously published data, the higher instrument count rates and better precision in the measured values, all suggest that the isotopic composition values obtained by NTIMS are more accurate then those obtained by ICP-MS. The data suggests that the samples have not lost Os between the time it took to distil them, and that there is no or little difference between the adsorption characteristics of Teflon and glass bottles. The difference in Os concentration between eastern Pacific seawater (this thesis) and Indian Ocean seawater (Levasseur et al., 1998) cannot be explained by adsorption, as glass bottles were used in both sets of samples. There is direct evidence that ship-distilled samples have higher blank contamination than laboratory-distilled samples, as blank contamination introduced by the reagents and the microdistillation alone account for 0.90 pg of Os blank.

There is a strong correlation between dissolved oxygen and Os concentration in this area of the eastern Pacific Ocean. Two processes may contribute to the decrease in Os in the dissolved oxygen minimum: the advection and mixing of a water mass of low Os concentration (created by the removal of dissolved Os to sediments at the continental slope) and the adsorption onto sinking particles driven by the suboxic conditions. These two processes are known to affect the concentrations of other trace metals in this area of the eastern Pacific Ocean. Without sediment trap data from the open ocean, or concentration values for seawater Os at the continental slope, it is difficult to assess the contribution from each process.

A comparison between filtered and unfiltered samples shows that the majority of Os, in both the seawater and vent-influenced samples, is in the dissolved phase. A maximum of 8.2% of the Os in seawater, and 3.7% of Os in the vent-influenced samples, was measured in the particulate phase. Osmium concentrations of hydrothermal vent samples are lower than those of deep-water samples, which suggests that Os may be scavenged from seawater by hydrothermal vent plumes and that vent fluid is not highly enriched in Os relative to seawater, or that the Os was quickly removed or diluted with the surrounding seawater before the samples were collected.

The process by which Os is removed from seawater to organic rich sediments under reducing conditions is not known. The results of this study suggest that both the adsorption of Os onto particles sinking to the sea floor, and the removal of dissolved Os at the seawater-sediment boundary, contribute to the flux of Os from seawater to the sediments. The Os concentration has been used to calculate a new estimate of the Os oceanic residence time of ~33,000 years, which suggests that Os should be uniformly distributed throughout the oceans.

The radiotracer and seawater results provide new light to the question of the speciation of Os in seawater. It is suggested that Os exists in several oxidation states and chemical species in seawater. Suboxic conditions force seawater Os to change oxidation state. At medium to high dissolved oxygen concentrations, Os exists in a non-particle reactive, oxidised form (possibly in the +8 oxidation state as the oxyanion $[H_3OsO_6]^-$) and therefore, the majority of the Os is in the dissolved phase. In suboxic conditions the Os, or at least a certain fraction of the Os, is reduced, made particle reactive and is adsorbed onto fast sinking particles. This behaviour is analogous in some respects to the aquatic geochemistry of Cr.

Appendix I: Reagents

- Osmium standard solution 1000 μg/mL in 20% HCl, Alfa Aesar.
- Osmium ICP/DCP standard solution 1000 μg/mL in 20% HCl, Johnson Matthey.
- Tamapure Super Clean (TMSC), Wako Chemicals.
- Conc. Nitric acid Primar grade, Fisons.
- Tin solution AAS grade 1000 ppm in approx. 1 M HCl, Fisons.
- AR grade ammonia solution SG 0.88, Fisons.
- ^{190}Os-isotopically enriched (96.93%) metal, Oak Ridge National Laboratory.
- Sodium peroxide powder, grade and supplier unknown.
- Sodium hypochlorite solution 5.25%.
- Sand-filtered seawater, collected from Newport, OR, USA.
- Vinylacetic acid Reagent grade, Fischer Scientific.
- 30% H_2O_2 Ultrex grade, VWR Scientific.
- 30% H_2O_2 Reagent grade, Fischer Scientific.
- Conc. H_2SO_4 Optima grade, Fischer Scientific.
- Conc. HBr, Axys Seastar Chemicals Inc.
- Conc. HCl, Axys Seastar Chemicals Inc.
- Conc. HNO_3 Reagent grade, Fischer Scientific.
- Conc. HCl Reagent grade, Fischer Scientific.
- Conc. H_2SO_4 Reagent grade, Fischer Scientific.
- Chromium trioxide, grade and supplier unknown.
- Milli-Q water (reverse osmosis deionised water).

Appendix II: $^{187}Os/^{186}Os$ Ratios in Marine and Geological Materials

Meteorites, chondrites, tektites and mesosiderites

$^{187}Os/^{186}Os$ Ratio	Origin and Type of Material	Literature
0.805±0.011	at the origin of the Solar System (calculated by regression analysis)	(Luck et al., 1980)
0.91	Allende carbonaceous chondrite	(Lichte et al., 1986)
0.91±0.11, 1.02±0.10	East Clearwater crater, Quebec melt rock	(Fehn et al., 1986)
0.98-1.01	Tlacotepec iron meteorites	(Luck et al., 1980)
1.03±0.04	Canyon Diablo iron meteorite	(Fehn et al., 1986)
1.06±0.05	Estherville mesosiderite	(Luck and Allègre, 1983)
1.07-1.16	range of 10 chondrites	(Luck and Allègre, 1983)
1.164±0.015	St Severin chondrite	(Luck et al., 1980)
1.122±0.08	Canyon Diablo iron meteorite	(Luck et al., 1980)
1.27-1.73	Ivory Coast tektites	(Koeberl and Shirley, 1993)
0.91-1.73	**range in meteorites, chondrites, tektites and mesosiderites**	

Igneous material: basalts, peridotites and mafic / ultramafic rocks

^{187}Os/^{186}Os Ratio	Origin and Type of Material	Literature
0.98-1.12	Ronda, Spain ultramafic rocks	(Reisberg et al., 1991)
0.99-1.15	Mont Trapeze, Kerguelen Islands peridotite xenoliths	(Hassler and Shimizu, 1998)
0.99-1.12	range in ultramafic intrusions (late Precambrian to Tertiary age)	(Hattori and Hart, 1991)
0.994-1.061	range in Izu-Bonin-Mariana forearc (Proterozoic age) mantle peridotites	(Parkinson et al., 1998)
≈1	Os used in industry, medicine and commerce (mined from ore deposits)	(Esser and Turekian, 1993a)
1.0032-1.173	range in ultramafic and mafic rocks	(Martin, 1991)
1.019-1.071	range in North Atlantic ridge, East Pacific Rise and Indian Ocean abyssal peridotites	(Roy-Barman and Allègre, 1994)
1.0261-1.1275	Samoa and Tahaa, south Pacific Ocean EMII basalts	(Hauri and Hart, 1993)
1.04-1.08	Lac Superieur, Kerguelen Islands peridotite xenoliths	(Hassler and Shimizu, 1998)
1.082±0.001	Reunion basalts	(Roy-Barman and Allègre, 1995)
1.10±0.02	Hawaiian basalts	(Martin et al., 1994)
1.10	Loihi basalts	(Pegram and Allègre, 1992)
1.11	Reunion basalts	(Pegram and Allègre, 1992)
1.1159-1.2473	HIMU Rurutu, Tubuai and Mangaia, south Pacific Ocean basalts	(Hauri and Hart, 1993)
1.117-3.534	mid-ocean ridge basalts (MORB) from the North Atlantic ridge, East Pacific Rise and Indian Ocean	(Roy-Barman and Allègre, 1994)
1.12-1.64	Comores basalts	(Reisberg et al., 1993)
1.13-1.59	La Palma, Canary Islands sub-aerial lavas	(Marcantonio et al., 1995)
1.13-1.16	Samoa basalts	(Reisberg et al., 1993)
1.13	Mauna Loa Volcano, Hawaii basalts	(Pegram and Allègre, 1992)
1.14	Mauna Loa Volcano, Hawaii aerosols	(Krähenbühl et al., 1992)
1.18-1.71	St Helena basalts	(Reisberg et al., 1993)
1.25	Mangaia basalts	(Reisberg et al., 1993)
1.33	Kerguelen basalts	(Reisberg et al., 1993)
1.35	Pitcairn basalts	(Reisberg et al., 1993)
1.485±0.045	Mangaia basalts	(Roy-Barman and Allègre, 1995)
1.7-47.9	Ronda, Spain mafic layer samples	(Reisberg et al., 1991)
6.31-7.76	Atlantic Ocean peridotite crusts	(Palmer et al., 1988)
6.8-14.3	Ries crater, Germany crustal rocks	(Fehn et al., 1986)
0.98-14.3	**range in Igneous material: basalts, peridotites and mafic/ultramafic rocks**	

Clays and sediments

$^{187}Os/^{186}Os$ Ratio	Origin and Type of Material	Literature
1.12±0.16	Woodside Creek, New Zealand Cretaceous/Tertiary boundary clays	(Lichte et al., 1986)
1.29	Raton Basin, Colorado K-T boundary samples	(Luck and Turekian, 1983)
1.3-8.7	TAG hydrothermal mound metalliferous deposits	(Ravizza et al., 1996)
1.65±0.03	Stevns Klint, Denmark K-T boundary clay	(Luck and Turekian, 1983)
1.8-5.0	New Haven Harbour surface sediment (industrial influence)	(Esser and Turekian, 1993a)
5.7-7.1	Black Sea sediments	(Ravizza et al., 1991)
6.2±3.3	Bakken Shale rock isochron (Mississippian/Devonian boundary)	(Ravizza and Turekian, 1989)
6.5	DOMES sites, North Pacific pelagic clay	(Esser and Turekian, 1988)
7.9-8.2	Bauer Basin metalliferous sediments	(Ravizza and McMurtry, 1993)
8-11	Atlantic and Pacific red clays	(Ravizza, 1992)
8.4-8.6	East Pacific Rise metalliferous sediments	(Ravizza and McMurtry, 1993)
8.8	Long Island Sound preindustrial sediments	(Esser and Turekian, 1993a)
1.12-8.8	**range in clays and sediments**	

Mn nodules

$^{187}Os/^{186}Os$ Ratio	Origin and Type of Material	Literature
5.27-10.96	Atlantic Ocean Mn nodules	(Palmer and Turekian, 1986)
5.95-8.91	Pacific Ocean Mn nodules	(Palmer and Turekian, 1986)
5.95±0.18	South Pacific Ocean Mn nodules	(Luck and Turekian, 1983)
6.68±0.10	South Atlantic Ocean Mn nodules	(Luck and Turekian, 1983)
7.02-8.33	Indian Ocean Mn nodules	(Palmer and Turekian, 1986)
7.20-8.07	range in marine Mn nodules from different ocean basins	(Palmer et al., 1988)
7.65±0.07	North Pacific Ocean Mn nodules	(Luck and Turekian, 1983)
7.97±0.11, 8.09±0.06	North Atlantic Ocean Mn nodules	(Luck and Turekian, 1983)
8.33±0.09	Indian Ocean Mn nodules	(Luck and Turekian, 1983)
8.38±0.19	Antarctic Ocean Mn nodules	(Luck and Turekian, 1983)
12.4-21.2	Baltic Sea Mn nodules	(Peucker-Ehrenbrink and Ravizza, 1996)
5.27-21.2	**range in Mn nodules**	

Seawater: direct and indirect analysis

$^{187}Os/^{186}Os$ Ratio	Origin and Type of Material	Literature
~2 → 3.5 → 6	increase in seawater ratio from the K-T boundary → 63 Ma → 15 Ma (inferred from metalliferous sediments)	(Peucker-Ehrenbrink et al., 1995)
6.1 →8.6	increase in seawater ratio over the past 15 Ma (inferred from metalliferous carbonates)	(Ravizza, 1993)
6.3±3.1	the first direct measurement of seawater, unknown location	(Koide et al., 1996)
6.9±0.4	the direct analysis of ambient seawater around the Juan de Fuca Ridge	(Sharma et al., 1997)
7.5→8.6	increase of ratio in seawater over the past 3.5 Ma (determined from sediment analysis)	(Ravizza, 1995; Ravizza and Esser, 1993)
~8.1	seawater late in the last two glacial maximums at 20 and 160 ka (determined from sediment analyses)	(Oxburgh, 1998)
8.6±0.2	indirect analysis of seawater (determined by analysing the hydrogenous Os released during leaching of pelagic clays and metalliferous sediments)	(Pegram et al., 1992; Ravizza, 1993; Ravizza and Esser, 1993; Ravizza and Turekian, 1992; Ravizza et al., 1991)
8.7±0.3	direct analysis of Central Pacific and North Atlantic deep ocean seawater	(Sharma et al., 1997)
8.80±0.07	direct analysis of Indian Ocean seawater	(Levasseur et al., 1998)
8.89±0.09	direct analysis of eastern Pacific Ocean seawater	this thesis
6.3±3.1 - 8.89±0.09	**range for present day seawater**	

River water, continental runoff and terrigenous sediments

$^{187}\text{Os}/^{186}\text{Os}$ Ratio	Origin and Type of Material	Literature
8.22-10.86	East China Sea terrigenous sediments	(Esser and Turekian, 1993b)
8.6-11.0	continental runoff from the Phanerozoic sedimentary platform south of the Baltic Sea	(Peucker-Ehrenbrink and Ravizza, 1996)
8.76-10.43	Amazon Shelf terrigenous sediments	(Esser and Turekian, 1993b)
8.8	Connecticut river water	(Sharma and Wasserburg, 1997)
9.28-10.85	Mississippi Delta terrigenous sediments	(Esser and Turekian, 1993b)
10-11	present-day erosion of upper continental crust	(Esser and Turekian, 1993b)
10.1-21.5	range in US, Ganges and Rio Maipo Rivers sediment leaches	(Pegram et al., 1994)
10.27-10.72	Roxana Silt terrigenous sediments	(Esser and Turekian, 1993b)
10.4	Mississippi river water	(Sharma and Wasserburg, 1997)
10.43-10.94	Peoria Loess terrigenous sediments	(Esser and Turekian, 1993b)
10.7	Vistula river water	(Sharma and Wasserburg, 1997)
12.5	bulk glacial Lake Hitchcock sediment	(Esser and Turekian, 1988)
14.4	Columbia river water	(Sharma and Wasserburg, 1997)
20.5-37.8; 30 (average)	calculated range and average for continental crust (mass balance approach to Os measurements of Pacific Ocean Mn nodules)	(Palmer and Turekian, 1986)
31.2-65.4	continental runoff from the Precambrian Baltic Shield	(Peucker-Ehrenbrink and Ravizza, 1996)
8.8-14.4	**range for the direct analysis of river water**	
8.6-65.4	**range for continental runoff and terrigenous sediments**	

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