JAAS

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/jaas

High precision osmium elemental and isotope measurements of North Atlantic seawater

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Abstract

This study presents new Os isotope and elemental data for seawater from the North Atlantic Ocean. Two techniques have been optimised and used to achieve tracer-seawater equilibration: i) heating of seawater-tracer mixture at 100°C with Br_2, CrO_3 and H_2SO_4 in Teflon bombs and solvent extraction of OsO_4 with Br_2; and ii) heating of seawater-tracer mixture to 300°C with CrO_3 and H_2SO_4 in sealed glass tube (HPA-S-s) at 125 bars and back extraction with Br_2. Both techniques yield similar total procedural blanks in the range of 14-18 fg, and have a total Os yield that ranges from 86 to 92%. For the 200 fg Os standard, the effective ionisation efficiency is between 6 and 10% demonstrating that single filament ionization is capable of achieving significant Os sensitivity.

To assess the external reproducibility on the ^{187}Os/^{188}Os ratio, both methods have been systematically applied to a single sample from a water depth of 2000m and yield an indistinguishable ^{187}Os/^{188}Os ratio of 1.026 ± 0.017 (n=11) and 1.020 ± 0.013 (n=3), for techniques (i) and (ii), respectively. The external reproducibility on the ^{187}Os/^{188}Os ratio and Os concentration is 1.6% and 3.7% respectively, demonstrating the capability of both methods for analysing Os in natural waters.

Both procedures have been applied to a seawater profile from north east Atlantic (IB13: 60°29.4' N, 19°59.2' W, 2650 m water depth). The results show little measurable variability in either Os concentration or isotope composition with depth and the overall average for the whole profile is 1.024 ± 0.031 (3%) for the ^{187}Os/^{188}Os ratio and 9.68 ± 0.48 (4.9%) pg/kg for the Os concentration. Therefore, for this locality at least, Os appears to behave conservatively.

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1. Introduction

Osmium (Os) isotopes have emerged as a powerful tracer of the changes in ocean chemistry that occur in response to variations in continental weathering, ocean anoxic events, extraterrestrial impacts and anthropogenic contamination[1]. Nevertheless, direct analysis of modern seawater remains challenging, in part, because of the very low Os concentrations, but also, in part, because the speciation and oxidation state of Os in seawater remain poorly constrained[2-6]. Femtomolar concentrations and the possibility of multiple oxidation states have therefore necessitated the development of ultra low blank analytical techniques capable of oxidizing all the Os present to a common oxidation state (OsO_4).[3,5-6]

These techniques have superseded all earlier attempts to isolate seawater Os indicating Os concentrations between 4-5 times higher than previous work[2]. The bromine method combines the oxidation and extraction of seawater Os in a single step through the addition of Br_2(l), H_2SO_4 and CrO_3 to the sample and spike, heated together in a Teflon bomb at 90-110°C in an oven[3,7]. This is then followed by liquid-liquid extraction of the OsO_4 in Br_2(l) into HBr. The distillation method also combines the oxidation and extraction of Os in one step[4]. The H_2SO_4 and H_2O_2 are combined with seawater and spike, and the solution is then heated to ~100°C while Os is distilled and trapped in HBr. The Carius tube method separates the oxidation and extraction steps by first oxidizing the sample and spike with CrO_3 in sealed glass (Carius tubes) heated to temperatures of 180°C[6], in an oven, or up to 320°C, in a High Pressure Asher (HPA-S)[6]. The Os extracted using each of these techniques is further purified by using micro-distillation and then measured using negative thermal ionization mass spectrometry (N-TIMs).[8,9]

Recently it has been suggested that much of the published Os isotope and elemental data for seawater has been compromised[6]. Evidence suggests the need for extended heating at high temperatures for complete equilibration of spike and sample Os. Indeed, East Pacific seawater samples heated to 300°C yield Os concentrations in seawater that are up to 35% higher than any other technique described above, consistent with a study of groundwaters comparing low and high temperature techniques. In parallel, it was discovered that widely used, pre‐cleaned high‐ and low‐density polyethylene (HDPE and LDPE) bottles appear to contaminate seawater Os, where the contamination seems to be caused by the use of ultrapure nitric acid during cleaning[10].

This study presents a comprehensive comparison of Os isotope and elemental measurements of seawater using the low-temperature bromine and high-temperature HPA-S method on the very same sample. These data show that the two techniques can yield an indistinguishable Os isotope composition and Os concentration at the level of precision obtained in this study, ± 1.6% for the $^{187}Os/^{188}Os$ ratio and ± 3.7% for the Os concentration. The bromine method is simple to use, has high yields (>90%) during extraction and purification of Os, and low blanks (~12-14 femtograms). When coupled with N-TIMS ionization efficiencies of up to 10% for 500 fg of Os this technique is capable of yielding precise and accurate isotope ($^{187}Os/^{188}Os$) and elemental data for aqueous samples, if the characteristic time for sample-spike equilibration is carefully identified.

2. Sampling and analytical techniques

2.1 Samples

2.1.1 Sampling North East Atlantic seawater

The RRS Discovery Cruise 253 'FISHES' was conducted in the north east Atlantic (60º29.4'N, 19º59.2'W) for the Southampton Oceanography Centre[11] (Fig. 1). A vertical seawater profile was obtained by sampling the CTD Rossette Niskin bottles (Station 13979, IB13). The temperature of the water in the Niskin bottles, at the time of sampling, was measured using a hand held electronic thermometer probe. One litre polycarbonate sample bottles were filled from 12 Niskin bottles selected to make a suitable vertical water profile for each station. The assembled bottle combinations were then placed in individual zip lock plastic bags. Upon receiving the samples at the Open University, they were filtered through 0.2 µm cellulose acetate filters using a manual frontal filtration unit and transferred into pre-cleaned 1L Teflon bottles and stored at low temperature (5°C) unacidified until analysis. Each Teflon bottle was cleaned using the following steps: 1) Rinsed with acetone, 2) Rinsed with MQ water, 3) steam-cleaned with ultrapure HBr, by filling the bottle with 30 ml of concentrated HBr and heating at 100°C for 7 days, 4) Rinsed with MQ water, 5) Steam-cleaned with MQ water by filling the bottle with 100 ml of MQ water and heated at 80°C for 2 weeks, 6) the water was discarded and the bottle air-dried under a laminar flow hood. After the cleaning procedure, the osmium blank for the Teflon bottle was determined by introducing 10 ml of ultrapure 8.8M HBr in the bottle and heating it on a hot plate at 100°C for 7 days. The acid was then collected, spiked and evaporated to dryness. The Os was purified by microdistillation and measured using NTIMS. This yielded a blank of 0.35 fg/g which is identical to the reagent blank itself.

2.1.2 Eastern Pacific seawater samples

These seawater samples were obtained during RV Atlantis cruise A3-11 to the eastern Pacific Ocean (9º46'N, 104º11'W) during November – December 1997; sampling locations and information on light transmission are given in Woodhouse et al.[4]. The samples were collected using PVC Niskin bottles (10 l) on a rosette-CTD package. The Niskin bottles were pre-cleaned by rinsing with Milli-Q water and scrubbing with a plastic brush, followed by soaking in 0.6 M HCl for 48 h two times. These samples were kindly provided by G. Ravizza (University of Hawaii). Investigated samples were from depth of 104, 459, 603 and 2480 m. Samples were stored in glass and/or Teflon bottles. The majority of the samples were not filtered except the 2480m sample which was filtered through a 0.4 µm Nuclepore polycarbonate membrane.

2.2 Preparation and purification of reagents involved in Os chemistry

Almost all reagents require one or several purification steps prior to use in the aqueous chemistry of osmium.

Bromine. Liquid bromine contains the highest levels of impurity by far. A range of commercial bromine liquids have been tested and all grades give values of osmium blank between 4 and 10 pg/ml (Table 1). To achieve an acceptable blank level it took no less than three distillations of a commercial solution with the blank stabilizing at Os levels around 2 - 4 fg/ml. Overall, this operation improves the Os blank of bromine by a factor greater than 1000.

Sulfuric acid. The only acid used without purification was the 18M sulfuric acid and once a clean batch was identified, a large quantity (of some 10L) was purchased and stored. This allowed us to operate with a stable blank for this acid of around 3 fg/ml throughout this study (Table 1). However when this acid is used for preparing the oxidizing solution containing chromium (CrO_3) it undergoes further purification by sparging, which involves bubbling clean air through the hot reagent.

Sodium dichromate dihydrate ($Na_2Cr_2O_7$, $2H_2O$) dissolved in 40% H_2SO_4 (50 g of CrO_3 in 50 ml H_2O + 35 ml 98% H_2SO_4 which is equivalent to dissolve 60g of CrO_3 in 100 ml of 40% H_2SO_4) was used in this study as the oxidizing agent. It was preferred to hydrogen peroxide (H_2O_2) because of its high relative oxidizing strength. The evidence for this comes when mixing dichromate ions with hydrogen peroxide resulting in the formation of a green-coloured solution. The following half reactions show what occurs during this process :

Reduction half reaction: $Cr_2O_7^{2-} + 14H^+ + 6e^- \Longrightarrow 2Cr^{3+} + 7H_2O$ $E^o_r = +1.33$ V

Oxidation half reaction: $3\ (H_2O_2 \Longrightarrow 3O_2 + 2H^+ + 2e^-)$ $E^o_r = -0.68$ V

Balanced net equation: $Cr_2O_7^{2-} + 8H^+ + 3H_2O_2 \Longrightarrow 2Cr^{3+} + 7H_2O + 3O_2$ $E^o_{cell} = +0.65$V

The reaction is spontaneous without any external source of energy and the overall potential $E°_{cell}$ is positive[12]. So the hydrogen peroxide is oxidized by the dichromate ions under acidic conditions. Despite the relative toxicity of sodium dichromate compared to H_2O_2, and its potential contamination by osmium, it was preferred as an oxidizing agent of Os in seawater samples. Furthermore the Os chemistry yield using H_2O_2 was always 20% less than CrO_3 during oxidation tests under the same conditions.

Ba, Na Emitter solution. A mixture of 1.85 g of Barium hydroxide octahydrate ($Ba(OH)_2•8H_2O$, AnalaR NORMAPUR®, VWR) is dissolved in~ 100 ml of sodium hydroxide 0.1 M (AVS TITRINORM®, VWR). Only between 0.4 and 0.6 µl of such saturated solution is used for each single Os load in order to promote OsO_3^- emission during N-TIMS measurements.

H_2O. 18.2 MΩ.cm MilliQ water from our Millipore water purification system yields a rather high blank of 3-5 fg/ml for what is considered to be the cleanest solution. We used water at two stages in the chemistry, first in making the CrO_3 solution with H_2SO_4, and secondly in evaluating the procedural blank where 3-4 ml of MQ water is used to extenuate the exothermic reaction caused by the addition of 18M H_2SO_4 to the solution. The MQ water was purified by sub-boiling distillation in a closed system, which reduces the Os blank to around 1 fg/ml.

Hydrobromic acid. Eight different grades of HBr from four different suppliers were tested. It was surprising to see that so-called high purity HBr acids (and therefore more expensive) were the most contaminated in osmium (> 100 fg / ml for Romil SPA). Commercial HBr with a relatively low contamination in osmium (26-50 fg/ml) from Fisher Scientific was chosen. Double distillation of this reagent brought the osmium blanks to very low levels of 0.4-1.5 fg/ml.

2.3 Separation of osmium from seawater

The first technique for the chemical separation of Os used in this study follows that originally developed by Birck et al.[9] and later modified for natural waters[3,7]. This method is based on the affinity of osmium tetroxide (OsO_4) for liquid bromine (Br_2). In brief, 50 g of water sample is introduced into 120 ml Savillex® PFA-Teflon pressure vessel (Savillex, Eden Prairie, MN, USA) together with 2 ml of Br_2, ^{190}Os spike, 2 ml of CrO_3 solution (CrO3 dissolved in 40% H_2SO_4) and 1.5 ml of 98% H_2SO_4. The pressure vessel is then closed and heated to 100 °C in the oven for 72h. This oxidation technique achieves complete spike-sample equilibration and the conversion of all Os species present to OsO_4. Extensive tests have shown that with 2 ml of the CrO_3 solution there was always an excess of Cr at the end of the oxidation stage. A drop of the aqueous phase is pipetted and dropped into 3% v/v H_2O_2 solution. Complete oxidation occurs if excess CrO_3 remains present in the solution. If so it will react with H_2O_2 by producing intense bubbling with a transient dense blue colour. If complete oxidation is confirmed, osmium is then extracted from the water into liquid bromine[3,7]. With this technique Os oxidation (by CrO_3) and extraction (by Br_2) are accomplished in the same step. Recent studies have suggested that this low temperature technique is unable to oxidize and recover all the Os present in natural water samples.[5-6]

In order to assess this supposition a second technique was used for Os extraction, where 50 g of water and ^{190}Os spike (in 8.8 M HBr) are combined in a quartz glass Carius tube and frozen at -20°C. To the frozen mixture, 2 ml of CrO_3 dissolved in 40% H_2SO_4 and 1.5 ml of 98% H_2SO_4 were added and the glass tubes were immediately sealed and placed in a High Pressure Asher (HPA-S, Anton Paar GmbH, Graz, Austria). The sample chamber was pressurized to 125 bars with nitrogen gas. After waiting for the sample to thaw, the tubes are heated to 300°C for 12 h. Once the sample chamber has cooled to room temperature, the HPA-S is vented and the sample transferred into 120 ml Savillex® PFA-Teflon with 2 ml of Br_2, and Os is extracted following the same procedure described above (Fig. 2). A second step of addition and extraction of 1 ml of bromine liquid was used in both techniques. After cooling the content of the 120ml Savillex bomb (~5-10°C) bromine was removed and directly mixed with 1 ml of concentrated HBr. The resulting hexabromoosmate (H_2OsBr_6) fraction is then gently dried and purified using micro-distillation[9]. Both techniques are outlined in fig. 2 and interlaboratory comparison of analytical parameters for different Os extraction methods used here and in other labs are summarised in Table 2. Our HPA-S method differs from that of Chen and Sharma[6] in the sense that the extraction of Os is carried out by the liquid bromine in Teflon bomb and not by distillation in the quartz glassware[6]. It also differs from that of Paul et al.[5] by using CrO_3 as oxidizing agent instead of H_2O_2.

The total procedural blank for the HPA-S technique obtained during the course of this study was 17.5 ± 2 fg (2σ, n=18) with a weighted mean ^{187}Os/ ^{188}Os of 0.18 ± 0.03 (2σ). For the Teflon bomb technique the blank was 14.4 ± 2.5 fg (2σ, n=26) with a weighted mean ^{187}Os/ ^{188}Os of 0.20 ± 0.04 (2σ). These blanks account for between 2.7 and 3.8 % of the total Os present in the seawater samples.

2.4 Mass spectrometry

2.4.1 Loading on Pt filaments

The purified Os fractions are loaded at about 0.6 A on pre-cleaned Pt filaments by acid leaching and outgassing in air for 3-5 minutes at 2.4 A (Pt of 99.999% purity, H Cross Company, Moonachie, USA). In order to remove osmium traces from the Pt filaments they were surface etched with a 15M HNO_3 solution at 100°C for 24 h, rinsed with water and acetone. After mounting on the filament holder the Pt was again cleaned with water and acetone and outgassed for 3 min at 3A under atmospheric pressure. During this procedure Os is oxidized to its volatile tetraoxide, and completely evaporated. A binocular microscope was used to load the sample, covering 1-2 mm of the filament length. The load is covered with a freshly prepared saturated solution of $Ba(OH)_2$ in 0.1 M NaOH for the purpose of enhancing ion emission. The filament is then heated to complete dryness, and incipient melting (~ 1.2-1.4 A) after which it was immediately cooled to avoid any loss of Os by evaporation of OsO_4. The purpose of this step is mainly to suppress the organic interferences at masses 233-235. This cleaning and heating procedure minimises the background level of Re, and other organic interferences monitored at mass 233 ($^{185}Re^{16}O_3^-$) in the range of 0–3 cps. The Os contribution from the Pt ribbon is quantified by analyzing 0.2 µl of ^{190}Os spike directly loaded onto the filament. The measured loading blank was always less than 1 fg for all cleaned Pt ribbon batches used in this study.

2.4.2 Isotope and elemental measurement

The Os isotope ratios were measured by Negative Thermal Ionization Mass Spectrometry (NTIMS)[8] on a Thermo Fisher Scientific Triton (Thermo Scientific, Bremen, Germany). The analyses were performed by using the secondary electron multiplier in ion counting mode as a detector. High purity O_2 gas is bled into the ion source at a pressure of ~2.10^{-7} mbar. The Os isotopic compositions for all samples are determined by peak jumping on masses 233, 235, 236, 238 and 240 of the OsO_3^- ion beam. Osmium isotopic ratios are normalised to ^{192}Os/^{188}Os of 3.08271[13] and corrected off-line to remove the spike and oxygen contribution using ^{18}O/^{16}O and ^{17}O/^{16}O ratios of

0.002047 and 0.0003708 respectively[14]. Repeated analyses of the JM Os standard obtained on separate loads of 0.2 pg (n=24) and 1 pg (n=43) yield an average $^{187}Os/^{188}Os$ of 0.1743 ± 0.0015 (0.86%) and 0.1738 ± 0.0008 (0.5%), respectively (Fig. 3). These values are in good agreement with published Faraday cup N-TIMS values of 0.173947 ± 0.000014[6,15]. Similar measurements were also made on separate loads of 0.2 pg (n=21) and 1 pg (n=44) of the LOsTD Os standard which yield an average $^{187}Os/^{188}Os$ of 0.1066 ± 0.0016 (1.5%) and 0.1067 ± 0.0009 (0.8%), respectively (Fig. 3), both averages being within error of the true value of the standard (0.1069).[16]

2.4.3 Ionisation yield

The ionization efficiency (IE) was calculated for different sample amounts ranging from 0.2 pg to 25 ng. The ionization efficiency is taken as the ratio of the number of detected ions against the number of loaded atoms. The IE increases significantly with decreasing Os loads, in agreement with already well established observations for TIMS for both positive and negative ions[17-18]. This behaviour, sometimes termed the "self poisoning effect" varies significantly between elements[17]. For Os the highest IE were observed in the range between 1 pg and 1 ng (e.g. 25-35%) however, these efficiencies are reduced below Os levels of 1 pg. This is the opposite to what was observed for radium[17] and thorium[18]. For the 200 fg Os standard, the I.E. varies between 6 and 10% (Fig. 4), significantly higher than the yield recently reported by Sharma et al.[10] on standards of similar size, demonstrating that the use of double filaments does not bring any significant improvement in Os sensitivity, over the use of single filaments.

3. Method optimisation

3.1 Duration of oxidation

An oxidation experiment was undertaken to determine the time required to achieve complete tracer-sample equilibration. A sequence of test measurements on the seawater sample from 100 m depth are given in Table 3 and plotted in Fig. 5. The oxidation curves were obtained at high (300°C) and low (100°C) temperatures for batches of the same sample using ~50 g of seawater at each step. At high temperature, the kinetics of equilibration of Os between seawater and the ^{190}Os tracer is rapid. Samples were heated at 300°C and held for 3, 5, 8, 12 or 15 hours. We did not observe any variability of $^{187}Os/^{188}Os$ ratio with time. However for the 3 h experiment, we recovered only 60% of the Os present in the sample. A plateau is attained after 12 h using the HPA-S. At lower temperatures complete oxidation takes more time and a plateau is not reached until some time after 48 h. As for the high temperature experiment in HPA-S, we did not observe any variation in the $^{187}Os/^{188}Os$ ratio over time. Consequently, both methods display a ramp up to the final concentration of Os, but with no change in the $^{187}Os/^{188}Os$ ratio. For the high temperature HPA-S and low temperature teflon methods, the duration of the oxidation step was fixed at 12 h (300°C) and 72 h (100°C), respectively.

3.2 Temperature of oxidation

Temperature has a marked effect on the kinetics of chemical reaction required in order to achieve full sample-tracer equilibration. Chen and Sharma[6] showed that the Os concentration measured by equilibrating the seawater-tracer at 300°C is some 30% higher than the concentration obtained after equilibration at 180°C[6]. We explore this dependency between Os concentration and temperature by investigating two different seawater samples (at 800 and 1600 m depths) and applying the HPA-S technique at reaction temperatures of 100, 150, 200, 250 and 300°C. In order to fully quantify the effect of temperature, all other parameters were left unchanged (2 ml CrO_3 solution, 1.5 ml H_2SO_4 and oxidation time of 12 h). The results are given in Table 4 and illustrated in Fig. 6, showing that over this range of temperatures, the Os isotope ratios are indistinguishable within error. However, Os concentrations do increase gradually with temperature reaching a plateau at around 250°C. We find that at 100°C the recovery of Os from both samples is around 60% twice that obtained by Chen and Sharma at the same temperature[6]. This is probably due to the nature and amount of the oxidizing reagent used. The results of our experiment and those of Chen and Sharma strongly contrast with those of Paul et al.[5] in which a high apparent Os concentration is obtained at 100°C even higher than the plateau values themselves, attributed by these authors to spike oxidation

3.3 Long term storage effect on seawater samples

The material used and length of time of storage both appear to affect the stability of osmium in seawater, noted for the first time by Koide et al.[19]. These authors suspected that osmium was adsorbed to the walls of the storage vessel to varying degrees depending on the material used, including polycarbonate, polyethylene and Pyrex. These tests were undertaken using a radioactive spike (^{185}Os) and estimated loss of this tracer in the Pyrex bottle was found to be around 0.5% per day. Two years later, Levasseur et al.[3] challenged the outcome of Koide et al study by the direct measurement of osmium aliquots from one sample of seawater. They found that the osmium concentration remained constant over a period of several months within the precision of measurement. The same test was conducted on a water sample from the Seine River stored in borosilicate and in polypropylene bottles. For both types of storage material, no significant modification of the concentration or of the isotopic composition of Os were observed over a period of 1.5 years.[20]

In contrast, Sharma et al.[10] document evidence for substantial modification of a seawater sample during storage in high density Polyethylene bottles[10]. In this case these authors observed an increase in Os concentration (i.e. from 8.8 to 9.1 pg/kg) accompanied by a significant decrease in the $^{187}Os/^{188}Os$ ratios (i.e. from 1.046 to 0.953).

As stated above, our seawater samples were stored in pre-cleaned 1L Teflon bottles and kept unacidified at a low temperature. One seawater sample from 2000m depth from the North Atlantic ocean was measured at irregular intervals from 2001-2008, and a total of 14 measurements were made using the low temperature oxidation technique (110°C). These measurements were then later complemented following the acquisition of a high pressure Asher, enabling equilibration of water samples and acid in closed vessel (capacity 90 ml) inside a pressure vials at high temperature (300°C) and high pressure of 125 bar. The results are reported in Table 5 and shown in Fig 7. The low temperature oxidation technique yields an average $^{187}Os/^{188}Os$ ratio of 1.026 ± 0.017 (2 S.D) and average concentration of 9.76 ± 0.38 pg/kg (2 S.D.; n=11). These results are indistinguishable from those obtained with high temperature technique with $^{187}Os/^{188}Os$ of 1.020 ± 0.013 (2 S.D.) and average Os concentrations of 9.72 ± 0.37 pg/kg (2 S.D.; n=3). Its is therefore concluded that the Os in the seawater stored in these Teflon bottle has preserved a constant concentration and isotope composition over an interval of more than seven years, and that the techniques used here yield indistinguishable isotope and elemental results.

4. Results and discussion

4.1 Interlaboratory calibration

We have undertaken a comparison of the results produced using different analytical technique on the same seawater profile analysed previously by Woodhouse et al.[4] and Chen and Sharma[6] from the eastern Pacific ocean. Investigated samples were from depths of 104, 459, 603 and 2480 m. The results here were obtained using the two different oxidation techniques described above and are reported in Table 6 and illustrated in Fig. 8. Although each of these studies claimed a complete homogenisation of sample and tracer osmium, comparison of the results obtained, including those here, does not yield consistent results (Fig. 8). The common feature observed for surface water 0-100 m deep is that the Os concentration is almost 30 to 40% lower than the concentration in the deep waters. This observation contributed to the suggestion that Os is not uniform in the water column in this part of the East Pacific ocean. As for the isotope data, if the results of the distillation technique are excluded because they were obtained under very different conditions from this work and that of Chen and Sharma, the ^{187}Os/^{188}Os ratio appears to be constant throughout the water profile. Our average ^{187}Os/^{188}Os composition, obtained with the low temperature oxidation technique, of 1.028 ± 0.040 (2 S.D.; n=4) is consistent with HPA-S technique of 1.034 ± 0.033 (2 S.D.; n=4) and compares with the averages obtained by Chen and Sharma of 1.015 ± 0.095, 1.045 ± 0.053 and 1.048 ± 0.038 for bromine, CT300 and CT180 techniques (Carius tube at 300°C and 180°C), respectively.[6] All indistinguishable within the analytical uncertainties.

Crucially however, and in marked contrast to the study of Chen and Sharma where their CT300 method yielded 25 to 35% more osmium compared to other techniques[6], our CT300 method yields the same quantity of osmium to that obtained using the low temperature bromine technique within the given uncertainties.

4.2 Os in North Atlantic seawater profile

4.2.1 On the reproducibility of Os measurements in seawater

The external reproducibility was calculated by repeat measurement on independent aliquots of the same seawater sample. Chen and Sharma compared several methods and found that the bromine technique yield an external reproducibility (2×standard deviation) of 4.4% and 9.9% for ^{187}Os/^{188}Os ratio and Os concentration respectively[6]. The CT180 method improves the reproducibility of the osmium concentration (i.e. to 1.9%) but not that of the isotope composition (5.6%). Their optimised high temperature oxidation technique (CT300) gave the best precision of 1.3 and 2.2% on ^{187}Os/^{188}Os and Os concentration, respectively.[6]

In assessing the long-term effects of storage on the sample from 2000m water depth, this study also obtained data that demonstrates the long-term analytical reproducibility of both techniques. The low temperature bromine technique yields a mean ^{187}Os/^{188}Os of 1.026 ± 0.017, that is a reproducibility of 1.6%, and a mean Os concentration of 9.76 ± 0.38 pg/kg (a reproducibility of 3.9%). In comparison, the high-temperature HPA-S technique yields mean ^{187}Os/^{188}Os of 1.020 ± 0.013, a reproducibility of 1.3%, and a mean concentration 9.72 ± 0.37 (a reproducibility of 3.8%). Taken together, both low and high-temperature methods of oxidation on this water sample gave a reproducibility of 3.8% on Os concentration (9.75 ± 0.37 pg/kg) and 1.6% on ^{187}Os/^{188}Os ratio of 1.025 ± 0.016 (n = 14).

The external precision obtained on the ^{187}Os/^{188}Os isotope composition is two times better than that reported by Woodhouse et al.[4] and Levasseur et al.[3] but close to the external reproducibility obtained on the 200 fg standard both in this study and that of Chen and Sharma.[6]

4.2.2 Application to North Atlantic seawater

We have measured the Os concentration and isotope composition for a seawater profile from the North Atlantic ocean (Station 13979, 60º29.4'N, 19º59.2'W). A total of 13 samples from different depths ranging from 0 to 2600 m were analysed using the two different techniques described in this study. The detailed results are reported in Table 5 while a summary of the averages for analyses obtained at each given depth is presented in Table 7.

To date, published Os isotopic and elemental data in seawater have failed to establish a consensus on the behaviour of this element in the ocean. Levasseur et al documented conservative behaviour similar to that of Ir, Re and Mo, with little variation in Os concentration with depth[3]. In contrast others have observed apparent non conservative behaviour with a nutrient-like distribution[4,6]. In such a profile Os is depleted near the surface and becomes enriched at 500m, and this has been taken to suggest that at least some part of Os resides in an organic phase and is thereby removed from seawater. Despite the relative low Os concentration found in 100 m surface sample, the profile measured here for the north Atlantic shows little variability within depth. The average ^{187}Os/^{188}Os value for the whole profile is 1.024 ± 0.031 (2 S.D., 3%) and the average Os concentration is 9.68 ± 0.46 pg/kg (2 S.D, 4.8%). Taking an average for each analytical method does not significantly alter the overall estimates above, and ^{187}Os/^{188}Os values of 1.023 ± 3.3% and 1.024 ± 2.9% and Os concentrations of 9.69 ± 5.9% and 9.68 ± 5.5% are obtained for Teflon and HPA-S techniques respectively (Fig. 9).

The best statistical estimate of the mean ^{187}Os/^{188}Os value obtained for the North Atlantic profile is within uncertainty of the value reported for North Atlantic and Central Pacific deep ocean water of 1.04 ± 0.02/0.04[2], but some 2-4% less than the reported values for Eastern Pacific and Indian ocean of 1.067 ± 0.011 and 1.056 ± 0.008, respectively.[3-4]

The best statistical estimate of the mean concentration of the samples is 9.67 ± 0.46 pg/kg (normalised to 35‰ salinity). This concentration is ~10% less than that reported for Indian Ocean (10.86 ± 0.07 pg/kg)[3] but close to the highest value found in 2401 m depth sample from Eastern Pacific Ocean of 9.82 ± 0.08 pg/kg[4]. However, no vertical variation is observed between surface and deep seawater suggesting that Os behaves conservatively in seawater, at least, in this part of the Ocean (Fig. 10).

5. Concluding remarks

Here we document optimised methods for the determination of the Os concentration and isotope composition of seawater. We have used two different oxidation techniques to achieve tracer-sample equilibration: i) the low temperature Os extraction method which entails heating of the sample-tracer mixture at 100°C with Br_2, Cr and H_2SO_4 in Teflon bombs and solvent extraction of OsO_4 with Br2; ii) the high temperature Os extraction method which consist of heating to 300°C with Cr and H_2SO_4 in sealed glass tube (HPA-S) at 125 bars and back extraction with Br_2. Such conditions were optimised after testing the effects of several parameters such as the nature and the quantity of the oxidant, the duration time and the temperature.

The low Os total procedural blanks (14-18 fg) obtained for both methods together with the high total yield of the chemical procedure (~ 90%) and the high effective ionisation efficiency (6-10%) allowed us to document the Os elemental and isotope composition of a seawater profile from north east Atlantic ocean. The external reproducibility on the $^{187}Os/^{188}Os$ ratio was assessed by repeat measurement using both methods, applied to a single sample from a depth of 2000m which yield a similar $^{187}Os/^{188}Os$ ratio of 1.026±0.017 (n=11) and 1.020±0.013 (n=3), for low and high temperature oxidation techniques respectively, demonstrating the robustness of both methods in analysing Os in natural waters. The external reproducibility on the Os concentration and $^{187}Os/^{188}Os$ ratio are 3.7 and 1.6% respectively similar to that reported in the most recent studies [6,10]. We applied both procedures to a seawater depth profile from north east Atlantic (IB13: 60°29.4' N, 19°59.2' W, 2650 m water depth). Our results show little variability with depth and the overall average for the whole profile is 1.024 ± 0.031 (3%) for $^{187}Os/^{188}Os$ and 9.68 ± 0.48 (4.9%) pg/kg for the Os concentration, leading us to suggest that at this site, at least, Os appears to behave conservatively.

Acknowledgements

We are indebted to Dr J.T. Allen (University of Southampton) who sampled the north east Atlantic seawater during RRS Discovery Cruise 253 (May-June 2001). We gratefully acknowledge Prof. G. Ravizza (University of Hawaii) for providing us with the eastern Pacific seawater samples. This work was supported by the Natural Environment Research Council (under contract NE/B502701/1).

This research was also financed by the French Government Laboratory of Excellence initiative n°ANR-10-LABX-0006, the Région Auvergne and the European Regional Development Fund. This is Laboratory of Excellence ClerVolc contribution number 113. We are also grateful for the constructive reviews of two anonymous referees which lend to improve this manuscript. We thank Mary MacLeod for her express editorial handling. Discussions with Dr. Christan Pin and Dr. Karine David were much appreciated.

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Figure captions

Fig. 1. Location map of the station 13979 (IB 13) where seawater samples were collected during the RRS Discovery cruise 253 in the North Atlantic Ocean.[11]

Fig. 2. Summary of the two protocols of osmium extraction from seawater used in this study.

Fig. 3. Plot of ^{187}Os/^{188}Os ratio of repeat measurements of Os standard. All runs of 200 fg and 1 pg loads of LOsTD and Os JM (DTM aliquot) were collected over the period of 2001-2008. Error bars show 2σ standard errors. The mean of each population of analyses are indicated on the lower portion of the panel with the corresponding 2σ external reproducibilities. The mean is plotted as dark line and the horizontal grey zones represent the 2σ external reproducibilities for the ^{187}Os/^{188}Os ratio.

Fig. 4. Experimental measurement ionisation efficiencies (I.E) for OsO_3^- of various Os loads. Literature I.E. are also reported for comparison[6,17,21]. I.E. increases when decreasing Os quantities loaded reaching I.E. of 30%. However below 1 pg , the I.E. drops down to 10%.

Fig. 5. Effect of variable duration of oxidation (in hours) on Os concentration (A) and isotopic compositions (B) of 100 m north Atlantic seawater sample. Error bars represent 2xS.D. This external reproducibility was calculated by repeat measurements of 2000 m seawater sample.

Fig. 6. Effect of changing temperature on Os isotopic compositions and concentrations.

Fig. 7. Plots showing the temporal evolution of Os isotopic composition (A) and concentrations (B) since the first measurement in north Atlantic 2000 m seawater sample stored unacidified in a 1L Teflon bottle. The Os concentration and isotopic compositions are constant through time yielding the mean of 9.75 ± 0.37 pg/kg (3.8%) and of 1.025 ± 0.016 (1.6%) respectively, despite using two different oxidation methods.

Fig. 8. Interlaboratory comparison of Os extraction methods on an East Pacific seawater profile. Investigated samples were from depths of 104, 459, 603 and 2480 m. The common feature with

literature data[4,6] on the same profile is the relative depletion (30 to 40%) of surface water (0-100 m) compared to the deep waters.

Fig. 9. Comparison of Os isotopic compositions (A) and Os concentrations (B) between HPA-S and Teflon method applied to North Atlantic seawater for a given depth. From all eleven different depths data obtained between both methods are consistent within 5% and 2% for Os concentration and isotopic compositions respectively.

Fig. 10. Seawater profile of Os concentration and isotopic composition from North Atlantic ocean (station IB13). The reported Os concentrations are normalized to 35 per mil salinity. Each data point represent an average of all measurements for a given depth. Error bars which are 2 SD are derived from the same measurements. Average of the whole profile are represented by the dark line and the vertical grey shading shows the 2σ external deviation on calculated averages for the whole profile. Salinity and potential temperature data are from[11].

Table 1. Reagent and procedural blanks

Reagent grade	Supplier	Number	[Os][j]	^{187}Os/^{188}Os
Bromine (commercial)[a]				
AnalaR®	VWR	1	9.6 pg/ml	1.12
AristAR®	VWR	8	4.2 - 5.8 pg/ml	0.14
Primar®	Fisher Scientific	3	6.4 pg/ml	0.73
Certified AR	Fisher Scientific	2	8.6 pg/ml	1.43
GR for Analysis	Merck chemicals	1	10.5 pg/ml	0.42
Suprapur	Merck chemicals	2	7.3 pg/ml	0.54
Bromine AristAR® purified[b]				
1st distilled	VWR	15	0.13-0.25 pg/ml	0.43
2nd distilled	VWR	19	0.018-0.036 pg/ml	0.29
3rd distilled	VWR	33	0.002-0.004 pg/ml	0.15
Sulphuric acid (commercial)[c]				
Primar®	Fisher Scientific	2	0.041 pg/ml	0.25
AristAR®	VWR	7	0.003 pg/ml	0.21
Suprapur®	Merck chemicals	2	0.08 pg/ml	0.22
Veritas®	GFS Chemicals	2	0.17 pg/ml	0.30
Romil	Romil	2	0.25 pg/ml	0.13
CrO_3 in 40% Aristar sulphuric acid[d]				
Sodium dichromate Rectapur	VWR	5	42 fg	0.37
Sodium dichromate Specified	Fisher Scientific	3	35 fg	0.34
Sodium dichromate GR for Analysis	Merck chemicals	8	26 fg	0.41
Sodium dichromate Suprapur	Merck chemicals	5	6-10 fg	0.38
Sodium dichromate Suprapur sparged[e]	Merck chemicals	17	3 - 5 fg	0.35
Hydrobromic acid (commercial)[f]				
Certified AR	Fisher Scientific	3	80 - 110 fg/ml	0.71
Primar®	Fisher Scientific	3	72 - 80 fg/ml	0.58
Specified	Fisher Scientific	12	26 - 50 fg/ml	0.35
Rectapur®	VWR	4	35-76 fg/ml	0.45
AnalaR®	VWR	3	60 - 87 fg/ml	0.29
AristAR®	VWR	3	75 - 92 fg/ml	0.38
Suprapur®	Merck chemicals	3	50 - 78fg/ml	0.25
SPA ™	Romil	3	145 - 175 fg/ml	0.21
HBr Specified purified[g]				
Specified 1st distilled	Fisher Scientific	8	12-17 fg/ml	0.19
Specified 2nd distilled	Fisher Scientific	48	0.4-1.5 fg/ml	0.16
MilliQ water				
18.2 MΩ	Millipore	4	3-5 fg/ml	0.45
18.2 MΩ 1st distilled	Millipore	9	0.8-1.1 fg/ml	0.27
Loading blank[h]				
Platinum 99.999% purity	H. Cross	21	2.5-4.3 fg	0.28
Platinum (leached)	H. Cross	35	0.2-1.1 fg	0.20
Total procedural blank[i]				
HPA-S method		18	15.9-19.3 (17.5) fg	0.18 ± 0.03
Teflon method		26	12-17 (14.4) fg	0.20 ± 0.04
Os chemistry yield				
1st extraction		5	70-77 %	
2nd extraction		5	86-92 %	

[a] Bromine blank includes 1 ml of HBr and microdistillation blank

[b] Purified using Savillex sub-boiling still with 120 ml vessel. Low temperature distillation was performed in the presence of 5% v/v distilled 8.8M HBr.

[c] CrO_3 and Br_2 blanks were subtracted

[d] This blank reflects the contribution of the exact amount of reagents used during the oxidation step of Os in seawater (CrO_3, MQ H_2O, H_2SO_4). However HBr and Br_2 blanks were subtracted

[e] Cleaned by removing the volatile specie of Os (OsO_4) by evaporation, to do so clean air being bubbled through the hot reagent (~50°C).

[f] 5 ml of HBr were spiked, dried and purified by micro-distillation

[g] Purified using Savillex sub-boiling still with 1000 ml jar then checked for their blank as for [f].

[h] 0.2 microliter of ^{190}Os tracer were loaded on Pt filament using a micro syringe.

[i] Includes the same volumes of all reagents involved in Os seawater chemistry (Cr_2O_3, H_2SO_4, Br_2 and HBr).

[j] Range of values indicates min and max of the given blank while number in parentheses represents the average

Table 2. Interlaboratory comparison of analytical parameters for different Os extraction methods in natural waters

Laboratory	Authors	Quantity (ml)	Reagents used	Equipment used	Processing time (days)	Equilibration Temp. (°C)	Equilibration time (h)	TPB (fg)
IPGP / Paris (FR)	Levasseur et al. [ref. 3]	50	CrO_3, H_2SO_4, Br_2, HBr	Teflon Bomb / Oven	5	90	72	22
Darmouth (USA)	Chen and Sharma [ref. 6]	50	CrO_3, H_2SO_4, HBr	Quartz Carius tube / Oven	4	180	40	10;
Darmouth (USA)	Chen and Sharma [ref. 6]	50	CrO_3, H_2SO_4, HBr	Quartz Carius tube / HPA-S	2	300	16	3,
Darmouth (USA)	Chen and Sharma [ref. 6]	50	CrO_3, H_2SO_4, Br_2, HBr	Teflon Bomb / Oven	5	90	72	12.2
WHOI (USA)	Woodhouse et al. [ref. 4]	1500	H_2SO_4, H_2O_2, Br_2, HBr	Distillation Apparatus	1	100	4	120
CRPG / Nancy (FR)	Paul et al. [ref. 5]	50	H_2O_2, H2SO4, Br_2, HBr	Quartz Carius tube / HPA-S	2	250	10	69
CRPG / Nancy (FR)	Paul et al. [ref. 5]	50	CrO_3, H_2SO_4, Br_2, HBr	Quartz Carius tube / HPA-S	2	250	10	202
Open University (UK)	This work	50	CrO_3, H_2SO_4, Br_2, HBr	Teflon Bomb / Oven	5	100	72	14.4
Open University (UK)	This work	50	CrO_3, H_2SO_4, Br_2, HBr	Quartz Carius tube / HPA-S	2	300	12	17.5

Table 3. Os isotopic compositions and concentrations data for North Atlantic 100 m sample under various experimental conditions for the purpose of optimising the duration of oxidation.

Method	Time (hours)	$^{187}Os/^{188}Os$	[Os] (pg/kg)	Blank (%)
Savillex 100°c	10	1.015	5.75	4.8
	24	1.020	7.20	3.8
	48	1.030	10.29	2.7
	72	1.041	9.81	2.9
	96	1.037	10.02	2.8
HPA-S 300°C	3	1.008	6.23	5.3
	5	1.031	7.56	4.4
	8	1.019	8.80	3.8
	12	1.029	9.78	3.5
	15	1.027	9.90	3.4

Table 4 Os isotopic compositions and concentrations for North Atlantic 800 and 1600 m seawater samples under various temperature of oxidation.

Water sample	Temperature (°C)	$^{187}Os/^{188}Os$	2SE	[Os] (pg/kg)	Blank (%)
Depth -800 m					
HPA-S	100	1.002	0.02	6.27	5.3
HPA-S	150	1.021	0.018	7.71	4.3
HPA-S	200	1.006	0.015	8.46	4.0
HPA-S	250	1.028	0.012	9.41	3.6
HPA-S	300	1.039	0.013	9.61	3.5
HPA-S	300	1.024	0.012	9.63	3.5
Depth -1600 m					
HPA-S	100	0.997	0.023	5.57	5.9
HPA-S	150	1.011	0.019	6.82	4.9
HPA-S	200	1.016	0.017	8.05	4.2
HPA-S	250	1.021	0.013	9.56	3.5
HPA-S	300	1.035	0.015	9.72	3.5
HPA-S	300	1.027	0.014	9.95	3.4

Table 5. Os isotopic compositions and concentrations in the North Atlantic seawater profile

Depth (m)	Temperature (°C)	Salinity (‰)	Technique used	$^{187}Os/^{188}Os$	2 S.E.	2 S.E. (%)	[Os] (pg/kg)	$[Os]_N$ (pg/kg)	Blank (%)
-25	8.90	35.23	Teflon bomb@100°C	1.006	0.010	1.02	9.25	9.19	3.0
-25			Teflon bomb@100°C	1.011	0.012	1.19	9.12	9.06	3.1
-25			HPA-S@300°C	1.009	0.012	1.19	8.94	8.88	3.8
-25			HPA-S@300°C	0.996	0.014	1.37	9.50	9.44	3.6
-100	8.81	35.22	Teflon bomb@100°C	1.030	0.013	1.24	10.29	10.23	2.7
-100			Teflon bomb@100°C	1.037	0.014	1.31	10.02	9.96	2.8
-100			Teflon bomb@100°C	1.041	0.009	0.85	9.81	9.75	2.9
-100			HPA-S@300°C	1.029	0.013	1.24	9.78	9.72	3.5
-100			HPA-S@300°C	1.027	0.014	1.40	9.90	9.84	3.4
-300	8.25	35.21	Teflon bomb@100°C	1.016	0.008	0.79	9.54	9.48	2.9
-300			Teflon bomb@100°C	1.026	0.010	0.94	9.75	9.69	3.5
-300			HPA-S@300°C	1.022	0.012	1.17	9.81	9.75	3.4
-800	7.00	35.14	Teflon bomb@100°C	1.020	0.010	0.94	9.95	9.91	2.8
-800			Teflon bomb@100°C	1.034	0.009	0.85	9.81	9.77	2.9
-800			HPA-S@300°C	1.039	0.014	1.39	9.61	9.57	3.5
-800			HPA-S@300°C	1.024	0.014	1.33	9.63	9.59	3.5
-1200	4.40	34.96	Teflon bomb@100°C	1.039	0.009	0.85	9.77	9.78	2.9
-1200			Teflon bomb@100°C	1.028	0.008	0.78	9.56	9.57	2.9
-1200			HPA-S@300°C	1.031	0.012	1.16	9.71	9.72	3.5
-1200			HPA-S@300°C	1.011	0.013	1.27	9.66	9.67	3.5
-1400	3.83	34.92	Teflon bomb@100°C	0.987	0.010	0.97	9.52	9.54	2.9
-1400			HPA-S@300°C	1.002	0.012	1.20	10.00	10.02	3.4
-1600	3.49	34.90	Teflon bomb@100°C	1.026	0.012	1.17	10.23	10.26	2.7
-1600			HPA-S@300°C	1.035	0.015	1.47	9.72	9.75	3.5
-1600			HPA-S@300°C	1.027	0.014	1.40	9.95	9.98	3.4
-1800	3.24	34.89	Teflon bomb@100°C	1.006	0.010	0.95	9.44	9.47	3.0
-1800			HPA-S@300°C	1.018	0.012	1.18	9.68	9.71	3.5
-2000	3.12	34.90	Teflon bomb@100°C	1.022	0.011	1.10	9.75	9.78	2.9
-2000			Teflon bomb@100°C	1.036	0.013	1.24	10.03	10.06	2.8
-2000			Teflon bomb@100°C	1.021	0.009	0.86	9.48	9.51	2.9
-2000			Teflon bomb@100°C	1.032	0.012	1.16	9.94	9.97	2.8
-2000			Teflon bomb@100°C	1.029	0.012	1.17	9.55	9.58	2.9
-2000			Teflon bomb@100°C	1.016	0.009	0.87	9.60	9.63	2.9
-2000			Teflon bomb@100°C	1.024	0.013	1.25	10.03	10.06	2.8
-2000			Teflon bomb@100°C	1.034	0.014	1.39	9.81	9.84	2.9
-2000			Teflon bomb@100°C	1.011	0.013	1.27	9.81	9.84	2.9
-2000			Teflon bomb@100°C	1.036	0.014	1.31	9.76	9.79	2.9
-2000			Teflon bomb@100°C	1.028	0.012	1.17	9.58	9.61	2.9
-2000			HPA-S@300°C	1.013	0.014	1.42	9.75	9.78	3.5
-2000			HPA-S@300°C	1.021	0.013	1.27	9.88	9.91	3.4
-2000			HPA-S@300°C	1.026	0.014	1.40	9.52	9.55	3.5
-2250	3.03	34.95	Teflon bomb@100°C	1.036	0.010	0.93	9.48	9.49	2.9
-2250			Teflon bomb@100°C	1.044	0.012	1.15	9.65	9.66	2.9
-2250			HPA-S@300°C	1.051	0.012	1.14	9.38	9.39	3.6
-2250			HPA-S@300°C	1.048	0.014	1.30	8.92	8.93	3.8
-2592	2.38	34.98	Teflon bomb@100°C	1.051	0.012	1.14	9.78	9.79	2.9
-2592			Teflon bomb@100°C	1.041	0.010	0.92	9.50	9.51	2.9
-2592			HPA-S@300°C	1.038	0.008	0.77	9.69	9.70	3.5
-2592			HPA-S@300°C	1.048	0.013	1.22	10.12	10.13	3.3

Table 6. Results of intercomparison of Os extraction methods on an East pacific seawater profile

						Total procedural blank	
Depth (m)	Origin of the data	Method	$^{187}Os/^{188}Os$	2 S.E.	[Os] (pg/kg)	$^{187}Os/^{188}Os$	[Os] (fg)
104	This work	HPA-S 300	1.014	0.008	7.82	0.18	17.5
459	This work	HPA-S 300	1.036	0.011	9.02	0.18	17.5
603	This work	HPA-S 300	1.054	0.010	11.1	0.18	17.5
2480	This work	HPA-S 300	1.031	0.009	12.35	0.18	17.5
Mean ± 2 S.D			**1.034 ± 0.033 (3.2%)**				
104	This work	Teflon / Br_2	1.002	0.009	7.52	0.20	14.4
459	This work	Teflon / Br_2	1.022	0.009	9.86	0.20	14.4
603	This work	Teflon / Br_2	1.039	0.008	11.61	0.20	14.4
2480	This work	Teflon / Br_2	1.047	0.010	11.21	0.20	14.4
Mean ± 2 S.D			**1.028 ± 0.040 (3.9%)**				
Mean ± 2 S.D	Chen and Sharma [ref.6]	HPA-S 180	1.048 **± 0.038 (3.6%)**			0.34	54.0
Mean ± 2 S.D	Chen and Sharma [ref.6]	HPA-S 300	1.045 **± 0.053 (5.1%)**			0.27	3.60
Mean ± 2 S.D	Chen and Sharma [ref.6]	Teflon / Br_2	1.015 **± 0.095 (9.3%)**			0.19	12.2
Mean ± 2 S.D	Woodhouse et al. [ref.4]	Distillation	1.066 **± 0.040 (3.8%)**			0.31	120

Table 7. Calculated averages of Os isotopic composition and concentration at all investigated depths of IB13 North Atlantic seawater profile.

Depth (m)	Temperature (°C)	Salinity (‰)	$^{187}Os/^{188}Os$	2 S.D.	2 S.D %	Dev$^{\$}$. (%)	[Os] (pg/kg)	$[Os]_N$ (pg/kg)	2 S.D.	2 S.D. (%)	Number of analyses
-25	8.90	35.23	1.005	0.013	1.32	-1.8	9.20	9.14	0.47	5.08	4
-100	8.81	35.22	1.033	0.012	1.15	0.9	9.96	9.90	0.41	4.13	5
-300	8.25	35.21	1.021	0.010	0.99	-0.3	9.70	9.64	0.28	2.91	3
-800	7.00	35.14	1.029	0.018	1.70	0.5	9.75	9.71	0.32	3.29	4
-1200	4.40	34.96	1.027	0.024	2.29	0.3	9.68	9.69	0.18	1.84	4
-1400	3.83	34.92	0.995	0.021	2.13	-2.9	9.76	9.78	0.68	6.97	2
-1600	3.49	34.90	1.029	0.010	0.96	0.5	9.97	9.99	0.51	5.14	3
-1800	3.24	34.89	1.012	0.017	1.68	-1.2	9.56	9.59	0.34	3.56	2
-2000	3.12	34.90	1.025	0.016	1.59	0.1	9.75	9.78	0.37	3.76	14
-2250	3.03	34.95	1.045	0.013	1.24	2.0	9.36	9.37	0.63	6.68	4
-2592	2.38	34.98	1.045	0.012	1.15	2.0	9.77	9.78	0.52	5.31	4
Average whole profile			**1.024**	**0.031**	**3.00**		**9.68**	**9.67**	**0.48**	**4.94**	

[\$] Deviation from the whole average (in %)

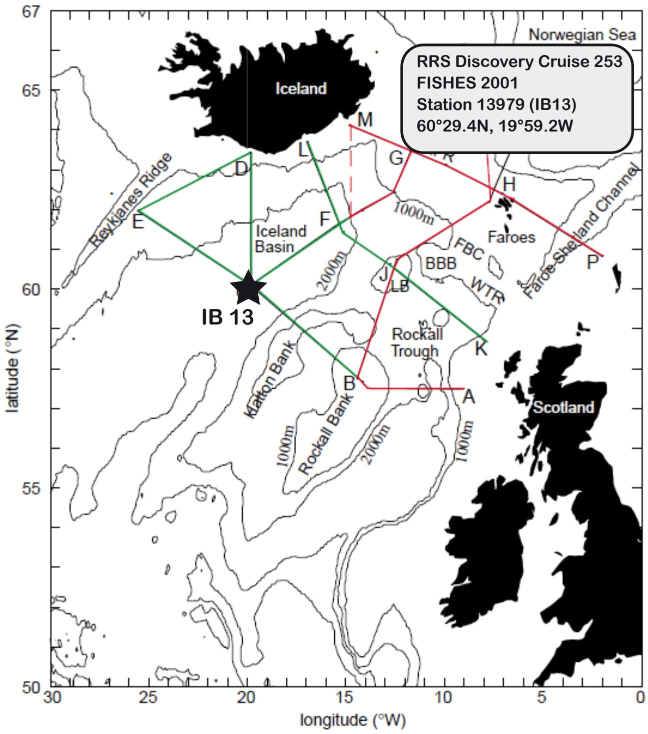

Norwegian Sea
RRS Discovery Cruise 253
FISHES 2001
Station 13979 (IB13)
60°29.4N, 19°59.2W
Iceland
Reykjanes Ridge
Iceland Basin
IB 13
Faroes
Faroe-Shetland Channel
FBC
WTR
BBB
LB
Rockall Trough
Hatton Bank
Rockall Bank
Scotland
1000m
2000m
A
B
D
E
F
G
H
J
K
L
M
P
67
65
60
55
50
30
25
20
15
10
5
0
latitude (°N)
longitude (°W)

Fig. 1

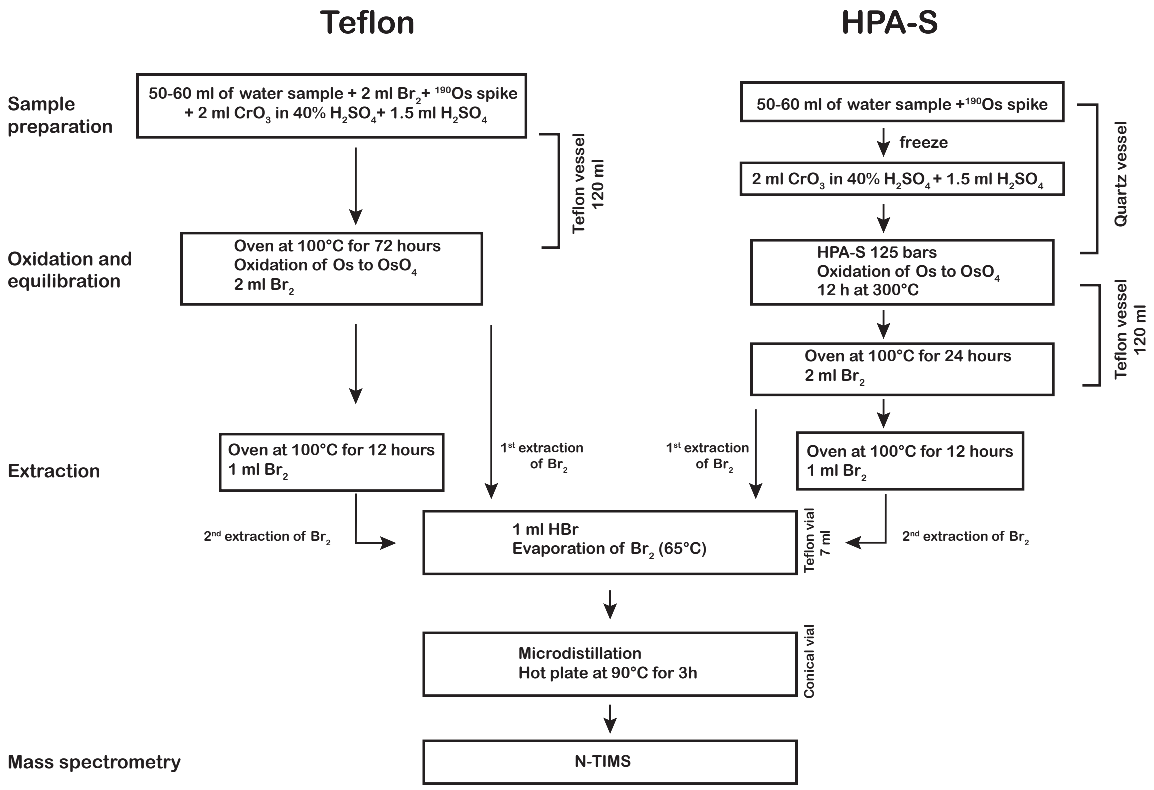
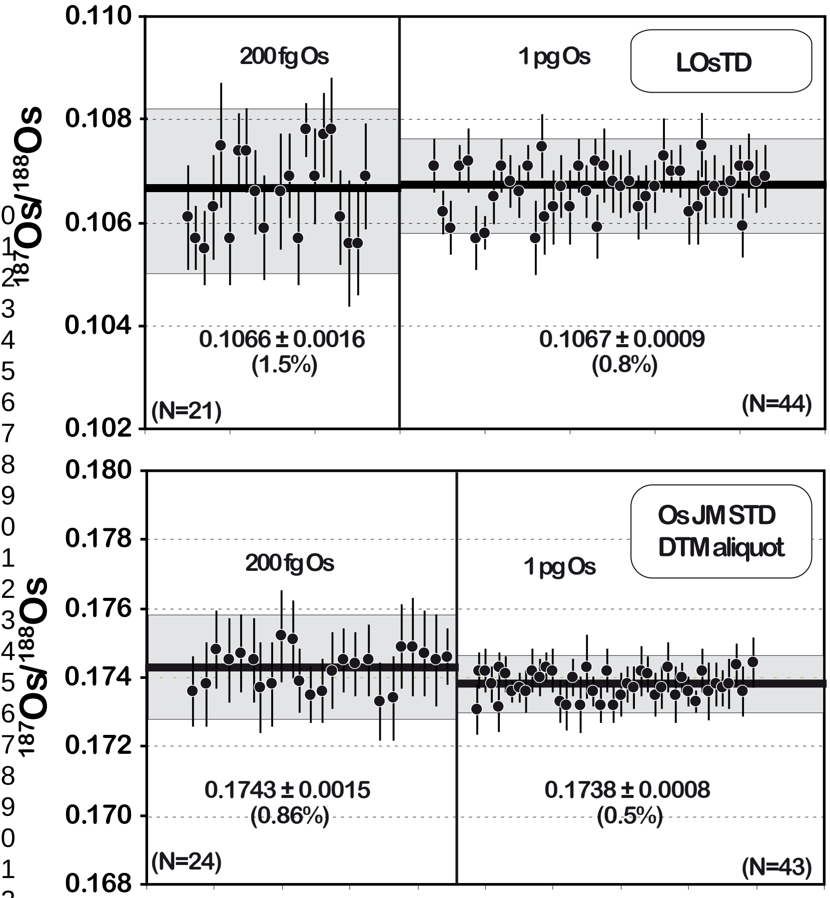

Teflon
HPA-S
Sample preparation
50-60 ml of water sample + 2 ml Br_2 + ^{190}Os spike + 2 ml CrO_3 in 40% H_2SO_4 + 1.5 ml H_2SO_4
Teflon vessel 120 ml
50-60 ml of water sample + ^{190}Os spike
freeze
2 ml CrO_3 in 40% H_2SO_4 + 1.5 ml H_2SO_4
Quartz vessel
Oxidation and equilibration
Oven at 100°C for 72 hours
Oxidation of Os to OsO_4
2 ml Br_2
HPA-S 125 bars
Oxidation of Os to OsO_4
12 h at 300°C
Teflon vessel 120 ml
Oven at 100°C for 24 hours
2 ml Br_2
Extraction
Oven at 100°C for 12 hours
1 ml Br_2
1st extraction of Br_2
1st extraction of Br_2
Oven at 100°C for 12 hours
1 ml Br_2
2nd extraction of Br_2
1 ml HBr
Evaporation of Br_2 (65°C)
Teflon vial 7 ml
2nd extraction of Br_2
Microdistillation
Hot plate at 90°C for 3h
Conical vial
Mass spectrometry
N-TIMS

Fig. 2

Fig. 3


0.110
0.108
0.106
0.104
0.102
^{187}Os/^{188}Os
200 fg Os
1 pg Os
LOsTD
0.1066 ± 0.0016
(1.5%)
0.1067 ± 0.0009
(0.8%)
(N=21)
(N=44)
0.180
0.178
0.176
0.174
0.172
0.170
0.168
^{187}Os/^{188}Os
200 fg Os
1 pg Os
Os JM STD
DTM aliquot
0.1743 ± 0.0015
(0.86%)
0.1738 ± 0.0008
(0.5%)
(N=24)
(N=43)

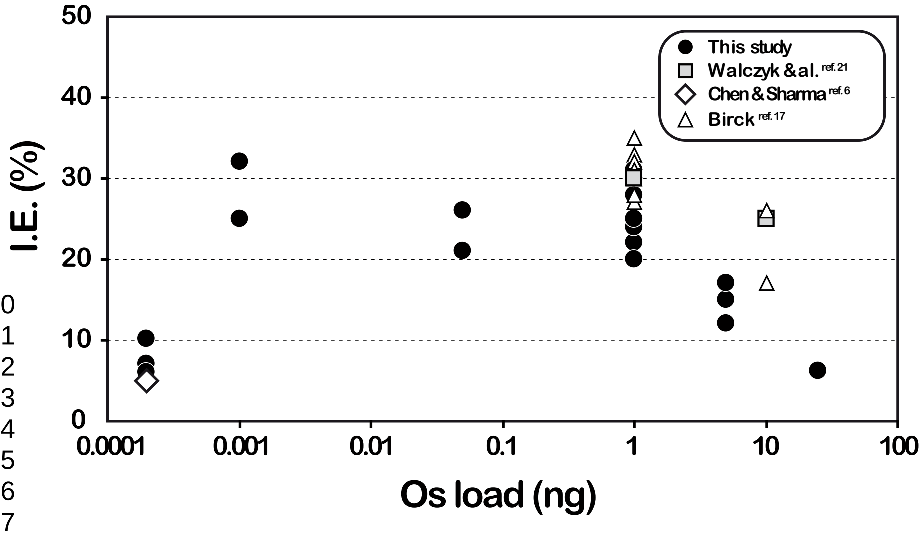

50
40
30
20
10
0
I.E. (%)
0.0001
0.001
0.01
0.1
1
10
100
Os load (ng)
● This study
▨ Walczyk &al. ref. 21
◇ Chen & Sharma ref. 6
△ Birck ref. 17

Fig. 4

Fig. 5

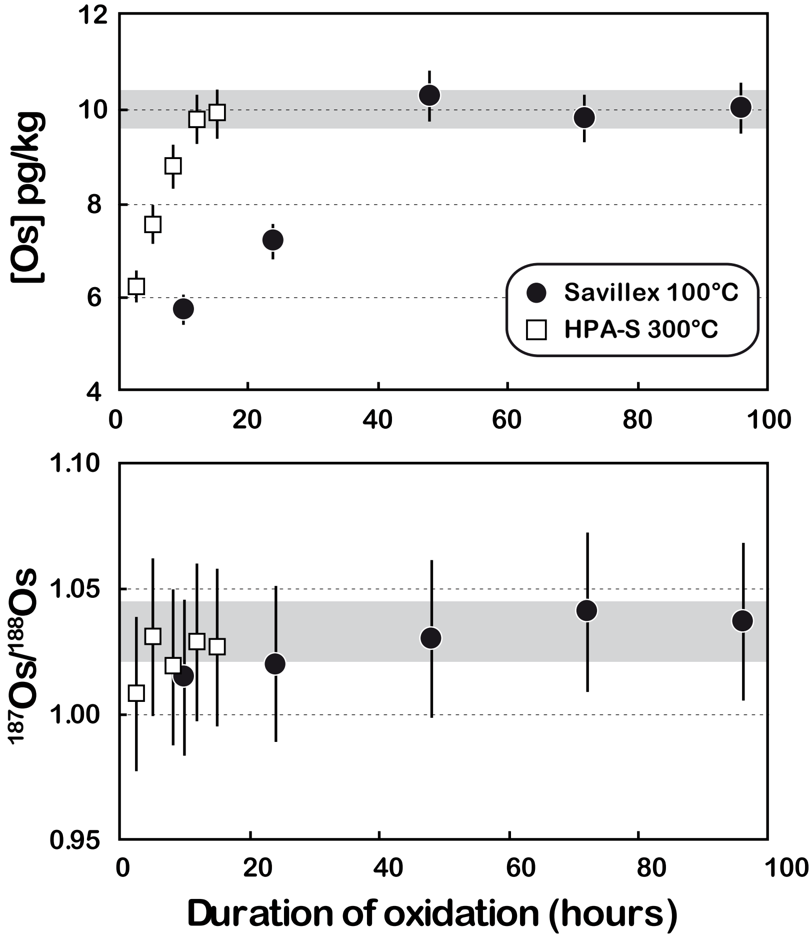
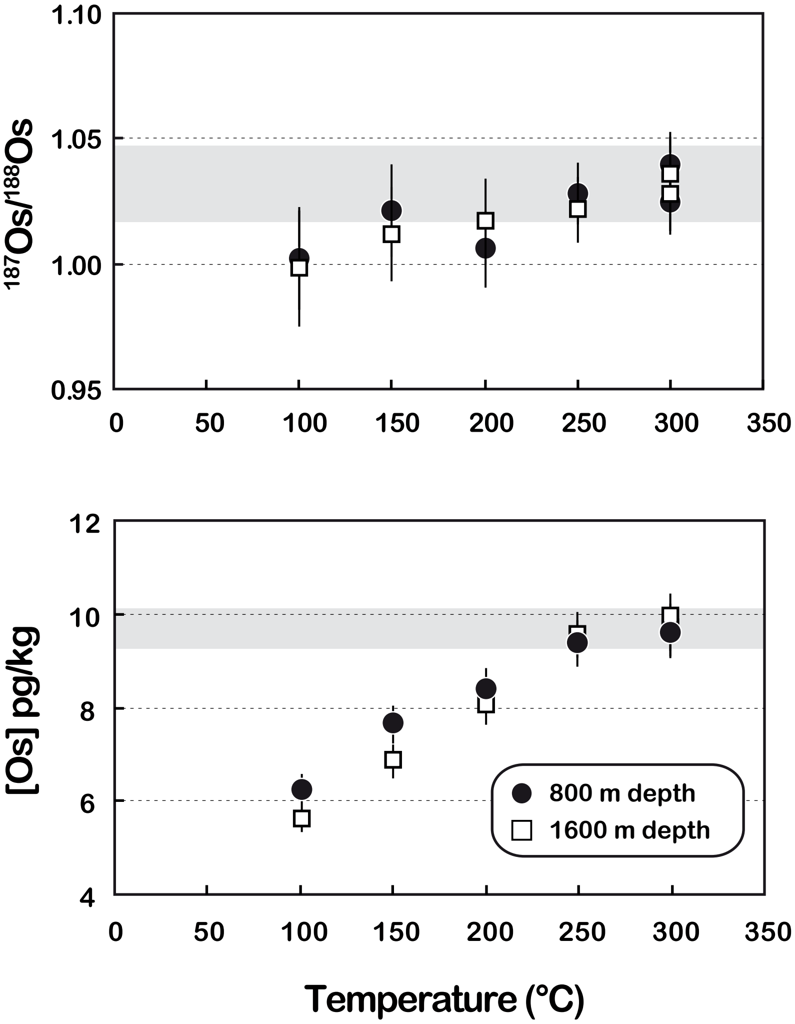

[Os] pg/kg
12
10
8
6
4
0
20
40
60
80
100
● Savillex 100°C
☐ HPA-S 300°C
^{187}Os/^{188}Os
1.10
1.05
1.00
0.95
0
20
40
60
80
100
Duration of oxidation (hours)

Fig. 6



1.10
1.05
1.00
0.95
^{187}Os/^{188}Os
0
50
100
150
200
250
300
350
12
10
8
6
4
[Os] pg/kg
● 800 m depth
□ 1600 m depth
Temperature (°C)

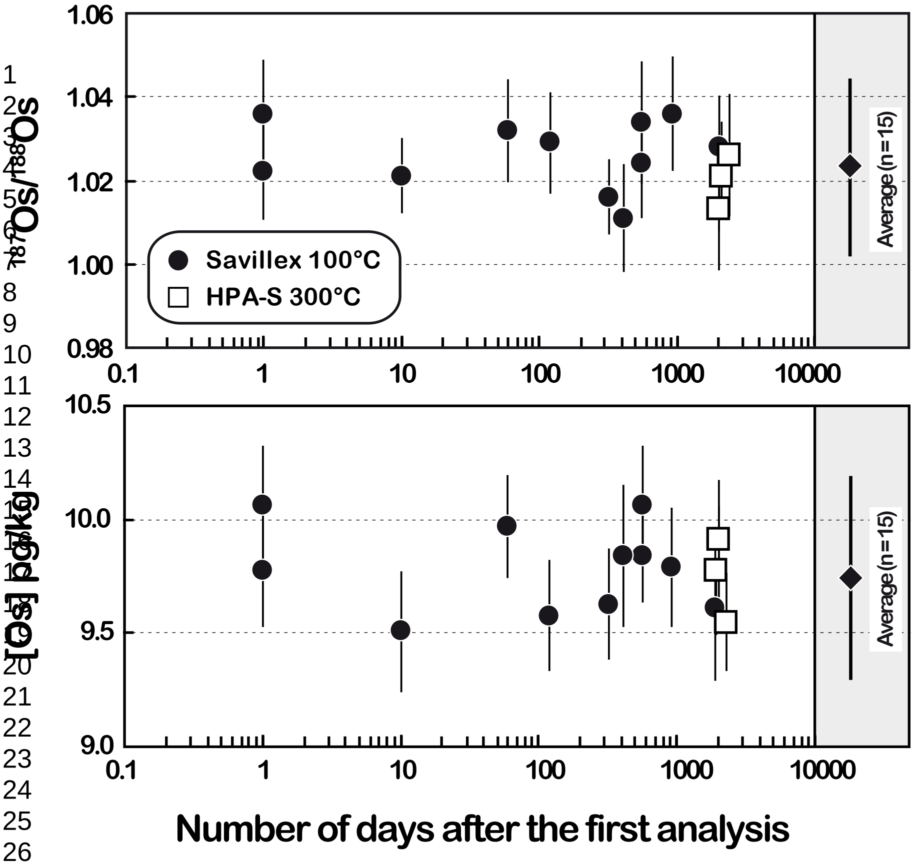

^{187}Os/^{188}Os
1.06
1.04
1.02
1.00
0.98
Savillex 100°C
HPA-S 300°C
Average (n=15)
0.1
1
10
100
1000
10000
[Os] pg/kg
10.5
10.0
9.5
9.0
Average (n=15)
0.1
1
10
100
1000
10000
Number of days after the first analysis

Fig. 7

Fig. 8

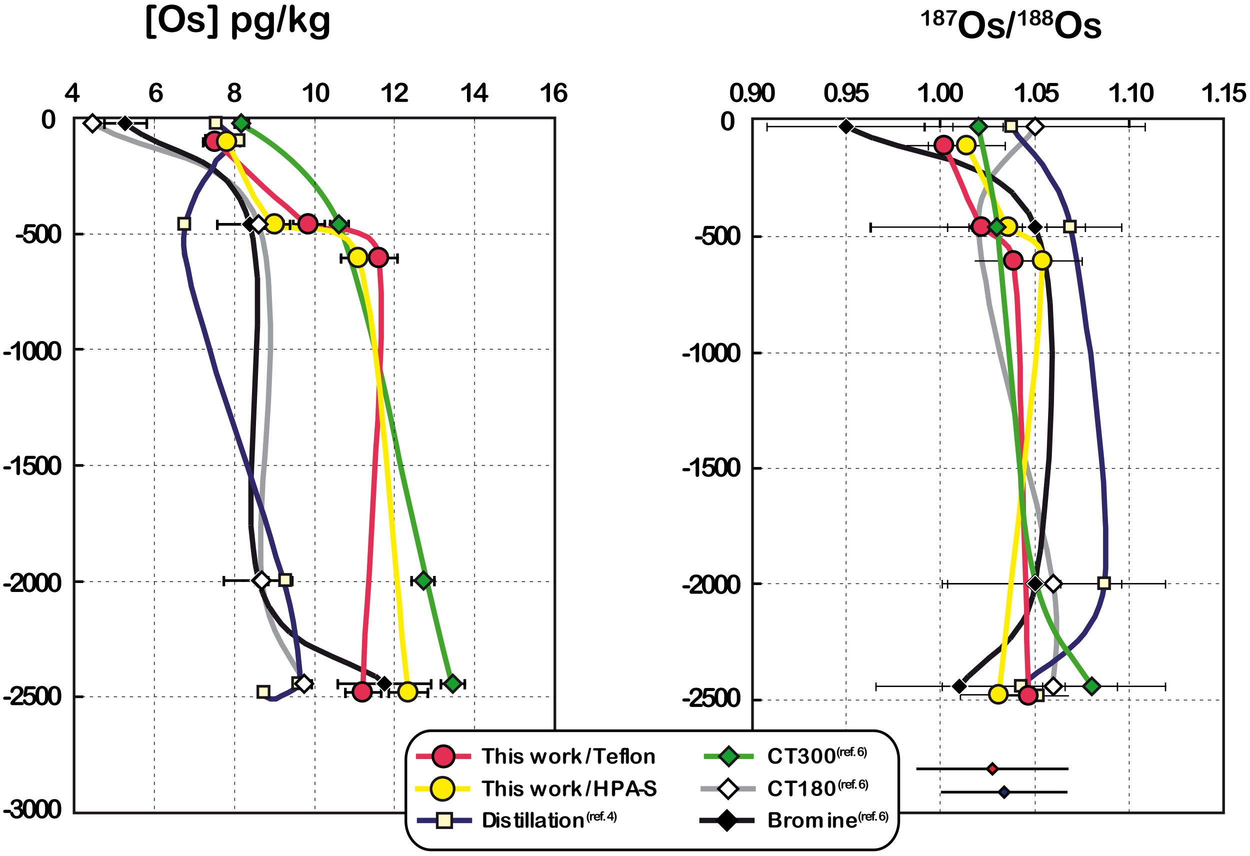
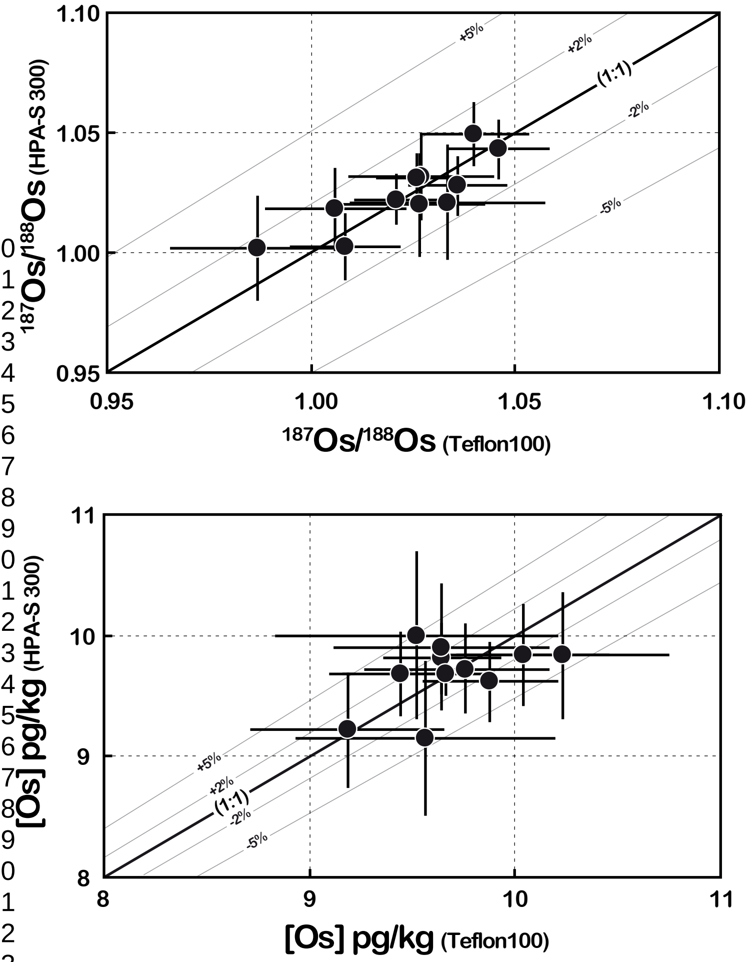

[Os] pg/kg
4
6
8
10
12
14
16
0
-500
-1000
-1500
-2000
-2500
-3000
^{187}Os/^{188}Os
0.90
0.95
1.00
1.05
1.10
1.15
This work/Teflon
This work/HPA-S
Distillation(ref. 4)
CT300(ref. 6)
CT180(ref. 6)
Bromine(ref. 6)

Fig. 9


1.10
1.05
1.00
0.95
+5%
+2%
(1:1)
-2%
-5%
0.95
1.00
1.05
1.10
^{187}Os/^{188}Os (HPA-S 300)
^{187}Os/^{188}Os (Teflon100)
11
10
9
8
+5%
+2%
(1:1)
-2%
-5%
8
9
10
11
[Os] pg/kg (HPA-S 300)
[Os] pg/kg (Teflon100)

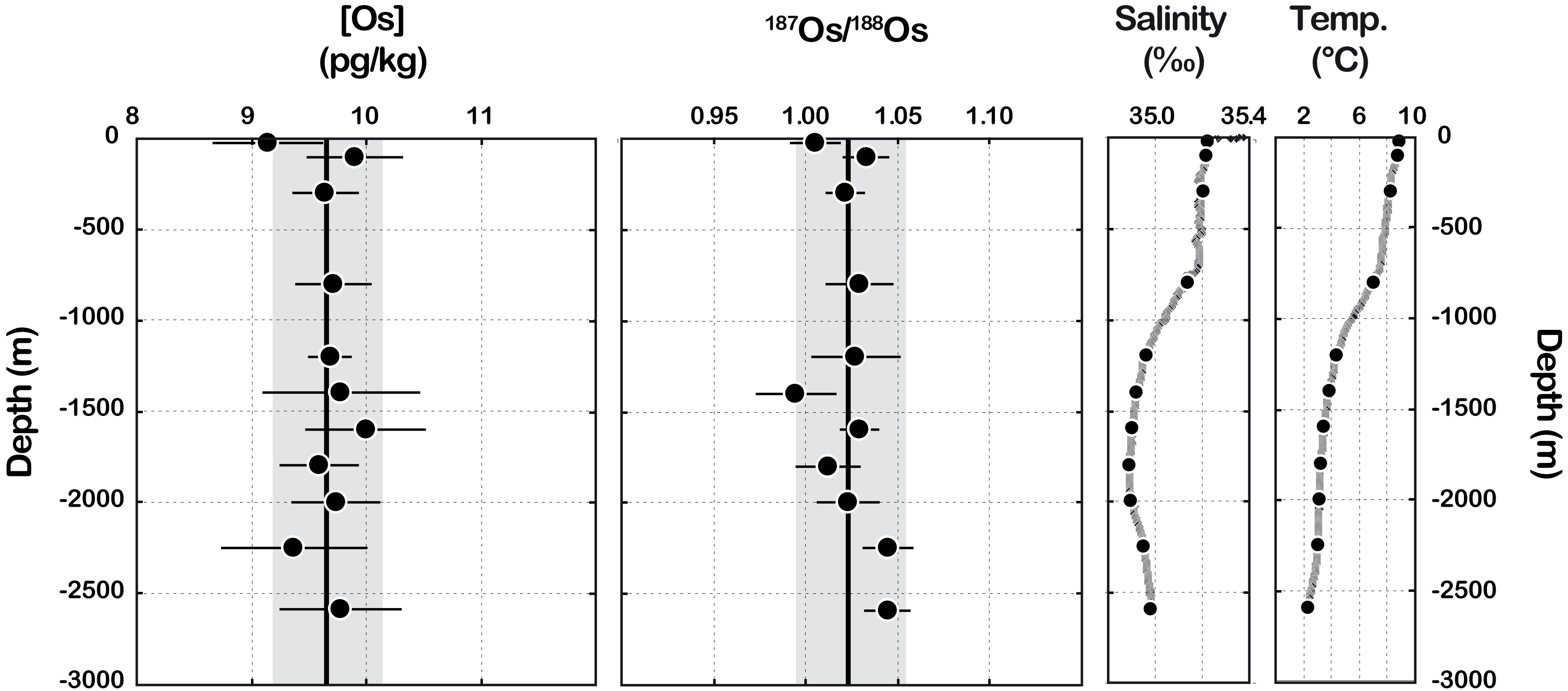

[Os]
(pg/kg)
8
9
10
11
^{187}Os/^{188}Os
0.95
1.00
1.05
1.10
Salinity
(‰)
35.0
35.4
Temp.
(°C)
2
6
10
Depth (m)
0
-500
-1000
-1500
-2000
-2500
-3000
Depth (m)

Fig. 10