LETTER

Rhenium in seawater: Confirmation of generally conservative behavior

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Abstract—A depth profile of the concentration of Re was measured in the Pacific Ocean using a technique
we have developed for the clean chemical separation and the precise measurement of Re by isotope
dilution and negative thermal ionization mass spectrometry (ID-NTIMS). This technique permits Re
concentrations to be determined from 200 mL of seawater with a typical precision of ±5%. This is an
improvement of at least a factor of 100 over the techniques used in previously published determinations
of Re in seawater. We obtain a narrow range for Re from 7.20 ± 0.03 to 7.38 ± 0.03 ng/kg for depths
between 45 m and 4700 m. This demonstrates that Re is relatively well mixed throughout the water
column and confirms the theoretical prediction that the behavior of Re in the oceans is conservative.
When examined in detail, both salinity and the concentration of Re increase by approximately 1.5%
between 400 and 4700 m, a correlation consistent with conservative behavior. However, Re appears to
be depleted relative to salinity by 1.0–1.5% at 100 m, and enriched by approximately 4% at the surface.
These observations suggest a minor level of Re scavenging in near surface waters, and an input of Re to
the ocean surface. This work demonstrates the utility of ID-NTIMS for geochemical investigations of
certain trace elements that have not previously been amenable to detailed study.

INTRODUCTION

The geochemistry of the Platinum Group Elements (PGE) and their periodic table neighbors is poorly understood, despite increasing interest in recent years in the use of these elements as isotopic and elemental tracers, and for geochronometry. This problem is particularly acute in the marine environment, where the surface abundances of Os, Ir, Ru, and Rh are poorly constrained, and their depth profiles are unknown. Depth profiles have been measured for Pt, Pd, and Re (e.g., Pt: GOLDBERG et al., 1986; JACINTO and VAN DEN BERG, 1989; Pd: LEE, 1983; Re: MATTHEWS and RILEY, 1970; OLAFSSON and RILEY, 1977; KOIDE et al., 1987), but these data have raised as many questions as they have answered. For example, the studies of the marine distribution of Pt have each yielded a different trend with depth. The cause of these differences is undetermined.

Uncertainty has also surrounded the marine geochemistry of Re. The concentration of Re in oxygenated seawater is expected to be fairly uniform with depth, as the stable form of Re in these waters should be the perrhenate anion, ReO₄⁻ (BRULAND, 1983; BROOKINS, 1986). Thus, the behavior of Re should be conservative in seawater. This expectation is consistent with the apparent enrichment of Re in seawater relative to its periodic table neighbors (KOIDE et al., 1987), which suggests that Re has an extremely long residence time in the oceans (GOLDBERG et al., 1988). However, the published measurements of the concentration of rhenium in seawater indicate a range of approximately 3 to 11 ng/kg (SCADDEN, 1969; OLAFSSON and RILEY, 1972; MATTHEWS and RILEY, 1970; KOIDE et al., 1987). These variations probably reveal a lack of precision and sensitivity in the analytical methods used, so that the content of Re in seawater is determined by these data to no better than a factor of three.

Our understanding of the geochemistry of Re and the PGE is limited largely by their low abundances and, until recently, the lack of analytical techniques which are sensitive, precise, and accurate enough to obtain reliable abundance measurements. The application of NTIMS to these elements (ZEININGER, 1984; DELMORE, 1987; HEUMANN, 1988; VÖLKENING et al., 1991; CREASER et al., 1991) introduced a highly sensitive new tool for their study. In order to resolve the problem of the Re concentration of seawater and its distribution with depth, we have applied ID-NTIMS to the study of Re in a Pacific Ocean profile.

SAMPLING AND ANALYSIS

Seawater samples were collected in January 1992, on the HOT-33 cruise (R/V Woman) at Station Aloha, approximately 100 km north of Oahu (22.5°N, 158.5°W). Nine samples were collected using PVC Niskin bottles with Teflon-coated internal springs, lowered on a steel cable. One sample (at 45 m) was collected using a Go-Flo bottle on a Kevlar line. Pressure, temperature, conductivity, and dissolved oxygen were monitored continuously using a conductivity-temperature-depth probe (CTD) and an oxygen sensor (KARL and WINN, 1991). The depth, salinity, and oxygen data reported in this study were derived from the CTD and oxygen sensor data (Table 1; D. Karl and R. Lukas, pers. commun.). After recovery, all samples were filtered within 48 h through 0.2 μm nitrocellulose filters using a peristaltic pump, then acidified by adding 2 mL of 12 N HCl to each liter of seawater, and stored in acid-washed high density polyethylene bottles for later analysis.

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TABLE 1. Re concentrations in the Pacific Ocean

<table>
<thead>
<tr>
<th>Sample</th>
<th>Depth (m)</th>
<th>Re (ng/kg)</th>
<th>ReN (ng/kg)</th>
<th>Salinity</th>
<th>Oxygen (μmol/kg)</th>
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<tbody>
<tr>
<td>6(a)</td>
<td>7.70</td>
<td>7.50</td>
<td>0.07</td>
<td>35.002</td>
<td>205.4</td>
</tr>
<tr>
<td>45</td>
<td>7.66</td>
<td>7.35</td>
<td>0.03</td>
<td>35.006</td>
<td>205.4</td>
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<tr>
<td>51</td>
<td>7.25</td>
<td>7.35</td>
<td>0.03</td>
<td>35.089</td>
<td>205.4</td>
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<tr>
<td>100</td>
<td>7.04</td>
<td>7.39</td>
<td>0.03</td>
<td>34.108</td>
<td>154.3</td>
</tr>
<tr>
<td>402(a)</td>
<td>7.20</td>
<td>7.39</td>
<td>0.03</td>
<td>34.104</td>
<td>154.3</td>
</tr>
<tr>
<td>402(b)</td>
<td>7.24</td>
<td>7.43</td>
<td>0.03</td>
<td>34.653</td>
<td>111.6</td>
</tr>
<tr>
<td>749</td>
<td>7.30</td>
<td>7.44</td>
<td>0.03</td>
<td>34.354</td>
<td>26.8</td>
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<tr>
<td>1489</td>
<td>7.31</td>
<td>7.40</td>
<td>0.03</td>
<td>34.361</td>
<td>62.5</td>
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<tr>
<td>2188</td>
<td>7.32</td>
<td>7.40</td>
<td>0.03</td>
<td>34.622</td>
<td>74.8</td>
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<tr>
<td>2800(a)</td>
<td>7.34</td>
<td>7.41</td>
<td>0.03</td>
<td>34.653</td>
<td>111.6</td>
</tr>
<tr>
<td>2800(b)</td>
<td>7.36</td>
<td>7.44</td>
<td>0.03</td>
<td>34.645</td>
<td>138.4</td>
</tr>
</tbody>
</table>

ReN is the Re concentration normalized to 35 % salinity. The uncertainty of each measurement is derived from uncertainties in the measured 249/251 ratio, tracer concentration, and all gravimetric determinations, (see text). Replicate samples (6, 402 and 2800 m) were processed separately, and indicate that the analytical variability was within the uncertainties of the individual measurements. Samples 6 (a), and 2800 (b) were spiked using the Dil-2 tracer. All other samples were spiked with Dil-1.

Accurately weighed 200 mL fractions from all samples, except for the 6 m sample, were spiked with a 188Re-enriched tracer solution approximately 3 months after collection. The 6 m sample was spiked aboard ship, following filtration and acidification. In all spiked solutions, the measured 188Re/187Re ratio was close to the optimal value needed to minimize the error propagation factor. After the addition of the tracer, the solutions were periodically shaken and stirred over 24-48 h, which was deemed sufficient time for complete equilibration of the Re isotopes, since Re is presumed to be present as ReO42−. The isotopic composition of the tracer solutions was determined by NTIMS in our laboratory ('188/187Re = 37.14 ± 0.04). The uncertainty of this measurement is only a reflection of the uncertainty in the relative ionization efficiency for both samples and standards than was possible using other Ba salts, such as Ba(NO3)2 or Ba(OH)2 (CREASER et al., 1991; HEUMANN, 1988). The ionization efficiency for Re standards was 20%. The ionization efficiency was lower for separated samples due to the presence of organic material in the final load, and ranged from 1 to 10% for the samples analyzed in this study.

Rhenium was separated from the seawater samples by anion exchange chromatography using two small Teflon columns (e.g., HUFFMAN et al., 1956). Primary separation was used to concentrate 200 μL Bio-Rad AG1-X8, 100-200 mesh resin, onto which ReO42− was adsorbed directly from the spiked, acidified seawater. The column was rinsed with 10 ml ultrapure H2O, followed by 650 μL 4 N HNO3 to remove Mo and W. These elements are both present as oxyanions in seawater at concentrations much lower than 21.5% amu−1, consistent with mass dependent isotope fractionation associated with sample depletion. No other drift was observed (e.g., as would be obtained from a variable filament blank), even when beam intensities were increased by an order of magnitude under different operating conditions. Replicate analyses of samples at 6 m, 402 m, and 2800 m were in agreement to ±3% (Table 1), consistent with this source of uncertainty. The close agreement of the two 2800 m fractions, spiked with different tracer solutions, indicates that the calibrations of the Dil-1 and Dil-2 tracer solutions are well within the analytical uncertainties.

An uncertainty propagation calculation was made for each sample, including the uncertainties in all gravimetric measurements, as well as the uncertainties in the concentration and isotopic composition of the Re tracer solution, and the uncertainty in the isotopic composition of the standard Re. An uncertainty of ±3% was assigned to the measured isotopic ratio of each spiked sample, due to the mass-fractionation uncertainty discussed above. An uncertainty of ±50% was assigned to the 3 pg chemical blank. The cumulative uncertainties from these sources (at 95% confidence) are reported in Table 1, and

The chemically separated Re was loaded using polyethylene tubing on a microsyringe, onto a high purity Pt filament on which Ba had been loaded as BaSO4 (used to enhance negative ion emission), and analyzed in a Lytac mass spectrometer configured for negative ions (WASSERBURG et al., 1969; CREASER et al., 1991). When prepared as a fine precipitate, BaSO4 forms an even coat on the filament, on which the sample may be easily loaded. The BaSO4 was found to provide a reproducible and efficient method of obtaining a higher ionization efficiency for both samples and standards than was possible using other Ba salts, such as Ba(NO3)2 or Ba(OH)2 (CREASER et al., 1991; HEUMANN, 1988). The ionization efficiency for Re standards was 20%. The ionization efficiency was lower for separated samples due to the presence of organic material in the final load, and ranged from 1 to 10% for the samples analyzed in this study.

Re was analyzed as ReO42− at masses 249 and 251, and the ion intensity at 251 was corrected for the contribution from 188ReO42− using 188O/16O = 0.002085 to obtain the ratio 188/187Re. This 188O/16O ratio has been measured directly for normal Re, using the 187ReO42− ion beam (CREASER et al., 1991). The contribution from 188ReO42− at mass 251 is negligible. When running seawater samples, ion currents corresponding to 10−10 counts per second (equivalent to ~6−10−11 A) were measured. Hence, 249 and 251 were maintained for approximately 30−40 min on a Faraday collector, at filament temperatures of 840−890°C, as determined by an optical pyrometer.

To determine the level of the ion current due to background contamination, BaSO4 was loaded on a filament without any sample or tracer. Ion currents corresponding to 10−10−10−11 counts per second (equivalent to ~6−10−11 A) were measured. Hence, 249 and 251 were maintained for approximately 30−40 min on a Faraday collector, at filament temperatures of 840−890°C, as determined by an optical pyrometer.

In order to establish the level of the filament blank under controlled conditions, we loaded 36 pg of Re tracer on a Pt filament with BaSO4, and obtained a stable signal at mass 249 equivalent to ~10−10 counts per second (equivalent to ~6−10−11 A) at filament temperatures of 840−890°C. The initial ion current of 10−10−10−11 A was measured and recorded, and the filament was allowed to run for 30−40 min. The ion currents were measured at approximately 3% of the initially loaded Re tracer had been ionized and detected (determined by integration of the ion beam intensities over time). If a constant, but initially unknown, blank contribution to the measured ion beam intensities is present, the ion currents measured from this experiment can be used to determine the magnitude of the blank contribution. This contribution corresponds to ~5 × 10−3 counts per second at mass 251.

The Re blank contributions determined from these two experiments are in general agreement. It follows that for our current generation of "clean" Pt filaments, the background current, using BaSO4 as the emitter, corresponds to ~10−10−10−11 counts per second at mass 251. This low level of Re blank has broad applicability in Re−Os geochemical studies.

During analyses of seawater samples, the observed drift in the measured ratios led to a typical uncertainty in these ratios of less than ±1.5% amu−1, consistent with mass dependent isotope fractionation associated with sample depletion. No other drift was observed (e.g., as would be obtained from a variable filament blank), even when beam intensities were increased by an order of magnitude under different operating conditions. Replicate analyses of samples at 6 m, 402 m, and 2800 m were in agreement to ±3% (Table 1), consistent with this source of uncertainty. The close agreement of the two 2800 m fractions, spiked with different tracer solutions, indicates that the calibrations of the Dil-1 and Dil-2 tracer solutions are well within the analytical uncertainties.

An uncertainty propagation calculation was made for each sample, including the uncertainties in all gravimetric measurements, as well as the uncertainties in the concentration and isotopic composition of the Re tracer solution, and the uncertainty in the isotopic composition of the Re sample. An uncertainty of ±3% was assigned to the measured isotopic ratio of each spiked sample, due to the mass-fractionation uncertainty discussed above. An uncertainty of ±50% was assigned to the 3 pg chemical blank. The cumulative uncertainties from these sources (at 95% confidence) are reported in Table 1, and
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FIG. 1. The concentration of Re at various depths in the Pacific Ocean. The solid circles are data from this study; other points are from KOIDE et al. (1987). Our samples were taken at 22°N 158°W. Other samples were taken at 33°N 139°W (open circles); 35°N 122°W (triangles), and 35°N 138°W (crosses).

were typically within ±5%. This is consistent with mass fractionation as the primary source of uncertainty for most samples.

RESULTS AND DISCUSSION

The results are shown in Table 1. The Re concentrations are presented both as direct determinations, and on a salinity-normalized basis (normalized Re, Re_{sal} = Re_{sample} \times 35/saline salinity). A comparison of the depth profile determined in this study with the Pacific Ocean profiles of KOIDE et al. (1987) is shown in Fig. 1. In contrast to the previous studies, our data clearly demonstrate that the concentration of Re is essentially constant with depth, and that the chemistry of Re is generally conservative, as was predicted on thermodynamic grounds (BRULAND, 1983; BROOKINS, 1986). This result is consistent with less precise recent measurements using isotope dilution–inductively coupled plasma mass spectrometry (ICP-MS), which yield marine profiles that are uniform with depth to within ±4% (COLODNER, 1991).

The consistency of our data is a significant improvement over the previous measurements of Re in seawater. Our best estimate of the average Re concentration of seawater is 7.31 ± 0.11 ng/kg, or 7.42 ± 0.04 ng/kg on a salinity-normalized basis. These values were obtained by averaging all the data below 400 m, where the salinity-normalized Re concentrations are most uniform. The uncertainties are ±2σ of the data used to calculate the averages. The samples from depths shallower than 400 m appear to deviate somewhat from conservative behavior, but it is not clear whether these deviations represent actual variations in the concentration of Re in the water column (see the following text and Fig. 2). Thus, these measurements are omitted from the best estimate. Table 2 compares our best estimate of the concentration of Re in seawater with the corresponding estimates from other studies. Our determination is within the wide range of the analyses of SCADDEN (1969), MATTHEWS and RILEY (1970), and KOIDE et al. (1987), but is substantially higher than the value from the Atlantic Ocean study of OLAFSSON and RILEY (1972). As suggested by KOIDE et al. (1987), we suspect that the uncertainties in these earlier studies are due, in large part, to variability in the yields of the chemical separation of Re from seawater. A systematically low yield could also explain the shift between our average value and that of OLAFSSON and RILEY (1972). Since, in our isotope dilution analyses, the tracer was added prior to chemical separation, yield uncertainties were not a source of error, as long as the sample and tracer isotopes equilibrated. The reproducibility of our data provide support that this was the case.

Our average seawater value is significantly lower than the best estimate by COLODNER (1991) of 8.19 ± 0.37 ng/kg.
reported on a salinity normalized basis with 2σ uncertainty. There appears to be a systematic offset between our data and those of Colodner (1991). This discrepancy may in part be due to the fact that the results of this study are based on filtered seawater samples, as compared to the unfiltered samples used by Colodner (1991). For example, Krishnaswami et al. (1981) and Cochran et al. (1983, 1990) have shown that a significant fraction of the $^{210}$Pb in seawater is bound to particles. This is true for many trace elements (e.g., Bruland, 1983; Whitfield and Turner, 1987). However, if this mechanism alone were to account for the discrepancy between the data sets, it would indicate a much greater reactivity of Re than is implied by the general uniformity of Re concentrations with depth. Further work is needed to determine the source of the discrepancy, and whether differences in acidification or storage procedures are important.

It should be noted that some of the previous studies included data from several locations (see Table 2). Thus, some of their variability could be due to real geographical variations in the Re content of seawater. We believe such variability is unlikely, however, due to the apparently conservative behavior of Re, as illustrated in Fig. 1, and because, for the less precise earlier work, there appears to be as much variability within a depth profile at one location as there is between samples collected at different sites (see, especially, Koide et al., 1987).

The precision of our data allows detail in the Re profile to be resolved for the first time. The Re concentration decreases from a value of 7.34 ± 0.04 ng/kg at 4705 m to an average value of 7.22 ± 0.04 at 402 m, and then rises to an average of 7.69 ± 0.07 at 6 m (Fig. 2a). The decrease in the Re concentration between 4705 and 402 m is comparable to the percent decrease in salinity over the same depth range (≈1.5%), which is consistent with conservative behavior. However, at 100 m, the Re concentration does not exceed the deep-water value, although there is a pronounced salinity maximum at this depth. A good correlation with salinity should be reflected in a Re concentration of ~7.4 ng/kg at 100 m (Fig. 2b). Although the sampling was not ideally spaced at these depths, this predicted value is nearly 1.0-1.5% higher than the average of the measured values at 100 m, and, therefore, should be detectable well within our analytical uncertainty. The salinity-normalized data suggest that the 51 m sample may also be somewhat depleted in Re relative to the deep waters, although this variation is within the uncertainties of the measurements. The surface enrichment is reflected only in the 6 m sample, and persists in the salinity-normalized data. The measured Re concentration at the surface is ≈4% higher than the average of the other samples, which is well above the analytical uncertainties.

These observations suggest that while the behavior of Re is essentially conservative, its distribution may be modified by two types of processes. The first process is a slight depletion due to biological or inorganic scavenging near the surface, and subsequent regeneration at depth; this mechanism could account for the apparent depletion at 100 m. The second process is an input of possibly anthropogenic Re to the ocean surface, probably via the atmosphere, which could be reflected in the surface Re enrichment. This mechanism is analogous to that observed for lead (Schaule and Patterson, 1981).

The interpretation of small variations in the Re concentration calls for caution, however, due to potential problems of Re contamination during sample collection, or removal of dissolved Re from solution during sample storage. Although the possibility of contamination cannot be ruled out, particularly for samples from shallow depths, the fact that the samples from 45 and 51 m are identical within errors, despite being collected using different types of sampling equipment, indicates that there was little or no Re contamination from the sampling procedure itself. As for Re removal during storage, it is possible that a small, but detectable, quantity of Re was lost due to adsorption on the walls of the polyethylene bottles, or reduction of ReO₄ following addition of HCl to these samples (Cotton and Wilkinson, 1988). This interpretation would demand that a nearly constant amount of Re was lost from most of the samples, to account for the uniformity of the salinity-normalized values below 402 m. Although this seems unlikely, it could account for the apparent enrichment of the 6 m sample, which was spiked aboard ship soon after sample collection, as well as the non-conservative behavior of the 100 m sample. Clearly, further work is needed to ascertain the importance of such sample collection and storage processes before these data are interpreted to the limits of the analytical precision.

These problems notwithstanding, our data confirm that Re is among the more conservative of elements in seawater, as exemplified by its relatively constant concentration with depth. These results also demonstrate that the refined chemical techniques described above, coupled to the ID-NTIMS technique, have the potential to improve substantially our understanding of the geochemistry of trace elements previously studied only with difficulty. We are currently extending this approach to the study of several platinum group elements in seawater.

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<table>
<thead>
<tr>
<th>Location</th>
<th>Re (ng/kg)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pacific Ocean</td>
<td>7.42 ± 0.04</td>
<td>(a) This study</td>
</tr>
<tr>
<td>Pacific Ocean</td>
<td>9.1 ± 4.4</td>
<td>(b) Koide et al., 1987</td>
</tr>
<tr>
<td>Pacific Ocean</td>
<td>8.4 ± 2.4</td>
<td>(c) Scaddon, 1969</td>
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<td>Atlantic Ocean</td>
<td>4.0 ± 2.1</td>
<td>(d) Olafsson and Riley, 1972</td>
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<tr>
<td>Atlantic Ocean</td>
<td>6.9 ± 2.1</td>
<td>(e) Matthews and Riley, 1970</td>
</tr>
<tr>
<td>Average Ocean</td>
<td>8.19 ± 0.37</td>
<td>(f) Colodner (1991)</td>
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</tbody>
</table>

Depth profiles were measured in all studies except (c), which included only surface samples. In (b) and (d), no data at depths shallower than 200 m were obtained. Studies (b), (c), (d) and (f) included samples from more than one location. Uncertainties in (b), (c) and (f) were reported by the authors as ±1σ of the measurements, but have been converted to ±2σ for comparison with this study. No uncertainty estimates were included in (d) and (e); by analogy to (b) and (c), we have calculated their uncertainties as ±2σ. Our average, (a), includes all measurements below 400 m, and the uncertainty is reported as ±2σ of these values. Average values from studies (a) and (f) are reported on a salinity-normalized basis.
kindly provided unpublished data from the HOT-33 cruise. We appreciate the helpful comments of K. K. Turekian and a second, anonymous reviewer. This work has been supported by NASA grant NAG 9-43 and NSF grant OCE 9018534. Ship time on the R/V Wecoma was supported by NSF grants OCE-8800329 (D. Karl) and OCE-8717195 (R. Lukas). Division contribution No. 5159 (777).

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REFERENCES


