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The geochemical cycle of rhenium: a reconnaissance

Debra Colodner [a], Julian Sachs [b], Gregory Ravizza [b], Karl Turekian [c], John Edmond [d] and Edward Boyle [d]

[a] *Lamont-Doherty Earth Observatory of Columbia University, Palisades, NY 10964, USA*
[b] *Woods Hole Oceanographic Institution, Woods Hole, MA 02543, USA*
[c] *Department of Geology and Geophysics, Yale University, New Haven, CT 06511, USA*
[d] *Earth, Atmospheric and Planetary Sciences, Massachusetts Institute of Technology, Cambridge, MA 02139, USA*

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ABSTRACT

Rhenium (Re) is one of a suite of elements (including uranium and molybdenum) that display conservative behavior in seawater and are enriched in anoxic sediments. The decay of ^{187}Re to ^{187}Os provides a geochronometer in ancient sedimentary rocks and gives rise to Os-isotopic variations in nature. In order to better characterize its sources to seawater, Re was measured in three major rivers (Amazon, Orinoco, Ganges–Brahmaputra) and some of their tributaries. Re concentrations span four orders of magnitude (from < 0.02 to 400 pmol/kg), with the highest concentrations found in rivers draining black shales in the Venezuelan Andes. Mainstream Re levels in the three rivers are between 1 and 10 pmol/kg, with a flux weighted average of 2.3 pmol/kg. The residence time for Re in the oceans is estimated to be 750,000 yr with respect to river inputs.

Re profiles from the Atlantic and Pacific Oceans confirm that Re behaves conservatively in seawater, with no significant uptake onto particles and/or recycling within the water column. This is also true in the anoxic water column of the Black Sea. Re removal into anoxic sediments occurs at or below the sediment water interface, as demonstrated in sediment pore waters from Chesapeake Bay. In oxic sediments, Re is not cycled with manganese oxides, and it is not enriched in very slowly accumulating pelagic sediments with a large hydrogenous iron and manganese component, or in manganese nodules. Burial of Re in anoxic sediments, which accumulate on 0.3% of the ocean floor, removes approximately 50% of the riverine Re flux to the oceans. Hence, oceanic Re concentrations may be very sensitive to changes in the area of anoxic sedimentation.

1. Introduction

The marine geochemistry of rhenium (Re) has attracted interest in recent years due to its extreme enrichment in reducing sediments compared to oxic sediments and the utility of the rhenium–osmium geochronometer for dating ancient sedimentary rocks [1,2]. Rhenium, element number 75, is one of the rarest elements in the Earth's crust, with concentrations generally lower than 0.5 ppb [3]. Despite this low crustal abundance, Re occurs in relatively high concentrations in seawater due to the solubility of the oxyanion, ReO_4^-, in oxidizing aqueous environments. Based on parallels between the chemistries of Re and molybdenum (Mo), Koide et al. [4] predicted that Re should have a long residence time in seawater and display conservative behavior (covary with salinity). Anbar et al. [5] recently confirmed that Re is indeed one of the few trace elements that display nearly conservative behavior in the oceans.

Re is removed from solution under anoxic conditions, leading to its strong enrichment in reducing marine sediments. Re concentrations in modern anoxic sediments were surveyed by Koide et al. [1] and Ravizza et al. [6], who found concentrations ranging from 5 to 130 ppb in various environments, with an average of 30 ppb (weighted for accumulation rate and depositional area). Koide et al. [1] also measured Re in oxic pelagic clays and manganese nodules, and found concentrations less than 0.1 ppb, less than or equal to crustal values. Although anoxic sediments have been found to contain enhanced concentrations of many metals, Re is unmatched in the degree of its enrichment. For example,

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molybdenum and uranium, whose geochemistries show many similarities to that of Re, are enriched in anoxic over oxic sediments by factors of 10 to 50, whereas this enrichment for Re is about a factor of 300.

The more abundant of the two Re isotopes, ^{187}Re, decays to ^{187}Os (β^-) with a half-life of about 46 billion years. Because nearly all the Re in organic-rich sediments is accumulated from seawater at or close to the time of deposition (i.e., an insignificant amount is in detrital minerals), the Re–Os clock may be used to determine sediment ages. The age calculation requires certain assumptions and preconditions: the system (bulk sediment) must remain closed with respect to Re and Os, the initial Re/Os ratio of the sediment must be heterogeneous, and the initial $^{187}Os/^{186}Os$ ratio must be homogeneous. Ravizza and Turekian [2] successfully applied this technique to Mississippian and Devonian black shales (200–400 Ma old), although they noted scatter in the data from some of the sites which they suggested might be attributed to post-depositional mobility of Re and/or Os. The conditions under which Re might be mobile, and the origin of variable Re/Os ratios are not well-understood.

The magnitude and specificity of its enrichment in anoxic sediments suggests that Re might also be utilized to determine the environment of deposition of organic-rich sediments in the geologic record. Although there is a range of Re concentrations in reducing sediments (from 6 ppb in Saanich Inlet to 96 ppb on the Chile Shelf [1]), it is not yet clear which environmental parameters determine these concentrations, and whether the level of enrichment may be used to reconstruct environmental conditions.

Additionally, Re may be studied as an analog for technecium, which occurs just above Re in the periodic table, and has only unstable isotopes and no natural sources. The two elements have strikingly similar chemistries [7]. Technecium has been introduced into the environment by nuclear weapons testing and in nuclear reactor wastes. ^{99}Tc (produced by fission of ^{235}U) raises environmental concern due to its relatively long half life (2.13×10^5 yr) and the solubility of TcO_4^- under surface conditions.

The application of Re to geochronology, and to paleoredox and environmental studies will benefit from a more complete understanding of its geochemistry. Here, we begin to fill some of the gaps in our knowledge of its geochemical cycle. In order to characterize the sources of Re to the oceans we present the first data for Re in major world rivers and begin to characterize its behavior in estuaries. We examine the mechanism(s) for Re removal from seawater with data from oxic and anoxic sediment pore waters, and from open ocean (oxic) and the Black Sea (anoxic) water columns. Results from oxic and anoxic marine sediments expand the existing data set significantly, and coupled with the riverine data, allow us to construct a preliminary ocean budget for Re.

2. Methods

Two different techniques were employed in this study: all water samples and some sediment samples were analyzed by inductively-coupled plasma mass spectrometry (ICP-MS), and most sediment samples were analyzed using secondary ion mass spectrometry (SIMS). Both techniques employed isotope dilution to correct for variable recoveries and/or instrumental instability. The techniques were compared for sediment samples and gave indistinguishable results [8–10]. Due to the number of different types of samples and different techniques used, the methods will only be summarized here. More complete descriptions may be found in [8–10].

2.1 Sample collection and storage

2.1.1 River samples

Sampling protocols for the waters included in this study varied somewhat, as they were collected by different people over several years. Orinoco and Amazon River Basin samples were filtered in the field through 0.4 μm filters into acid-cleaned polyethylene bottles, and acidified with triply distilled 6N HCl. A comparison of acidified and unacidified samples from the Orinoco Basin showed that Re values were unaffected by storage at different pH. Amazon Estuary samples were filtered through 0.22 μm Millipore Millipack filter cartridges in the field and acidified with distilled HCl. The Ganges–Brahmaputra River samples were filtered as above, and acidified with HNO_3.

2.1.2 Pore water samples

Sediment pore waters were collected in the Northeast Pacific Ocean and in Chesapeake Bay. The Pacific samples are from two gravity cores raised from 4400 m water depth at approximately 34°48′N and 122°58′W aboard the R.V. *New Horizon* in February, 1990. Upon recovery on deck, the sediments were extruded in one centimeter sections at in situ temperatures (~ 1°C) in a nitrogen-filled glove bag. Pore waters were separated by centrifugation and filtered through 0.2 μm syringe filters. Two Chesapeake Bay cores were collected aboard the R.V. *Ridgely Warfield* in July, 1990: one gravity core (Station 2) and one box core (Station 6). Sediments were sectioned at ship laboratory temperatures (25–30°C) and then cooled to bottom water temperature (22–23°C) in an incubator before centrifuging. Sectioning and filtration were carried out under nitrogen. Filtered pore water samples (10–20 ml) were acidified with 100 μl triply-distilled 16N HNO_3.

2.1.3 Seawater samples

North Atlantic (32°10′N; 64°30′W) samples were collected in May 1990. Unfiltered samples were acidified to pH = 2 with triply-distilled 6N HCl. North Pacific (24°16′N; 169°32′E) samples were collected in May 1985, and acidified as above. All samples were stored in acid-cleaned high-density polyethylene bottles.

2.1.4 Black Sea samples

Black Sea water samples were collected in the summer of 1988 during the R.V. *Knorr* expedition to the region. They were filtered through 0.4 μm filters and acidified with HCl at sea using trace-metal clean techniques.

2.2 Sample preparation

2.2.1 Water samples

In preparation for analysis, water samples were spiked with a stable ^{185}Re isotope-dilution tracer and stored for at least 24 h to assure equilibration between sample and spike. Re was purified and preconcentrated on an anion exchange resin (Biorad AG1-x8). ReO_4^- was retained by the resin in dilute acid solutions, and eluted with 8N HNO_3.

For Mo determinations, a spike enriched in ^{95}Mo was added to the samples. River water samples were run directly and pore water samples were diluted 40-fold.

2.2.2 Sediment samples

Sediments were dried at 90 to 100°C and disaggregated using a ceramic mortar and pestle. Two methods of sample dissolution were compared: high-temperature fusion (1000°C) was used to prepare samples for SIMS, whereas acid dissolution was used prior to ICP-MS. The fusion technique employed a mixed sodium carbonate–sodium tetraborate flux to which elemental nickel and sulfur were added, along with the sample and the ^{185}Re-enriched tracer. Nickel sulfide forms an immiscible melt which concentrates most of the Re. Although recovery of Re was not quantitative, isotopic equilibration between the nickel sulfide bead and the fusion glass takes place, so that concentration data can be obtained [10]. Following the fusion, the NiS bead was separated from the glass and dissolved in HCl. The sulfide residue from this dissolution was dissolved in 4N H_2SO_4 and Re was separated from the solution by extracting ReO_4^- with tribenzyl amine in chloroform, and back-extracting into concentrated NH_4OH. The NH_4OH solution was then evaporated to dryness, and the solid residue redissolved in dilute HNO_3. Re was purified by separation on an anion exchange resin (Biorad AG1-x8); ReO_4^- was retained on the column in dilute HNO_3 and was eluted in 4N HNO_3.

For the acid decomposition technique, the sediment was first combusted at 550°C over night to oxidize most of the organic matter. The sample was then dissolved in an HF–HNO_3–HCl mixture in teflon bombs in a microwave oven, with ^{185}Re-enriched tracer added at the start of the dissolution. The sediment solution was taken to dryness and redissolved in HCl. Re was preconcentrated from the resulting solution as ReO_4^- using anion exchange, as above.

2.3 Inductively coupled plasma-mass spectrometry

Column eluants from the anion exchange procedure were evaporated to a small volume (< 100 μl) in conical teflon vials. The sample was then rediluted with 250 μl 0.8N HNO_3, and introduced to the ICP-MS (VG Plasmaquad at MIT) using a 200 μl flow-injection loop downstream of

a peristaltic pump. The $^{185}Re/^{187}Re$ ratio (or $^{95}Mo/^{98}Mo$ ratio for Mo determinations) was measured by peak jumping for 20 s during the period of maximum intensity of the transient sample signal. Ratios were adjusted for mass discrimination by correcting to a standard solution of known isotopic composition which was measured several times during each run.

2.4 Secondary ion mass spectrometry

Column eluants from the anion exchange procedure were evaporated to a volume of 1 μl or less. Using microbore teflon tubing and a syringe, the sample was deposited in a small spot on a silicon wafer for isotopic analysis. Measurements were performed on a Cameca IMS 3F ion microprobe (SIMS) at MIT. Ratios were corrected for instrumental mass discrimination as above.

3. Results and discussion

3.1 Sources of rhenium to rivers

Re was measured in the Amazon, Orinoco and Ganges–Brahmaputra Rivers and some of their tributaries, with the most detailed coverage in the Orinoco Basin. These are the first, third and fourth largest rivers in the world in terms of water discharge and together provide approximately 23% of world riverine input to the ocean [11]. In order to identify important sources of the element, Re concentrations were determined in rivers draining a variety of lithologies. Re is known to be concentrated in organic-rich sedimentary rocks [2], and is collected in economic quantities as a byproduct from the processing of molybdenite ores, and some copper, platinum, potash and uraninite deposits. It is expected to be highly mobile in oxic waters, as the perrhenate anion (ReO_4^-) is stable over the entire pH range of river waters [7]. Dissolved riverine Re concentrations will therefore reflect the geologic substrate and its rate of weathering, with minimal direct influence from river chemistry.

3.1.1 The Orinoco River Basin

The catchment area of the Orinoco is geologically diverse and relatively undisturbed by human activity, providing an ideal setting in which to survey the variability of Re in river waters. The right (southern) bank of the Orinoco is dominated by the Guyana Shield, a vast area of Precambrian rocks nearly devoid of younger Paleozoic rocks and of biogenic and chemical sediments [12]. The terrain is covered by thick jungle, and weathering occurs in the subsurface, with river chemistries indicating nearly complete alteration of basement rocks to gibbsite, quartz and kaolinite [13]. Transport-limited weathering in this region is reflected by very dilute river waters with low Re concentrations (< 0.02–0.4 pmol/kg).

The northwestern tributaries of the Orinoco arise in the Venezuelan Andes, with terrain typical of "an average global river basin" [12], containing shales, limestones, evaporites, sandstones, and metamorphic, granitic and calc-alkaline volcanic rocks, but dominated by shales and impure limestones. The highest Re concentrations were found in this region (up to 400 pmol/kg, or $10 \times$ seawater concentration), particularly in the catchment of the Portuguesa River (Acariguau, Ospino, Cojedes and Morador Rivers). The headwaters of these rivers drain widely distributed exposures of Cretaceous black shales and bituminous limestones, as well as Paleozoic evaporite deposits [14]. The Andean rivers traverse a broad floodplain before joining the mainstream Orinoco, and Re concentrations are progressively diluted. The Apure, a major tributary which joins the Orinoco from the northwest, reaches its highest Re levels downstream of its junction with the Portuguesa (at S. Fernando). Other rivers in the Andes/Floodplain region have Re concentrations between 1 and 22 pmol/kg.

Re correlates with both SO_4 and Ca in the northern (left bank) rivers ($r^2 = 0.977$ and 0.899, respectively; Fig. 1), and with total cation concentrations ($TZ^+ = Na + K + 2Mg + 2Ca$, $r^2 = 0.837$), although not with any other major ion (Na, K, Mg, Cl, HCO_3 or Si). These relationships would be consistent with an evaporite (gypsum) source for Re; however, the Re/SO_4 molar ratio in the high-Re rivers (3×10^{-7}) is much larger than that in seawater (2×10^{-9}), implying concentration of ReO_4^- over SO_4^{2-}. This is unlikely given the high solubilities of the common salts of the perrhenate ion [15]. For example, $Ca(ReO_4)_2 \cdot 2H_2O$ is approximately $1000 \times$ more soluble than $CaSO_4 \cdot 2H_2O$ (gypsum). The Re/SO_4 ra-

tios of the rivers are more similar to the Re/S ratio of black shales ($\sim 5 \times 10^{-7}$ [2]), and suggest that Re is being weathered congruently with sulfur from these rocks. Additionally, these rivers have elevated selenium concentrations, consistent with a black shale source [16]. Molybdenum, which is also concentrated in black shales, was measured in several left bank rivers and this metal correlates with Re ($r^2 = 0.984$), excepting the Cojedes River (Table 1).

3.1.2 *The Amazon River Basin*

The relationship between Re concentrations and the presence of black shales is not as clear in the samples from the Amazon Basin, and the correlation between Re and SO_4 concentrations is weak (Table 1). Re was measured in rivers of two sub-basins, the Marañon and Madeira, which drain the Peruvian and Bolivian Andes, respectively. The major lithologies in the catchment of each river sampled were summarized by Stallard

TABLE 1

Rhenium in some major rivers and their tributaries

River	Re ± 1σ(n) (pmol/kg)	SO_4 (μmol/kg)	Mo (nmol/kg)	Sample date
Orinoco and tribuaries				
Orinoco—Ciudad Bolivar	4.4	73.5		3/86
Right bank — Guyana Shield rivers				
Cataniapo	0.24	4.1		10/84
Yuruman	0.40			10/84
Cuchivero	0.09	3.0		6/87
Caroni	0.03	1.2		3/83
Atabapo	< 0.02			10/84
Ventuari	0.06	4.1		10/84
Sipapo	< 0.02			10/84
Paragua	0.34			10/84
Aro	0.02			10/84
Padamo	< 0.02			10/84
Left bank — Andean Floodplain rivers				
Apure—Portuguesa	8.5 ± 0.6 (2)	78.1	6.4	6/87
Apure—S. Fernando	38.4 ± 0.9 (3)	223.0	16.0	2/88
Apure—el Perro	21.6	62.0	8.7	10/84
Capanaparo	0.8	4.6		10/84
Meta	5.0	66.6	4.4	10/84
Venezuelan Andes rivers				
Masparro	21.9	264.0	10.9	2/88
Acariguau	254.1 ± 2.2 (3)	1230.0	102.5	6/87
Tamanaco	8.2 ± 0.1 (2)	45.0		2/88
Ospino	50.4	345.2		6/87
Morador	22.0 ± 0.1 (2)	392.2		6/87
Cojedes	411.8	1885.0	24.6	2/88
Canagua	2.1 ± 0.1 (2)	30.0		2/88
Caparo	5.7	51.0		2/88
Arauca	3.4	73.7	1.8	10/84
Uribante	16.3	192.4	19.7	6/86
Eastern Venezuela Basin rivers				
Manapire	1.3	58.6		10/84
Caris	0.3	4.2		10/84
Pao	1.0	24.0		10/84

Fig. 1. Re (pmol/kg) vs. SO_4 and Ca in the left bank tributaries of the Orinoco River.

and Edmond [17] and Stallard [18]. Where Re is elevated (Cana, Huallaga, Guapay/Grande and Mamore Rivers), the drainage lithologies contain black shales [17,18]; however the converse is not always true (the Espritu Santo also drains black shales). The highest Re concentration was measured in the headwaters of the Madeira sub-basin, where river chemistry is indicative of black shale weathering, i.e., high SO_4, high SO_4/Cl, relatively high silica and radiogenic $^{87}Sr/^{86}Sr$ [12,17]. Sulfate concentrations are strongly influenced by evaporite weathering in this region, leading to decoupling of the Re–SO_4 relationship. A saline spring with very high SO_4 contains little Re (Table 1), supporting the conclusion that evaporites are not an important source of Re.

TABLE 1 (continued)

River	Re ± 1σ(n) (pmol/kg)	SO_4 (μmol/kg)	Mo (nmol/kg)	Sample date
Amazon and tributaries				
Amazon—mouth	1.1			7/89
Maranon Basin rivers				
Cana	16.2	2080		11/78
Huallaga	19.9	246		5/77
Maranon	3.5	52		11/78
Salt Spring—Tingo Maria	2.9	9300		5/77
Shanusi	2.1	37		11/78
Paranapura	3.5	82		11/78
Madeira Basin rivers				
Espiritu Santo	3.2	200		11/78
Guapay/Grande	46.0	2190		11/78
Mamore	9.0	306		11/78
Ganges and tributaries				
Ground waters				
Ganges—Gurhmukteshwar	21.7			11/83
Yamuna—Agra	23.6		22.9	11/83
Lowland rivers				
Ganges—Aricha Ghat	9.1			11/83
Son—Ara	3.9	37		3/82
Gomati—Dobni	15.0	250	22.1	11/83
Brahmaputra				
—Aricha Ghat	5.6			11/83

(n) = number of replicates.
Where $n = 2$, standard deviation (1σ) is taken to be the difference from the mean Pooled standard deviaion (PSD) for six samples where duplicates or triplicates were run = 3.5%, where: PSD = $\sqrt{\sigma n_i (rsd)_i^2 / \Sigma n_i}$ and rsd = relative standard deviation.
For samples with very low Re concentrations (< 0.05 pM, errors are estimated to be ±50%, due largely to uncertainty in the blank correction. Sample size was 50 ml, except for the main channel Orinoco—C. Bolivar, where sample size was 200 ml. Additional data may be found in [12,13,16–21].

3.1.3 *The Ganges–Brahmaputra Rivers*

The source of the Ganges is at 7000 m in the Kumaun Himalayas, a region consisting of dolomitic limestones (commonly replaced by gypsum), calcareous shales, sandstones, quartzites, schists, gneisses and granites [19]. The carbonates in many regions are associated with pyritic carbonaceous shales and slates [20]. From there the river descends through the Siwalik Range (sandstones, clays and conglomerates) to a broad alluvial plain. The Brahmaputra originates farther north, in the Tibetan Himalayas, and flows parallel to the main Himalayan Range until it descends through the Assam Valley to meet the Ganges at Aricha Ghat. The geology of the high Tibetan Himalayas is poorly known, but the lithology of the southern slopes along the Brahmaputra is dominated by black shales, gneisses and volcanic rocks [19].

Re concentrations near the mouths of the rivers (measured during moderate flow conditions), at the Ganges–Brahmaputra confluence (Aricha Ghat), are relatively high compared to mainstream values for the Amazon and Orinoco Rivers. This is probably due to the higher dissolved loads in the Indian rivers, which result from high chemical denudation rates in the Himalayas [19]. Additionally, cyclic wetting and drying of the Indo-Gangetic alluvial plain leads to the formation of saline/alkali soils and groundwaters which are an important source of dissolved material to the rivers [19]. Sarin et al. [21] reported that uranium concentrations are also elevated (up to 33 nM) in the Ganges River and its highland tributaries.

Re and U concentrations are positively correlated in the six rivers and groundwaters sampled here, and both elements are positively correlated with total cation contents of the rivers (Fig. 2). Based on the similarity of the U/Σcations ratios in dissolved and suspended phases in the rivers, Sarin et al. [21] concluded that congruent weathering of U and major cations was taking place, although the source of the high-U material was not obvious. Although carbonate weathering dominates the major-ion chemistry of the highland rivers [19], U/Ca ratios in typical carbonates ($\leqslant 1$ μmol U/mol Ca in a limestone with $\leqslant 3$ ppm U) are at least an order of magnitude lower than U/Ca ratios measured in the highland rivers

Fig. 2. Re and U vs. total cations in the Ganges–Brahmaputra River System. Open symbols = river waters; filled symbols = ground waters.

(10–30 μmol U/mol Ca). This suggests that there may be an additional source of U, perhaps in the granites and gneisses of the region. Carbonaceous shales are a possible source for both Re and U, however, the U/Re molar ratio (~ 2000) is greater than one would expect from the weathering of typical organic-rich sediments (10–300). For example, the black shale-influenced rivers of the Orinoco system have U/Re ratios of 10–30. Higher ratios in the Himalayan rivers are not simply due to stabilization of U by carbonate ions, as the Andean and Himalayan rivers have similar carbonate contents [Orinoco U data from M. Palmer, pers. commun.; also 13,19]. Mechanisms which might have fractionated U and Re in the source rocks or during weathering are not yet known, and more detailed sampling will be necessary to determine the sources of Re to these rivers.

3.2 *Behavior of Re in the Amazon Estuary*

The riverine contribution of trace elements to the oceans can be substantially modified by chemical and physical processes within estuaries. Even elements which display conservative behavior in seawater and are fairly mobile under freshwater conditions, such as U, can be added to or removed from the dissolved phase within estuarine systems. These effects can be very sensitive to conditions in a particular estuary. For example, McKee et al. [22] suggested that dissolved U

Fig. 3. Re vs. salinity in surface waters of the Amazon Estuary. The solid line is the conservative mixing line between Amazon River waters (1.1 pmol/kg Re, 0‰ salinity) and seawater (46.2 pmol/kg Re, 36.5‰ salinity). The dashed line is the best fit through the data, with a zero salinity intercept at 4.7 pmol/kg Re. Error bars are ±1 pooled standard deviation (4%). The data is available in [8], or from the senior author on request.

concentrations are enhanced in the Amazon Estuary due to mobilization of U from reducing sediments seaward of the estuary, whereas Butts and Moore [23] demonstrated that U is removed from the dissolved phase into sediments within the Ganges–Brahmaputra mixing zone.

Re was measured in 13 surface samples from the Amazon Estuary covering a salinity range from 0 to 36.4‰. If there are no sources or sinks of Re within the estuary, Re should vary linearly with salinity from river water to open ocean concentrations. The results show that Re is nearly conservative through the outer portion of the mixing zone (Fig. 3). However, three points at low salinity show a positive departure from the linear mixing line, suggesting a source of Re to the dissolved (< 0.22 μm) phase within the inner Amazon shelf. If these samples are generally representative of the Amazon, the overall flux of Re to the oceans from this river system could be approximately four times that calculated from the endmember concentration (intercept of 4.7 vs. 1.1 pM in Fig. 3).

A source of Re in the inner estuary might result from desorption of Re from suspended solids, or mobilization of Re out of shelf sediments. The evidence regarding Re adsorption from oxic solutions is somewhat contradictory. Olaffson and Riley [24] reported that ReO_4^- is not coprecipitated with $Fe(OH)_3$ from seawater at pH = 8, but that it is significantly adsorbed by illite, kaolinite and argillaceous deep sea sediments. However, its concentrations in oxic pelagic sediments and ferromanganese nodules are lower than crustal values, indicating insignificant ad-

Fig. 4. Re profiles in the (a) Atlantic (32°10′N, 64°30′W) and (b) Pacific (24°16′N, 169°32′E) Oceans. Plotted Re concentrations are corrected to 35‰ salinity. Error bars are ±2.2%, which is the pooled standard deviation of the six triplicate measurements. The vertical line shows the mean of the data set. The data are available in [8], or from the senior author on request.

sorption from seawater (see below). Its behavior in fresh waters is even more poorly constrained, and it is possible that Re is adsorbed by ferric-oxyhydroxide coatings on mineral grains, or on mineral surfaces, and is desorbed in the inner Amazon mixing zone. Alternatively, reduced Re which has been sequestered in anoxic or suboxic sediments may be released to the dissolved phase if these sediments are re-oxygenated [25]. In this case, the observed enhancement might be due to a local, transient, sediment disturbance, or to seasonal changes in the redox properties of the sediments.

3.3 *Open ocean behavior*

Thermodynamic predictions indicate that Re should occur in seawater as the unreactive oxyanion, ReO_4^- [7]. By analogy with molybdenum, which is present as MoO_4^{2-}, it was expected that Re would display conservative behavior in the oceans, i.e., covary with salinity [4]. Early studies [4,24,26] of Re in seawater yielded similar Re concentrations (20–50 pmol/kg) but were not able to demonstrate conservative behavior of the metal due to poor precision of the available techniques. Recently, Anbar et al. [5] measured Re by negative thermal ionization mass spectrometry in a depth profile from the central Pacific Ocean, and confirmed its generally conservative behavior, with a mean concentration of 38.9 pmol/kg.

Our results for two profiles in the Atlantic and Pacific Oceans are consistent with previous work, and demonstrate the unreactive nature of the element in the water column (Fig. 4). The mean value determined here, 44.3 ± 0.3 pmol/kg ($\pm 2\sigma_{mean}$) is higher than that reported by Anbar et al. [5], 38.9 ± 0.4 pmol/kg (both corrected to 35‰ salinity). This systematic offset between the two methods will be resolved by intercalibration in the near future. Re shows constant concentrations relative to salinity in the Atlantic samples, within analytical uncertainties ($\pm 2\%$). There is more variability in the surface waters of the Pacific profile, but it cannot yet be shown whether this reflects natural variability or analytical/sampling artifacts. Anbar et al. [5] also noted a slight depletion from mean values in near-surface waters (300–400 m), and measured a surface enrichment of the element that is not evident in our data. The average Re concentrations in the two profiles are 44.6 ± 0.4 pmol/kg in Atlantic and 43.9 ± 0.6 pmol/kg in the Pacific ($\pm 2\sigma_{mean}$), normalized to 35‰ salinity. These values agree

Fig. 5. (a) Re profile in the Black Sea. The horizontal line marks the O_2–H_2S boundary at 85 m. Note that isopycnals are approximately 20 m deeper at Station 6 than at Station 2. (b) Re vs. salinity in the Black Sea. The horizontal line marks the salinity at the O_2–H_2S interface. The data are available in [8], or from the senior author on request.

within $2\sigma_{mean}$, thus no inter-ocean fractionation is discerned from the data, as expected for a conservative element.

3.4 Re in the Black Sea

The Black Sea is the world's largest anoxic basin and is permanently devoid of oxygen below approximately 100 m due to sluggish renewal of its deep waters. Stable density stratification arises from the excess of fresh water inputs over evaporative losses, and the inflow of saline waters from the Mediterranean Sea. Exchange with Mediterranean waters occurs via the Sea of Marmara, restricted by the narrow Dardanelles and Bosporus Straits. Warm, saline (~ 38‰) waters from the Sea of Marmara spill into the Black Sea over the shallow (32–34 m) Bosporus sill, and entrain colder, fresher waters from intermediate depths to create a deep water mass with a salinity of about 22‰ [27]. Surface circulation is dominated by two large cyclonic gyres in the eastern and western basins, causing doming of isopycnal surfaces in the Black Sea. The position of the oxic–anoxic boundary has varied, although the causes and timing of the changes are not well understood [27–29].

Water column profiles from two stations were analyzed: BS3-2 in the center of the western gyre, and BS3-6 in the central Black Sea, between the two gyres. In the summer of 1988, when these samples were collected, the sulfide interface ($H_2S > 0.4\ \mu M$) at Station 2 occurred at about 85 m and was overlain by a 30 m zone of low-oxygen waters ($O_2 < 10\ \mu M$). This sub-oxic zone is coincident with the pycnocline which restricts mixing between lower salinity (~ 18‰) surface and higher salinity (~ 22‰) deep waters. Re concentrations decrease smoothly through the upper water column (Fig. 5a), with the exception of a single point with lower Re at 80 m (discussed below). In deeper waters (below 600 m), Re levels are fairly constant at about 9 pmol/kg. Re covaries with salinity below the pycnocline, indicating conservative behavior in the anoxic water column (Fig. 5b). The decrease in Re with increasing salinity (and depth) is due to its removal to highly reducing bottom sediments (Re in Black Sea sediments ~ 40 ppb [6]). Above the pycnocline, high Re values in Black Sea surface waters are the result of elevated concentrations in rivers flowing into the Black Sea, possibly as the result of anthropogenic contamination [8].

Re does not appear to be removed within the anoxic water column itself, although sedimentary pore waters are not significantly more reducing than the bottom waters of the Black Sea. This was also noted for U [30] and Mo [31] in the Black Sea water column. This suggests that the reduction or complexation that is required for Re removal is kinetically hindered. It is possible that removal of Re from anoxic waters requires the presence of mineral surfaces, as suggested for U [30]. Analysis of suspended and sinking particles from the Black Sea and other anoxic basins will be necessary to confirm the inert behavior of Re in the anoxic water column.

A single point at 80 m (BS3-2) deviates significantly from the Re mixing line in surface waters (Fig. 5a). This sample is also depleted in Mo and V [31], and coincides with the deeper of two maxima in particulate Mn [32]. Manganese oxides are known to scavenge Mo and V, but other data suggests little removal of Re from seawater via this mechanism (see below, with respect to manganese nodules and oxic pore waters). The other particulate Mn maximum, at 70 m, is not accompanied by depletions in Re, Mo or V. Therefore, it is possible that another phase, such as bacterial matter, is responsible for oxyanion scavenging at 80 m. There is no particulate Fe maximum above the sulfide interface, although some Fe oxidation is undoubtably occurring, and may also play a role in the removal of Re, Mo and V. Further evidence that Re may be scavenged by particles under some conditions is discussed below with results for hydrothermal sediments.

3.5 Sediment pore waters

Conservative behavior of Re in oxic and anoxic water columns implies that "hydrogenous" (originating from seawater) accumulation of the element must occur at or below the sediment–water interface. In the simplest case, Re would diffuse into sediment pore waters along a concentration and redox gradient from bottom waters to the depth at which it is reduced and removed from solution. This removal pathway has been shown to largely control the enrichment of U (occurring

in seawater as the oxyanionic complex, $UO_2(CO_3)_3^{4-}$) in reducing sediments [33–35]. This is true for Mo as well, if there is no oxidized layer in surficial sediments [31,36]. Where an oxic layer exists, MoO_4^{2-} is cycled with Mn-oxides in shallow sediments, before being reduced and removed from deeper pore waters [36].

In order to determine the removal pathway for Re, pore waters from one oxic and one anoxic site were examined. The oxic sediments were collected in the North Pacific, west of Point Conception, California at a depth of approximately 4400 m. This is a site of an ongoing study of seasonal variations in carbon flux and benthic

Fig. 6. (a) Re, Mo and NO_3 in pore waters from an oxic Pacific site (34°47′N, 122°59′W). The Mo profile in core F shows evidence for cycling with Mn. (b) Re, Mo and H_2S in pore waters from Chesapeake Bay: station 2 (38°40′N, 76°24′W) and station 6 (38°56′N, 76°23′W). The horizontal lines mark the sediment–water interface. The uppermost points represent Re and Mo concentrations in water recovered with the core, overlying the sediment. Standard deviation for Re measurements (1s) is 6%, based on duplicate determinations of five 10 ml bottom water samples from Chesapeake Bay. Standard deviation for Mo is 8%, based on counting statistics, and uncertainty in background corrections. The data are available in [8], or from the senior author on request.

activity [37]. Primary productivity in the overlying waters of the California Current varies by a factor of three annually, giving rise to variations in the deep water flux of particulate organic matter of a factor of ten or more, with a maximum in June [37,38]. In February, when these samples were collected, the sediment was capped by a 2–3 cm oxic (red-brown) layer, overlying suboxic grey-green sediment.

Re was measured in two cores from this site

TABLE 2

Rhenium sediment concentrations

Sample	Sediment Type	Location	Re (ppb)
AII 54-2			
Sta. 29, 14PC 2–5 cm	Calcareous ooze	8S 102W Flank, East Pacific Rise	0.046 ± 0.010
Sta. 14, 8PC 1–11.5 cm	Calcareous ooze	5S 107W East Pacific Rise	0.023 ± 0.009
CHN 96-4			
Sta. G4 4PG 0–11 cm	Calcareous ooze	24N 41W Mid-Atlantic Ridge	0.025 ± 0.006
AII 15			
Sta. 765 (HC) 2–20 cm	Calcareous ooze	32S 49E North of SW Indian Ridge	0.023 ± 0.006
LL44-1 GPC3			
87–93 cm	Pelagic clay	30N 157W	0.163 ± 0.012
260–270 cm	Pelagic clay	Abyssal N Pacific	0.116 ± 0.011
565–570 cm	Pelagic clay		0.253 ± 0.019
ESOPE52			
1580–1609 cm (Avg. 15 samples)	Pelagic clay	23N 63W Abyssal N Atlantic	0.060 ± 0.014
CHN 100-11			
Sta. 137 91PG	Metalliferous pelagic clay	10S 103W	2.98 ± 0.13
Chesapeake Bay			
Sta. 2 1–2 cm	Anoxic mud	39N 76W	1.34 ± 0.05
Sta. 6 0–1 cm	Anoxic mud		2.75 ± 0.38
San Pedro Matir Basin			
20–35 cm	Laminated, diatomaceous	28N 112W Gulf of California	15.3 ± 0.5
Carmen Basin			
10–20 cm	Laminated, diatomaceous	26N 110W	26.3 ± 1.2
30–40 cm	Lam., diat.	Gulf of California	26.5 ± 1.1
60–70 cm	Lam., diat.		31.2 ± 1.5
80–95 cm	Lam., diat.		30.8 ± 2.2
Walvis Bay			
10–36 cm	Diatomaceous mud	23S 14E SW African Shelf	18.9 ± 1.7
Jelly Fish Lake			
10–20 cm	Biogenic ooze	7N 134E Republic of Palau	34.5 ± 1.3
Peru Shelf	Phosphorite crust	8S 81W	34.3 ± 3.2

and results are illustrated in Fig. 6a, along with accompanying Mo and NO_3 data. There is no unidirectional trend in Re concentrations over the depth interval sampled in either core. In core F, Re begins to decrease through the top 18 cm, but then increases again in deeper pore waters. In contrast, the Mo profile in this core shows evidence for uptake onto Mn-oxides at about 2 cm, and release back to pore solutions where these oxides are reduced at 6 cm. Similar structure in Mo pore water profiles was noted at other sites in the California borderlands by Shaw et al. [36]. Similar inflections are not discerned in the Re profile, suggesting that Re is not cycled with sedimentary Mn-oxides. This finding is in agreement with previous measurements of Re in Mn-nodules; whereas nodules were found to have extremely low Re concentrations (< 0.1 ppb), they are highly enriched in Mo, with concentrations up to hundreds of ppm [1].

Anoxic sediments were collected in Chesapeake Bay, the seasonally anoxic estuary of the Susquehana, Potomac and several smaller rivers. Sampling was carried out at two sites in July, when bottom waters were anoxic from about 15 m to the bottom at 29 m. The first core (Station 2, off the mouth of the Choptank River) was taken in fairly coherent sediment that had the characteristic grey color of finely disseminated pyrite. Sulfide increases smoothly with depth in the pore waters below 8 cm (Fig. 6b). Re decreases through the top 3 cm, and is nearly completely removed between 4 and 8 cm. It reappears in pore waters below this depth at a nearly constant value of about 10 pmol/kg. There is currently no explanation for the two high points at 4.5 and 27.5 cm, although possibilities include physical disturbance of the sediment during sampling, contamination, or oxidation before separation of pore waters from solids.

The second core (Sta. 6) was taken in more highly reducing sediments due East of Annapolis, MD. The pore waters were homogenized to some extent by the evolution of methane within the core, and sediment texture was more gelatinous than at the first site. Sulfide was detected in pore waters between 1 and 14 cm, with a maximum at 6–7 cm (Fig. 6b). The rapid decrease of sulfide toward the base of the core is the result of depletion of pore water sulfate at these depths. Re decreases smoothly through the surficial 5 cm to concentrations of between 4 and 12 pmol/kg below this depth.

Re diffusion into anoxic sediments can be inferred from the pore water profiles at both sites. At Sta. 2, Re is nearly completely removed from pore waters between 3 and 8 cm, but reappears below this depth at concentrations of about half that in overlying waters. In the second core (Sta. 6) Re is never depleted to the very low levels (< 1 pmol/kg) observed in Sta. 2 pore waters, but decreases steadily through the top 5 cm to a similar deep value of approximately 10 pmol/kg. Incomplete removal from pore solutions has also been noted for U [33,34], and may be due to the association of these two metals with a colloidal (< 0.4 μm) phase [39]. The Chesapeake pore water data suggest that sulfide may be indirectly responsible for stabilization of Re in solution, as its reappearance in Sta. 2 pore waters coincides with the depth at which H_2S is first observed. If this is the case, one would not expect to see the near-surface (3–8 cm) depletion of Re in Sta. 6 samples because sulfide is elevated through this depth interval. Solubility of a Re sulfide phase does not appear to directly control Re concentrations, as Re does not correlate with sulfide in the pore solutions. Indirect control might be attributed to the presence of colloidal sulfides (< 0.2 μ) which might incorporate Re.

The depth at which Re concentrations reach their minimum value marks the zone of most rapid Re removal from pore waters. If removal is simply redox-controlled, this depth is presumably the point in the redox gradient at which Re is reduced. However, some Re removal may be occurring above this "reduction boundary", as near-surface sediments from these cores are enriched (1–3 ppb Re; Table 2) compared to crustal materials (~ 0.3 ppb Re), although this might also be due to seasonal cycles in the estuary. It is likely that Re is ultimately incorporated into pyrite in reducing sediments, as has been shown to be the case for Mo [40].

3.6 Re in modern sediments

The extreme enrichment of Re in reducing sediments compared to oxic sediments or crustal values implies that these sediments are a signifi-

cant sink in its oceanic cycle. Koide et al. [1] surveyed Re concentrations in modern sediments and found an average concentration in anoxic sediments of about 50 ppb (with a range of 2–127 ppb). Ravizza et al. [6] reported similar concentrations in anoxic Black Sea sediments, with a range of 20–184 ppb Re. In contrast, concentrations in oxic sediments and manganese nodules are < 0.1 ppb [1], which is lower than our best estimate of crustal Re values (~ 0.4 ppb Re) [69]. In a second study, Boyko et al. [41] found slightly higher Re concentrations in nodules (0.2–2 ppb) and pelagic sediments (0.2–0.5 ppb). This indicates that ReO_4^- is only very weakly adsorbed, if at all, on ferromanganese oxide minerals in nodules or dispersed in pelagic sediments. This is surprising in view of the chemical similarity of Mo and Re, and the strong enrichment of Mo in manganese nodules. The preference of ferromanganese oxides for MoO_4^{2-} over ReO_4^- is not yet understood, and is not due simply to the difference in their seawater concentrations. If Re were incorporated into Mn-nodules in proportion to Mo, one would expect Re concentrations in nodules of approximately 100 ppb. Thus, although anoxic sediments accumulate over only 0.3% of the ocean floor [31], it is likely that they represent the most significant sedimentary sink for Re.

In order to further test this hypothesis, we have expanded the sedimentary Re data set to include calcareous oozes from mid-ocean ridge flanks, metalliferous sediments and additional pelagic and anoxic sites (Gulf of California, Walvis Bay, Jelly Fish Lake, Peru margin). The results (Table 2) are in general agreement with the previous works. Concentrations in anoxic sediments range from 15 to 34 ppb. Calcareous oozes from the Atlantic, Pacific and Indian oceans have very low Re concentrations (< 0.05 ppb) demonstrating the lack of Re incorporation into calcitic shells at levels significant for the oceanic mass balance. Pelagic brown clay from the Nares Abyssal Plain (ESOPE 52) and from the abyssal North Pacific (LL44-1, GPC3) have similarly low Re levels with Re/Al ratios less than or equal to crustal values ($Re/Al_{crust} = 5x10^{-9}$, $Re/Al_{ESOPE} = 0.5 \times 10^{-9}$ and $Re/Al_{GPC3} = 2 \times 10^{-9}$; Al data from [42,43]). It is therefore likely that all the Re in these sediments can be accounted for by that incorporated in mineral lattices.

Evidence that Re may indeed be scavenged from seawater into sediments by ferromanganese oxides comes from metalliferous sediments near the East Pacific Rise (Re ~ 3 ppb). Previously, Boyko et al. [41] had reported relatively enriched Re levels (0.8 ppb) in EPR metalliferous sediments. Certain hydrothermal sulfide deposits have also been shown to be highly Re-enriched [1], but it is not clear whether the source of Re lies in the hydrothermal fluid or in seawater. Preliminary data for hydrothermal solutions indicate that the exiting fluid is not a Re source (Re < 0.1 pmol/kg in endmember hydrothermal solutions from the Mid Atlantic Ridge [Colodner, unpubl.]) and that enrichments in metalliferous sediments probably arise from seawater. These sediments have also been shown to accumulate uranium from seawater, presumably by adsorption onto ferromanganese oxides, with iron (rather than manganese) likely to be the controlling phase [44,45]. Unlike most particles in the ocean which have a negative surface charge (imparted by organic coatings), freshly precipitated iron oxide in hydrothermal plumes is known to be an efficient scavenger of many oxyanions. More data from metalliferous sediments and hydrothermal plume particulates will be necessary to understand and quantify Re removal via this pathway.

4. Summary and conclusions

4.1 Toward a marine Re budget

With the available data, one can begin to evaluate the geochemical cycle of Re. Re is easily mobilized during weathering by oxic aqueous solutions, and is delivered to the oceans primarily by rivers. Its behavior through most of the amazon mixing zone is essentially conservative, with an apparent addition of dissolved re to the innermost shelf waters. It is not yet clear whether this enrichment at low salinities is generally representative of its estuarine behavior. An average value for Re in rivers, based on the water flux-weighted mainstream concentrations of the Amazon, Orinoco And Ganges–Brahmaputra rivers, is 2.3 pM Re (Table 3). Using a global river flux of 3.6×10^{16} l [11], the annual riverine input of Re to the oceans is 83,000 moles. With a mean seawater concentration of 45 pM Re, the resi-

TABLE 3

The riverine flux of Re to the oceans

River	Water discharge (km^3/yr)	Re * (10^{-12} mol/l)
Amazon	6300	1.1
Orinoco	1100	4.4
Ganges	450	9.1
Brahmaputra	603	5.6
Flux-weighted average		2.3

Water fluxes from [11].

* The Amazon River concentration is taken to be its endmember value until further confirmation of a desorptive flux is available. A true Orinoco endmember value is not known, and the concentration is taken to be that of the main channel at Ciudad Bolivar. The Ganges and Brahmaputra values are taken just before their confluence.

dence time of Re in the oceans with respect to river inflow is estimated to be 750,000 yr. This is similar to the oceanic residence times of Mo and U of 780,000 and 250,000–500,000 yr, respectively [46–48].

Re concentrations covary with salinity in oxic seawater and in the anoxic Black Sea. Re is not significantly cycled with biogenic matter in the water column, although mineral surfaces, specifically ferromanganese oxides, may have a limited ability to scavenge Re, as seen in a particle-rich layer in the Black Sea. Metalliferous hydrothermal sediments may also accumulate Re from seawater. In contrast, manganese nodules and oxic pelagic sediments with a large hydrogenous component are depleted in Re relative to crustal values, and Re does not cycle with Mn in the pore waters studied here. The kinetic or thermodynamic factors controlling Re scavenging by various surfaces, as well as the difference in adsorptive behavior between Re and other oxyanions (e.g., Mo and V) require further study. In addition to enhancing our understanding of Re geochemistry, this may provide insight into the nature of the "scavenging" reaction by which anions are adsorbed or precipitated from seawater onto negatively charged oxide surfaces.

Re is removed from seawater into anoxic sediments via diffusion into anoxic pore waters to the depth where it is adsorbed or precipitated from solution. Its removal presumably involves reduc-

TABLE 4

Calculation of the global burial flux of Re in organic-rich sediments

Locality	Re (ng/g)	S (cm/yr)	ρ (g/cm^3)	F Re ($ng/cm^2 \cdot yr$)	Area [a] (10^{15} cm^2)	Regional Burial Flux (10^6 g/yr)
SW African Shelf					0.25	0.53
Walvis Bay	19	1 [b]	0.11 [b]	2.1		
Gulf of California					0.8	1.1
Carmen Basin	28	0.2 [b]	0.25 [b]	1.4		
San Pedro Matir	15	1 [b]	0.1 [c]	1.5		
California Margin					0.8	0.6
Santa Barbara Basin	9 [d]	0.3	0.25 [b]	0.7		
Peru–Chile Margin					1.9	3.5 [i]
Chile Shelf	96 [d]	0.15 [e]	0.22 [b]	3.2		
Peru Shelf	20 [d]	0.11 [b]	0.22 [b]	0.5		
Baltic Sea	?			0.14 [h]	3.8	0.53
Black Sea (Unit 1)	36 [f]	0.016 [g]	0.24 [g]	0.14	2.7	0.38
Sea of Azov	?			0.14 [h]	0.4	0.06
Total burial (10^6 g/yr)						6.7

S = accumulation rate; ρ = in situ (or dry bulk) sediment density.

[a] Areas from [50]. [b] [51,52]; [c] based on Walvis Bay sediments with similar accumulation rate; [d] [1]; [e] [53]; [f] [6]; [g] [54]; [h] Re burial flux assumed to be same as Black Sea; [i] Regional flux derived by taking an average of the Peru and Chile burial fluxes. This may bias the burial flux toward higher values if the high Re values found in the Chile core are not representative of the region.

tion of the $Re(VII)O_4^-$ to Re(IV). Using the available data, one can calculate the burial flux of Re in organic-rich sediments (Table 4). Approximately 36,000 moles of Re, or about 43% of the riverine input, are annually removed into sediments which cover about 0.3% of the ocean floor. Thus, as suggested for the elements U, Mo and V [31,49], the Re content of the oceans may be very sensitive to changes in the area of anoxic sedimentation. There is currently not enough data to quantify the other Re sinks, but important removal fluxes are likely to occur in suboxic coastal and hemipelagic sediments, and in hydrothermal systems and their associated deposits.

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