

The Geochemistry of Rhenium

by

Julian P. Sachs

SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF
BACHELOR OF SCIENCE

at the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

May, 1991

© Massachusetts Institute of Technology 1991

Signature of Author _____
Department of Earth, Atmospheric and Planetary Sciences
Massachusetts Institute of Technology
May, 1991

Certified by _____
Edward A. Boyle, Thesis Supervisor

Accepted by _____
Tom Jordan, Department Head
Department of Earth, Atmospheric and Planetary Sciences
Massachusetts Institute of Technology

ABSTRACT

A systematic characterization of the geochemistry of rhenium was undertaken. Three regimes were studied: (1) a major river basin (the Orinoco), (2) a large estuary (the Amazon), and (3) the open ocean (Atlantic and Pacific).

In 29 rivers throughout the Orinoco basin, Re concentrations were found to vary by more than 4 orders of magnitude, from <0.02 pmol/kg to 412 pmol/kg. The highest values were observed in the Portuguesa Basin, a region in the southeastern Andean foothills containing substantial black shale deposits. The lowest values were measured in tributaries draining the intensely-weathered Precambrian Guyana Shield on the right bank of the Orinoco.

Measurements of dissolved Re from 13 locations in a transect of the Amazon estuary fall on or close to the conservative mixing line, although a positive deviation below 5 per mil salinity suggests the existence of a Re source on the inner shelf.

In depth profiles from both the North Atlantic and North Pacific oceans, Re shows vertical conservative behavior to $\pm 3.5\%$ at the 95% confidence level. Based on the 17 analyses comprising each profile, average [Re] in the Atlantic is 44.68 ± 0.34 pmol/kg, and 43.91 ± 0.46 pmol/kg in the Pacific. Between basins, average [Re] is therefore conservative at the 95% confidence level.

Finally, Re was calculated to have a residence time in seawater, with respect to riverine inputs, of 300,000 to 2,000,000 years, and, within uncertainties, to be in steady state.

All analyses were made using the technique of isotope dilution-inductively-coupled plasma mass spectrometry.

ACKNOWLEDGEMENTS

I would like to thank Debra Colodner for the knowledge she shared with me, her patience, her kindness, and her generosity. She made this work possible, and taught me everything I know about trace metal analysis, most of what I know about geochemistry, and a sizeable chunk of what I know about geology. I would also like to thank Ed Boyle for his seemingly endless wisdom on all matters, and his generosity.

I would like to thank John Edmond for sharing his knowledge of the Amazon and Orinoco Rivers, for the samples he was able to provide, and for the use of his laboratory and ICP-MS facility. I am also grateful to Ed Brook, Debra Colodner and Ed Boyle for the use of the samples they collected.

Finally, I would like to thank Yair Rosenthal for his advice and lively discourse, and the rest of the people around the lab who offered me advice on numerous occasions.

This work was partially funded by Sea Grant and UROP at the Massachusetts Institute of Technology. It is dedicated to my parents, who fostered in me a love of the sea; to my twin brother, Jeff, the best friend I have; and to my brother Lee, a role model to whom I may aspire.

TABLE OF CONTENTS

Abstract	2
Acknowledgements	3
Table of Contents	4
List of Figures	5
I Introduction	6
II Methods	9
2.1 Sample Collection Information	9
2.2 Laboratory Preparation of Samples for Re Analysis by Isotope Dilution	10
2.3 Isotope Dilution Technique	11
2.4 Inductively-Coupled Plasma Mass Spectrometric Technique for Re Analysis	13
2.5 Maximizing Precision: Correcting for Background Noise, Spurious Re, and Machine Variability and Bias	13
2.6 Machine Variability and Bias	14
2.7 pH Experiment	14
2.8 Precision Experiment	15
III Data Analysis and Discussion	16
3.1 Re in the Orinoco River Basin	16
3.2 Re in the Amazon Estuary	26
3.3 Re in the North Atlantic and North Pacific Oceans	31
IV Geochemical Calculations and Discussion	37
V Conclusion	39
VI Summary	40
References	41

LIST OF FIGURES

Figure 3.1.1	Map of the Orinoco basin.	17
Figure 3.1.2	Re oncentrations in the Orinoco Basin. 18	
Figure 3.1.3	[Re] vs [SO ₄ ⁻²] for the Andean rivers (region 3) of the Orinoco.	22
Figure 3.1.4	[Re] vs [SO ₄ ⁻²] for the Llanos (region 2) of the Orinoco.	23
Figure 3.1.5	[Re] vs [SO ₄ ⁻²] for the Guyana Shield (region 1) of the Orinoco.	24
Figure 3.1.6	[Re] vs [Mo] and [U] for the Llanos (region 2) of the Orinoco.	25
Figure 3.2.1	[Re] vs Salinity for the Amazon estuary.	29
Figure 3.3.1	Conservative depth profile of Re in the North Atlantic (Station S: 32°10'N; 64°30'W).	32
Figure 3.3.2	Conservative depth profile of Re in the North Pacific (24°16'N; 169°32'W).	34

I Introduction

This study was undertaken to characterize rhenium's geochemistry in an effort to learn more about its efficacy as a paleoredox tracer in the ocean. There were three reasons why it was thought that Re might be employed in such a fashion. First, its seawater concentration was reported to be at least 20 times its concentration in crustal rocks (9 ng/L versus 0.1-0.5 ppb) (Koide, Hodge et al., 1987), suggesting low reactivity in the ocean. Second, it was observed to be depleted in pelagic sediments (<0.1 ppb) relative to its crustal abundance, while being enriched exclusively in reducing sediments (1.8-127 ppb) (Boyko, Baturin et al., 1985);(Koide, Hodge et al., 1986). This suggested its use as a sensitive indicator of environmental redox processes. Finally, Re was believed to exhibit conservative behavior in the ocean (Koide, Hodge et al., 1987), suggesting little, if any, particle-reactivity.

The underlying explanation for the observed behavior of Re in seawater is the unreactivity of the perrhenate ion (ReO_4^-) (Koide, Hodge et al., 1986), the primary Re species found in natural waters (Turner, Whitfield et al., 1981).

Rhenium, discovered in, 1925, was one of the last stable elements to be found. Although predicted much earlier by Mendeleev, its scarcity prevented its isolation (Morris and Short, 1965). Naturally occurring Re (atomic number 75) has two isotopes. ^{185}Re , with a cosmic abundance of 37.07%, is stable, while ^{187}Re , with a cosmic abundance of 62.93%, is radioactive. The latter nuclide decays to ^{187}Os with the emission of a β^- particle, and has a half-life of 4.3×10^{10} years.

Among the most important compounds formed by Re is the tetrahedral oxoanion, perrhenate (ReO_4^-) (Cotton and Wilkinson, 1988). It has been shown that heptavalent Re, as perrhenate, is the primary speciation of rhenium in both seawater and fresh-water (Turner, Whitfield et al., 1981).

The inertness of perrhenate in solution is responsible for rhenium's high concentration in seawater, its observed depletion in pelagic sediments, and its enrichment only in highly reducing sediments. As Koide, *et al.* (1986) point out, crustal rocks weathering under oxidizing conditions become depleted in Re as it gets oxidized to the thermodynamically favored ReO_4^- species and carried off in solution. If the Re-depleted rocks are further weathered and the products are deposited under oxidizing conditions, Re-depleted pelagic sediments are the result. Only strongly reducing sediments appear capable of reducing perrhenate (Koide, Hodge et al., 1986);(Koide, Hodge et al., 1987).

There is abundant evidence supporting this hypothesis. For instance, Re is highly enriched in black shales (Morris and Short, 1965);(Poplavko, Ivanov et al., 1977);(Ravizza and Turekian, 1989);(Martin, 1990). This was observed, indirectly, in this study, when Andean rivers of the Portugueza Basin, draining known black shale deposits (Macellari and De Vries, 1987), were found to contain extremely high concentrations of dissolved Re (here, defined as all Re species that passed through a $0.4 \mu\text{m}$ filter).

The hypothesized unreactivity of dissolved Re, as perrhenate, in seawater (Koide, Hodge et al., 1986);(Koide, Hodge et al., 1987) was confirmed, in this study, when depth profiles of the element in both the North Atlantic and North Pacific Oceans were found to be conservative. Further evidence of the inertness of perrhenate is the close correlation of

dissolved Re to the conservative mixing line in the Amazon estuary. The final piece of evidence suggesting dissolved rhenium's inertness is its long residence time in seawater, calculated in this study to be between 300,000 and 2,000,000 years.

II. Methods

II.1 Sample Collection Information

Orinoco

1) Major (MAJ) and trace (TE) samples collected by John Edmond and Erik Brown during 7 expeditions between March, 1983, and February, 1988, (see Table 3.1.a).

2) For TE samples, 500 mL of river water was filtered through 0.4 μm Nucleopore filters, then acidified with 1 mL 3x redistilled 6 N HCl. For MAJ samples, 500 mL of water was filtered through 0.45 μm Millipore filters, and not acidified.

Amazon Estuary

1) Collected by Ed Brook in August, 1989.

2) In the field, 500 mL samples were filtered through 0.22 μm Millipore Millipacks, then acidified with 2 mL 6 N HCl.

North Atlantic Ocean (Station S: 32°10'N; 64°30'W)

1) Collected by Ed Boyle in May, 1990.

2) In the field, 2 l unfiltered samples were acidified with 25 mL 6 N HCl.

North Pacific Ocean (24°16'N; 169°32'E)

1) Collected by Chris Measures on May 10, 1985.

2) In the field, 1 l samples were acidified with 4 mL 6 N HCl.

II.2 Laboratory Preparation of Samples for Re Analysis by Isotope Dilution

A 50 mL aliquot of a sample is spiked with an appropriate volume (discussed below) of 97.4% ^{185}Re spike (Oak Ridge National Laboratories, TN), and left to equilibrate for 24 hours. Separation of Re from a sample is facilitated by running it through a 0.8x4 cm anion exchange resin column containing 1.5 mL AG 1-X8 (100-200 mesh, Cl^- form) resin capped with a porous polyethylene frit; both the columns and resin are from BioRad Laboratories, Richmond, CA.

Pre-preparation of the columns consists of running through (1) 10 mL 3x redistilled 8 N HNO_3 , (2) 20 mL Corning Distilled Water (CDW), (3) 10 mL 6 N HCl , and (4) 20 mL 0.5 N HCl . The columns are allowed to drip at 1 atmosphere pressure.

After a sample is run through a column, the column is rinsed with 50 mL 0.1 N HCl , and 50 mL CDW. The sample is then eluted into a 50 mL teflon beaker with 30 mL 8 N HNO_3 .

Concentration of the sample is facilitated by evaporation in a teflon evaporation chamber under a filtered air stream (and inside a fume hood), at $\sim 80^\circ\text{C}$. When <5 mL of liquid remains in the beaker, the sample is transferred to a 5 mL conical teflon vial. The evaporation is stopped when the sample has been concentrated to $<250 \mu\text{L}$ (a drop in the base of the conical vial).

Finally, $250 \mu\text{L}$ 0.8 N HNO_3 is added to the sample and mixed before injection into the ICP-MS (VG PlasmaQuad).

All bottles, beakers, columns, and accessory equipment are acid-leached in 10% HNO_3 , or 50% HNO_3 for teflon components. Furthermore, unless otherwise specified, the above steps are carried out in a laminar flow

bench, 3x redistilled acids are used, and the standard precautions against contamination followed during trace metal analysis are practiced.

These methods are described in more detail in (Colodner, 1991a).

II.3 Isotope Dilution Technique

In isotope dilution (ID) analysis, the quantity of an element is estimated from the change produced in its isotopic composition by the addition of a known quantity of a stable isotopic tracer of that element (Heumann, 1986). The general formula for an element with n isotopes is

$$x = y * \frac{B_{ik} - C_{ik}}{C_{ik} - A_{ik}} * \frac{\sum_{i=1 \text{ to } n} A_{ik} * M_i}{\sum_{i=1 \text{ to } n} B_{ik} * M_i}$$

where x=the quantity of the element in the sample;

y=the quantity of the tracer (or "spike");

A_{ik}=the "cosmic" (e.g., crustal) ratio of the of the isotopes i and k in the sample;

B_{ik}=the ratio of the isotopes i and k in the spike;

C_{ik}=the measured ratio of the isotopes i and k in the mixture of sample and spike;

M_i=the atomic weight of the isotope i.

For Re, with two isotopes, the ID equation simplifies to

$$S = \frac{\%187Re_t}{\%187Re_s} * T * \frac{R_t - R_m}{R_m - R_s}$$

where S=# moles of Re in the sample

T=# moles of spike added to the sample;

R=the ratio of ¹⁸⁵Re to ¹⁸⁷Re;

t=tracer (or spike);

s=sample;

m=mixture of sample and spike.

Since the Oak Ridge National Laboratories Re spike is 97.40% ^{185}Re , and the crustal abundance of ^{185}Re is 37.4% (in, 1991), the ID equation for Re simplifies to

$$S = \frac{2.60}{62.6} * T * \frac{37.46 - R_m}{R_m - 0.5974}$$

Determining T, the correct amount of spike to add to a sample, is the only tricky part. What makes its determination arbitrary is the fact that the actual amount of Re in the sample is unknown. For seawater or estuary samples that does not pose much of a problem, because Re was expected (and observed) to be conservative. For the river water samples, though, where more than 4 orders of magnitude in Re concentration are observed, determining the proper amount of spike to add to a sample can affect precision considerably. Therefore, some samples were run twice, both unspiked and spiked.

The ideal ratio one aims for in spiking a sample is somewhere between 1, which is ideal for the ICP-MS, and 4.7, which is ideal given the aforementioned spike and crustal isotopic ratios. The former results from the assumption that the ICP-MS experiences the same background (noise) for both isotopes, and the latter is simply the geometric mean between the spike ratio and the crustal (or sample) ratio. This ratio minimizes the error introduced into results calculated with the ID equation by the error in the measured ratio. In most cases, I attempted to spike all samples such that the isotopic ratio of the mixture would be around 3 (Colodner, 1991b).

II.4 Inductively-Coupled Plasma Mass Spectrometric Technique for Re Determination

Samples, prepared as outlined above, were introduced into the ICP-MS by a flow injection device with a 250 μL loop. A peak jumping mode was employed for all analyses.

For every 3 samples injected into the ICP-MS, 1 blank (0.8 N HNO_3) and 1 monitor solution (defined here as a spiked standard with $^{185}\text{Re}/^{187}\text{Re}=3.62$) were run. Furthermore, 1 procedure blank was prepared with every 5 or 11 samples (samples were prepared in batches of 6 or 12 for logistical purposes). The procedure blank was subject to all aspects of preparation that the samples were, excluding the addition of a sample or Re spike.

II.5 Maximizing Precision: Correcting for Background Noise, Spurious Re, and Machine Bias and Variability

Precision was maximized by taking the following steps: (1) background noise was corrected for by subtracting the average number of counts per second (cps) recorded for each isotope of the blank (0.8 N HNO_3), for all blanks run on a particular day, from each of the monitor solution measurements of those isotopes; (2) spurious Re introduced during the preparation of the samples was eradicated from the recorded signal by subtracting the average number of cps recorded for each isotope of the procedure blank, for all blanks run on a particular day, from each of the sample measurements of those isotopes; and (3) the effects of machine bias on a particular day were minimized by multiplying the corrected isotopic ratio of the sample by the ratio of the theoretical isotopic ratio of the

monitor solution (3.62) and the average of the measured isotopic ratios of the monitor solution.

Counts per second on the blank (0.8 N HNO₃) typically fell between 1 and 10 for either isotope, whereas for the procedure blank, they typically fell between 2 and 15. Total cps for either isotope of a sample with spike varied by day, and with the particular set of cones used, but typically fell between: (1) 1100 and 18,000 for seawater samples; (2) 500 and 14,000 for estuarine samples; and (3) 200 and 20,000 for river water samples. Only in some of the Orinoco samples (specifically those from the Guyana Shield) did the background account for more than 1% of the total signal.

II.6 Machine Variability and Bias

Variability in the response of the ICP-MS can account for approximately 1.4% of the error associated with the measurements made during these experiments. That number represents the average standard deviation of the monitor solution ratios measured each day the machine was run. The average of the averages of measured isotopic ratios (¹⁸⁵Re/¹⁸⁷Re) of the monitor solution for all days the machine was used during these experiments is 3.52. Therefore, during the entire period from 10/31/90 to 3/31/90, there was a $2.8 \pm 1.4\%$ bias for the heavier isotope (¹⁸⁷Re), since the theoretical ratio of the monitor solution is 3.62.

II.7 pH Experiment

A test was run to determine the effect of sample pH on Re recovery. This was done since the samples used had been acidified to varying pH's.

A 58 pM Re monitor solution was acidified with 3x redistilled 6 N HCl, to pH's of: 3.1 (duplicates made), 1.8, and 0.5 (duplicates made). After

elution from the columns, the samples were each spiked with 100 μL 50.5 nM Re tracer (97.40% ^{185}Re), and concentrated in the aforementioned fashion. Recoveries were $>98\%$, and did not show any trend with varying pH. The standard deviation of the measured isotopic ratios was 5.5% on a day when the standard deviation of the isotopic ratio of the monitor solution was 3.8%. It was therefore determined that pH did not affect the recovery of Re using the above stated procedure. Koide, *et al.* (1987) made a similar test and concluded that pH did not affect the recovery of Re by a similar procedure.

These results were confirmed by the fact that Orinoco TE and MAJ samples from the same location were observed to have the same Re concentrations, even though the former had been acidified, and the latter had not.

II.8 Precision Experiment

An experiment was conducted to determine the precision of the method of recovery and analysis of Re from a natural water using the above procedure. Five replicates of the same bottle of North Pacific seawater ($35^{\circ}03.20'\text{N}$; $123^{\circ}19.29'\text{W}$) were prepared in the above fashion. Each was then split into two aliquots before injection into the ICP-MS. The standard deviation of all ten analyses was 3.07%, while the standard deviation of the isotopic ratio of the monitor solution was 0.6%. The precision of the combined method of recovery and analysis of Re was thus thought to be at least as good as 3%.

III Data Analysis and Discussion

III.1 Re in the Orinoco River Basin

The Orinoco River is the third largest in the world in terms of annual water discharge, surpassed only by the Amazon and Zaire Rivers. In its entirety, the Orinoco basin occupies 830,000 km²--most of Venezuela and Colombia (Figure 3.1.1). Yee, *et al.* (1987), divided its geology crudely into three regions: (1) the Precambrian Guyana Shield constituting the right bank of the river; (2) the floodplain, or Llanos, consisting of recent fluvio-lacustrine sediments deposited by rivers originating in the Colombian and Venezuelan Andes; and (3) the Colombian and Venezuelan Andes, consisting of the Cordillera de Merida and Portugueza Basins (Palmer and Edmond, 1990). The latter two regions comprise the left bank of the Orinoco (Figure 3.1.2).

Rhenium was measured in 29 rivers and tributaries throughout the Venezuelan Orinoco Basin. The samples were collected during 7 expeditions between March, 1983 and February, 1988, by John Edmond and Erik Brown. A listing of rivers sampled, dates of collection, and flow conditions may be found in Table 3.1.a. Concentrations of dissolved Re-- defined here as all Re that passed through a 0.4 μ m filter--were found to span more than four orders of magnitude in the basin. The lowest values were below 0.02 pmol/kg, the detection limit for 50 ml water samples. The highest Re concentration measured was 412 pmol/kg--nearly 10 times the Re concentration in seawater. The highest concentrations of dissolved Re were observed in rivers from region 3: those draining the eastern foothills of the Venezuelan Andes. More specifically, the rivers of the Portugueza Basin in the eastern part of region 3 were found to contain extremely high Re concentrations. Samples taken at Ciudad Bolivar, thought to be

Figure 3.1.1: Map of the Orinoco Basin.

<u>Region</u>	<u>Map Number</u>	<u>River</u>	<u>Date Collected</u>	<u>Water Level</u>
1	1	Cataniapo	Oct-84	Median: falling
1	2	Yuruman @ S. Ignacio	Oct-84	Median: falling
1	3	Cuchivero	Jun-87	Median-high: rising
1	4	Caroni @ Ordaz	Mar-83	Low
1	5	Atabapo	Oct-84	Median: falling
1	6	Ventuari @ Cacuri	Oct-84	Median: falling
1	7	Sipapo @ mouth	Oct-84	Median: falling
1	8	Paragua ab Karun	Oct-84	Median: falling
1	9	Aro ab falls	Oct-84	Median: falling
1	10	Padamo	Oct-84	Median: falling
2	11	Apure @ Portuguesa	Jun-87	Median-high: rising
2	12	Apure @ S. Fernando	Feb-88	Low
2	13	Apure @ el Perro	Oct-84	Median: falling
2	14	Capanaparo	Oct-84	Median: falling
2	15	Meta	Oct-84	Median: falling
3	16	Masparro @ Apure conf.	Feb-88	Low
3	17	Acariguau @ Rt. 5	Jun-87	Median-high: rising
3	18	Tamanaco near Macapa	Feb-88	Low
3	19	Ospino	Jun-87	Median-high: rising
3	20	Morador Rt. 5	Jun-87	Median-high: rising
3	21	Cojedes @ S. Rafael Rt. 5	Feb-88	Low
3	22	Canagua	Feb-88	Low
3	23	Caparo	Feb-88	Low
3	24	Flood plain Arauca	Oct-84	Median: falling
3	25	Uribante	Jun-86	Median: rising
	26	Manapire	Oct-84	Median: falling
	27	Caris	Oct-84	Median: falling
	28	Pao	Oct-84	Median: falling
Mainstream	29	Orinoco @ C. Bolivar	Mar-86	Low

Table 3.1.a: Rivers in the Orinoco basin in which dissolved Re was measured. Included in the table are region, name, sampling location, sampling date, and water level.

representative of mainstream Orinoco water (Edmond,1991), contained 4.40 pmol/kg dissolved Re. The pooled standard deviation on all Re measurements in the Orinoco Basin, based on replicate analyses, is 2.04% (Table 3.1.b).

The range in riverine Re concentrations can be explained by the geology of the Orinoco basin. The Portuguesa basin contains black shales and bituminous limestones, deposited during the maximum transgression of the late Cretaceous seas (Macellari and De Vries, 1987), while the entire right bank of the river is an intensely-weathered (transport-limited) Precambrian shield (Palmer and Edmond, 1990).

Rhenium geochemistry can account for the high dissolved Re load in rivers draining black shales and bituminous limestones. Black shales have been observed by other researchers to be highly enriched in Re (Poplavko, Ivanov et al., 1977);(Ravizza and Turekian, 1989). Furthermore, Re is known to be enriched in marine anoxic sediments (typically the precursors to black shale deposits), relative to its crustal abundance (Boyko, Baturin et al., 1985);(Koide, Hodge et al., 1987). Under the strongly reducing conditions associated with anoxic sediments, heptavalent Re, as the unreactive oxoanion, perrhenate (ReO_4^-), may be reduced to the tetravalent oxide (Morris and Short, 1965); or, in the presence of sulfur, the hexa-, tetra-, or trivalent sulfides, or $\text{Re}(0)$ (Brookins, 1986). The significant correlation observed between Re and SO_4^{2-} in the Andean rivers of region 3 is further evidence of a black shale source for the element; the high sulfate concentrations in these rivers are believed to originate from the oxidizing weathering of reduced sulfur in black shales (Figure 3.1.3).

Region	Map #	Sample #	[Re] pmol/kg	AVG	SD	[SO4] μmol/kg	[U] pmol/kg	[Mo] nmol/kg
1	1	549 MA	0.24			4.10	150	
1	2	507 TE	0.40			0.00	37	
1	3	826 TE	0.09			3.00	229	
1	4	450 TE	0.03			1.20	89	
1	5	545 MA	0.01			0.00	39	
1	6	544 MA	0.06			4.10	83	
1	7	580 MA	<0.02			0.00	199	
1	8	506 TE	0.34			0.00	63	
1	9	556 TE	0.02			0.00	59	
1	10	584 MA	<0.02			0.00	156	
2	11	822 TE	7.87					
2	11	822 TE	9.09	8.48	0.86	78.14	297	6.40
2	12	924 TE	39.36					
2	12	924 TE	38.35					
2	12	924 MA	37.54	38.42	0.91	223.00	1589	16.00
2	13	523 TE	21.64			62.00	206	8.70
2	14	527 TE	0.80			4.60	52	
2	15	532 TE	4.98			66.63	40	4.40
3	16	919 TE	21.90			264.00	3256	10.90
3	17	801 MA	253.20					
3	17	801 MA	252.60					
3	17	801 TE	256.60	254.13	2.16	1230.00	6333	102.50
3	18	901 TE	8.27					
3	18	901 TE	8.23	8.25	0.03	45.00	258	
3	19	802 TE	50.43			345.17	928	
3	20	803 TE	21.89					
3	20	803 MA	22.16	22.03	0.19	392.21	472	
3	21	903 TE	411.80			1885.00	5787	24.60
3	22	912 MA	2.16					
3	22	912 TE	2.02	2.09	0.10	30.00	95	
3	23	914 TE	5.70			51.00	227	
3	24	561 MA	3.38			73.70	46	1.80
3	25	788 MA	16.28			192.41	1140	19.70
	26	522 TE	1.34			58.60	140	
	27	515 MA	0.33			4.20	153	
	28	517 TE	1.03			24.00	120	
Mainst.	29	721 MA				71.61		
		736 MA	4.40			75.33		
				PSD	2.04			
				(%)				

Table 3.1.b: Re in the Orinoco. Included in the table are Re concentrations, with averages and standard deviations for replicate analyses, as well as available SO₄²⁻, U (Edmond, 1991), and Mo (Colodner, 1991b) concentrations. The "PSD" is a pooled standard deviation based on all replicate analyses in the Orinoco. It is of the form $[(\sum n(i)\sigma(i)^2)/\sum n(i)]^{0.5}$, where sigma is the standard deviation (SD) of n replicates. The mainstream Re measurement was made on 200 ml of water (100 ml from each sample); all other Re measurements were made on 50 ml of water.

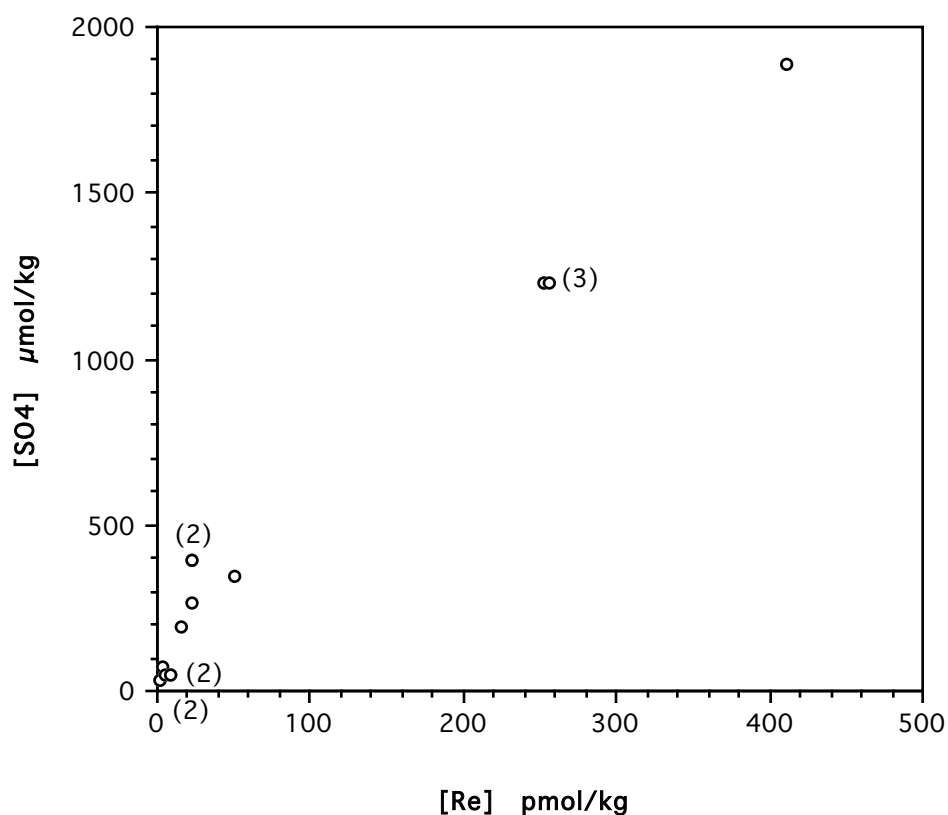


Figure 3.1.3: [Re] vs [SO₄²⁻] for the Andean rivers (region 3) of the Orinoco. Numbers in brackets indicate quantity of replicate analyses.

The Llanos, or region 2 of the Orinoco basin, represents a large floodplain that receives the waters from the Andean rivers (Palmer and Edmond, 1990) (Figure 3.1.2). During the wet season (roughly July-September), when the river attains its highest stand, the entire region becomes flooded, making navigation, and hence, sampling, virtually impossible. Another consequence of the annual flooding is a topological metamorphosis. Tributaries are lost, created, and rerouted (Edmond, 1991). At any given time, though, such tributaries would be expected to exhibit chemistries similar to the Andean rivers. The dissolved load carried

by Andean rivers (resulting from intense weathering which occurs in the Andes) is inherited by floodplain rivers. The suspended load from Andean rivers is deposited and reworked in the Llanos (Palmer and Edmond, 1990). Further weathering of floodplain sediments may therefore add Re and SO_4^{2-} to these rivers, but the major process affecting Re concentration in the Llanos is simply dilution. Evidence of this is shown in Figure 3.1.4, where Re and SO_4^{2-} are observed to be relatively high in the floodplain, and correlated as in Figure 3.1.3. (For comparison, see Figure 3.3.5, a plot of [Re] vs [SO_4^{2-}] for region 1 of the Orinoco--the precambrian Guyana Shield--in which the concentrations of both species are low and not well correlated).

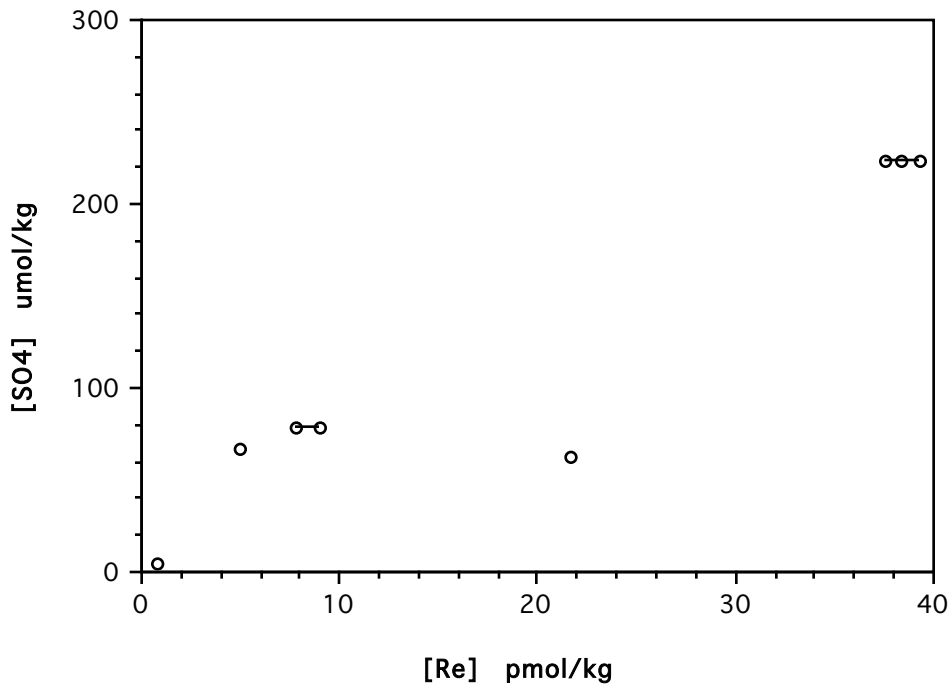


Figure 3.1.4: [Re] vs [SO_4^{2-}] for the Llanos (region 2) of the Orinoco. Replicate Re measurements were made on two of the five samples from the floodplain. The results of all region 2 analyses are plotted.

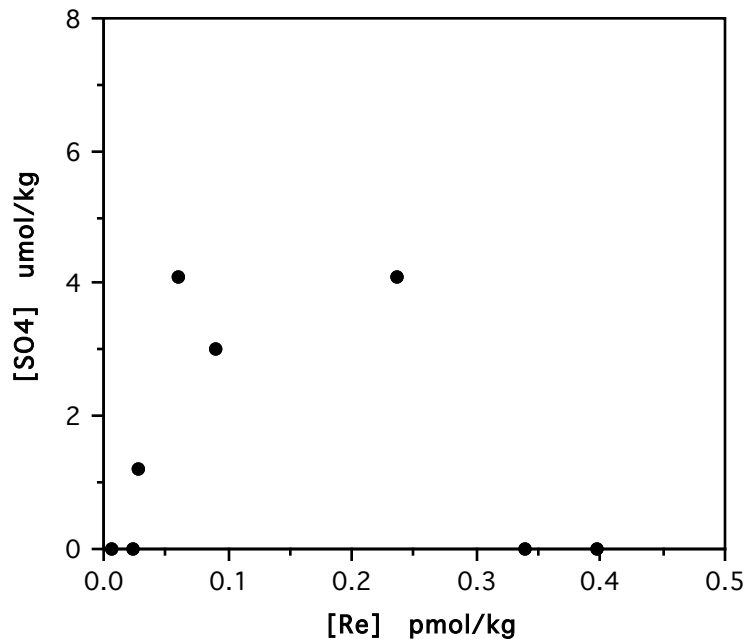


Figure 3.1.5: [Re] vs [SO₄⁻²] for the Guyana Shield (region 1) of the Orinoco.

Another indication that black shales are the primary source of Re in the Orinoco is the correlation of Mo and U with Re in the floodplain rivers (Figure 3.1.6). The former two species are known to exhibit similar geochemical behavior to that observed for Re. For instance, they are both enriched in anoxic sediments (Bertine and Turekian, 1973);(Calvert and Price, 1983);(Jacobs, Emerson et al., 1987);(Francois, 1988) and black shales (Vine and Tourtelot, 1970). Furthermore, both Mo and U, like Re, are conservative in the ocean (Bruland, 1983);(Chen, Edwards et al., 1986) and have long residence times in seawater (Broecker and Peng, 1982).

Finally, it is consistent with our understanding of the geology and weathering processes occurring on the Guyana Shield (region 1) to find extremely low Re concentrations in rivers draining that region. The

lithologically diverse Precambrian terrain is undergoing intense transport-limited weathering (Palmer and Edmond, 1990). This is evidenced by the observed Si/(Na+K) ratios, which are in excess of 3 in most sampled rivers (Palmer and Edmond, 1990). Any Re originally present in the basement rock would most likely have been mobilized by oxidative weathering processes.

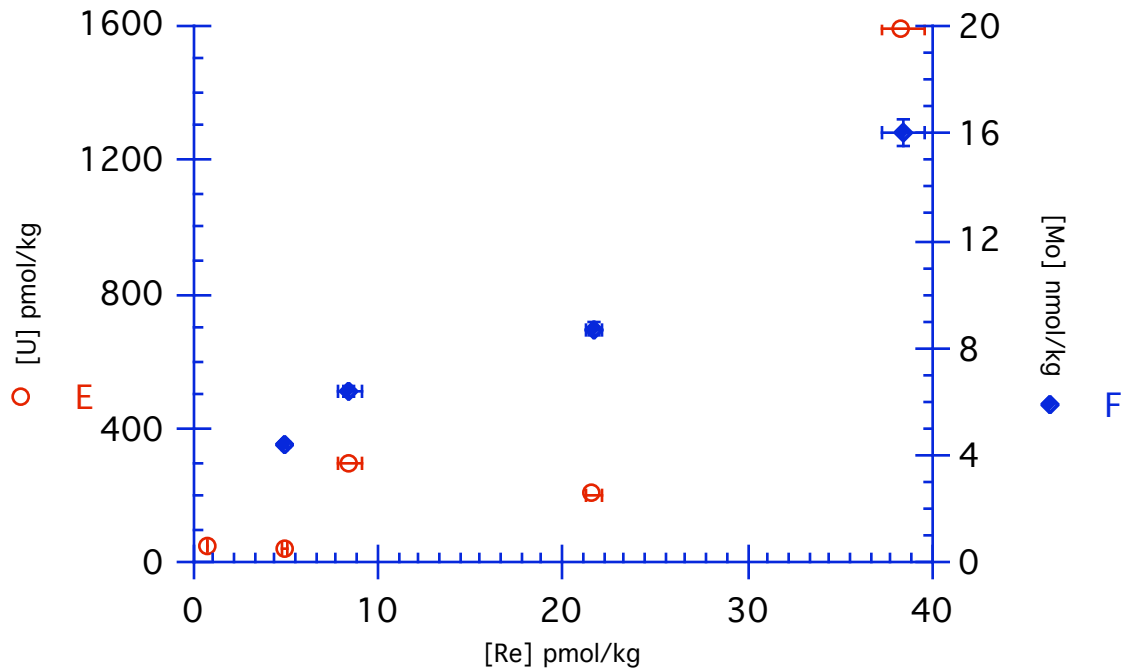


Figure 3.1.6: [Re] vs [U] and [Mo] for the Llanos (region 2) of the Orinoco Basin. Mo measurements were made by D. Colodner (Colodner, 1991b); U measurements by M. Palmer (Edmond, 1991). Error bars on the Mo measurements are 3%, while those on the Re measurements are a pooled standard deviation (2.04%) divided by the square root of the number of replicates. The pooled standard deviation is of the form $[(\sum n(i)\sigma(i)^2)/\sum n(i)]^{0.5}$, and is derived from all replicate analyses performed in the Orinoco Basin.

III.2 Re in the Amazon Estuary

Initial studies of the marine geochemistry of Re suggested a long residence time for this element in seawater due to the stability of its thermodynamically-favored (Turner, Whitfield et al., 1981) dissolved form in seawater, the perrhenate anion (ReO_4^-) (Koide, Hodge et al., 1986). In order to quantify its residence time with respect to river inflow, the dissolved concentration of Re in rivers and the behavior of Re in estuaries must be determined. If an estuary is a system in steady state with inflowing river water and seawater, the concentration of a conservative dissolved species is a linear combination of the concentrations in river water and seawater (Evans, Cutshall et al., 1977). In other words, the dissolved concentration of a conservative species should increase linearly from its fresh-water value to its open-ocean value in a typical estuary. This implies that a plot of such a species versus salinity should be linear, with endpoints at zero salinity and the "local" open-ocean salinity.

Estuaries are dynamic systems, however, where chemical and physical processes interact to produce deviations from the ideal mixing behavior described above. For example, uranium, which also exhibits conservative behavior in seawater, has been shown to be added to the dissolved phase in the Amazon estuary (McKee, DeMaster et al., 1987) but removed from the dissolved phase in the Ganges-Brahmaputra mixing zone (Butts and Moore, 1988). In both cases, the input of uranium by rivers to the oceans is substantially modified by interactions of the element with deltaic sediments.

The Amazon River is the world's largest river in terms of water discharge, and the second largest source of fluvial sediment to the world ocean (Meade, Dunne et al., 1985), and therefore was chosen for this study of Re estuarine geochemistry. On the Amazon shelf, strong tidal currents

and wave activity rework the seabed and suspended sediment concentrations increase toward shore (McKee, DeMaster et al., 1987). Rhenium was measured at 13 locations along a transect of the Amazon estuary. The low and high salinity end-members were taken to be Amazon river water from Macapa and Atlantic surface water from Bermuda, respectively (Table 3.2.a). Re shows nearly conservative behavior in the estuary. In a plot of Re concentration versus salinity, a straight line is observed that closely traces the line between zero salinity (the fresh-water end-member) and 36.4 per mil salinity (the seawater end-member). At salinities below about 5 per mil, though, Re deviates substantially from the conservative mixing line (Figure 3.2.1). The data suggest that a source for rhenium exists on the inner Amazon shelf.

Similar observations were reported by McKee, *et al.* (1987) in their study of uranium geochemistry on the Amazon shelf. They also observed a positive deviation from their straight-line plot of dissolved ^{238}U versus salinity at 5 per mil salinity (McKee, DeMaster et al., 1987). The most likely source of the added dissolved uranium on the shelf is desorption from the ferric-oxyhydroxide coatings of resuspended fluvial bottom sediments. The ferric-oxyhydroxide coating on particles is the most important transport phase for transition metals in the Amazon River (Gibbs, 1977), and Re might also be adsorbed on this phase. Under suboxic conditions on the Amazon shelf, iron-hydroxide coatings are reduced and dissolved, and may release adsorbed metals such as uranium and rhenium to pore waters. Under reducing conditions one would expect both U and Re to be reprecipitated in the sediments, however, frequent resuspension of bottom sediments could release both metals to oxic shelf waters.

Sample	Salinity ppt	[Re] pmol/kg	AVG pmol/kg	SD pmol/kg	SD (%)	Error Bar (1 SD)
Am1a	0.00	1.06				
Am1b	0.00	1.17	1.11	0.07	6.57	0.03
A7	0.30	9.10				0.39
A1	2.60	10.64				0.45
A8	2.61	10.45				0.44
A2	4.90	10.18				
v.11 (A2)	4.90	9.57	9.88	0.43	4.36	0.30
AmE2	14.78	19.54				0.83
A3	16.40	22.90				0.97
A9	17.60	24.72				1.05
A4	21.60	28.93				1.23
A10	26.50	31.69				1.34
A5	27.30	41.25				
v.10a (A5)	27.30	41.33				
v.10b (A5)	27.30	40.80	41.12	0.29	0.69	1.01
AmE6	34.45	44.50				1.89
AmE4	36.36	44.13				1.87
			PSD pmol/kg	0.30		
			PSD (%)		4.24	

Table 3.2.a: Re measurements in the Amazon estuary. Samples Am1a and Am1b are replicates of the fresh-water end-member. Sample AmE4 is the seawater end-member. PSD stands for the pooled standard deviation, which is derived from all replicate analyses performed in the Amazon estuary, and is of the form $[(\sum n(i)\sigma(i)^2)/\sum n(i)]^{0.5}$, where σ is the standard deviation (or SD), and n is the number of replicates. The error bar is $((\text{PSD}\% \times [\text{Re}] \text{pmol/kg}) / 100 / \sqrt{n})$. The error bars plotted in Figure 3.2.1 are \pm that value.

Additionally, reworking of these sediments maintains suboxic conditions in the seabed where anoxic conditions would otherwise prevail [Aller, 1986 #16]. It is also possible that Re and U escape reduction and simply diffuse out of the sediments into bottom water. This would probably be more likely on the outer shelf, where wave and tidal actions would have less of an effect on bottom sediments. A combination of these processes would provide a Re source capable of producing a positive deviation from the conservative mixing line.

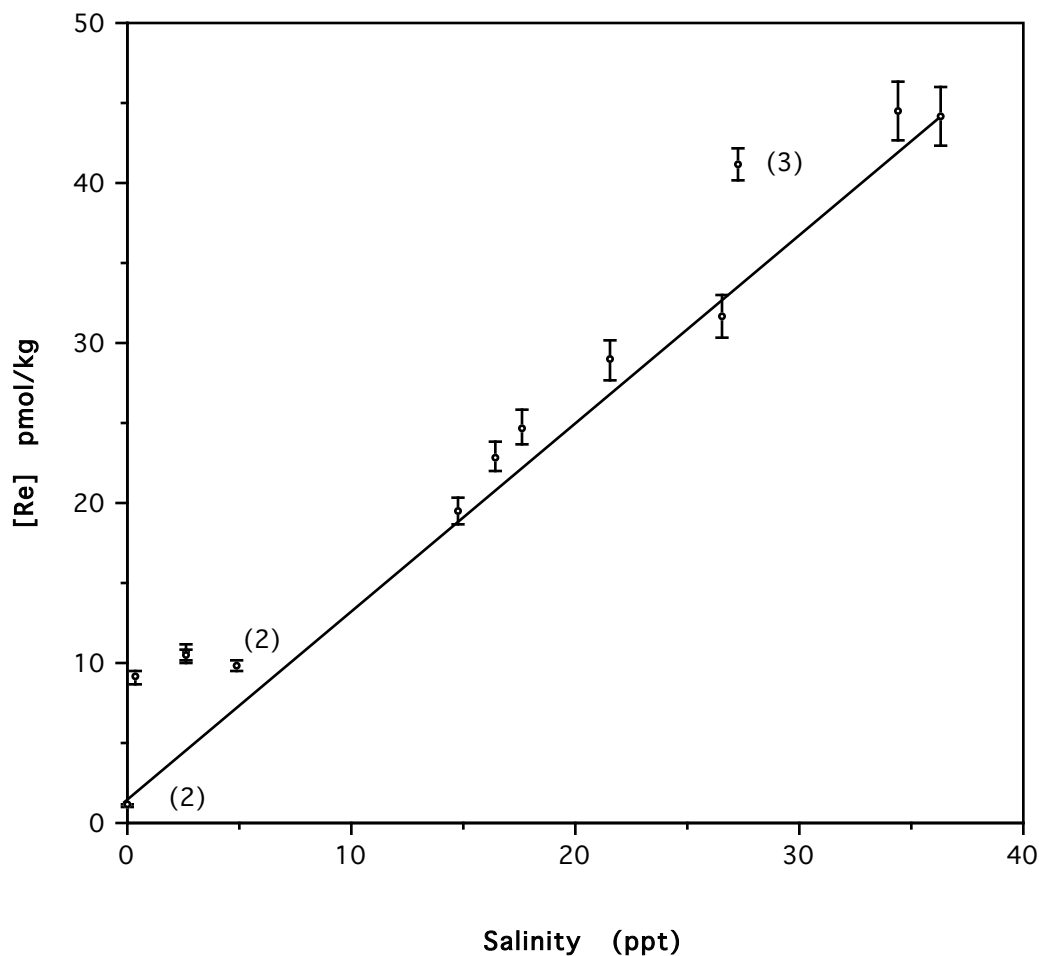


Figure 3.2.1: [Re] vs salinity for the Amazon estuary. The plotted line is the conservative mixing line. The error bars are the pooled standard deviation, based on all replicate analyses in the estuary, divided by the square root of the number of replicates. The numbers in brackets indicate the number of replicate measurements performed on the sample.

Unlike U, though, the Re source appears to be localized on the inner Amazon shelf. In the case of U, the sediments appear to be a source for the element along the entire shelf. This may indicate that a smaller proportion of the Re load of the Amazon is carried in the ferric oxyhydroxide phase, or that Re desorption occurs more quickly in the inner shelf sediments.

Alternatively, a different mechanism may be controlling the Re distribution in the Amazon estuary. Assuming that there are no external sources of Re, such as other fresh-water sources or industrial pollution, the additional source of dissolved Re may be attributed to desorption from fluvial particulate matter within the water column. It has been shown that many trace metals and radionuclides, such as Mn and ^{54}Mn (Johnson, Cutshall et al., 1967);(Kharkar, Turekian et al., 1968);(Evans and Cutshall, 1973), and Ba (Edmond, Boyle et al., 1978);(Bruland, 1983) are carried on suspended particulate matter in rivers, and released upon contact with seawater. Evans *et al.* (1977) suggest that such behavior can be explained on the basis of simple ion exchange displacement. For instance, Evans *et al.* (1973) showed that Columbia River suspended matter released 30-60% of its ^{54}Mn upon contact with seawater. Analyses of Re in Amazon Shelf sediments and in suspended particulate matter will be necessary in order to determine which of these processes dominates Re behavior in this environment.

III.3 Re in the North Atlantic and North Pacific Oceans

A conservative oceanic depth profile for an elemental species is one that shows "a constant concentration relative to salinity as a result of the low reactivity of the element in seawater" (Bruland, 1983). The depth profiles of Re in both the North Atlantic (Station S: 32°10'N; 64°30'W) and North Pacific (24°16'N; 169°32'E) show constant concentrations of dissolved Re relative to salinity to $\pm 3.2\%$ and $\pm 4.4\%$, respectively, at the 95% confidence level (Figures 3.3.1&2, Tables 3.1.a&b). Based on the 17 analyses comprising each profile, average dissolved Re concentration in the Atlantic is 44.68 ± 0.34 pmol/kg, and 43.91 ± 0.46 pmol/kg in the Pacific. On an inter-ocean basis, then, average [Re] is conservative at the 95% confidence level.

Sample	Depth (m)	Salinity ppt	[Re] pmol/kg	[Re] corr 35 ppt	SD pmol/kg	SD (%)	Error Bar (1 SD) pmol/kg
At1.a	101	36.685	48.53	46.30			
At1.c	101	36.685	45.31	44.20			
At1.d	101	36.685	46.03	44.61			
		AVG	46.63	45.04	1.69	3.62	0.64
At2	366	36.567	46.33	44.34			1.10
At3	551	36.308	46.76	45.07			1.11
At4	920	35.169	44.52	44.31			1.05
At5	1053	35.083	44.61	44.50			1.05
At6	1323	35.066	43.90	43.82			1.04
At7.a	1593	35.043	44.59	44.53			
At7.c	1593	35.043	44.44	44.66			
At7.d	1593	35.043	45.21	45.37			
		AVG	44.75	44.85	0.41	0.91	0.61
At8	2119	35.003	44.72	44.71			1.06
At9	2597	34.953	45.42	45.48			1.07
At10	3075	34.924	44.34	44.43			1.05
At11.a	3553	34.899	43.20	45.48			
At11.c	3553	34.899	44.64	44.39			
At11.d	3553	34.899	44.24	43.26			
		AVG	44.03	44.38	0.74	1.69	0.60
Average of 17 Analyses (pmol/kg)			45.11	44.68			
Standard Deviation (pmol/kg)			1.25	0.71			
95% Conf. Interval (pmol/kg)			± 2.50	± 1.91			
95% Conf. Interval (%)			$\pm 5.55\%$	$\pm 3.16\%$			
Pooled Standard Dev. (pmol/kg)			0.01				
Pooled Standard Deviation (%)			2.36%				

Table 3.3.a: Data for the Atlantic depth profile (Figure 3.3.1).

Figure 3.3.1: Conservative depth profile of Re at Station S, off Bermuda, in the North Atlantic.

Sample	Depth (m)	Salinity ppt	[Re] pmol/kg	[Re] corr 35 ppt	SD pmol/kg	SD (%)	Error Bar pmol/kg
P1.a	27	35.25	44.50	44.18			
P1.b	27	35.25	43.10	42.79			
P1.c	27	35.25	43.45	43.14			
		AVG	43.68	43.37	0.73	1.67	0.48
P2	287	34.696	42.16	42.53			0.79
P3	566	34.136	45.16	46.30			0.85
P4	880	34.254	43.67	44.62			0.82
P5	1142	34.453	43.39	44.08			0.81
P6	1730	34.579	43.01	43.54			0.81
P7.a	2436	34.64	44.57	45.03			
P7.b	2436	34.64	44.75	45.22			
P7.c	2436	34.64	42.62	43.07			
		AVG	43.98	44.44	1.18	2.68	0.48
P8	3354	34.667	43.37	43.79			0.81
P9	4495	34.684	42.95	43.34			0.80
P10	5310	34.692	43.51	43.89			0.81
P11.a	6180	34.695	43.21	43.59			
P11.b	6180	34.695	42.96	43.33			
P11.c	6180	34.695	43.59	43.97			
		AVG	43.25	43.63	0.32	0.74	0.47
Average of 17 Analyses (pmol/kg)			43.53	43.91			
Standard Deviation (pmol/kg)			0.80	0.96			
95% Conf. Interval (pmol/kg)			±1.60	±1.91			
95% Conf. Interval (%)			±3.68%	±4.36%			
Pooled Standard Dev. (pmol/kg)			0.81				
Pooled Standard Deviation (%)			1.87%				

Table 3.3.b: Data for the Pacific depth profile (Figure 3.3.2).

Since the uncertainty introduced by the analytical technique (represented as an error bar on each point in the profiles) on the 17 Atlantic and Pacific analyses ranges from 2.8% to 4.7%, and 2.2% to 3.7%, respectively, and the total variance of those analyses is 1.1% and 2.1%, respectively (Tables 3.3.a and 3.3.b), it is statistically safe to say that no structure may be elucidated in the Re depth profiles. In other words, there are no processes causing changes in rhenium's concentration in the North Atlantic and North Pacific Oceans. At the 95% confidence level, 1 out of 20 points (with its associated two-sigma error bar) would be expected to fall outside the confidence interval; the single point in 34 analyses that does is therefore statistically irrelevant.

Figure 3.3.2: Conservative depth profile of Re in the North Pacific (24°16N; 169°32'E).

What appears on the face to be a boring story turns out to be quite noteworthy for a trace element in the sea. Of the 5 distinct basic types of vertical elemental profiles observed in typical seawater--conservative, nutrient-type, surface enrichment and depletion at depth, mid-depth minima, mid-depth maxima--conservative is relatively rare (Bruland, 1983).

It should be noted that similar findings were previously predicted by Koide and Goldberg, *et al.* (1987); however, their measured Re concentrations at 6 depths in the North Pacific (33°N; 139°W) varied by nearly a factor of 3. Their measurements ranged from 27.8 pmol/kg to 79.5 pmol/kg (assuming an average seawater density of 1.026 kg/L), with an average concentration of 57.48 pmol/kg (Table 3.3.c) (Koide, Hodge *et al.*, 1987). Due to the observed variations, Koide, *et al.* were not able to prove rhenium's conservative behavior.

<u>Depth</u>	<u>[Re] pmol/kg</u>
200	66.5
750	79.5
1000	61.8
2000	41.3
3000	27.8
4500	68.0
Average	57.5

Table 3.3.c: Data from Koide *et al.* (1987).

As stated previously, it is the stability of the oxoanion, perrhenate (ReO_4^-), in solution that is responsible for rhenium's chemical inertness. Turner *et al.* (1981) lend some insight into why ReO_4^- is the predominant Re species in natural waters.

The speciation of the positive oxidation states of elements in seawater is dictated largely by hydrolytic processes (Turner, Whitfield *et al.*, 1981).

To use Turner's example, Na^+ can be thought of as a weakly hydrolysed (or hydrated) species, while SO_4^- can be viewed as the hydrolysis product of S^{+6} followed by condensation. The degree of hydration can be semi-quantitatively estimated by the free energy of hydration, given by z^2/r , where z is the charge on the cation and r is the ionic radius (Phillips and Williams, 1965);(Williams and Hale, 1966). This term has also been referred to as the "polarizing power" of the cation (King, 1965);(Millero, 1977), and can be considered to be a measure of the cation's ability to attract electrons from water molecules (Turner, Whitfield et al., 1981). Therefore, the greater the polarizing power of the cation, the farther to the right the hydrolysis reaction will proceed. Re^{VII} , according to Turner, is "fully hydrolyzed" in natural waters; the free cationic species does not exist even in strongly acid solutions (Baes and Mesmer, 1976).

In summation, heptavalent Re, as the tetrahedral oxoanion ReO_4^- , is predicted by thermodynamic models to be the primary species of elemental Re in natural waters. The inertness of perrhenate is evidenced by its conservative depth profile. It is not surprising, then, that Re is observed to have a very long residence time in seawater. That will be shown in chapter IV.

IV Geochemical Calculations and Discussion

Two important pieces in the puzzle of rhenium's geochemistry may now be addressed. One is the element's residence time in seawater, and the other is whether it is in steady state.

With the data collected during this study, a seawater residence time for Re, with respect to riverine inflow, may be calculated. This is done by dividing the total amount of dissolved Re in the ocean by the annual riverine input of that element. Using the measured mainstream Orinoco and Amazon estuary fresh-water end-member Re concentrations (4.40 and 1.11 pmol/kg, respectively; this work), and the percentage of world riverine output those rivers represent (3.4% and 20.3%, respectively (Edmond, 1991)), one can extrapolate an "average" riverine Re concentration (1.58 pmol/kg). By multiplying this number by the total yearly input of river water to the oceans (3.6×10^{16} L/yr (Palmer and Edmond, 1990)), a yearly riverine flux of Re to the oceans of 57,000 mol-Re/yr is derived. Taking the average oceanic Re concentration to be 44 pmol/kg (this work), the average density of seawater to be 1.028 kg/L, and the world ocean volume to be 1.37×10^{21} L (Emerson and Husted, 1990) a total dissolved Re reservoir of 6.20×10^{21} mol-Re is calculated. Dividing this number by the yearly riverine flux of Re yields a residence time, with respect to riverine inflow, of 1.1×10^6 years.

A long residence time for Re was expected based on its conservative behavior in the ocean. However, the calculated value has a tremendously large "error bar" associated with it. As Bruland (1983) states, "estimates [of residence times] are [highly] dependent upon the choice of effective river end-member concentrations." In my estimation, average riverine Re concentration probably lies in the range between 1 and 5 pmol/kg.

Accounting only for dilution effects, the Orinoco value may be high since the sample was taken when the river was low (Table 3.1.a), and the Amazon value may be low since the sample was taken when the river was high (outflow of the Amazon changes by a factor of about 2.5 between wet and dry seasons (Edmond, 1991)). Another reason for the uncertainty in the calculated residence time is that the Amazon and Orinoco Rivers only account for 23.7% of the total riverine input to the oceans. The other 66.3% of world river water entering the oceans may have a Re concentration somewhat different to that of the Orinoco or the Amazon. Other determinations of the dissolved Re content of major rivers are not known to this author. Lastly, additional sources of dissolved Re--as observed on the inner shelf of the Amazon estuary--or sinks--as observed for U in the Ganges-Brahmaputra mixing zone--may exist, introducing another source of error into the estimation of a worldwide average riverine Re concentration, or an associated residence time determination.

With these uncertainties, the residence time of Re, with respect to riverine inflow, then, probably falls between 300,000 and 2,000,000 years. Even if the former were the correct value, Re would still be classified as a conservative element (given that it has a non-nutrient type depth profile), when compared to elements having similar residence times (and non-nutrient type depth profiles) (Broecker and Peng, 1982);(Bruland, 1983).

The second question to be addressed is whether or not dissolved Re is in steady state in the oceans. An element in steady state in seawater should have a removal rate to sediments equal to its input rate from rivers (and the atmosphere) (Broecker and Peng, 1982);(Bruland, 1983). Ravizza (1990) estimates the total flux of Re to anoxic sediments, assumed to be the only significant sink for the element (Koide, Hodge et al., 1986), to be 44×10^3

mol/yr. Comparing this to the estimated yearly riverine flux of the element, 57×10^3 mol/yr (this work), it can be concluded that Re is in steady state in seawater, within uncertainties.

V Conclusion

The purpose of this work was (1) to characterize rhenium's geochemistry, and (2) to study its efficacy as a paleoredox tracer in the ocean. Much was discovered about the former, while little was concluded about the latter (see (Colodner, 1991a) for more on that story). Questions I would like to see answered before drawing conclusions about (2), above, are: what the behavior of reduced Re on riverine suspended particulates is when contacted by seawater, what the rate of removal of perrhenate from seawater to anoxic sediments is, what extent of sub-oxia is required for the removal to take place, what the rate of remobilization of reduced Re is if oxic conditions return to an anoxic sedimentary layer, under what geochemical conditions might such remobilization be enhanced/decreased.

At the present time, I see Re being used effectively as a sentinel of an oxidizing atmosphere in the Precambrian. Koide *et al.* (1987) suggested this, and it still seems a perfect application of Re as a paleoredox tracer, given what we know about its geochemistry. If Re is detected in Precambrian black shales in concentrations in excess of 1 ppb (twice the crustal abundance), then oxidizing weathering processes must have been occurring, and the atmosphere would have had to contain oxygen. If Re concentrations were found to be <1 ppb, it would not necessarily mean that the atmosphere was oxygen-free; all of the Re initially present in the sample may have simply been oxidized during the past 2+ billion years. However,

with enough samples and perseverance, such a study would likely be fruitful.

VI Summary

- 1) Dissolved [Re] was found to span more than 4 orders of magnitude in the Orinoco basin: from <0.02 to 412 pmol/kg. The lowest values were observed in rivers draining the Precambrian Guyana Shield on the right bank of the river, while the highest were measured in the rivers of the Portuguesa Basin, in the southeastern foothills of the Andes.
- 2) The source of Re in the Orinoco basin is believed to be the oxidizing weathering of black shales.
- 3) Dissolved [Re] was found to closely follow the conservative mixing line in the Amazon estuary, except on the inner shelf (below 5 per mil salinity), where there appears to be a source for the element.
- 4) Dissolved Re was found to have a conservative depth profile in both the North Atlantic (Bermuda: Station S) and North Pacific ($24^{\circ}16'N$; $169^{\circ}32'E$) Oceans. In the former, its vertical concentration varied by $\pm 3.16\%$ at the 95% confidence level, while in the latter, it varied by $\pm 4.36\%$ at the 95% confidence level. Furthermore, average [Re] was 44.68 ± 0.34 pmol/kg in the Atlantic, and 43.91 ± 0.46 pmol/kg in the Pacific, making Re conservative, on an inter-ocean basis, at the 95% confidence level.
- 5) Re was calculated to have a residence time between 300,000 and 2,000,000 years.
- 6) Re was calculated to be in steady state in seawater, within uncertainties.

REFERENCES

- Aller, R. C., J. E. Mackin and R. T. Cox. (1986). "Diagenesis of Fe and S in Amazon Inner-Shelf Muds: Apparent Dominance of Fe Reduction and Implications for the Genesis of Oolitic Ironstones." *Cont. Shelf Res.* **6**: 263-289.
- Baes, C. F. and R. E. Mesmer. (1976). *The Hydrolysis of Cations*. John Wiley & Sons.
- Bertine, K. K. and K. K. Turekian. (1973). "Molybdenum in Marine Deposits." *GCA.* **37**: 1415-1434.
- Boyko, T. F., G. N. Baturin and A. D. Miller. (1985). "Rhenium in Recent Ocean Sediments." *Geokhimiya.* **11**: 1662-1671.
- Broeker, W. S. and T. H. Peng. (1982). *Tracers in the Sea*. Palisades, New York, Eldigio Press.
- Brookins, D. G. (1986). "Rhenium as Analog for Fissiogenic Technetium: Eh-pH Diagram (25°C, 1 bar) Constraints." *Applied Geochemistry.* **1**: 513-517.
- Bruland, K. W. (1983). *Trace Elements in Sea-water*. *Chemical Oceanography*. London, Academic Press.
- Butts, J. L. and W. S. Moore. (1988). "Uranium Removal in the Ganges-Brahmaputra Mixing Zone." *EOS.* **69**(44): 1255.
- Calvert, S. E. and N. B. Price. (1983). *Geochemistry of Nambian Shelf Sediments. Coastal Upwelling and its Sedimentary Record*. Plenum Press.
- Chen, J. H., R. L. Edwards and G. J. Wasserburg. (1986). "U(238), U(234) and Th(232) in Seawater." *EPSL.* **80**: 241-251.
- Colodner, D. (1991). (*Marine Geochemistries of the Platinum Group Elements*). PhD thesis, Massachusetts Institute of Technology (not yet published).
- Colodner, D. C. (1991). Personal Communication.
- Cotton, F. A. and G. Wilkinson. (1988). *Advanced Inorganic Chemistry*. New York, John Wiley & Sons.

Edmond, J. M. (1991). Personal Communication.

Edmond, J. M., E. D. Boyle, D. Drummond, B. Grant and T. Mislick. (1978). "Desorption of Barium in the Plume of the Zaire (Congo) River." *Netherlands Journal of Sea Research*. **12**(3/4): 324-328.

Emerson, S. and S. S. Husted. (1990). Ocean Anoxia and the Concentration of Molybdenum in Seawater. Unpublished manuscript.

Evans, D. W. and N. H. Cutshall. (1973). Effects of Ocean Water on the Soluble-Suspended Distribution of Columbia River Radionuclides. Vienna, International Atomic Energy Agency.

Evans, D. W., N. H. Cutshall, F. A. Cross and D. A. Wolfe. (1977). "Manganese Cycling in the Newport River Estuary, North Carolina." *Estuarine and Coastal Marine Science*. **5**: 71-80.

Francois, R. (1988). "A Study on the Regulation of the Concentrations of Some Trace Metals (Rb, Sr, Pb, Cu, V, Cr, Ni, Mn and Mo) in Saanich Inlet Sediments, British Columbia, Canada." *Marine Geology*. **83**: 285-308.

Gibbs, R. J. (1977). "Transport Phases in the Amazon and Yukon Rivers." *Geol. Soc. Amer. Bull.* **88**: 829-843.

Heumann, K. G. (1986). Isotope Dilution Mass Spectrometry. Chemical Analysis. New York, John Wiley & Sons.

Jacobs, L., S. Emerson and S. S. Husted. (1987). "Trace Metal Geochemistry in the Cariaco Trench." *Deep-Sea Research*. **34**(5/6): 965-981.

Johnson, V. G., N. H. Cutshall and C. L. Osterberg. (1967). "Retention of Zn(65) by Columbia River Sediments." *Water Resources Research*. **3**: 99-102.

Kharkar, D. P., K. K. Turekian and K. K. Bertine. (1968). "Stream Supply of Dissolved Silver, Molybdenum, Antimony, Selenium, Chromium, Cobalt, Rubidium and Cesium to the Oceans." *GCA*. **32**: 285-298.

King, E. J. (1965). Acid-Base Equilibria. Pergamon Press.

Koide, M., V. Hodge, J. S. Yang and E. M. Goldberg. (1987). "Determination of Rhenium in Marine Waters and Sediments by Graphite Furnace Atomic Absorption Spectrometry." *Anal. Chem.* **59**(14): 1802-1805.

Koide, M., V. F. Hodge, J. S. Yang, M. Stallard and E. G. Goldberg. (1986). "Some Comparative Marine Chemistries of Rhenium, Gold, Silver and Molybdenum." *App. Geochem.* **1**: 705-714.

Kuehl, S. A., D. J. DeMaster and C. A. Nittrouer. (1986). "Nature of Sediment Accumulation on the Amazon Continental Shelf." *Cont. Shelf Res.* **6**: 209-225.

Macellari, C. E. and T. J. De Vries. (1987). "Late Cretaceous Upwelling and Anoxic Sedimentation in Northwestern South America." *PPP.* **59**: 279-92.

Martin, C. E. (1990). Rhenium-Osmium Isotope Geochemistry of the Mantle. PhD Thesis, Yale University.

McKee, B. A., D. J. DeMaster and C. A. Nittrouer. (1987). "Uranium Geochemistry on the Amazon Shelf: Evidence for Uranium Release from Bottom Sediments." *GCA.* **51**: 2779-2786.

Meade, R. H., T. Dunne, J. E. Richey and U. Santos. (1985). "Storage and Remobilization of Suspended Sediment in the Lower Amazon River of Brazil." *Science.* **228**: 488-490.

Millero, F. J. (1977). Thermodynamic Models for the State of Metal Ions in Sea Water. *The Sea*. John Wiley & Sons.

Morris, D. F. C. and E. L. Short. (1965). Rhenium. Handbook of Geochemistry. Chapter 75. Heidelberg, Springer-Verlag.

Nittrouer, C. A., T. B. Curtin and D. J. DeMaster. (1986). "Concentration and Flux of Suspended Sediment on the Amazon Continental Shelf." *Cont. Shelf Res.* **6**: 151-174.

Palmer, M. R. and J. M. Edmond. (1990). Controls Over the Sr Isotope Composition of River Water: Examples from the Ganges, Orinoco, Amazon, Chinese and East African Rift Valley Basins. Unpublished manuscript.

Phillips, C. S. G. and R. J. P. Williams. (1965). Inorganic Chemistry. Clarendon Press.

Poplavko, Y. M., V. V. Ivanov, L. G. Longinova, V. S. Orekhov, A. D. Miller, I. I. Nazarenko, R. N. Nishankhodzhayev, N. I. Razenkova and Y. A. Tarkhov.

(1977). "Behavior of Rhenium and Other Metals in Combustible Central Asian Shales." *Geokhimiya*. **2**: 273-283.

Ravizza, G. (1990). Personal Communicatiuon.

Ravizza, G. and K. K. Turekian. (1989). "Application of the Re(187)-Os(187) System to Black Shale Geochronometry." *GCA*. **53**: 3257-3262.

Turner, D. R., M. Whitfield and A. G. Dickson. (1981). "The Equilibrium of Dissolved Components in Freswater and Seawater at 25°C and 1 atm Pressure." *GCA*. **45**: 855-881.

Vine, J. D. and E. B. Tourtelot. (1970). "Geochemistry of Black Shale Deposits--A Summary Report." *Economic Geology*. **65**: 253-272.

Williams, R. J. P. and J. D. Hale. (1966). "The Classification of Acceptors and Donors in Inorganic Reactions." *Struct. Bonding*. **1**: 249-281.

Yee, H. S., C. I. Measures and J. M. Edmond. (1987). "Selenium in the Tributaries of the Orinoco in Venezuela." *Nature*. **326**(6114): 1805-1811.