An Investigation of the Marine Geochemistry of Gold

by

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B.A. Chemistry, Reed College

(1983)

SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

at the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
and the
WOODS HOLE OCEANOGRAPHIC INSTITUTION

February, 1989

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Submitted to the Department of Earth, Atmospheric and Planetary Sciences
on January 20, 1989 in partial fulfillment of the requirements for
the Degree of Doctor of Philosophy in Oceanography

ABSTRACT

An analytical method has been developed for the analysis of gold (Au) in seawater and was applied to a suite of samples in order to conduct a preliminary assessment of the marine geochemical behavior of Au. The method involved preconcentration by anion exchange of Au complexed with cyanide ion and detection by flow injection-inductively coupled plasma quadrupole mass spectrometry (FI-ICPMS). An aliquot of a radiotracer (Au-195, $t_{1/2}$=183 d) was added to each sample to monitor recoveries. Preconcentration of two to eight liters of seawater into one milliliter was carried out nearly quantitatively under the conditions specified. Analysis by FI-ICPMS resulted in a practical detection limit, expressed as the concentration of Au in seawater, of about 10 fmol/liter for a four liter preconcentrate. Corrections for the stable Au in the radiotracer and that contributed by reagents were significant, constituting up to 60% of the overall signals measured. Reproducibility, based in the analyses of five four-liter samples of Mediterranean seawater obtained from a single 30-liter Niskin bottle, was about 15% at the 140 fmol/liter level.

Gold profiles from the Atlantic Gulf Stream, Northeast Pacific, Mediterranean and Black Seas and hydrothermal fluids from 21°N, on the East Pacific Rise were analyzed. In general, the concentrations of Au in seawater (20-200 fmol/l) are nearly three orders of magnitude less than reported in the literature prior to 1988. This does not reflect a decrease in the Au concentrations with time, rather it indicates contamination problems with the earlier data. Gold is a non-conservative element in seawater. It does not appear to undergo appreciable recycling in the water column under oxic conditions as is evidenced by its fairly homogeneous distribution over the water column and similar average values in the Atlantic (53±22 fmol/l) and Pacific (55±36 fmol/l). Further data is required to be certain of this since relatively large errors in the Pacific data leave open the possibility of an enrichment or depletion by up to a factor of 2.5 between the deep Atlantic and deep Pacific.

The surface Mediterranean contains about the same Au concentrations as North Atlantic waters (≈50 fmol/l) whereas the deeper Mediterranean is enriched (100-150 fmol/l) with respect to North Atlantic waters. The source of this enrichment may be due to atmospheric dust which has been shown by other workers to be enriched in Au in this region or less likely to riverine inputs. In the Black Sea, Au concentrations decrease from 200 fmol/l in the surface water to about 20 fmol/l in the deep anoxic waters. A plot of Au versus salinity suggests that the decrease from the surface is due to mixing with depleted deeper waters with no abrupt changes at the redox boundary. Removal of Au is occurring either under the reducing conditions in the deeper waters which have a relatively long residence time (900-2000 years) or at the sediments. Upper limit calculations indicate that the Au removed in the deep Black Sea would contribute negligably to the sedimentary inventory which is dominated by detrital materials.

Budget considerations suggest that rivers and atmospheric dust are likely to provide the bulk of Au to the oceans and may be equally important, although their fluxes are presently ill-constrained. While Au is enriched in hydrothermal fluids (30-250 pmol/l) with respect to ambient seawater (≈50 fmol/l), hydrothermal Au is not likely to be widely disseminated in the oceans. Accordingly, its influence on the oceanic budget of dissolved Au is probably limited. The data would suggest an overall residence time for Au in the oceans on the order of a few hundred to a few thousand years.

Thesis Supervisor: Dr. John M. Edmond, Professor of Oceanography

Acknowledgements

This work would not be complete without acknowledgement of the support of the people who made it all possible. My interest in oceanographic research was kindled under the guidance and encouragement of Mike Bacon during those early Summer Fellowship days in his laboratory at Woods Hole. The expertise, patience and good humor of Mike, Allan Fleer, Becky Belastock and Debbie Shafer made those summers a truly pleasureable learning experience. I would like to thank John Farrington and members of his laboratory for allowing me to delve into the realm of organic geochemistry during my first year in graduate school. I owe a special thanks to Hovey Clifford who so valiantly handled those midnght floods!

My thesis work has benefitted from the assistance of many individuals: Susan Chapnick and Chris Measures both helped me to become oriented in the lab at M.I.T. Dong Soo Lee provided the springboard for this work with his masterful analytical skills. Shir Filler's diligence while working with me as a UROP student was essential to getting the ZGFAA work going. Mitch Galanek of the Radiation Protection Office generously loaned equipment and advice which enabled the successful employment of the new gamma counting system. I am grateful to Fred Frey and Pillalamarri Ila for accomodating my samples on their counting equipment during a hectic period. Steve Recca's expertise with the electron microprobe was essential to characterizing those pesky residue problems. Only with the electronic wizardry of Ken Burrhus and Tim Barrash and the aid of Andy Campbell, could I have managed to keep the ICPMS going in those early days. Chris Measures, Andy Cambell, Ken Bruland, Kristin Orians, Erik Brown, Debbie Colodner, Rob Sherrell, Chris German and John Bullister all collected samples critical to this work. In addition Bill Smethie, Ed Boyle and John Edmond allowed me to join their field programs to obtain samples and generously provided the ancillary data in the tables of this thesis.

During the course of this work, I have benefitted from discussions with many people; I would like to thank all of my fellow students, faculty, staff and the members of my committee for sharing their thoughts which challenged my thinking and made this a better thesis. I owe special thanks to Terri Bowers for her efforts toward enlightening me on the transport of hydrothermal Au, Ed Boyle for his unfailing willingness to lend his valuable wisdom and Chris Measures for sticking with me through the highs and lows and for helping me to 'link this series of cock-ups'. I am very grateful to have had the opportunity to work in the laboratory of my advisor, John Edmond, and to have been inspired by his insights. Last and most certainly not least, I thank Jean-Jacques Ouisel for putting up with another round of madness.

Funding for this work was provided by the Woods Hole Oceanographic Institution, a National Science Foundation Graduate Fellowship, the National Science Foundation (equipment grant OCE-8709403), the Massachusetts Institute of Technology and the Office of Naval Research (contract # N00014-86-K-0325).

Dedication

This thesis is dedicated to Mary and Redwood Wright whose generous support and understanding of my aspirations made all the difference.

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Chapter 1

1.1 Introduction

The potential of many trace metals to act as indicators of both biogeochemical and physical processes in the oceans has been realized through extensive investigations of their distributions and chemical properties in the marine environment (e.g. Bruland, 1983 and ref. therein; Boyle, 1988; Measures and Edmond, 1988). An understanding of the geochemical cycling of a metal has been an essential prerequisite for exploiting its tracer capabilities. The principle aim of this study was to conduct a preliminary investigation of the marine geochemistry of gold (Au) and ultimately, to explore its potential as a tracer of oceanic processes. In addition, it is of interest to explain why anomalously high Au concentrations have been found to be coincident with anomalously high iridium (Ir) concentrations in the sediment layer marking the Cretaceous-Tertiary (K-T) boundary in some locations (Brooks *et al.*, 1984) but not in others (Officer and Drake, 1985). Gold, like Ir and the other platinum group elements, is highly enriched in meteoritic materials with respect to crustal materials (see below). If the excess Ir in K-T sediments is derived from a giant meteorite which impacted with the earth as has been proposed (e.g. Alvarez *et al.*, 1980), it would seem that Au and Ir were segregated either by processes occurring within the water column or after deposition during sedimentary diagenesis. In this regard, it is important to determine the relative mobilities of Au and the platinum group elements both in the water column and in the sediments. This study represents an initial effort towards characterizing the behavior of Au in the water column so that the unusual conditions governing the depositional record of the K-T transition might eventually be addressed.

At the time this work was begun, little was known regarding the behavior of Au in the oceans. This was due, in part, to formidable analytical difficulties associated with the very low levels of Au present in seawater (see section 1.2.1). A major part of this research effort went into establishing a reliable and practical analytical technique for the determination of Au concentrations in seawater. The methods development phase and a recommended procedure involving anion exchange preconcentration and detection by flow injection-inductively coupled plasma quadrupole mass spectrometry (FI-ICPMS) are summarized in Chapter 2. Data are presented in Chapter 3, including Au profiles from the Black Sea, Mediterranean Sea, Atlantic Gulf Stream and northeast Pacific along with initial analyses for hydrothermal fluids. The conclusion, Chapter 4, discusses the implications of the current data set and delineates areas of future interest for furthering our understanding of the cycling of Au in the marine environment.

1.2 Background

1.2.1 General

Recent estimates of the abundance of Au in various materials are listed in Table 1.1. Due to its strongly siderophilic nature, Au is believed to have been preferentially concentrated with iron in the earth's core during its early formation thus depleting the crust and mantle with respect to primitive matter of the solar system (Goldschmidt, 1958). The Au content of the majority of the earth's crustal rocks, both volcanic and plutonic continental igneous types and mid-ocean ridge basalts, falls within an unusually narrow range for a trace element (Crocket, 1974). For the most part, Au is not strongly associated with particular rock forming minerals and occurs predominantly in the elemental form, whose occlusion in such minerals may be controlled by structural factors and the amount of Au present in the magma during crystallization (Crocket, 1974).

Gold does not combine with oxygen or sulfur but can form minerals with tellurium (Te), such as calaverite ($AuTe_2$) and silver (Ag) bearing sylvanite ($AuAgTe_2$), and to lesser extent with antimony and bismuth (Jones and Fleischer, 1969). The few known minerals of Au are quite rare being found in only a few ore settings (Crocket, 1974). In most ore deposits, Au occurs in the metallic form often alloyed with some Ag. Its high density in the native state, 19.3 gm/cm^3, leads to its concentration by preferential settling in placer deposits. The body of literature concerning the occurrence of Au in ores is quite extensive; a summary description of various types of Au deposits and theories of their genesis may be found in Boyle (1987).

Table 1.1: Au abundances in various solid materials

material	*abundance ppb*	*reference*
C1-chondrite*	145±15%	Anders and Ebihara, 1982
crustal rocks	0.5-5	Crocket, 1974
	1.5	Crocket and Kuo, 1979
	4	Taylor, 1964
marine		
pelagic sediments	1.5 (0.6-5.3)	Crocket and Kuo, 1979
	1.9 (0.1-6.3)	Koide, *et al.*, 1986
anoxic coastal sediments	2.4 (0.4-5.9)	Koide, *et al.*, 1986
manganese-nodules	2.9 (0.2-8.3)	Crocket and Kuo, 1979
	1.1 (0.1-7.4)	Koide, *et al.*, 1986
hydrothermal deposits		
Pacific sites	2-510	Koide, *et al.*, 1986
Pacific sites	20-6700	Hannington, *et al.*, 1986
mid-Atlantic Ridge	800-16,400	Hannington, *et al.*, 1988

*best estimate of cosmic abundance

1.2.2 Au in seawater

The presence of dissolved Au in seawater was first reported as early as 1872 (Sondsadt). From that time, motivated by hopes of financial gain, many have unsuccessfully attempted to recover Au from seawater. Perhaps the most famous such endeavor was that of Fritz Haber who set out to recoup Germany's WWI debt in the 1920's and ultimately forsook nearly a decade of research when he concluded, from the analyses of a large number of samples from all over the world, that the Au content of seawater was several orders of magnitude less than previously reported (Haber, 1927 and 1928).

According to Haber (1928), the average Au content of samples taken at open ocean stations was $\approx 20\text{x}10^{-12}$ mol/liter (20 pmol/l). Widely ranging values of similar or greater magnitude have been reported in the subsequent literature. The results of determinations of Au in seawater between 1927 and 1970 have been summarized by Jones (1970)-also see Schutz and Turekian (1965). Recent efforts (Koide *et al.*, 1988; this work) indicate that actual concentrations of Au in open ocean water are two to three orders of magnitude less than those Haber found or in the range of $10\text{-}100\times10^{-15}$ mol/liter (10-100 fmol/l). As with other trace metals (Bruland, 1983), earlier workers were doubtlessly hampered by the inadequacy of available analytical instrumentation and failed to recognize sample contamination problems. Conclusions about the behavior of Au in the oceans based on data published before 1988 are therefore unlikely to be valid and are not reviewed here. The findings of the other contemporary study of Au in the oceans by Koide *et al.* (1988) are discussed in the context of the results of this work in Chapter 4.

Inorganic thermodynamic considerations predict that Au should exist in seawater predominantly in the +I oxidation state as $[AuCl_2]^-$ with much lesser amounts of $[AuBrCl]^-$ and other Br, I and OH complexes present (Sillen, 1961; Sillen and Martell, 1971; Peshchevitskii, *et al.*, 1970). The total solubility of these complexes in seawater with respect to metallic Au is on the order of 100 nmol/l (Sillen, 1961; Peshchevitskii, *et al.*, 1970). Since this greatly exceeds measured concentrations and the supply of Au to the oceans has not been limiting over geologic time (see below), the concentration of dissolved Au in seawater is not controlled by the solubility.

Although it is not predicted to be stable with respect to conversion to Au(I) in seawater, the one other possible form of Au is the +III oxidation state which also forms complexes and if present would be in the dissolved state. Dissolved Au (I and III) can readily be converted to the metal in the presence of reducing agents (Puddephatt, 1978), such as organic coatings on particulate materials or compounds associated with organisms present in oxic seawater. There is in fact some evidence to show that Au is accumulated by absorption and reduction in certain algal species (Greene, *et al.*, 1986). No specific biochemical function of Au is known and the influence of bioaccumulation on the oceanic cycling of Au has yet to be investigated. Once in the metallic form, Au is kinetically inert to reoxidation which may have important implications for its removal onto particulate phases in the oceans. This point is further examined in Chapter 4.

1.2.3 Au in rivers

As is the case for seawater, earlier literature for dissolved Au in rivers and streams appears suspect; values range widely, from a few pmol/l to µmol/l (Crocket, 1974 and references therein), raising the possibility of contamination artifacts. More recently, investigators have found levels of dissolved Au in stream and river waters to be at or below their detection limits of a few pmol/l (McHugh, 1988) except, perhaps, in drainage areas of high Au content (Brooks, *et al.*, 1981; Hamilton, *et al.*, 1983a &b; Hall, *et al.*, 1986; McHugh, 1988). Inorganic thermodynamic considerations predict the solubility of Au in river waters to be considerably less than that for seawater: For a mean (Cl^-) content of 2.2×10^{-4} M, the maximum concentration of dissolved Au in river water would be ≈30 pmol/l at 25°C with $[AuCl_2]^-$ the predominant species at pH=4 and $[AuO_2]^-$ at pH=9 (Ong and Swanson, 1969). Since measured concentrations are lower than predicted, solubility does not appear to be the primary control of the concentration of Au dissolved in rivers. Further study is required to uncover the factors that govern the riverine transport of Au. The fate of riverine Au as it enters the oceans is also unknown since there is no information about the behavior of Au in the estuarine environment.

1.2.4 Eolian Au

Atmospheric input is known to be an important source for many trace elements in the oceans (Bruland, 1983). Several workers have reported enrichments of Au in marine aerosols (Rahn *et al.*, 1979; Buat-Menard and Chesselet, 1979; Arnold *et al.*, 1982; Arnold, 1985). Defining the enrichment factor to be the ratio of Au to Al in the aerosols divided by the average Au to Al ratio in the crust, enrichment factors ranging from 10 to 5000 have been measured.

The source of the enrichment in aerosols is not certain. There are no known anthropogenic sources of atmospheric Au. The boiling point of elemental Au (3080°C) is quite high and so Au would not be atomized under normal environmental conditions and there are no known volatile compounds of Au which would be stable in the atmosphere (Puddephatt, 1978). Measurements of Au in aerosols from Mauna Loa (Zoller, *et al.*, 1983; Olmez, *et al.*, 1987) and particulate plume and hot vent samples from Mount Etna (Buat-Menard and Arnold, 1978) show extremely large enrichment factors (10^3-10^6) indicating that volcanic exhalations could be a source of the Au enrichment in atmospheric aerosols. The mechanism of enrichment in volcanic aerosols is unclear. It may be that the volatile compound, Au_2Cl_6, is formed under volcanic conditions. This compound can be created in the laboratory under a chlorine atmosphere at temperatures greater than 200°C but is immediately deposited as elemental Au in the presence of air (Puddephatt, 1978). Thus, it seems likely that Au volatilized as Au_2Cl_6 would be rapidly reduced to elemental Au on particulate aerosols as it is carried away from the hot vent site. Buat-Menard and Arnold (1978) found the enrichment of Au in aerosols diminished rapidly with distance (10-100's of meters) from the plume which would be consistent with this mechanism.

Whether the influence of volcanic Au is local or widespread is not known. It is conceivable that some Au associated with fine fraction of volcanic aerosol would become widely dispersed while Au enriched particles that are deposited near the volcanic site could exert a more localized influence under later remobilization. Since much of the atmospheric dust is known to originate from desert regions (Prospero, 1981), it may be that desert soils have been enriched by past or present volcanic activity. Alternatively such soils may be enriched in Au because it is resistant to mobilization by weathering processes.

1.2.5 Au in marine sediments

Within the precision of the available data, the Au content of various types of marine sediments falls within the same concentration range as for crustal rocks (see Table 1.1). A study by Crocket, *et al.* (1973) of glacial Arctic nearshore sediments, which are highly physically weathered, and sediments near Tahiti, which are highly chemically weathered, would suggest that very little effect if any is had by weathering on the Au concentration of predominantly clay sediment with respect to its source rocks.

In a separate investigation, the average Au content of marine sediments (1.50±0.9ppb) showed very little variation over a suite of deep sea cores despite large variability in the proportions of biogenic and lithogenic components (Crocket and Kuo, 1979). A positive correlation of Au with $CaCO_3$ was noted for a core from the Caribbean described as a calcareous ooze but not for another $CaCO_3$-rich core (Globigerina ooze) from the Pacific-Antarctic basin. Analysis of the >150μm fraction of the $CaCO_3$ cores, principally Globigerina tests, did not show preferential incorporation of Au in this phase. The correlation may have arisen from the association of Au with some medium to fine-grained biogenic constituent associated with the productivity of carbonate organisms. No correlation was found for Au and Si in a siliceous ooze core from the Pacific and as the organic carbon contents for these sediments were not reported, it remains unclear how Au is associated with the biogenic fraction of sediments. Likewise, no relationship of Au with Mn was found. Whatever processes control Au in the non-lithogenic fraction of these sediments appear to generate concentrations on a weight basis that are similar to clay materials.

Natural anoxic coastal sediments also seem to contain about the same levels of Au as pelagic ones (see Table 1.1) and so reducing conditions in sediments do not seem to give rise to preferential incorporation of Au. Exceptionally high Au levels (100's ppb) found in California coastal sediments near Los Angelos were attributed sewage outfall (Koide *et al.*, 1986) and so, at least locally, anthropogenic activities can influence the Au contents of marine sediments.

The most spectacular natural enrichments of gold found in the marine environment occur in association with sulfide deposits produced by hydrothermal venting (see Table 1.1). In 1973, before the discovery of submarine hydrothermal vents (Corliss *et al.*, 1979), Crocket *et al.* reported elevated Au and palladium (Pd) concentrations in metalliferous sediments across the East Pacific Rise. While Pd showed a smooth increase centered on the rise crest, the pattern for Au was more irregular and did not correlate with iron (Fe) or manganese (Mn). More recent measurements at the TAG Mid-Atlantic ridge site and Endeavor Ridge indicate that, while Au is quite heterogeneously distributed in the vent areas it is most concentrated in phases that contain high levels of lead, silver, arsenic, antimony and silica, representative of mature, late-stage venting (Hannington *et al.*, 1986&1988). The source of the Au in the enriched phases, either scavenged from seawater or deposited from the vent fluid, cannot be distinguished on the basis of the solid phase measurements alone. The first measurements of Au in vent fluids, reported here in Chapter 3, do show substantial enrichment with respect to ambient seawater. The significance of this hydrothermal Au to the oceanic budget is examined in Chapter 4.

Chapter 2

2.1 Methods Development

2.1.1 Radiotracers

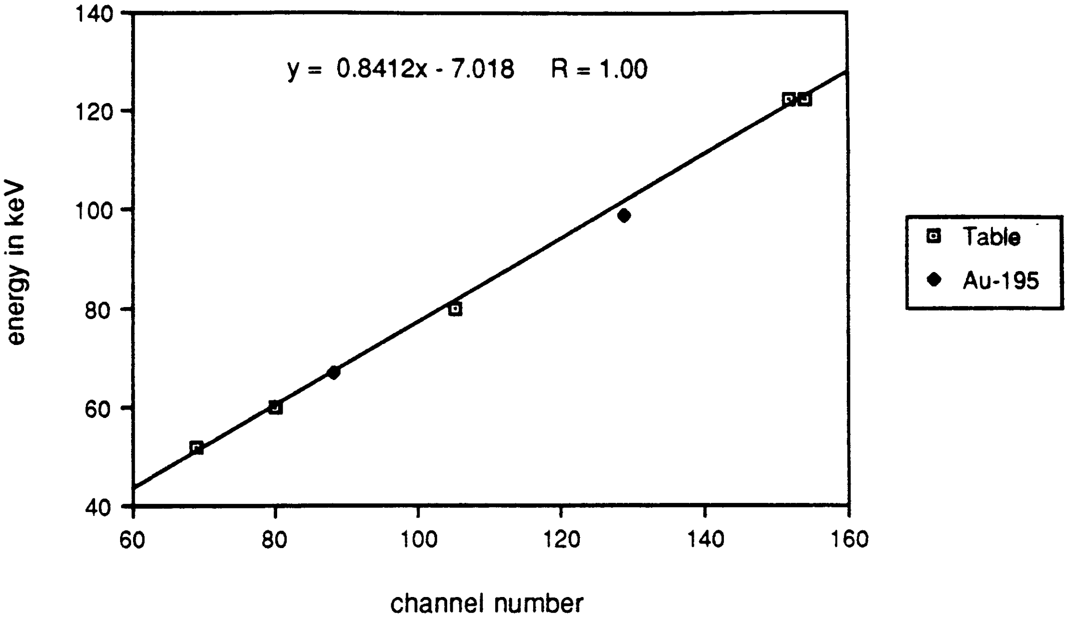
Initial developmental work was carried out with ^{198}Au which is readily produced in a conventional reactor by the thermal neutron capture reaction of natural ^{197}Au: ^{197}Au(n, γ)^{198}Au. Gold-198 decays by β^- emission ($t_{1/2} = 2.696$ d) to stable ^{198}Hg with gamma rays accompanying the decay at 412 keV (96%), 675 keV (1.2%) and 1087 keV (0.26%) (Lederer and Shirley, 1978). Approximately 5 mCi of ^{198}Au was supplied by New England Nuclear in a HCl-HNO_3 solution that contained >40 Ci/gm gold. Its activity per unit volume was reduced to a working range by dilution to 10 ml with 10% aqua regia (abbreviated AR, see section 2.2.2.1 for definition) and the solution stored in a polyethylene scintillation vial. The brief half-life of this tracer limited its utility to short term (several week) studies.

Yield-monitoring and longer term studies were carried out with ^{195}Au which is produced by bombardment of a Pt target with deuterons and decays by electron capture ($t_{1/2} = 183$ d) to stable ^{195}Pt. Prominent emissions accompanying the decay of ^{195}Au include X-rays (Pt, K-shell) at 67 keV (≈100%) and 76 keV (≈10%) and a gamma ray at 99 keV (11%) (Lederer and Shirley, 1978). Gold-195 was obtained from New England Nuclear in 100 μCi aliquots in ≈4M HCl that contained >20 Ci/gm gold. The first batch (12JUL86) was diluted with 5% AR to ≈15 ml and transferred to a glass scintillation vial for storage. The stable gold level in the diluted tracer solution was determined directly by Zeeman graphite furnace atomic absorption spectrophotometry (ZGFAA) to be 84±3 nmol/l. The second batch (23SEP87) was diluted with 56% AR to 20 ml and transferred to a Teflon vial for storage. The stable gold in this tracer solution was determined by FI-ICPMS using standard additions to be 6.4±0.8 nmol/l.

2.1.2 Gamma counting

The Au radiotracers were monitored by NaI gamma spectroscopy on two separate counting systems. Preliminary work was performed on a 1" by $1^1/2$" NaI(Tl) crystal (Nucleus P2000 detector) connected to a 256 channel multi-channel analyzer (MCA) with a built-in amplifier (Nucleus Model 256 MCA). The system was operated in the pulse height analysis mode and data output to a parallel printer (Addmaster Model 156-3). Yield monitoring was performed on a $1^1/2$" by $1^1/2$" NaI(Tl) crystal (Harshaw, Type 12S12/E) with an attached amplifier (Canberra, Model 2007P) connected to a 4096 channel MCA (Canberra, Model 1004, Series 10). Spectra were reduced by conventional background stripping and integration of the peak areas of interest followed by any corrections required for radiodecay.

All experiments were designed so that counts were acquired on a relative basis for a given counting geometry, negating the necessity for determining the absolute efficiencies of the detectors. Counts were accumulated for preset live-times even though count rates were always low enough such that corrections for instrumental dead-time (<1%) were insignificant . A set of typical operating parameters for recovery monitoring is outlined in Appendix A. Peaks were assigned on the basis of known spectral characteristics of the tracers and energy calibrations with a suite of radioisotopic standards (Table 2.1; Fig. 2.1). Aliquots of the ^{195}Au tracer solution were also counted on a calibrated GeLi system at MIT (Canberra GeLi crystal and Model 8180 MCA) as an independent confirmation of peak identities.



Energy Calibration for NaI(Tl) Detector

Figure 2.1: This calibration was carried out on July 2, 1988; see Table 2.1 for the radioactive standards used. See Appendix A for the system description and operating parameters. The equation is a regression of the data in Table 2.1 excluding ^{195}Au.

Table 2.1: Radionuclide standards used for NaI(Tl) detector calibration

nuclide	*particle*	*particle energy (keV)*	*channel no.*
Am-241	γ	60	80
Ba-133	γ	80	105
	I-esc of γ	52	69
Eu-152	γ	122	152
Co-57	γ	122	154
(Au-195)	Pt K-α X-ray	67	88
	γ	99	129

For ^{198}Au, the area of the most intense gamma peak (411 keV) was monitored. For ^{195}Au, the induced X-rays of Pt (K_α at 67 keV and K_β at 76keV) and 99 keV gamma peaks overlapped. In addition, the predominant Pt-K_α X-ray peak was overlapped on its low energy side by its own iodine escape peak and less intense iodine escape peaks of the other emissions. Iodine escape peaks arise from the loss of a characteristic X-ray of I (25 keV) when primary radiation interacts with the NaI crystal close to the detector surface. Such interactions result in peaks shifted 25 keV below the main photo peak and become increasingly probable with lower primary radiation energy and larger detector surface to volume ratios (Friedlander *et al.*, 1981 p.263; Knoll, 1979 p.319, 329). Since the Pt-X-rays, gamma ray and iodine escape peaks could not be resolved, their combined area was integrated for the purpose of comparing samples.

Background corrections limited counting precision for this work. Initially, lead brick (1") shielding was employed to reduce the high background typical for NaI type detectors (Friedlander *et al.*, 1981 p. 263). The counting precision for ^{195}Au yield monitoring, expressed as the relative standard deviation of at least triplicate counts for a sample in a given geometry, ranged from 3-10% for samples having greater than 20% recoveries (>30,000 counts in 20 minutes). Lead foil shielding, added around the detector and sample chamber, while lowering the overall background, revealed the 77 keV Pb-K_α X-ray peak (Knoll, 1979) arising from interaction of the Pb shielding with background and cosmic radiation. A sandwich of Cu-Cd-Al shielding between the lead and NaI crystal (Fig. 2.2) eliminated this X-ray peak, as described in Knoll (1979) and counting precision was improved to 1-3% for samples with greater than 20% recoveries.

Care was taken to ensure uncertainties due to geometry were minimized by placing vials into a well holder whose position was fixed relative to the crystal and by matching both solution volumes and vial types. The linearity of the detector response to a range of activities in a fixed solution volume was determined for each vial/solution volume combination used. The ranges were chosen to encompass activities measured in actual experiments and samples and in all cases, the detector response was highly linear (Fig. 2.3). This validated the application of activity ratios for sample and standard comparisons in yield monitoring and permitted the direct addition of activities as described in the elution fraction experiment.

2.1.3 Adsorption onto containers

Loss of significant amounts of Au by adsorption onto container walls can pose a serious problem for quantification of Au in natural waters (Benes, 1964; Benes and Smetana, 1966; Chao *et al.*, 1968). For this reason a series of experiments using ^{195}Au as a tracer were undertaken to determine conditions required to keep Au in solution in seawater samples. One liter borosilicate glass, Teflon and high density polyethylene containers were pretreated with 10% AR. Containers were 2/3 filled with the acid and placed in a 60°C oven overnight. The next morning they were removed from the oven, inverted for an additional day of leaching at room temperature, and then thoroughly rinsed with distilled dionized water (DDW). This leaching process was employed to remove any contaminant Au from the containers under conditions at least as harsh as those under which the storage of samples was to be tested. The oxidation potential of AR may cause development of ion exchange sites on polyethylene (Laxen and Harrison, 1981 and references therein) and so it must be emphasized that the results of th

Schematic Cross-Section of NaI(Tl) Gamma Counting System

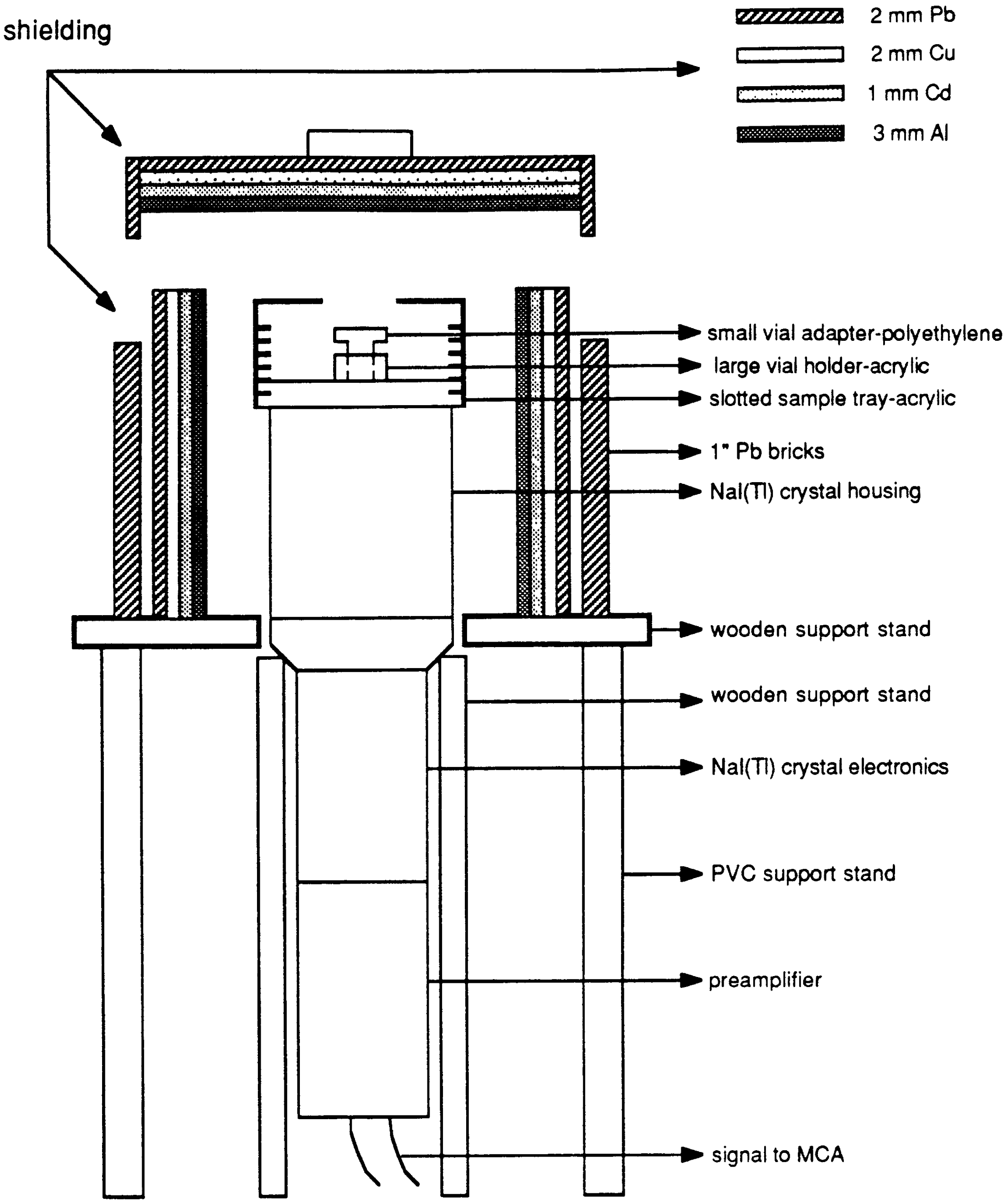


Figure 2.2: For counting system description, see Section 2.1.2. and Appendix A.

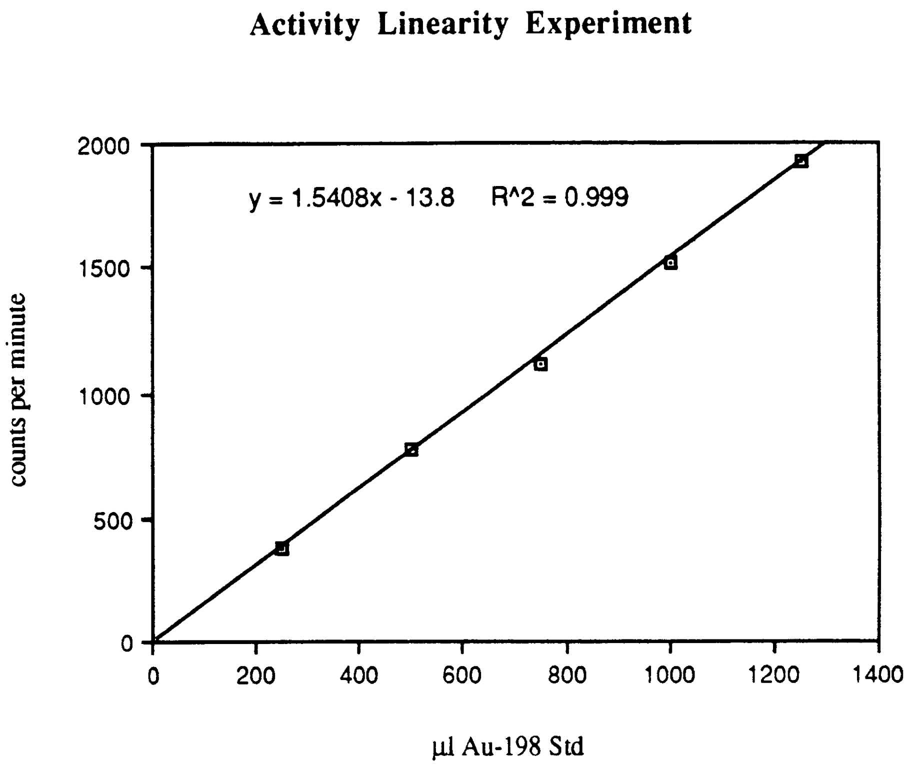


Figure 2.3: The plot is an example of testing whether count rate increased linearly with activity for a given geometry, solution volume and activity range. In this case, aliquots of ^{198}Au were diluted to 20 ml with 5% AR in 20 ml polyethylene vials and counted in the NaI(Tl) gamma counting system used for preliminary work. For the system description, see section 2.1.2.

following experiments apply to containers prepared by this AR method and not necessarily to those cleaned by other methods.

Preliminary adsorption experiments with unfiltered seawater yielded highly scattered results. This is thought to have been caused by adsorption of ^{195}Au onto particulate matter which may not have been sampled in a representative fashion and even if properly subsampled would have compromised the counting geometry. Therefore, for the long term storage experiments, seawater was filtered through 0.4 μm polycarbonate Nuclepore filters. Instrumental drift was monitored with a ^{195}Au standard and found to be less than 0.5% over the course of this experiment.

Filtered seawater was weighed into the containers and acidified as outlined in Table 2.2. Radiotracer was added, the sample quickly mixed and an aliquot of 3.0 ml withdrawn immediately for reference counting. Subsequent aliquots were taken over the course of a year (see Table 2.3). Samples were stored at room temperature ($\approx$21°C) in a fume hood with no precautions taken to prevent their exposure to room lighting. The stable Au concentrations ($\approx$45 pmol/l) listed in Table 2.2 were calculated from the known Au contents of the added tracer. This is likely to be the principal source of Au, as the concentration of ^{195}Au in the tracer is negligible with respect to stable Au, seawater itself contains less than 0.5 pmol/l and the redistilled acids contained no detectable blank. In addition, the seawater had been stored unacidified in 1 liter polyethylene bottles for more than one year before filtration and it is likely, as demonstrated in this experiment, that most of the Au present naturally would have been adsorbed under these conditions.

Table 2.2: Adsorption Experiment Parameters

container	*volume (ml)*	*acid*	*pH*	*Au(pmol/l)*
glass(1)	1058	aqua regia	1.5	40
glass(2)	914	HCl	2.3	46
glass(3)	918	none	7.7	46
Teflon(1)	846	aqua regia	1.4	50
Teflon(2)	515	HCl	2.3	41
Teflon(3)	836	none	7.9	50
poly(1)	970	aqua regia	1.5	43
poly(2)	989	HCl	2.3	43
poly(3)	966	none	7.3	44

Results (Fig. 2.4) are plotted as percent tracer remaining in solution versus time for the three different container types. Over the 350 day storage period no gold is lost from solution, within the measurement error (±3%), from aqua regia bearing solutions in either glass, Teflon or polyethylene. Likewise, samples acidified to pH 2.3 with HCl in Teflon also appear to retain gold in solution over this time period. Unacidified filtered seawater in Teflon experienced minimal losses (<5%). Seawater samples with HCl added to pH 2 stored in either polyethylene or glass were viable for two weeks but exhibited significant losses by one month. Polyethylene without acid was the poorest choice of container; within five hours approximately 10% of the gold was lost to the container walls, within one day 20% was lost and by two weeks more than half of the gold originally present was no longer in solution. The addition of KCN (0.3 mM in solution) to filtered, unacidified seawater was found to reduce the adsorption of Au (24 pmol) onto polyethylene for one month from about 50% to ≤10% due to the ability of CN^- to strongly complex Au.

Attempts to resolubilize ^{195}Au from 10% aqua regia solutions that had been evaporated to dryness in 20 ml glass and polyethylene vials resulted in ≤ 10% being remobilized in DDW, 5% and 10% AR, and 10% HCl solutions even when vials bearing the desorption solutions were placed in a 60°C oven for one week. Only 100% AR quantitatively mobilized adsorbed

^{195}Au Adsorption Experiment Data

storage media	time (AR)	% (AR)	time (HCl)	% (HCl)	time (no acid)	% (no acid)
borosilicate glass	0	100	0	100	0	100
	0.13	104	1.1	99	0.24	96
	0.13	103	1.8	98	0.92	99
	1.4	102	6	99	3	98
	3.1	101	16.2	95	6.2	96
	6.2	101	50.1	84	16.4	93
	16.4	100	112	66	50.3	85
	50.3	102	346	71	112	93
	112	99			345	56
	345	98				
Teflon	0	100	0	100	0	100
	0.22	101	0.22	100	0.19	101
	1.1	101	1.1	94	0.98	96
	4.1	99	4.2	100	4.1	98
	14.3	99	14.3	100	14.3	97
	48.3	99	48.2	98	48.2	93
	110	101	110	98	110	96
	343	98	344	98	344	94
polyethylene	0	100	0	100	0	100
	0.65	98	0.1	99	0.19	89
	0.89	100	0.98	99	1	81
	1.7	99	4.1	98	4.2	70
	4.9	99	14.2	97	14.9	43
	15.1	96	48.1	90	48.2	44
	48.9	100	109	60	110	56
	111	96	344	59	344	46
	345	94				

Table 2.3: Adsortion experiment data are expressed as % radiotracer remaining in solution for the given time in days. The designations "AR", "HCl" and "no acid" indicates adsorption was followed in separate containers with AR (pH=1.5), HCl (pH=2) and no acid (pH≈8) added to the seawater. See Fig. 2.4 for plot of these results and section 2.1.3 for experimental details.

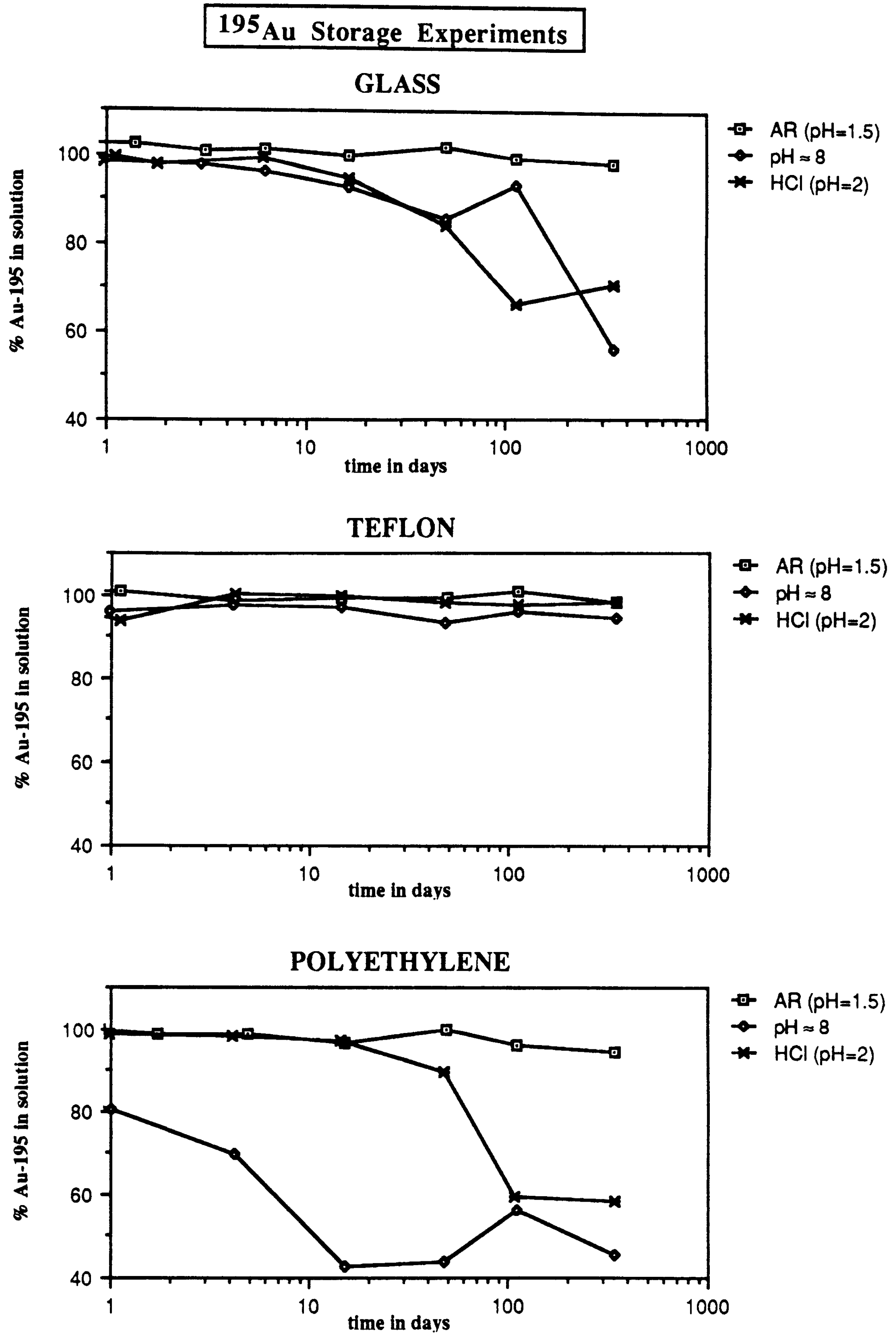


Figure 2.4: Losses of ^{195}Au from filtered (0.4 μm) seawater to the walls of 1 liter borosilicate glass, Teflon and high density polyethylene containers were monitored for one year under the conditions outlined in Table 2.2. The activity remaining in solution is expressed as the percentage of the activity of an aliquot of the sample at time zero. Uncertainty in this ratio is ±5% up to day 10 and increases of to ±8% by day 350. The data is given in Table 2.3. See Section 2.1.3 for a discussion of these results.

Au, indicating reduction of Au to the metallic state was occurring on the surfaces during evaporation.

The remobilization of a small fraction of adsorbed Au by the non-AR solutions indicates, however, that some degree of reversibility of the Au adsorption occurs on an hours to days time-scale. In an experiment designed to further investigate the reversibility of adsorption, seawater held unacidified for one year in the polyethylene container during one of the storage experiments was retained in the same container, spiked with additional tracer and adjusted to pH 1.5 with AR. This brought the total stable Au content of the container to 106 pmol/kg. A new reference aliquot was taken immediately after acidification and the activity of the solution was followed over the course of a week. It was expected that the activity would remain constant if adsorption was entirely irreversible since acidification with aqua regia had already proven to be adequate for keeping Au in solution in polyethylene.

In fact, the activity fell off during the few days the solution was monitored at roughly the same rate as it had originally while unacidified in the container (Fig. 2.5). One possible explanation is that isotope exchange took place with the radioisotope redistributing itself between the Au adsorbed from the previous experiment and that in solution. Since the amount of Au adsorbed onto the walls from the initial storage experiment, the Au in solution and the specific activities of the spikes were all known, the activity expected in solution at isotopic equilibration can be calculated (see Appendix D). The results predict 118±6 cps for a 3 ml aliquot, in good agreement with the 10 day sample of 111±2 cps, lending support for the case of isotopic equilibration.

As a further test of whether isotope exchange occurred, a large amount of stable gold (5.5 nmol-$[AuCl_4]^-$) was added to this same seawater solution while the pH was maintained at 1.5. Virtually all of the radiotracer should have returned to solution if the amount of gold on the walls was not increased and isotopic equilibration took place. However, only about 30% of the tracer on the walls returned to solution by the eleventh day after the stable Au addition, in seeming contradiction to a simple isotope exchange mechanism. Apparently, a large fraction of

^{195}**Au on Polyethylene Adsorption Experiment**

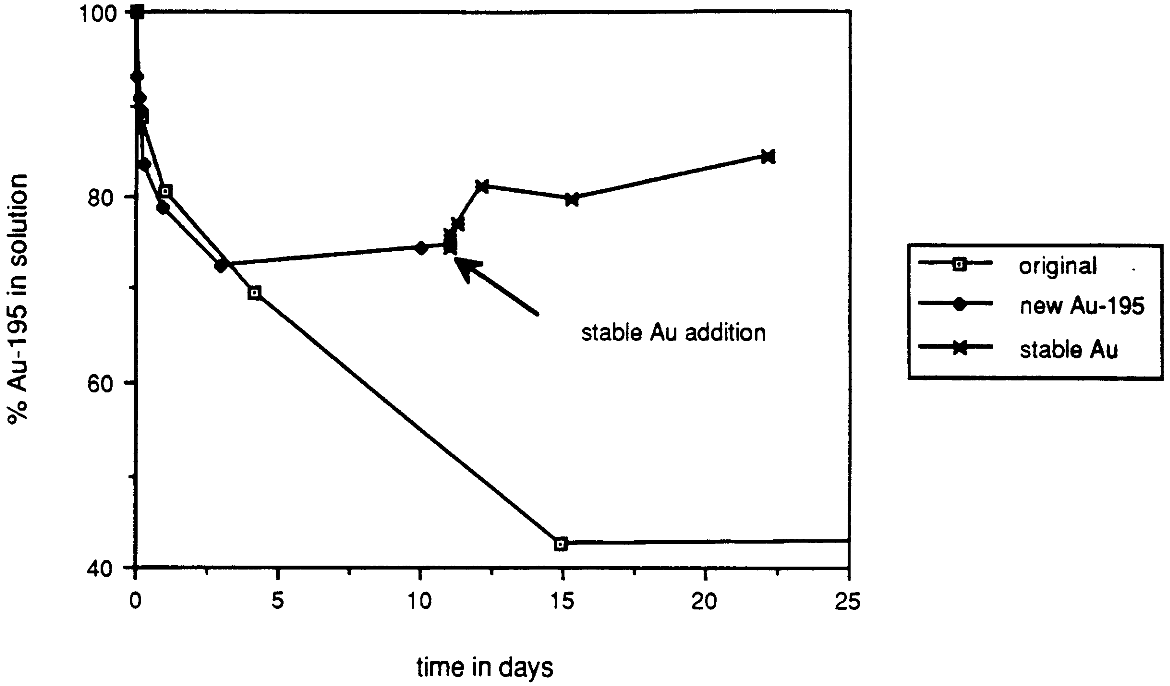


Figure 2.5: The percent ^{195}Au remaining in a filtered seawater solution in a polyethylene container was followed with time under various conditions. See Section 2.1.3. for experimental details. The squares are for the original condition (no acid added), the diamonds are for the additional tracer and 57% AR to pH 1.5 and the stars are for the excess stable Au.

the adsorbed Au had become unavailable for isotope exchange on this time scale in this latter experiment.

Although further experimentation would be necessary to fully explain these results, it seems that adsorbed Au can exist in two fractions: one is likely to be the refractory metallic form and the other an oxidized species which can readily undergo exchange with the Au in solution. The partitioning of Au between these fractions is presumably a complex function of Au speciation and the surface area and surface character which in turn can be expected to depend upon the pH and the solution composition.

Two important conclusions can be drawn on the basis of these adsorption experiments for the storage of seawater samples: 1) Aqua regia, which is strongly oxidizing and contains the complexing agent Cl^-, effectively guards against adsorptive losses of Au at pM and presumably lower concentrations at pH 1.5 in all three container types. 2) In addition to the serious problem of contamination by dissolution of surface bound material, isotope exchange with previously adsorbed Au can cause the results of yield monitoring by radiotracers to be misleading. It is essential in this regard that a sample container be precleaned by a procedure at least as harsh as that used to store the samples in order to remove the exchangeable fraction of contaminant Au.

It is doubtful that the harsh cleaning procedure employed here and consequent production of adsorption sites was entirely responsible for the adsorptive losses, since other workers have observed significant Au adsorption in containers pretreated with only HCl and DDW rinses (Benes, 1964; Benes and Smetana,1966; Chao *et al.*, 1968). Their studies all consisted of short term experiments which followed adsorption and desorption of ^{198}Au from solutions as a function of pH and time. The container surface to volume ratios, solution compositions and total Au contents used were not directly germane to the issue of preservation of seawater samples but do lend insight into the adsorption process and so their results are reviewed briefly in the following paragraphs.

For both glass (Benes, 1964) and polyethylene (Benes and Smetana, 1966; Chao *et al*, 1968), adsorption was found to vary as a function of pH. When the pH was adjusted with just HCl, HNO_3, or acetic acid and NaOH, adsorption tended to be minimal at low pH, increased steeply to a maximum in the pH range 2-4 and decreased somewhat throughout the higher pH range. Adsorption on polyethylene was found to be independent of the Au concentration or the presence of various electrolytes. Desorption of ^{198}Au adsorbed on polyethylene was not readily effected in either DDW or HCl solutions but was carried out in high yield in 0.01M KCN and quantitatively in 100% AR (Benes and Smetana, 1966) and in Cl^--bearing Br_2-solutions (Chao *et al.*, 1968). In glass, on the other hand, percent adsorption decreased with increasing Au concentration and was suppressed in the presence of electrolytes (Benes, 1964). Adsorbed Au could be resolubilized in concentrated HCl and to a lesser extent in 1N HCl. Clearly, the mechanism of adsorption differs for these two container types which is not surprising considering their different surface characteristics.

The dependence of the extent of adsorption on Au concentration for glass suggests a site limited process and the suppression by other cations competing for the sites is consistent with an ion exchange mechanism known to occur at oxyhydroxy-silicate groups on glass surfaces (Benes, 1964; Adams, 1972 and references therein). Benes and Smetana (1966) suggested that lack of adsorption suppression in the presence of other cations rules out an ion-exchange process for polyethylene, however, it could be argued that the Au-surface bond is strong enough that the other cations (Na, Ba, La, Fe(III)), even in excess concentrations cannot effectively compete for the sites. They proposed that the adsorption mechanism for Au onto polyethylene is a physical one, determined by the oxidation state and speciation of Au in solution and postulated the adsorbed species to be a hydrolyzed Au(III) chloride. To explain diminished adsorption at higher pH's, Benes and Smetana (1966) invoked electrostatic repulsion between negatively charged increasingly hydrolyzed Au(III) and the negative surface charge of polyethylene brought about through the primary adsorption of OH^- ions at pH>3. Contrary to this, however, most hydrolyzed metals do not show diminished adsorption at high pH's; in fact, the same chemical tendency for more extensive hydrolysis with increasing pH gives rise to increasing interaction of metals with surface hydroxyl groups (Dzombak, *et al.*, 1987). The unusual pH-adsorption trend observed for Au cannot be dismissed as an artifact of the observation period (15 hours) chosen for the experiments, since longer observation periods only exaggerated the trend (Benes and Smetana, 1966). One possibility they did not consider was that the adsorption of Au onto polyethylene may involve reduction of Au(III) to Au(I) at the surface. In such case, Au(I), which doesn't undergo hydrolysis (Smith and Martell, 1976), and Au(III) would be expected to display different adsorption behaviors with different kinetics and so give rise to the apparently complex adsorption characteristics of Au.

The difficulty of desorption of Au from polyethylene in DDW and HCl solutions was probably not due to diffusion of Au into the container since adsorbed Au was quantitatively removed by 100% AR (Benes and Smetana, 1966) and Cl^--bearing Br_2-solutions (Chao *et al.*, 1968). Benes and Smetana (1966) proposed a slow secondary reduction of adsorbed Au to the metallic form on the polyethylene surface to account for the ability of only strongly oxidizing solutions to quantitatively desorb Au. This is consistent with the findings of the desorption experiments presented here. Quantitative desorption from glass into 12N HCL (Benes, 1964) would suggest that at least over the unspecified time period of their experiment, reduction to Au(0) did not occur.

One curious aspect of these studies which was not explained was the slight but consistent increase in the pH of maximum adsorption with increasing Au concentration for both glass (Benes, 1964) and polyethylene (Benes and Smetana, 1966). It is doubtful that isotope exchange processes confounded their results because the Au levels in the solutions (nmol/l-µmol/l) were relatively high with respect to probable contamination. Likewise, colloids of Au probably do not occur in sufficient concentration to be responsible for this phenomenon. The possible influence of foreign impurities such as trace metals or organics in the test solutions or residual on the polyethylene or glass cannot be ruled out and may contribute to the apparent complexity of the adsorption mechanisms. Alternatively, this may be a consequence of interplay between the kinetics and thermodynamics of Au(III) and Au(I) adsorption as mentioned earlier. Further study is required to fully understand the factors governing the adsorption of Au onto these surfaces.

Although questions regarding the adsorption mechanisms of Au remain, the ^{198}Au studies do raise issues pertinent to the preservation of natural water samples: 1) Indiscriminate acid additions can actually promote adsorptive losses of Au in both polyethylene and glass and so specification of the pH for storage is critical. 2) A set of conditions which successfully retains Au in solution in a polyethylene container cannot be assumed to do so in glass and vice versa. 3) Adsorbed Au can be desorbed by adding excess Br_2 to Cl^--bearing samples, however, unless the sample container was pretreated in a manner that liberates metallic Au, there is a risk of introducing contaminant as well as adsorbed Au into solution. The method used for storing samples for this work is presented in section 2.2.3.

2.1.4 Preconcentration scheme

2.1.4.1 General

The very low levels of Au in natural water samples (fM-pM) necessitate a preconcentration step in an analytical scheme for even the most sensitive of current detection instrumentation. The preconcentration method adopted for this work involves separation of anionic complexes of Au with ion exchange resin which was investigated and first used for this purpose by Koide *et al.* (1984). Analytical grade AG 1-x2, 50-100 mesh, strongly basic, Cl^--form, anion exchange resin (Bio-Rad Laboratories-abbreviated here as AG 1-x2), a styrene divinylbenzene copolymer with quaternary ammonium functional groups, was used for all column work described here. As discussed below, Au can readily be retained from solution on this resin, however it is not a simple matter to achieve quantitative elution. This is probably the result of reductive retention of some fraction of the Au by the resin and so the term extraction, rather than ion exchange, is used below. The larger mesh size and low cross-linkage (2%) resin were deliberately chosen to promote the removal of Au from the resin. The columns used were made of polyethylene (20 ml capacity) and fitted with a polyethylene frit (Econo-columns, Bio-Rad Laboratories).

2.1.4.2 Complexation and extraction

A series of investigations with radiotracer were performed to determine optimum complexation and extraction conditions for Au since near quantitative recoveries are essential to be able to perform analyses on a practical sample volume ($\leq$ four liters) of seawater. The effectiveness of both Cl^- and CN^- as complexing agents was tested in the intial phase. Koide *et al.*. (1984) reported that HCl additions to seawater resulted in 70-90% extraction of a ^{195}Au spike, and that KCN additions resulted in 100% extraction of ^{103}Pd by the AG 1-x2 resin. Although they did not report on the effectiveness of $[Au(CN)_2]^-$ extraction, Au is known to form stronger complexes with CN^- than Cl^- (Puddephatt, 1978).

The experimental conditions and results of the first round of testing of these complexing agents are shown in Table 2.4. Approximately one liter aliquots of seawater (unfiltered, acidified to pH 2 with HCl) were poured into 1 liter polyethylene containers and 3 ml of 16N HNO_3 was added, to simulate the AR concentrations used for stored samples. The samples were spiked with ^{198}Au ($\approx$40 pmol/kg stable Au) and allowed to equilibrate for various time periods. Either HCl or KCN was added to the sample and in the case of KCN additions, the pH was adjusted to about 9 with NH_4OH and the samples allowed to equilibrate again for the times noted. At the end of the equilibration period, samples were passed through approximately 1.5 ml of the resin (pre-rinsed with 0.12N HCl) at a rate of 2 ml/min. Columns were rinsed with 20 ml each of 0.12N HCl and DDW, which never eluted significant amounts of the tracer, and then were eluted with 20 ml aliquots of various reagents.

The initial recoveries (>70%) were encouraging but not quantitative. As they represent the overall procedure, these initial recovery experiments did not distinguish between inefficient extraction and inefficient elution. However, monitoring the ^{198}Au activity of seawater after it had passed through the resin revealed that Au in samples with added KCN had been efficiently

^{198}Au Preconcentration Experiment Data

No.-eluant	Complex	Spike equil hrs	Reag equil hrs	% Recovery
1-HNO3	0.5 ml KCN	3.3	1.2	70
1-TOTAL				70
2-HNO3	18 ml HCl	3.4	1	77
2-TOTAL				77
3-HNO3	18 ml HCl	15.6	1.6	50
3-AR				6
3-TOTAL				56
4-HNO3	0.5 ml KCN	15.6	1.3	85
4-AR				6
4-TOTAL				91
5-HNO3	0.5 ml KCN	115	8.8	76
5-HNO3				14
5-acetone				0
5-TOTAL				90
6-HNO3	0.5 ml KCN	115	54	100
6-HNO3				0
6-H2SO4				0
6-TOTAL				100
8-HNO3	0.5 ml KCN	95	4.5	76
8-HNO3				19
8-HNO3				3
8-TOTAL				98
10-HNO3	5 ml KCN	95	4.5	78
10-HNO3				12
10-HNO3*				0
10-TOTAL				90
11-HNO3	50 ml KCN	95	4.5	74
11-HNO3				19
11-HNO3*				0
11-TOTAL				93

Table 2.4: The elution sequence for each sample consisted of 0.12N HCl (not shown) then DDW (not shown) neither of which carried significant tracer activity followed by 20 ml of the eluants in the table in vertical order. The HNO_3 was 16N, 90°C; H_2SO_4 18N, 60°C; AR 100%, 35°C and "$(HNO_3)*$" indicates the acid had cooled to near room temperature. "Complex." indicates the amount of complexing agent added to the ≈ 1 liter seawater (unfiltered Antarctic water) samples. The stock KCN solution was 4% or 0.62M and the HCl 6N. "Spike equil. hrs." is the time from ^{198}Au addition to the time of complexing agent addition in hours. "Reag. equil. hrs." is the time from complexing agent addition to the time the sample was passed through the resin. Percent recovery is with respect to the ^{198}Au originally added to the seawater sample.

extracted whereas in samples with HCl added, extraction efficiency was variable. Counts of radioactivity in the columns showed elution was incomplete for both sample types. Hence, at this stage it was decided to use CN^- as a complexing agent and to optimize the elution step.

2.1.4.3. Elution

Previous experiments (not reported in Table 2.4) showed that neither polar nor non-polar organic solvents were efficient eluting agents. Warm AR and H_2SO_4 did efficiently remove Au but destroyed much of the resin in the process which manifested itself as a sludge upon evaporating the eluant. The most effective eluting agent (Table 2.4) was 12N HNO_3 at 90°C but at lower temperatures this acid was considerably less efficient at removing Au. The requirement of a harsh oxidative treatment to remove Au implies either a very large distribution coefficient for the Au cyanide complex onto the resin or more likely, as with container surfaces, some portion of the Au partitioned into a more refractory reduced phase on the resin surface. The oxidative removal may be brought about in part by actual cleavage of the resin as evidenced by organic residues in evaporates of the eluant. Since hot HNO_3 adversely affects the resin properties, columns were disposed of after being used once.

The amount of resin required depends upon the sample volume and its Au content as well as the sample flow rate. Excess resin results in unnecessarily large volumes of eluant and increased blanks; conversely insufficient resin results in breakthrough. Determining the amount of Au in seawater and the requisite sample volume was an iterative process. Experiments with radiotracers were scaled to the volume desired (1, 2, or 4 liters) and to 100x the upper limit expected Au concentration (1 pmol/l) in order to ascertain the amount of resin, sample flow rate and elution conditions. In practice, the resin was pretreated with hot HNO_3 to remove contaminant Au, the sample flow rates were kept at $\leq$6 ml/min and the amount of resin increased until breakthrough did not occur. The total amount of acid required for elution was determined by profiling the elution (Fig. 2.6). It was found that about 1.8 ml of resin

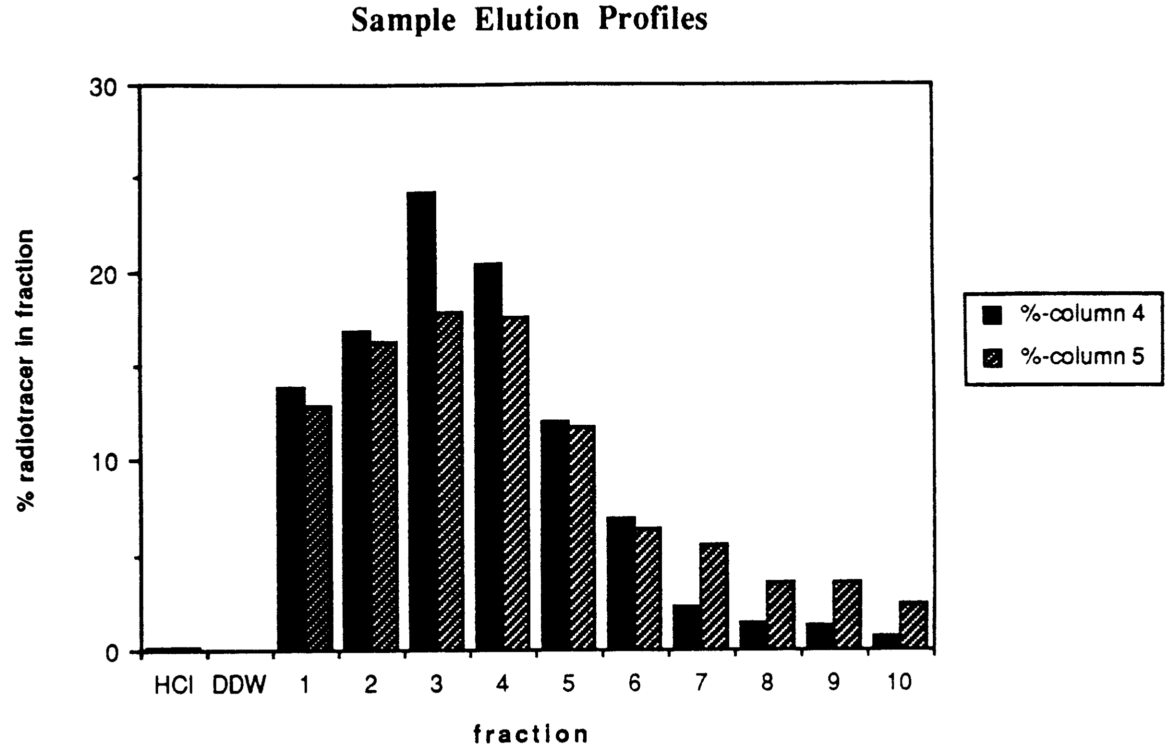


Figure 2.6: This graph shows examples of elution profiles (column numbers refer to experiments) used to determine the optimum amount of resin. In this case, 1 liter ^{198}Au-spiked seawater samples were passed through 0.8 ml (wet volume) AG-1 x2 anion exchange resin. Percent of the spike recovered per fraction is plotted; For both columns 100% of the spike was recovered as indicated by comparing the sum of the counts in the fractions to a radiotracer standard. The following were eluted in succession: 20 ml 0.12N HCl, 20 ml DDW and ten 1 ml fractions 90°C, 16N HNO_3. The actual resin and eluant volumes used were larger to avoid breakthrough at higher Au concentrations (see section 2.1.4.3).

quantitatively retained ≈100 pmol Au in 4 liters of seawater and that 40 ml of 90°C, 16N HNO_3 quantitatively eluted the Au.

2.1.4.4 Tracer equilibration

Because several steps in the analytical procedure present the possibility of Au losses, approximately 0.1 µCi of ^{195}Au radiotracer spike was added to each sample, as $[AuCl_4]^-$, at the time of collection and was monitored for recovery after preconcentration. Implicit in this approach, is the assumption that the radiotracer equilibrated with and so was representative of the stable Au in the sample. As outlined below, both thermodynamic predictions and empirical observations suggest that this assumption is valid and that recovery of the radiotracer can be applied to naturally occurring stable Au in a sample.

In theory, dissolved Au is present in seawater as $[AuCl_2]^-$ (Sillen, 1961; Peshchevitskii, *et al.*, 1970), but as discussed earlier may be present in the metallic state or less likely, in the more oxidized form, $[AuCl_4]^-$. At the Cl^- concentration of seawater (≈0.5M), thermodynamics strongly favors the conversion of the radiotracer added as $[AuCl_4]^-$ to $[AuCl_2]^-$ (Puddephatt, 1978):

$$[AuCl_4]^- + 2e^- \Leftrightarrow [AuCl_2]^- + 2Cl^- \qquad E° = +0.93V$$

Both Au(III) and Au(I) form considerably stronger complexes with CN^- than with Cl^- (Sharpe, 1976; Puddephatt, 1978). In the presence of CN^-, the reduction potential of Au(III) to Au(I) has been estimated to be about +0.5V (Remick, 1947) so thermodynamics again would predict the conversion of any radiotracer present as $[Au(CN)_4]^-$ to $[Au(CN)_2]^-$ in the seawater samples (Sharpe, 1976). The unusually high stability of $[Au(CN)_2]^-$ also promotes the oxidation of finely divided Au(0) at pH>7 in the presence of O_2 and is, in fact, commonly exploited to separate Au from crushed ores (Puddephatt, 1978):

$$4Au + 8CN^- + O_2 + 2H_2O \longrightarrow 4[Au(CN)_2]^- + 4OH^- \qquad E° \approx +1.0V$$

Therefore, in all three of its possible oxidation states, Au is predicted to be converted to $[Au(CN)_2]^-$ in seawater bearing excess CN^- (0.3 mM for this work) facilitating isotopic equilibration.

Of course, kinetic factors may inhibit attainment of equilibrium and there may be species of Au present, such as organic complexes, that were not considered, so empirical evidence showing that the radiotracer represents the stable Au in a sample is required. One approach is to compare results of different methods for measuring Au in seawater. The one other recent study of Au in seawater is by Koide *et al.*, (1988). They used ^{195}Au, added as $[Au(Cl)_4]^-$, as a recovery monitor but extracted Au onto anion exchange resin with Cl^- as the complexing agent and then performed a second single resin bead preconcentration step before determination by graphite furnace atomic absorption spectrophotometry. Their recoveries tended to be low (25-50%) but their Au concentrations for seawater are similar (within a factor of 2) to ones reported here. In addition, they performed alternative procedures, involving exhaustive oxidation (Cl_2 gas) and reduction (copper sulfide precipitation) of Au before preconcentration, on separate aliquots of the same seawater samples. They found no statistically significant differences between the results of the three methods. This would suggest that ^{195}Au adequately monitors the major fraction of Au in seawater for the technique of Koide *et al.* (1988) and because our levels are comparable, for the technique reported here.

It remains ambiguous what the form of Au in seawater is since thermodynamic equilibrium may not be attained but perhaps both (I) and (III) species, and possibly Au(0) can be efficiently retained by the resin. The highly oxidative elution step used both for this work and by Koide *et al.* (1988) forces all forms of Au to the (III) state so from that point on in the procedure the ^{195}Au radiotracer represents a single pool of Au and can be expected to track subsequent losses of stable Au proportionately. This would result in the accurate determination of Au in a seawater sample in spite of incomplete isotopic equilibration prior to passing it through the resin. Further work would be necessary to address the speciation of Au in seawater. Adding Au species in (I) and (0) states to seawater would show whether the resin selectively retains a particular oxidation state-species of Au. If all species appear to be retained it would not be possible to distinguish between rapid conversion to the preferred form and non-selective retention. It would be desirable to repeat comparison of exhaustively oxidative and reductive analyses with high precision to check if some fraction of either Au (III) or (0) occurs within the levels of precision (6-50%) reported by Koide *et al.* (1988).

It is conceivable, that Au exists in some additional form in seawater that neither the method of Koide *et al.*, (1988) nor the one reported here detects. Such an entity would have to be resistant to the extreme redox conditions of the alternative methods employed by Koide *et al.* (1988), thus its existence seems highly unlikely. If it does exist, it does not appear to participate in isotopic equilibration over a 40 day period since quantitative tracer recoveries were achieved in this work for equilibration periods as short as one hour (Table 2.4) and as long as 40 days.

2.1.4.5 Evaporative concentration of the eluant

Several problems were experienced upon evaporative concentration of the eluant. Excessive heat seemed to promote the adsorptive losses of Au in both Teflon and glass beakers and upon evaporation to dryness a large amount of residue that resisted dissolution and seemed to retain Au was observed. This residue was shown by electron microprobe analysis to be predominantly silica and organic matter with lesser amounts of Ca and Mg (Fig. 2.7). The organic matter probably originates from both the resin and sample. Silica, Mg and Ca were not present in eluants of reagent blank columns, but were most predominant for seawater samples that had been adjusted to $pH \approx 9$. This indicated Si, Mg and Ca were derived from the seawater and were probably retained on the resin as Si oxyanion and Ca and Mg hydroxide complexes or precipitates. Upon going to dryness, the Si precipitated as amorphous Si which was not readily redissolved; the Au was variably retained in this phase probably assisted by its reduction in the presence of organic matter and surfaces. The small volumes of acid eventually

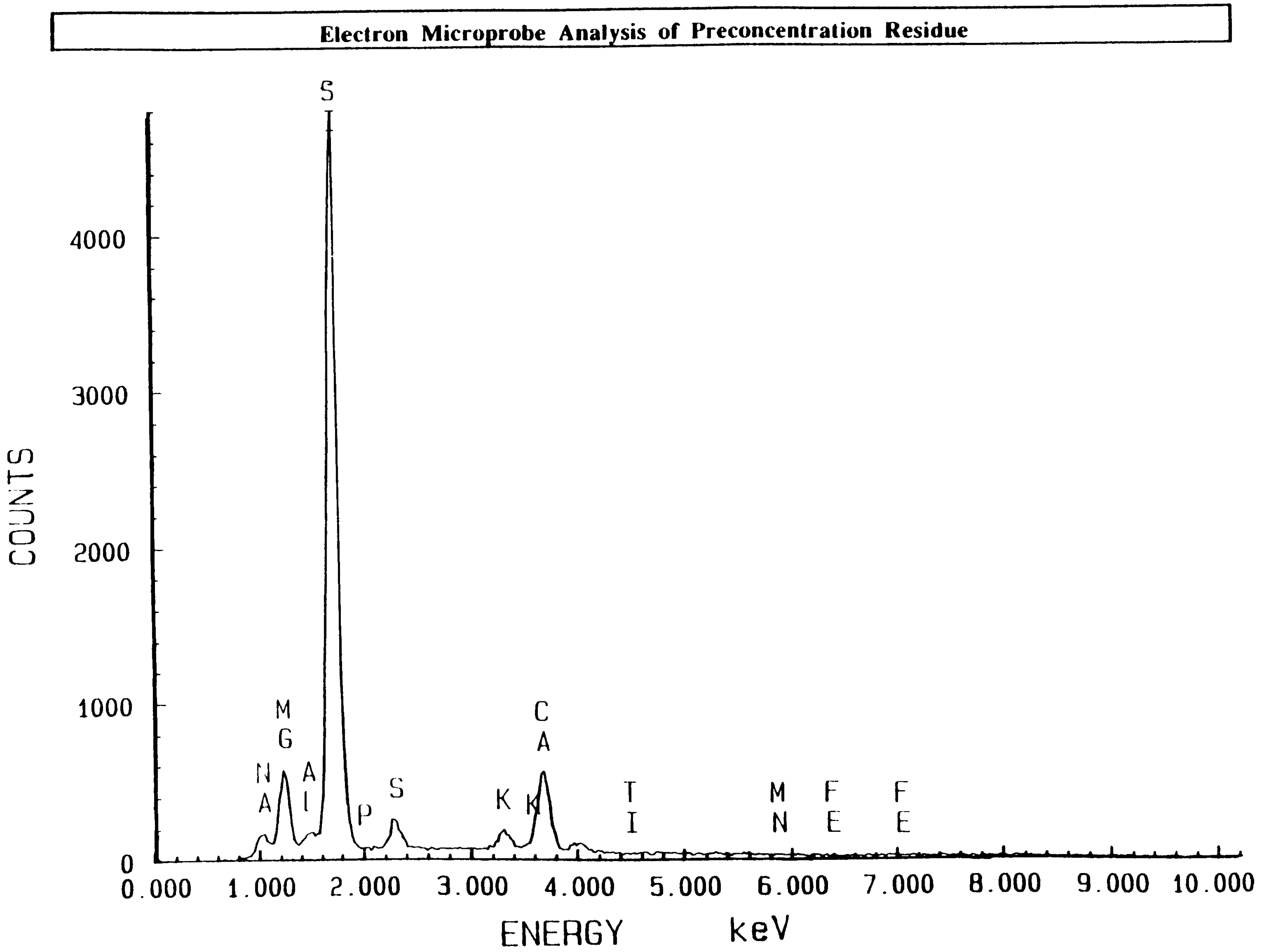


Figure 2.7: The spectrum shows the results of a qualitative electron microprobe (JEOL Model 733 Superprobe) analysis of an eluant residue for preconcentrated seawater. The beam current was 10 nanoamps and the accelerater voltage 15 keV. The sample was a typical residue from the evaporative concentration of the eluant before the corrective measures of extra column rinses and HF treatments were applied (see Section 2.1.4.5).

required for analysis could only resolubilize a small fraction of the Au and carried along some of the residue posing both matrix and viscosity problems discussed in greater detail below.

Several steps were added to the method to diminish the residues. First, the effect of sample pH on extraction of Au was tested by radiotracer experiments as lowering the pH of a sample would reduce the amounts of Si, Ca and Mg present in anion exchangeable form. It was found that quantitative extraction of the Au cyanide complex onto the resin could be achieved at the natural pH of seawater (≈8). The extent to which the pH can be adjusted downward before loss of CN^- as HCN gas ($pKa \approx 9.3$ in H_2O) outcompetes complex formation was not determined. Rinsing the resin before elution with 0.12N HCl and DDW was found to remove most of the Ca and Mg and some Si but no Au. Adding 6N HCl to the HNO_3 eluant was carried out to to ensure that Au would remain dissolved and UV irradiating this AR solution in quartz tubes was found, by visual inspection of residues, to oxidize much of the organic matter.

Adsorptive losses during evaporation were minimized by using Teflon beakers and employing gentle heating under infra-red lamps (≈80°C). When samples were reduced to small volume (<2ml), they were transferred to small (5 ml capacity) conical Teflon vials (Savilex) for the final evaporation step as these vials were more convenient for bringing the sample into the final solution. Adding HF in the final stage of evaporation was found to effect removal of Si via formation of volatile SiF_4 when evaporation was carried out at ≈80°C. Even after these treatments, taking the final solution to dryness resulted in highly variable recoveries thought to be due to the presence of persistent organic matter (small amount of visible residue) and the surfaces of the container bringing about the reduction of Au and rendering it insoluble. When evaporation is stopped at 20μl and the sample is transferred into the final volume as described in section 2.2, consistent nearly quantitative overall recoveries (>90%) are readily achieved.

2.1.4.6. Alternative approaches

Another strategy explored for preconcentrating Au involved its extraction from acidic solutions with organic solvents. Mechanistically, Au(III) anionic complexes can associate with a protonated oxygen-containing organic solvent (Das and Bhattacharyya, 1976 and references therein). Two solvents were tested for their ability to extract ^{195}Au from 100% and 57% AR; such an extraction step would allow separation of Au in the eluant from Mg, Ca and Si and the solvent extract might be directly injected into the Zeeman graphite furnace atomic absorption spectrophotometer (ZGFAA). Quantitative extraction from 2 ml of 100% AR with and without 25 µl of Br_2-water (DDW saturated with Br_2) was achieved with two 1 ml methyl isobutyl ketone (MIBK) extracts (3 min shaking each) with 95% extracted in the first 1 ml. However, while reducing the volume of the extracts by evaporation under an air stream the solvent first became purple, then brownish orange and finally dried to a brown sludge from which very little radiotracer could be recovered into 250 µl of 57% AR. Ethyl acetate could also be used to obtain quantitative extraction of Au, but if allowed to contact the acid for more than 3 minutes, the organic phase became miscible with the aqueous phase due to the formation of acetic acid and ethanol through acid catalyzed hydrolysis of ethyl acetate. The Au, however, was extracted quantitatively when a second portion of ethyl acetate was added and quickly separated. Ethers have also been shown to efficiently extract Au but were not tested as they tend to form hazardous peroxides (CRC Handbook of Laboratory Safety, 1971).

Injecting MIBK and ethyl acetate extracts directly into the ZGFAA resulted in poor reproducibility as the solvents have low viscosities and tended to spread irregularly over the graphite surface presenting a variable atom vapor to the light beam. Taking the ethyl acetate extracts to dryness and resolubilization of the Au with 250 µl of 57% AR resulted in low and variable recoveries. Though extraction of Au by organic solvents did not prove beneficial for the analytical method employed in this work, it may find application in graphite furnace-ICPMS as is discussed in section 2.1.6.5.

As a final note, no evidence for volatilization of Au during preconcentration as has been invoked by other workers (Dong Soo Lee, pers. comm., 1985) was found under the analytical conditions used for this work; all losses of Au were accounted for by adsorption.

2.1.5. Zeeman graphite furnace atomic absorption spectrophotometry

In the sections that follow, detection limits are defined as the amount of Au that produces an analytical signal equal to three times the standard deviation (σ) of the background signal. For detection limits determined for standards in simple matrices the background signals approached the noise limitations of the instrument and standard curves were extrapolated to an estimate of 3σ to calculate detection limits.

It was originally intended that preconcentrated samples be analyzed via Zeeman graphite furnace atomic absorption spectrophotometry (ZGFAA). Zeeman GFAA, as opposed to conventional GFAA, was chosen for its superior background correction capabilities which are based on the splitting and polarizing of spectral lines in the presence of a magnetic field (Van Loon, 1980). The sacrifice in sensitivity for Au by ZGFAA with respect to conventional GFAA is about 16% (Slavin *et al.*, 1983). A Perkin Elmer Zeeman 5000 instrument system (HGA500 graphite furnace, AS40 autosampler and 3600 data station) was used and compared to a conventional GFAA system (PE5000, HGA400 graphite furnace, AS40 autosampler) throughout the optimization phase. In general it was found that in simple standard matrices, detection limits were comparable for the systems but in more complex sample matrices, ZGFAA exhibited far less noise and afforded significantly better detection limits.

Radiotracer experiments showed that dilute (< 15%) HNO_3 or HCl solutions were incapable of retaining Au in solution in the 1 ml polyethylene sample cups used in the autosampler for even ten minutes. Testing of 0.01%, 0.1%, 1% and 5% AR indicated that Au was maintained in solution in $\geq 1\%$ AR solutions. When introduced to the graphite furnace in AR, however, Au distributed itself inconsistently between two species that were atomized at different rates over a 4 second atomization step resulting in broad overlapping peaks (see spectrum B in Fig.2.8). This irregular peak shape prevented accurate determination by either peak height or integration of peak area.

In an attempt to improve the peak shape, various commonly used matrix modifiers (Van Loon, 1980) were tested. Excess NH_4NO_3, ascorbic acid, H_2SO_4 and HCl injected with a Au standard in 5% AR, were not found to help. Lining the inside of a graphite tube with tantalum foil can result in improved GFAA sensitivity for some elements (Sen Gupta, 1984), but did not work for Au. The matrix modifier that did improve the Au peak shape was Ni. Other workers (Slavin *et al.*, 1983 and references therein) have suggested that in the graphite furnace Ni can amalgamate other metals which then are effectively retained until the Ni itself is atomized. The addition of excess Ni as a standard solution in 5% AR to the Au standard in 5% AR produced a single Gaussian shaped peak that resulted in both improved sensitivity and very good reproducibility under the conditions outlined in Appendix B. The optimum amount of Ni was found to be 0.52 μmol/ml sample. An extra cleaning step in the furnace program was necessary to completely remove residual Ni which could otherwise degrade a subsequent injection.

The best sensitivity and detection limits for the Ni-bearing Au standard solutions were achieved using a L'vov platform in a pyrolytically coated graphite tube and atomizing with a 1 second ramp; maximum power heating, i.e. instantaneous ramping, was found to diminish sensitivity. Integration of peak area was used for the determinations since they were found to be more reproducible than peak height determinations. The detection limits achieved for 20 μl injections of Au standards under the optimized conditions were 50 fmol (10 pg) for ZGFAA and 60 fmol for GFAA with standard curve slopes of 1.5×10^{-4} abs-units/fmol Au and 2.4×10^{-4} abs-units/fmol Au respectively.

In real samples, the presence of residues in the preconcentrate posed interference problems; Si strongly suppressed the Au signal, necessitating the use of standard additions, and the high viscosity of the small volume preconcentrates made it difficult to deliver the sample volume reproducibly. Only preconcentrated hydrothermal solutions contained enough

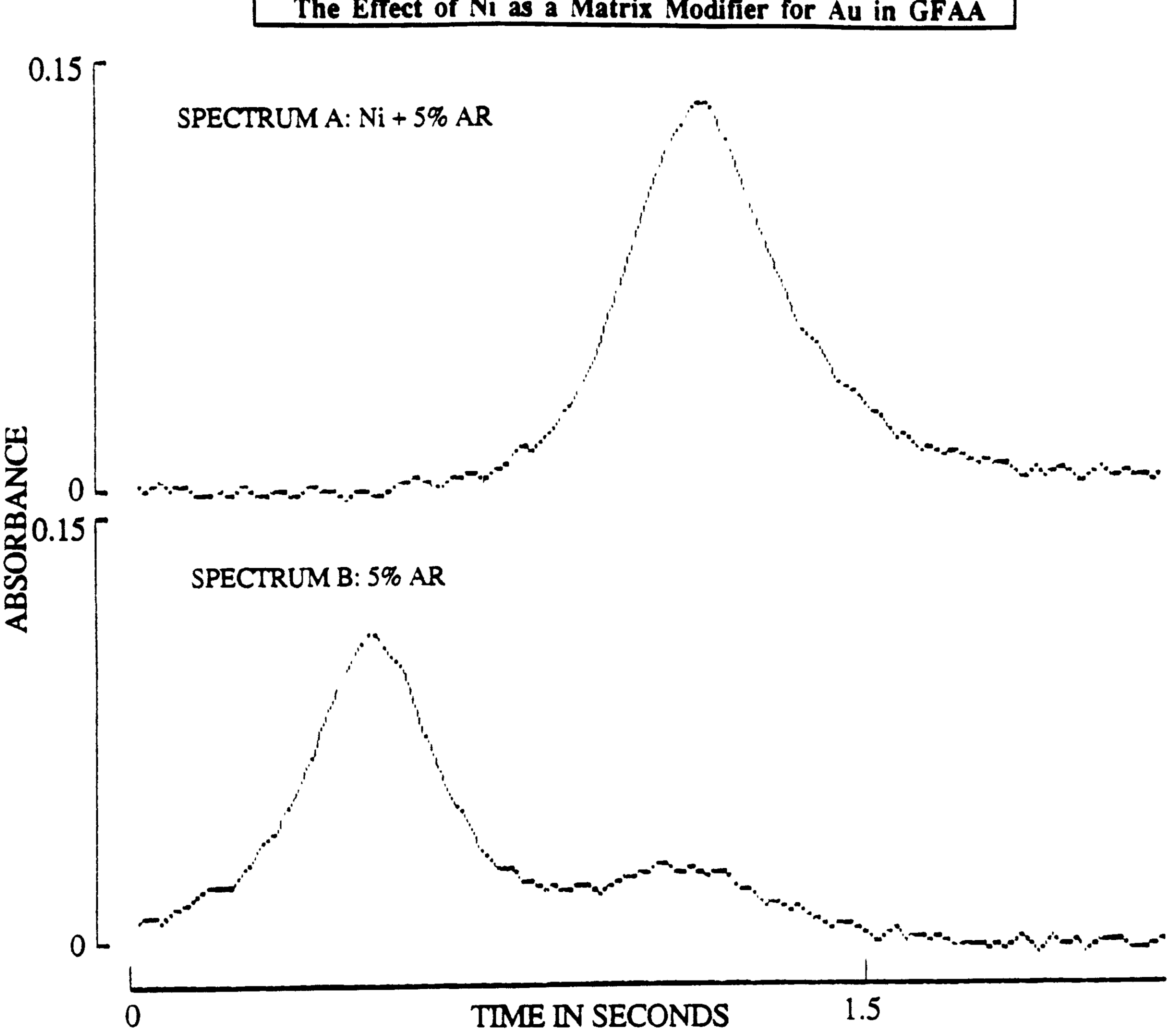


Figure 2.8: The spectra are graphite furnace atomic absorption peaks for Au (20 µl of 50 nmol/l Au in 5% AR) with and without Ni (0.52 µmol/ml sample) as a matrix modifier. The samples were atomized from a L'vov platform in a pyrolytically coated graphite tube under the conditions outlined in Appendix B for the ZGFAA system. It can be seen that, in the presence of Ni, the peak shape is nearly Gaussian whereas it is quite irregular for the AR only matrix. Refer to Section 2.1.5. for further discussion.

Au to be analyzed by the standard additions ZGFAA method. Preconcentrated 4 liter seawater samples could not be analyzed by this approach since suppression by the matrix caused absorbance signals to be near or at the detection limits. In addition, correction for the significant reagent blanks was difficult since suppression caused their smaller signals to be indistinguishable from baseline noise. The difficulty of this approach was exacerbated by poor recoveries of Au that were experienced when taking up evaporated samples in the maximum volume (100 µl) of acid that could be used yet still exceed detection limits for 4 liters seawater. Although these problems might have been circumvented by processing of larger sample volumes, the acquisition of an inductively coupled plasma quadrupole mass spectrometer (ICPMS) offered a superior analytical solution without increased sample size and the ZGFAA work was not pursued further.

2.1.6 Inductively coupled plasma quadrupole mass spectrometry

2.1.6.1 Background

Inductively coupled plasma quadrupole mass spectrometry (ICPMS) is a recently developed analytical tool; the first report of the technique appeared in 1980 (Houk *et al.*.) and the first commercial instruments became available in 1983. Being so new, there remain many aspects of the technique to fully explore; the increase in understanding of ICPMS thus far has been rapid and further improvements in performance are anticipated in the short term (Koppenaal, 1988). The analytical method reported here should be considered a stepping stone from which to apply advances as they become available. In light of this, immediate possibilities for enhancement of ICPMS for the analysis of Au are outlined in the conclusion of this section.

2.1.6.2 General characteristics

ICPMS involves the introduction of ions from an argon (Ar) gas plasma, through a specialized sampling interface, into a high vacuum region where a quadrupole mass analyzer separates them on the basis of their charge to mass ratio for detection (see Fig. 2.9). In the conventional mode of operation samples are introduced into the plasma as an aerosol by natural aspiration or peristaltic pumping of a fluid through a concentric glass nebulizer. The aerosol created is directed through a spray chamber which acts as a low pass filter for aerosol droplets $\leq$ 10 microns in diameter. Such small droplets can be efficiently desolvated, atomized and ultimately ionized in the plasma but constitute only about 1% of the original aerosol with 99% of the sample directed to waste (Gustavsson, 1987). More efficient systems of nebulization exist but tend to be costly, inconvenient and unreliable for various reasons (Gustavsson, 1987).

The plasma used is virtually the same as that used for conventional ICP emission spectroscopy except that it is mounted horizontally rather than vertically. Electromagnetic energy is coupled at a radio frequency into flowing Ar gas by means of a water cooled Tesla coil. Sample aerosol is introduced in the central channel of the Fassel type torch at typical Ar flow rates of 0.1-1 liters/min. Cool gas and auxillary flows are introduced tangentially at typical Ar flow rates of 10-14 liters/min and 0-1.0 liters/min respectively. Plasma temperatures of ≈7000K promote the efficient ionization of most elements of the periodic table (Douglas and Houk, 1985).

The plasma is sampled through a small orifice (≈1 mm diameter) in a high purity Ni sampling cone attached to a water cooled plate into the first vacuum stage (Fig. 2.9). As the plasma gases undergo supersonic expansion, they are further subsampled through the orifice (≈0.75 mm diameter) of a skimmer cone and ions are then directed toward the ion optics. The ion optics contain a photon stop which reduces the background due to stray light and a series of lens plates to which variable focusing voltages are applied. Ions are guided by the ion optics to the quadrupole housed in a high vacuum stage (1-3x10^{-6} mbar operating pressure).

The mass range from lithium to uranium can be scanned at speeds of up to 3000 atomic mass units (amu) per second by rapidly varying the voltages applied to the rods of the quadrupole. Alternatively, the voltages may be set to monitor a single ion energy, scan limited

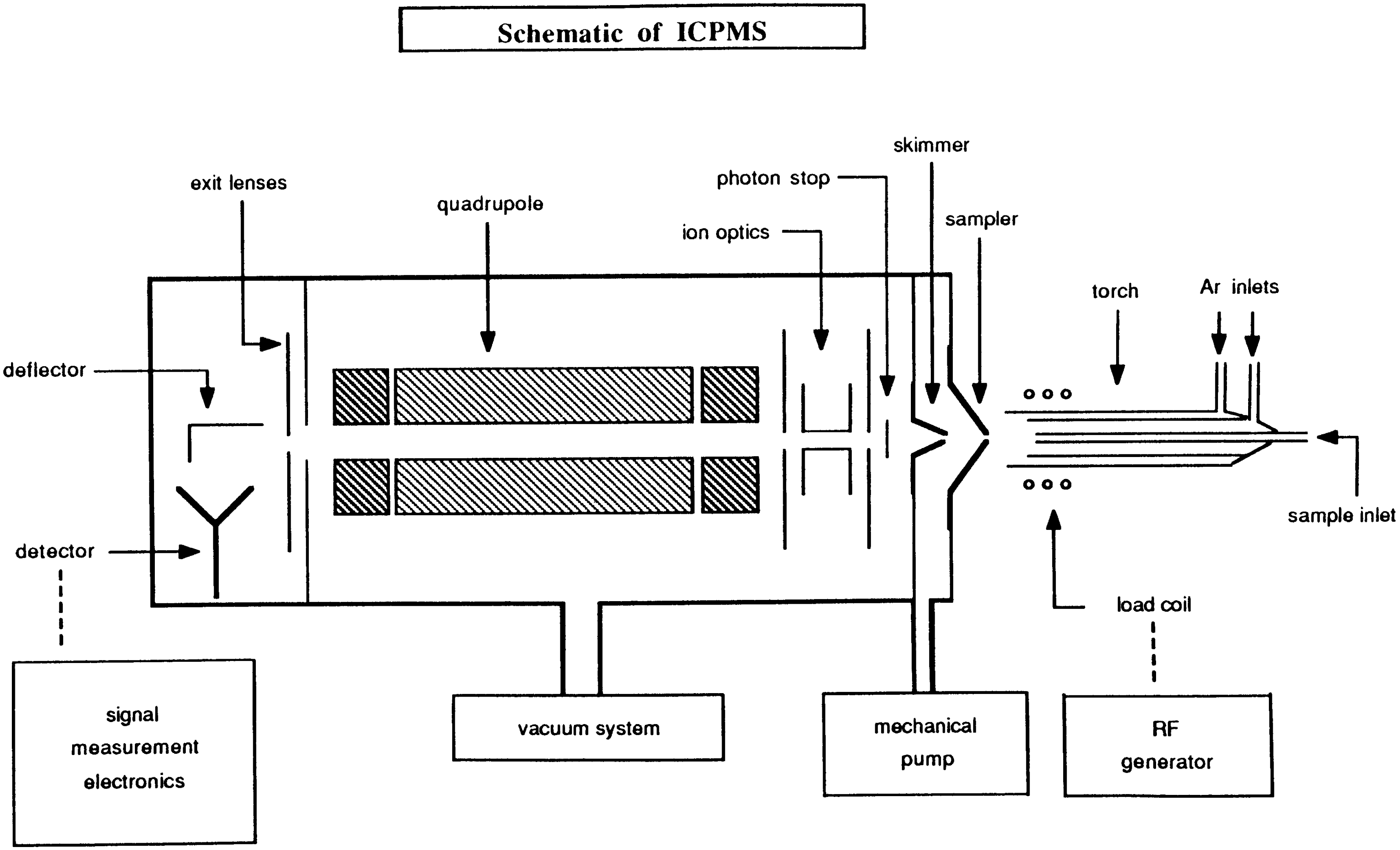


Figure 2.9: This shematic of ICPMS is not to scale. See section 2.1.6 for the principles of operation.

mass ranges, or peak hop. Ions are detected with an electron multiplier. Data is collected directly by a computer or by a multi channel analyzer and passed to a computer for manipulations.

2.1.6.3 System description

The ICPMS system used for this work was a VG Plasmaquad (PQ). Sample solutions were pumped with a Gilson Minipuls 2 peristaltic pump through a concentric Meinhard, TR-30-A3 glass nebulizer and the aerosol created was directed through a Scott-double bypass, borosilicate glass spray chamber, water-cooled to 15°C. Power for the ICP was supplied at an RF frequency of 27.12 MHz by a 2kW Henry Model 2000D RF Generator. All Ar gas flows for the ICP were controlled by mass flow controllers. The RF generator for the VG Quadrupole (Model 12-12S) operated at a frequency of 2.631 MHz and ions were detected with a continuous dynode electron multiplier (Galileo Model 4870). Data were collected with a VG 4096 channel multi channel analyzer and passed to an IBM-XT 286 computer for subsequent manipulations.

2.1.6.4 Gold analysis

Using the conventional mode of sample introduction with a sample flow rate of ≈1 ml/min, optimizing gas flows and ion optics for Au (mass 197) and operating the quadrupole in a scanning mode (masses 195-205), a detection limit of 16 nM (3 ppb) and standard curve slope of ≈7 cps/nM was readily attained for Au standards in 5% AR. Under these conditions, about two ml of solution are required to achieve a steady state signal equating to an absolute detection limit of ≈800 fmol Au. Single ion monitoring, i.e. setting the quadrupole to monitor only mass 197, improved this detection limit by a factor of about 10 making it comparable to ZGFAA for simple matrices.

In general, ICPMS sensitivity exhibits a broad maximum with sample flow rate due to the competing effects of increasing the amount of analyte delivered and decreasing the efficiency of the plasma as an ion source by solvent loading. Although, it was possible to achieve optimum sensitivity for Au by introducing a small volume (0.5 ml) of sample at a low flow rate (0.15 ml/min) (Bakowska *et al.*, 1988) this was found to be impractical. The peristaltic pumping required to control the low flow rate, necessitates the use of flexible (usually Tygon) tubing which contains additives and plasticizers that are highly reactive toward many elements and proved particularly problematic for Au. Gold was adsorbed onto the tubing from DDW and dilute HCl or HNO_3 solutions but was partly desorbed over time with $\geq 5\%$ AR or BR_2/HCl solutions resulting in a slow rise to noisy steady state signals and persistent memory effects.

The strategy employed to allow introduction of small sample volumes yet get around the flexible tubing difficulty was to introduce the sample downstream of the peristaltic pump by means of a flow injection valve. A Rheodyne type 50 Teflon 4-way rotary valve was inserted in the Teflon tubing (0.022"ID) downstream of the flexible tubing so that the sample contacted only Teflon before arriving at the nebulizer. The quadrupole was set to transmit a fixed ion energy at the maximum of the Au-197 peak and transient signals of small volume injections monitored (see Fig. 2.10 for sample output).

Gold also displayed a memory effect associated with the spray chamber and torch. For this reason, these items were cleaned thoroughly in 100% AR before analyses. As discussed below, samples were taken up in 10% AR, so 10% percent AR was pumped through new pieces of flexible tubing until the contaminant Au count rate decreased to background. The same concentration of AR was used as the eluant for the flow injection work. The acidic eluant did not seem to cause undue degradation of the sample or skimmer cones but did degrade o-rings in the nebulizer/spray chamber system more rapidly than dilute HNO_3 or HCl eluants. The O-rings did not contribute to contamination but air leakage due to their degradation affects plasma stability and adds a large degree of noise to signals.

Because of the memory effect it proved expedient not to use Au to optimize the ion optics. Optimal settings were found to be comparable for Pb-208 and Au-197 so Pb was used

FI-ICPMS
Spectrum

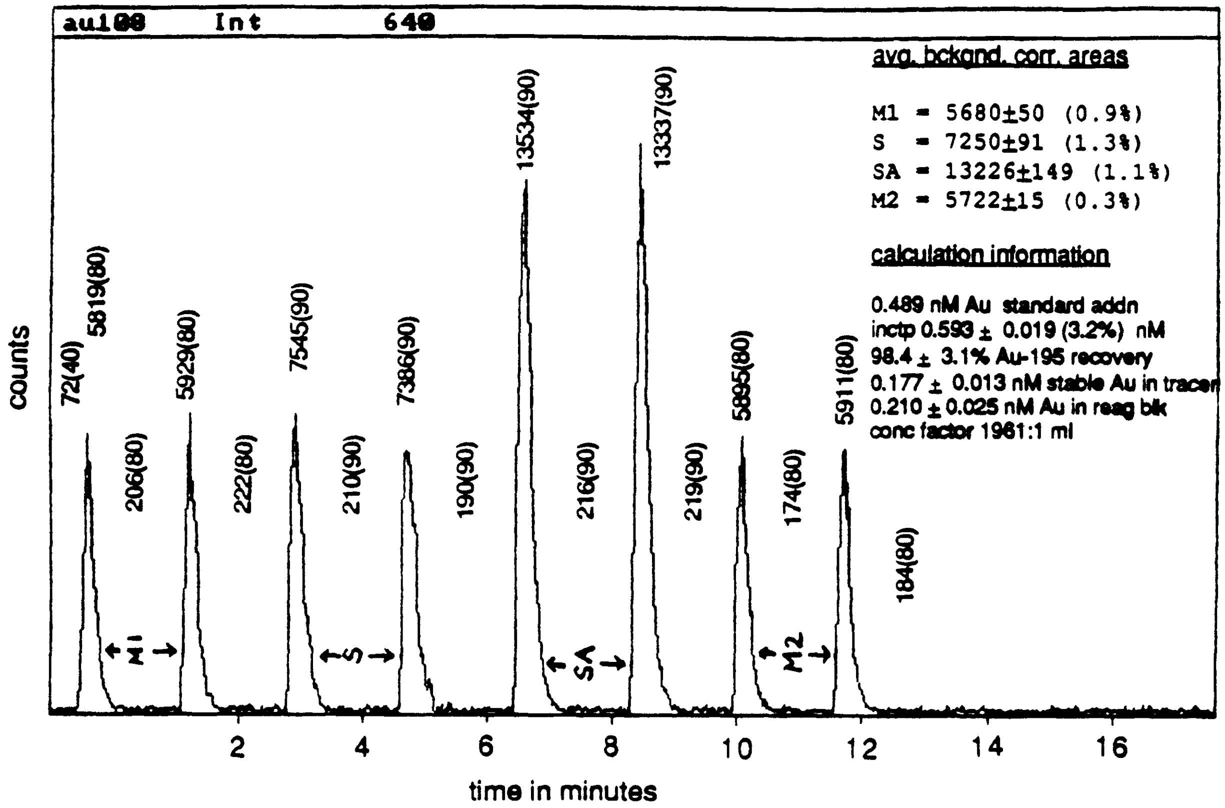


Figure 2.10: This is a plot of typical FI-ICPMS data output. The peaks represent transient signals for Au at mass 197 based on 120 µl injections. The standard was injected in duplicate before (M1) and after the sample (M2) and the sample was injected in duplicate (S) followed by a standard addition in duplicate (SA). Uncorrected areal counts for the number of channels in parentheses are given. The average of counts before and after a peak was used for background correction. Duplicates were then averaged and assigned a 1σ error. The standard was checked for signs of instrumental drift and the data processed as described in Section 2.1.6.4. This particular sample was from the Black Sea and contained 110±20 fmol/l. See section 2.1.6 and Appendix C for instrumental operating conditions and section 2.2 for the preconcentration procedure.

as a proxy for Au for tuning the PQ. At mass 197 there are few isobaric interferences: A hydride of 25% abundant Pt-196 or oxide of the 99.9% abundant Ta-181 could have interfered if these elements had been present in high enough concentrations. Scanning of the 181 and 196 mass regions showed that neither Pt nor Ta occurred in high enough levels in the final concentrates to pose interference complications assuming that such molecular species were present at ≤1% and ≤5% respectively of their free ion concentrations (Horlick et al., 1987).

In general for ICPMS, the quadrupole resolution can be reduced in order to gain increased sensitivity. The extent to which the resolution could be sacrificed for monitoring Au was limited by Pt in the preconcentrated sample and background Hg which both have two masses neighbor to 197. For this work, the resolution was adjusted downward until tailing from the more abundant Hg-198 was at background levels at mass 197.5. Overlap by Pt in the samples was insignificant.

Minimizing the length of the Teflon tubing between the valve and the nebulizer reduced diffusive spreading of the transient peaks and led to excellent reproducibility of integrated peak areas (2% relative std. deviation for twelve 220 µl injections of a 0.25 nM Au standard in 5%AR) when the PQ was operating stably. The detection limit using 220 µl injections of Au standards in 5% AR was 10 fmol (Fig. 2.11). Practical detection limits were about a factor of two greater than this: Four liters of seawater concentrated to 1 ml allowed four determinations for this sample loop size and the detection limit expressed as the concentration of Au in the seawater was 20 fmol/l.

Since for FI-ICPMS a larger final preconcentrate volume (1 ml) could be used than was possible for ZGFAA (100 µl), problems with the radiotracer recovery of the final preconcentrate were eliminated. Provided samples were not evaporated completely to dryness, 1 ml reliably provided near quantitative recovery of the radiotracer. The viscosities of samples preconcentrated to 1 ml were still higher than for 5-10% AR and varied slightly between samples. Viscosity can affect the efficiency of aerosol production and may have generated the small differences in sensitivity found between standards and samples

Au Standard Curve by FI-ICPMS

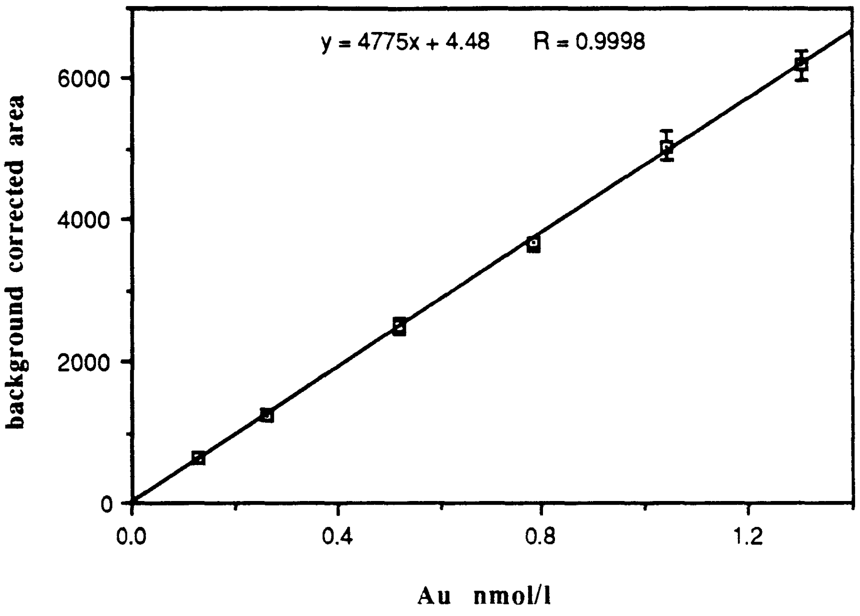


Figure 2.11: This is a plot of FI-ICPMS analysis (June 3, 1988) of Au standards in 5% AR. Each point represents the average of triplicate injections with 1σ errors. A 220 μl loop was used with instrumental parameters given in section 2.1.6.4 and Appendix C. Assuming 3σ of the background signal is 250 areal counts, an absolute detection limit of 10 fmol per injection is obtained.

While in general ICPMS is relatively more tolerant of high concentrations of matrix elements than GFAA, a variety of matrix effects do occur (Horlick et al., 1987). High concentrations of refractory oxide forming elements such as Al and Si can build up on the sample cone and diminish the size of the orifice. This tends to occur slowly and is not likely to be a problem for the Au preconcentrates since the bulk of residual Si is volatilized by HF in the final evaporation step. Suppression of the Au signal was found in the presence of Br at 10 mM or greater concentrations, independently of whether the Br was added as Br2 or HBr (Fig. 2.12). This type of suppression has been found to be general for any element in the presence of high concentrations of another and exhibits a mass dependence (Olivares and Houk, 1986). For a given analyte, the higher the mass of the matrix element the greater the suppression. Also lighter analyte masses tended to show more extensive suppression by a given matrix element than heavier masses. Modeling of space charge effects of Ar+ at the sample orifice accounts for some of these observations but not all (Gillson et al., 1988). Matrix effects for ICPMS have yet to be fully explained and are the subject of ongoing investigation.

Due to effects on the signals by the viscosity and sample matrix, standard additions were employed for flow injection ICPMS (FI-ICPMS) analysis. The sample was injected in duplicate followed by two injections of sample with a standard addition. An example of a typical sample run by ICPMS is shown in Figure 2.10. Operating parameters are outlined in Appendix C. The smaller (120 µl) injection loop was used in conjunction with a set of cones that provided 70% increased sensitivity without increasing the background thereby reducing the practical detection limit to 10 fmol per injection. The reason for differences in sensitivities between cone sets, once gas flow rates, torch box position and ion optics are optimized, is not clear and is currently under investigation.

The standard, injected in duplicate before and after a sample, was used as an indication of the stability of the PQ over the course of the ≈15 minute sample runs. If the difference between the duplicates was >10% and/or the the difference between the average before and after the run was >8%, a run was rejected. Long and short term stability tests of the PQ over

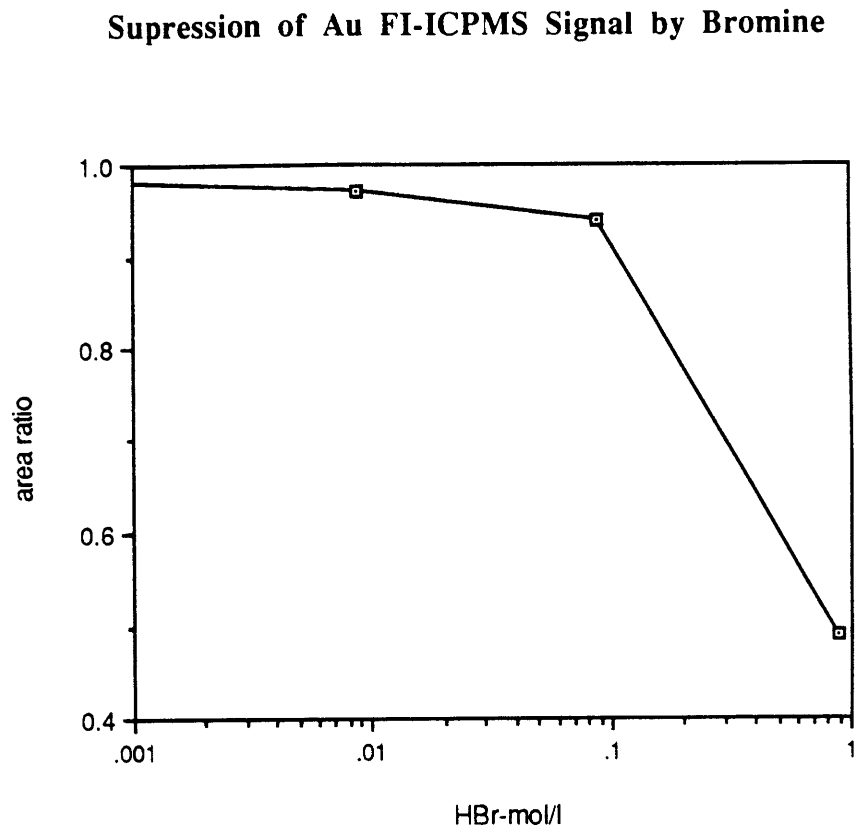


Figure 2.12: This is a plot of Br concentration versus Au signal suppression expressed as the ratio of the peak area with the Br addition to the peak area without for a Au standard (0.25 nmol/liter) in 10% AR. Bromine was added as HBr but the same affect is observed for equal molar concentrations of Br_2.

the course of this work indicated that the PQ could operate stably over 15 minute periods but did not do so reliably. Instability manifested itself both as gradual drift and sporadic fluctuations. Factors that contributed to instability included a deteriorating electron multiplier, damaged or worn sampling and skimmer cones, air leakage through worn o-rings in the nebulizer mounting block, drafts and environmental temperature fluctuations and a variety of electronics failures. As these problems were identified and controlled, the stability improved but unexplained sensitivity fluctuations still occasionally occurred.

2.1.6.5 Possible enhancements

Because the PQ was not acquired until the late stages of this work, there was not sufficient time to investigate several probable enhancements of ICPMS for the analysis of Au. They are outlined briefly below for the sake of future work:

1. To improve precision and recover data otherwise jeopardized during unstable operation, it would be desirable to add an internal monitor to the samples. It is suggested that bismuth, being monoisotopic at mass 209 and close in mass to Au, could be added in high concentration with respect to its concentration (presently unknown) in the preconcentrate and be used for normalization. Software that has become available since the analyses reported here were completed, which permits the examination (by rapid peak-hopping) of multiple transient signals could be used to monitor both Au-197 and Bi-209. In addition, without any changes to the preconcentration method, the injection loop could be made larger by nearly a factor of two (240µl) to partly offset the sacrifice in sensitivity for Au incurred by spending time on another element.

2. The spray chamber was chilled to 15°C throughout this work. Studies have clearly shown that lowering the temperature of the spray chamber to 2°C reduces the water

vapor loading of the plasma and results in a more efficient plasma (Hutton and Eaton, 1987). It is suggested that the spray chamber temperature be lowered to check for improved detection limits for Au by FI-ICPMS.

3. ICPMS does not require that samples be introduced in solution. Introduction of a sample in a gaseous form such as hydrides (Robbins and Caruso, 1979; Nakahara, 1983; Thompson *et al.*, 1978) or Os as OsO_4 (Summerhays *et al.*, 1983) or as an atomic or molecular vapor through thermal atomization from a filament (Park *et al.*, 1987) or graphite (Hall *et al.*, 1988) or through laser ablation of solids (Routh and Tikkanen, 1987) lessens dilution of an analyte and avoids the problems associated with excess solvent loading (Hutton and Eaton, 1987). As demonstrated in the ZGFAA work, Au can be readily thermally ionized in a graphite furnace so it is conceivable that this mode of sample introduction could provide at least an order of magnitude better detection limit than nebulization where 99% of the sample goes to waste. Since it is the ability to sweep the atom vapor into the plasma and not the exact location of the vapor in a light beam that is at issue here, an aliquot of a partly evaporated solvent extract of the column eluant could be introduced directly to a graphite cup and the solvent evaporated and charred at a relatively low temperature. A nickel solution could then be added to effect a Gaussian type atomization as in ZGFAA along with an internal monitor of mass closer to Au of similar atomization characteristics. The gas stream could be diverted to the plasma before atomization and the transients of Au and the internal monitor followed. If one order of magnitude improvement in detection limits is attainable, Au could be analyzed on < 1 liter of seawater and sampling could be made part of more routine hydrographic work making detailed investigations of the marine geochemistry of this element more convenient.

2.2 Analytical Procedure

2.2.1 General

Labware was cleaned before use by soaking in 100% AR followed by copious rinsing with DDW and drying in a laminar flow bench. As much as possible, work was carried out under filtered air either in a laminar flow bench or enclosed in vessels with filtered air supplies. For safety, the KCN solution and hot acids were dealt with in a well ventilated hood with precautions taken to avoid unnecessary exposure of the samples to unfiltered air. The relatively easy reduction and loss of Au from solution tends to minimize contamination levels in DDW and reagents, however, analysis at the fM level was only possible by purification of reagents and careful tracking of blanks.

2.2.2 Reagents

2.2.2.1 Acids

Reagent grade HNO_3 (16N) and HBr (8.9N) were triply distilled in a Vycor still with collection into AR cleaned polyethylene or Teflon containers. Hydrochloric acid was likewise prepared from reagent grade HCl (12N) diluted 2 fold with DDW for distillation of the 6N azeotrope. For the purpose of this work, the classical definition of AR (3 parts 12 N HCl to 1 part 16 N HNO_3 by volume) was taken as being equivalent to 100% and dilutions were expressed as percentages maintaining the 2.3 HCl/HNO_3 molar ratio. The most concentrated aqua regia possible from the Vycor triply distilled acids by this definition is $\approx$57% and was made from 6 parts 6N HCl to 1 part 16 N HNO_3 by volume. Reagent grade hydrofluoric acid (28.9N) was triply distilled in a two bottle Teflon still.

2.2.2.2 Other

Bromine was triply distilled in a Pyrex still and sealed until used in glass ampoules that had been precleaned in hot AR. Ammonium hydroxide was purified by allowing open containers of reagent grade NH_4OH (≈14 N) and DDW to equilibrate for two days within a closed polyethylene vessel that was gently swirled on a shaker table. The 4% KCN solution was made by dissolving 40 gm of reagent grade KCN in 1000 gm DDW and was purified by passing this solution (2 ml/min) through an AR precleaned disposable polyethylene ion exchange column containing ≈2.0 ml analytical grade AG 1-x2, 50-100 mesh strongly basic anion exchange resin (Bio-Rad Laboratories).

2.2.2.3 Standards

Stable Au standard was obtained commercially (VWR Scientific Atomic Absorption Reference Standard) as a 1000 ppm Au solution in dilute aqua regia. The concentration of this standard was found by GFAA to be consistent within analytical uncertainties (±5%) with a standard prepared in the laboratory by dissolving high purity Au wire in a small amount of AR and diluting with DDW. The primary standard was stored in an amber bottle kept out of the light when not in use. However, unlike silver which is very photosensitive, Au does not seem to undergo adverse photo-reactions; working standards (≈50 nM) in 5% AR solutions stored in glass volumetric flasks exposed to laboratory lighting for up to a year showed no signs of diminished Au contents with respect to freshly prepared working standards.

A dilution of a commercial 1000 ppm Ni standard in dilute nitric acid (VWR Scientific Atomic Absorption Reference Standard) was used as a matrix modifier for the Zeeman GFAA Au determinations.

2.2.3 Sample storage

Teflon, as was shown in section 2.1.3, is the container of choice for storing samples but was prohibitively expensive for routine use. Since glass containers present awkward handling difficulties, polyethylene was used to contain samples. Gold-195 radiotracer (≈0.1 µCi) was added to each sample as soon as possible after collection (and filtration if done). Whenever possible, 0.5 ml of a 4% KCN solution (see section 2.1.4.2) was added to a container before a sample was drawn and samples were preconcentrated shipboard, otherwise the samples were acidified to pH 1.5 with 56% AR. The approach taken for preserving individual samples for this work is annotated with the results in Chapter 3. In all cases, sample containers were leached in 10% AR at 60°C overnight and rinsed with DDW before use to avoid contamination or isotope exchange with contaminant Au.

2.2.4 Column preparation

Approximately 1.8 ml of the anion exchange resin was added as a slurry in DDW to the precleaned polyethylene columns. The resin was pretreated by elution with 15 ml 90°C 16N HNO_3 to remove contaminant Au followed by 20 ml rinses with DDW and 6N HCl. Columns were then capped and stored in sealed plastic bags until use.

2.2.5 Seawater analysis

2.2.5.1 Preconcentration

The pH of stored samples was adjusted with NH_4OH from 1.5 to 8, as determined by indicator paper, followed immediately by the addition of 0.5 ml of a 4% KCN solution per liter sample. Samples processed at sea received the same amount of KCN without pH adjustment. For both stored and unstored samples at least one hour was allowed for Au cyanide complex formation before passing the samples through the resin by means of the apparatus shown in Fig. 2.13. Flow rates were adjusted to 2-6 ml/min by the 2-way Teflon valves. The volume of seawater processed varied for this work as noted with the results in Chapter 3 and the

Preconcentration Apparatus

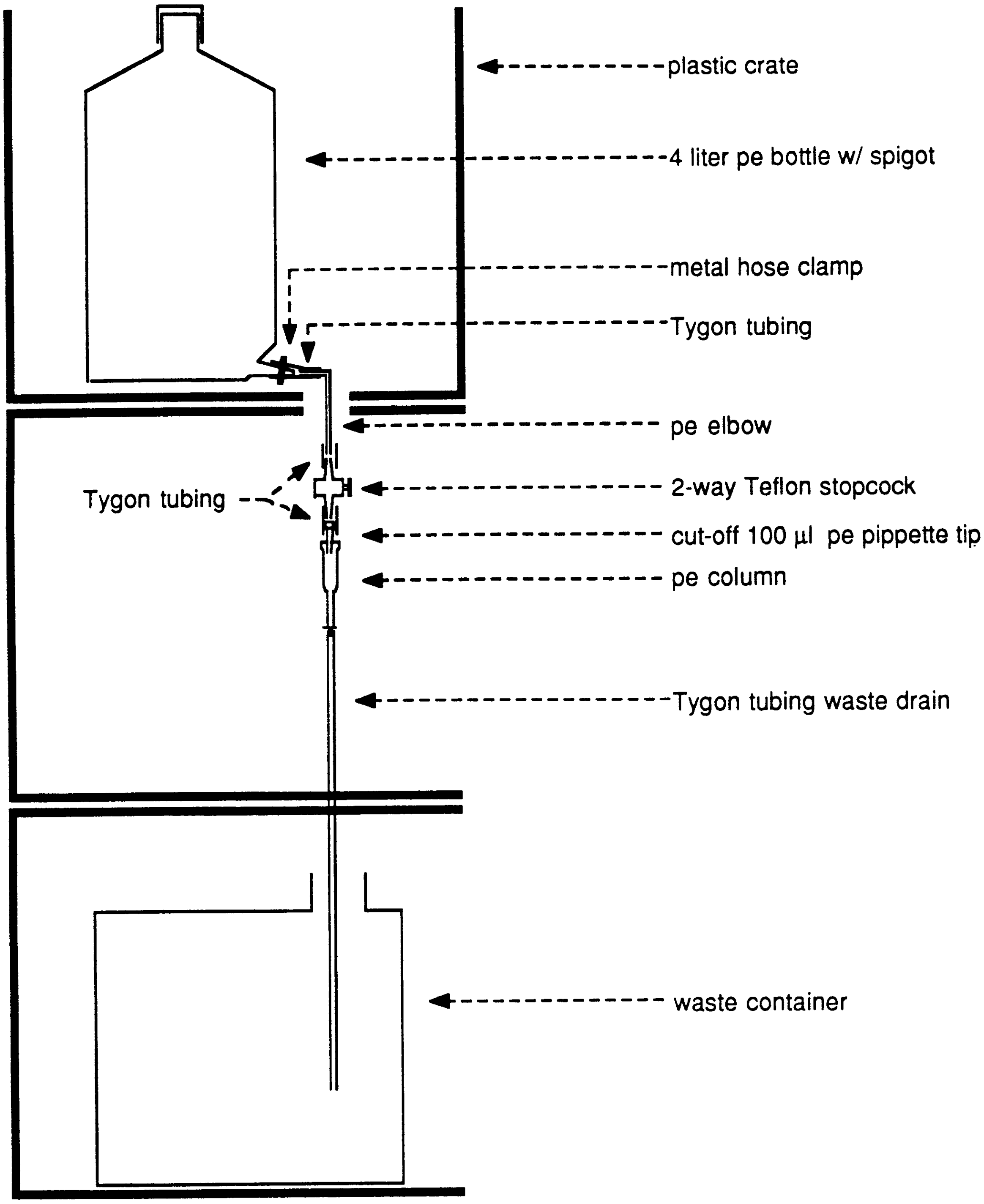


Figure 2.13: This is a sideview, cross-sectional shematic of the apparatus used to preconcentrate 2-8 liter seawater samples. The abbreviation pe is for polyethylene. The metal hose clamp for securing the Tygon-tubing piece to the spigot was wrapped in parafilm to prevent corrosion. The end of the tubing at the spigot wrapped in Teflon tape to help prevent leakage. Tygon was used to connect pieces and had minimal contact with the samples before the column. At sea, the plastic crates were fastened together with tie-wraps and the waste container secured with bungy cord. The 4-liter pe bottle was secured upright in its crate with bungy cord until most of the sample had drained through the column and then the bottle was tilted forward and resecured to allow the remaining sample to pass through the column. See section 2.2 for further details.

conditions specified here were used for samples of ≤ 4 liters. Eight liter samples were passed through two columns in 4 liter aliquots and the eluants were combined. After samples had passed through, the exteriors of the columns were rinsed with DDW. The columns were then capped with their ends wrapped in Parafilm and put into plastic bags.

All elution work was carried out in the laboratory. Columns were rinsed with 40 ml of 0.12N HCl and 40 ml of DDW, followed by elution into quartz tubes with 40 ml of 90°C 16N HNO_3. After 40 ml of 6N HCl was added, the eluants were UV-oxidized for 24 hours, transferred to 100 ml Teflon beakers and evaporated under filtered air with gentle heating (≈80°C) under IR lamps. When reduced to ≈1 ml, the sample solutions were transferred to 5 ml conical Teflon vials (Savilex). One ml of concentrated HF was added to volatilize any Si present and the samples were evaporated in a Teflon coated heating element (75°C) housed in a laminar flow box until only 20-50 µl remained. At this point, 250 µl of 57% AR was added to resolubilize the Au and the vials were capped and placed in a laminar flow bench (room temperature) for at least 24 hours. Finally, the samples were diluted to 1 ml (±1%) with DDW.

Reagent blanks were prepared by spiking a mixture of the reagents with ^{195}Au, with both the spike and reagents in the same quantities used for the samples, and preconcentrating in the same way as was done for the samples.

2.2.5.2 Yield Monitoring

Preconcentrated samples and reagent blanks were transferred with a 1 ml pipet to 1.5 ml polyethylene vials which were capped for NaI(Tl) γ-counting. Standards were made in the same type of vial by diluting aliquots of the radiotracer, equal to that added to the samples (≈ 0.1 µCi), to 1 ml such that the final AR concentration was 10%. Samples, reagent blanks and standards were each counted three times in a set geometry and recoveries were calculated from averaged counts (see Appendix A for operating parameters). Provided samples had not been evaporated to dryness, radiotracer recoveries ranged from 90-100% with uncertainties of ≤ 2% based on the relative standard deviations of the replicate counts. Consistently high recoveries would suggest that as more experience is gained with this technique it will be possible to eliminate the tracer addition and hence the uncertainties associated with correction for the stable Au in the tracer. However, information would be lost on samples which been completely evaporated because their recoveries varied from 0-70% .

2.2.5.3 *FI-ICPMS determination*

After counting, 250 µl aliquots of each sample were transferred to four 500 µl polyethylene centrifuge vials for determination by standard additions FI-ICPMS as described in section 2.1.6. Additions (10µl) of a standard in 10% AR was made to two vials of each sample set and a 120 µl injection loop was used for sample analysis. Refer to Appendix C for typical operating parameters.

Uncertainties for regressions were calculated by assuming that the error associated with the concentration of Au added was insignificant, using a standard deviation as an estimate of the error in the average peak areas and propagating these errors in the usual way (Skoog and West, 1982). Calculated uncertainties ranged from 5-20% depending upon the Au content of a sample.

2.2.5.4 *Precision*

Uncertainties reported with the samples were propagated from the regression errors and recovery and blank corrections. The reproducibility of the method is estimated to be 15% at the 140 fM level based on the analysis of five 4 liter shallow Mediterranean seawater samples drawn from a single 30 liter Niskin bottle (see Table 2.5).

Table 2.5: Reproducibility of anion exchange preconcentration-FI-ICPMS

sample 1	sample 2	sample 3	sample 4	sample 5	average±1σ
141±17 fM	132±40 fM	110±23 fM	168±55 fM	145±56 fM	139±21 fM

Blank corrections constituted a significant fraction of the signals measured for this work. The Au contributed by the radiotracer amounted to 160 fmol and the blank ranged from 140-280 fmol compared to ≈250 fmol contributed by 4 liters of seawater. Whereas the measured contribution of Au by the radiotracer was consistent (±10%) from run to run, significant variability was found for the reagent blanks. The average of replicate reagent blank determinations for a given run (± 1σ) was used to correct samples of that run. The uncertainty associated with the reagent blank corrections (up to 50% of the reagent blank Au concentrations) constituted the largest single source of error to the measurements.

Preliminary work in the laboratory indicates that the 4% KCN solution contributed most of the Au to the reagent blank. It may be possible to reduce the Au contents of this reagent by a second column clean-up step and to reduce the amount of KCN (<0.3 mmol/l) added to the samples. In addition, short of eliminating the radiotracer, the amount of fresh ^{195}Au added to the samples could be decreased by a factor of four to ≈ 0.025µCi yet still provide sufficient radioactivity for yield monitoring.

2.2.6 Fresh water analysis

The same method used for seawater can be applied to filtered freshwater samples. Due to their generally higher particulate matter content, it is recommended that fresh waters be filtered with a Teflon-based filter system through 0.4 µm Nuclepore filters immediately upon collection and then spiked with radiotracer and either preserved (AR-pH 1.5) or preconcentrated as soon as possible. The filters can be pretreated by rinsing in 5% AR and soaking in DDW. The pH of freshwater samples should be adjusted to ≈8 with NH_4OH after adding the 4% KCN solution (0.5 ml/liter) and otherwise processed as for seawater.

2.2.7. Hydrothermal fluids analysis

A few submarine hydrothermal fluid samples, preserved with AR (pH 1.5), were available for this work. Their actual analytical treatments are described in Chapter 3. What follows here is a recommended procedure based on preliminary experience with those samples.

Several complications can arise in the collection of hydrothermal fluids which can adversely affect Au analysis. Since Au can be highly concentrated in solid phases around vent areas (Hannington *et al.*, 1986 and 1988), particulate matter from a vent or suspended sediment sampled with the fluid presents the possibility of gross contamination. It is therefore recommended that aliquots of vent fluids be filtered shipboard as soon as possible and then spiked with ^{195}Au and preserved with AR (100 µl of 57% AR per 20 ml hydrothermal fluid). Based on the results of the 21°N, 332°C fluids (section 3.1), 25 ml should be an adequate for Au analysis with extra volume allowed for seawater entrainment. Even with acid additions, amorphous Si and sulfide minerals can precipitate in stored hydrothermal fluids. A minimum amount of Br_2-HF-HNO_3 should be added to resolubilize this material. Excess Br_2 should be allowed to evolve and then 4% KCN added in excess (300 µmol/liter) and the pH adjusted to about 8 with NH_4OH. As the pH is adjusted upward a mixed Fe-Si oxyhydroxide gel will precipitate, however CN^- complexation is sufficiently strong that Au stays solubilized. The solution should be filtered with pH 8 (DDW-NH_4OH) rinses and then passed through anion exchange resin and further processed as for seawater.

Chapter 3

3.1 Results

3.1.1 Atlantic Gulf Stream profile

The first profile of samples for Au analysis for this work was taken on 1-Nov-87 in the Atlantic Gulf Stream at 36'8.2"N, 69'29.1"W (391 nautical miles from the Virginia coast), as part of the R/V Knorr South Atlantic Ventilation Experiment (SAVE) Expedition, Intercalibration Leg 00. Sampling (Station 4-Cast 2) was conducted with 30-liter Niskin bottles equipped with epoxy-coated internal springs and Viton rubber o-rings, hung on a stainless steel hydrowire. As soon as the Niskins were on deck, and directly after gas samples were taken, 8 liters of seawater were drawn into polyethylene containers containing 4 ml 4% KCN solution and were spiked with ^{195}Au within 20 minutes. These unfiltered samples, along with reagent blanks, were passed through anion exchange columns at sea, and the columns returned to the laboratory for further processing as described in section 2.2.

The results are presented, along with ancillary data, in Table 3.1 and are plotted in Fig. 3.1. Excluding the bottom maximum, the values over the water column are uniform within the uncertainties at an average of 53±22 fmol/l. Unfortunately, a surface sample was not available and so it cannot be determined whether these waters are enriched or depleted with respect to deeper waters at this site. Uncertainties in the data make it difficult to resolve any mid-depth features for Au. The near bottom maximum may be associated with a detached turbidity maximum, known to occur sporadically in this region (Biscaye and Ettreim, 1977; McCave, 1986). Since the water was unfiltered, the increased concentrations may result from Au stripped from particulate material. No independent measure of suspended matter was obtained on this expedition, however, an upper limit of the amount of material required to supply the excess Au can be estimated by assuming that suspended matter has a continental crust Au concentration (1.5 ppb); 1 mg/l of such material would be necessary to produce the observed 75 fmol/l Au concentration anomaly with respect to the upper water column. Values of several mg/l of suspended detrital matter have been reported for deep waters of this region (Ewing and

Atlantic Gulf Stream Data: 36'8.2'N, 69'29.1"W

SAMPLE	DEPTH *m*	GOLD CONC *fmol/l(unc)*	TEMP *deg C*	THETA *deg C*	SALT *psu*
201	200	56(14)	19.573	nd	nd
202	485	56(8)	16.188	16.109	36.2
203	873	37(9)	7.309	7.22	35.114
204	1252	nd	4.603	4.525	35.014
205	1721	56(13)	4.01	3.867	34.99
206	2189	43(10)	3.59	3.408	34.978
207	2659	15(9)	3.087	2.865	34.962
208	3136	nd	2.709	2.445	34.928
209	3622	82(16)	2.369	2.06	34.912
210	4122	125(14)	2.247	1.884	34.895
211	4327	79(31)	2.242	1.855	34.897
212	4379	≤ 2	2.248	1.854	34.892

Table 3.1: Au concentrations are for unfiltered 8-liter seawater samples from Stn. 4, Cast 02 of Leg 00 of the R/V Knorr Save Expedition, 1-Nov-87. Depths have been corrected by comparison of protected and unprotected thermometers and salinities are reported in practical salinity units. The radiotracer correction was 166±22 fmol and the reagent blank 355±52 fmol for this suite of samples. See section 3.1.1 for details.

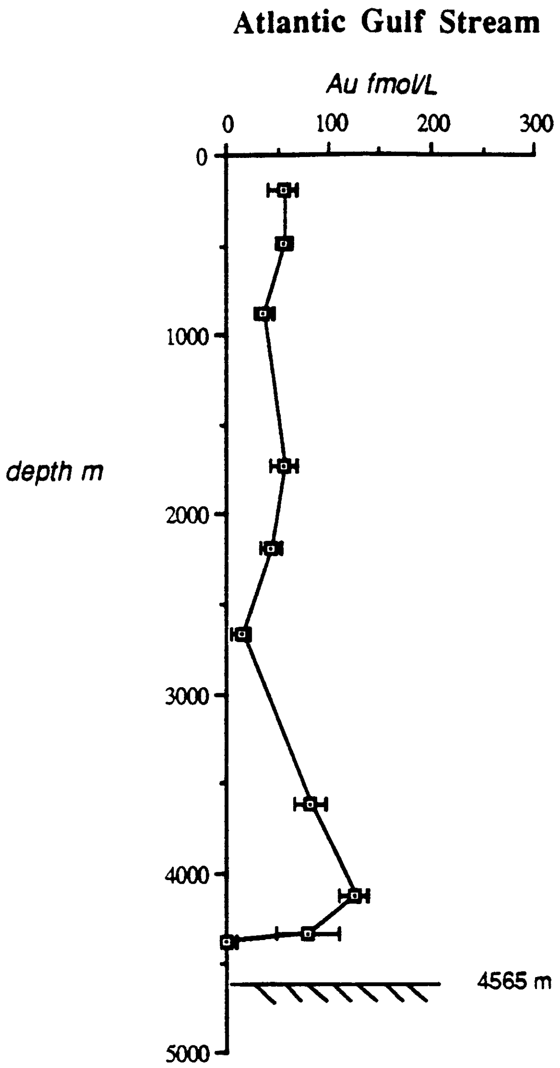


Figure 3.1: Au profile at 36'8.2"N 69'29.1"W. See Table 3.1 for data.

Thorndike, 1965) and so a particulate source for the excess Au is reasonable. The very low bottom water value could be due to uptake at the sediments or may be an advective feature associated with Antarctic bottom water. Since the gradients of bottom water hydrographic properties are not very steep at this location (see Station 121 (35'59"N, 67'59"W) of the GEOSECS Atlantic Expedition Atlas), the latter possibility is less likely. Further studies are needed to clarify the origin of this depletion. The complex hydrography of this site (Stommel, 1965) coupled with low sampling density, make it difficult to draw any firm conclusions regarding the behavior of Au in the oceans on the basis of this profile.

3.1.2 Northeast Pacific profile

A second profile was collected in the Northeast Pacific (41'00"N, 127'30"W) during the R/V Atlantis II-DSRV Alvin Escanaba Trough Expedition 118/35. This station, situated in the California current, is about 180 nautical miles from the California coast (Fig. 3.2). Multiple casts were made during nightly reoccupations of the station location over the period 31-May-88 through 14-Jun-88. Samples were collected with 5-liter Niskins equipped with epoxy-coated internal springs and red silicone rubber o-rings, hung on a galvanized steel hydrowire. Four-liter samples were drawn soon after collection into polyethylene bottles containing 2 ml 4% KCN solution and were spiked with ^{195}Au within 24 hours of collection. These unfiltered samples were shipped back to the laboratory and processed, as described in section 2.2, one month after collection.

The results are presented, along with ancillary data, in Table 3.2 and are plotted in Fig. 3.3. Recoveries were essentially quantitative for this suite of samples, however, there is a fairly large degree of uncertainty associated with the measured concentrations because the blank corrections constituted a large fraction (60%) of the signals. Within these uncertainties, the concentration of Au appears to be fairly uniform with depth at an average concentration of 55 ± 36 fmol/l, similar to the Atlantic average of 53 ± 21 fmol/l. There is no evidence for an enrichment of Au in the surface waters. If anything, there may be a surface water depletion,

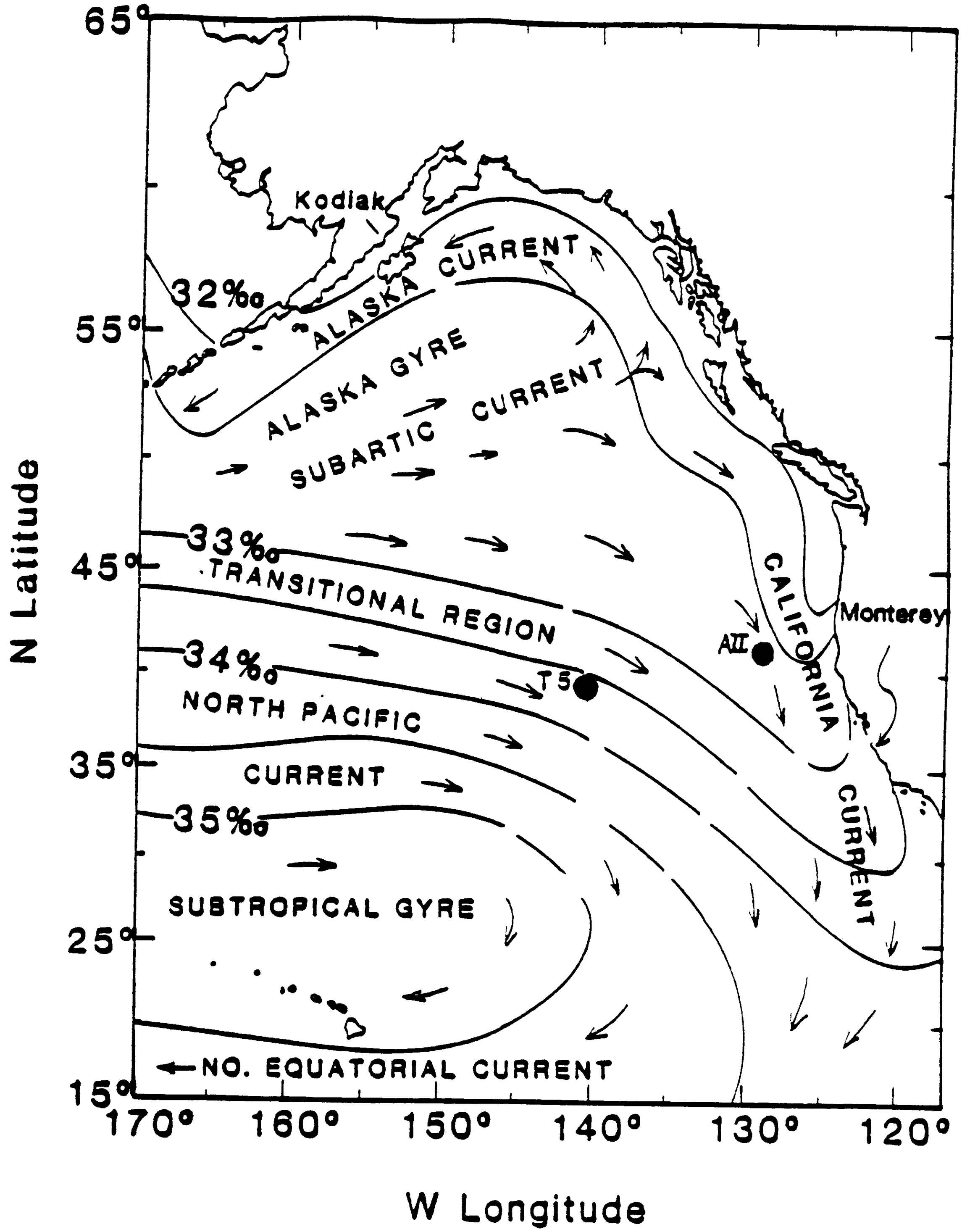


Figure 3.2: Pacific station locations: AII refers to the Atlantis II Expedition and T5 refers to the Vertex Expedition. Arrows show direction of surface circulation. See section 3.1.2. for details.

Pacific California Current Data: 41'00'N, 127'30"W

depth m	sal psu	in-situ T deg C	PO4 µM	SiO2 µM	O2 mM	Au fM	∂ Au fM
0				3 364		8	49
10	32.439		0.52	3.714	260.5		
15			0.41	3.524	281.1		
20				2.667			
40			0.79	6.286	288.3		
40	32.656		0.81	6.952			
65			1.33	16.571	229.4		
84	33.253		1.55	20.381	211.1		
90			1.90	22.762	171.7		
90				28.381			
96	33.392			22.952		69	45
110	33.538	8.77	1.86	26.483	183 3		
173				41.041			
177	33.923		2.15	37.754	170.6		
193	33.984	7.62	2.29	42.216	119.6	36	53
270	34.025	6.69	2.59	53.487	96.7		
288				52.313			
295				58.037		6	45
308			2.60	55.131	95.5		
363	34.060		2.88	68.516			
387				65.228			
393				80.000		47	
407			2.89	68.516	63.0		
461	34.087	5 20	3.04	79.996	54.2		
479	34.110			83.797			
481	34.097			82.847			
486	34.091	5.03	3.23	81.897	49 1		
491		4.85		85.607		114	59
600	34.185			96.150			
610	34.200			97.100			
666	34.285			105.652			
676	34.274	4.33	3.33	106.127	68.4		
723	34.301			109.452		73	50
733	34.302		3.33	110.878	19.1		
847	34.370			118.479			
857	34.371	3.90	3.39	119.905	16.5		
953	34.420	3.62	3.34	126.556	26 4		
959	34.410			124.656			
973	34.426			126.081			
974	34.425	3 57	3 40	128.456	22 0		
1187	34.473		3 36	138.879	31 3		
1221				141.284			
1231	34.491			142.234		21	47
1400	34.521			151.736		98	46
1419	34.538			154 112			
1429	34.540	2.55	3.29	153 637	49.9		
1467	34.540		3.33	154.587	80.3		
1666	34.562			159 439		21	46
1876	34.607			169.315		89	52
1899	34.602			171.216			
1909	34.602		3.07	171.691	70 9		
1961	34.590		2.98	170.741			
2154				169.720		72	47
2333	34.632			176.917			
2343	34.626	1.80	3 04	175.016	90.3		
2454	34.630	1.81	2.99	176.917			
2862		1 70		170.654			

Table 3.2: Au concentrations are for unfiltered 4-liter seawater samples collected June 1988. Depths have been corrected by comparison of protected and unprotected thermometers; salinities are reported in practical salinity units; ∂ Au is the uncertainty associated with Au in fmol/l; the radiotracer correction was 163±61 fmol and the reagent blank was 245±180 fmol for this suite of samples. See section 3.1.2 for details.

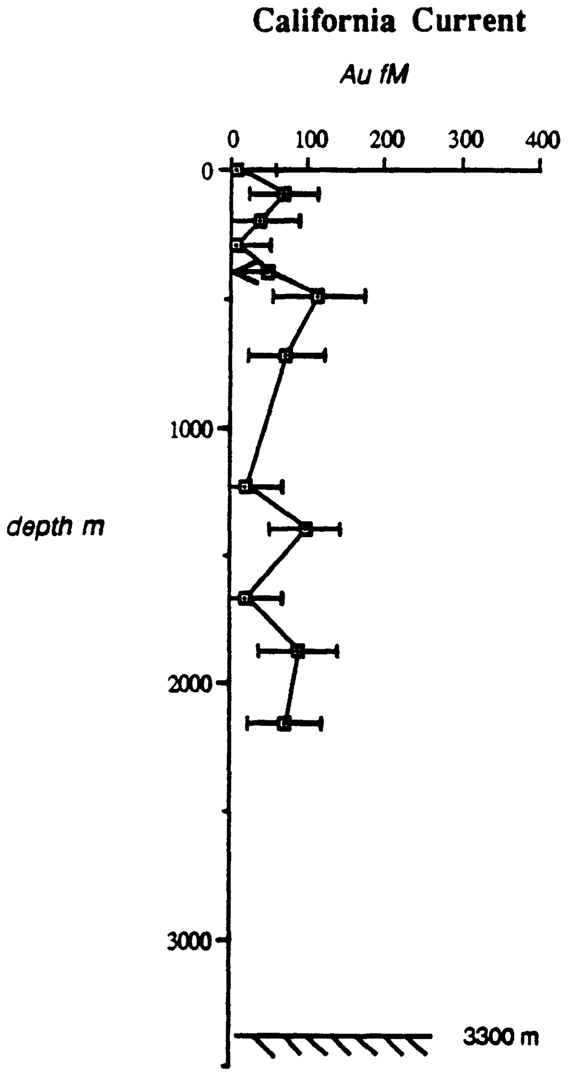


Figure 3.3: Au profile at 41'00"N 127'30"W. See Table 3.2 for data.

although the data are not sufficient to be conclusive. Since the concentration is uniform (within uncertainties) throughout the water column, Au shows no correlations with the hydrographic properties in Table 3.2.

Samples were also collected from four depths in the Northeast Pacific (39'N,141'W) during the Vertex VII Expedition, August 1987. This location (Stn. T-5) is in an oligotrophic transitional region, between the Subarctic Current to the north, the California Current to the east and the North Pacific Current and Subtropical Gyre to the south (Fig. 3.2). Samples were obtained from 30-liter Teflon lined Go-Flo bottles hung on a Kevlar line. Four-liter samples were filtered through 0.4 μm Nuclepore filters using 8 psi nitrogen gas overpressure and collected into 4-liter polyethylene bottles containing 10 ml 57% AR. Samples were then shipped back to the lab and spiked with ^{195}Au two months later. One year after they were spiked, the samples were processed as described in section 2.2.

The results are presented in Table 3.3. Though the storage period was more than one year the radiotracer recoveries were quite high, 80-87%. As for the other Northeast Pacific Station, the precisions were limited by large blank corrections (up to 60% of the signal). Apart from the sample at 500 m, the Au concentrations are comparable to ones found for the Gulf Stream and the other Northeast Pacific station; the average, 50±17 fmol/l, is the same, within errors, as the averages for these other stations. The sample at 500 m (219±49 fmol/l) has a relatively high Au concentration compared to any other sample from these stations. Because this sample was filtered, the elevated level cannot be attributed to leaching of Au from particles during processing. The salinity of this sample suggests that no leakage occurred during sampling. The lack of a detailed profile makes it extremely difficult to determine the cause of the enrichment or to rule out the possibility of contamination.

Table 3.3: Vertex Station T5

Depth (m)	200	500	1000	2000
Au (fmol/l)	38±36	219±49	42±31	70±46

3.1.3 Mediterranean profiles

Two profiles for Au analysis were taken in early April, 1988 in the Mediterranean during Leg 0 of the R/V Knorr Black Sea Expedition. Station 1 was located at 37'27"N, 2'30"E between the Alboran and Balearic Seas and Station 3 was located at 35'28"N, 17'22" in the Ionian Sea (Fig. 3.4). Samples were collected with 30 liter Niskin bottles equipped with epoxy-coated internal springs and red silicone-rubber o-rings, that had been previously leached in an EDTA solution using the ship's freshwater supply. The Niskins were either hung on a stainless steel hydrowire (Station 1) or mounted on a painted steel rosette frame equipped with a conductivity-temperature-depth probe (CTD) system (Station 3). As soon as the Niskins were on deck and immediately following sampling for gases, 4-liter samples were drawn into 4-liter polyethylene bottles containing 2 ml of 4% KCN solution. The samples were spiked with ^{195}Au within one hour of collection. The unfiltered samples, along with reagent blanks were passed through anion exchange columns at sea and the columns returned to the laboratory for further processing as described in section 2.2.

The results are presented, along with ancillary data, in Tables 3.4 and 3.5 and are plotted in Fig. 3.5. The water budget of the Mediterranean is dominated by surface inflow of North Atlantic water and subsurface outflow of Mediterranean intermediate water into the Atlantic. An excess of evaporation over precipitation and run-off in the Mediterranean basin causes its waters to be more saline (36-39 ppt) than open ocean waters (Hopkins, 1978). The Au profile for Station 1, particularly the upper water column, is quite erratic. While salinity measurements were not available for this station, the oxygen (O_2), nutrients and freons display smooth, regular behavior indicating that the bottles had not pre-tripped or leaked. Since this was the first use of the Niskins after leaching in EDTA (carried out for collection of other trace metal samples) it is possible that the Niskins contributed contaminant Au, however, higher levels of Au were found in the second cast (upper water column) than the first. Alternatively, it is possible that Au was partly derived from particles in these unfiltered samples. Substantial concentrations of Au (20-85 fmol/l) have been reported in suspended particulate matter

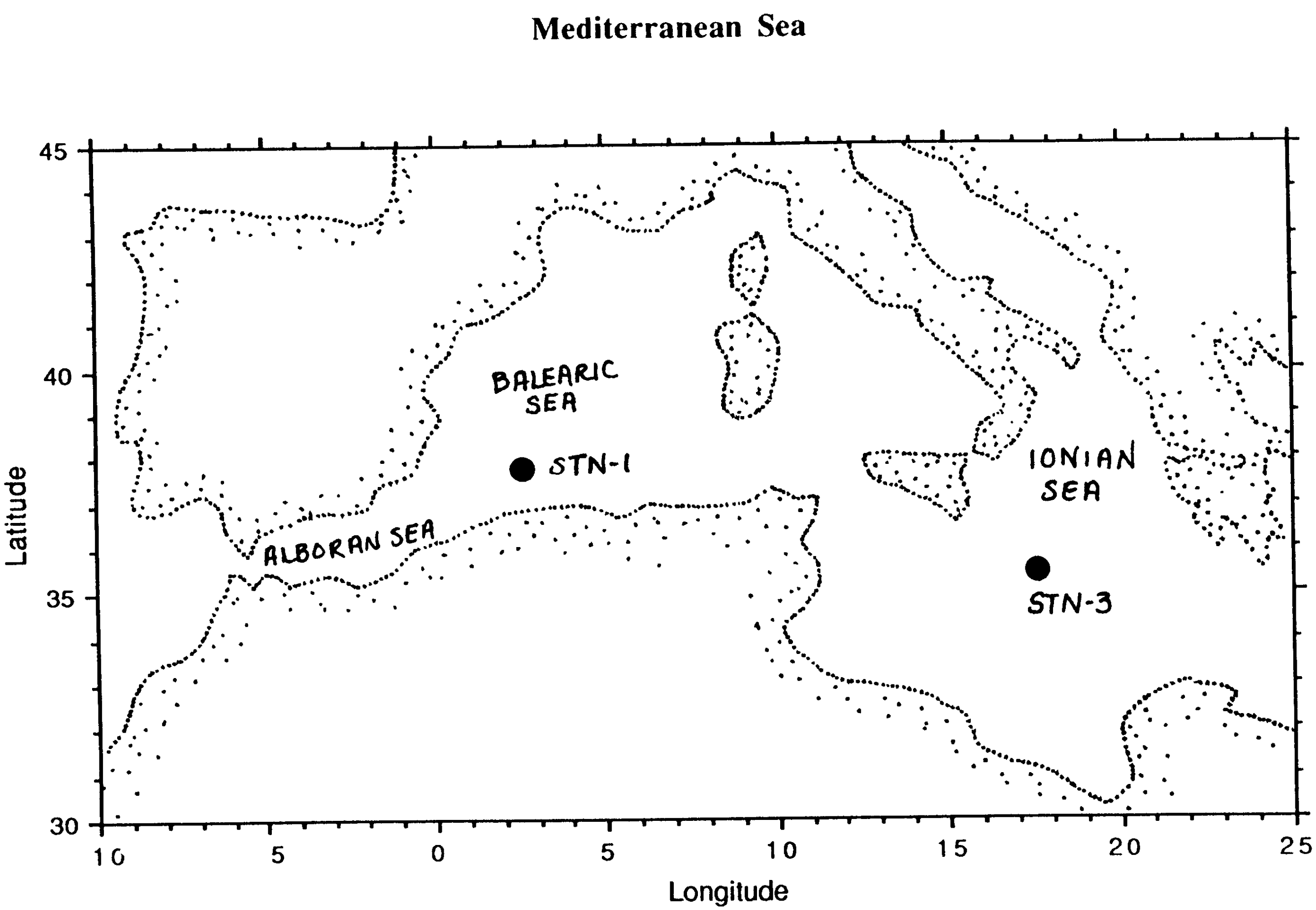


Figure 3.4: Mediterranean station locations. See section 3.1.3 for details.

Mediterranean Data: Station 1 37'27"N, 2'30"W

sample	depth m	Au fM	∂Au fM	sal psu	sigma theta	NO3+NO2 µM	Si µM	PO4 µM
S1C2-9	25	133	16	37.1438	27.5908	0	0.66	NA
S1C2-10	50	66	27	37.4783	27.9986	0.28	0.93	NA
S1C2-11	100	180	20	38.1502	28.7163	3.99	3.25	NA
S1C2-12	150	100	24	38.4296	28.9185	6.31	3.54	NA
S1C2-13	200	240	28	38.3465	28.9848	7	4.26	NA
S1C2-14	300	182	88	38.4597	29.0448	8.1	5.96	NA
S1C2-15	350	318	58	38.4776	29.016	8.2	6.64	NA
S1C2-16	400	117	19	38.4763	29.0665	8.2	7.05	NA
S1C2-17	500	150	29	38.4673	29.0781	8.1	7.65	NA
S1C2-18	600	170	33	38.4483	29.0821	8.04	8.04	NA
S1C2-19	700	85	17	38.4366	29.0829	7.99	8.35	NA
S1C1-1	800			38.4279	29.0842	7.8	8.22	NA
S1C1-2	1000	220	43	38.4199	29.0856	7.63	8.37	NA
S1C1-3	1400	60	21	38.4151	29.0857	7.45	8.5	NA
S1C1-4	1600	315	35	38.4163	29.0866	7.4	8.46	NA
S1C1-5	1800	107	12			7.31	8.26	NA
S1C1-6	2000	111	16			7.24	8.19	NA
S1C1-7	2400	135	15			7.25	8.37	NA
S1C2-8	2800	142	24			7.1	8.28	NA

Table 3.4: Au concentrations are for unfiltered 4-liter seawater samples taken in April 1988; depths are uncorrected; salinities are reported in practical salinity units; ∂Au is the uncertainty associated with Au in fmol/l; the radiotracer correction was 161±22 fmol and the reagent blank was 147±24 fmol for this suite of samples. See section 3.1.3 for details.

Mediterranean Data: Station 3 35'28"N, 17'22"W

sample	depth m	Au fM	∂Au fM	sal psu	sigma theta	NO3+NO2 µM	Si µM	PO4 µM
S3C5-4	30	69	13	38.1655	28.2518	0	0.53	0.03
S3C3-18	90	58	23	38.1706	28.2603	0.003	0.58	
S3C4-3	200			38.5876	28.7517	1.35	1.13	0.04
S3C4-2	275	61	28	38.7541	29.0104	3.01	2.83	0.09
S3C4-1	350		80	38.7789	29.0854	4.44	3.89	0.16
S3C3-17	400	96	23	38.8246	29.1033	4.5	4.42	0.17
S3C2-16	650	109	26	38.7481	29.1352	4.89	6.16	0.21
S3C2-15	1000	111	44	38.6979	29.1469	4.91	8.81	0.21
S3C2-14	1400	93	26	38.6706	29.1515	4.81	8.12	0.2
S3C1-13	2000	133	12	38.6527	29.1561	4.52	7.93	0.2
S3C1-12	2500	136	17	38.6507	29.1585	4.39	7.78	0.18
S3C1-11	3000	142	29	38.6473	29.16	4.25	7.4	0.17
S3C1-10	3400	240	53	38.6446	29.1609	4.18	7.28	0.17
S3C1-9	3770	153	11			4.05	6.81	0.18

Table 3.5: Au concentrations are for unfiltered 4-liter seawater samples taken in April 1988; depths were determined by the CTD; salinities are reported in pratical salinity units; ∂Au is the uncertainty associated with Au in fmol/l; the radiotracer correction was 161±22 fmol and the reagent blank was 147±24 fmol for this suite of samples. See section 3.1.3 for details.

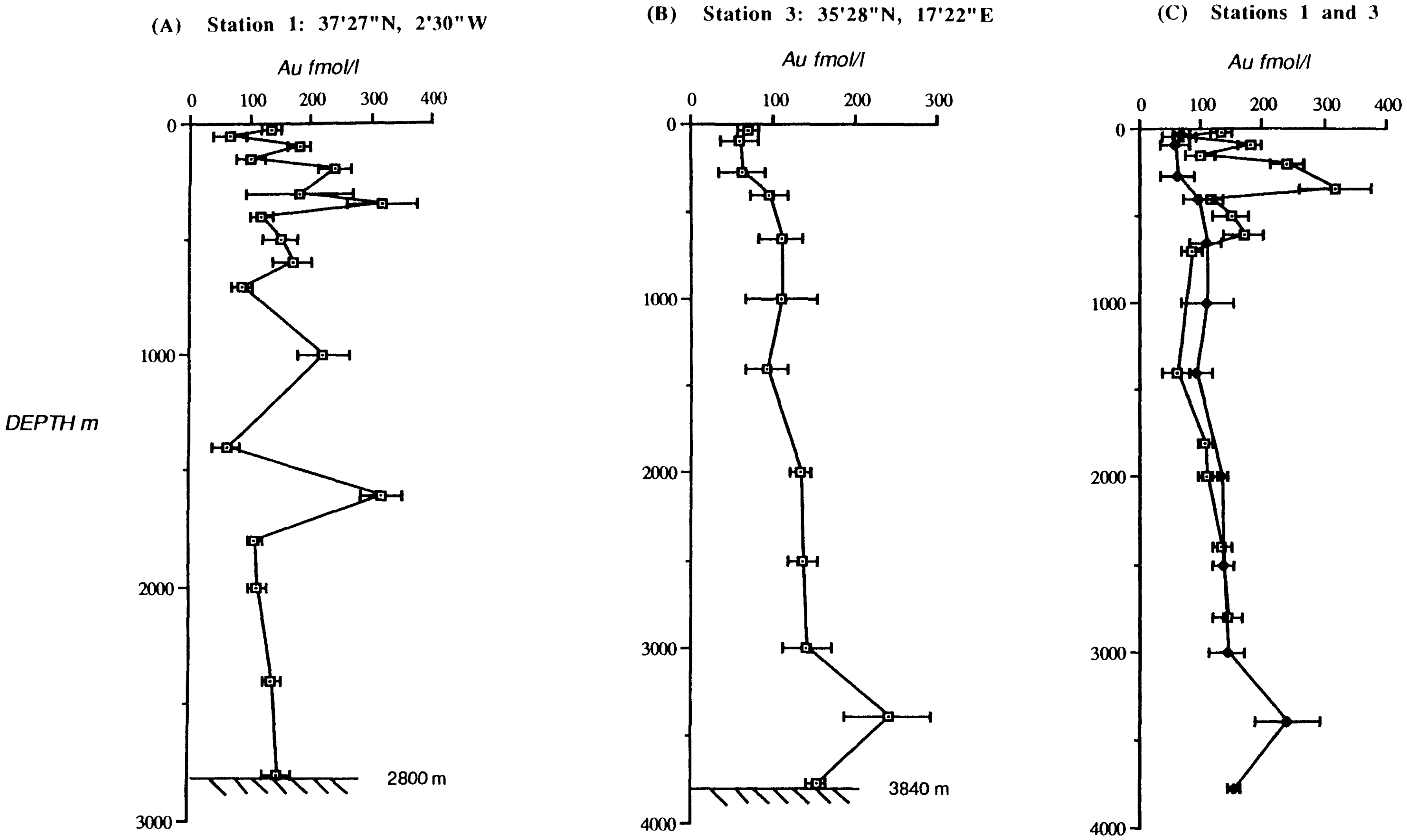


Figure 3.5: Mediterranean Au profiles: (C) is Stations 1 and 3 plotted to the same scale with points from Station 1 deleted as described in section 3.1.3. See Tables 3.4 and 2.5 for data.

throughout the water column at a nearby station in the Mediterranean (36'17"N, 0'06'W) (Risler, 1984). Such levels constitute a significant fraction (5-100%) of the values reported here and if correct, inclusion of particulate Au could have given rise to elevated variable concentrations. The concentration of Au in the suspended matter varied considerably and non-systematically over the water column which may indicate problems with the data, however.

The Au profile from Station 3 (Fig. 3.5b) showed much less erratic behavior within the reported errors. There appears to be a small but significant (2 fold) surface depletion in the mixed layer (≈100 m) with respect to waters deeper than 500 m. Surface values are very similar to the average values found in Atlantic samples at about 50 fmol/l which may be due to surface Mediterranean water having originated in the Atlantic (Hopkins, 1978) or may be coincidental. Below the surface, Au concentrations gradually increase with depth reaching 130 fmol/l at about 3000 m.

A comparison of the upper waters of the two profiles implies either enrichment or contamination of the samples from the surface cast at Station 1 (Fig. 3.5c). When the two samples with high Au content from Station 1 deep waters are disregarded, the concentration levels and depth trends below 500 m are very similar for the two profiles (Fig. 3.5c). On average, these deep water values (100-130 fmol/l) are about twice as high as the Atlantic and Pacific concentrations (≈50 fmol/l). The source of this enrichment is discussed in section 4.1.2.

3.1.4 Black Sea profile

A profile of samples for Au analysis was collected 29-Jun-88 in the Black Sea (43'05"N 34'01"E) during Leg 4 of the R/V Knorr Black Sea Expedition (Fig. 3.6). Samples were obtained from 30 liter Teflon-lined Go-Flo bottles mounted on the same rosette system used in the Mediterranean. Two-liter samples were collected directly into 2-liter Teflon bottles and shipped back to the laboratory. Three months later, the samples were vacuum filtered through 0.4 μm Nuclepore filters (precleaned by soaking in 1% HCl for one day followed by

Black Sea

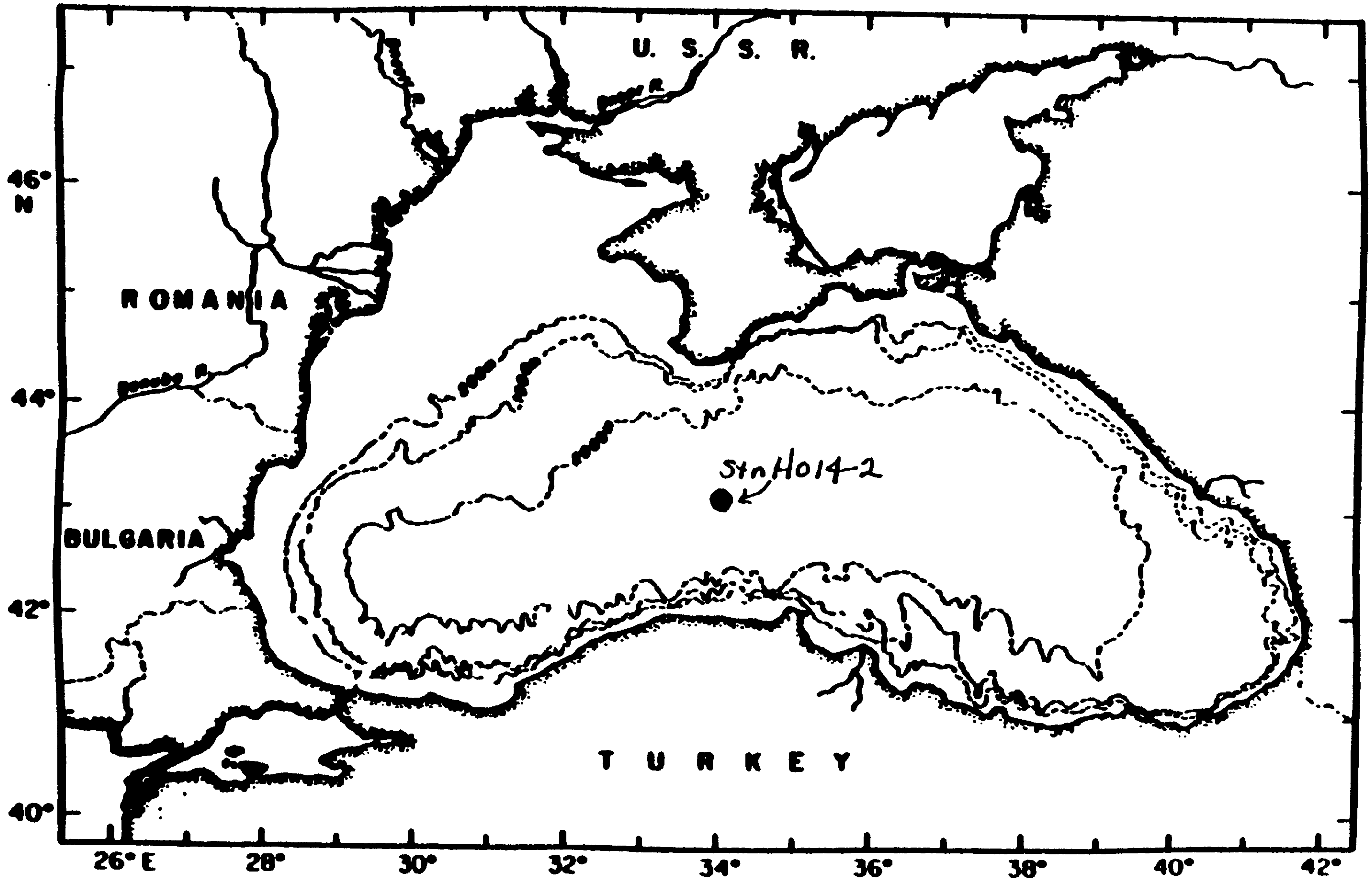


Figure 3.6: Black Sea station location. See section 3.1.4. for details.

soaking in DDW rinses) using a polycarbonate-polypropylene filter holder with a red silicone rubber o-ring (Millipore). The samples were then spiked with ^{195}Au and processed as described in section 2.2.

The results, along with ancillary data and qualitative descriptions of the appearance of the filtered material, are given in Table 3.6 and are plotted in Figure 3.7. The Black Sea derives its surface waters predominantly from a combination of river water and precipitation (Shimkus and Trimonis, 1974). Unlike the Mediterranean, freshwater input exceeds evaporation in the Black Sea Basin and surface waters have very low salinities (18 ppt). At the Strait of Bosporus, these less saline waters flow out at the surface into the Sea of Marmara and a smaller amount of denser, saltier water originating in the Mediterranean (38.5 ppt) flows along the bottom into the deep Black Sea causing it to be more saline (≈22 ppt) (Gunnerson and Ozturgut, 1974). Strong density stratification restricts renewal of the deeper waters and consequently deep Black Sea water is anoxic.

Gold levels are highest in the less saline surface waters (200 fmol/l). Concentrations steadily decrease through the oxic surface waters to below the oxic/anoxic interface, demarcated by the onset of reduced sulfide (Fig. 3.7). Deeper water Au levels were close to the detection limit; within the uncertainties reported, the values are 20±20 fmol/l representing a 10-fold depletion with respect to the surface concentration.

3.1.5 Submarine hydrothermal fluids

Submarine hydrothermal fluids for Au analysis were collected at 21°N on the East Pacific Rise during the R/V Atlantis-DSRV Alvin Guayamas Expedition 112-29 in August, 1985. Sampling was conducted with DSRV Alvin, whose mechanical arm was used to operate piston-driven titanium (Ti) samplers (Von Damm *et al.*, 1985). Two samples, taken at the vent known as Hanging Gardens (Von Damm *et al.*, 1985; Campbell *et al.*, 1988), were drawn from the Ti bottles into 1-liter polyethylene bottles containing 2 ml 57% AR and were shipped back to the laboratory.

Black Sea Data: Station HO14-2 43'05"N, 34'01"W

depth m	temp deg C	sal psu	sigma-t	oxygen ml/l	PO4 µM	SiO2 µM	nitrate µM	nitrite µM	NH4 µM	H2S µM	Au fM	∂ Au fM
10	17.067	18.289	12.721	7.137	0.09	2	0.22	0.02	0.1	0	201	27
30	9.318	18.364	14.086	7.228	0.08	2	0.18	0.01	0.1	0		
60	7.223	19.223	14.996	2.311	0.81	31	6.31	0.02	0.1	0	185	31
90	8.172	20.415	15.825		1.28	63	2.52	0.05	0.2	0		
120	8.503	20.934	16.191		5.27	84	0.2	0.01	5.7	0	110	20
200	8.751	21.512	16.611		4.84	119			19.1	38	75	28
300	8.84	21.799	16.824		5.27	156			33.3	84		
401	8.871	21.951	16.939		5.7	185			43.2	123	29	16
500	8.888	22.045	17.01		6.11	212			52.8	157		
600	8.897	22.126	17.072		6.67	237			63	192		
701	8.908	22.187	17.118		6.99	257			69.8	219		
800	8.923	22.227	17.147		7.25	273			75.6	229	81	47
901	8.94	22.256	17.167		6.9	257			68.7		43	22
1000	8.957	22.276	17.181		7.78	306			85.2	246		
1100	8.974	22.291	17.19		7.82	310			87.5	258		
1201	8.989	22.301	17.196		7.92	317			90.5	269		
1350	9.013	22.31	17.2		7.99	322			92.2	273	67	23
1500	9.034	22.315	17.201		8.03	328			93.2	281		
1600	9.049	22.318	17.202		8.15	329			95.1	289		
1700	9.063	22.32	17.201		8.06	333			95	285	12	19
1800	9.083	22.324	17.202		8.2	339			97.8	302		
1900	9.096	22.323	17.199		8.19	339			98	305		
2050	9.112	22.324	17.198		8.19	338			97.9	308		
2165	9.126	22.323	17.195		8.19	341			97.9	300	36	23

Table 3.6: Data for Black Sea: ∂Au is the uncertainty associated with Au in fmol/l; the radiotracer correction was 177±13 fmol and the reagent blank was 210±25 fmol for this suite of samples. See section 3.1.4 for details.

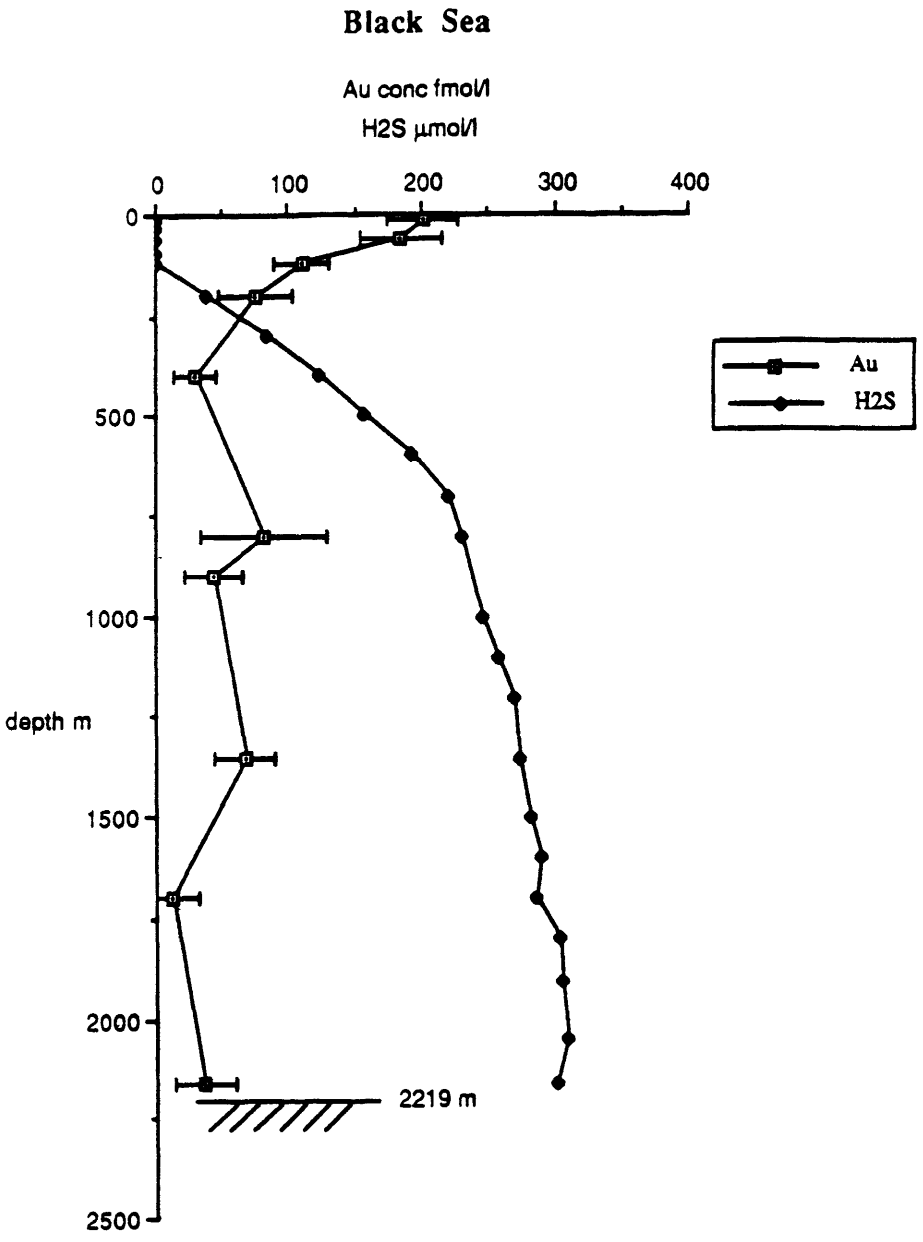


Figure 3.7: Black Sea Au and H_2S profiles at 43'05.15"N, 34'00.59"E, 7-July-88. See Table 3.6 for data and section 3.1.4. for details.

Since these were the first hydrothermal samples analyzed for Au, the procedure differed somewhat from that recommended in section 2.2.7. One month after collection the samples were spiked with ^{195}Au. At the time the samples were spiked, a transparent amorphous Si precipitate, embedded with fine dark sulfide minerals, adhered to the bottoms of the bottles and fine dark sulfide minerals were suspended in solution. The solutions were filtered through 0.4μm Nuclepore filters (precleaned by rinsing in 5% AR followed by soaking in DDW) using a polycarbonate-polypropylene filter holder with a red silicone rubber o-ring (Millipore). The filtered materials along with the filters were transferred back into the original sample containers and 10 ml each of 16N HNO_3 and 28.9N HF and 500 μl of Br_2 were added. Blanks were prepared by placing clean filters in 1-liter polyethylene bottles containing the reagents. After 1 day at room temperature, the bottles were put into a 60°C oven for 4 days to aid digestion of the Si-sulfide precipitates and filter. The solutions were partly evaporated in order to evolve excess Br_2, HF and SiF_4, and then transferred to quartz tubes and UV irradiated for 48 hours to oxidize the remaining filter material. Finally, the solutions were transferred to Teflon beakers, evaporated to a few ml, checked for ^{195}Au recovery and analyzed using standard additions by ZGFAA (section 2.1.5).

One ml of 4% KCN was added to the filtered hydrothermal fluids and upon adjusting the pH≈9 with NH_4OH, an orange colored gel-like iron oxyhydroxy precipitate formed. The samples were refiltered and preconcentrated along with reagent blanks using anion exchange resin (section 2.1.4), checked for ^{195}Au recovery and analyzed using standard additions by ZGFAA (section 2.1.5). The gel was redissolved in a minimal volume of 57% AR and checked for ^{195}Au recovery. The results are shown in Table 3.7.

Table 3.7: Results for Hanging Gardens fluids (332°C)*

dive no.	vol(ml)	% Au-195				total Au fmol/l
		fluid	precip.	gel	total	
1645-5c	263	62	29	0	91±8	250,000±70,000
1644-2c	199	41	64	0	105±5	37,000±8000

*The general chemistry of this vent site can be found in Edmond *et al.*, 1982 and Campbell *et al.*, 1988.

No radioactivity was found in the gel fraction even though the gel formed in the presence of ^{195}Au. This suggests Au was retained in solution, probably by strong complexation with CN^-, so it was assumed that this fraction carried no stable Au. Essentially all ^{195}Au originally added to the samples was recovered in the sum of the fluid plus precipitate fractions (Table 3.7). Since the analytical conditions used forced both ^{195}Au and naturally occurring stable Au in each of these fractions to the same chemical state and all the ^{195}Au was recovered, the Au recoveries of the individual fractions were assumed to be quantitative. Corrections for Au in the blanks were negligible for both fractions. The Au concentrations for the samples were calculated by adding the stable Au contents of the fluid and precipitate fractions. Most of the stable Au (>80%) was associated with the precipitate fractions which was not directly reflected by the ^{195}Au recoveries (Table 3.7). This indicates that isotopic equilibration between the fluid and precipitates was not achieved before the samples were filtered the first time and is not surprising since the ^{195}Au spike was added to the samples after precipitate formation.

The extent of dilution of the vent water by entrainment of seawater during sampling was minimal as indicated by the very low Mg contents of the samples (<2 mmol/l, A. Campbell, pers. comm.). Assuming that the vent water contains no Mg (Edmond *et al.*, 1979) and sea water contains 53 mmol/l Mg and 100 fmol/l Au (section 2.2.2), correction of the Au concentrations in the vent samples for dilution with entrained seawater amounts to <4% which is well within analytical errors of the measured concentrations.

It was not expected that the Au concentrations of these samples should have differed significantly since the same vent was sampled over a few days. Contamination from chimney materials may have contributed to the higher levels in 1645-5c since sizeable pieces of dark solids were observed in the fluids of the companion Ti-sampler whose nozzle was band-clamped to the Ti-sampler this sample came from. Since solid phases around vent areas can be quite enriched in Au (Hannington *et al.*, 1986 &1988), the presence of even minute quantities would pose a considerable risk of contamination. Only 10 micrograms of the most enriched sulphide sample yet measured (16 ppm Au) (Hannington *et al.*, 1988) would need be included to generate the higher concentration here.

Chapter 4

4.1 Discussion

4.1.1 Sampling procedure

In general, it is only since about 1975 that oceanic trace metal data reported in the literature began to be reliable (Bruland, 1983). Earlier work was fraught with contamination problems and only with careful attention toward eliminating contamination during sample collection and handling, did trace metal distributions consistent with known properties of the oceans begin to emerge (Bruland, 1983). The results of Koide *et al.* (1987) and the work presented here appear to extend this generality to the case of Au in seawater.

Reliability of trace metal data for seawater is demonstrated by interlaboratory agreement and oceanographic consistency (Boyle *et al.*, 1977). The latter implies that detailed profiles should be smooth and their features compatible with known chemical and physical processes in the oceans (Boyle *et al.*, 1977). The first of these criteria is met by comparing the levels for Au in seawater recently found by Koide *et al.* (1988) to the ones reported here; the results of the independent determinations of Au concentrations in open ocean Pacific waters agree to within a factor of two (or within reported precision). Most importantly, these recent data are nearly three orders of magnitude less than previously reported values (Jones, 1970).

While the interlaboratory agreement lends confidence to the newly reported levels, the data of Koide *et al.* (1988) are not very precise making it difficult to ascertain trends in their profile. With the possible exception of the Station 1 in the Mediterranean, the profiles presented in this report are smoothly trending and so it would appear that the samples were not randomly contaminated. Possible oceanographic processes leading to the observed Au distributions are discussed in the following section. The compatibility of these Au profiles with known oceanographic properties can only be fully demonstrated when more is known about distributions of Au in seawater.

Relatively smooth profiles tentatively suggest that viable Au samples can be collected by a variety of methods, i.e. Niskins equipped with epoxy-coated inner springs and Teflon-lined Go-Flo bottles either hung on a stainless steel hydrowire or Kevlar line or mounted on a painted-steel rosette frame. Samples must be drawn from the sampling bottles as soon as possible since Au can be lost by adsorption to container walls. In addition, unnecessary exposure of the interior of the sampling bottles and of the samples to the air must be avoided because Au can be highly enriched in atmospheric aerosols (Buat-Menard and Chesselet, 1978; Rahn *et al.*, 1979; Arnold *et al.*, 1982; Arnold, 1985) presenting the potential for contamination. In spite of these precautions, high variability was observed in the profile at Station 3 in the Mediterranean. Since it is possible that the variability was due to Au partially stripped from particulate matter in the samples, for future work, collection of filtered samples is recommended to help permit the assessment of the occurrence of contamination.

4.1.2 Au in the water column

Elements can be broadly classified as either reactive or conservative in the oceanic regime. Conservative elements are noted by the constancy of their dissolved concentrations with respect to the salinity. Examination of this data shows that Au concentrations vary independently of salt concentrations and so, like most trace metals (Bruland, 1983), Au falls into the reactive category. Reactive metals engage in interactions with particulate matter in the oceans and exhibit a wide variety of distributions that are reflective of differences in their input mode, degree of reactivity and removal mechanisms (Bruland, 1983).

Several trace elements (e.g cadmium, selenium, zinc, germanium; Bruland, 1983 and references therein) have been observed to show nutrient-like distributions in the oceans; such elements are depleted in surface waters and enriched at depth implying, by analogy with the nutrients, their uptake in surface waters by biologically generated particles and regeneration with depth as these particles are degraded in the water column. Furthermore, as deep water is transported along the path of its advective flow lines from the North Atlantic to the Antarctic and Indian Oceans and eventually to the North Pacific, the concentrations of nutrients and nutrient-like elements increase as a result of the continual input of particulate matter from the overlying water; the result is higher concentrations in the deep Pacific compared to the deep Atlantic and generally more pronounced vertical gradients in the Pacific than the Atlantic (Broecker and Peng, 1982).

Gold does not appear to exhibit nutrient-like behavior. Within the uncertainties, the Atlantic and Pacific profiles do not show marked increases in concentration with depth. Comparison of the average deep water Atlantic Au values (55±22 fmol/l) with the Pacific values (53±36 fmol/l) would suggest no inter-ocean enrichment although, due to relatively large uncertainties, the possibility of an inter-oceanic fractionation of up to a factor of 2.5 in either direction cannot be ruled out. The profile at Station 3 in the Mediterranean shows a nutrient-like shape but in this sea such a profile can be an artifact of circulation: depleted surface waters, having originated in the Atlantic, overlie enriched deep waters formed by convection in the Eastern and Northern Mediterranean (Miller *et al.*, 1970). In the Black Sea, gold shows negative correlations with the nutrients Si and P (Fig. 4.1) whose vertical distributions are again affected primarily by biological uptake in surface waters and remineralization at depth (Fonselius, 1974). Since the concentration of Au remains low throughout the deep anoxic Black Sea waters, it does not undergo net remineralization along with the nutrients.

That Au would not undergo extensive nutrient-type recycling would not be very surprising given its chemical properties observed in the laboratory, i.e. its strong tendency to adsorb onto containers, its ready reduction in the absence of strong oxidizing agents from dissolved states to the metallic form and its kinetic resistance to resolubilization. Since extensive regeneration does not appear to occur within the water column, the distributions of dissolved Au are primarily affected by the nature of its sources and its rate of removal in the particulate form.

The Au enrichment in Mediterranean deep waters with respect to Deep Atlantic and Pacific waters may be due to proximal riverine or eolian sources. River water constitutes only a small fraction (0.4%) and North Atlantic water constitutes the bulk (≈97%) of the water input

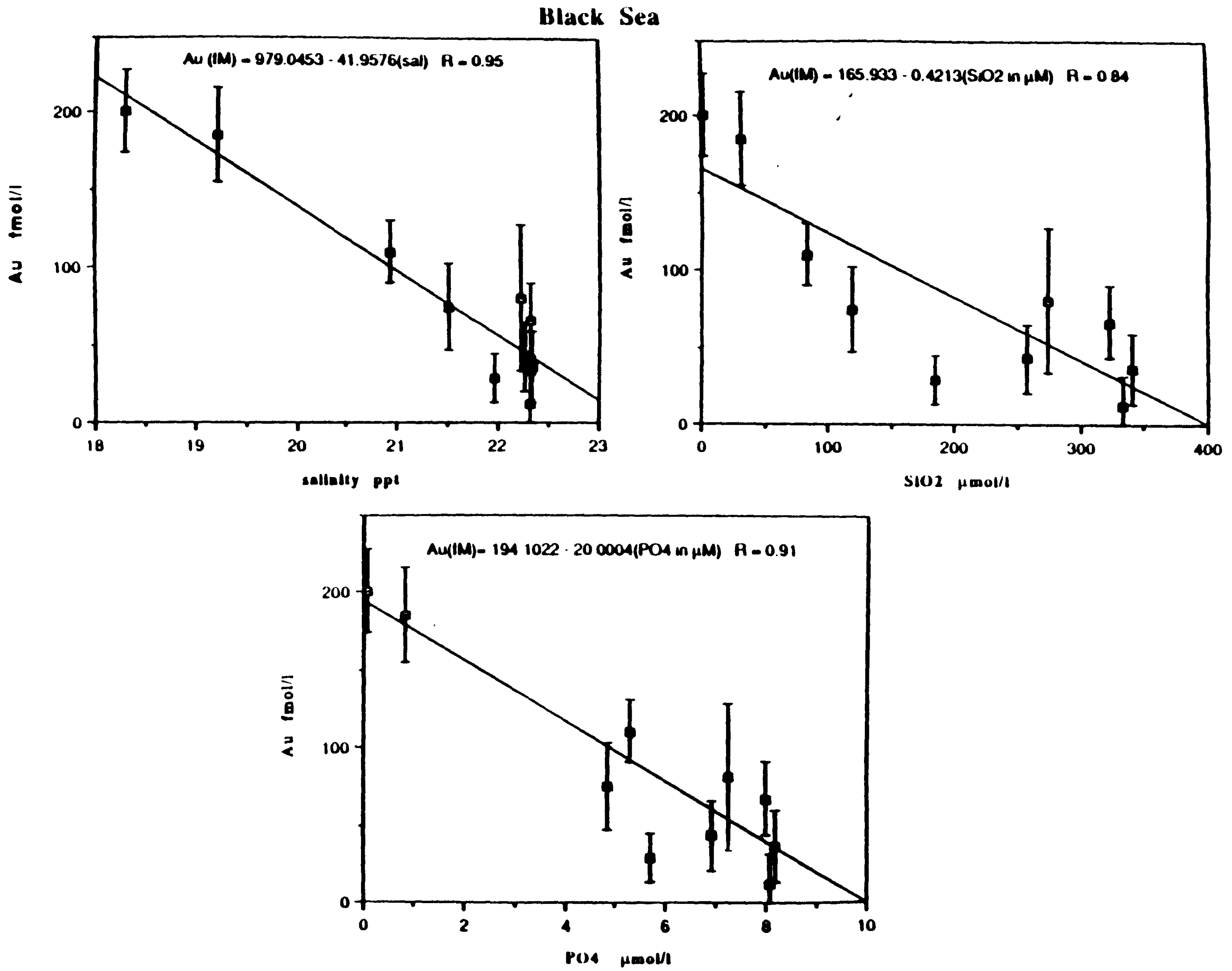


Figure 4.1: Regressions of Au versus salinity, phosphate and silicate for the Black Sea: for station location and data see section 3.1.4.

to the Mediterranean (Sverdrup *et al.*, 1942). Assuming a North Atlantic Au concentration of 55 fmol/l and no losses of Au within the Mediterranean due to scavenging, river water would have to contain 25 pmol/l Au to generate the levels (150 fmol/l) found in the deep Mediterranean. If Au is removed to a large extent in the estuarine environment, even higher river water Au concentrations would be necessary. Because surface water enrichments are not observed at Station 3, any such riverine Au would have to be rapidly removed from the surface and regenerated in the deep waters. No data for Au in river waters of the Mediterranean are available and so it is difficult to assess whether 25 pmol/l is a reasonable river water Au concentration. However, this value is at least a factor of 4 higher than more recently reported values for Au in rivers (McHugh, 1988) and 20 times higher than the estimated riverine input to the Black Sea (see below).

While unusually high Au concentrations would be required in a riverine source, a large amount of Au could readily be derived from dust input. Concentrations of Au associated with aerosols in air of the Mediterranean region show considerable temporal and spatial variability, but it seems that the enrichment factor for Au in the aerosols with respect to crustal materials (using Al for normalization) is consistently high at about 100 (Arnold *et al.*, 1982; Arnold, 1985). The enrichment is probably to due remobilization of soils enriched in Au by volcanic activity in this region (Buat-Menard and Arnold, 1978). Using an annual dust input of $\approx 24\text{x}10^9$ kg to the Mediterranean (Ganor and Mamane, 1982 and Loye-Pilot *et al.*, 1986) and assuming an Al content of 8.23% and Au/Al weight ratio in crustal materials of $4.9\text{x}10^{-8}$ (Taylor, 1964), the amount of Au input by this dust would be the equivalent of 13 fmol/l per year for total dissolution (assuming the volume of the Mediterranean is $3.70\text{x}10^6$ km^3; Sverdrup *et al.*, 1942).

Eolian dust input is thought to be the predominant source of aluminum in the deep Mediterranean (Measures and Edmond, 1988) and interestingly, the ratio of dissolved Au (≈120 fmol/l) to dissolved Al (≈135 nmol/l; Measures, pers. comm., 1989) in central Mediterranean deep water (Station 3), $6.6\text{x}10^{-6}$ gm/gm, is the same as that measured in the aerosols or ≈100 times the crustal ratio of 4.9×10^{-8} gm/gm (Taylor, 1964). Based on laboratory experiments, much of the dissolution of Al occurs within a few hours of the delivery of dust to surface waters (Maring and Duce, 1987). Photo-oxidative reactions during the transport of aerosols could conceivably provide the highly oxidative conditions required to solubilize Au from dusts, so Au may also be quickly solubilized upon contact with seawater. In such case, as for Al (Measures and Edmond, 1988), the enrichment of Au in Mediterranean deep waters is envisioned to result from the convective formation of these waters during times of high winds and consequently high dust input. Alternatively Au may be more slowly mobilized from the aerosol particles by some unknown mechanism as they are carried to deeper water .

To balance the Al lost from the Mediterranean in the outflow at the Straits of Gibraltar, 2-5% dissolution of Al input from dust is required (Measures and Edmond, 1988) which is same amount of dissolution of Al from dusts measured in laboratory experiments (Maring and Duce, 1987). No information is available on the solubility of Au associated with dust. An estimate of the amount of dissolution needed to supply all of the Au in Mediterranean deep water can be made assuming the deep waters integrate dust input over their ≈100 year residence time (Broecker and Gerard, 1969) and the enrichment factor for Au in the dusts is constant with time at the measured value of 100 (Arnold *et al.*, 1982). Under these assumptions, only 10% dissolution of the Au from the dust, or about the same magnitude of dissolution believed to occur for Al, would be required. Since there does not appear to be extensive removal of dissolved Al over the residence time of the deep water within the Mediterranean (Measures and Edmond, 1988), the fact that dissolved Au and Al are present in the same ratio as in the dusts may indicate that Au also is not extensively removed. Further work is required to determine whether the measured measured enrichment factor for Au in aerosols (Arnold *et al.*, 1982; Arnold, 1985)) is representative of the dust input to the Mediterranean over long time period (100's of years) and how much dissolved Au this material contributes. Of course, it may be that elevated Au in rivers or from as yet identified sources fortuitively cause the dissolved Au to Al ratio to be the same as that measured in the aerosols.

The levels of Au in Black Sea surface water were twice as high as those in Mediterranean deep water. In contrast to the Mediterranean, rivers are the largest source of water input to the Black Sea (Shimkis and Trimonis, 1974). A plot of Au versus salinity (Fig. 4.1) suggests that, within the reported errors, the decrease of Au below the surface waters of the Black Sea could be explained by conservative mixing of the enriched surface layer with the depleted deeper waters. Extrapolation of this regression line implies a freshwater end member of about 1 pmol/l Au. If it is assumed that no Au is associated with the input from rain or dry deposition of dust, the calculated river water concentration would be increased to 1.3 pmol/l Au since about 25% of the fresh water input to the Black Sea is from precipitation (Shimkus and Trimonis, 1974). No river water Au concentrations are available for this region, but this concentration appears to be reasonable with respect to recent values obtained in other river systems (McHugh, 1988). If, however, Au is removed to a large extent in estuaries, an eolian source may be significant as in the Mediterranean. The converse assumption, that no Au is derived from rivers, leads to an upper limit of 4 pmol/l for the integrated Au concentration associated with rain.

Assuming steady state, the shape of the profile suggests that removal of dissolved Au is occurring in the deep anoxic zone or in the sediments of the Black Sea. Uncertainties associated with the deep water Au concentrations make it impossible to ascertain whether removal is occurring within the water column. An upper limit for the amount of removal occurring can be calculated by considering the Au contents of the Mediterranean water and fresh water supplying the Black Sea deep water: Mediterranean water input into the Black Sea has a salinity of 38.5 ppt before undergoing dilution by mixing at the Straits of Bosporus (Gunnerson and Ozturgut, 1974). On the basis of the salt balance, this would imply that Black Sea deep water (≈22 ppt) is comprised of 57% Mediterranean seawater and 43% fresh water. Assuming a seawater Au concentration of 100 fmol/l, as measured at 38.5 ppt salinity in the

Mediterranean (Station 3) and an upper limit fresh water concentration of 1000 fmol/l Au (see above), the expected Au concentration for conservative mixing of these endmembers is 490 fmol/l. This exceeds the measured bottom water Au concentrations of ≈20 fmol/l by 470 fmol/l. If loss of Au from the Mediterranean endmember occurs during mixing at the Bosporus or in the sea of Marmara this would overestimate removal.

Removal of Au in the Black Sea may be brought about by reduced solubility of Au under reducing conditions or precipitation onto sulfide mineral surfaces in the water column or by processes occurring in the sediments. Studies in the laboratory indicate reductive adsorption of both Au(I) and Au(III) complexes is catalyzed on sulfide mineral surfaces (Jean and Bancroft, 1985) which might explain the smooth shape of the profile through the redox boundary since sulfide mineral formation tends to occur below the redox interface and into the anoxic zone (Brewer and Spencer, 1974). The smooth shape would also suggest that Au is not affected by Mn/Fe recycling at the redox boundary that has been shown to affect other elements (i.e. phosphorus, Shaffer, 1986; cobalt, Brewer and Spencer, 1974; rare earth elements, German, pers. comm., 1989). More detailed sampling at the redox boundary and examination of deep water particulate matter would be needed to determine the factors governing the removal of Au in the Black Sea.

No measurements are available for the Au contents of the sediments of the Black Sea but the upper limit for the removal of dissolved Au (470 fmol/l per year; see above) can be used to assess the whether a Au enrichment would be expected for these anoxic sediments. Given a mean residence time of 900 years for Black Sea deep water (Ostlund, 1974) and an area of 423,000 km^2 and volume of 534,000 km^3 for the Black Sea (Ross *et al.*, 1974), the upper limit for the removal rate of Au is calculated to be 66 fmol/cm^2 per year. For an average sedimentation rate of ≈10 cm/1000 yr and sediment density of ≈2 gm/cm^3 (Ross and Degens, 1974), the upper limit for the Au concentration in Black Sea sediments due to removal of dissolved Au is ≈0.7 ppb. This is not very different than the average Au content of the crust and deep sea sediments (1.5-4 ppb; see Table 1.1) and since continental detritus constitutes the bulk of Black Sea sediments (Muller and Stoffers, 1974), the sediments are not expected to be markedly enriched in Au over deep sea sediments.

4.1.3 Budget considerations

Given the limited data set to date, the calculations presented below are not intended to imply certain knowledge but rather are presented as a framework with which to guide further investigation of the marine geochemistry of Au.

4.1.3.1 Riverine flux

Recent determinations of Au concentrations for several US stream and river waters, would suggest that such waters carry between 1-20 pmol/l with an average of about 5 pmol/l (McHugh, 1988). Recent data are not available for other world rivers so it is difficult to know how representative these numbers are. In addition, there is no information concerning the behavior of Au in estuaries. Given the reactivity of Au, it is very doubtful that it undergoes net desorption from riverine particles in the estuarine environment such as Ba (Hanor and Chan, 1977; Edmond *et al.*, 1978) and so the contribution of Au to the oceans by rivers is probably not greater than would be predicted from dissolved river water concentrations. If anything its input may be considerably less, due to net removal in the estuary. Until more information is available, a value of 5 pmol/l is used to estimate an upper limit on the input of riverine Au to the oceans. Using this value and an annual world river flow of 4.7×10^{16} liters (Holland, 1978), an input of 2.4×10^{5} mol Au/yr to the world's oceans is calculated.

4.1.3.2 Eolian flux

The annual flux of mineral aerosol deposition to the oceans is estimated to be $532\text{-}851 \times 10^{12}$ gm (Prospero, 1981). Available measurements of Au in aerosols all show enrichment with respect to its abundance in crustal materials (Rahn, 1970; Buat-Menard and Arnold, 1978; Buat-Menard and Chesselet, 1979; Arnold *et al.*, 1982; Arnold, 1985). The reported enrichment factors vary from 10 (Rahn, 1970) to as high as 500 (Buat-Menard and Chesselet, 1979). Calculations for the Mediterranean suggested that 10% dissolution of Au in aerosols was necessary to completely supply the deep water enrichment (section 4.1.2). On the basis of laboratory experiments on the dissolution of Al from marine aerosols (Maring and Duce, 1987), 2% is assumed to be a lower limit of solubility of Au from dusts. Applying the range of estimates for all these parameters, the contribution of Au to the oceans by atmospheric dust could be as small as $4.3\text{x}10^5$ mol Au/yr or as large as $1.7\text{x}10^8$ mol Au/yr.

4.1.3.3. Hydrothermal flux

The input of hydrothermal fluids to the oceans based on ^{3}He and heat flux considerations has been estimated to be $2.3\text{x}10^{14}$ liters of 350°C water per year (Jenkins *et al.*, 1978). Geophysical modeling would suggest that the amount of 350°C water is only ≈10% of this number (Sleep and Wolery, 1978; Morton and Sleep, 1985), however a smaller amount of high temperature water would not affect the conclusions below. If a Au concentration range of 37-250 pmol/l based on the measurements of fluids from Hanging Gardens (21°N, EPR) is assumed, an annual hydrothermal input of $8.5\text{x}10^3$ to $5.8\text{x}10^4$ mol Au is calculated. This estimate is likely to be an upper limit for two reasons: 1) Much of the Au in hydrothermal fluids is probably removed close to the vent sites and is not widely disseminated in the oceans since the deposition of Au from solution has been shown to be catalyzed by sulfide mineral surfaces which form in hydrothermal plumes (Jean and Bancroft, 1985). The fact that this deposition occurs is attested to by the spectacular enrichments associated with sulfides in submarine hydrothermal areas (Hannington *et al.*, 1986; Hannington *et al.*, 1988). 2) The solubility of Au is highly dependent on temperature and the values measured for these samples at 332°C are probably close to the maximum Au concentrations for submarine hydrothermal systems. Modeling of the high temperature thermodynamics of a pyrite-Fe-chlorite-magnetite buffered system suggests that the maximum Au solubility is obtained (for a given Cl^- concentration) at 300°C through complexation of Au(I) by HS^-: Solubility increases rapidly between 250 and 300°C due to increasing HS^- and falls off steeply between 300 and 350°C due to a decrease in the concentration and dissociation constant of H_2S (Cathles, 1986). The solubility of gold Cl^- complexes is insignificant at these high temperatures. In fact, increasing Cl^- decreases the pH which diminishes the dissociation of H_2S causing lowered Au solubility (Cathles, 1986). While hydrothermal Au may not constitute a significant fraction of the oceanic Au budget, its concentration in vent waters may be a very sensitive indicator of the temperature of vent systems. If a sample had been available from the previous visit, Au might have been used to confirm the type of cooling (340 to 332°) that apparently occurred between expeditions for the Hanging Gardens vent site (Campbell *et al.*, 1987).

4.1.3.4 Cosmic flux

Input of Au to the oceans by cosmogenic sources is estimated by considering an upper limit of the flux of such material to be 1.5×10^5 tons/yr based on the accumulation of Ir in deep sea sediments (Crocket *et al.*, 1973). The flux of cosmogenic Au to the earth is calculated to be 110 mole per year which is insignificant with respect to the other sources discussed above.

4.1.3.5 Sedimentary sink

The data for Au in marine sediments are sparse: the few measurements available suggest that the concentration of Au in marine sediments shows very little variation with location and sediment type with values tending to cluster around its crustal abundance of 1.5-4 ppb (Table 1.1). Enhanced accumulations of Au do appear to take place at mid-ocean ridges in association with hydrothermal activity (Table 1.1; Crocket *et al.*, 1973; Hannington *et al.*, 1986 &1988). A meaningful estimate of the output of Au to marine sediments cannot be made at the present time due to a lack of information concerning fluxes of Au in various sedimentary regimes.

4.1.3.6 Residence time

An overall residence time of an element in seawater can be calculated by dividing the total amount of the element dissolved in seawater by the flux of the element into or out of the oceans provided that the residence time is longer than the mixing time of the oceans (≈1000 years; Broecker and Peng, 1982). Residence times that are found to be shorter than the mixing time of the oceans are not a true indication of the time an element resides in the oceans before being removed but can be taken as an indication of the degree of reactivity of that element (Bruland, 1983). Assuming an average seawater Au content of 50 fmol/l and the volume of the world's oceans of 1.37×10^{21} liters (Sverdrup *et al.*, 1942), the total amount of dissolved Au in the oceans is estimated to be 6.9×10^{7} mol.

The total flux of Au into the oceans depends highly upon what value is chosen for the atmospheric input. The upper limit of the range of atmospheric flux (1.7×10^{8} mol Au/yr) given in section 4.2.2.2 generates an unrealistically short 150 day residence time, which indicates that either the enrichment or solubility factors applied for atmospheric dust are unreasonably high for a global estimate. If the low enrichment and solubility factors (section 4.2.2) are used, the atmospheric flux obtained is on the same order as the upper limit riverine flux and the total flux based on these values gives a residence time of about 200 years or less which is significantly shorter than the ≈1000 year mixing time of the oceans (Broecker and Peng, 1982). Using just the upper limit riverine flux, a residence time of 350 years is calculated. With a residence time less than the mixing time of the oceans and predominantly riverine and eolian sources, Au might be expected to be somewhat depleted in deep Pacific waters compared to deep Atlantic waters as is the case for highly reactive Al which has a residence time of 100-200 years and similar sources (Orians and Bruland, 1985; Measures *et al.*, 1986). Due to uncertainties in the Pacific profile, such a depletion for Au cannot be discounted. However, the flux need only be smaller by a factor of about two for the residence time of Au to be increased to on the order of the mixing time of the oceans. In such case, Au concentrations in deep Atlantic and Pacific waters would be predicted to be similar as is suggested by the average of the measured values. If however a significant amount of Au is injected into the deep water by hydrothermal venting along the mid-ocean ridge crests, comparison of deep water values cannot be interpreted as suggested here.

4.2 Summary

The concentrations of dissolved Au in seawater (20-200 fmol/l) are nearly three orders of magnitude less than have previously been reported in the literature. This indicates contamination problems with the earlier data. Gold profiles from the Atlantic Gulf Stream, Northeast Pacific, Mediterranean and Black Sea allow a preliminary assessment of its marine geochemical behavior. Gold is a non-conservative element in seawater. It does not appear to undergo appreciable recycling in the water column under oxic conditions and its removal is probably enhanced under reducing conditions in accordance with its observed behavior in the laboratory. Rivers and atmospheric dust are likely to provide the bulk of the Au to the oceans and may be equally important, although their fluxes are presently ill-constrained. An understanding of the behavior of Au in the estuarine environment and of the enrichment in and solubility from atmospheric dust are needed to better estimate the relative contribution of these sources. While Au is enriched in hydrothermal fluids with respect to ambient seawater, it would seem that most of the hydrothermal Au is not widely disseminated in the oceans, limiting its influence on the oceanic budget of dissolved Au. The overall residence time of Au in the oceans is likely to be less than the mixing time of the oceans or on the order of a few hundred years.

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Appendix A: Operating Parameters: Au-195 on Gamma Counting System*

high voltage: +800V
amplifier: input=positive, time constant=fast, gain=200
analog to digital converter: gain=1024, offset=0, zero=0%; PHA=ADD
SCA: LLD=0%, ULD=110.0%
ROI: ch 9-132

*$1^1/2$" by $1^1/2$" NaI(Tl) Crystal-Harshaw,Type 12S12/E
Attached Preamplifier (Canberra, Model 2007P)
Canberra Series 10 MCA (V1004-D2)

Appendix B: INSTRUMENTAL PARAMETERS: PE 5000 GFAA

Element: Gold Matrix: 1-5% aqua regia w/Ni

Tube Type: pyrolized new style with platform

Sample Aliquot: 25 µl

HGA-400 Keyboard Entries

STEP	1	2	3	4	5	6	7	8
TEMP (°C)	90	150	1000	1200	2800	2800	2800	20
RAMP TIME (s)	10	35	15	1	1	1	1	1
HOLD TIME (s)	30	30	7	2	4	4	4	5
RECORD					0			
READ					0			
BASELINE				2				
FLOW ml/min				10	10			

Notes:

λ = 242.8 nm
slit = 0.7 nm low
energy ≈ 52 at 12 mA
4 sec read
gas = argon
working range for standards in 10 expand scale: 1-100 nM Au
0.52 µmol/ml Ni

Appendix B: INSTRUMENTAL PARAMETERS: PE Zeeman 5000 GFAA

Element: Gold Matrix: 1-5% aqua regia w/Ni

Tube Type: pyrolized new style with platform

Sample Aliquot: 25 µl

HGA-500 Keyboard Entries

STEP	1	2	3	4	5	6	7	8
TEMP (°C)	90	150	1000	1200	2700	2700	2700	20
RAMP TIME (s)	10	35	15	1	1	1	1	1
HOLD TIME (s)	30	30	7	2	4	4	4	5
RECORD				1	0			
READ					1			
BASELINE								
FLOW ml/min				10	10			

Notes:

$\lambda = 242.8$ nm
slit = 0.7 nm low
energy ≈ 52 at 12 mA
4 sec read
gas = argon
working range for standards in 10 expand scale: 1-100 nM Au
0.52 µmol/ml Ni

Appendix C: Operating Parameters for Au in Seawater* by FI-ICPMS**

injection loop: 120 µl
teflon tubing ID: 0.022"
eluent: 10% AR
eluent flow rate: 0.85 ml/min
injection interval: 110 sec
spray chamber temp: 15°C (not optimized)
gas flow rates (liters/min): cool=13.5 neb=0.72 aux=0.32
ICP: forward power=1350W reflected power<10W

scan parameters: mode=internal, mass=197.0, nominal mass range 196-198,
1 sweep, 500,000µs dwell, 2048 channels

*samples preconcentrated as described in section 2.2
**ICPMS system described in section 2.1.6.3

Appendix D: Isotope Exchange Calculations for Adsorption Mechanism Experiment

1. stable gold concentrations in tracer solutions and amount added

    a. original spike (10/86): 84 nmol/l=> 42 pmol added to container
    b. original spike at time specific activity determination (10/87): 54.7 nmol/l (adsorption in spike container occurred but is accounted for in these calculations)
    c. new spike (10/87): 12nmol/l=> 60 pmol added to container

2. stable gold distribution before new spike added:

    a. 45.6% in soln=>19.2 pmol
    b. 54.4% on walls=>22.8 pmol

3. assume amount on walls fixed and the rest remains in solution to find % stable Au in soln.:

$$\% \text{ stable Au in soln} = \frac{60 \text{ pmol} + 19.2 \text{ pmol}}{60 \text{ pmol} + 42 \text{ pmol}} \times (100) = 77.7$$

4. specific activity of spikes determined by 25 µl in 3ml 5% aqua regia in same counting system (10/87):

    a. orig. spike: 148±4 cps/((54.7 nmol/L)x(25 µl)) = 113±3 cps/pmol
    b. new spike: 216±2 cps / ((12 nmol/L)x(25 µl)) = 720±7 cps/pmol

5. total activity in container (10/87):

$$\text{orig.} + \text{new} = (113 \text{ cps/ pmol})(42 \text{ pmol}) + (720 \text{ cps/ pmol})(60 \text{ pmol})$$
$$= 4.79 \times 10^4 \text{ cps}$$

6. predicted activity in solution at isotopic equilibration of 3 ml aliquot (10/87):

    (% stable Au in soln)(total activity)(3 ml/947 ml) = **118±6 cps**

7. measured activity in solution at 10±1 days of 3 ml aliquot (10/87):

    average of decay corrected cps = **111±2 cps**

Biographical Note

The author was born on March 1, 1960 in Lancaster, New Hampshire. She graduated from Concord High School in Concord, New Hampshire in 1978 and then attended Reed College in Portland, Oregon, graduating in 1983 with a B.A. in chemistry and minor in Russian. In the summer of 1981, she participated in the Woods Hole Summer Fellowship Program and conducted research in the laboratory of Dr. Michael Bacon. Following college, she began her graduate studies at the Woods Hole Oceanographic Institution in the W.H.O.I./M.I.T. Joint Program in Oceanography. Accompanied by her husband, James Allan Falkner, she moved to Boston, Massachusetts in 1984 to complete her Ph.D. research at M.I.T. in the laboratory of Dr. John. M. Edmond. The author is a member of Phi Beta Kappa, the American Geophysical Union, the Geochemical Society and the Association for Women in Science.