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MODELING OF DISSOLVED ELEMENTS IN SEA WATER

M.S. Quinby-Hunt
P. Wilde

Marine Sciences Group
Department of Paleontology
University of California
Berkeley, California 94720

ABSTRACT

The distribution of elements dissolved in sea water is reviewed with special emphasis on occurrence in the tropical oceans where potential OTEC (Ocean Thermal Energy Conversion) sites are most likely to be found. The distribution of elements in order of atomic number and by chemical affinity is discussed, examining both geographical and depth variability. This study identifies major interrelationships among the various elements, which can be used for predictive models to estimate concentrations of elements in lieu of expensive and difficult multi-element chemical analyses of water samples in regions of potential OTEC interest. The inputs to the model algorithms are the concentrations of oceanic constituents, such as salinity (chlorinity), nutrients (phosphate, nitrate, silicate), dissolved gases, and carbonate alkalinity, which are easily measured. Elements related to salinity have been designated as "conservative" and include: Li, B, F, Na, Mg, S as SO_4, Cl, K Ca. V, Br, Rb, Sr, Mo, Sb. Cs, and U. Nutrient-related elements include Cr, Ni, Zn, Ge, Se, Cd, I as IO_3, Ba and Hg. Other elements are non-conservative, non-reactive, non-nutrient gases whose concentration is related directly to their solubility. For some elements (such as Pb or Mn) whose chemistry and distribution in sea water is not related to easily measured constituents by simple algorithms, numerical models have not been proposed, although the relationships observed are discussed. Other elements whose chemistry or distribution in the ocean is poorly known are not categorized.

These algorithms have been applied to two potential OTEC sites: Kahe Point and Ke-ahole Point, Hawaii, to model concentrations in the surface, mixed layer and at the proposed depth of the cold water intake. Little variation with depth is

predicted for conservative elements due to the small variation in Salinity with depth. However, nutrient-related elements show a marked increase with depth due to the general increase in nutrient concentrations with depth. Thus, water from the cold water intake will have significantly increased concentrations of Cr, Ni, Zn, Ge, Se. Cd, I. Ba, and possibly Hg (see caveat in text) over that found in water from warm water intakes situated at shallow depths. Of concern for any proposed use of deep water or surface mixed discharge are the trace metals Ni (2x the concentration at the surface), and Zn, Se, Ge, Cd (10x or greater over surface concentrations). Simple 1:1 dilution by surface waters would still yield high concentrations in the discharge. Appropriate discharge strategies should be considered to avoid this problem. Such high concentrations of trace metals may be the cause of inhibition of Primary productivity noted in aquacultural studies of the use of deep ocean water.

INTRODUCTION

The data available describing the chemical composition of the oceans may provide a basis for prediction of composition at any depth or location in the oxic open ocean oceans. Among other uses, this type of information will be of assistance in assessing the impact of pumping deep water in the operation of an Ocean Thermal Energy Conversion (OTEC) plant or certain aquaculture facilities. Typically 5–10 $m^3 sec^{-1}$ per megawatt of electrical capacity of water from about 1000 m depth will be pumped to the surface for OTEC operations.

Although OTEC plants are restricted to tropical regions generally (Chase et al., 1986), the deep water masses are different in each area. Deep water in the American Mediterranean (Caribbean and Gulf of Mexico), for example, is different from deep water of the North Pacific so far as the nutrient elements are concerned. Thus an OTEC plant off the Florida Keys will be

processing deep water lower in phosphate, nitrate and silicate (any any other elements that have distributions similar to these species) than a plant off Hawaii.

The chemical composition throughout the water column must be known at each potential OTEC site. For some constituents, for example the nutrients, procedures for determination have been standardized (Strickland and Parsons, 1972; Grasshoff, 1976). For others. like the trace metals, determination can be an expensive and difficult procedure, requiring sophisticated sampling and analysis procedures and highly skilled personnel (Patterson and Settle. 1976: Bruland et al., 1979).

This report suggests a method for estimating concentrations of trace elements in the oxic open ocean (Quinby-Hunt and Turekian, 1983) and applies it to two sites off Hawaii. The method does not address the problem of estimating the effects of local releases from bottom sediments, or of human activity. It addresses the problems of estimating concentrations when continental sources, upwelling (see. for example. Boyle et al., 1982; Bruland and Franks. 1983) or fluvial inputs are important (Hanor and Chan. 1977; Boyle et al., 1982; 1984).

Method of Approach

The salinity of the open ocean ranges between 33°/$_{oo}$ and 38°/$_{oo}$ (Sverdrup et al., 1942). Dittmar (1884) showed that despite variation in total salt concentration the proportions of the major ions making up most of the salt content (i.e. Na, K, Mg, Ca, Cl, Br, SO_4) were constant within analytical limitations. These ions

were termed conservative; variations in their concentration can be ascribed to the addition or subtraction of pure water to a solution of fixed elemental proportions. Their concentrations relative to total salinity or chlorinity are well-known; from a single salinity measurement they can be calculated. The concentrations of some trace elements also correlate with chlorinity within analytical limits and these too can be classified as behaving conservatively extending the concept beyond that of Dittmar.

Oxidized species of certain elements, the micronutrient or biolimiting elements (phosphorus, nitrogen and silicon), are not conservative: generally, concentrations of these species ace low in surface waters and are significantly higher in underlying deep water (Riley, 1965a; Brandt, 1916–1920; Atkins and Harvey, 1925; Broecker and Peng, 1982). Any other element having a similar vertical distribution could be described as being a nutrient, nutrient-related, or biolimiting (Quinby-Hunt and Turekian, 1983). Analytical limitations prevented demonstration of correlation between the concentrations of trace elements with nutrients until the past decade because of analytical limitations, although the concept had been suggested (Schutz and Turekian. 1965a,b; Goldberg et al., 1971). Once such a relationship was demonstrated for Sr (Brass and Turekian, 1974) and Cd (Knauer and Martin, 1973), similar relationships were reported for many trace constituents. Some elements have been observed to be only partially depleted in the surface waters. Broecker and Peng (1982) refer to these elements as biointermediate.

Some elements show complex distributions that have not been related by simple mathematical equations to easily measured quantities (For additional review articles see Bruland, 1983; Broecker and Peng, 1982). These include the biologically-and chemically-active gases and those involved in the carbonate system; elements whose concentrations are effected by particle scavenging, bottom release terms, or by redox chemistry; and elements whose main source term is anthropogenic releases.

Distributions of gases initially are determined by the solubility of atmospheric gases in surface water: in principle. the surface concentration of each gaseous component could be determined by the temperature of the water in contact with the atmosphere and the measure relative abundance of the gases in the atmosphere (Henry's Law), but corrections must be made for bubble trapping and supersaturation (Kester, 1975). To a first approximation, the concentrations of non-reactive gases can be predicted from Henry's Law (Kester, 1975). Concentrations of biologically-active or chemically reactive gases. such as O_2, N_2, CO_2, N_2O, H_2S, H_2, and CO, can vary with consumption and metabolism, as well as changing redox conditions. Thus. oxygen is produced by photosynthesis and used up during respiration and decay processes. Carbon dioxide participates in the oceanic buffering system; its concentration depends on complex equilibria with that system.

Fluxes of some species from the ocean boundaries modify their distribution patterns, significantly. Aluminum concentrations are particularly sensitive to source terms (Orians and Bruland, 1986).

Mn may be released from sediments due to changing redox conditions in the sediments (Landing and Bruland, 1980); Cu may be released as carrier particles decompose (Boyle et al., 1977). Primitive He is released from the interior at oceanic ridge rise systems (Craig and Lupton, 1981). Mn correlates with He in such areas (Weiss, 1977). Fluvial inputs, coastal upwelling, transport from the continental shelf effect elemental concentrations - sometimes for great distances from land (Hanor and Chan, 1977; Boyle et al., 1982, 1984; Bruland and Franks, 1983).

Removal processes, such as scavenging at various depths in the water column or particle resuspension and precipitation at the sediment-water interface, also influence the distribution patterns of the elements, as has been shown for ^{210}Pb produced from the decay of ^{226}Ra in sediment (Craig et al., 1974; Nozaki et al., 1980).

Redox chemistry can affect distribution patterns. Under oxic conditions, elements such as Mn and Fe are highly insoluble and show complex distributions related to nutrient concentrations, particle scavenging and other factors. Under more reducing conditions, their solubility increases dramatically. Depending on the extent of the reducing conditions, oceanic chemistry varies dramatically.

The presence of elements whose oceanic distribution is due to anthropogenic inputs is clearly seen by the presence of atom bomb-Produced nuclides, such as ^{90}Sr, ^{137}Cs, ^{3}H, % (bomb), and plutonium and lead generated by internal combustion engines. The distribution of these species is controlled by aeolian and coastal sources. and their concentrations generally decrease with depth.

As the composition of sea water at a particular location and depth is a function of all source and removal terms. [Species] = f(geology, biology, physics, chemistry, source), and practically, can be expressed as a sum:

$$[\text{Species}] = \Sigma\, c[C_i] + b[C_i] + a[C_i] + r[C_i] - s[C_i] + \ldots$$

where "c" represents the geological controls demonstrated by conservative elements, "b" biological controls, "a" aeolian source terms, "r" redox chemistry, and "s" scavenging and other removal terms. If "b" or "c" are much greater than the other factors then the concentration of the species will correlate with salinity ("c" predominates), or the nutrients ("b" predominates), or' some intermediate combination (Broecker and Peng's (1982) biointermediate). The distributions of such trace elements can be predicted using regression formulae. Elements whose multiplicative factors representing boundary effects, scavenging components, aeolian or anthropogenic source terms or redox chemistry, and so on dominate the series require more extensive information before calculation is feasible.

The literature reporting elemental distributions in seawater and the correlations they exhibit was reviewed with the idea of using those correlations to predict trace element concentrations at OTEC or aquaculture sites. Table 1 and Figure 1 summarize the best available concentrations of the elements in seawater and the correlations they exhibit. Radionuclides were not considered.

TABLE 1

Atomic Number	Element	Correlation Expression	Concentration	Location	Reference
1	Hydrogen (as H2O)	Biogenic or hydrothermal origin			
2	Helium	Non-Nutrient Gas	Depth (m) Conc (nmol/kg) 2 1.74 209 1.88 511 1.79 917 1.87 1955 1.80	1 Pacific 28o29'N, 121o38'W	Clarke et al. 119101
3	Lithium	Conservative Li/CL = 9.4 x 10E-6	170 ug/kg	N. Atlantic 10o56'N, 49o30'W	Fabricand et al. (1966, 19611
4	Beryllium	Pacific: nutrient-related, Cu-like Atlantic: non-conservative, not nutrient-related	Depth (m) Conc (pg/kg) 40 36 110 36 206 45 336 54 497 63 593 108 691 144 789 144 986 126	1 Pacific 30oN, 158oW	Measures and Edmond (1982); Measures and Edmond (1983); Measures et al. (1984)
5	Boron (inorganic boron)	Conservative B/CL = 2.3 x 10E-4	4.4 mg/kg (profile available)	Gulf of Mexico 25o27'N, 79o56'W	Noakes and Hood (1961)

Atomic Number	Element	Correlation Expression	Concentration		Location	Reference
b	Carbon (carbon dioxide)		Depth (m)	Conc (umol/kg)	S Pacific 14o03'S, 126o16'W	Broecker and Takahashi (1978)
			1	2039		
			83	2045		
			197	2085		
			363	2252		
			114	2264		
			1846	2334		
			1916	2326		
7	Nitrogen (N2 gas)	Non-Nutrient Gas	YO umol/kg		4o22'S, 149o28'W	Craig et al. (1967)
	(as Nitrate)	Nutrient	Pacific: 19o52'N, 163o15'W		Atlantic: 7o56'S, 28o12'W	Pacific: Bainbridge (1979a) Atlantic: Bainbridge (1979b)
			Depth (m)	Conc (umol/kg)	Depth (m) Conc (umol/kg)	
			22	0.0	31 0.0	
			89	0.0	90 0.7	
			170	2.5	170 15.7	
			244	7.2	256 25.1	
			347	14.8	349 28.7	
			444	25.1	459 33.6	
			596	37.1	610 34.1	
			692	40.3	111 34.9	
			891	41.3	909 34.0	
8	Oxygen (as dissolved 021	Biological Dependence	Pacific: 19o52'N, 163o15'W		Atlantic: 7o56'S, 28o12'W	Pacific: Bainbridge (1979a) Atlantic: Bainbridge (1979b)
			Depth (m)	Concentration (umol/kg) mL/L	Depth (m) Concentration (umol/kg) mL/L	
			22	205 (4.7)	32 207 (4.8)	
			89	223 (5.1)	90 210 14.81	
			170	192 144)	170 124 (2.8)	
			244	186 14.31	256 101 (2.3)	
			347	181 1421	149 141 13.21	
			444	139 1321	459 121 12.81	
			596	52 1121	610 126 12.9)	
			692	37 1081	711 141 (3.2)	
			891	41 11.1)	909 160 (3.7)	

(continued)

(Table 1 cont.)

Atomic Number	Element	Correlation Expression	Concentration	Location	Reference
9	Fluorine	Conservative F/CL = 6.7 x 10E-5	1.3 mg/kg	N_Atlantic	Bewers et al. 119731
10	Neon	Non-Nutrient Gas	Depth (m) Conc (nmol/kg) 10 7.0 515 7.6 1086 8.0 1876 8.3	Pacific 9o26'N, 113o16'W	Craig et al. (1967)
11	Sodium	Conservative, Na/CL = 0.5565	10.782 g/kg		Millero and Leung (1976)
12	Magnesium	Conservative Mg/CL = 0.06626	1.284 g/kg	Sargasso Sea 32o16'N, 64o30'W	Carpenter md Manella 119731
13	Aluminum	Non-conservative, depends strongly on source terms and scavenging	Pacific: 28o15'N, 155o07'W Depth (m) Conc (ng/kg) 15 110 50 73 125 33 150 23 200 37 300 34 500 13	Atlantic: about 26oN, 31oW Depth (m) Conc (ng/kg) 23 703 99 756 250 324 352 216 502 243	Pacific: Orians and Bruland (1986) Hydes (1983) - Atlantic

Atomic Number	Element	Correlation Expression	Concentration				Location	Reference
			750	8	756	162		
			1100	2	1002	162		
			1300	12	1260	162		
14	Silicon (silicate)	Nutrient	Pacific: 19o52'N, 163o15'W		Atlantic: 7o56'S, 28o12'W			Pacific: Bainbridge (1979a) Atlantic: Bainbridge (1979b)
			Depth (m)	Conc. (umol/kg)	Depth (m)	Conc. (umol/kg)		
			22	2.0	52	1.2		
			89	2.0	90	1.2		
			170	3.4	170	5.5		
			244	7.0	256	10.9		
			347	17.3	349	17.1		
			444	38.7	459	21.8		
			596	71.0	610	26.3		
			692	87.1	711	29.2		
			891	100.8	909	35.5		
15	Phosphorus (as phosphate)	Nutrient	Pacific: 19o52'N, 163o15'W		Atlantic: 7o56'S, 28o12'W			Pacific: Bainbridge (1979a) Atlantic: Bainbridge (1979b)
			Depth (m)	Conc (umol/kg)	Depth (m)	Conc (umol/kg)		
			22	0.08	32	0.10		
			89	0.08	90	0.10		
			170	0.27	170	1.09		
			244	0.50	256	1.64		
			347	1.00	349	1.90		
			444	1.78	459	2.18		
			596	2.60	610	2.50		
			692	2.80	711	2.30		
			891	2.84	909	2.29		

(continued)

(Table 1 cont.)

Atomic Number	Element	Correlation Expression	Cmrmtrrtion	Location	Reference
16	Sulfur (SO4)	Conservative, SO4/CL = 0.1400	2.112 g/kg	Irish Sea	Morris and Riley (1966)
17	Chlorine	Conservative, Cl/CL = 0.99896	19.35 g/kg		Wilson (1975)
18	Argon	Non-nutrient gas	Depth (m) Conc (umol/kg) 10 10.0 515 13.9 1086 15.6 1876 15.6	Eastern N. Pacific 9o26'N, 113o16'W	Craig et al. (1967)
19	Potassium	Conservative, K/CL = 0.0206	399 mg/kg		Culkin and Cox (1966)
20	Calcium	Correlates with carbonate alkalinity Ca = 366.7 + 21.14 CR 1st Approx.: Conservative Ca/CL = 0.02126	Depth (m) Conc (ug/kg) 30 417.7 99 422.6 298 418.4 498 400.9 649 408.0 800 408.0 900 409.2 1000 410.4 1391 411.5 1709 412.3 2015 412.1	Western S. Pacific between American Samoa and Tonga 15o22'S, 170o05'W	Horibe et al. (1974)
21	Scandium		0.4 - 1.0 ng/kg	N. Atlantic 35o46'N, 67o60'W	Brewer et al. (1972)

Atomic Number	Element	Correlation Expression	Concentration	Location	Reference
22	Titanium		0.9 ng/kg	Puget Sound	Griel and Robinson (1952)
23	Vanadium	Conservative, near surface evidence of scavenging V/CL = 6 x IOE-8	1.2 ug/kg	N. Atlantic	Morris (1975), Zhou et al. (1982), Huizenga and Kester (1982) -Look up
24	Chromium	Wutrient-correlated Cr = 210 + 1.1[Si] = 1.0[Si] - 7.6[P04] + 210 = 1.0[Si] + 0.47[N03] + 230	Depth (m) Conc (ng/kg) 10 268 80 226 150 259 250 230 400 222 600 385 800 202 1000 296	Guatemala Basin	Cranston (19791, Crtnston and Murray (1978)
25	Manganese	Complex, nutrient-related; 02, nitrate, deep water scavenging	Pacific: 18oN, 108oW Depth (m) Conc (ng/kg) 05 137 100 148 150 192 220 214 295 275 590 192 785 82 900 47 1955 34	Atlantic: 34o15'N, 66o17'W Depth (m) Conc (ng/kg) 0 137 100 71 136 66 597 27 1036 39 1441 42	Pacific: Martin and Knauer (1984); Atlantic: Bruland and Franks (1983)

(continued)

(Table 1 cont.)

Atomic Number	Element	Correlation Expression	Concentration		Location		Reference
26	Iron	Tentative correlation uith oxygen and nutrients	W Pacific Depth (m)	Conc (ng/kg)	Atlantic: 34o58'N, 68o03'W Depth (m)	Conc (ng/kg)	Gordon et al. (1982) Atlantic: Symes and Kester (1985)
			0	7.8			
			30	35.1			
			50	40.8	54	95	
			70	100.5	75	100	
			90	145.2			
			150	100.5	174	145	
			295	55.8			
			395	40.0			
			590	42.4	519	95	
			785	40.2	735	128	
			980	44.7	944	223	
			1955	33.5	1043	212	
27	Cobalt	Much l i b Mn, surface anthropogenic input	Depth (m)	Conc (ng/kg)	N. Pacific 36a30'N, 123, 05'W		Knauer et al. (1982)
			0.2	6.8			
			100	5.6			
			200	3.9			
			300	3.8			
			400	3.4			
			520	2.8			
			700	2.0			
			PRO	1.8			

Atomic Number	Element	Correlation Expression	Concentration	Location	Reference
28	Nickel	Nutrient-related both oceans; Atlantic about 80% below that predicted in equation Ni = 161 + 56[PO4] + 1.9(Si)	Pacific: 32°41'N, 145°00'W Depth (m) Conc (ng/kg) 0 146 75 161, 180 185 222, 223 375 320, 298 595 440 780 541, 524 985 566 1505 575 2025 633, 605	Atlantic: 34°15'N, 66°17'W Depth (m) Conc (ng/kg) 0 114, 126 100 114, 126 375 169, 176 597 174, 180 715 260, 255 1036 335 1441 323 2030 339	Pacific: Bruland (1980); Atlantic: Bruland and Franks (1983)
29	Copper	Non-conservative, resembles nutrients, but with release at sediment-water interface scavenging in intermediate and deep water.	Pacific: 32°41'N, 145°00'W Depth (m) Conc (ng/kg) 0 34 75 38, 49 185 61, 55 375 83, 87 595 121 780 126, 121 985 130 1505 133 2025 212, 192	Atlantic: 34°15'N, 66°17'W Depth (m) Conc (ng/kg) 0 77, 70 136 80 375 81 597 73 715 85 1036 98, 95 1441 103 2030 108	Pacific: Bruland (1980); Atlantic; Bruland and Franks (1983)
30	Zinc	Nutrient-related, Atlantic concentrations are about 2x that predicted by equation. Zn = 1.3 + 3.5(Si)	Pacific: 32°41'N, 145°00'W Depth (m) Conc (ng/kg) 0 b, 7 15 7, 12 185 24, 21 375 123, 124 595 325 780 383, 408 985 418 1505 529 2025 542, 528	Atlantic: 34°15'N, 66°17'W Depth (m) Conc (ng/kg) 0 3 100 17 375 20 597 31 715 84 1036 122 1441 130 2030 99	Pacific: Bruland (1980); Atlantic: Bruland and Franks (1983)

(continued)

(Table 1 cont.)

Atomic Number	Element	Correlation Expression	Concentration	Location	Reference
31	Gallium		15-30 ng/kg		Burton et al. (1959) Ishibashi et al. (1961)
52	Germanium	Nutrient-correlation Ge = 5 x 10E-5 (Si)	0.5-0.5 ng/kg (data not qivm in profile)	25o00'N, 179o05'E	Froelich and Andreae (1981)
53	Arsenic (as As(V))	Nutrient-related	1-2 ug/kg (data not given ia profile)	[illegible]htifir 30o46'N, 163o30'W	Andreae (1979), Andreae 119031
34	Selenium (as Se(tot)) Cruise 79 Cruise 88 GEOSECS I	Nutrient-related Se(t) = 27.2 +0.76[Si] +28[PO4] = 42 + 0.54[Si] + 33[PO4] = 42 + 0.58[Si] + 14[PO4]	Depth (m) Conc (ng/kg) 1 27 91 29 235 56 484 54 732 65 1632 80 2091 10	[illegible]_Atlantic 23o06'N, 27o52'W	Cruises 19 and 88: Measures and Burton (1980); GEOSECS I: Measures et al. (1980)
35	Bromine	Conservative, Br/Cl = 0.003413	67 ug/kg		Morris and Riley (1966)
36	Krypton	Non-nutrient gas	Depth (m) tom-(nmol/kg) 10 1.0 48 2.3 99 2.7	[illegible]_Atlantic 5o13'N, 23o30'W	Bieri et al. (1968)

Atomic Number	Element	Correlation Expression	Concentration		Location	Reference
			198	3.0		
			298	3.2		
			486	3.5		
			698	1.6		
			810	5.1		
			1010	3.1		
31	Rubidium	Conservative Rb/Cl = 6.41 x 10E-6	124 ug/kg		N. Pacific 28o29'N, 121o38'W	Spencer et al. (1970)
38	Strontium	Nutrient-correlation Sr/S = 0.2184 + 0.0578[PO4]/S 1st approx.: conservative Sr/Cl = 3.99 x 10E-4	Drpth (m) 10 700 2000	Conc (mg/kg) 1.404 1.720 7.715	N. Pacific 28o29'N, 121o38'W	Brass and Turekian (1974)
39	Yttrium		13 ng/kg		N. Atlantic deep	Nogdahl et al. (1968)
40	Zirconium		0.4-1.4 ug/kg		Indian Ocean 19o45'N, 72o36'E	Sastry et al. (1969)
41	Niobium		<5 ng/kg		N. Atlantic, SW of Plymouth Sound	Carlisle and Hunnerstone (1958)
42	Molybdenum	Conservative Mo/Cl = 5.8 x 10E-7	10 ug/kg		I. Atlantic N. Pacific	Morris (1975) Collier (1985)
43	Technecium					

(continued)

(Table 1 cont.)

Atomic Number	Element	Correlation Expression	Concentration		Location	Reference
44	Ruthenium		Depth (m)	Conc (ng/kg)	Western Gulf of Mexico, 25°03'N, 86°59'W	Dixon et al. (1966)
			10	0.7		
			670	0.6		
			880	0.5		
			1800	0.6		
45	Rhodium	NA				
46	Palladium	Nutrient-related	Depth (m)	Conc (pg/kg)	29°42'N, 118°04'W	Hodge et al. (1985) Lee (1983)
			5	21		
			200	30		
			300	a		
			800	38		
			1200	47		
			1800	53, 40		
47	Silver	Nutrient-related, Cu-like	Depth (m)	Conc (ng/kg)	hcific, off Mexico 18°N, 108°W	Martin et al. (1983);
			0	0.15		
			60	0.04		
			100	0.22		
			150	0.15		
			220	0.11		
			295	0.01		
			490	0.26		
			690	0.60		
			880	1.00		
			980	1.17		
			2440	2.46		

Atomic Number	Element	Correlation Expression	Concentration	Location	Reference
48	Cadmium	Nutrient-correlations in the Atlantic about 15% lower than predicted by equation: Pacific: Cd = 39 [PO4] - 16 r = 0.991 Atlantic: = 29.7[PO4] + 1.0 r = 0.958 Gulf of Mexico: = 30.3[PO4] + 7.9	Pacific: 32o41'N, 145o00'W Depth (m) Conc (ng/kg) 0 0.26 75 0.3 185 19, 18 375 56 595 93 780 110, 117 985 111 1505 113 2025 104, 102 Atlantic: 34o15'N, 66o17'W Depth (m) Conc (ng/kg) 0 0.22 100 0.9 136 1 375 2 597 10 715 19 1036 31 1441 31, 30 2030 31	Pacific: Bruland (1980); Atlantic: Bruland and Franks (1983); Olaffson (1983) Gulf of Mexico: Boyle et al. (1984)
49	Indium	NA	Depth (m) Conc (ng/kg) 2 0.30 500 0.12 1000 0.10 2090 0.11	N_Atlantic off W coast of Africa, 23o00'N, 18o42'W	Matthews and Riley (1970a)
50	Tin (as Sn[tot])	Non-conservative, anthropogenic; bottom release tern	Depth (m) Conc (ng/kg) 0 2.6 800 2.1 1600 0.6 2800 0.0 3600 0.2	Gulf Stream 28o50'N, 78o08'W	Byrd and Andreae (1982)
51	Antimony	Conservative	0.21 ug/kg	N_Atlantic	Brewer et al. (1972)

(continued)

(Table 1 cont.)

Atomic Number	Element	Correlation Expression	Concentration	Location	Reference
		Sb/CL = 1.1 x 10E-8		Sargasso Sea 35o46'N, 68o00'W	
52	Tellurium	?Selenium- or polonium-like Strong evidence of scavenging by particles	Pacific: 07o00'N, 78o40'W Depth (m) Cnnc (ng/kg) Surface 0.22 2500 0.06	Atlantic: 14o59'S, 01o00'E Depth (m) Conc (ng/kg) Surface 0.16 2500 0.07	Lee and Edmond (1985)
53	Iodine, as iodate as I[tot]	Nutrient-correlated IO3 = 0.35 [NO3] + SO = 5.46 [PO4] + 48	Depth (m) Conc (ng/kg) 2 48 126 55 353 55 533 57 729 60 1036 60	Western S. Atlantic 32o31'S, 42o00'W	Wong and Brewer (1974)
54	Xenon	Non-nutrient gas NA	Depth (m) Conc (nmol/kg) 10 0.26 5010 0.52 5329 0.44	Pacific	Mazor et al. (1964)
55	Cesium	Conservative Cs/CL = 1.54 x 10E-8	0.29 ug/kg	NE Pacific	Spencer et al. (1970)
56	Barium	Nutrient-correlated, but dependent upon water mass [Ba] = 0.063[Si] + 4.8	Depth (m) Conc (ug/kg) 13 4.81 55 4.96 154 5.22 304 5.13 430 6.59 566 8.52 776 11.06 997 11.32 1196 14.97	NE Pacific off Hawaii 31o23'N, 150o2'W	Chan et al. (1976, 19771

Atomic Number	Element	Correlation Expression	Concentration	Location	Reference
57	Lanthanum	Nutrient-related, particle and possibly boundary scavenging	Pacific: 18oN, 108oW Depth (m) Conc (ng/kg) 15 2.64 100 4.44 150 6.53 200 2.36 500 2.70 750 4.72 1000 4.86 1250 4.50	Atlantic: 28o01'N, 25o59'W Depth (m) Conc (ng/kg) 0 5.10 100 1.80 200 2.36 600 3.12 700 3.50 900 2.89 1500 3.17	Elderfield and Greaves (1982) DeBaar et al. 119851
58	Cerium	Redox controlled	Pacific: LBo~-108oW Depth (m) Conc (ng/kg) 15 1.54 100 1.40 150 3.50 200 2.58 500 1.02 750 1.18 1000 1.04 1250 0,59	Atlantic: 28o01'N, 25o59'W Orpth (m) Conc (ng/kg) 0 9.29 100 235 200 3.12 600 2.58 700 3.46 900 1.35 1000 2.91 1500 1.36	Elderfield and Greaves (1982) DeBaar et al. (1985)
59	Praeseodymium	Mutirent-related, particle and possibly boundary scavenging	Depth (m) Conc (ng/kg) IS 0.45 100 0.46 150 0.61 200 0.35 500 0.44 750 0.59 1000 1.07 1250 0.01	Pacific: 18oN, 108oW	DeBaar et al. (1985)

(continued)

(Table 1 cont.)

Atomic Number	Element	Correlation Expression	Concentration				Location		Reference
60	Neodymium	Nutrient-related, particle and possibly boundary scavenging	Pacific: 18oN, 108oW				Atlantic: 28o01'N, 25o59'W		Elderfield and Greaves (1982) DeBaar et al. (1985)
			Depth (m)	Conc (ng/kg)			Depth (m)	Conc (ng/kg)	
			15	1.88			0	4.95	
			100	2.16			100	1.85	
			150	3.46			200	2.28	
			200	1.88			600	2.84	
			500	2.16			700	3.16	
			750	2.45			900	3.04	
			1000	4.90			1000	3.29	
			1250	3.61			15M	2.74	
61	Promethium	NA							
62	Samarium	Nutrient-related, particle and possibly boundary scavenging	Pacific: 18oN, 108oW				Atlantic: 28o01'N, 25o59'W		Elderfield and Greaves (1982) DeBaar et al. (1985)
			Depth (m)	Cant (ng/kg)			Depth (m)	Conc (ng/kg)	
			15	0.41			0	0.90	
			100	0.39			100	0.40	
			150	6.60			200	0.68	

Atomic Number	Element	Correlation Expression	Concentration		Location		Reference
			200	0.39	600	0.58	
			500	0.38	700	0.64	
			150	0.47	900	0.65	
			1000	0.96	1000	0.68	
			1250	0.68	1500	0.56	
63	Europium	Nutrient-related, particle and possibly boundary scavenging	Pacific: 18oN, 108oW		Atlantic: 28o01'N, 25o59'W		Elderfield and Greaves (1982) DeBaar et al. (1985)
			Depth (m)	Conc (ng/kg)	Depth (m)	Conc (ng/kg)	
			15	0.11	0	0.093	
			100	0.12	100	0.091	
			150	0.19	200	0.129	
			200	0.11	600	0.120	
			500	0.11	700	0.115	
			750	0.12	900	0.125	
			1000	0.24	1000	0.153	
			1250	6.19	1500	0.145	
64	Gadolinium	Nutrient-related, particle and possibly boundary scavenging	Pacific: 18oN, 108oW		Atlantic: 28o01'N, 25o59'W		Elderfield and Greaves (1982) DeBaar et al. (1985)
			Depth (m)	Conc (ng/kg)	Depth (m)	Conc (ng/kg)	
			15	0.63	0	0.819	
			100	0.63	100	0.536	
			150	0.99			
			200	0.58	600	0.762	
			500	0.66	700	0.822	
			750	0.64	900	0.818	
			1000	1.35			
			1250	1.12	1500	0.855	

(continued)

(Table 1 cont.)

Atomic Number	Element	Correlation Expression	Concentration		Location	Reference
65	Terbium	Nutrient-related, particle and possibly boundary scavenging	kpth (m)	Conc (ng/kg)	Pacific: 18oN, 108oW	DeBaar et al. (1985)
			15	0.09		
			100	0.09		
			150	0.14		
			200	0.09		
			500	0.09		
			750	0.11		
			1000	0.12		
			1250	0.18		
66	Dysprosium	Nutrient-rrlated, particle and possibly boundary scavenging	kplh (m)	Conc (ng/kg)	Atlantic: 28o01'N, 25o59'W	Eldcrficll and Greaves (1982) DeBaar et al. (1985)
			0	0.81		
			100	0.78		
			200	0.86		
			600	0.88		
			700	0.88		
			900	0.91		
			1000	0.98		
			1500	098		
67	Holeium	Nutrient-related, particle and possibly boundary scavenging	Depth (m)	Conc (ng/kg)	Pacific: ~BoW, 108oW	Debar et dl. 119851
			15	0.16		
			100	0.12		
			150	0.25		
			200	0.18		
			500	0.25		
			750	0.23		
			1000	0.58		
			1250	0.39		

Atomic Number	Element	Correlation Expression	Concentration	Location	Reference
68	Erbium	Nutrient-related, particle and possibly boundary scavenging	Depth (m) Conc (ng/kg) 0 0.61 100 0.68 200 0.77 600 0.77 700 0.77 900 0.83 1500 0.89	28o01'N, 25o59'W	Elderfield and Greaves (1982)
69	Thulium	Nutrient-related, particle and possibly boundary scavenging	Depth (m) Conc (ng/kg) 15 0.06 100 0.09 150 0.15 200 0.10 500 0.11 750 0.13 1000 0.31 1250 0.25	Pacific: 18oN, 108oW	DeBaar et al. (1985)
10	Vttrrbium	Nutrient-related, particle and possibly boundary scavenging	Pacific: ~DoH, 108oW Depth (m) Conc (ng/kg) 15 0.38 100 0.48 150 5.75 200 0.61 500 0.69 750 0.95 1000 2.28 Atlantic: 28o01'N, 25o59'W Depth (m) Conc (ng/kg) 0 0.545 100 0.614 200 0.704 600 0.716 100 0.104 900 0.806		Elderfield and Greaves (1982) DeBaar et al. (1985)

(continued)

(Table 1 cont.)

Atomic Number	Element	Correlation Expression	Concentration	Location	Reference
			1250 1.57 1500 0.863		
71	Lutetium	Nutrient-related, particle and possibly boundary scavenging	Depth (m) Conc (ng/kg) 15 6.06 100 0.08 150 0.17 200 0.10 500 0.12 750 0.17 1000 0.13 1250 0.29	Pacific 18oN, 108oW	De8aar el al. 119851
72	Hafnium	NA	<8 ng/kg	Various	Schutz and Turekian (1965a)
73	Tantalum	NA	<2.5 ng/kg	Variour	Schutz md Turekian (1965a)
74	Tungsten	NA	0.1 ug/kg	Japanese coastal Irish Sea, surface	Ishibashi 119531; Chan and Riley (1967)
75	Rhenium	HA	Depth (m) Conc (ng/kg) 0 5.6 900 4.3 1500 4.2	N. Atlantic 62o58'N, 19o51'W	Olafsson and Riley (1972)
76	Osmium	NA	NA		
77	Iridium	RA	10 pg/kg	Coastal Pacific	fresco el dl. (1985)

Atomic Number	Element	Correlation Expression	Concentration	Location	Reference
78	Platinum	Nutrient-like profile	Depth (m) Conc (pg/kg) Surface 106 10 105 50 130 300 170 700 160 800 170 1000 70 1200 150 2000 370	29°42'N, 118°04'W	Hodge et al. (1985)
79	Gold	NA	4-26 ng/kg	Atlantic	Schutz and Turekian (1965a)
80	Mercury	Nutrient-correlated (but with caveats) Hg = 2.28 + 0.22 (Si)	Depth (m) Conc (ng/kg) 250 3 500 4 1000 4 1900 4.5	N. Atlantic 39°10'N, 65°30'W	Mukherji and Kester (1979)
81	Thallium	?Conservative	Depth (m) Conc (ng/kg) 0 12.4 400 16.4 1000 13.6 2070 12.1 3470 12.1	34°15'N, 66°17'W	Flegal and Patterson (1985)

(continued)

(Table 1 cont.)

Atomic Number	Element	Correlation Expression	Concentration	Location	Reference
82	Lead	Non-conservative, anthroPacific: 32o41'N, 145o00'W Depth (m) Conc (ng/kg) 0.2 13.6 15 12.2 200 13.1 400 14.0 600 0.9 860 5.1 1000 45 2000 20	Atlantic: 34o15'N, 66o17'W Depth (m) Conc (ng/kg) 0.2 53.2 35 51.1 150 33.2 400 35.2 600 51.1 750 26.9 1000 16.0 2010 8.9	Pacific: Schaule and Patterson (1981) Atlantic: Schaule and Patterson 119831
83	Bismuth	Non-conservative, aeolian source possible correlation with Lead; Atlantic higher thatn Pacific Depth In) Conc (pg/kg) 25 36 60 35 75 33 100 34 200 55 400 73 600 105 750 79 900 64 1100 56 2000 28	VERTEX IV, N. of Hawaii	Let et al. (1985/6) Lee (1982)
92	Uranium	Conservative U = 1.7 x 10E-7	3.2 ug/kg	7o25'N, 20o35'W	Ku et al. (1977)

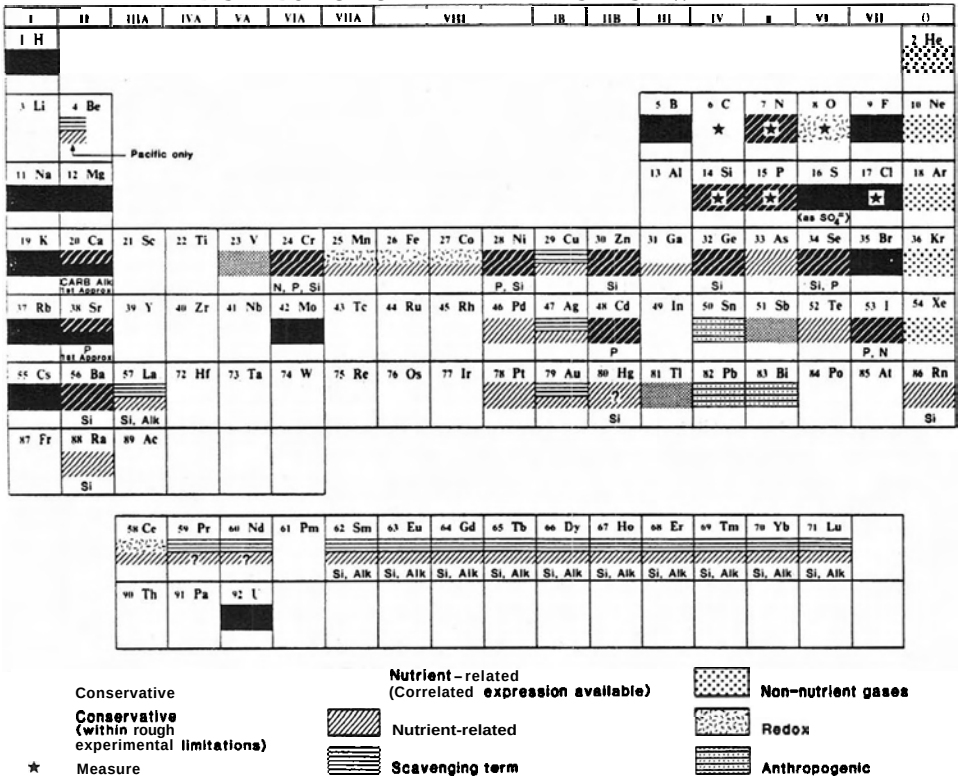

Fig. 1. Concentrations and correlations of the elements in seawater.

Although data have been published in a number of units, elemental data (for other than nutrients and gases are expressed in g/kg and multiples thereof. The nutrients and gases are given in μm/kg (for dissolved O_2, the commonly used mL/L is in parentheses). We will generally refer to total elemental concentration. If several species were addressed, they are identified. For conservative elements, the average concentration in seawater, normalized to

35‰ and the relation to chlorinity (CL) is reported. For elements correlated to the nutrients, a profile, the correlation, correlation expression and coefficients are given as available. The correlation expressions are presented so that the resultant elemental concentration in "x"g/kg corresponds to the observed concentrations in seawater. To convert to approximate kg^{-1} from L^{-1}, we have divided by 1.025 as suggested by Bainbridge (1979a,b,c).

CONCENTRATIONS AND CORRELATIONS OF THE ELEMENTS IN SEAWATER

The discussion of the elemental abundance patterns in the oceans follows the periodic table. The Main Croup Elements are discussed first, by group and then the Transition Elements, Lanthanides and Actinides are discussed by row.

Group IA: The Alkali Metals, Lithium, Sodium, Potassium, Rubidium and Cesium

Evidence indicates that all the alkali metals are conservative to the precision of current analytical methods (Wilson. 1975) and their concentrations can be predicted everywhere in the open ocean from salinity (chlorinity, CL).

Li concentrations are about 180 µg/kg in seawater normalized to 35‰ salinity and is conservative (Table 1; Fabricand et al., 1966, 1967; Chow and Goldberg, 1962; Riley and Tongudai, 1964). Although there is some evidence of spatial variability in the tropical oceans (Riley and Tongudai, 1967; Angino and Billings, 1966; Fabricand et al., 1967), the differences were not statistically significant.

Sodium and potassium are major constituents of sea water, historically, thought to be conservative (Dittmar, 1884; Forchhammer, 1865; Cox, 1965; Culkin, 1965), a finding still supported (Culkin and Cox, 1966; Mangelsdorf and Wilson, 1972; Millero and Leung, 1976). No significant variation with depth has been reported for the cation to chlorinity ratios (Table 1). Concentrations of these elements can be predicted reliably from salinity measurements. The concentrations reported in the few papers available with data from tropical sites (Fabricand et al., 1966; Barker and Zeitlin, 1972; Froelich et al., 1978) are in agreement with the above findings.

Seawater contains about 124 µg/kg rubidium (at 35‰ salinity). It is conservative and its concentration may be calculated using the expression appearing in Table 1 (derived from Spencer et al., 1970). Most researchers (Bolter et al., 1.964; Spencer et al., 1970; Brewer et al., 1972) have reported cesium concentrations of 0.3 µg/kg at 35 ‰ salinity and no significant variation with depth. About 1 % variation between surface samples taken at sites in the North Pacific Ocean and for subsurface samples has been reported (Folsom, 1974). Even if this variation is real, to a first approximation Cs can be considered conservative (Table 1).

The Group IIA Elements: the Alkaline Earths - Beryllium, Magnesium, Calcium, Strontium. Barium, and Radium

The distribution of beryllium in the Pacific resembles copper, that is, it shows nutrient-like behavior except that high values

are found near the sediment–water interface and near ridge–rise systems (Measures and Edmond, 1982, 1983). There is some scavenging in intermediate and deep water. The distribution of Be in the Atlantic near the equator is not like any of the nutrients or trace elements. In the Atlantic, its concentration is enriched relative to the Pacific (Measures et al., 1984).

Magnesium, a major constituent, is conservative within analytical limitations (Dittmar, 1884; Forchhammer, 1865; Cox, 1965; Culkin, 1965; Culkin and Cox, 1966; Carpenter and Manella, 1973). Data for the tropical oceans is similar (Atwood et al., 1973; Barker and Zeitlin, 1972; Billings and Harris, 1965; Carpenter. 1972; Sen Gupta et al., 1978).

Calcium carbonate is removed from surface water by the biological deposition of calcareous tests. Accordingly, since Dittmar (1884), researchers have predicted that calcium should not behave conservatively (Culkin and Cox, 1966; Riley and Tongudai, 1967; Mangelsdorf and Wilson, 1972). To a first approximation, calcium concentrations can be predicted using the conservancy relation reported in Table 1. In 1974, (and later Shiller and Gieskes, 1980) 'variation of calcium concentration with depth was observed (Horibe et al., 1974: Shiller and Cieskes. 1980): about 1% variation over 5000 m (Table 1) and a direct correlation of calcium concentration with carbonate alkalinity.

Strontium exhibits a correlation ($r = 0.88$) with phosphate (Figure 2) (Brass and Turekian, 1974). Using their data and that of Bainbridge (1979b) for PO, and salinity at the same station, the

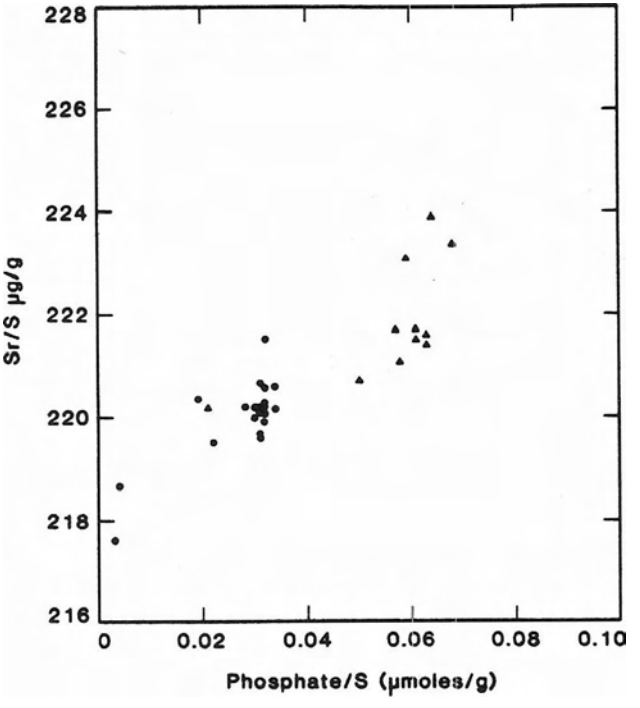

Fig. 2. Strontium concentration vs phosphate concentration (data from Brass and Turekian, 1974). o represents data from Station 3 at 51°01'N, 43°07'W. x represents data from Station 68 at 48°39'S, 45°09'W.

correlation expression in Table 1 may be derived. The variation of [Sr] with depth deviates by less than 0.3% over 4000 m from that predicted by Sr/Cl = 3.99 x 10^{-4} (based on data in Brass and Turekian, 1974).

Several profiles of barium have been reported (Wolgemuth, 1970; Bacon and Edmond. 1972; Bender et al., 1972; Bernat et al., 1972). The extensive and reliable data of Chan et al. (1976, 1977) shows a nutrient-like distribution (Figure 3). They report a

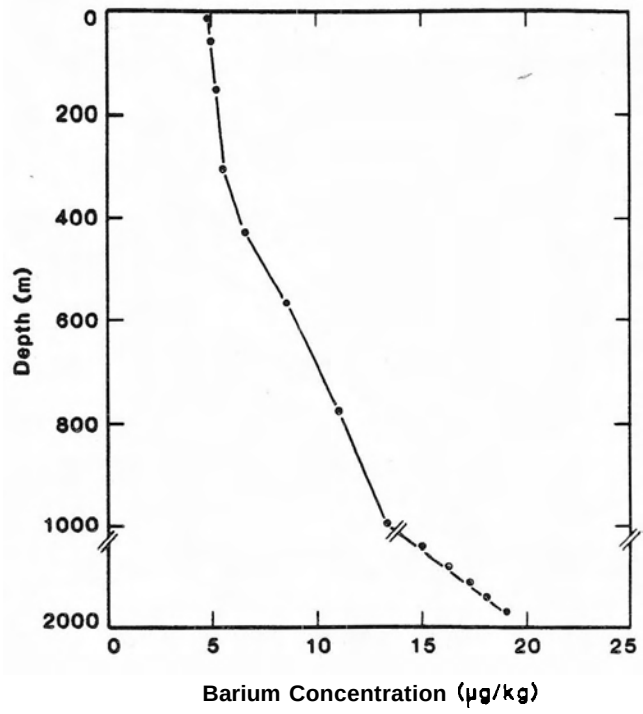

Fig. 3. Barium concentration in seawater vs depth (data from Chan et al., 1976, Station 204, 31°23'N, 150°02'W.

linear relationship between barium and silicate, however the ratio varies with water mass (Figure 4). Using the [Ba] reported by Chan (Chan et al., 1976) and the [Si] of Bainbridge (1979a) for GEOSECS station 204, a correlation expression may be derived (Table 1).

Although radium exists in a number of isotopes, only ^{226}Ra will be considered. Radium-226 has been determined in seawater by a number of researchers (Broecker et al., 1970; Ku et al., 1970;

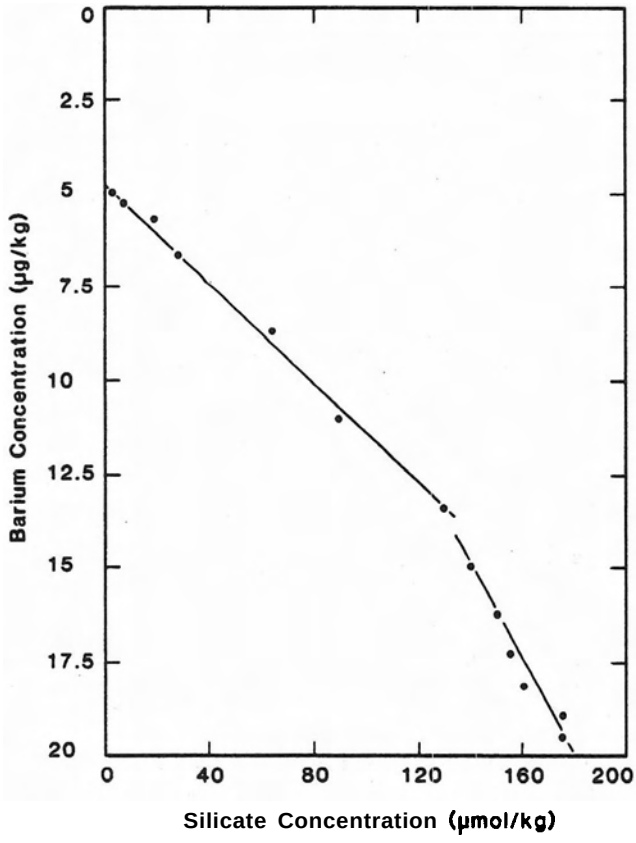

Fig. 4. Barium concentration vs silicate concentration (data from GEOSECS Station 204, 31°23'N, 150°02'W). Ba data: Chan et al. (1976); Si data: Bainbridge (1979a). Chan et al. demonstrated that the ratio of [Ba]/[Si] varies with water mass.

Chung and Craig. 1973; Bruland et al., 1974; Chung, 1974. 1976. 1980; Chan et al., 1976; Bacon et al., 1976; Broecker et al., 1976; Ku and Lin, 1976; Knauss et al., 1978). Broecker et al. (1976) report a profile 9.1 dpm/100kg at 149 m increasing to 15.0 dpm/100kg at 4170 m at a station in the western tropical North

Atlantic. Chan et al., (1976) using data from the same site (and others in the North Atlantic) report a linear correlation between radium and barium concentrations and, therefore, also to silicate, confirming an earlier report of Li et al. (1973). However, they further report that at some station, notably one in the North Pacific. northwest of Hawaii, that the relationship does not hold at great depths.

The Group IIIA Elements - Boron, Aluminum, Gallium, Indium and Thallium

Boron is conservative and its concentration in seawater as approximately 4.4 mg/kg at salinity °/₀₀ (Table 1: Culkin, 1965; Cast and Thompson, 1958; Noakes and Hood, 1961; Williams and Strack (1966); Gassaway, 1967).

The oceanic distribution of aluminum is complex and data has been seemingly contradictory (Measures et al., 1986). Sackett and Arrhenius (1962) reported seawater has an [Al] of about 1 µg/kg. Moore (1981) reported no correlation of aluminum with nutrients in the Arctic. Hydes (1979) reported open ocean profiles of dissolved aluminum with concentrations ranging from 1.0 µg/kg at the surface, a minimum of 0.5 µg/kg at about 1000 m, increasing with depth to about 0.9 µg/kg. He suggested a negative correlation with silica, but did not resent a regression formula or correlation constant. In the Atlantic, Hydes (1983) reported that Al is non-conservative, with a surface maximum (0.9 µg/kg), minimum in intermediate waters (0.2 µg/kg), increasing toward the sediment-water interface or the continent. In the Mediterranean is

considerably higher than in the Atlantic and correlates with silicate at least in the upper 1500 m (Mackenzie et al., 1978; Stoffyn and Mackenzie. 1982; Caschetto and Wollast, 1979) perhaps due to uptake by siliceous organisms. The results from the Mediterranean may not be applicable to the open ocean (Hydes, 1983).

Recently, the oceanic distribution of Al has been described in terms of external, aeolian and fluvial source terms and extensive scavenging by particles (Orians and Bruland, 1986; Measures et al., 1986). Concentrations can vary from 1 µg/kg to 13 pg/kg depending season and location. The deep Pacific contains 50 times less Al than does the deep Atlantic. It appears unlikely that any simple correlations will be derived that permit calculation of aluminum concentrations from simply measured oceanic constituents.

Al data from the Tongue of the Ocean in the Bahamas, are in general agreement with Hydes, although with considerably greater scatter (Alberts et al., 1976). As aluminum concentrations ars potentially important is OTEC operations, this element and its relation to biological activity should be examined further in conjunction with measurements at potential OTEC sites.

Gallium has been determined in seawater (Table 1), but no profiles are available. In the north Atlantic, near the British Isles, concentrations of about 30 ng/kg have been reported (Culkin and Riley. 1958; Burton et al., 1959). In the Pacific off Japan, concentrations of 15–20 ng/kg were reported (Ishibashi et al., 1961).

Matthews and Riley (1970a) report indium concentrations ranging from 0.3 ng/kg at the surface to 0.1 ng/kg at 2000 m for a station in the north Atlantic off the coast of Africa, concentrations significantly lower than the values reported by the same coworkers for inshore waters (Matthews and Riley. 1970b). More detailed studies are needed to determine if the surface enrichment which they observed in open ocean waters is real. The data were insufficient to assign a correlation category.

Thallium determinations, like those of indium and gallium, are rare. Matthews and Riley (1970d) reported a profile from the Bay of Biscaye giving an average concentration of 10 ng/kg, which was somewhat less that the 19 ng/kg reported for the Irish Sea (Matthews and Riley, 1969). More recent thallium determinations at various depths in the Pacific and Atlantic report measuring similar concentrations (Table 1) and suggest that it is conservative within analytical limitations (Flegal and Patterson, 1985). More detailed observations may reveal a more complex distribution with a dependence on redox species.

The Croup NA Elements - Carbon, Silicon, Germanium, Tin, and Lead

Carbon and its compounds make up many of the important biological, organic and inorganic species in sea water. Carbon tied into the biochemical cycle can be predicted roughly from the Redfield-Richards equation (Redfield et al., 1963; Richards, 1965): 106C:16N:1P. Carbon dioxide and the carbonate system participate in the oceanic buffering system. In considering the potential environmental effects of OTEC plants, the possibility of releasing

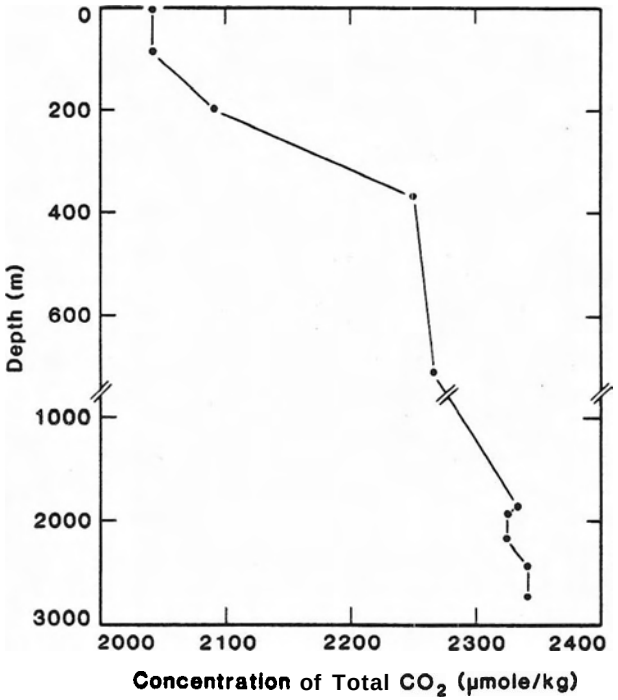

Fig. 5. CO_2 dissolved in sea water vs depth (data from Broecker and Takahashi 1978, GEOPAC 10, Station 326, 14°03'S, 126°15'W).

excess CO_2 into the atmosphere must be considered. Thus, a reliable estimate of $[CO_2]$ at OTEC sites is required. Total CO_2 profiles (Table 1, Figure 5) have been determined in the oceans (Li et al., 1969; Takahashi et al., 1970; Edmond, 1974) and will be published as part of the GEOSECS atlas. Bradshaw et al. (1981) report that the original GEOSECS calculations should be corrected by about +12 μmol/kg for the Pacific–Indian Ocean data and +5 μmol/kg for the Atlantic. In addition to the GEOSECS data (Bainbridge, 1979a,b,c), much data is available for the tropical

oceans (e.g. Broecker and Takahashi, 1978; Edmond. 1974; Skirrow, 1975).

Vast quantities of data are available for silicate in water (Grasshoff, 1964; Brewer and Bradshaw, 1975; Bainbridge, 1979a,b,c). Table 1 and Figure 6 show the typically low concentrations found in surface waters with increasingly higher values at greater depths. As can be seen in Figure 6, silicate concentrations in Pacific deep water are distinctively higher than those in Atlantic deep water (Sverdrup et al., 1942; Bainbridge, 1979a,b). Profiles determined in the tropical oceans are reported in Bainbridge and many other sources.

Germanium rarely has been detected in sea water. Germanium co-varies with silicate (Froelich. and Andreae, 1981; Andreae, 1983) typically ranging from <0.5-9 ng/kg from near the surface to about 2800 m (Table 1). Germanium has not been reported for the tropical oceans, although Braman and Tompkins (1978) reported that in samples taken in the Gulf of Mexico off Tarpon Springs Florida, germanium was undetected using a technique with a minimum detection limit of 4 ng/kg. It is possible, however, to predict the Ge concentration from the Si concentration on the basis of Froelich and Andreae's work.

Only few data are available for the concentration of tin in seawater, recent papers indicate that the concentration in the open oceans are very low, non-conservative, with strong anthropogenic inputs (Byrd and Andreae, 1982). Riverine inputs were found to be small relative to inputs from aeolian sources.

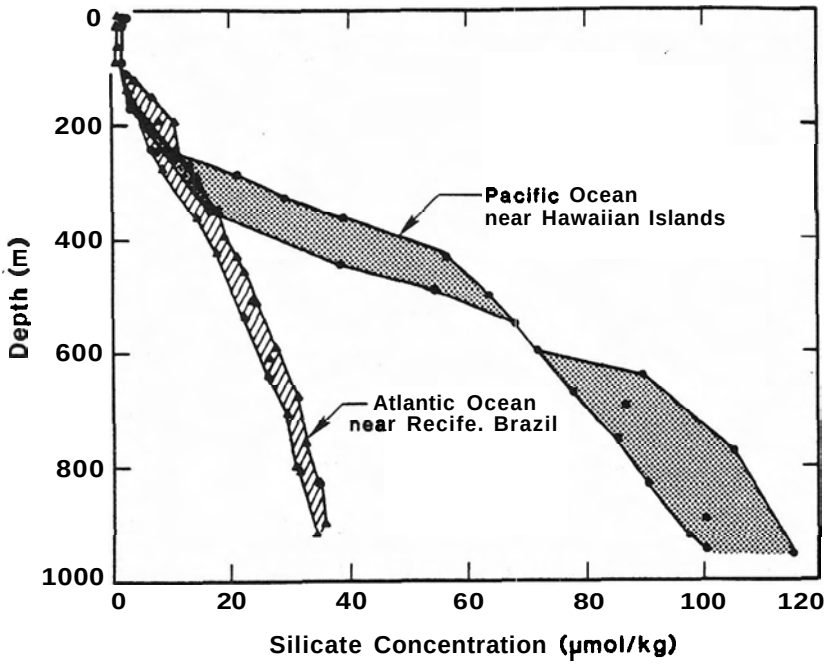

Fig. 6. Silicate concentrations vs depth in the Atlantic and Pacific oceans. Data observed by GEOSECS (Bainbridge, 1979a, b). Atlantic stations: 48 (4°00'S, 29°00'W), 49 (7°56'S, 28°12'W), and 53 (12°00'S, 28°01'W). Pacific stations: 234 (19°52'N, 163°14'W), 235 (16°45'N, 161°23'W), and 206 (22°09'N 153°50'W).

In the Gulf Stream and Sargasso Sea, Andreae (Byrd and Andreae, 1982; Andreae, 1983) reports concentrations ranging from a maximum at the surface of 2.5 ng/kg decreasing to a minimum (below the detection limit, < 0.1 ng/kg) at about 3000 m, increasing to 0.6 ng/kg a few hundred meters off the bottom. They observed significant concentrations of organotin compounds, which have toxicities comparable to that for organomercury compounds. Hodge et al. (1979) report 0.3–0.8 ng/kg of [Sn(IV)] in subsurface

samples (12–17 m) taken off San Francisco. Other species such as organotin compounds were undetected. Braman and Tompkins (1979) have reported higher concentrations of Sn(tot) in the Gulf of Mexico (3.5 ng/kg).

Lead has been studied extensively. However, most of the analyses prior to 1974 were contaminated (Patterson. 1974), primarily due to anthropogenic lead from the atmosphere. Schaule and Patterson (1978, 1981,1983) have found lead concentration in the ng/kg range. Profiles (Figure 7) from the central north Pacific show higher concentrations in surface waters (for example 13.6 ng/kg) decreasing to 1.2 ng/kg at depth. Lower surface concentrations are reported in areas less exposed to anthropogenic pollution. Variations in concentration appear to be due to transport of anthropogenic lead through the water column. At depths greater than 2500 m a constant concentration of 1 ng/kg is observed; presumably the pre-pollution value, although Schaule and Patterson argue that the Pb concentration would have been a factor of two to five lower. In the upper 2000 m concentrations reported in the Atlantic are almost a factor of three times those observed in the Pacific (Schaule and Patterson, 1983).

The Croup VA Elements - Nitrogen, Phosphorus, Arsenic, Antimony, and Bismuth

Nitrogen, like carbon, oxygen, and hydrogen, appears in sea water in a wide variety of compounds: as a dissolved gas, in the nutrients, nitrate, nitrite, ammonia, urea and in numerous organic compounds. Table 1 gives profiles of two of the more important species - dissolved N_2 and nitrate.

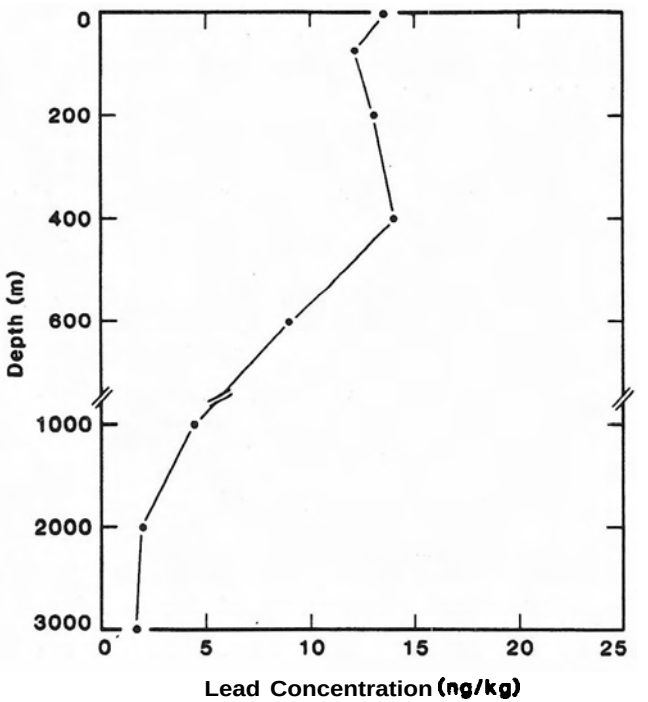

Fig. 7. Lead concentrations vs depth from the central northeast Pacific (data from Schaule and Patterson. 1981. 32°41'N, 145°00'W.

The distribution of dissolved N_2 (Craig et al., 1967) is typical of the profiles exhibited by the non-reactive gases in seawater (Kester, 1975; Konig et al., 1964). Its concentration can be predicted from known solubilities (Weiss, 1970) and bubble formation. Modifications locally can occur due to biological effects.

Nitrate is the dominant nitrogen-containing nutrient species in seawater (Vaccaro, 1965). It has been determined extensively and virtually hundreds of papers report data. The profiles given

in Table 1 are typical of the tropical Atlantic and Pacific Oceans. Concentrations at great depths in the Atlantic are usually less that In the Pacific (Figure 8). Nitrate concentrations are correlated with the concentrations of chromium, iodate and (away from the continental shelf manganese, chromium and iodate (Wong and Brewer, 1974; Cranston, 1979; Klinkhammer and Bender, 1980).

The atlas by Bainbridge (1979a,b,c) includes numerous profiles from the Atlantic. Pacific, and Indian Oceans, Including the tropics. Additional data is available for Hawaii (e.g. Gunderson et al., 1972; Gunderson and Palmer, 1972; Cunderson and Mountain, 1973), Gulf of Mexico (Cummings et al., 1977; Nowlin and McClellan, 1967; Morrison and Nowlin, 1977; El-Sayed et al., 1972), the Caribbean (Lee et al.. 1978) and off the coast of Morocco (Treguer and Le Corre, 1979). Many of the papers presenting trace metal data also give nutrient data.

Phosphorus also exists in a variety of compounds in the ocean; its dominant form is reactive phosphate (Brewer, 1975). Profiles typical of the Pacific and Atlantic Oceans are found in Table 1. Figure 9 compares distributions typical of the tropical Atlantic and Pacific Oceans. Phosphate is relatively easy to determine and is correlated with arsenic, cadmium and nickel (Johnson and Pilson, 1972: Andreae, 1977. 1978. 1979; Bruland et al., 1978a, 1979; Bruland, 1980).

Vast quantities of phosphate data are in the literature. Data for the tropics can be found in most of the sources suggested for nitrate, especially the CEOSECS reports (Bainbridge, 1979a,b,c) and

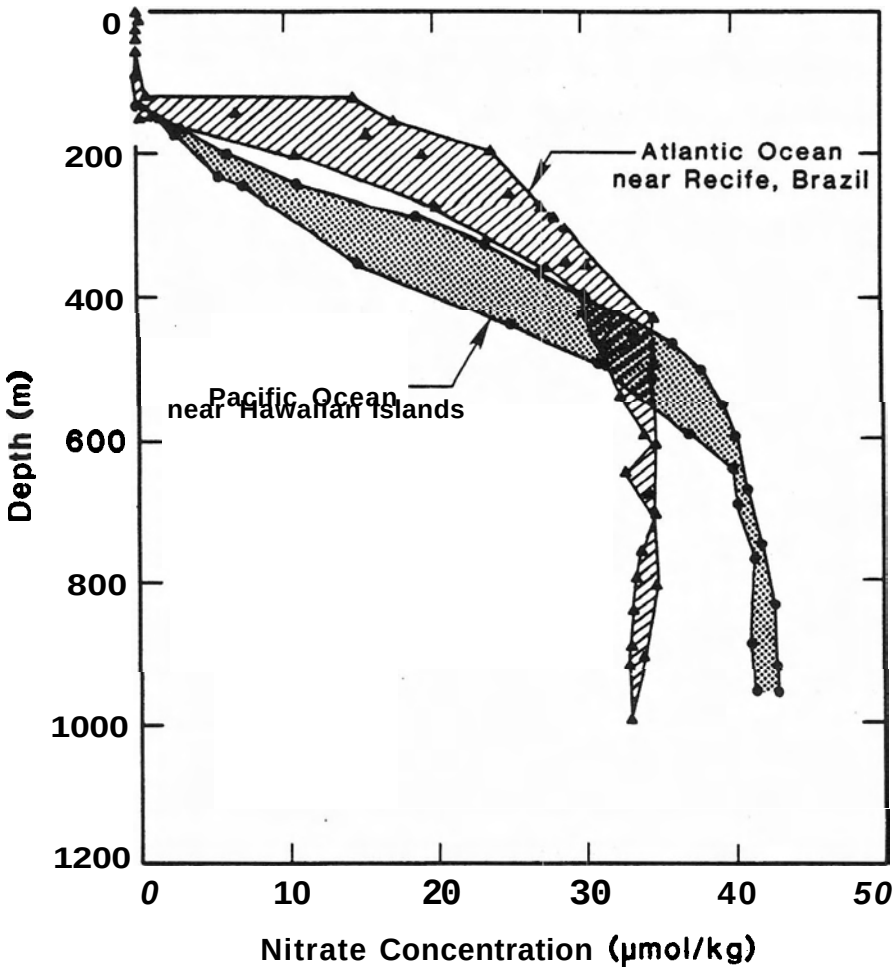

Fig. 8. Nitrate concentrations vs depth in the Atlantic and Pacific oceans. Data observed by GEOSECS (Bainbridge, 1979a, b). Atlantic stations: 48 (4°00'S, 29°00'W), 49 (7°56'S, 28°12'W), and 53 (12°00'S, 28°01'W). Pacific stations: 234 (19°52'N, 163°14'W), 235 (16°45'N, 161°23'W), and 206 (22°09'N 153°50'W).

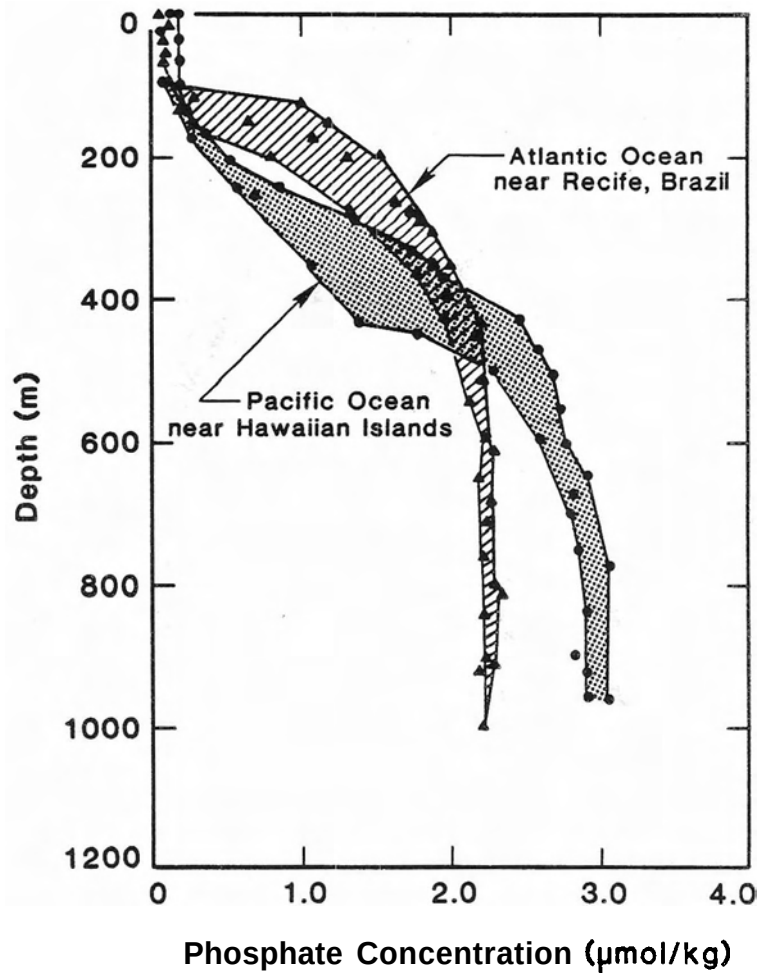

Fig. 9. Phosphate concentrations vs depth in the Atlantic and Pacific oceans. Data observed by GEOSECS (Bainbridge, 1979a, b). Atlantic stations: 48 (4°00'S, 29°00'W), 49 (7°56'S, 28°12'W), and 53 (12°00'S, 28°01'W). Pacific stations: 234 (19°52'N, 163'1 4'W), 235 (16°45'N, 161°23'W), and 206 (22°09'N 153°50'W).

in Richards (1958), Churgin and Halminski (1974), Culberson and Pytkowicz (1975), Halminski (1975), and Voituriez and Herbland (1979).

Arsenic exists as As(V), As(III) and as several organoarsenic species, which are of importance due to varying toxicity and carcinogenicity (EPA, 1976; NRC, 1977). Johnson and Pilson (1972) reported arsenic concentrations in the Caribbean, Gulf of Mexico and northwest Atlantic which range from 2.0 µg/kg (surface) to 3.2 µg/kg (at depth). They reported that arsenate maxima occur at the same depth as phosphate maxima. Andreae (1977, 1978, 1979) reported determined profiles of several arsenic species (Figure 10). In the Pacific Ocean, he observed a partial correlation between arsenate and phosphate concentration. Concentratlons, 1 µg/kg (surface) to 2 µg/kg (>1000 m) were about a factor of two lower than those reported by Johnson and Pilson. The methylated species, dimethylarsenate (DMA) correlated to ^{14}C uptake or chlorophyll a. Analytical variability prevented the derivation of correlation expressions.

Antimony rarely has been determined in seawater. Generally, researchers have found antimony to be conservative within analytical limitations (Schutz and Turekian. 1965a; Portman and Riley, 1966a; Spencer et al., 1970; Brewer et al., 1972; Gilbert and Hume, 1973; Godha, 1975). The correlation expression (Table 1) is based on the limited data in Brewer et al. (1972). More recently, four species of Sb - Sb(V), Sb(III), monomethylantimony and dimethylantimony have been detected in seawater. A profile of

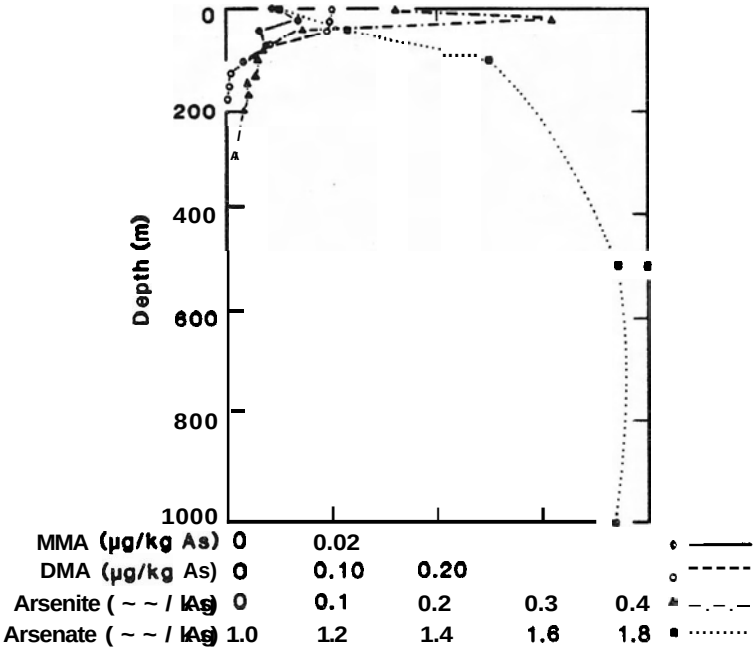

Fig. 10. Arsen'ate, arsentie, and dimethylarsenate concentrations vs depth (data from Andreae, 1979, 30°46'N, 163°30'W).

Sb(V), the dominant form, measured in the Pacific Ocean showed concentrations ranging from 0.09-0.14 µg/kg with no trend in the vertical distribution; the authors report possible storage problems (Andreae, 1983). The discrepancy with earlier results is not as large as might be expected, but it is clear that analytical problems need to be resolved, before the vertical distribution of Sb in the ocean is understood.

Recent analyses of bismuth in the Atlantic and Pacific suggest that its distribution resembles that of lead: it is non-conservative with a possible aeolian anthropogenic source term

(Lee, 1982; Lee et al., 1985/6). As with lead. concentrations are higher in the Atlantic than in the Pacific.

The Group VIA Elements - Oxygen,, Sulfur. Selenium, and Tellurium

Oxygen is found as the dissolved gas and in many other compounds in the ocean. The concentration of the dissolved gas is easily measured and often reported. Figure 11 compares the distributions commonly observed in the Atlantic and Pacific Oceans. In the tropical Pacific, oxygen shows a deep minimum of about 40 µmol/kg (0.8 mL/L) at about 700 m. In the Atlantic, Caribbean, and Gulf of Mexico, the minimum generally is not so pronounced and is shallower, although there are anoxic basins which are exceptions. Tropical data can be found in Bainbridge. (1979a,b,c) and in many of the papers referenced in this report. Dissolved oxygen may be an important control on the concentration of dissolved manganese, iron, cobalt, cerium and europium (Klinkhammer and Bender, 1980; Bacon et al., 1980; Knauer et al., 1982; Klinkhammer and Elderfield, 1982).

Sulfur as sulfate is a major anion in the ocean, historically regarded as conservative (Dittmar, 1884; Forchhammer, 1865; Bather and Riley, 1954). A more recent report confirms the concentration as 2.712 g/kg and the SO4/Cl ratio as 0.1400 (Morris and Riley. 1966). In the oxic oceans. S^{2-} occurs in very low concentrations, however, in anoxic basins its concentration increases considerably. For example, H_2S in the Cariaco Trench is virtually undetected until a depth of about 250 m. As the waters become anoxic with depth. H_2S increases to about 1.3 g/kg (Scranton et al., in press).

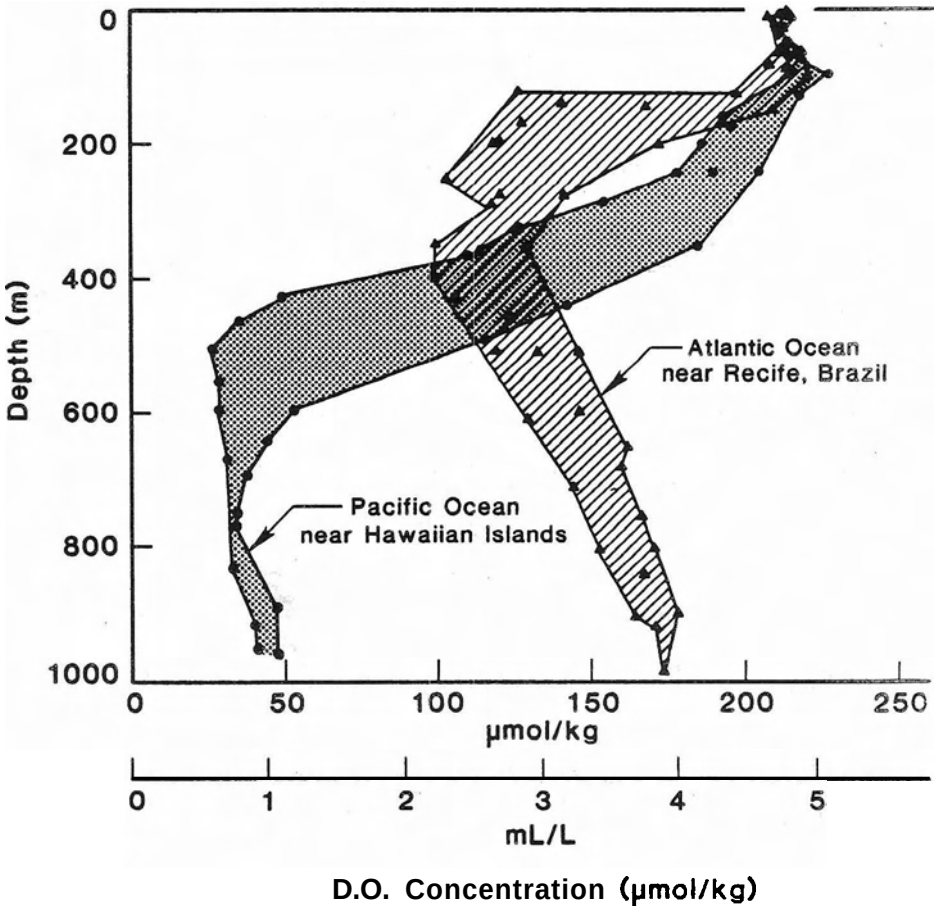

Fig. 11. Dissoved oxygen profiles in the Atlantic and Pacific oceans. Data observed by GEOSECS (Bainbridge, 1979a, b). Atlantic stations: 48 (4°00'S, 29°00'W), 49 (7°56'S, 28°12'W), and 53 (12°00'S, 28°01'W). Pacific stations: 234 (19°52'N, 163°14'W), 235 (16°45'N, 161°23'W), and 206 (22°09'N 153°50'W).

Under anoxic conditions, sulfate cannot be considered conservative. Clearly, the presence of anoxic waters containing high concentrations of S^{2-} would be a serious concern for many aspects of operations involved in pumping deep ocean waters to the surface.

Both selenate and selenite have been determined (Cutter, 1978; Measures and Burton, 1980; Measures et al., 1980, 1983). Total Se concentrations are at ng/kg levels increasing with depth with a nutrient-like distribution (Figure 12). Concentrations of Se(tot) in the North Pacific vary from 27-85 ng/kg. In the north Pacific, vertical distributions of Se(VI) can range from 40-110 ng/kg and Se(IV) from 4-62 ng/kg; concentrations are about 30-40% higher than in the Atlantic. Surface [Se(tot)] vary from 15-60 ng/kg in the Pacific. Correlation expressions have been derived, however, they vary considerably with site (Measures and Burton, 1980: Measures et al., 1980, 1983) as can be seen from the expressions given in Table 1. At the surface anomalies have been reported that can been understood in terms of hydrographic features.

Tellurium has been measured only recently in seawater by Lee and Edmond (1985). Its profile appears to be like that of selenium (Table 1), that is nutrient-like with strong evidence of scavenging by particles. No correlation expressions have been derived.

The Halogens - ~~Fluorine, Chlorine, Bromine, and Iodine~~

The halogens, primarily as halides, constitute a majority of the anions in seawater. Salinity is strongly related to the

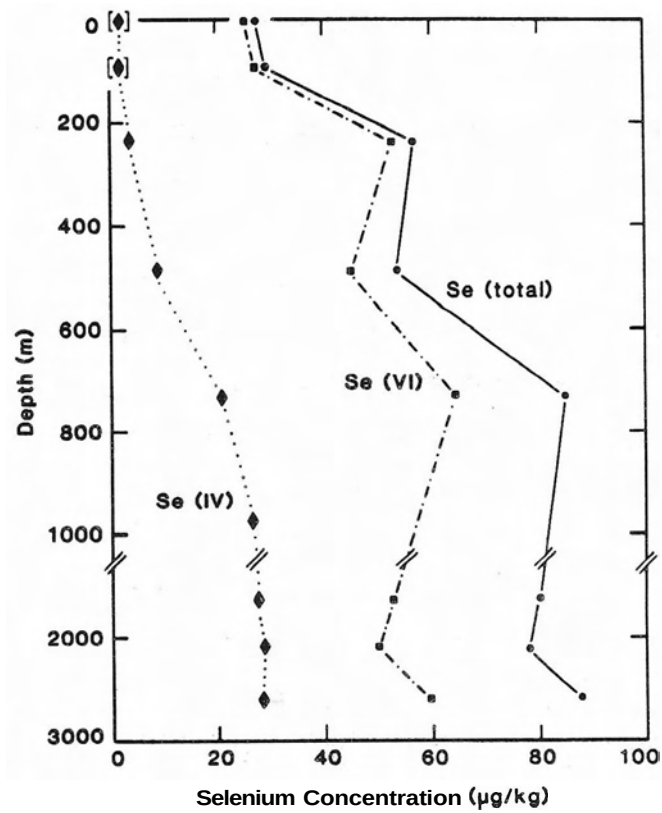

Fig. 12. Profiles of the concentrations of several selenium species vs depth (data from Measures and Burton. 1980, 230°86'N, 27°52'W).

concentration of the halides. Salinity is defined as "the weight in grammes [sic] in 1 kg of seawater, after all bromide and iodide have been replaced by chloride, and all carbonate converted to oxide" (Cox, 1965 quoting Knudsen, 1901). The median salinity of the ocean is 34.69 °/₀₀ (Knauss, 1978).

Fluoride occurs at about 1.3 mg/kg and is generally thought to be conservative (Riley, 1965b; Wilkniss and Linnenbom, 1968;

Kester, 1971; Bewers. 1971; Warner, 1971; Bewers et al., 1973; Greenhalgh and Riley, 1973; Kullenberg and Sen Gupta, 1973; Sen Gupta et al., 1978). The relationship has been questioned at certain sites (Riley, 1965b; Brewer et al., 1970; Kester, 1971), although there is some disagreement (Bewers, 1971; Bewers et al.. 1973). In any case. the non-conservative condition is considered an anomaly.

Chloride. Cl^-, the most abundant anion in the oceans, is conservative (Table 1). A salinity of 35 $^o/_{oo}$ includes a chloride concentration of 19.353 g/kg (Millero and Leung, 1976). Investigators are also in general agreement that bromide, Br^- is conservative, and that the Br/CL ratio is 0.003473 (Morris and Riley, 1966).

Iodate $(IO_3)^-$ is the more abundant and thermodynamically stable species of iodine in seawater, although small but significant quantities of iodide have also been detected (Wong, 1980). The species balance may be linked to the productivity of a region, although the correlation of iodide with productivity is not quantitative (Wong, 1980). Iodate has been found to increase with depth from a level of about 48 µg I/kg at the surface to 58 µg/kg at approximately 4000 m (Figure 13, Tsunogai. 1971; Tsunogai and Hemni, 1971; Wong, 1977; Wong and Brewer, 1974, 1976, 1977; Liss et al., 1973). Wong and Brewer established the correlation between iodate with reactive phosphate and nitrate. Using the mole ratios presented by Wong and Brewer we have determined correlation equations (Table 1). Later studies confirmed the correlation (Wong

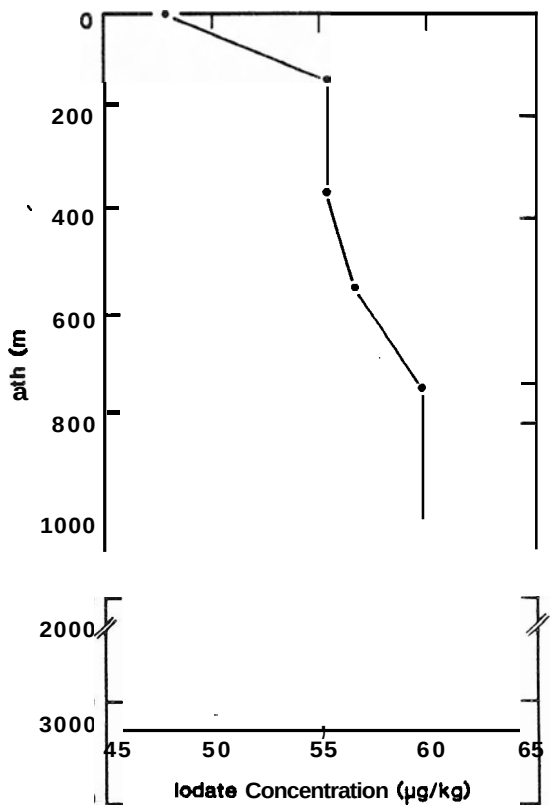

Fig. 13. Iodate concentration vs depth (data is from Wong and Brewer. 1974. 32°31'S, 12° W.

and Brewer, 1976; Wong, 1980; Elderfield and Truesdale, 1980). The correlation is not valid in anoxic basins where iodide shows a pronounced increase with depth (Wong and Brewer, 1977).

The Rare Gases - Helium Neon, Argon, Kryption, Xenon and Radon

The rare gases all have been detected in seawater (Bieri et al., 1966, 1968; Mazor et al., 1964; Konig et al, 1964; Clarke et al., 1969, 1970; Craig et al., 1975). Some of the earlier work

shows a lack of analytical precision, however, the more recent work gives data which is reproducible. Table 1 and Figure 14 give sample profiles. With the exception of radon, the concentrations of the rare gases in sea water depend upon their solubility and entrapment by bubble formation. The degree to which they deviate from their solubility depends largely on physical processes, for instance, the partial dissolution of air bubbles, or mixing of waters of different temperatures (see, for example, Kester, 1975), rather than on chemical and biological interaction.

The profile of radon throughout most of the water column is directly related to its parent isotope, ^{226}Ra. Relative to ^{226}, Rn shows a deficiency in the top 100 m and an excess in near bottom waters (Broecker. 1966; Broecker et al., 1967: Broecker and Kaufman, 1970; Broecker and Peng, 1971; Wilkening and Clements, 1975; Sarmiento et al, 1978). Reported concentrations range from 5.6 dpm/100kg (normalized to 35‰ salinity) near the surface to 17.05 dpm/100kg (at 35‰ salinity) near 4000 m (Broecker and Peng, 1971). These excesses and deficiencies have been used to determine eddy diffusion constants for bottom water and surface water. Throughout the rest of the water column, radon concentrations can be predicted from known ^{226}Ra, Ba, or Si concentrations.

The First Transition Series - Scandium, Titanium, Vanadium, Chromium, Manganese, Iron, Cobalt, Nickel, Copper and Zinc

Concentrations of the first three elements of the first transition series. Sc, Ti and V rarely have been reported in ocean

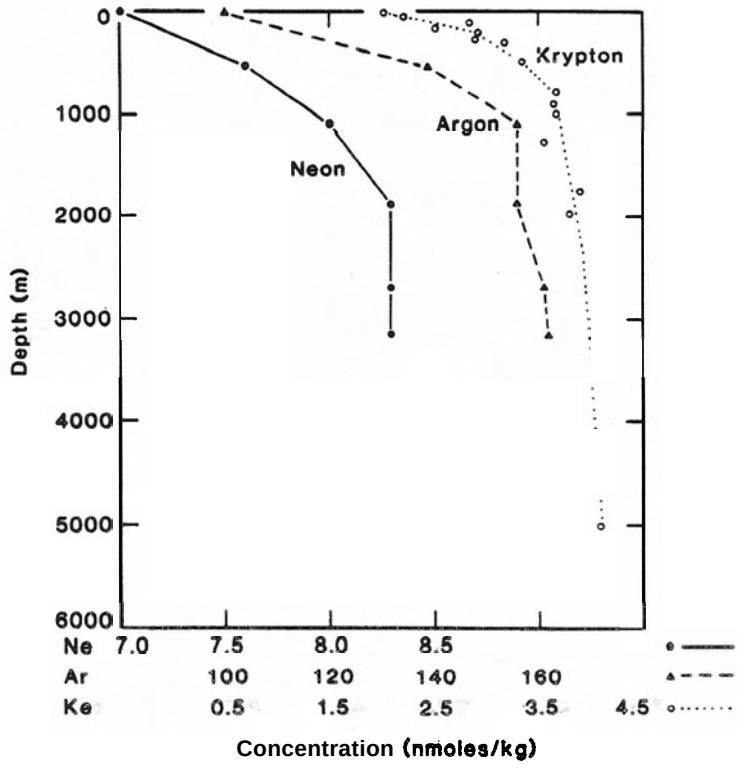

Fig. 14. Neon. argon and krypton concentrations vs depth. Data from Ne and Ar is from Craig et al. (1967), 9°26'N, 113°16'W. Kr data are from Bieri et al. (1968), 5°15'N, 23°30'W.

water. Scandium concentrations reportedly vary from 0.4–1 ng/kg in the Atlantic (Spencer et al., 1970; Brewer et al., 1972; Robertson et al., 1968). No prediction of its correlation category has been made. In Puget Sound. 0.9 - 1.9 μg/kg Ti were measured (Griel and Robinson, 1952), but no open ocean concentrations have been published. No correlation category has been assigned. Morris (1975) reported a profile of V in the northeast Atlantic Ocean, in

which V varies from 1.0-1.2 µg/kg. No consistent variation with depth was apparent. therefore within this degree of precision, V is conservative and using Morris' data, a V/Cl is 6 x 10^{-6}. Recent examinations of V have shown scavenging in surface water and somewhat higher average concentration, about 2 µg/kg (Zhou et al., 1982; Huizenga and Kester. 1982).

Dissolved chromium exists in two oxidation states in seawater: Cr(III) and Cr(VI). In a study of northwest Atlantic waters. Campbell and Yeats (1979, 1981) found chromium concentrations slowly increased with depth and then leveled off. They reported a positive correlation with silicate but with a correlation coefficient of 0.66. Cranston (1979) determined profiles of Cr(VI), Cr(III) and Cr(tot) in the Guatemala Basin (Figure 15). Concentrations average 297 ng/kg Cr(tot), 44 ng/kg Cr(III), and 9 ng/kg particulate Cr. The [total Cr] correlated with Si. or Si and PO or NO,. Cr(III) may correlate with biological production and regeneration of biogenic debris.

Manganese profiles have been reported from the Atlantic and Pacific Oceans (Bender et al.. 1977; Klinkhammer and Bender. 1980; Landing and Bruland, 1980; Martin and Knauer, 1980, 1982, 1984 1985). Mn correlates with the labile nutrients and inversely with oxygen (Landing and Bruland, 1980). [Mn] is at a maximum at the surface (about 140 ng/kg), declining to minimum at the top of the thermocline (Figure 16) then increasing. If the dissolved oxygen concentration drops below 2.3 mL/L, then Mn apparently is released as particles pass through the oxygen minimum and a maximum may be

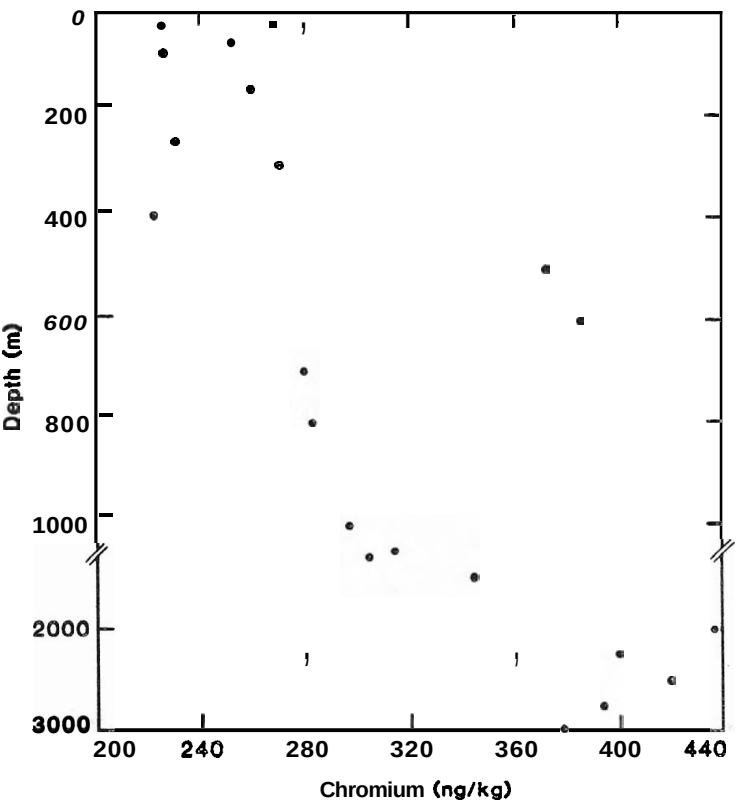

Fig. 15. Chromium concentration vs depth (data is from Cranston, 1979, Guatemala Basin).

observed near the oxygen minimum (Knauer and Martin, 1984). In the Atlantic, concentrations apparently decline with greater depth (Bruland and Franks. 1983). In anoxic basins, Mn concentrations can increase dramatically as is observed in the Cariaco Trench (Figure 16: Bacon et al., 1980). The data from the Cariaco Trench show considerable scatter and the surface data are questionable, however similar conditions have been reported for the Black Sea.

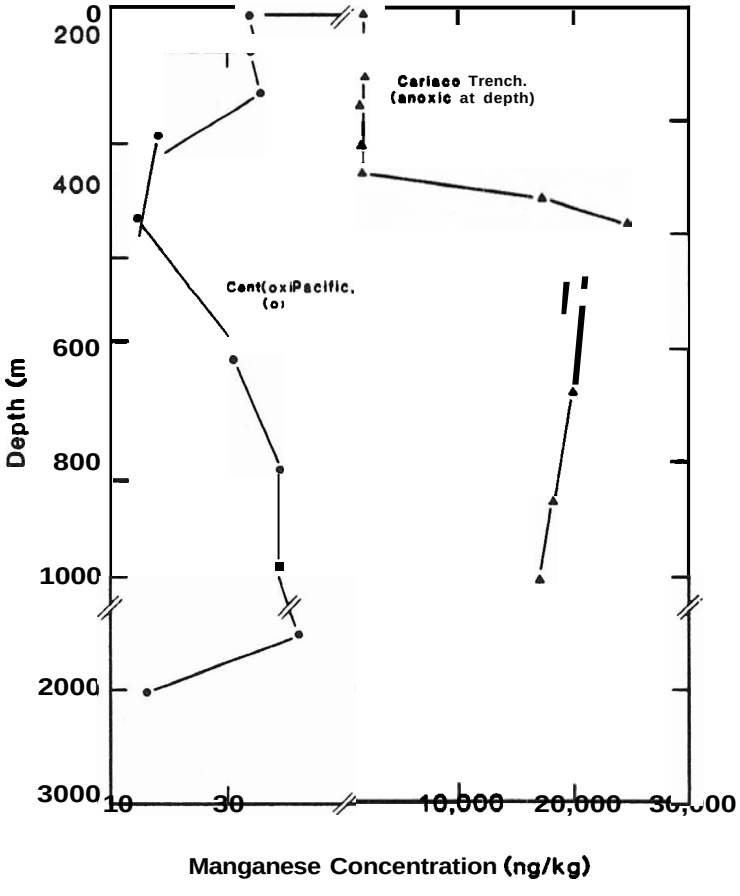

Fig. 16. Manganese concentration vs depth. Concentrations observed in the oxic eastern Pacific (32°41'N, 145°00'W, Landing and Bruland, 1980) are compared with concentrations observed in the Cariaco Trench, and anoxic basin (Bacon et al., 1980).

As the California coast is approached, surface values increase indicating a coastal source for the surface Mn (Landing and Bruland, 1980). A significant Mn flux is associated with the hydrothermal vents of ridge rise systems (Klinkhammer et al.,

1977), therefore Mn concentrations depend strongly on location. No correlation expressions have been proposed for Mn.

A correlation between manganese and oxygen could have serious implications for OTEC or other operations requiring pumping of water from great depth. If waters rich in dissolved manganese were released into a water mass with high oxygen concentration, the dissolved/particulate equilibrium might be disrupted, causing the precipitation of a large number of fine MnO_2 particles.

Iron is essential to many forms of life, and might be expected to show a correlation with the nutrients or biochemical species (Corcoran. 1967). Only a preliminary correlation, however, can be suggested. Iron is extremely difficult to determine. It is an all-pervasive contaminant making ultra-clean techniques mandatory. Under normal oceanic conditions, iron oxides can exist as extremely fine particles, which render normal filtration techniques useless and standard methods of detection meaningless. Concentrations of 8-400 ng/kg (greater near the continental shelf and bottom) have been reported and an apparent correlation between dissolved iron and the nutrients. inverse to dissolved oxygen noted (Gordon et al., 1982; Symes and Kester, 1985). In anoxic basins, iron concentrations increase dramatically, similar to manganese increases (Bacon et al., 1980). Some evidence of an association of iron maxima with an excess of primordial ^3He has been reported, but not confirmed (Brewer et al., 1972; Spencer et al., 1970).

The cobalt distribution in the eastern North Pacific is similar to that of manganese (Knauer et al., 1982). From the surface maximum (6.8 ng/kg) concentrations decrease to 1.4 ng/kg

at 2350 m. No increase in concentration was found at the oxygen minimum, although in anoxic basins the Co concentration has been reported to increase dramatically (Kremling, 1983). The profiles, taken off the California coast, showed an inverse relationship between [Co] and salinity which indicates a fresh water source for the high Co, probably San Francisco Bay, resulting at least in part from anthropogenic releases.

Nickel distributions ranging from 140-340 ng/kg at the surface increasing to 600-700 ng/kg at depth (Figure 17) have been reported (Bender and Gagner, 1976; Sclater et al., 1976; Bruland et al.. 1979; Bruland. 1980). Bruland (1980) has shown a correlation with reactive phosphate and silicate (Table 1). Nickel concentrations in the Atlantic are nutrient-like and are lower than are observed in the Pacific. Concentrations predicted using the above expression for the Atlantic are actually lower than those observed for that ocean. In the Atlantic, shelf concentrations that are significantly higher than open ocean values have been interpreted to indicate a continental source, whereas in the Pacific, enhanced concentrations have been associated with upwelling (Bruland and Franks, 1983). Nickel concentrations in the Gulf of Mexico are similar to those in the open Atlantic ocean (Boyle et al., 1984).

Copper has been determined successfully in seawater (Boyle and Edmond, 1975: Moore and Burton. 1976; Boyle et al., 1977; Bruland et al., 1977; Moore, 1978; Bruland, 1980; Boyle et al., 1981: Bruland and Franks. 1983: Boyle et al, 1984). Bruland (1980)

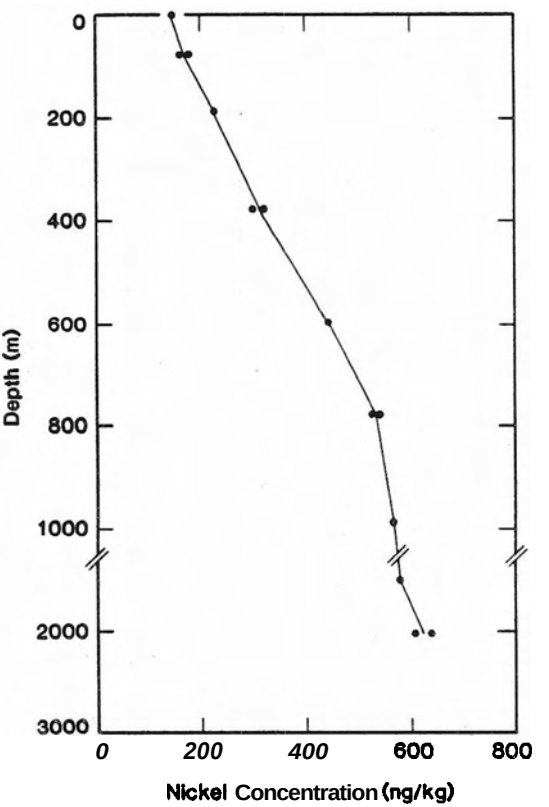

Fig. 17. Nickel concentration vs depth (data from Bruland, 1980, 32°41'N, 145°00'W).

reports levels of Cu at the surface of about 35–100 ng/kg increasing to greater than 300 ng/kg near 4000 m (Figure 18). Copper is depleted at the surface, replenished in the bottom water by supply from sediments (Bruland, 1980; Boyle et al., 1977) with scavenging in the intermediate and deep water. No correlation expression has been formulated relating [Cu] to salinity, the nutrients or easily determined biological parameters, although it

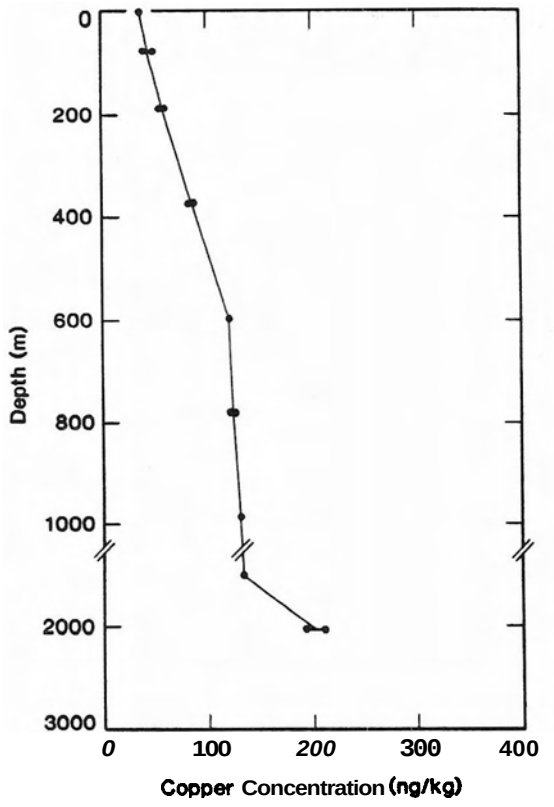

Fig. 18. Copper concentration vs depth (data from Bruland, 1980, 32°41'N, 145°00'W).

most closely behaves like phosphate. In the Gulf of Mexico, the importance of riverine and continental sources of copper has been demonstrated (Boyle et al., 1982; 1984).

Zinc concentrations in the Pacific Ocean are correlated linearly with silicate (Table 1) (Bruland, 1980; Bruland et al., 1978b). Approximately 6–10 ng/kg Zn in surface waters increases to about 600 ng/kg at depths greater than 2000 m for the northwest Pacific (Figure 19).

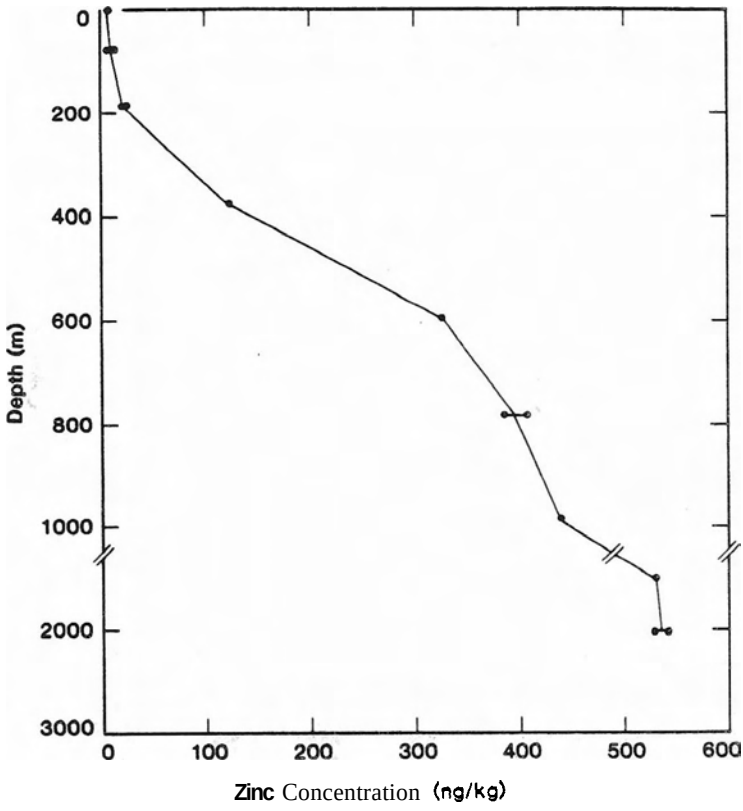

Fig. 19. Zinc concentration vs depth (data from Bruland, 1980, 32°41'N, 145°00'W).

The Second Transition Series - Yttrium, Zirconium, Niobium, Molybdenum, Ruthenium, Rhodium. Palladium, Silver, and Cadmium

Of the second transition series, only cadmium has been studied extensively in seawater. For the rest of the metals in this series only minimal information is available. No data are available for rhodium. The only data for yttrium available report concentrations of 12–13 ng/kg in the Gulf of Mexico and tropical

North Atlantic (Hogdahl et al., 1968; Hayes et al., 1966). No significant variations with depth were observed. Concentrations of zirconium ranging from 0.4-1.4 µg/kg have been reported in Indian coastal waters (Sastry et al., 1969) and 0.01-0.04 µg/kg in open ocean water (Shigematsu et al., 1964). Neither data set is sufficient to define a profile much less a correlation. The only concentration reported for niobium is 5 ng/kg in Plymouth Bay (Carlisle and Hummerstone (1958). In open ocean water southwest of Plymouth Bay, none was detected. No correlation has been predicted for this element.

Molybdenum concentrations vary from 8.6-12.7 µg/kg, averaging 10.4 µg/kg and show no significant variation spatially or to a depth of 1000 m (Morris, 1975). Although the scatter is not insignificant, to this level of precision molybdenum is conservative. Using Morris' data, a correlation expression may be derived: $Mo/Cl = 5.8 \times 10^{-7}$. Recent data from the northeast Pacific, confirm that molybdenum is conservative with a concentration of 10 µg/kg (Collier, 1985).

Ru concentrations in seawater are reported for the Gulf of Mexico (Dixon et al., 1966). In several profiles, surface concentrations vary from 0.1-1.4 ng/kg; at depth concentrations vary from 0.5-0.9 ng/kg. These concentrations are of the same order as those reported by Bekov et al., 1984. No consistent variation with depth was observed and no correlation category has been assigned.

Palladium exhibits a nutrient-like profile with concentrations varying from 21-53 pg/kg (Lee, 1983; Hodge et al., 1985).

Preliminary results suggest that the profile is similar to that for Ni and Pt which occur just above and below Pd in the periodic table.

Recent determinations of Ag suggest that it behaves much like Cu in seawater; it is non-conservative, resembling the nutrients with a release term at the sediment-water interface and scavenging in intermediate waters (Martin et al., 1983). Concentrations vary from 0.1 to 2.5 ng/kg.

Cadmium has been determined with accuracy at extremely low levels, ranging from 0.2 ng/kg in subsurface waters of the north Atlantic to around 100 ng/kg below 600 m (Boyle et al., 1976; Bruland et al., 1978a; Bruland, 1980; Bruland and Franks, 1983 Olafsson, 1983; Boyle et al., 1984). It displays a nutrient-like profile (Figure 20). A number of correlation expressions have been derived (Table 1). The expression predicts concentrations about 15% higher than are observed in the Atlantic. These correlations are nor valid at subnanogram levels of Cd. Concentrations of Cd can change radically during upwelling season, notably in the tropical Pacific when surface concentrations can increase from <1 ng/kg to 9 ng/kg. Clearly, under these conditions, the correlation expressions (Table 1) are not valid.

The Third Transition Series - Hafnium, Tantalum, Tungsten, Rhenium, Osmium, Iridium, Platinum, Gold and Mercury

In the third transition series, no elements can be assigned a correlation category with certainty, although Mukherji and Kester (1979) and Hodge et al. (1985) have suggested possible correlations for Hg and Pt. Three elements remain undetected in seawater: Hf,

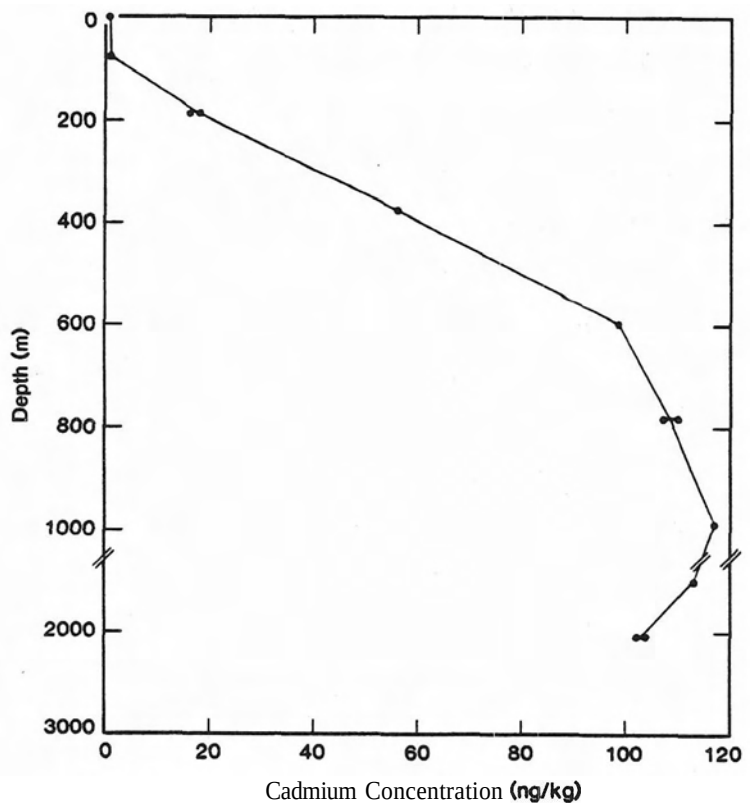

Fig. 20. Cadmium concentration vs depth (data from Bruland, 1980, 32°41'N, 145°00'W).

Ta, and Os. Schutz and Turekian (1965b) did not detect Hf and Ta using neutron activation analysis using a procedure which had a minimum detection limit for these elements of 8 and 2.5 ng/kg, respectively.

Tungsten concentration of 0.1 µg/kg have been reported (Ishibashi, 1953; Chan and Riley, 1967; Kawabuchi and Kuroda, 1969). No profiles are available and no correlation category has been

assigned. Rhenium concentrations of 4–8 ng/kg have been reported (Scadden, 1969; Matthews and Riley, 1970c; Olafsson and Riley, 1972). No significant variation with depth has been reported and no correlation category has been assigned. Iridium concentrations of 10 pg/kg have been reported for coastal Pacific water (Fresco et al., 1985). No open ocean data is available. Platinum is nutrient-like, ranging from 106 pg/kg near the surface to 320 pg/kg at 2000 m (Hodge et al., 1985). No correlation expression was reported.

The most probable concentration of gold in seawater is about 4 ng/kg, first reported by Haber (1927) and confirmed later by Schutz and Turekian (1965b). A number of researchers attempted to determine Au in the interim with varying results (Brewer, 1975). No trends with depth are evident at the levels of precision reported.

Mercury and mercury complexes are important due to their extreme toxicity when concentrated in marine systems. Mercury has been studied extensively. Since Brewer's review (1975), a number of analysts have reported mercury in seawater: about 5 ng/kg in the open ocean off Japan (Matsunaga et al., 1979), and similar concentrations for the northwest Atlantic Ocean (Fitzgerald and Hunt, 1974; Fitzgerald and Lyons, 1975; Fitzgerald, 1976). One profile showed an average oceanic concentration of 4 ng/kg: 3 ng/kg in Atlantic subsurface water (about 25 m) increasing to 5 ng/kg at greater depth (Mukherji and Kester, 1979) and a correlation between mercury and silicate (Table 1).

At depths greater than 2200 m, the correlation of mercury with silicate did not hold. The correlation was derived using data from the Atlantic, where silicate concentrations in the upper 2000 m are generally <20 μmol/kg. As the correlation may not exist at depths greater than 2200 m or when silicate concentrations are >20 μmol/kg, its application on a world-wide scale may not be justified. Olafsson (1983) has investigated Hg concentrations at more northerly latitudes in the Atlantic and reports concentrations of the same order of magnitude but higher. He did not observe a correlation between [Hg] and any of the nutrients. This report supports the view that use of a correlation expression to predict [Hg] would not be justified until its distribution in the ocean is better understood.

Lanthanum and the ~~Lanthanides~~

In addition to lanthanum, the lanthanides or rare earth elements (REEs) are cerium, praeseodymium, neodymium. promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium. The chemical properties of the series are similar with the exception of Ce and Eu. All the others are found in the +3 oxidation state in sea water. Ce can occur as Ce(III) and Ce(IV); Eu as Eu(II) and Eu(III). Because of their chemical similarities, REEs are generally considered as a group. The concentrations of REEs as a series often are examined relative to chondrite (Haskin et al., 1966) or shale (Haskin and Haskin, 1966) concentrations. Profiles of most have determined in the Atlantic and the Pacific. Example profiles are in Table 1; Figure 21 gives data for the Atlantic and Pacific near the surface

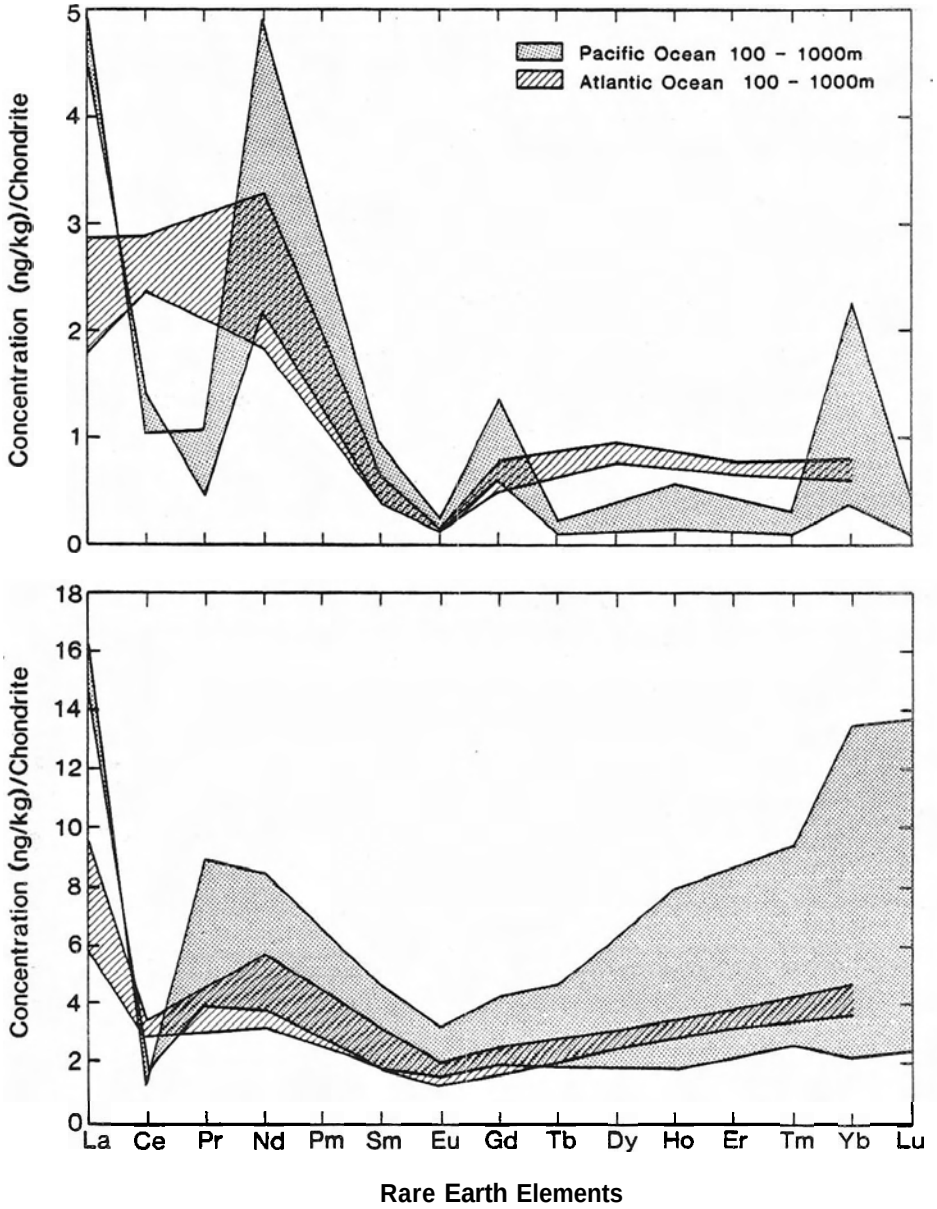

Fig. 21. Concentrations of the rare earth elements near the surface and at depth (Data from Elderfield and Greaves, 1982, 28°01'N, 25°59'W; DeBaar et al., 18°N, 108°W). Absolute concentrations and concentrations relative to chondrlte (Haskin et al., 1966) are shown.

and at depth (both absolute concentrations and relative to chondrite).

Concentrations of all the REEs except Ce increase with depth in both the Atlantic and Pacific, the more for the heavy REEs than the light. The distribution of the REEs is nutrient-like with evidence of scavenging by particles in deep water (DeBaar et al., 1985a). The heavy REEs follow a typical silicate distribution, whereas the light REEs are less systematic (Klinkhammer and Elderfield. 1982). In North Atlantic Deep Water (NADW) and Pacific Equatorial Deep Waters, a correlation between Lu and Si has been demonstrated (DeBaar et al., 1985a):

Atlantic: $[Lu] = 5.36[Si] + 76$ $r = 0.99$

Pacific: $[Lu] = 4.72[Si] - 372$ $r = 0.8$

Units: [Lu], pg/kg (original expression in pmol/kg)

[Si], μmol/kg

A similar expression can be derived using alkalinity that has been corrected for nitrate formation (DeBaar et al., 1985a):

Atlantic: $[Lu] = 4.02\ Alk_{corr.} - 9210$ $r = 0.98$

pacific: $[Lu] = 3.85\ Alk_{corr.} - 9030$ $r = 0.8$

The correlation expression is valid only for the deep waters. No expressions have been reported for the other REEs. The qualitative correlation with alkalinity or silicate indicates mechanisms associated with the biogeochemical cycle of skeletal material, such as actual incorporation into the lattices or adsorption.

The distribution of Ce is dominated by its redox chemistry as is the distribution of Fe and Mn. In areas of low pE, its concentration is greatly enhanced (DeBaar et al., 1985a 1985b).

The Actinides - Uranium

Only Uranium will be discussed. Plutonium and americium exist only as the result of man's activities. Most researchers agree that uranium is conservative in sea water and that its concentration is about 3.2 µg/kg normalized to 35°/₀₀ salinity, (Rona et al., 1956; Moore and Sackett, 1964; Somyajulu and Goldberg, 1966; Noakes et al., 1967; Sackett and Cook, 1969; Turekian and Chan, 1971; Brewer et al., 1972; Ku et al., 1977). Using the data of Turekian and Chan (1971), a correlation expression, U/CL = 1.7 x 10^{-7}, was derived. Sackett and Cook (1969) report greater fluctuations in coastal zones. In open ocean water, however, the conservative relationship has proven reliable and can be used to predict uranium concentrations.

CONCENTRATIONS PREDICTED AT PROPOSED OTEC SITES

It has been shown that for a number of elements correlations between the elemental concentration and other chemical oceanographic parameters exist (Table 1, Figure 1). We conclude that using chemical oceanographic data measured at a specific site and known correlations between those parameters and other species, the concentration of many elements can be predicted for any time or location.

To test the viability of this conclusion, elemental concentration have been predicted for the proposed OTEC sites in

Hawaii at (I) Kahe Point off the southwest coast of Oahu (Table 2) and (II) Ke-ahole Point off the Kona Coast of the Island of Hawaii (Table 3). Calculations were made using nutrient and salinity measurements made at Kahe Point by Noda et al. (1981, 1982). For the conservative elements and nutrient-related elements, concentrations have been calculated at the surface in the mixed layer and at 680 m, approximating depths of warm and cold water intakes for OTEC. The range of concentration for other depths can be made by substituting the appropriate salinity and nutrient values at that depth in the algorithm for a particular element. Variations in the concentrations at the same depth of salinity and the nutrients are indicated in the tables as average, maximum, and minimum values. Such variations, in excess of instrument or analytical error are like due to seasonal variations in nutrient productivity and water mass flow and locally due to patchiness and the action of internal waves.

As Tables 2 and 3 indicate, both sites have similar salinity-nutrient depth distribution reflecting their close proximity and the relative homogeneity of the open oligotrophic ocean. Conservative elements do not vary appreciably with depth reflecting the uniform salinity of the ocean in this area. There is a slight seasonal salinity maximum at depth due to changes in water masses. However. such small changes do not influence the model calculations. The nutrient-related elements do show significant increase with depth related to the increase of nutrient with depth to about 1000 m. As the nutrient increase is within

TABLE 2

Observed Concentrations at Kahe Point

	Chlorinity (pp thousand1		Average Phosphate (uM)		Average Nitrate (uM)		Silicate (uM)	
	Mix.Layer	CWI	Mix.Layer	CWI	Mix.Layer	CWI	Mix.Layer	CWI
Average	19.26	18.99	0.2	2.8	0.01	36	2	90
Minimum	19.10	18.90	0.01	1.8	0	28	0	75
Maximum	19.50	19.10	0.5	3.8	3	40	8	120

Predicted concentrations (Beware caveats, see text

Atomic Number	Element	Mixed Layer Average	Mixed Layer Minimum	Mixed Layer Maximum	Units	CWI Average	CWI Minimum	CWI Maximum	Units
3	Lithium	181	180	183	ug/kg	178	178	180	ug/kg
5	Boron	4.4	4.4	4.5	rglkg	4.3	4.4	4.5	ag/kg
9	Fluorine	1.3	1.3	1.3	ag/kg	1.3	1.3	13	ag/kg
11	Sodium	10.720	10.628	10.849	glkg	10.566	10.520	10.628	g/kg
12	Magnesium	1.276	1.265	1.292	glkg	1.26	1.25	1.27	g/kg
16	Sulfur (SO4)	2.697	2.674	2.729	glkg	2.658	2.646	2.674	g/kg
17	Chlorine	19.243	19.077	19.475	g/kg	18.967	18.884	19.077	g/kg
19	Potassium	397	393	402	rglkg	391	389	393	ag/kg
20	Calcium								
	based on carb. alk	413.3	carb alk, 2.28	meq/kg	rglkg	415.2	carb alk, 2.3	meq/kg	rglkg
	based on conserv.	409.5	406.0	414.5	ag/kg	403.7	401.9	406.0	ag/kg
23	Vanadium	1.2	1.1	1.2	ug/kg	1.1	1.1	1.1	ug/kg

Atomic Number	Element		Predicted Concentrations (Beware caveats, see text) Mixed Layer Average	Minimum	Maximum	Units	CWI Average	Minimum	Maximum	
24	Chromium									
	silicate rel.		212	210	219	ug/kg	309	293	342	uqlkq
	silicate, PO4 rel.		240	240	244	ug/kg	309	301	331	ug/kg
	silicate, NO3 rel.		232	230	239	ug/kg	337	318	373	uqlkq
28	Nickel		176	162	204	ng/kg	489	404	602	nqlkq
30	Zinc		8.3	1.3	29.3	ng/kg	316.3	263.8	421.3	nglkq
32	Germanium		0.1	0	0.4	ng/kg	45	3.75	6	nqlkq
34	Selenium	Site 1	34.3	27.5	47.3	ng/kg	174.0	134.6	224.8	nqlkq
		Site 2	49.7	42.3	62.8	ng/kg	183.0	141.9	232.2	nqlkq
		GEOSECS I	46.0	42.1	53.6	ng/kg	133.4	110.7	164.8	nqlkq
35	Bromine		66.9	66.3	67.7	ag/kg	65.9	65.7	66.3	ag/kg
37	Rubidium		123.5	122.4	125.0	uqlkg	121.7	121.2	122.4	uqlkq
38	Strontium	Phosphate	7.6	7.5	7.7	ag/kg	7.7	7.6	7.8	ag/kg
		Conservat	7.7	7.6	7.8	ag/kg	7.6	7.5	7.6	ag/kg
42	Molybdenum		11.2	11.1	11.3	ug/kg	11.0	11.0	11.1	uqlkq
48	Cadmium	Pacific	0.2		11.9	ng/kg	101.6	62.6	140.6	nqlkq
51	Antimony		0.21	0.21	0.21	uqlkg	0.21	0.21	0.21	uqlkq
53	Iodine	Nitrate	50	50	51	ng/kg	63	60	67	ng/kg
		Phosphate	49	48	51	ng/kg	63	58	69	nglkq
55	Cesium		0.30	0.29	0.30	ug/kg	0.29	0.29	0.29	ug/kg
56	Barium		4.9	4.8	5.3	ug/kg	10.5	9.5	12.1	uqlkg
80	Mercury		2.70	2.3	40	ng/kg	22.1	18.8	28.7	ng/kg
92	Uranium		3.3	3.2	3.3	ug/kg	3.2	3.2	3.2	uqlkq

TABLE 3

Observed **Concentrations** at Kahe Point

	Chlorinity (pp thousand)		**Average** Phosphate **(uM)**		Average Nitrate lull		Silicate lull	
	Mix.Layer	**CWI**	**Mix.Layer**	**CWI**	**Mix.Layer**	CYI	**Mix.Layer**	**CWI**
Average	19.18	**19.01**	0.2	2.9	0.01	30	2	85
Minimum	18.91	18.99	0.01	25	0	32	0	50
Maximum	19.50	19.04	0.4	3.2	3	43	8	**100**

Atomic Nurber	Element	Predicted **Concentrations (Beware** caveats, see **text** Average	**Minimum**	**Maximum** Units	Average	**Minimum**	**Maximum**
		--------- **Mixed Layer** ----------			---------	**CWI**	
3	Lithiur	**180**	**178**	183 uglkg	**179**	**179**	179 uglkg
5	**Boron**	**4.4**	**4.3**	4.5 qlkg	**4.4**	**4.3**	4.5 **ag/kg**
9	Fluorine	**1.3**	**1.3**	1.3 rglkg	**1.3**	**1.3**	1.3 **ag/kg**
11	**Sodium**	**10.674**	**10.523**	10.849 **g/kg**	**10.579**	**10.568**	**10.596 g/kg**
12	**Magnesium**	**1.271**	**1.253**	1.292 glkg	**1.26**	**1.26**	1.26 glkg
16	Sulfur **(SO4)**	**2.685**	**2.647**	2.729 glkg	**2.661**	**2.659**	**2.666** glkg
17	Chlorine	**19.160**	**18.890**	19.475 glkg	**18.990**	**18.970**	19.020 **g/kg**
19	Potassium	**395**	**390**	402 rglkg	**392**	**391**	392 rqlkg
20	**Calcium**						
	based on carb. **alk**	413.3	carb **alk,** 2.29	**aeq/kg** rglkg	415.2	**carb alk,** 23	**aeq/kg** rglkg
	Cased **on** conserv.	407.8	402.0	**$14.5 ag/kg**	404.2	403.7	**404.B ag/kg**
23	Vanadium	1.2	**1.1**	**1.2 ug/kg**	1.1	1.1	1.1 **ug/kg**

Atomic Number	Element		Predicted Concentrations (Beware caveats, see text) Mixed Layer Average	Mixed Layer Minimum	Mixed Layer Maximum Units	CWI Average	CWI Minimum	CWI Maximum
24	Chromium							
	silicate rel.		212	210	219 ug/kg	304	265	320 uqlkg
	silicate, POI rel.		240	240	245 ug/kg	303	271	316 ug/kg
	silicate, NO3 rel.		232	230	239 uglkq	333	295	350 ug/kg
28	Nickel		176	162	199 nglkg	485	396	530 nglkq
30	Zinc		8.3	1.3	29.3 nglkq	298.8	176.3	351.3 nglkg
32	Germanium		0.1	0	0.4 nglkg	4.25	2.5	5 ng/kg
34	Selenium	Site 1	34.3	27.5	44.5 nglkg	173.0	135.2	192.0 ng/kg
		Site 2	49.7	42.3	59.5 nglkg	183.6	151.5	201.6 ng/kg
		GEOSECS I	46.0	42.1	52.2 nglkg	131.9	106.0	144.8 ng/kg
35	Bromine		66.6	65.7	67.7 rglkg	66.0	66.0	66.1 mgikg
37	Rubidiun		122.9	121.2	125.0 uglkg	121.9	121.7	122.0 ug/kg
38	Strontium	Phosphate	7.6	7.5	7.7 mg/kg	7.7	7.6	7.7 mg/kg
		Conservat	7.7	7.5	7.0 mg/kg	7.6	7.6	7.6 mg/kg
42	Molybdenum		11.1	11.0	11.3 uglkg	11.0	11.0	11.0 ug/kg
48	Cadmium	Pacific	0.2		0.0 nglkg	105.5	89.9	117.2 ng/kg
51	Antimony		0.21	0.21	0.21 uglkg	0.21	0.21	0.21 uglkg
53	Iodine	Nitrate	50	50	51 ng/kg	63	61	65 ng/kg
		Phosphate	49	48	50 nglkg	64	62	65 nglkq
55	Cesium		0.30	0.29	0.30 uglkg	0.29	0.29	0.29 ug/kg
56	Barium		4.9	4.8	5.3 ug/kg	10.2	8.0	11.1 ug/kg
80	Mercury		2.70	2.3	4.0 nglkg	21.0	13.3	24.3 ng/kg
92	Uranium		3.3	3.2	3.3 ug/kg	3.2	3.2	3.2 uglkq

the range of depths required for cold water withdrawal, changes in depth of the cold water pipe intake will also change the concentration of nutrients and nutrient-related elements used by the OTEC plant. For engineering and economic reasons the depth of the cold-water intake is kept as shallow as possible to produce the required thermal difference to operate the OTEC heat exchangers. Thus any increase in depth to gain better thermal efficiency also produces an Increase in nutrient-related metal concentrations in the intake water.

Of particular concern are the nutrient-related trace metal which have potential environmental effects if released in the metal-depleted surface water. The very fact that such metals are related to nutrient concentration indicates they are readily taken up by organism in the near surface waters. This is emphasized in the nomenclature that Broecker and Peng (1982) use to describe those elements that they identified as biolimiting or biointermediate. Their increase with depth show their release from organic matter through oceanic decay processes. Natural processes such as upwelling bring up water from depth into the photic zone. However, the depth of the source of naturally-upwelled water is on the order of 10's of meters rather than the nearly 1000 meters required for OTEC operations. Thus, natural marine populations do not see metal concentrations of the values predicted for cold water intakes for OTEC plants. Based on the model in Tables 2 and 3, nutrient-related elements such as Ni (2x surface) and Zn, Se, Ge, and Cd (10x surface or greater) show

significant increase in concentration over surface values. Accordingly, the effects of a discharge of this deep water into the photic zone or use of such water in biologically sensitive processes, such as aquaculture, must be examined. The toxic effects of these elements at such concentrations are not well known. Mitigation to acceptable concentrations might be effected by use of mixed discharge with the spent water from the warm water (near surface) intake used as a diluant. A 1:1 mixture would only half the metal concentration. However, by proper design, minimizing mixing and proper depth location of the combined discharge. the increased density of the mixed discharge could be made to descend to below the photic zone before mixing with the ambient sea water.

CONCLUSIONS

It should be possible in the future to predict the concentrations of many trace elements in the world's oceans using correlation expressions derived by experts in the field. It is now important to test these hypotheses in order to get a good approximation of the chemistry of the seawater involved in an OTEC operation. Appropriate use of such model concentrations with depth would focus direct and costly analytical studies on significant elements while eliminating the need for expensive studies on other elements. More refined analyses and techniques are required if the bottom effects prove to be significant as these models are based on open ocean conditions. Any additional chemical studies should be related to parallel biological and

biochemical studies on the effect of deep water concentrations on surface and near-surface biota near proposed OTEC sites. Without accepted toxic and chronic exposure studies using deep water. a prudent mitigating strategy for discharge of water from the cold water intake is to insure its return to depths below the photic zone.

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