

Distribution patterns of the elements in the ocean: A synthesis

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(Received September 10, 1990; accepted in revised form September 6, 1991)

Abstract—The observed partition patterns of elements between a marine solid phase (e.g., pelagic clays, deep sea manganese nodules, seamount manganese crusts, and plankton) and seawater can be, to the first approximation, explained by the James and Healy adsorption model, except for Ce, Co, Mn, Pb, and Tl, which are concentrated in the solid phase through oxidative uptake processes. In other words, the composition of seawater is mainly controlled by the compositions of source materials (i.e., the crustal igneous rocks and primary magmatic volatiles) and the physicochemical principles regulating the adsorption processes of various chemical species in seawater onto oceanic pelagic clays.

INTRODUCTION

THE CRUSTAL igneous rocks reacted with the primary magmatic volatiles (including H₂O, CO₂, HCl, H₂S, H₂, N₂, As, B, Bi, Br, Cd, I, Sb, Se) to produce the presently observed seawater and various sedimentary rocks (e.g., RUBEN, 1951; GOLDSCHMIDT, 1954; HORN and ADAMS, 1965; GARRELS and MACKENZIE, 1971; LI, 1972). The relative global abundances of sedimentary sandstone, limestone and oceanic carbonates, and shale and oceanic pelagic clays are roughly 11:15:74% (GARRELS and MACKENZIE, 1971). According to the average compositions of these sedimentary rock types given by TUREKIAN and WEDEPOHL (1961), the sandstone is essentially a mixture of 70% quartz (SiO₂) and 30% shale with minor zircon (ZrO₂, HfO₂), and the limestone is a mixture of 90% calcite (CaCO₃, enriched in Sr, Mg) and 10% shale with minor apatite. Therefore, shale and seawater are the most important end products of repeated weathering cycles.

How are the elements partitioned between shale and seawater? What factors control the chemistry of seawater? How are the compositions of solid phases such as marine manganese nodules and marine living organisms, which are all formed from seawater, related to that of seawater? and why? These questions have been dealt with by many researchers (e.g., SILLEN, 1961, 1967; SCHINDLER, 1975; WHITFIELD and TURNER, 1979, 1983; BALISTRIERI et al., 1981; LI, 1981, 1984; KUMAR, 1983a,b; SANTSCHI, 1984; FISHER, 1986; GREEN and CHAVE, 1988). In light of the many new concentration data for seawater and various marine solid phases, especially for ultra trace elements, it is worthwhile to re-examine these questions. The observed distribution patterns of elements between seawater and various marine solid phases have been related to the geochemical parameters such as ionization energies (LI, 1982b), ionic potentials (BANIN and NAVROT, 1975; KUMAR, 1983a), crystal lattice energies (GREEN and CHAVE, 1988), hydrolysis constants (SCHINDLER, 1975; LI, 1981), solubility products (FISHER, 1986), electronegativities (WHITFIELD and TURNER, 1979), etc. However, these geochemical parameters are all closely inter-related quantities (LI, 1991). Therefore, for illustration purposes, the so-called electron binding energy to gaseous cation M^{+z} , I_z , which is equivalent to the z th ionization energy of

gaseous cation M^{z-1} (i.e., $M^{z-1} + I_z \rightarrow M^{z+} + e^-$), is chosen here.

As discussed by LI (1981, 1982a and references within), the chemical bond (i.e., mainly electron pair sharing) strengths between the adsorbed cations and the oxygen atoms of the hydrolyzed (or hydrous) oxide surface are linearly correlated to the first hydrolysis constants ($\log *K_1$'s) of the cations, which are in turn roughly proportional to their I_z . In contrast, the chemical bond strengths between the adsorbed oxyanions and the metal atoms of the hydrolyzed oxide surface are inversely related to the first or second dissociation constants of oxyacids ($\log K_1$ or $\log K_2$), which are in turn proportional to the I_z of the central metal of oxyanions. Therefore, the I_z is a convenient overall parameter which can, to the first approximation, represent the chemical bond strength of adsorbed cations and anions onto the hydrolyzed oxide surface (LI, 1982b). Another advantage of adopting I_z is that I_z data for various cations and anions are quite extensive and accurately determined. One predicts that the distribution coefficients of the elements ($K_d =$ the concentration of any element in a given solid phase divided by that in the seawater) increase with the I_z of adsorbed cations and decrease with the I_z of the central metals of adsorbed oxyanions, if the chemical bond formation is the predominant process controlling the adsorption of ions onto the hydrolyzed oxide surface (LI, 1981, 1982b).

According to the adsorption model of JAMES and HEALY (1972), the Gibbs free energy of an adsorption reaction (ΔG_{ads}) involves not only the chemical bond energy (ΔG_{chem}) but also the coulombic electrostatic energy (ΔG_{coul}) and the secondary solvation or hydration energy (ΔG_{solv}), i.e.,

$$\Delta G_{\text{ads}} = \Delta G_{\text{coul}} + \Delta G_{\text{solv}} + \Delta G_{\text{chem}}$$

The negative ΔG_{ads} value enhances the adsorption reaction. ΔG_{coul} is equal to $Ze\psi$, where Z is the charge valence of adsorbing ion, e is the charge of an electron, and ψ the potential at the equilibrium position of the adsorbing ion in the solid-liquid interface. ψ is, in turn, a function of $(\text{pH}_{\text{zpc}} - \text{pH})RT/e$ and ionic strength of solution, where pH_{zpc} is the zero point of charge pH. ψ is negative for clay minerals in a seawater of pH = 8, since pH_{zpc} for clay minerals ranges from about 2 to 4.6 (PARKS, 1967). The negative ψ enhances

the adsorption of positively charged ionic species ($\Delta G_{\text{coul}} < 0$) and hinders the adsorption of negatively charged ionic species ($\Delta G_{\text{coul}} > 0$). The ΔG_{solv} is related to the energy needed to replace part of hydration water molecules around hydrated cation by the solid and by the interfacial adsorbed water on the solid during the adsorption process, and has an expression

$$\Delta G_{\text{solv}} = Z^2 e^2 / (16\pi\epsilon_0) \{ 1 / [2(r + 2r_w)] + r_w / [(r + 2r_w)^2] \} \{ (1/\epsilon_{\text{int}} - 1/\epsilon_{\text{bulk}}) + Z^2 e^2 / [32\pi\epsilon_0(r + 2r_w)] \{ 1/\epsilon_{\text{solid}} - 1/\epsilon_{\text{int}} \} \}$$

for a hydrated cation moving from the bulk solution to the inner Helmholtz plane at the solid-liquid interface (JAMES and HEALY, 1972) where ϵ_{bulk} , ϵ_{int} , and ϵ_{solid} are the dielectric constants for the bulk solution, the solid-liquid interface region, and the solid respectively, and are dimensionless. The crystallographic radii of cation and water molecule ($=1.38 \text{ \AA}$) are represented by r and r_w , respectively. ϵ_{water} is equal to 78.5 at 25°C and ϵ for clay minerals ranges from 4.5 to 8 (KELLER, 1966). ϵ_{int} has an average value lying between ϵ_{bulk} and ϵ_{solid} . Therefore ΔG_{solv} is always positive and hinders the adsorption of hydrated cations. Also the larger the radius of adsorbed cation, the less positive the ΔG_{solv} term. ΔG_{chem} is, as discussed earlier, roughly proportional to $-I_z$ for cations and to I_z for anions. The relative importance of ΔG_{coul} , ΔG_{solv} , and ΔG_{chem} terms will be discussed later. The application of the James and Healy model to geochemical problems is also discussed by MURRAY and BREWER (1977) and JAMES and MACNAUGHTON (1977).

The dissolved organic ligands in seawater may form organometallic complexes or compete with other ion species for the adsorption sites of solid particles, and may enhance or retard the adsorption of other ions on the solid particles (e.g., DAVIS and LECKIE, 1978). However, adsorption experiments with and without dissolved organic matter (LI et al., 1984) show that dissolved organic matter concentrations in deep ocean are generally too low to affect discernibly the adsorption of most elements by oceanic pelagic clays except for a few elements such as Hg and Au. The organic particles both adsorb and absorb ions from seawater, and the gravitational settling of organic-rich particles like fecal pellets are probably the most important transport mechanisms of elements from surface to deep oceans and to sediment-water interface (e.g., FOWLER, 1977). However, most of the organic matter is quickly reoxidized by microbial activities, and associated elements are mostly released back to deep water and sediment porewater. Because organic contents in oceanic pelagic clays, manganese nodules, and seamount crusts are low, the particulate organic matter cannot be an important final sink in the ocean (excluding coastal regions) for the element inputs from rivers and oceanic hydrothermal vents.

DATA BASE

The concentration data of various elements in average seawater (C_{sw}), shale (C_{sh}), oceanic pelagic clays (C_{op}), deep sea manganese nodules (C_{mn}), and marine organisms (C_{org}) are summarized in Table 1 along with their data sources. The

Table 1: The average concentrations of the elements in seawater (C_{sw}), shale (C_{sh}), oceanic pelagic clays (C_{op}), manganese nodule (C_{mn}) and marine organisms (C_{org}). C_{sw} 's are in 10^{-12}g/g and the rest in ppm (notice $\text{Ex}=10^x$).

	C_{sw} [1]	C_{sh} [2]	C_{op} [2]	C_{mn} [3]	C_{org} [4]
Ag	2.5	0.07	0.11	0.09	0.22
Al	300	80000	84000	27000	62
As	1700(V) 5.2(III)	13	20 b	140	15
Au	0.03 ko	0.0025 we	0.002 b	0.002	0.008 f
B	4.5E6	100	230	300	120
Ba	15000	580	2300	2300	19
Be	0.21	3	2.6	2.5	0.0028
Bi	0.0042	0.43 m	0.53 m	7	
Br	67E6	20 we	-0	21	440
C	28E6	12000 v	4500	1000	345000
Ca	448E6	16000 we	10000	23000	14000
Cd	79	0.3	0.42	10	0.72
Ce	1.7	70 ha	106 r	530 h	0.23 e
Cl	18.8E9	180	-0	-0	4700
Co	1.2	19	74	2700	0.43
Cr	250(VI) 2.6(III)	90	90	35	1.8
Cs	306	5	6	1	0.072
Cu	210	45	250	4500	12
Dy	1.5	4 ha	12 r	31 h	
Er	1.3	3.4 ha	7.2 r	18 h	
Eu	0.21	1.2 ha	3.5 r	9 h	
F	1.3E6	740	1300	200	4.5
Fe	250	47200	65000	125000	160
Ga	1.7 or	19	20	10	0.5

Table 1. (Continued)

	C _{sw} [1]	C _{sh} [2]	C _{op} [2]	C _{mn} [3]	C _{org} [4]
Gd	1.3	5.2 ha	13 r	32 h	
Ge	4.3	1.6	1.6 b	0.8	0.01 ei
Hf	3.4 bo	4.6 go	4.1	8	
Hg	0.42		0.1 m	0.15 h	0.03
Ho	0.45	1.04 ha	2.8 r	7 h	
I	58000(V) 4.4(-I)	19 be	28 b	400	1020
In	0.1 bu	0.1	0.08	0.25	
Ir	0.002 g	80 E-6 fe	0.0004 g	0.007	20E-6 w
K	390E6	26600	25000	7000	52000
La	5.6	32 ha	42 r	157 h	0.14 e
Li	0.18E6	66	57	80	5.4
Lu	0.32	0.48 ha	1.1 r	1.8 h	
Mg	1.29E9	15000	21000	16000	94000
Mn	72	850	6700	186000	20
Mo	10000	2.6	27	400	0.39
N	0.42E6	1000 v	600 b	200	18000
Na	10.8E9	9600	28000	17000	33000
Nb	10 br	11	14	50	
Nd	4.2	31 ha	51 r	158 h	
Ni	530	68	230	6600	1.4
Os		50E-6 es	140E-6 es	0.002 es	
P	65000	700	1500	2500	2800
Pb	2.7	20	80	900	8.7
Pd	0.07	0.004 la	0.006 b	0.006	
Pr	0.87	7.9 ha	13 r	36 h	
Pt	0.27		0.005 b	0.2	0.0002 ho
Ra	130E-6		28E-6		0.1E-6
Rb	0.12E6	140	110	17	1.8
Re	8 ko		0.0003 b	0.001	0.013 f
Rh			0.0004 b	0.013	
Ru	≤0.005 ko		0.0002 b	0.008	
S	898E6	2400	2000 b	4700	8300
Sb	150 bu	1.5	1	40	0.16
Sc	0.86	13	19	10	0.07
Se	100(VI) me 55(IV) me	0.6	0.2 b	0.6	0.063
Si	2.5E6	0.28E6	0.25E6	77000	1500
Sm	0.84	5.7 ha	13 r	35 h	
Sn	0.6	6	4 r	5	0.29
Sr	7.8E6	300	180	830	1100
Ta	≤2.5 bu	0.8	1	10	
Tb	0.21	0.85 ha	1.9 r	5.4 h	
Te	0.05(VI) 0.02(IV)	0.08 go	1 b	10	
Th	0.05 co	12	13 k	30	0.1
Ti	10 or	4600	4600	6700	11
Tl	14	1.2 m	1.8 b	150	0.2 fl
Tm	0.25	0.5 ha	1.1 r	2.3 h	
U	3200	3.7	2.6 k	5	0.8
V	2150 j	130	120	500	3.5
W	100	1.8	4	100	0.035 f
Y	13	26	60 r	150	
Yb	1.5	3.1 ha	7.3 r	20 h	
Zn	320	95	170	1200	39
Zr	17 bo	160	150	560	0.7 ei

[1] Whitfield and Turner (1987), [2] Turekian and Wedepohl (1961), [3] Baturin (1988), [4] Bowen (1979). b: Baturin (1988), be: Becker et al. (1972), bo: Boswell and Elderfield (1988), br: Brewer (1975), bu: Bruland (1983), co: Cochran et al. (1987) and Huh et al. (1989), e: Elderfield and Greaves (1982), ei: Eisler (1981), es: Esser (1991), f: Fukai and Meinke (1962), fe: Fenner and Presley (1984), fl: Flegal et al. (1986), g: Goldberg et al. (1986), go: Govindaraju (1989) SCO-1 shale, h: Haynes et al. (1986), ha: Haskin and Haskin (1966), ho: Hodge et al. (1986), j: Jeandel et al. (1987), k: Ku (1966), ko: Koide et al. (1986a and b, 1987, 1988), la: Laul et al. (1972; average of two part granite and one part basalt, m: Marowsky and Wedepohl (1971), me: Measures et al. (1983 and references therein), or: Orians and Bruland (1988a and b), Shiller (1988), Orians et al. (1990), r: Rankin and Glasby (1979), v: Vinogradov (1959), w: Wells et al. (1988), we: Wedepohl (1969-1978).

C_{sw} are essentially the average of the deep Atlantic and deep Pacific waters as summarized by WHITFIELD and TURNER (1987) unless noted otherwise [note that the concentrations of Li and Te(IV) for the deep Pacific water in Table 17.4 of Whitfield and Turner should be $26 \mu\text{M}$ and 0.1 pM , respectively]. The C_{org} are mainly from the brown algae data of BOWEN (1979). If a range was given for any C_{org} , its geometric mean is listed in Table 1. As shown by BOWEN (1979) and LI (1984), the composition of brown algae is also, in general, representative of phytoplankton and zooplankton. Recent determinations of plankton compositions (e.g., KNAUSS and KU, 1983; COLLIER and EDMOND, 1984) and compilation of marine organisms compositions (EISLER, 1981) are in good agreement with the Bowen data. For the oceanic pelagic clays and manganese nodules, the sea salt components are subtracted assuming all chloride is of seawater origin. As shown in Table 1 and Fig. 1, the C_{sh} and C_{op} for most elements are the same within a factor of two or better. The obvious exceptions are Mn, Na, Ba, Cu, Ni, Co, Pb, Mo, Te, Ir, and Os, which are mostly related to MnO_2 phases of pelagic clays according to factor analysis (LI, 1982a). These elements are enriched in the pelagic clays as compared to shale (Fig. 1). The pelagic clays are also slightly depleted in Ca, Sr, Se, and U (Fig. 1). However, for the purpose of this paper, these minor differences are not critical. Any conclusion drawn from the oceanic pelagic clays is equally applicable to the average shale.

CHEMICAL SPECIATIONS AND TYPES OF THE CONCENTRATION PROFILE IN THE OCEAN

Table 2 summarizes the most probable major chemical species of the elements in normal oxygenated seawater, the

types of elemental concentration profiles in the ocean, the electron binding energies (I_z) corresponding to the valency of metals in the given chemical speciations, and the distribution coefficients calculated from data given in Table 1 (except for radionuclides, which will be discussed later).

The chemical speciations are mainly based on BYRNE et al. (1988) with close reference to TURNER et al. (1981), STUMM and BRAUNER (1975), and BRULAND (1983). Additional results are from VLASSOPOULOS and WOOD (1990) for Au, and KIM (1986) and CHOPPIN (1983) for some actinides.

One can also easily read off the dominant chemical speciation of each element from the stability fields of species $[\text{MCl}^{z-1}]$, $[\text{MCO}_3^{z-2}]$, $[\text{MOH}^{z-1}]$, and $[\text{M}^{+z}]$ as shown in Fig. 2, without going through a more rigorous but elaborate calculation (e.g., BYRNE et al., 1988; TURNER et al., 1981). Figure 2 also provides a useful perspective view on chemical speciation. In Fig. 2, the β_1^L values are the first complexation constants of metal M^{+z} with ligand L (such as OH^- , Cl^- , CO_3^{2-} , etc.) at ionic strength $I = 0$ and 25°C , and are conveniently summarized by TURNER et al. (1981). However, β^{CO_3} values for REE are taken from CANTRELL and BYRNE (1987), and β^{CO_3} values for other trivalent- and oxy-cations are estimated from Fig. 3, which shows a linear relationship between the first or second cumulative complexation constants of trivalent REE, Th^{+4} , and UO_2^{2+} for carbonate at $I = 0$, and those for oxalate at $I = 1$. The extensive data on the oxalate complexation constants at $I = 1$ are given or can be estimated from data at $I = 0.1$ (SMITH and MARTELL, 1976, 1989). Additional β^L data are from COTTON and WILKINSON (1988) for Ir and Rh, and RARD (1985) for Ru.

The solid lines in Fig. 2 represent the activity ratio of one

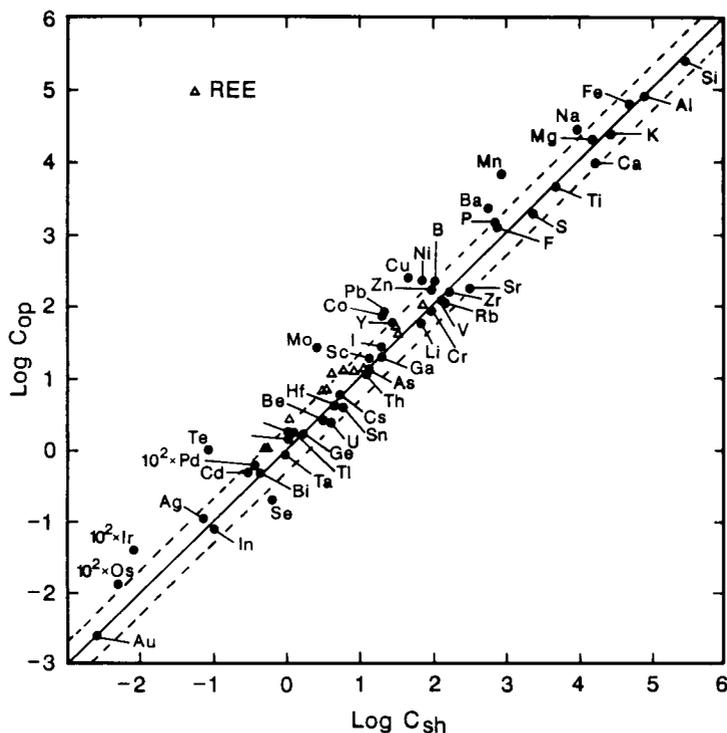


FIG. 1. The concentrations of elements in the oceanic pelagic clays (C_{op}) vs. those in the average shale (C_{sh}). The dashed lines represent a factor of two deviations from the solid concordia line.

between the adjoining species for seawater with $\text{pH} = 8$, $m_{\text{Cl}^-} = 0.53 \text{ M}$, and $m_{\text{CO}_3} = 80 \mu\text{M}$ (i.e., deep Antarctic waters; BROECKER et al., 1982), assuming the total activity coefficients of $\gamma_{\text{Cl}^-} = 0.63$ and $\gamma_{\text{CO}_3} = 0.02$ (WHITFIELD, 1979). The dashed boundary lines represent the concentration ratio of one between the adjoining species, assuming a maximum probable activity coefficient ratio of $\gamma_{\text{ML}}/\gamma_{\text{M}} + z \approx 2$. According to Fig. 2, the hydrated cations ($[M^{+z}]$) in normal oxygenated seawater include the alkalis and alkaline earths (minus Be), whereas Ag, Cu, Cd, Hg are mostly chloride complexes. Both hydrated cationic forms and chloride complexes are important for Tl, Mn, Ni, Co, and Zn, in good agreement with Table 2. The β_1^{OH} value for Pd^{+2} and Pt^{+2} have a large uncertainty and β_1^{Cl} values for Rh^{+3} and Ir^{+3} are still unknown, but considering their high electric polarizability (LI, 1991), their chloride complexes are probably important (Fig. 2). As will be discussed later, the relatively low $\log C_{\text{op}}/C_{\text{sw}}$ for Pd, Pt, and Ir (thus probably also for Rh) also suggest the importance of their chloride complexes. The $*K_1$ values for OsO_4^0 and RuO_4^0 are small (BAES and MESMER, 1976), and their $\log \beta_1^{\text{Cl}}$ are probably small also. Therefore, OsO_4^0 and RuO_4^0 could be the stable species in an oxygenated seawater (Fig. 2), as also suggested by BROOKINS (1987) and XUE and OSSEAO-ASARE (1989). However, as will be discussed later, OsO_4^0 and RuO_4^0 are probably not the most stable species in the ocean where biological activities are omnipresent.

Carbonate complexes are the dominant species for the rare earth elements as well as Y^{+3} , tri-valent actinides, Pb^{+2} , Cu^{+2} , PuO_2^{+2} , and UO_2^{+2} , in Fig. 2, and are again in good agreement with Table 2. Although the $[\text{MCO}_3^{z-2}]/[\text{MOH}^{z-1}]$ ratios for Hg, Th, Sc, and Al are greater than one, the high order chloride (for Hg) and hydroxo complex species probably dominate over the carbonate complex species. The elements Zr^{+4} , Hf^{+4} , Fe^{+3} , Ga^{+3} , In^{+3} , Be^{+2} , and probably Cr^{+3} and Ti^{+4} , are mostly in hydroxo complex forms.

The importance of high order chloride complexation can be easily checked by the condition for $[\text{MCl}_i^{z-i}]/[\text{MCl}_{i-1}^{z-i+1}] \geq 1$ in seawater with $m_{\text{Cl}^-} = 0.53 \text{ M}$ and $\gamma_{\text{Cl}^-} = 0.63$, i.e.,

$$\log \beta_i^{\text{Cl}} - \log \beta_{i-1}^{\text{Cl}} + \log [\text{Cl}^-] \geq 0 \quad (1a)$$

or

$$\log \beta_i^{\text{Cl}} - \log \beta_{i-1}^{\text{Cl}} \geq -\log [\text{Cl}^-] = 0.48$$

where β_i^{Cl} is the i th cumulative chloride complexation constant (for a reaction of $M^{+z} + i \text{Cl}^- \rightarrow \text{MCl}_i^{z-i}$), and the bracket = activity. Similarly, the conditions for $[\text{M}(\text{CO}_3)_i^{z-2i}]/[\text{M}(\text{CO}_3)_{i-1}^{z-2i+2}] \geq 1$ and $M(\text{OH})_i^{z-i}/[M(\text{OH})_{i-1}^{z-i+1}] \geq 1$ in seawater with $m_{\text{CO}_3} = 80 \mu\text{M}$, $\gamma_{\text{CO}_3} = 0.02$, and $\text{pH} = 8$ are, respectively,

$$\log \beta_i^{\text{CO}_3} - \log \beta_{i-1}^{\text{CO}_3} \geq -\log [\text{CO}_3^{2-}] = 5.8 \quad (1b)$$

for carbonate ligand, and

$$\log \beta_i^{\text{OH}} - \log \beta_{i-1}^{\text{OH}} \geq -\log [\text{OH}^-] = 6 \quad (1c)$$

or

$$\log *K_i - \log *K_{i-1} \geq \log [\text{H}^+] = -8 \quad (1d)$$

for hydroxyl ligand where $*K_i$ is the i th cumulative hydrolysis constant (for a reaction of $M^{+z} + i\text{H}_2\text{O} \rightarrow M(\text{OH})_i^{z-i} + i\text{H}^+$). For example, the logarithms of β_1^{Cl} , β_2^{Cl} , β_3^{Cl} , and β_4^{Cl} for Hg^{+2} are, respectively, 7.4, 14.3, 14.5, and 15.3. Therefore, according to Eqn. (1a), the most abundant chloride complex is HgCl_4^{2-} . While $\log \beta_1^{\text{CO}_3}$ for Hg^{+2} is 11.3 and if $\log \beta_2^{\text{CO}_3} - \log \beta_1^{\text{CO}_3}$ is less than 5.8, then HgCO_3^0 is dominant carbonate complex. The condition for $[\text{HgCl}_4^{2-}]/[\text{HgCO}_3^0] \geq 1$ is

$$\log \beta_4^{\text{Cl}} - \log \beta_1^{\text{CO}_3} + 4 \log [\text{Cl}^-] - \log [\text{CO}_3^{2-}] \geq 0.$$

The left-hand side of the equation is equal to 8.1 for the present case, thus, HgCl_4^{2-} is dominant over HgCO_3^0 in seawater. Similarly, the $\log *K_1$ to $\log *K_4$ for Th^{+4} are -3.2 , -6.9 , -11.7 , and -15.9 , respectively; thus, according to Eqn. (1d), $\text{Th}(\text{OH})_4^0$ is the most abundant hydroxo complex. Values for $\log \beta_1^{\text{CO}_3}$ to $\log \beta_3^{\text{CO}_3}$ for Th^{+4} are 12.0, 22.7, and 29.5 respectively, and if $\log \beta_4^{\text{CO}_3} - \log \beta_3^{\text{CO}_3}$ for Th^{+4} is less than 5.8, then, according to Eqn. (1b), $\text{Th}(\text{CO}_3)_3^{2-}$ is the most abundant carbonate species. The condition for $[\text{Th}(\text{OH})_4^0]/[\text{Th}(\text{CO}_3)_3^{2-}] \geq 1$ is $\log *K_4 - \log \beta_3^{\text{CO}_3} - 3 \log [\text{CO}_3^{2-}] - 4 \log [\text{H}^+] \geq 0$. The left-hand side of this equation is 4 for the present case; thus $\text{Th}(\text{OH})_4^0$ is dominant over $\text{Th}(\text{CO}_3)_3^{2-}$. However, we badly need the $\log \beta_4^{\text{CO}_3}$ datum to verify the assumption that $\log \beta_4^{\text{CO}_3} - \log \beta_3^{\text{CO}_3}$ is less than 5.8 for Th^{+4} .

A note of precaution is warranted here. The speciation calculations are based on the assumption of thermodynamic equilibria, which are not always true in the oceanic environment. For example, according to thermodynamics calculation, the high oxidation state species of As, Cr, Se, Te, and Pu should be the stable forms, but low oxidation state species of these elements are also found in the ocean (Table 1), probably through biologically mediated reduction processes. Therefore, it is quite probable that large fractions of Ru and Os are also in lower oxidation states in the ocean (KOIDE et al., 1986b). As shown by SANTSCHI (1988), the fast removal of Chernobyl ^{103}Ru from the water column of Lake Zürich is also facilitated by the reductive uptake of Ru by lake plankton. As the data on complexation constants of ions with various ligands increase and improve, the speciation results will change accordingly. For example, chloride complexes of Au were predicted to be the dominant species in seawater according to BYRNE et al. (1988). But the most recent work by VLASSOPOULOS and WOOD (1990) indicates $\text{AuOH}(\text{H}_2\text{O})^0$ is the most probable species. There are large uncertainties in the $\log *K_i$ values for tri-valent actinides (Am, Cm, Bk, and Cf). If one uses $\log *K_i$ values for actinides given by SMITH and MARTELL (1976), which are about 1.4 units higher than those given by BYRNE et al. (1988), then, both carbonate and hydroxyl complexes may become important. One should keep in mind that data on the $\log \beta_3$ and $\log \beta_4$ for carbonate (or oxalate) complexes are still largely unknown, and many chloride complexation constants for platinum group elements are lacking. It is still not feasible to quantify thermodynamically the extent of metal complexation with mostly unidentified natural organic ligands which cover a wide range of molecular weights and sizes (including colloids) in seawater.

The concentration profiles of elements in the oceans are classified into four major types in Table 2:

Table 2: The types of concentration profiles; major chemical speciations; distribution coefficients of the elements for pelagic clays ($\log C_{op}/C_{sw}$), deep sea manganese nodule ($\log C_{mn}/C_{sw}$), marine organisms ($\log C_{org}/C_{sw}$) in seawater; and electron binding energy (I_z).

Z	Type*	Speciation**	$\log C_{op}/C_{sw}$	$\log C_{mn}/C_{sw}$	$\log C_{org}/C_{sw}$	I_z (eV) ***
Group Ia						
Li-3	c	Li ⁺	2.5	2.7	1.5	5.4
Na-11	c	Na ⁺	0.41	0.2	0.49	5.1
K-19	c	K ⁺	1.8	1.3	2.1	4.3
Rb-37	c	Rb ⁺	3.0	2.2	2.2	4.2
Cs-55	c	Cs ⁺	4.3	3.5	2.4	3.9
Fr-87	(c)	Fr ⁺				4.0
Group IIa						
Be-4	n	BeOH ⁺ , Be(OH) ₂ [°]	7.1	7.1	4.1	18.2
Mg-12	c	Mg ⁺²	1.2	1.1	1.9	15.0
Ca-20	c	Ca ⁺²	1.4	1.7	1.5	11.9
Sr-38	c	Sr ⁺²	1.4	2.0	2.2	11.0
Ba-56	n	Ba ⁺²	5.2	5.2	3.1	10.0
Ra-88	n	Ra ⁺²	5.3		2.9	10.1
Group IIIa						
Sc-21	s+n	Sc(OH) ₃ [°]	7.3	7.1	4.9	24.8
Y-39	(n)	YCO ₃ ⁺ , Y(CO ₃) ₂ ⁻	6.7	7.1		20.5
La-57	n	LaCO ₃ ⁺ , La(CO ₃) ₂ ⁻	6.9	7.5	4.4	19.2
Ac-89		Ac(CO ₃) ⁺ , Ac ⁺³				(19)
Group IVa						
Ti-22	s+n	Ti(OH) ₄ [°]	8.6	8.8	6.0	43.3
Zr-40	s+n	Zr(OH) ₅ ⁻	7.0	7.5	4.5	34.3
Hf-72	s	Hf(OH) ₅ ⁻	6.1	6.4		33.3
Group Va						
V-23	n	NaHVO ₄ ⁻ , HVO ₄ ⁻²	4.8	5.4	3.3	65.2
Nb-41	(n)	Nb(OH) ₆ ⁻ , Nb(OH) ₅ [°]	6.1	6.7		50.6
Ta-73	(n)	Ta(OH) ₅ [°] , Ta(OH) ₆ ⁻	≥5.6	6.6		(45)
Group VIa						
Cr-24	n	CrO ₄ ⁻² , NaCrO ₄ ⁻ (VI)	5.6	5.2	3.9	90.6
	s	Cr(OH) ₃ [°] , Cr(OH) ₂ ⁺ (III)	7.5	7.1	5.8	31.0
Mo-42	c	MoO ₄ ⁻²	3.4	4.6	1.6	68
W-74	(n)	WO ₄ ⁻²	4.5	6.0	2.5	(61)
Group VIIa						
Mn-25	s	Mn ⁺² , MnCl ⁺	8.0	9.4	5.4	15.6
Tc-43	c	TcO ₄ ⁻	0.4 b		0.4 b	(94)
Re-75	c	ReO ₄ ⁻	1.6	2.1	3.2	(79)
Group VIIIa						
Fe-26	s+n	Fe(OH) ₃ [°]	8.4	8.7	5.8	30.7
Co-27	s	Co ⁺² , CoCl ⁺	7.8	9.4	5.6	17.1
Ni-28	n	Ni ⁺² , NiCl ⁺	5.6	7.1	3.4	18.2
Ru-44	(n)	RuO ₄ [°] , reduced species	>4.6	>6.2		46 (IV)
Rh-45	(n)	Rh(OH) ₃ [°] , RhCl ₆ ⁻³ ?				31.1
Pd-46	n	PdCl ₄ ⁻² , Pd(OH) ₂ [°] ?	4.9	4.9		19.4
Os-76	(n)	OsO ₄ [°] , reduced species				40 (IV)
Ir-77	(n)	Ir(OH) ₃ [°] , IrCl ₆ ⁻³ ?	5.3	6.5	4.0	(27)
Pt-78	n	PtCl ₄ ⁻² , Pt(OH) ₂ [°] ?	4.3	5.9	3.1	18.6
Group Ib						
Cu-29	n	CuCO ₃ [°] , Cu-organic	6.1	7.3	4.8	20.3
Ag-47	n	AgCl ₂ [°]	4.6	4.6	4.9	7.6
Au-79	pc	AuOH(H ₂ O) [°]	5.0	5.0	5.4	9.2
Group IIb						
Zn-30	n	Zn ⁺² , ZnCl ⁺	5.7	6.6	5.1	18.0
Cd-48	n	CdCl ₂ [°]	3.7	5.1	4.0	16.9
Hg-80	s+n	HgCl ₄ ⁻²	5.4	5.6	4.9	18.8
Group IIIb						
B-5	c	B(OH) ₃ [°] , polyborates	1.7	1.8	1.4	37.9
Al-13	s	Al(OH) ₃ [°] , Al(OH) ₄ ⁻	8.5	8.0	5.3	28.4
Ga-31	s+n	Ga(OH) ₄ ⁻	7.1	6.8	5.5	30.7
In-49	n+s	In(OH) ₃ [°]	5.9	6.4		28.0
Tl-81	pc	Tl ⁺ , TlCl [°]	5.1	7.0	4.1	6.1
Group IVb						
C-6	n	HCO ₃ ⁻	2.2	1.6	4.1	64.5
Si-14	n	H ₄ SiO ₄ [°]	5.0	4.5	2.9	45.1
Ge-32	n	H ₄ GeO ₄ [°] , H ₃ GeO ₄ ⁻	5.7	5.3		45.7
Sn-50	s	SnO(OH) ₃ ⁻	6.8	6.9	5.7	40.7
Pb-82	s	PbCO ₃ [°] , PbCl ⁺	7.5	8.5	6.5	15.0
Group Vb						
N-7	n	NO ₃ ⁻	3.1	2.7	4.6	97.9
P-15	n	NaHPO ₄ ⁻ , HPO ₄ ⁻²	4.4	4.6	4.6	65.0

Table 2. (Continued)

Z	Type*	Speciation**	log C _{op} /C _{sw}	log C _{mn} /C _{sw}	log C _{ox} /C _{sw}	I _z (eV) ***
As-33	n	HAsO ₄ ²⁻ (V)	3.9	4.9	4.0	62.6
	s	As(OH) ₃ ⁰ , As(OH) ₄ ⁻ (III)	6.4	7.4	6.5	28.4
Sb-51		Sb(OH) ₄ ⁻	3.9	5.5	3.1	56
Bi-83	s	Bi(OH) ₃ ⁰	8.1	9.2		25.6
Group VIb						
S-16	c	SO ₄ ²⁻	0.35	0.72	1.0	88.0
Se-34	n	SeO ₄ ²⁻ (VI)	3.3	3.7	2.8	81.7
	n	SeO ₃ ²⁻ (IV)	3.6	4.0	3.1	42.9
Te-52	s	TeO(OH) ₄ ⁻ , Te(OH) ₆ ⁰ (VI)	7.3	8.3		70.7
	s	TeO(OH) ₃ ⁻ (IV)	7.7	8.7		37.4
Po-84		PoO(OH) ₃ ⁻ ?	7.0 ba		5.9 k	(38)
Group VIIb						
F-9	c	F ⁻ , MgF ⁺	3.0	2.2	0.54	3.4
Cl-17	c	Cl ⁻			-0.6	3.6
Br-35	c	Br ⁻		-0.5	0.82	3.4
I-53	n	IO ₃ ⁻	2.7	3.8	4.3	(71)
At-85						
Lanthanides						
La-57	n	LnCO ₃ ⁺ , Ln(CO ₃) ₂ ⁻	6.9	7.5	4.4	19.2
Ce-58	s	"	7.8	8.5	5.1	20.2
Pr-59	n	"	7.2	7.6		21.6
Nd-60	n	"	7.1	7.6		22.1
Pm-61	n	"				22.3
Sm-62	n	"	7.2	7.6		23.4
Eu-63	n	"	7.2	7.6		24.9
Gd-64	n	"	7.0	7.4		20.6
Tb-65	n	"	7.0	7.4		21.9
Dy-66	n	"	6.9	7.3		22.8
Ho-67	n	"	6.8	7.2		22.8
Er-68	n	"	6.7	7.1		22.7
Tm-69	n	"	6.6	7.0		23.7
Yb-70	n	"	6.7	7.1		25.0
Lu-71	n	"	6.5	6.8		21.0
Actinides						
Ac-89		AcCO ₃ ⁺ , Ac ⁺³				(19)
Th-90	s	Th(OH) ₄ ⁰	8.4	8.7	6.3	28.8
Pa-91		PaO ₂ OH ⁺	6.3 a			(44)
U-92	c	UO ₂ (CO ₃) ₂ ²⁻ , UO ₂ (CO ₃) ₃ ⁴⁻	2.9	3.2	2.4	(57)
Np-93		NpO ₂ ⁺ , NpO ₂ (CO ₃) ⁻	3.7 h		2.6 h	(53)
Pu-94		PuO ₂ (CO ₃) (OH) ⁻	6.0 co		5.4 h	(80)
		Pu(OH) ₃ ⁺ , Pu(OH) ₄ ⁰	6.8 co			(41)
Am-95		AmCO ₃ ⁺	6.5 i		5.5 i	(24)
Cm-96		CmCO ₃ ⁺	6.5 i		5.5 i	(24)
Bk-97		BkCO ₃ ⁺	(6.5) i		(5.5) i	(24)
Cf-98		CfCO ₃ ⁺	(6.5) i		(5.5) i	(24)

*: Types of the concentration profiles in the oceans. c = conservative ([M]/[Cl] = constant within 10%), pc = pseudo conservative (surface ≈ deep, deep Atlantic ≈ deep Pacific with large analytical uncertainty), n = nutrient type (surface < deep, Atlantic < Pacific), s = scavenged type (surface > deep, Atlantic > Pacific), s+n = mixed type I (surface < deep in Pacific, deep Atlantic > deep Pacific), n+s = mixed type II (surface > deep, deep Atlantic < deep Pacific). The types in parentheses are only educated guesses.

** : Mainly from Byrne et al. (1988) with close reference to Turner et al. (1981), Bruland (1983), except for Au (Vlassopoulos and Wood, 1990); Pa, U, Pu (Choppin, 1983; Choppin and Stout, 1989; Aston, 1980). The question marks are only educated guesses.

***: Data are mainly from Dean (1985) values in parentheses are less reliable and are given by Samsonov (1973) or extrapolated.

a: Anderson et al. (1983), b: Beasley and Lorz (1986), Fisher (1982), ba: Bacon (1976), co: Cochran et al. (1987), h: Holm (1981), i: IAEA (1985), k: Kharkar et al. (1976).

- 1) Conservative type (c) where the ratio of element to chloride concentrations is constant (within 10%) throughout the ocean
- 2) Nutrient type (n) where the concentration increases generally from the surface to deep waters and from the deep Atlantic to deep Pacific

- 3) Scavenged type (s) where the concentration decreases from the surface to deep waters and from the deep Atlantic to deep Pacific
- 4) Mixed type (s + n) where the concentration decreases from the deep Atlantic to deep Pacific as for the scavenged type, but the vertical profiles retain part of the nutrient

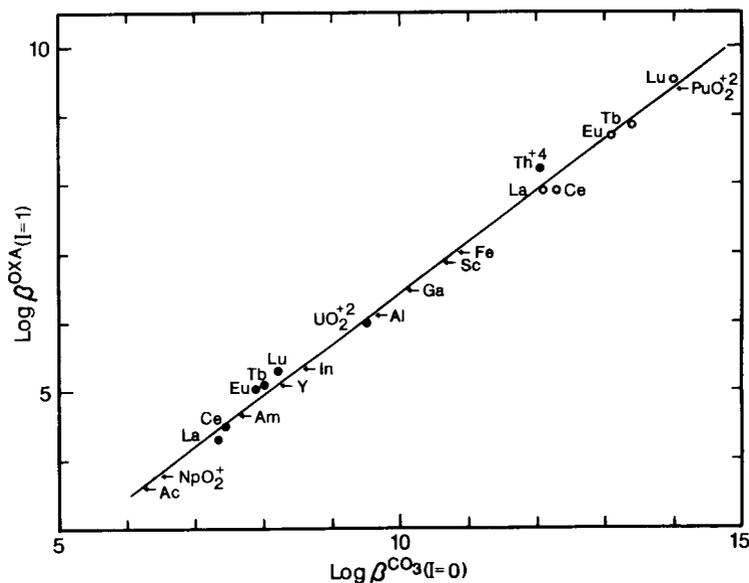


FIG. 3. The linear relationship between the complexation constants of trivalent REE, Th^{4+} , and UO_2^{2+} for carbonate at $I = 0$ and for oxalate at $I = 1$. Solid circles are for $\log \beta_1$ data and open circles for $\log \beta_2$ data at 20 to 25°C. The horizontal arrows represent the known β^{9a} values for given trivalent cations unless noted otherwise.

crease slightly with depth by no more than 10%, and thus are classified as the conservative type here. The classifications in the parentheses of Table 2 are only rough predictions based on $\log C_{op}/C_{sw}$ values and the chemistry of the elements. For verification, complete vertical concentration profiles in the Atlantic and Pacific are required for these elements (including Fr, Y, Nb, Ta, W, Ru, Rh, Os, and Ir).

THE SYSTEMATICS AMONG CHEMICAL SPECIATION, TYPES OF CONCENTRATION PROFILES, $\log C_{op}/C_{sw}$ AND I_z VALUES

The values of $\log C_{op}/C_{sw}$ from Table 2 are plotted versus I_z in Fig. 4. The elements with an asterisk are radionuclides whose $\log C_{op}/C_{sw}$ are calculated from the activities in filtered particles and seawater from the deep Atlantic (BACON, 1976; ANDERSON et al., 1983; COCHRAN et al., 1987). Only the $\log C_{op}/C_{sw}$ values for the reduced forms of As, Cr, Pu, Se, and Te are plotted in Fig. 4. Because the adsorbed species of these elements are predominantly the reduced species, as indicated by roughly 10^3 -fold differences in K_d between reduced and oxidized forms of these elements (SANTSCHI, 1988; NELSON et al., 1984; BALISTRERI and CHAO, 1990). The $\log C_{op}/C_{sw}$ is also related to the logarithm of the mean oceanic residence time of the element in the ocean, $\log \bar{T}$, according to the definition of $T = (v \cdot C_{sw}) / (s \cdot C_{op})$ or $\log C_{op}/C_{sw} = \log v / s - \log \bar{T}$, where v is the total water mass of the ocean and s is the total deposition rate of oceanic pelagic clays (LI, 1982a). In general, the $\log C_{op}/C_{sw}$ tend to increase with increasing I_z for cations from Na^+ up to Al^{3+} , Fe^{3+} , and Th^{4+} ; then decrease for elements whose charges are greater than three and exist in seawater as hydroxo-, hydroxo-oxo-, and oxocomplexes. This observed general trend (in the shape of an inverted V) is consistent with the prediction discussed earlier, and indicates the predominant effect of ΔG_{chem} term

for adsorption. However, some obvious exceptions to this trend need further discussion in the following sections.

The $\log C_{op}/C_{sw}$ for alkali and alkaline earth elements other than Li and Be decrease with increasing I_z . The I_z values (or $\log *K_1$) of alkali and alkaline earth cations other than Li and Be are small. Therefore, the contribution of the ΔG_{chem} term to the overall ΔG_{ads} is also negligible. The ΔG_{coul} term is negative and constant among alkali or alkaline earth cations (except Be). The only difference is the positive ΔG_{solv} term. For example, among alkaline earth cations other than Be, the ionic radius of cation r decreases from Ra^{+2} to Mg^{+2} , thus ΔG_{solv} increases from Ra^{+2} to Mg^{+2} . The net effect is that ΔG_{abs} is most negative for Ra^{+2} , thus facilitating adsorption and resulting in the highest $\log C_{op}/C_{sw}$ value, whereas ΔG_{abs} for Mg^{+2} is less negative, thus resulting in the lowest $\log C_{op}/C_{sw}$ value. For Be, its I_z (or $\log *K_1$) is large, thus, the large negative ΔG_{chem} term simply overwhelms the other terms, and results in a high $\log C_{op}/C_{sw}$ value. A similar argument can be applied to the alkali cations. In short, the introduction of the ΔG_{solv} term is an important feature of the JAMES and HEALY (1972) model.

The exceptionally high $\log C_{op}/C_{sw}$ values for Mn, Co, Pb, Ce, and Tl relative to the neighboring elements in Fig. 4 are probably caused by the oxidative uptake of these elements on the particle surfaces ($\text{Mn}^{+2} \rightarrow \text{Mn}^{+4}$, $\text{Co}^{+2} \rightarrow \text{Co}^{+3}$, $\text{Pb}^{+2} \rightarrow \text{Pb}^{+4}$, $\text{Ce}^{+3} \rightarrow \text{Ce}^{+4}$, and $\text{Tl}^{+2} \rightarrow \text{Tl}^{+3}$; GOLDBERG, 1954; MURRAY and DILLARD, 1979; LI, 1982b; WHITFIELD and TURNER, 1987). The exceptionally low $\log C_{op}/C_{sw}$ value for B may indicate the formation of yet unknown stable polyborate complexes in seawater (LI, 1981). Further studies are warranted. The relatively low $\log C_{op}/C_{sw}$ value for Se may be caused by the desorption of Se from the sediments through the gradual oxidation of adsorbed SeO_3^{-2} into more soluble SeO_4^{-2} at the particle surface (TAKEMATSU et al., 1990). Because the first hydrolysis constants ($\log *K_1$) for

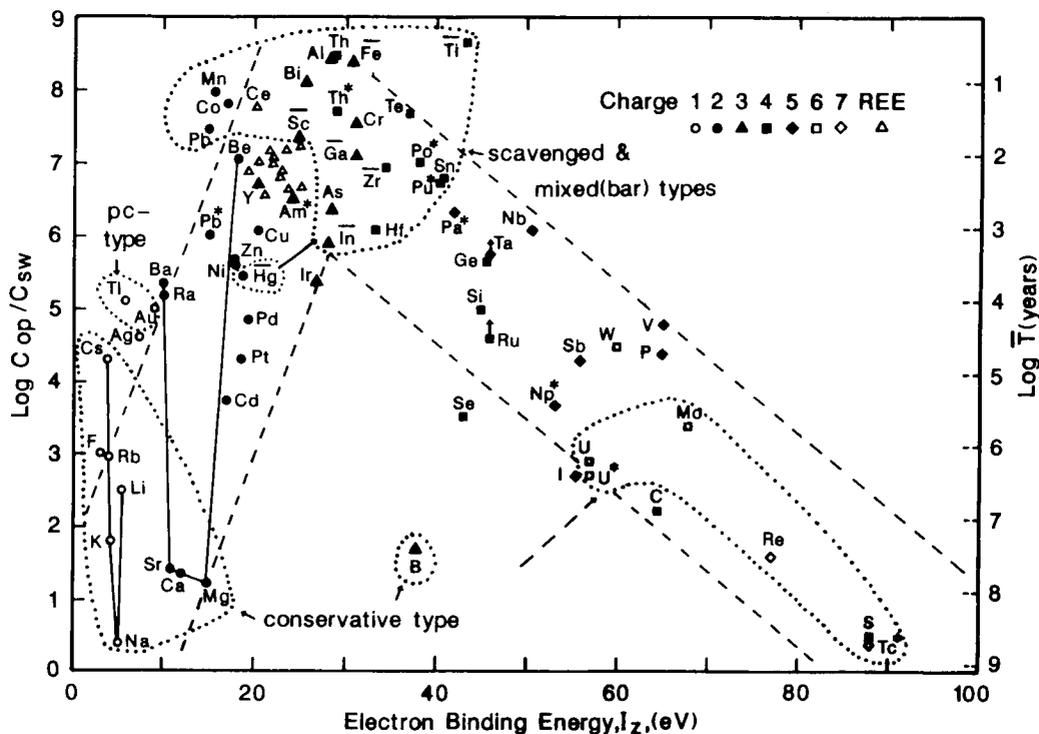


FIG. 4. The elemental concentrations in the oceanic pelagic clays divided by those in the seawater ($\log C_{op}/C_{sw}$) are plotted against the electron binding energies to cations (I_z). The alkali and alkaline earth elements are connected by solid lines. The conservative type (*c*), pseudo-conservative type (*pc*), and the scavenged (*s*) plus mixed (*s + n*) types (elements with bar) are grouped by the dotted enclosures. Ungrouped elements are nutrient types. The elements with an asterisk are radionuclide data. The Ta and Ru with vertical arrows are minima in their $\log C_{op}/C_{sw}$ values.

RuO_4^0 and OsO_4^0 are small, one would also expect their $\log C_{op}/C_{sw}$ values to be low, in direct contradiction with the observation for Ru (Table 2 and Fig. 4). Therefore, Ru and Os must exist in seawater as lower oxidation states species (e.g., II, III, and IV) through biological activities. For example, the $\log *K_1$ for Ru^{+3} is quite high (Fig. 2), and Ru^{+3} can, therefore, be readily absorbed by the hydrolyzed oxide surface and exhibit relatively high $\log C_{op}/C_{sw}$ value. Indeed, the chemical speciation of Ru in seawater can be very complicated (MARAZOVIC and PUCAR, 1967; DAWSON and DUURSMA, 1974).

For ease of comparison, the types of concentration profiles are also grouped in Fig. 4. The scavenged and mixed types are all clustered at the tip of "inverted V" with very high $\log C_{op}/C_{sw}$ values or short oceanic mean residence times. The conservative type elements all have very low $\log C_{op}/C_{sw}$ values or long oceanic mean residence times except for Cs. The apparent high $\log C_{op}/C_{sw}$ value for Cs may be in part caused by a large intra-lattice detrital component of Cs in the sediments, which, of course, are not adsorbed. According to factor analysis, the oceanic pelagic clays also contain a significant fraction of intra-lattice detrital components for Al, Si, Rb, K, Cr, etc. (LI, 1982a). The nutrient type elements have intermediate $\log C_{op}/C_{sw}$ values except I and C, which happen to have low C_{op}/C_{sw} values and the smallest concentration differences between the surface and deep waters and between the deep Atlantic and deep Pacific waters among all nutrient type elements, and thus are closer to the conservative type

elements. The plot of $\log C_{sh}/C_{sw}$ vs. I_z values would be similar to Fig. 4, with only minor adjustments according to Fig. 1, and was thus omitted here.

The systematic changes in the chemical speciation of elements in seawater with respect to $\log C_{op}/C_{sw}$ and I_z are summarized in Fig. 5. In general the speciation changes from hydrated cations \rightarrow chloride complexes \rightarrow carbonate complexes \rightarrow to fully hydrolyzed hydroxocomplexes when both $\log C_{op}/C_{sw}$ and I_z increase systematically from Na^+ to Th^{+4} . Then, the speciation changes to negatively charged hydroxo complexes \rightarrow weak oxyacids \rightarrow partly to totally deprotonated oxyacids \rightarrow to totally deprotonated strong acids, when the I_z of the central metal of hydroxocomplexes and of oxyanions continue to increase, but the $\log C_{op}/C_{sw}$ to decrease.

KINNIBURGH and JAMES (1978) showed that the adsorption of Hg^{+2} by hydrous iron oxide gel is considerably reduced by the presence of chloride ion, and there is no significant concurrent adsorption of added ^{36}Cl radiotracer. The implication is that Hg^{+2} exists in solution mainly as HgCl_4^{-2} but is adsorbed not as a chloride complex, but most likely as $\text{Hg}(\text{OH})_2^0$ (LECKIE and JAMES, 1979). It is apparent that chloride (and probably also carbonate) does not act as an effective bridging ligand onto a hydrous oxide surface during the adsorption process. In contrast, the OH^- ligand is an effective bridging ligand. Therefore, cations with high $\log *K_1$ values are most likely adsorbed by hydrous oxides as hydroxocomplexes, even though the predominant forms in solution may not necessarily be hydroxocomplexes (LECKIE and

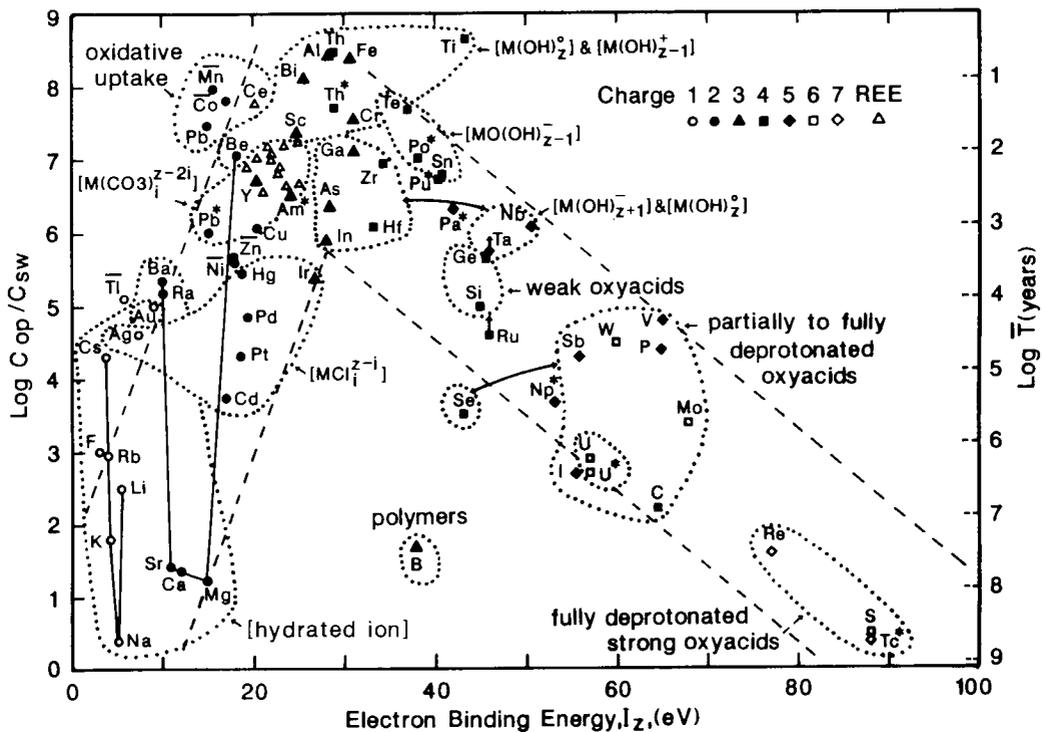


FIG. 5. The systematic change in the chemical speciations as functions of $\log C_{op}/C_{sw}$ and I_z . The elements with a bar indicate the dominance of both hydrated cationic and chloride complex forms. The elements within the same dotted enclosure or two dotted enclosures connected by a double headed arrow have the same type of complexation. The elements with an asterisk are radionuclide data.

JAMES, 1979). The $\log C_{op}/C_{sw}$ for elements forming negatively charged hydroxo- and hydroxo-oxocomplexes also become lower than those forming neutral or positively charged hydroxocomplexes (Fig. 5), probably partly reflecting the electrostatic repulsive effect by the negatively charged silicate particles (positive ΔG_{coll}).

DEEP SEA MANGANESE NODULES AND SEAMOUNT MANGANESE CRUSTS

Deep sea manganese nodules and seamount manganese crusts mainly consist of ferromanganese oxides and phosphate phases with minor detrital aluminosilicate phases. The major phases are precipitated from the seawater and many associated elements are also derived from seawater (so-called hydrogenous). Therefore, it is very instructive to find out whether or not the partition of elements between the manganese nodules (C_{mn}) and seawater (C_{sw}) is again related to the electron binding energies I_z . (Figure 6 provides such verification. The similarities between Fig. 6 and Fig. 4 are evident, including the reversed trends for alkali and alkaline earth elements, high K_d values for Mn, Co, Pb, Ce, and Tl, and low K_d values for B and Se. One can conclude that the partition of elements between manganese nodules (as well as manganese crusts) and seawater is again in accord with the adsorption model of JAMES and HEALY (1972).

Figure 7 shows the elemental concentrations in the deep sea manganese nodules (data from Table 1) and the Pacific seamount manganese crusts (data from MANHEIM and LANE-

BOSTWICK, 1989; APLIN, 1984 for REE; HALBACH et al., 1989 for Pd; AMOSSÉ and LE SUAVÉ, 1990 for Rh and Au) divided by those in the oceanic pelagic clays (Table 1), arranged more or less in the increasing order of $\log C_{op}/C_{sw}$ values. The elements are also classified according to their preference to todorokite, vernadite (i.e., δMnO_2), iron oxides, phosphates, and aluminosilicate phases of manganese deposits as previously discussed by LI (1982a), using statistical factor analysis and correlation matrix techniques. The classification of elements in seamount manganese crusts is based on the correlation matrices given by MANHEIM and LANE-BOSTWICK (1989).

The most important difference between the normal deep sea manganese nodules and seamount manganese crusts is that todorokite is dominant over vernadite in the nodules, while vernadite is the dominant manganese oxide phase in the seamount crusts (USUI, 1979). Todorokite forms tunnel structures with building blocks of octahedral $[(Mn^{+4}, Mn^{+2})O_6]$ units (OSTWALD, 1988, and references therein). The tunnels contain mono-, divalent cations (such as alkali, alkaline earths, etc.) and H_2O molecules, while the di-valent transition metals can easily substitute for Mn^{+2} in the $[(Mn^{+4}, Mn^{+2})O_6]$ units. An approximate schematic formula for todorokite is $(R_2O, RO)_{0.2} MnO_2 \cdot 0.6 H_2O$ where the R are the above-mentioned cations. Todorokite can hardly accommodate highly hydrolyzable cations (such as Au^+ , Be^{+2} , Pd^{+2} , tri- and tetravalent cations with high $\log * K_1$ values). Therefore, it is not surprising to find that only the mono- and di-valent cations with relatively low to moderate

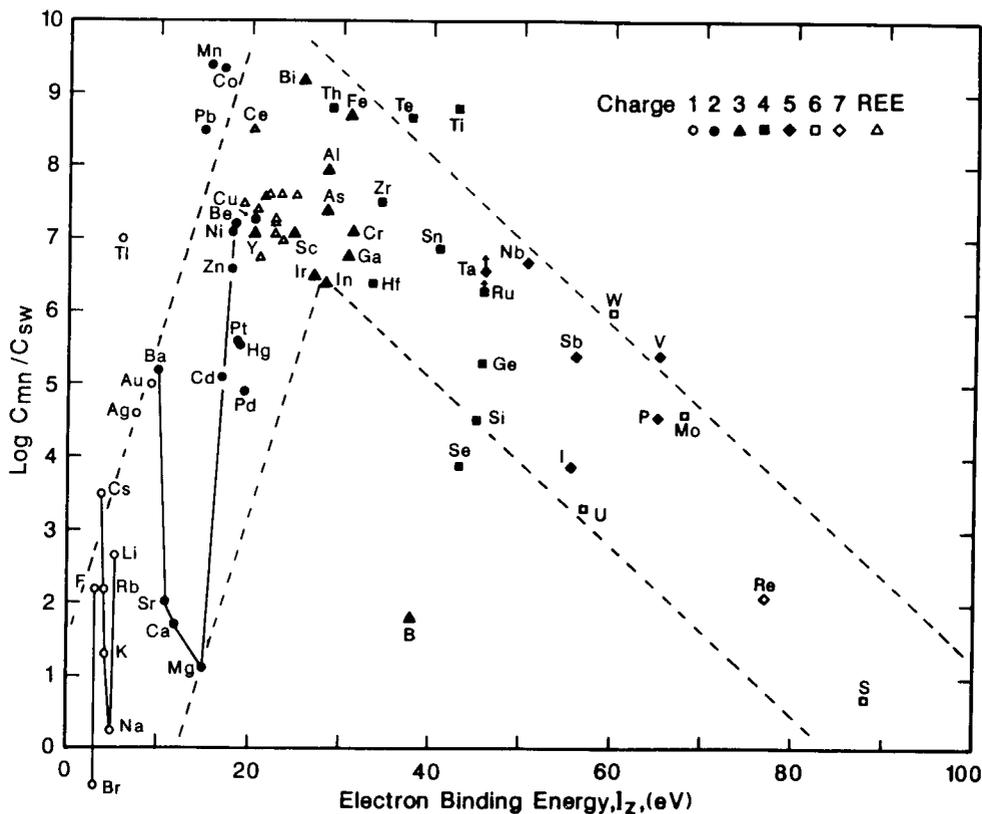


FIG. 6. The elemental concentrations in the marine manganese nodules over those in seawater ($\log C_{mn}/C_{sw}$) vs. the electron binding energy to cations (I_2).

hydrolysis constants are covariant with Mn contents in deep sea nodules (e.g., Na, Mg, Ag, Ba, Cd, Zn, Ni, Cu; LI, 1982a). The obvious exceptions are Co, Pb, and Pt, which are often covariant with Fe contents instead (SKORNYAKOVA, 1979; LI, 1982a; TERASHIMA et al., 1988), and are highly enriched in the nodules as compared to the pelagic clays. One plausible explanation has been that Co^{+2} , Pb^{+2} , and Pt^{+2} are easily oxidized into Co^{+3} , Pb^{+4} , and Pt^{+4} at the nodule surface, thus precluding their incorporation into todorokite but enhancing their sorption onto hydrous iron oxide phases (e.g., USUI, 1979; GOLDBERG et al., 1986). The similar enrichments of Rh, Ir, Ru (and probably Os also) but not Pd in the nodules may also be explained by their oxidation from di- or trivalent to tetra-valent states (GOLDBERG et al., 1986).

Vernadite, the dominant phase in seamount crusts, is a poorly ordered hydrated manganese oxide. Marine vernadite may be represented roughly by the formula $(R_2O, RO, R_2O_3)_{0.5} \cdot \text{MnO}_2 \cdot (1 \sim 2)\text{H}_2\text{O}$, where R represents mono- to tri- or even tetravalent cations which are incorporated into vernadite through both surface adsorption and substitution of Mn in the $[(\text{Mn}^{+4}, \text{Mn}^{+2})\text{O}_6]$ units. Vernadite also can easily form epitaxial intergrowths with goethite (OSTWALD, 1988). Among goethite, vernadite, and aluminosilicate phases, vernadite shows the highest K_d for divalent cations in seawater, while aluminosilicate shows the lowest (LI et al., 1984; TAKEMATSU, 1979). The pH_{zpc} for aluminosilicates is in the range of 2 to 4.6; for vernadite, 2.8; and goethite, 7.5 to 8.3 (STUMM and MORGAN, 1981). Therefore, both ver-

nadite and aluminosilicate are negatively charged in seawater pH of 8, and can electrostatically attract positively charged ions ($\Delta G_{\text{coul}} < 0$) in addition to the chemical bond formation (ΔG_{chem}). Goethite is only slightly charged or neutral in seawater pH of 8; thus, the adsorption of ions onto goethite is mostly through chemical bond formation. Vernadite and goethite are almost equally effective in adsorbing cations with high $\log^* K_1$ in seawater (LI et al., 1984), because the strong chemical bond formation (ΔG_{chem}) overwhelms any electrostatic (ΔG_{coul}) and solvation (ΔG_{soliv}) effects. Why vernadite and goethite have much higher K_d values for many cations than pelagic clays (LI et al., 1984; TAKEMATSU, 1979) may be explained as follows: The intrinsic acidity constants (for a reaction of $\equiv X - \text{OH} \leftrightarrow \equiv X - \text{O}^- + \text{H}^+$; SCHINDLER and STUMM, 1987) for hydrolyzed goethite and vernadite may be much smaller than those for pelagic clays; therefore, the chemical bond strength between the adsorbed metal and oxygen of hydrolyzed solid surface is much stronger for goethite and vernadite than for pelagic clays. Another possibility is that the dielectric constants for aluminosilicate minerals range from 4.5 to 8 (KELLER, 1966), and for vernadite about 32 (MURRAY, 1975), thus vernadite (and probably also goethite) has a much smaller positive ΔG_{soliv} term than clays, and inhibits adsorption of hydrated cations to a lesser extent.

According to the correlation matrices for the seamount manganese crust data from the whole Pacific Ocean and the Marshall Islands (MANHEIM and LANE-BOSTWICK, 1989), the elements are likely partitioned into (1) phosphate phases

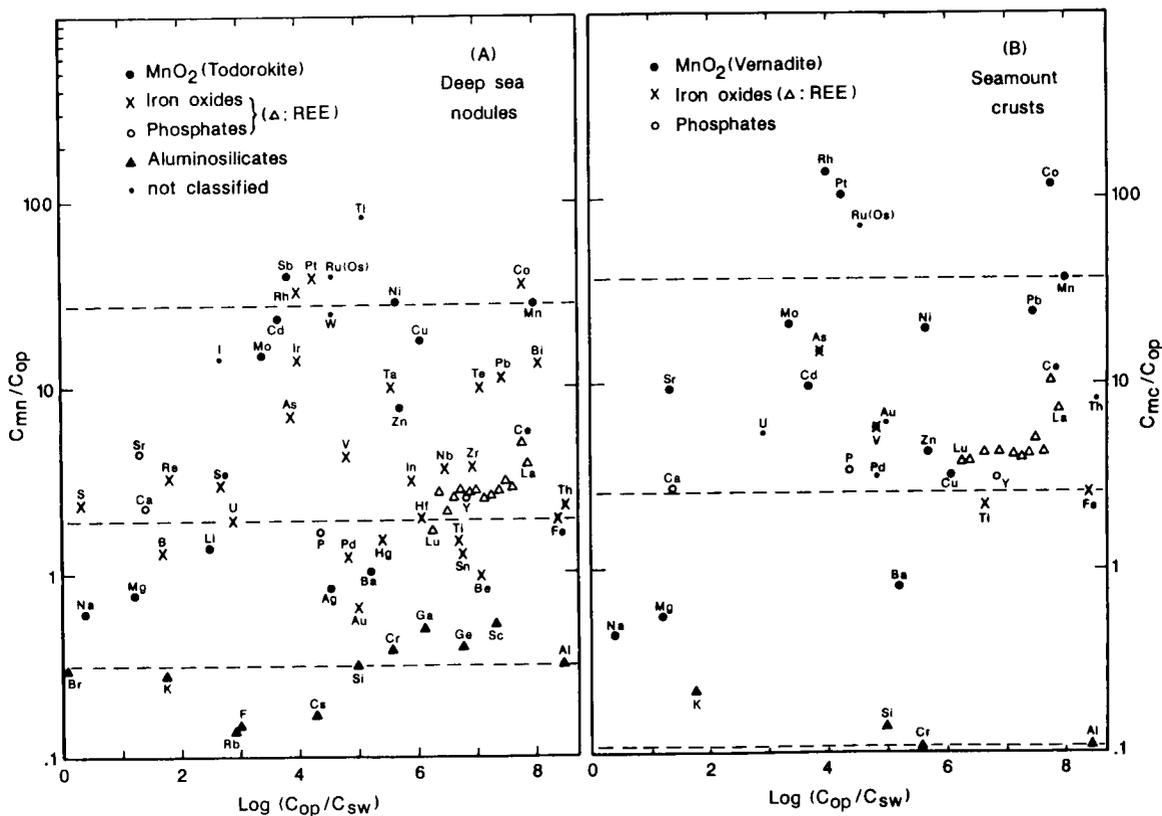


FIG. 7. The elemental concentrations in (A) the deep sea manganese nodules over those in the pelagic clays ($\log C_{mn}/C_{op}$) and (B) seamount manganese crusts over those in the pelagic clays ($\log C_{mn}/C_{op}$) are plotted against the $\log (C_{op}/C_{sw})$. The horizontal dashed lines pass through the Al, Fe, and Mn data points. The dominant residing phases for the elements are mostly based on the factor analysis and the correlation matrices.

(Ca, P, C, Y; partially Pt), (2) detrital aluminosilicate phases (Al, Si, K; partially Fe and Ti), (3) goethite (Fe, Ti; partially As and V), and (4) vernadite (Mn, Co, Ni, Cd, Zn, Mg, Na, Mo; partially As, V, Sr, and Pb) along with unidentified subphase (Cu, Ba, Ce; partially Ni, Pt, Sr, and Pb). Unlike in the manganese nodules, the Co, Pb, and Pt are no longer associated with iron oxide phases in crusts. The strong association of Pt with both phosphates and an unidentified subphase is intriguing and needs to be verified independently. HEIN *et al.* (1988) and AMOSSÉ and LE SUAVÉ (1990) show a close correlation between the concentrations of Pt and Rh in the seamount manganese crusts. The approximately one hundred-fold enrichment of the platinoids (Pt, Rh, Ru, but excluding Pd) and Co in seamount crusts relative to pelagic clays (Fig. 7b) may again be explained by the oxidative uptake processes at the crust surface as discussed earlier, in addition to vernadite as an efficient scavenger. In contrast, HALBACH (1986) advocated that the reduction of divalent Pt to metal Pt explains the Pt enrichment. However, a later calculation by HALBACH *et al.* (1989) indicated that the reduction of Pt^{+2} to Pt^0 can take place only under a condition of abnormally high Mn^{+2} concentration. Contrary to the argument of HALBACH *et al.* (1989), any negatively charged chloro-complex such as $PtCl_4^{-2}$ or $PtCl_6^{-2}$ can still be readily adsorbed by the negatively charged vernadite as long as the negative ΔG_{chem} term overwhelms the positive ΔG_{coul} term.

The higher contents of Na, Mg, Ba, Ni, Cu, Zn, and Cd in the deep sea nodules than in the seamount crusts (Fig. 7) can be explained by the mineralogical difference (todorokite vs. vernadite) superimposed over high concentrations of Ba, Ni, Cu, Zn, and Cd in the deep ocean water and the interstitial water of deep sea sediments as compared with those in the shallow ocean water. The interstitial water provide metal fluxes to deepsea nodules. The concentrations of REEs other than Ce in seawater increase with water depth (DE BAAR *et al.*, 1985), but the contents of REEs are higher in seamount crusts than in deep sea nodules. The implication is that both vernadite and goethite phases in the seamount crusts contribute to the scavenging of REEs. However, the covariance of REEs with Fe positively and with Mn negatively in the seamount crusts (APLIN, 1984) suggests that goethite is probably a more effective scavenger of REEs than vernadite, on a unit surface area or mass basis. In contrast, the REEs in the deep sea nodules are mostly associated with goethite and phosphate phases (ELDERFIELD *et al.*, 1981), because todorokite can hardly accommodate tri-valent REEs and actually dilutes the REE concentrations in the nodules.

LIVING MARINE ORGANISMS

The constituents of marine phytoplankton are almost entirely extracted from seawater. The incorporation of metals

should be primarily dependent on the binding of metals to hydrophilic functional groups (such as $-\text{COOH}$, $-\text{NH}_2$, $-\text{SH}$, $-\text{OH}$, etc.) of proteins, which are embedded in the lipid bilayer of cell membranes, and subsequent transport of organometallic complexes into the cell interior through complicated biochemical mechanisms (HUGHES, 1981; OCHIAI, 1987). The complexation constants of various metals to many organic ligands ($\log \beta^L$) are again shown to be linearly correlated with the $\log *K_1$ (BALISTRERI et al., 1981) or with I_z as shown in Fig. 8, using the EDTA ligand as an example. Therefore, one can expect again a systematic change of $\log C_{\text{org}}/C_{\text{sw}}$ as a function of I_z as demonstrated in Fig. 9. Although the $\log C_{\text{org}}/C_{\text{sw}}$ values change only about seven orders of magnitude, the general trend is again very similar to those for $\log C_{\text{op}}/C_{\text{sw}}$ (Fig. 4) and $\log C_{\text{mn}}/C_{\text{sw}}$ (Fig. 6), including the reversed trends for the alkali and alkaline earth elements and the high $\log C_{\text{op}}/C_{\text{sw}}$ for Mn, Co, Pb, and Tl. Apparently, the adsorption model of JAMES and HEALY (1972) applies to organic matter equally well. The high $C_{\text{org}}/C_{\text{sw}}$ for C, N, and P are as expected because these elements are the major building blocks of organic matter. The $C_{\text{org}}/C_{\text{sw}}$ for the radionuclides, designated with an asterisk in Fig. 9, were calculated from their activities in plankton and seawater samples from the Caribbean Sea (KHARKAR et al., 1976; HUH and BACON, 1985) or from laboratory culture (FISHER, 1982, 1985; for Tc, Pu, and Am).

Since both $\log C_{\text{org}}/C_{\text{sw}}$ and $\log C_{\text{op}}/C_{\text{sw}}$ are related to the I_z , the former two also should relate to each other as shown in Fig. 10. The often observed inverse relationship between $\log C_{\text{org}}/C_{\text{sw}}$ and the logarithm of the mean oceanic residence times of elements ($\log \bar{T}$; YAMAMOTO, 1972) is as expected, because $\log \bar{T}$ is inversely related to $\log C_{\text{op}}/C_{\text{sw}}$ as shown

earlier. Because the elements designated with solid circles in Fig. 10 all fall roughly on a 45 degree diagonal line (a slope of one), their relative abundances in the organisms and pelagic clays are similar. These elements are mainly the A-type ions (cations and anions with electron configurations of noble gases as well as $[\text{Xe}]4f^{14}$), the lanthanides, the first transition metal series other than Cu and Zn; and were called the "biophobe" elements by LI (1984), regardless of their actual biological function. In addition to C, N, and P, the elements highly enriched in marine organisms relative to pelagic clays [the open and solid triangles in Fig. 10 with an enrichment factor, defined here as $(C_i/C_{\text{Fe}})_{\text{org}}/(C_i/C_{\text{Fe}})_{\text{op}}$ in the order of 10 to 10^4] are mainly the A-type ions with very low $\log C_{\text{op}}/C_{\text{sw}}$ values, the B-type ions (with electron configurations of nd^{10} , $nd^{10}(n+1)s^2$), the platinoids, and the actinides. These elements are called the "biophile" by LI (1984), again regardless of their actual biological function. Their enrichments can be explained in the following:

The electrons in the d subshell of the B-type and platinoid cations are highly polarizable (LI, 1991), thus these cations form extra strong chemical bonding with organic ligands, especially those containing donor atoms of sulfur and nitrogen (e.g., $-\text{NH}_2$ and $-\text{SH}$). The severe toxicity of most highly polarizable cations like Cu^+ , Cu^{2+} , Ag^+ , Pd^{2+} , Rh^{3+} , Ru^{4+} , Au^+ , Au^{3+} , Hg^+ , Hg^{2+} , Pt^{2+} , Pt^{4+} , Ir^{3+} , Ir^{4+} , and Os^{4+} (LI, 1991) are in part caused by their blockage of vital functional groups in biomolecules (OCHIAI, 1987). The important difference between the actinide and lanthanide cations is that the energy level difference between 5f and 6d subshells in actinides is in general very small as compared to those between 4f and 5d subshells in lanthanides. Therefore, the electrons in the 5f subshell of actinides can easily move into the

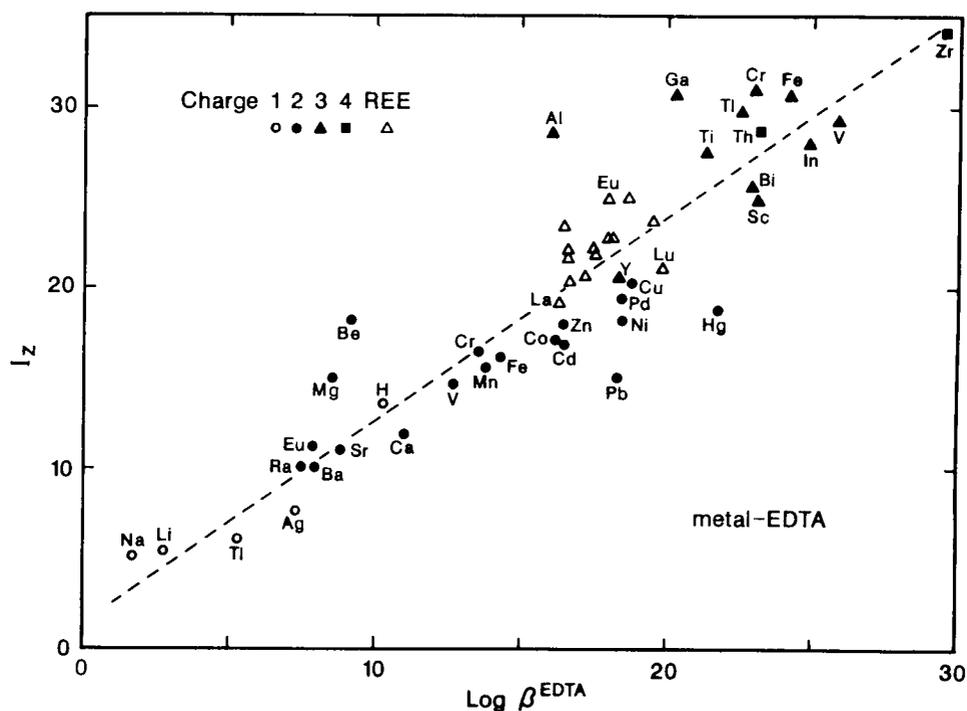


FIG. 8. The electron binding energies to cations (I_z) vs. the first complexation constants of cations to fully deprotonated EDTA ligand ($\log \beta^L$; SCHWARZENBACH, 1957; DEAN, 1985).

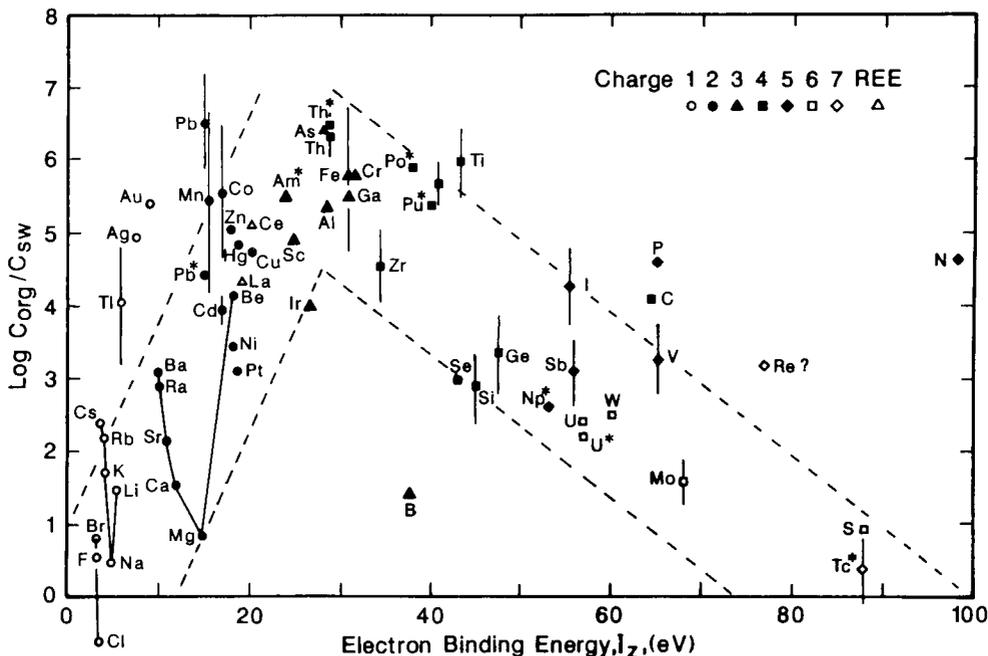


FIG. 9. The elemental concentrations in the living marine organisms over those in the seawater ($\log C_{org}/C_{sw}$) vs. the electron binding energies to cations (I_2). The elements with an asterisk are radionuclides. The vertical bars are the range of concentrations given by BOWEN (1979).

6d subshell (thus becoming highly polarizable) to form strong chemical bonds with various organic ligands, while no 4f subshell electrons of lanthanides can move to 5d subshell

(COTTON and WILKINSON, 1988). Na^+ , K^+ , Mg^{+2} , and Ca^{+2} can be effectively transported through the cell membrane by the so-called sodium pump (Na/K-ATPase) and calcium pump (Ca/Mg-ATPase), as well as by the so-called ionophores (ion-carrier) and channels for these cations (OCHIAI, 1987).

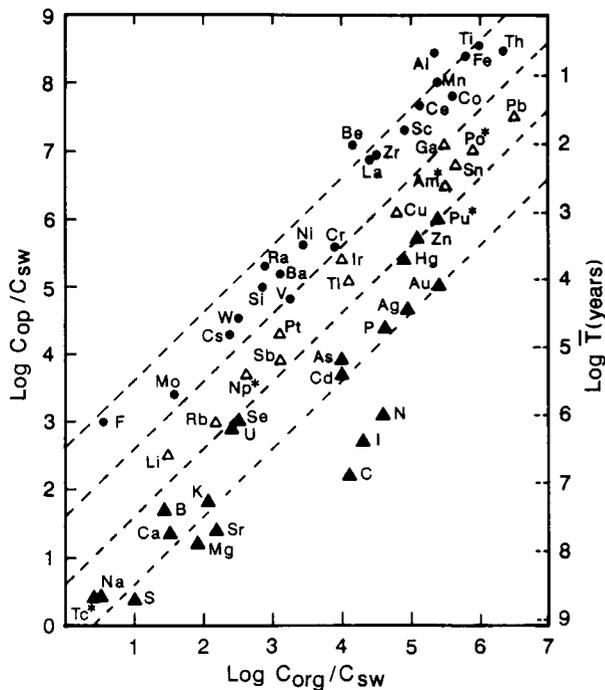


FIG. 10. The plot of $\log C_{op}/C_{sw}$ or $\log \bar{T}$ (mean residence time) vs. $\log C_{org}/C_{sw}$. The dashed lines have a slope of one and are one order of magnitude apart. The solid circles are the "biophobe" elements with the enrichment factors $(C_i/C_{Fe})_{org}/(C_i/C_{Fe})_{op}$ of roughly 1 to 10 and the triangles the "biophile" elements with the enrichment factors of greater than 10 to 100 (open) and of greater than 100 (solid). The elements with an asterisk are radionuclides.

CONCLUSIONS

- 1) The partition of elements between marine solid phases (pelagic clays, manganese nodules and crusts, living organisms) and seawater can be, to the first approximation, explained by the adsorption model of JAMES and HEALY (1972). The $\log K_d$ values for alkali and alkaline earth elements other than Li and Be are closely related to the ΔG_{soliv} term. However the $\log K_d$ values for most other elements are dominated by the ΔG_{chem} term (or I_2). Also, the high $\log K_d$ values for Tl, Mn, Co, Ce, and Pb are indicative of their oxidative uptake mechanisms at solid-liquid interface. The composition of seawater is ultimately controlled by the composition of its source materials (the crustal igneous rocks and the primary magmatic volatiles) and the physicochemical principles regulating the adsorption processes between the pelagic clays and seawater.
- 2) The conservative type elements in the ocean water column have the lowest C_{op}/C_{sw} values or the longest mean oceanic residence times, and the scavenged and mixed types the highest C_{op}/C_{sw} values or the shortest mean oceanic residence time (Fig. 4). The nutrient type elements are mostly in between.
- 3) The major difference between deep sea nodules and seamount crusts in terms of the concentrations of various elements and the inter-element relationship can be attributed to the difference in their manganese oxide phases, i.e.,

todorokite in nodules and vernadite (δMnO_2) in crusts. The enrichment of platinoids (Pt, Ir, Rh, Ru, thus probably Os, but not Pd) in both deep sea nodules and seamount crusts relative to pelagic clays can be explained by the oxidative uptake processes at the interfaces of the metal oxides.

- 4) The enrichment of the B-type and platinoid cations in living marine organisms relative to the pelagic clays (normalized to Al or Fe) are probably related to the formation of strong complexes between these cations and organic ligands which contain sulfur and nitrogen donor atoms. The enrichment of actinides but not lanthanides in marine organisms relative to pelagic clays is related to the fact that the 5f subshell electrons of actinides can move to 6d subshell to form stronger chemical bonds with many organic ligands.

Acknowledgments—Helpful comments by Drs. J. W. Murray, P. H. Santschi, D. R. Turner, and K. Chave are acknowledged. Dr. K. J. Orians kindly provided her unpublished data. The editorial help from Ms. D. Henderson and D. Sakamoto is greatly appreciated. This is SOEST contribution no. 2668.

Editorial handling: F. J. Millero Jr.

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