

THE SIGNIFICANCE OF OXYGEN AS OXIDES AND HYDROXIDES IN CONTROLLING THE ABUNDANCE AND RESIDENCE TIMES OF ELEMENTS IN SEAWATER

M.D. KUMAR

National Institute of Oceanography, Dona Paula, Goa 403 004 (India)

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ABSTRACT

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A model is presented which signifies the role of oxygen (as oxides and hydroxides) in controlling the composition of seawater. Using the regression equations

$$\log K_{sw} = -0.77 + 0.03\Delta O^2M \text{ and } [M]_{sw} = K_{sw}[M]_{crust}$$

$$\log \bar{t}_y = 4.73 + 0.04\Delta O^2M$$

respective concentration and residence times for the unknown elements can be estimated. Geometric and statistical indices of Legget and Williams (1981) are used to evaluate the accuracy of the model. This reveals from the known values of ΔO^2M that the present model estimates $\log \bar{t}_y$ values within a factor of 1.77. The predicted oceanic residence times for Am, Ir, Ra and Rh are 3.6×10^2 , 3.7×10^2 , 2.2×10^5 and 6.4×10^2 years, respectively.

INTRODUCTION

One of the recent topics in chemical oceanography, at present receiving much attention, is the understanding of the control of seawater composition. Apart from the atomic properties of elements (Whitfield and Turner, 1979; Kumar, 1983), oxygen plays a key role in the control of the composition of natural waters (Horne, 1979) by participating in biogeochemical reactions. The mineral particles and suspended particulate matter found in the marine environment consist of either hydroxides (of Al, Fe, Th, etc.) formed in-situ or terrestrial particles carried by rivers. The surface of these particles is coated with hydroxyl ions as a result of the interaction between oxides and seawater, or the adsorption of a hydroxyl ion in a carboxyl group onto the respective particle (Balistrieri et al., 1981; Li, 1981). Oxygen contributes to marine chemical reactions in the form of oxides, hydroxides and hydroxyl ions. Also, since the oxides constitute much of the mineral content in the earth's crust, oxygen (as its compounds) is significant in the control of seawater composition.

The present model assumes that seawater attains its cationic composition

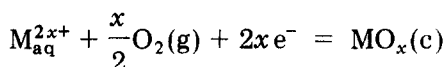
through the dissolution of the oxides of respective elements and subsequently that cations undergo adsorption-desorption equilibria as their hydrolysed complexes in seawater, before being deposited as sediments (Fig. 1).

CALCULATIONS AND DATA SOURCES

The parameter $\Delta O^{2-}M$ is defined as

$$\Delta O^{2-}M = \frac{1}{x}(\Delta G_f^0 MO_x - \Delta G_f^0 M_{aq}^{2x+})$$

where x = cation valence/2 (Tardy and Garrels, 1976). ΔG_f^0 is the Gibbs free energy of formation of an oxide or aqueous cation at 25°C and 1 atm. pressure. $\Delta O^{2-}M$ is the free energy of reaction when a metal oxide is formed from its aqueous metal ion and molecular oxygen.



Hence, $\Delta O^{2-}M$ is a negative value of free energy of the reaction (ΔG_r^0) in which aqueous metal ion is formed from its oxide. $\Delta O^{2-}M$ values (kcal mol⁻¹) are either obtained from Tardy and Garrels (1976) or calculated from the values of Latimer (1952).

Elemental concentrations in seawater ($\log [M]_{sw}$) are obtained from Whitfield (1979). $\log \bar{t}_y$ of an element y in seawater is calculated based on its sedimentation rate taken from Li (1982). Seawater-crustal rock partition coefficients of elements ($\log K_{sw}$) are calculated from the listed values of Turner et al. (1980). First hydrolysis constants of metal ions ($\log \beta^0 M(OH)^{(2x-1)+}$) are selected from Baes and Mesmer (1976) and Turner

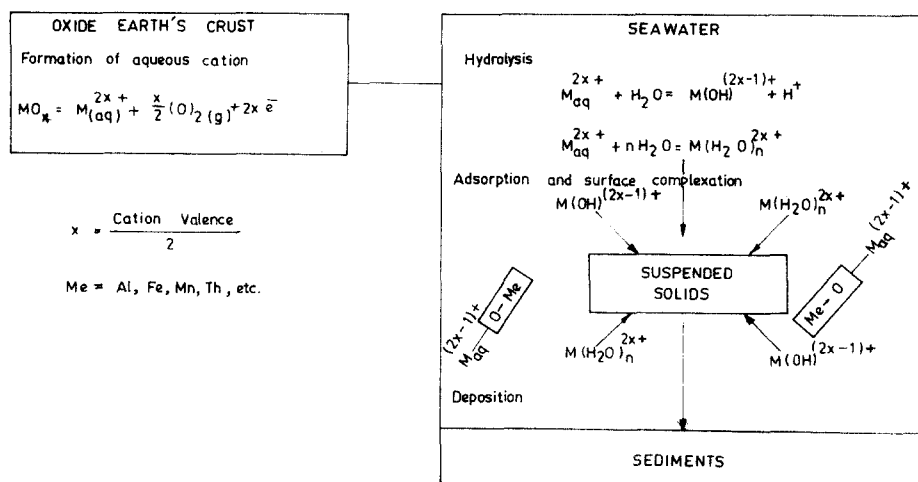


Fig. 1. Model considered for the role of oxygen in seawater composition.

et al. (1981) and corrected ($\log \beta^* M(OH)^{(2x-1)+}$) for seawater ionic strength (i.e., $I = 0.72$).

RESULTS AND DISCUSSION

With the increase in ΔO^2-M , the formation of the aqueous cation from its oxide is favoured. Usually, exogenic processes occur in the uppermost few kilometers of the earth crust. After formation, as a result of weathering and subsequent dissolution, these cations reach the sea via streams and rivers. Figure 2 shows the linear relationship between ΔO^2-M and $\log [M]_{sw}$. Many elements (except about six) fall within the 1σ limit and the plot has a correlation coefficient (r) of 0.55 (Table I, eq. 1) which is significant at the 0.001 level (Reeves and Brooks, 1978). The free energy of formation of aqueous alkali and alkaline earth cations from their oxides and oxide minerals is low (i.e., high ΔO^2-M) and as a result not only favours their formation in larger quantities but also stability in aqueous solutions. Since the same free energy is higher for transitional elements, these highly reactive ions might be formed in smaller quantities. Due to the dependence of the quantity of metal ion in seawater on its abundance in the earth's crust (Perel'man, 1967) it is felt that the latter should also be included in the model to predict $\log [M]_{sw}$ of unknown elements with relatively good accuracy. Figure 3 depicts the relation between ΔO^2-M and $\log K_{sw}$ and Table I shows the parameters of the regression analyses for $\log K_{sw}$ with ΔO^2-M (Table I, eq. 2), and $\log [M]_{sw}$ (Table I, eq. 3). In both the cases r is significant at the 0.001 level (Table I).

In Figs. 2 and 3 positively deviated Na, Mg and Ca have greater crustal abundance than negatively deviated Ce, Cs and Eu (Whitfield, 1979).

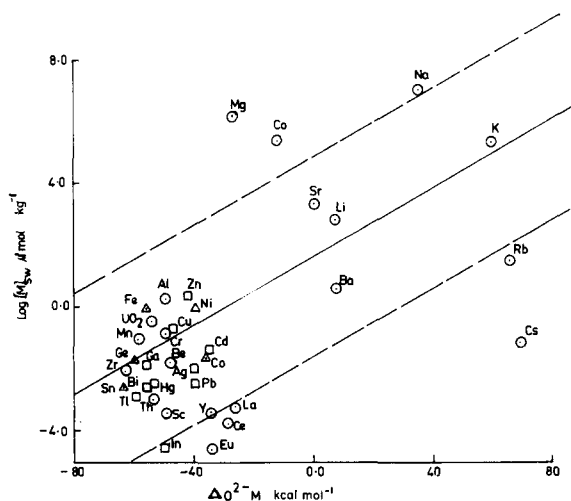


Fig. 2. Relationship between ΔO^2-M and $\log [M]_{sw}$. (○) lithophilic; (□) chalcophilic; and (△) siderophilic elements.

TABLE I

Regression relations ($y = mx + c$) found between various parameters for the present model

Equation No.	Number of points	x	y	m	c	r_{obs}^a	$\sigma_{y,x}^b$	r_{exp}^c
1	36	$\Delta\text{O}^{2-}\text{M}^d$	$\log [\text{M}]_{\text{sw}}^e$	0.05	+ 1.20	+ 0.55	3.23	0.52
2A	36	$\Delta\text{O}^{2-}\text{M}$	$\log K_{\text{sw}}$	0.03	- 0.77	+ 0.54	1.97	0.52
2B ^f	4	$\Delta\text{O}^{2-}\text{M}$	$\log K_{\text{sw}}$	0.07	+ 0.15	- 0.77	1.45	0.99
3	36	$\log K_{\text{sw}}$	$\log [\text{M}]_{\text{sw}}$	1.16	+ 1.28	+ 0.76	3.00	0.52
4	48	$\log \beta^*\text{M}(\text{OH})^{(2x-1)+}$	$\log \bar{t}_y$	0.24	+ 1.52	- 0.49	2.02	0.46
5A	34	$\Delta\text{O}^{2-}\text{M}$	$\log \bar{t}_y$	0.04	+ 4.73	+ 0.59	2.23	0.53
5B ^f	4	$\Delta\text{O}^{2-}\text{M}$	$\log \bar{t}_y$	0.10	+ 5.35	- 0.91	1.60	0.99

^a Correlation coefficient observed.

^b Standard deviation of y on x.

^c Correlation coefficient that must be exceeded for the correlation to be significant at the 0.001 significance level (Reeves and Brooks, 1978).

^d kcal mol⁻¹.

^e $\mu\text{mol kg}^{-1}$ seawater.

^f Alkaline earths (except Be).

Although Ag, Bi and Hg have relatively low crustal concentrations (Whitfield, 1979), they exhibit relatively higher values (Figs. 2 and 3), which might be due to their strong complexation with ligands (Ag-Cl, Bi-OH and Hg-Cl; Turner et al., 1981). Slight positive deviations for Ni and Zn can be attributed to additional fluxes from volcanic emanations, marine aerosols, pollution, etc. (Martin and Meybeck, 1979). In spite of relatively high contents in the crust, the low $\log [\text{M}]_{\text{sw}}$ and $\log K_{\text{sw}}$ values for La and Sc are due to either precipitation or adsorption onto particulate matter, of which the

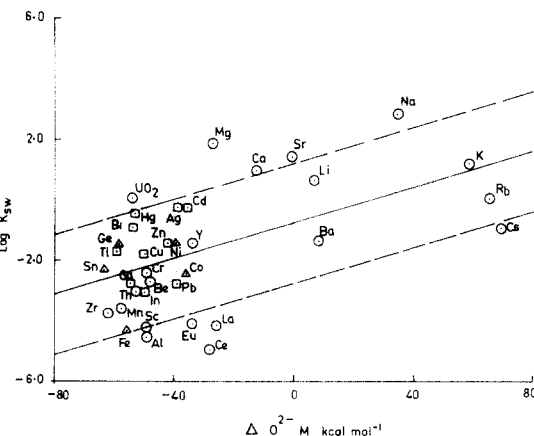


Fig. 3. The relationship of $\Delta\text{O}^{2-}\text{M}$ with $\log K_{\text{sw}}$ (symbols are as in Fig. 2).

latter process is more important in seawater. However, in natural waters metal concentrations are very low and their precipitation as hydroxides is not likely (Perel'man, 1967; Brewer, 1975), except for a few elements (e.g., Al, Fe, Mn, etc.). As the Ionic Potential (IP) increases up to about 7, the tendency to form metal hydroxides is enhanced (Perel'man, 1967) and elements show low $\log \bar{t}_y$ values (with a few exceptions); but a further increase in IP has shown long residence times (Kumar, 1983) owing to metal oxyanion formation. Mainly lithophilic elements contribute to the linear relationships (Figs. 2 and 3), supported by chalcophilic and siderophilic elements. From the above relations (Figs. 2 and 3), it is possible to find the expected concentrations for the unknown elements in seawater. After calculating the K_{sw} value (Table I, eq. 2A), the $[M]_{sw}$ values are calculated with relatively good accuracy for Ir, Ra and Rh (using their crustal abundances, $[M]_{crust}$ taken from Rösler and Lange (1972)) and they are listed in Table II. Simultaneously, $[M]_{sw}$ values are calculated from Am, Ir, Ra and Rh using eq. 1 (Table I) which are listed in parentheses in Table II. The observed concentration of radium in seawater ($1 \times 10^{-10} \mu\text{mol l}^{-1}$, Goldberg, 1965; Brewer, 1975) is nearer to the value ($1 \times 10^{-6} \mu\text{mol kg}^{-1}$) estimated from eq. 2A than to the value ($112 \mu\text{mol kg}^{-1}$) found from eq. 1. The value for $[Ra]_{sw}$ found from eq. 2B is $3.6 \times 10^{-7} \mu\text{mol kg}^{-1}$ which agrees well with the value obtained by eq. 2A. Obviously, calculation by consideration of the elemental crustal abundance (Table I, eq. 2A) gives relatively better values for $[M]_{sw}$. The deviation between observed $[Ra]_{sw}$ and the estimated $[Ra]_{sw}$ using eq. 2A might result from the increasing reactivity as the retention on clay minerals due to increased ionic radius (Goldberg, 1965). For instance, Bolter et al. (1964) noted the non-equilibrium exchange of Cs with deep-sea clays.

Before or during hydrolysis, cations in aqueous solution undergo

TABLE II

Estimated values for four elements from the observed relations of Table I

Element	$\Delta O^{2-}M^a$	$[M]_{sw}^b$	K_{sw}^c	\bar{t}_y^d
Am	-60.40	(- 0.016)	0.003	3.6×10^2
Ir	- 60.00	1×10^{-5} (0.016)	0.003	3.7×10^2
Ra (i) ^e	+ 17.00 ^f	1×10^{-6} (112.0)	0.532	2.2×10^5
(ii) ^g	+ 17.00 ^f	3.6×10^{-7}	0.081	5.2×10^3
Rh	- 53.53	1×10^{-4} (0.033)	0.005	6.4×10^2

^a Calculated from Latimer (1952) unless otherwise stated, kcal mol^{-1} .

^b $\mu\text{mol kg}^{-1}$ seawater (from eq. 2A; for values in parentheses eq. 1 is used).

^c Seawater—crustal rock partition coefficient (from eq. 2A).

^d Years (from eq. 5A).

^e From eqs. 2A and 5A.

^f From Tardy and Garrels (1976).

^g From eqs. 2B and 5B.

adsorption—desorption equilibria. Li (1981) stated that the hydrolysis of oxide surfaces produces surface hydroxide groups which have amphoteric properties. Balistreri et al. (1981) considered the surface of particles in the sea to be coated with —OH groups of metal oxides or —COOH groups of organic compounds. Li (1981) also noted that the relative energy of the metal—oxygen bond (during the replacement of protons from the surface —OH groups) is unaffected by the host metal on the other side of the oxygen bond. The stability constants of metal hydroxo complexes in solution are shown to have good correlation with the intrinsic stability constants for SiO_2 —metal interactions (Schindler et al., 1976). Although considerable scatter is seen in the plot between $\log K_1$ (first hydrolysis constants) and $C_{\text{op}}/C_{\text{sw}}$ (concentration ratio of an element in oceanic pelagic clay sediments to that in seawater), Li (1981) could derive some positive relations depending on the charges of the various cations.

Considering the above facts and in view of the fact that marine particulate matter bears a negative charge on its surface, first hydrolysis constants of aqueous metal ions ($\log \beta^* \text{M}(\text{OH})^{(2x-1)+}$) are plotted against observed \log (residence times) in seawater (Fig. 4). Here, $\log \beta^* \text{M}(\text{OH})^{(2x-1)+}$ can be related to the free energy of adsorption of the first hydrolysis complex on to suspended particles ($\Delta G_{\text{r(ads.)}}^0$) in seawater as

$$\Delta G_{\text{r(ads.)}}^0 \propto \frac{1}{(RT \ln \beta^* \text{M}(\text{OH})^{(2x-1)+})}$$

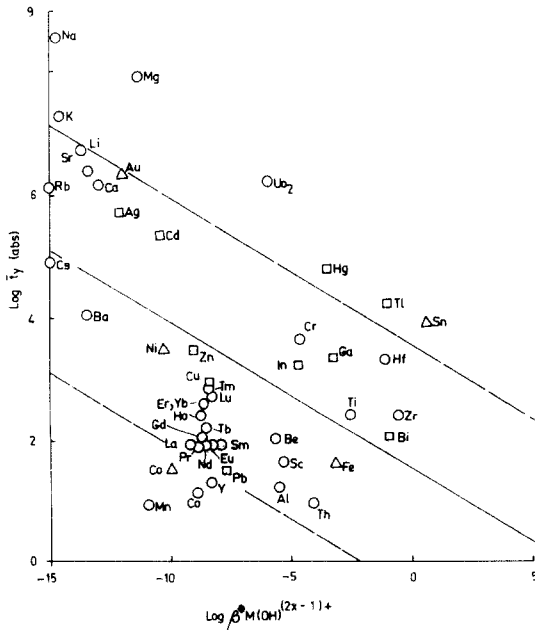


Fig. 4. Relationship between the first hydrolysis constant of metal ions ($\log \beta^* \text{M}(\text{OH})^{(2x-1)+}$) and $\log T_y$ in seawater (symbols are as in Fig. 2).

The tendency to adsorption should increase with the decrease in the free energy of the reactions or vice versa. Figure 4 supports this fact by exhibiting a negative relation between $\log \beta^* M(OH)^{(2x-1)+}$ and $\log \bar{t}_y$ (obs.). Having a low affinity for oxygen in aqueous solutions, due to their low ionic potentials, alkali and alkaline earths are present as solvated cations and they have long $\log \bar{t}_y$ (obs.) periods in seawater. Positive deviations for some elements (e.g., Hg, Tl, Sn and UO_2) can be attributed to additional sources or strong complexation to chloride (Hg, Tl), carbonate (UO_2) and hydroxyl (Sn) ligands in seawater (Turner et al, 1981). Negative deviation of Al, Mn, Ce, Th and Y is due to their ability to form amorphous hydroxides or strong hydrolysis complexes (Whitfield and Turner, 1979). About 58% of the Co can be in a free form which can adsorb on to available surfaces and has low $\log \bar{t}_y$ (obs.). The observed r value for Fig. 4 is -0.49 (Table I, eq. 4) which is significant at the 0.001 level (Reeves and Brooks, 1978). However, cations in aqueous solutions form positively ($M(OH)_b^{(a-b)+}$, $a > b$), or negatively ($M(OH)_b^{(a-b)+}$, $a < b$) charged hydroxyl complexes, or dissolved neutral complexes ($M(OH)_b^{(a-b)+}$, $a = b$) which undergo strong adsorption processes at solid solution interfaces (Stumm and Morgan, 1970; Parks, 1975). For instance, Be^{2+} forms either $[Be(H_2O)_2]^{2+}$ or $[Be_3(OH)_3]^{3+}$ complexes and has been strongly adsorbed to yield low $\log \bar{t}_y$ (obs.) (Fig. 4; Stumm and Morgan, 1970; Brewer, 1975). Of the considered chalcophilic and siderophilic elements, Au, Ag, Cd, Co and Pb exhibit pronounced deviations from the main body of elements.

Stumm and Morgan (1970) and Parks (1975) noted that OH^- or H_2O determines the potentials on solid surfaces and these can sequester positive metal ions or complexes from aqueous solutions. In marine waters this adsorption behaviour increases with an increase in ionic charge, provided that the cations are uncomplexed by strong ligands other than OH^- (Parks, 1975). The coordination behaviour of OH^- ions enhances the adsorption process. Free energy change in chemical adsorption of metals on solid phases decreases with an increase in the ionic charge (Parks, 1975) facilitating more adsorption for trivalent ions than uni- or divalent ions. Simultaneously, however, if an adsorbed metal ion is of low ionic potential, water molecules can desorb the ion by forming soluble hydroxy complexes or solvated cations. It is obvious from the literature (Brewer, 1975; Turner et al., 1981) that hydroxyl complexes exhibit more stability for a number of elements in seawater and IA and IIA group elements form solvated cations (Brewer, 1975). Li (1981) found the deposition of Al, Be, Cs, Rb and Se with the aluminosilicate detrital phase; Hg, Pb, Sn, U, Cr, In, Ge, rare earths, Th, Y and Zr with the iron oxide phase; and Ba, Tl, Co, Ni, Cu, Zn, Bi, Ag and Cd with the manganese oxide phases in oceanic pelagic clays and manganese nodules. The significance of oxygen at the oxide—solution interface in this respect and hence in removal processes is augmented by the observations of Li (1981). Figure 5, a plot of ΔO^2-M against $\log \bar{t}_y$ (obs.) with an r value of 0.59 (Table I, eq. 5A), strengthens the above discussion and also shows

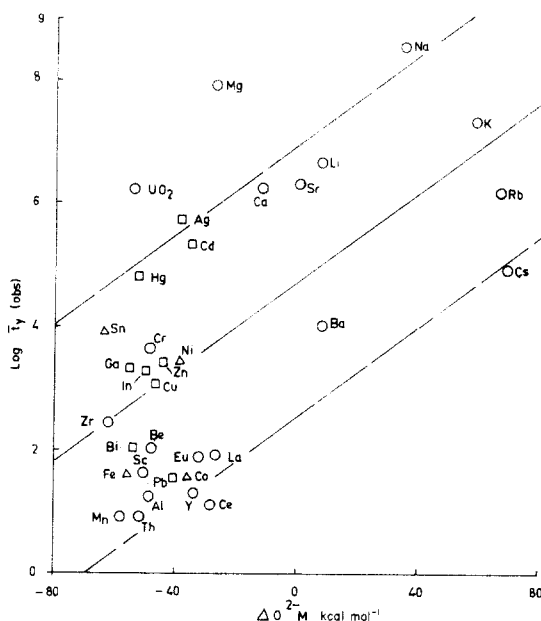


Fig. 5. Relationship between $\Delta G^{\circ}(\text{O}^{2-}\text{M})$ and $\log \bar{t}_y$ of various elements in seawater (symbols are as in Fig. 2).

that many trace elements with low $\Delta G^{\circ}(\text{O}^{2-}\text{M})$ values have relatively low residence times. Negative deviation for Ce would be a result of the oxidation of Ce(III) to Ce(IV) in seawater (Brewer, 1975).

The residence times of some elements calculated from eq. 5A (Table I), $\log \bar{t}_y$ (calc.), are related to the observed residence times (Li, 1981), $\log \bar{t}_y$ (obs.), in Fig. 6. A correlation coefficient of 0.59 is found between the calculated and observed residence times with the regression equation

$$\log \bar{t}_y(\text{calc.}) = 2.43 + 0.35 \log \bar{t}_y(\text{obs.}); \sigma_{y,x} = 1.31$$

Reactivities in seawater, similar to electrostatic attraction between Cs, K and Rb and negatively charged particles (Li, 1981) including complexation (UO_2), cause the observed deviations in Fig. 6. Significantly, lithophilic elements exhibit much deviation when compared to chalcophilic and siderophilic elements.

The reliability of the present model needs to be tested in order to know the accuracy of prediction of residence times in seawater. Recently, Legget and Williams (1981) proposed geometrical (K_g) and statistical (K_s) indices to estimate any model accuracy. A model prediction can be accurate within these factors (K_g and K_s). They are defined as (Legget and William, 1981):

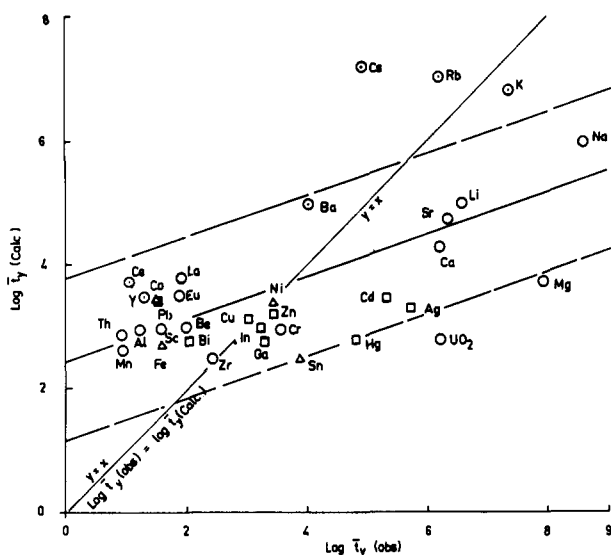


Fig. 6. A plot of $\log \bar{t}_y$ (obs.) and $\log \bar{t}_y$ (calc.) for elements in seawater (symbols are as in Fig. 2).

$$K_g = \frac{1 + \left(\frac{1}{n} \sum_{i=1}^n \left[\frac{1 - (y_i/x_i)}{1 + (y_i/x_i)} \right]^2 \right)^{1/2}}{1 - \left(\frac{1}{n} \sum_{i=1}^n \left[\frac{1 - (y_i/x_i)}{1 + (y_i/x_i)} \right]^2 \right)^{1/2}}$$

and

$$K_s = \exp \left(\frac{1}{n} \sum_{i=1}^n [\log (y_i/x_i)]^2 \right)^{1/2}$$

x_i and y_i are calculated (Table I, eq. 5A) and observed (Li, 1982) residence times in seawater, respectively. K_g and K_s are found to be 1.77 and 1.29, respectively. Legget and Williams (1981) claimed the superiority of K_g over K_s , because the former is simple and intuitive. Consequently, the present model predicts residence times in seawater within a factor of 1.77. In fact, the magnitude of these factors gives information on model accuracy but does not show how closely they are related to each other (L.R. Williams, personal communication). This evaluation confirms the validity of the deduced correlations and of the present model. The $\log \bar{t}_y$ (calc.) values for Am, Ir, Ra and Rh, estimated from $\Delta O^{2-}M$, are given in Table II. The $\log \bar{t}_{Ra}$ value obtained from eq. 5B (Table I) is lower than that with eq. 5A.

CONCLUSIONS

The model considered reveals that oxygen (as oxides and hydroxides) is highly significant and plays a major role, next to the individual atomic

properties of elements, in controlling the composition of seawater. The parameter $\Delta O^{2-}M$ can be used as a key for predicting elemental concentrations and residence times in seawater. These calculated and observed residence times agree within a factor of 1.77. The difference between the observed $[Ra]_{sw}$ ($10^{-10} \mu\text{mol kg}^{-1}$) and estimated $[Ra]_{sw}$ ($10^{-6} \mu\text{mol kg}^{-1}$) can be attributed to the reactivity of Ra in seawater and its tendency for adsorption on to particulate matter. The expected concentrations and residence times for Am, Ir, Ra and Rh are tabulated.

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