

## Ultimate removal mechanisms of elements from the ocean\*

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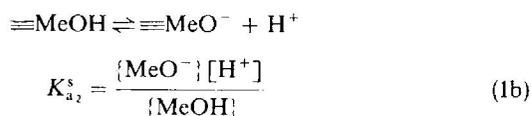
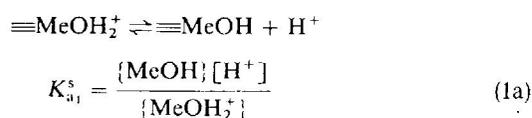
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**Abstract**—The surface complex formation model can adequately explain the observed partitioning of most of the elements between seawater and pelagic clays and between river water and river suspended particles. The adsorption of elements on the hydrous oxide surface of iron oxide, manganese oxide and clay minerals is the most important ultimate removal mechanism of most of the elements from the ocean.

IT HAS been demonstrated that the settling of fecal pellets and fecal aggregates is the most important mechanism for transporting most of the elements (Mn, Co and Ni are exceptions) from the surface to the deep oceans. A large fraction of Mn, Co and Ni currently depositing on the ocean floor may be transported from the continental margins to the deep ocean (Li, 1981a). Once elements are transported down to the deep ocean, a certain fraction of each element is remineralized and dissolved back to the water column and transported back to the surface ocean by upswelling. Another fraction is incorporated into pelagic clays and Mn-nodules. The R-mode factor analysis and the enrichment pattern of elements in Mn-nodules relative to pelagic clays have shown that, both in oceanic pelagic clays and in Mn-nodules, elements such as K, Rb, Cs, Be, Sc and Ga are mainly correlated with the aluminosilicate detritus phase. The elements related to or incorporated into iron oxide phases are anion or oxyanions (e.g. P, S, Se, Te, As, B, Sn, I, Br, F, U, Pb, Hg, etc.) and hydroxide complexes of tri- and tetravalent cations (e.g. Ti, Ge, Zr, Hf, Th, Y, rare earths, In, Pd, Cr, etc.) in seawater. The elements incorporated into manganese oxide phases are mono- and divalent cations (e.g. Mg, Ca, Ba, Tl, Co, Ni, Cu, Zn, Bi, Ag, Cd, etc.) and oxyanions with high affinity to Mn such as Mo, W and Sb in seawater. Mg, Ca and Ba in pelagic clays are also related to other phases, such as aluminosilicates, carbonates and barite (Li, 1981b).

Except for elements placed inside the crystal lattice of detrital phases or those forming their own authigenic minerals (CaCO<sub>3</sub>, apatite, BaSO<sub>4</sub>, etc.), the most important removal mechanisms of elements from the deep ocean is the adsorption of elements on the interface of fine particles (e.g. GOLDBERG, 1954; KRANSKOPF, 1956). Various theories have been proposed to describe the adsorption of ions at hydrous oxide interface (see brief summary by STUMM *et al.*, 1976). But the most simple and promising one is the surface

complex formation model (e.g. STUMM *et al.*, 1970; SCHINDLER, 1975). In this model the hydrolysis of oxide surfaces produces hydrous oxide surface groups such as ≡Si—OH, ≡Mn—OH and ≡Fe—OH. The surface hydroxyl groups have amphoteric properties. Protonation or deprotonation results in surface charge on the oxide surfaces, e.g.



where

Me = metal (e.g. Mn, Fe, Si, Al) of solid oxides  
 [ ] = concentration of species in aqueous phase  
 { } = concentration of surface species on solid oxides  
 K<sub>a1</sub><sup>s</sup> and K<sub>a2</sub><sup>s</sup> are acidity constants

The pH at which {MeOH<sub>2</sub><sup>+</sup>} = {MeO<sup>-</sup>} is called the pH of zero point of charge (pH<sub>zpc</sub>). At pH < pH<sub>zpc</sub>, {MeOH<sub>2</sub><sup>+</sup>} > {MeO<sup>-</sup>} and *vice versa*. The maximum exchange capacity of surface groups, {MeO<sub>T</sub>}, is equal to {MeOH<sub>2</sub><sup>+</sup>} + {MeOH} + {MeO<sup>-</sup>}.

For example, pH<sub>zpc</sub> of Goethite (α-FeOOH) ranges from 7.5 to 8.3 in NaCl solution (Hingston *et al.*, 1972; BALISTRERI and MURRAY, 1979); at oceanic pH of 8, the dominating surface species is {FeOH}, with a small amount of {FeOH<sub>2</sub><sup>+</sup>} or {FeO<sup>-</sup>} dependent on the precipitation history of Goethite (e.g. BALISTRERI and MURRAY, 1979; ASTON and CHESTER, 1973). YATES (1975) determined {FeO<sub>T</sub>} of Goethite to be equal to 27.8 μmol/m<sup>2</sup>. If one takes the surface area of the freshly precipitated FeOOH equal to 48.5 m<sup>2</sup>/g (YATES, 1975), then {FeO<sub>T</sub>} is equal to about 1400 μmol/g FeOOH.

The pH<sub>zpc</sub> of δMnO<sub>2</sub> (birnessite) in NaCl solution is about 2.8 ± 0.3 (MORGAN and STUMM, 1964).

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Therefore, at oceanic pH of 8, the dominating surface species are  $\{\text{MnO}^-\}$  and  $\{\text{MnOH}\}$ . The alkalimetric titration of  $\delta\text{MnO}_2$  suspension gives  $\{\text{MnO}^-\} \approx 3800 \mu\text{mol/g MnO}_2$  at pH 8 (MORGAN and STUMM, 1964). If one assumes  $\{\text{MnO}_T\}$  is also equal to  $27.8 \mu\text{mol/m}^2$  as  $\{\text{FeO}_T\}$ , then with the surface area of  $300 \text{m}^2/\text{g MnO}_2$  (MORGAN and STUMM, 1964),  $\{\text{MnO}_T\}$  is roughly about  $8300 \mu\text{mol/g MnO}_2$ .

For aluminosilicate clay minerals,  $\text{pH}_{zpc}$  are not given in literature, since at  $\text{pH}_{zpc}$  the clay minerals still exhibit a negative charge due to isomorphous substitution of Al (III) for Si (IV) at tetrahedral sites or of Mg (II) or Fe (II) for Al (III) at octahedral sites inside the mineral structure (PARKS, 1975). Therefore, the lower pH at which the net particle charge is zero (so-called Isoelectric point,  $\text{pH}_{IEP}$ ) is given instead, for example,  $\text{pH}_{IEP} = 3.3$  to  $4.6$  for kaolinite and  $< 2.5$  for montmorillonite (PARKS, 1967). At oceanic pH of 8, clay minerals freshly introduced to the ocean are negatively charged as shown by and ASTON and CHESTER (1973). The total exchange capacity ranges from about  $100 \mu\text{mol/g}$  for kaolinite to about  $1000 \mu\text{mol/g}$  for montmorillonite (e.g. BEETEM *et al.*, 1962; SAYLES and MANGELSDORF, 1977). The fine suspended particles ( $< 2 \mu\text{m}$ ) from the Amazon River give the exchange capacity of about  $400 \mu\text{mol/g}$  (SAYLES and MANGELSDORF, 1979) which can be taken as an average for the aluminosilicates freshly introduced to the ocean. However, a significant fraction of the exchange capacity of aluminosilicates must be contributed by negative charges which are produced by isomorphous substitution inside mineral structure. By knowing Fe, Mn and Al contents in pelagic clay, the calculated maximum exchange capacity contributed by  $\alpha\text{-FeO}(\text{OH})$ ,  $\delta\text{MnO}_2$  and aluminosilicates are 150, 40 and  $400 \mu\text{mol/g}$  of pelagic clay respectively (just to show the relative order of magnitude). Though clay minerals contribute the highest exchange capacity in pelagic clay sediments, apparently clay minerals mostly absorb alkaline and alkaline earth element as shown by SAYLES and MANGELSDORF (1977) and LI (1981b).

According to JAMES and HEALY (1972), the change in the Gibbs free energy during the adsorption of hydrated cation on solids ( $\Delta G_{\text{ads}}$ ) includes the contributions from the coulombic electrostatic interaction ( $\Delta G_{\text{coul}}$ ), the secondary solvation or hydration ( $\Delta G_{\text{solv}}$ ) and the chemical or noncoulombic interaction ( $\Delta G_{\text{chem}}$ ) at the solid-solution interface, i.e.

$$\Delta G_{\text{ads}} = \Delta G_{\text{coul}} + \Delta G_{\text{solv}} + \Delta G_{\text{chem}} \quad (2)$$

$\Delta G_{\text{coul}}$  is equal to  $Ze\psi$ , where  $Z$  is the charge of the adsorbing ion and  $\psi$  the potential at its equilibrium position in the interface.  $\psi$  is, in turn, a function of  $RT/e (\text{pH}_{zpc} - \text{pH})$  and ionic strength of solution. Therefore, at oceanic pH of 8,  $\psi$  is negative for aluminosilicates and  $\delta\text{MnO}_2$ . The negative  $\psi$  facilitates the adsorption of positively charged ion species ( $\Delta G_{\text{coul}} < 0$ ) and hinders the adsorption of negatively charged ion species ( $\Delta G_{\text{coul}} > 0$ ). Whereas  $\psi$  of

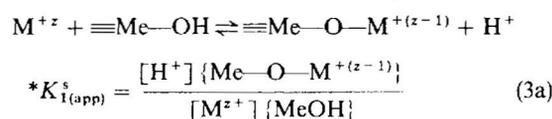
$\alpha\text{-FeOOH}$  is near zero at oceanic pH of 8, therefore  $\Delta G_{\text{coul}}$  term is relatively small for  $\alpha\text{-FeOOH}$  and is zero for neutral ion species. On the other hand, the change in the Gibbs free energy of solvation ( $\Delta G_{\text{solv}}^\circ$ ) during the adsorption of hydrated cation on solids is a function of

$$Z^2 e^2 / r' [1/\epsilon_{\text{interface}} - 1/\epsilon_{\text{water}}]$$

where  $r'$  = radius of hydrated cation, and  $\epsilon_{\text{interface}}$  and  $\epsilon_{\text{water}}$  are the dielectric constants of the solid-solution interfacial region and the bulk solution respectively.

Therefore, as long as  $\epsilon_{\text{interface}}$  is less than  $\epsilon_{\text{water}}$  ( $\sim 78$  at  $25^\circ\text{C}$ ),  $\Delta G_{\text{solv}}$  is always positive and hinders the adsorption of hydrated cations. The dielectric constants of aluminosilicates ( $\epsilon \sim 4.5$  to  $8$ ; KELLER, 1966) are much smaller than that of manganese oxide ( $\epsilon \sim 32$ ; MURRAY, 1975) and probably iron oxide. Therefore,  $\Delta G_{\text{solv}}$  is much greater for aluminosilicates than for manganese and iron oxides, especially for high valent, low ionic radius cations (e.g. transition metals). This may explain why aluminosilicate phases in the ocean mostly absorb alkaline and alkaline earth elements and not transition metals. For neutral ion species,  $\Delta G_{\text{solv}}$  is zero. In short, considering the fundamental differences in the physicochemical properties (e.g.  $\text{pH}_{zpc}$  or  $\text{pH}_{IEP}$  and  $\epsilon$ , etc.) among aluminosilicates, manganese oxide and iron oxide phases, the specific association between elements and these three important solid phases are not unexpected.

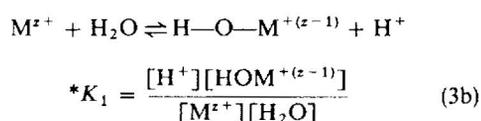
According to the surface complex model, the adsorption of cation,  $\text{M}^{z+}$ , on the surface hydroxyl groups can be visualized as:



where

$$*K_{1(\text{app})}^s = \text{apparent equilibrium constant} \\ = \exp(-\Delta G_{\text{ads}}/RT)$$

DUGGER *et al.* (1964) showed that the Gibbs free energy or the bond strength of single metal-oxygen bond (O-M) on silica gel for various cations are linearly correlated to their  $\log *K_1$ , where  $*K_1$  is the first hydrolysis constant for the reaction



SCHINDLER (1975) also showed that  $\log *K_{1(\text{app})}^s$  of silica gel for various cations are linearly correlated with  $\log *K_1$ . The implication is that the relative strength of metal-oxygen bonding is not affected much by the host metal on the other end of the oxygen bond (either Me or H in our case). If the surface complex model is realistic, then for a first approximation one would expect from eqn (3a) that the partitioning of

various cations between solid and liquid phases in the ocean ( $C_{op}^i/C_{sw}^i$  = the concentration ratio of element  $i$  in oceanic pelagic clay sediments and seawater) or in rivers ( $C_p^i/C_R^i$  = the concentration ratio of element  $i$  in river-suspended particles and river water) should be positively correlated with the relative bond-strength between cations and the oxygen of the hydrous oxide surface or with  $*K_1$ . For simplicity, the details of the complex formation of cations in seawater and on the hydrous oxide surface (e.g. SCHINDLER, 1975; BALISTRERI *et al.*, 1981) are ignored for the time being. Figure 1 (left) provides just this kind of plot.  $*K_1$  values are mainly the average of  $*K_1$  values in  $\text{NaClO}_4$  solution with ionic strength between zero and one and temperature at 25°C (SILLEN and MARTELL, 1964, 1971). The exceptions are Au and Be, which are predicted from the linear relationship between  $\log *K_1$  and the ionization potential, as will be discussed later.  $C_{op}$  data are mainly from TUREKIAN and WEDEPOHL (1961), except rare earths (PIPER, 1974), and U and Th (KU, 1966),  $C_{sw}$  data from BREWER (1975) except Cd, Zn, Ni and Cu (BRULAND, 1980) Se (MEASURES and BURTON, 1980) and Pb (SETTLE and PATTERSON, 1980),  $C_p$  data from MARTIN and MEYBAECK (1979) except Hg (LINDBURG *et al.*, 1975) and  $C_R$  from GOLDBERG *et al.* (1971) except rare earths, Al and Fe (MARTIN and MEYBECK, 1979) and Hg (LINDBERG *et al.*, 1975). The general positive correlations in Fig. 1 (left) are quite good for mono- and divalent cations. Few exceptions are explainable, e.g. the high  $\log C_{op}/C_{sw}$  values for  $\text{Ba}^{2+}$ , and  $\text{Tl}^+$  are probably caused by the formation of  $\text{BaSO}_4$  and

$\text{Ti}_2\text{O}_3$  phases in the pelagic clays instead of pure adsorption. The low  $C_{op}/C_{sw}$  values for  $\text{UO}_2^{2+}$  and  $\text{Hg}^{2+}$  are due to the formation of strong complex ions such as  $\text{UO}_2(\text{CO}_3)_2^{2-}$  and  $\text{HgCl}_4^{2-}$ . The low  $\log C_p/C_R$  for  $\text{Cu}^{2+}$  can be explained by the formation of strong Cu-organic complexes in rivers (SUNDA and HANSON, 1979).

The hydrolysis constants  $*K_1$  for Rb and Cs are too small to be measured, but the  $\log C_{op}/C_{sw}$  and  $\log C_p/C_R$  values for Rb and Cs are rather high as compared to Na (Fig. 1). Therefore the adsorption of Rb and Cs (and to some extent, K) on aluminosilicates is not due to the formation of strong chemical bond between cations and the oxygen of hydrous oxide surface, but rather due to the electrostatic attraction between cations and negatively charged particles. The selective adsorption in the affinity order of  $\text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{Na}^+$  on aluminosilicates may partly be explained by the increasing order of  $\Delta G_{\text{soliv}}$  (or  $1/r'$ ) for these elements (BERUBE and DE BRUYN, 1968).

The tri- and tetra-valent cations, which usually form hydroxyl complexes in natural water, form a broad maximum in Fig. 1. or even show a slight negative correlation. However, the low  $\log C_{op}/C_{sw}$  values for Hf, Ti, Zr, Ga and In are probably caused by too high  $C_{sw}^i$  values for these elements. Redetermination of  $C_{sw}^i$ 's for these elements in seawater is desirable.

The adsorption of a hydroxyl complex on a  $\text{FeO}(\text{OH})$  can be visualized as

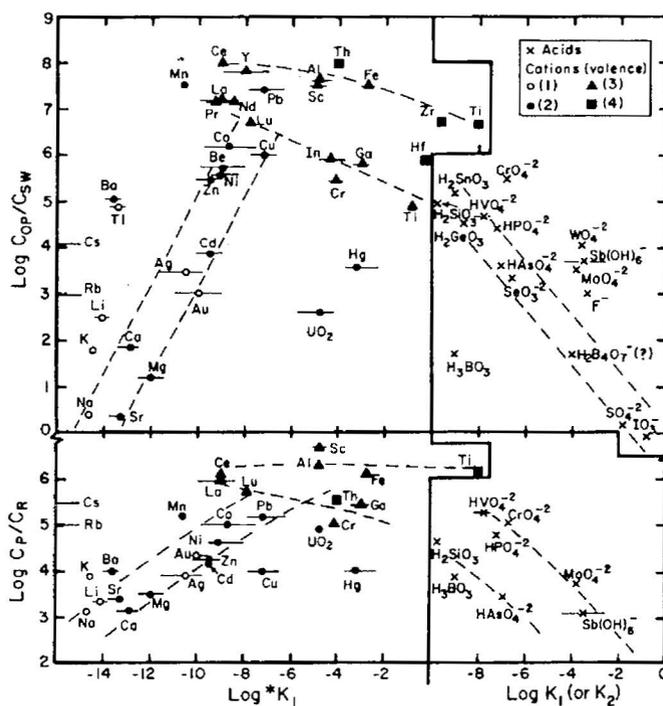
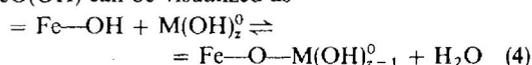
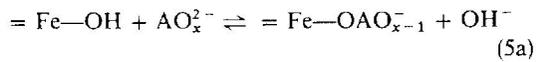


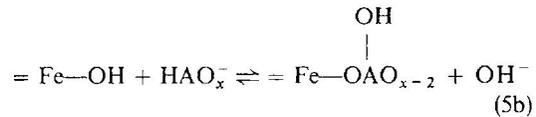
Fig. 1. The plots of  $\log C_{op}/C_{sw}$  and  $\log C_p/C_R$  vs  $\log *K_1$  (the first hydrolysis constant) and  $\log K_1$  (the first dissociation constant of acids) or  $\log K_2$  (the second dissociation constant of acids).

For elements whose  $\log *K_1$  are larger than that of Fe (i.e. O—M bond is stronger than that of O—Fe), the degree of adsorption probably depends more on the Fe—O bond strength than on that of M—O. This may explain why  $C_{op}/C_{sw}$  and  $C_p/C_R$  do not increase with  $*K_1$  for tri- and tetravalent cations.

The adsorption of oxyanions of dissociated acids by Goethite can be visualized as:



or



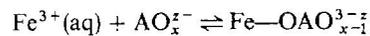
The strength of the bond between Fe of the iron oxide surface and the O of oxyanion in eqns (5a) and (5b) is inversely related to  $\log K_2$  (the second dissociation constant of acid  $\text{H}_2\text{AO}_x$ ) and  $\log K_1$  (the first dissociation constant of acid  $\text{H}_2\text{AO}_x$ ), respectively (HINGSTON *et al.*, 1972). The higher the  $\log K_1$  or  $\log K_2$ , the weaker is the bond between Fe or H and the dissociated acids; therefore the lower the  $\log C_{op}/C_{sw}$  ratio. The right-hand side of Fig. 1 shows just this kind of inverse correlation between  $\log C_{op}/C_{sw}$  (or  $\log C_p/C_R$ ) and  $\log K_1$  or  $\log K_2$ . The choice between  $K_1$  and  $K_2$  depends on the speciation of acid in seawater at pH = 8. For example,  $K_1$  is for dominantly undissociated acids and monovalent anions and  $K_2$  is for divalent anions (Fig. 1 right).  $K_1$  and  $K_2$  values are obtained from DEAN (1979).

The general inverse correlation in Fig. 1 (right) is fair. The high  $C_{op}/C_{sw}$  values for Mo, W and Sb are probably related to the formation of manganese com-

pounds of  $\text{MoO}_4^{2-}$ ,  $\text{WO}_4^{2-}$  and  $\text{SbO}_3^{3-}$  instead of pure adsorption (LI, 1981b). The high  $C_{op}/C_{sw}$  for  $\text{CrO}_4^{2-}$  may indicate that Cr in pelagic clays are in part absorbed as  $\text{Cr}(\text{OH})_3$ . The high  $C_{op}/C_{sw}$  for  $\text{F}^-$  is due to the formation of apatite in addition to the adsorption onto  $\alpha\text{-FeO}(\text{OH})$ , probably as  $=\text{Fe—F}$ . The Fe—F bond strength is again inversely related to  $\log K_1$ . Since  $\log K_1$  for HCl and HBr are so large (+ 6.1 and 9, respectively),  $\text{Cl}^-$  and  $\text{Br}^-$  are hardly absorbed by pelagic clays. The low  $C_{op}/C_{sw}$  for  $\text{H}_3\text{BO}_3$  is an enigma. One possible explanation is that boric acid forms stabilized polymers in seawater (e.g.  $\text{H}_2\text{B}_4\text{O}_7$ ) and becomes less reactive to particles (Fig. 1 right). SIGG and STUMM (1981) and STUMM *et al.* (1981) also show that the bond strength between Fe and the O of oxyanion is proportional to the logarithm of the complex formation constant  $K'_1$  where

$$K'_1 = \{ \text{Fe—OAO}_{x-1}^{3-z} \} / ( \{ \text{Fe}^{3+}(\text{aq}) \} \{ \text{AO}_x^{z-} \} )$$

for a reaction:



Unfortunately, there are only a few  $K'_1$  data available for the complex formation between  $\text{Fe}^{3+}(\text{aq})$  and various anions.

One should be aware of the fact that  $C_{op}/C_{sw}$  and the mean residence time of element in the ocean,  $\tau$ , are inversely related quantities, if  $\tau$  is defined as equal to  $(V \cdot C_{sw}) / (S \cdot C_{op})$ , where  $V$  is the volume of the ocean and  $S$  the mean sedimentation rate of pelagic clays. It is also interesting to notice that the  $\log *K_1$  and  $\log K_1$  (abscissas in Fig. 1) are highly correlated with the ionization potential,  $I$  (= minimum amount of energy required to remove the least strongly bound electron from a gaseous atom or ion), and moderately corre-

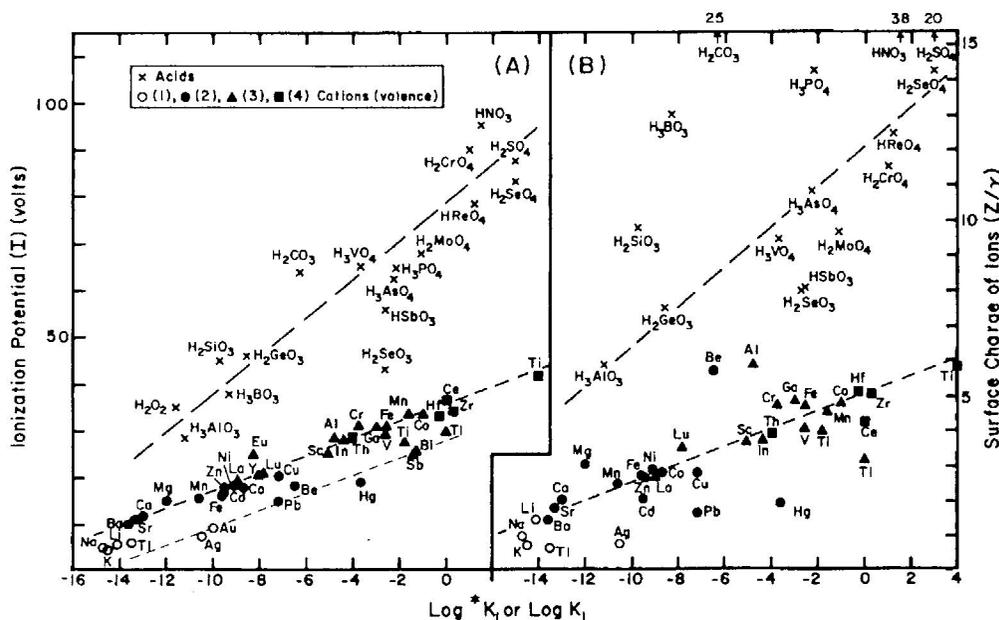


Fig. 2. The plots of (A) Ionization potential,  $I$ , and (B) ionic potential or surface charge of ions,  $Z/\gamma$ , vs  $\log *K_1$  for cations and  $\log K_1$  for acids.

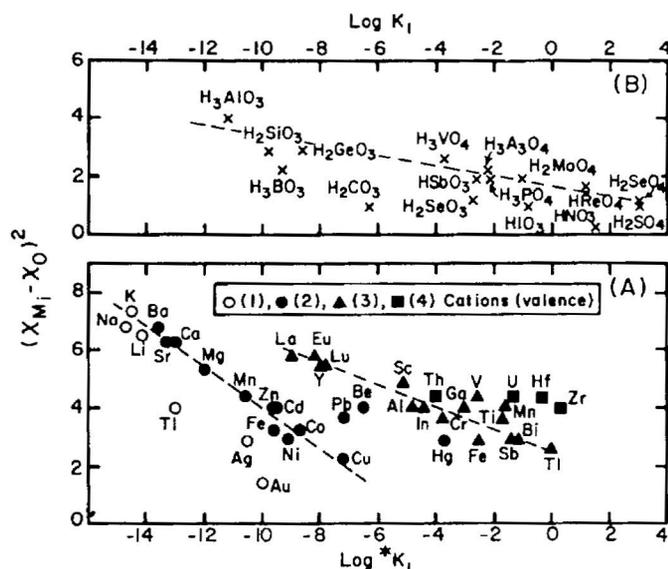


Fig. 3. The plots of  $(X_{M_i} - X_O)^2$  vs (A)  $\log *K_1$  for cations and (B)  $\log K_1$  for acids.

lated with the ionic potential or the surface charge of ions ( $= Z/\gamma$ , where  $Z$  = charge of ion,  $\gamma$  = ionic radius) as shown in Fig 2A and 2B. The ionization potentials of elements for successive stages of ionization are best summarized by DEAN (1979) and the ionic radii of various elements by AHRENS (1952). Except Be (probably bad  $*K_1$  datum), the elements which fall below the main correlation lines but with the same slope are always the B-metal cations (STUMM and MORGAN, 1970). The unknown  $\log *K_1$  can be predicted from Fig. 2A, if  $I$  is known. The plot of  $\log (C_{op}/C_{sw})$  vs  $I$  does produce a figure similar to Fig. 1, but the scattering of data mainly caused by the B-metals is too big to be desirable. The plot of  $\log C_{op}/C_{sw}$  vs  $Z/\gamma$  makes the scatter of data even worse.

Finally, according to PAULING (1960), the bond energy between metal and oxygen,  $D(M_i-O)$ , can be expressed by:

$$D(M_i-O) = 1/2 \{D(M_i-M_i) + D(O-O)\} + 23(X_{M_i} - X_O)^2 \quad (6)$$

where  $X_{M_i}$  and  $X_O$  are the electronegativity of metal  $M_i$  and oxygen at the common oxidation state. The electronegativity values are summarized by WEDEPOHL (1969).

As shown by DUGGER *et al.* (1964),  $D(M_i-O)$ 's are proportional to  $\log *K_1$  for various cations. By ignoring the  $D(M_i-M_i)$  term in eqn (6), WHITFIELD and TURNER (1979) proposed that  $D(M_i-O)$ 's are positively correlated with  $(X_{M_i} - X_O)^2$  according to their plot of  $\log C_{sw}/C_{ig}$  vs  $(X_{M_i} - X_O)^2$ , where  $C_{ig}$  is the concentration in average crustal igneous rocks. However, as shown in Fig. 3A,  $\log *K_1$ , and therefore  $D(M_i-O)$ , are inversely correlated with  $(X_{M_i} - X_O)^2$ , i.e. the stronger the  $M_i-O$  bond, the weaker the ionic contribution to the total bond energy. Therefore, their interpretations of their plot are erroneous.

In summary, the surface complex formation model appears to work quite well, both in riverine and marine environments except elements which form authigenic phases. The concentrations of many trace elements in the deep ocean and rivers must reflect a certain degree of the adsorption equilibrium between solution and solid phases.

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