Ultimate removal mechanisms of elements from the ocean*

YUAN-HUI LI
Lamont-Doherty Geological Observatory of Columbia University, Palisades, NY 10964, USA.

(Received 13 January 1981; accepted in revised form 9 April 1981)

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 upwelling. 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, Th, Eu, Tb, Ce, Nd, 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 (CaCO₃, apatite, BaSO₄, 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; Kranskoff, 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.

\[
=\text{MeOH} \leftrightarrow =\text{MeO}^- + \text{H}^+ \\
K_s^1 = \frac{[\text{MeOH}][\text{H}^+]}{[=\text{MeO}^-]} \quad \text{(1a)}
\]

\[
=\text{MeO}^- \leftrightarrow =\text{MeO}^- + \text{H}^+ \\
K_s^1 = \frac{[=\text{MeO}^-][\text{H}^+]}{[=\text{MeOH}]} \quad \text{(1b)}
\]

where

- \(\text{Me} = \text{metal} (\text{e.g. Mn, Fe, Si, Al})\) of solid oxides
- \([\text{]}\) = concentration of species in aqueous phase
- \([\text{]}\) = concentration of surface species on solid oxides
- \(K_s^1, K_s^2\) are acidity constants

The pH at which \([=\text{MeOH}^+] = [\text{MeO}^-]\) is called the pH of zero point of charge (pH_zpc). At \(pH < \text{pH}_{zpc}, [=\text{MeOH}^+] > [\text{MeO}^-]\) and vice versa. The maximum exchange capacity of surface groups, \([\text{MeO}^-]\), is equal to \([=\text{MeOH}^+] + [\text{MeOH}^-] + [\text{MeO}^-]\).

For example, pH_{zpc} of Goethite (\(\alpha\)-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 \([=\text{FeOH}^-]\), with a small amount of \([=\text{FeOH}_2^-]\) or \([\text{FeO}^-]\), dependent on the precipitation history of Goethite (e.g. Balistreri and Murray, 1979; Aston and Chester, 1973). Yates (1975) determined \([=\text{FeO}^-]\) of Goethite to be equal to 27.8 \(\mu\text{mol/m}^2\). If one takes the surface area of the freshly precipitated FeOOH equal to 48.5 \(\mu\text{m}^2/g\) (Yates, 1975), then \([=\text{FeO}^-]\) is equal to about 1400 \(\mu\text{mol/g}\) FeOOH.

The pH_{zpc} of \(\delta\text{MnO}_2\) (birnessite) in NaCl solution is about 2.8 ± 0.3 (Morgan and Stumm, 1964).

* Lamont-Doherty Geological Observatory Contribution No. 3202.
Therefore, at oceanic pH of 8, the dominating surface species are [MnO\textsuperscript{2+}] and [MnOH\textsuperscript{−}]. The alkalimetric titration of δMnO\textsubscript{2} suspension gives [MnO\textsuperscript{2+}] ≈ 3800 μmol/g MnO\textsubscript{2} at pH 8 (Morgan and Stumm, 1964). If one assumes [MnO\textsubscript{2+}] is also equal to 27.8 μmol/m\textsuperscript{2} as [FeO\textsubscript{2+}], then with the surface area of 300 m\textsuperscript{2}/g MnO\textsubscript{2} (Morgan and Stumm, 1964), [MnO\textsubscript{2+}] is roughly about 8300 μmol/g MnO\textsubscript{2}.

For aluminosilicate clay minerals, pH\textsubscript{pzc} are not given in literature, since at pH\textsubscript{pzc} 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, pH\textsubscript{iep}) is given instead, for example, pH\textsubscript{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 μmol/g for kaolinite to about 1000 μmol/g for montmorillonite (e.g. Bette et al., 1962; Sayles and Mangelsdorf, 1977). The fine suspended particles (<2 μm) from the Amazon River give the exchange capacity of about 400 μmol/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 α-FeOOH, δMnO\textsubscript{2} and aluminosilicates are 150, 40 and 400 μmol/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 elements and not transition metals. For neutral ion species, ΔG\textsubscript{exch} is zero. In short, considering the fundamental differences in the physicochemical properties (e.g. pH\textsubscript{pzc} or pH\textsubscript{iep} and ε, 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, M\textsuperscript{z+}, on the surface hydroxyl groups can be visualized as:

\[
M^{z+} + \equiv \text{Me--OH} \rightleftharpoons \equiv \text{Me--O--M}^{z+} (z-1) + H^+ 
\]

\[
K_i^{(app)} = \frac{[H^+] [\text{Me--O--M}^{z+} (z-1)]}{[M^{z+}] [\text{MeOH}]} \tag{3a}
\]

where

\[
K_i^{(app)} = \text{apparent equilibrium constant} 
\]

\[
= \exp (-\Delta G_{\text{ads}}/RT) 
\]

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 \text{*K}_1, where \text{*K}_1 is the first hydrolysis constant for the reaction

\[
M^{z+} + H_2O \rightleftharpoons H--O--M^{(z-1)} + H^+ 
\]

\[
*K_1 = \frac{[H^+][\text{HOM}^{(z-1)}]}{[M^{z+}][H_2O]} \tag{3b}
\]

Schindler (1975) also showed that log \text{*K}_1(app) of silica gel for various cations are linearly correlated with log \text{*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 \( \frac{C_{\text{so}}}{C_{\text{sw}}} \) = the concentration ratio of element \( i \) in oceanic pelagic clay sediments and seawater or in rivers \( \frac{C_{p}}{C_{\text{sw}}} \) = 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; BASTIAERTI 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 \( \cdot K_1 \) values in \( NaClO_4 \) 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. \( C_{\text{sw}} \) data are mainly from TUREKIAN and WEDEPOHL (1961), except rare earths (Piper, 1974), and U and Th (Ku, 1966). \( C_{\text{sw}} \) data from BREWER (1975) except Cd, Zn, Ni and Cu (BRLAND, 1980) Se (MEASURES and BURTON, 1980) and Pb (SETTLE and PATTERSON, 1980), \( C_{\text{sw}} \) data from MARTIN and MEYBECK (1979) except Hg (LINDBERG et al., 1975) and Cs 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 \( \log C_{\text{so}}/C_{\text{sw}} \) values for \( Ba^{2+} \) and \( Ti^{4+} \) are probably caused by the formation of \( BaSO_4 \) and \( Ti_2O_3 \) phases in the pelagic clays instead of pure adsorption. The low \( \log C_{\text{so}}/C_{\text{sw}} \) for \( UO_2^{2+} \) and \( Hg^{2+} \) are due to the formation of strong complex ions such as \( UO_2(CO_3)_2^{2-} \) and \( HgCl_4^{2-} \). The low \( \log C_{p}/C_{\text{sw}} \) for \( Cu^{2+} \) 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 \( \log C_{\text{sw}}/C_{\text{so}} \) and \( \log C_{p}/C_{\text{sw}} \) 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 \( Cs ^+ > Rb ^+ > K ^+ > Na ^+ \) on aluminosilicates may partly be explained by the increasing order of \( \Delta G_{ads} \) (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 \( \log C_{\text{so}}/C_{\text{sw}} \) values for Hf, Ti, Zr, Ga and In are probably caused by too high \( C_{\text{sw}} \) values for these elements. Redetermination of \( C_{\text{sw}} \)'s for these elements in seawater is desirable. The adsorption of a hydroxyl complex on a \( Fe(OH) \) can be visualized as:

\[
Fe-OH + M(OH)_2^2+ \rightleftharpoons Fe-O-M(OH)_{2-1} + H_2O
\]

Fig. 1. The plots of \( \log C_{\text{so}}/C_{\text{sw}} \) and \( \log C_{p}/C_{\text{sw}} \) 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 $C_{op}/C_s$ do not increase with $K_1$ for tri- and tetravalent cations.

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

$$= \text{Fe-OH} + AO^{-} \rightleftharpoons = \text{Fe-OAO}^{-} + \text{OH}^{-}$$

or

$$\text{OH}^{-} = \text{Fe-OH} + HAO_x \rightleftharpoons = \text{Fe-OAO}_x^{-} + \text{OH}^{-}$$

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 $K_1$ (the second dissociation constant of acid $H_2AO_x^-$) and log $K_1$ (the first dissociated constant of acid $H_2AO_x^-$), respectively (Hingston et al., 1972). The higher the $K_1$ 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 $C_{op}/C_s$) and $K_1$ 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 compounds of MoO$_4^{2-}$, WO$_4^{2-}$ and SbO$_4^{2-}$ instead of pure adsorption (Li, 1981b). The high $C_{op}/C_{sw}$ for CrO$_4^{2-}$ may indicate that Cr in pelagic clays are in part absorbed as Cr(OH)$_3$. The high $C_{op}/C_{sw}$ for F$^-$ is due to the formation of apatite in addition to the adsorption onto α-FeO(OH), probably as Fe-F. The Fe-F bond strength is again inversely related to log $K_1$.

Unfortunately, there are only a few $K_1$ data available for the complex formation between Fe$^{3+}$ (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, $T$, are inversely related quantities, if $T$ is defined as equal to $(V'C_{sw})/S'C_{op}$, 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, 1 (= minimum amount of energy required to remove the least strongly bound electron from a gaseous atom or ion), and moderately corre-
Ultimate removal mechanisms of elements from the ocean

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

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.

Acknowledgements—Discussions with Drs W. STUMM, P. W. SCHINDLER and P. H. SANTSCHI have been most inspiring and helpful. Constructive criticisms from Drs F. MILLER, C. P. CHANG, D. ADLER and J. W. MURRAY are acknowledged. The work is supported by grants from the Department of Energy (EY-76-S-02-2185) and from the Environmental Protection Agency (R803902-03).

REFERENCES


JAMES R. D. and HEALY T. W. (1972) Adsorption of hydro-


