

Interelement relationship in abyssal Pacific ferromanganese nodules and associated pelagic sediments

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Abstract—By R-mode factor analysis and enrichment factor calculations, most of the elements in abyssal ferromanganese nodules and associated pelagic sediments (excluding common authigenic minerals like apatite, barite, opal and carbonates) are found to be preferentially concentrated in one of the following three major phases: aluminosilicates (e.g., Al, Si, Sc, Ga, Cr, Be, Na, K, Rb and Cs), Fe-oxides (e.g., Fe, P, S, V, Se, Te, As, B, Sn, U, Hg, Pb, Ti, Ge, Y, Zr, Nb, Pd, In, rare-earth, Hf, Th, Pa, Pu, Am, Ru and Bi), and Mn-oxides (e.g., Mn, Tl, Ag, Cd, Mg, Ca, Ba, Ra, Co, Ni, Cu, Zn, Mo, Sb and probably W). The specific association of elements with these three phases can be explained by the difference in chemical forms of elements in seawater and by fundamental differences in physicochemical properties (e.g., the pH of zero point of charge and dielectric constant) of these three phases.

INTRODUCTION

THE importance of hydrous Mn and Fe oxides in controlling the concentrations of many elements in deep-sea sediments, ferromanganese nodules and seawater was emphasized by Goldberg (1954). Jenne (1968) also concluded that the concentration of heavy metals like Co, Ni, Cu and Zn in soils, stream sediments and continental waters are mainly controlled by hydrous Mn and Fe oxides.

The calculations of correlation coefficients or plots of correlation diagrams for various pairs of elements (on the basis of bulk or acid leachate chemical composition data) in pelagic clays (Cronan, 1969/70; Calvert and Price, 1977; Bischoff *et al.*, 1979; Piper *et al.*, 1979), marine ferromanganese nodules (Cronan, 1977; Calvert and Price, 1970, 1977; Calvert *et al.*, 1978; Piper *et al.*, 1979), East Pacific Rise sediments (Bostrom and Peterson, 1969; Horowitz, 1970; Crockett *et al.*, 1973), basal metalliferous sediment from the eastern Pacific (Cronan, 1976), stream sediments and concretionary Mn-Fe oxides (Nowlan, 1976), black coatings on stream boulders (Carpenter *et al.*, 1978) suspended particles of rivers (Gibbs, 1977; Teraoka and Kobayashi, 1980), ferromanganese-oxide crusts and nodules from Lake Michigan (Callender, 1973) all attest to the importance of hydrous Mn-Fe oxides as scavengers or accumulators of many elements. Furthermore, data for the chemical composition of ferromanganese nodules provide clues as to which elements associate preferentially with hydrous Mn oxides or with hydrous Fe oxides. For example, Calvert and Price (1977) showed that Mg, Ba, Cu, Mo, Ni and Zn in ferromanganese nodules from the eastern central Pacific are strongly correlated with Mn content, whereas Ti, P, As, Pb, Sr, Y, Ce, Zr and Co are correlated with Fe content.

The purpose of the present paper is 1) to summarize the interelement relationship in abyssal Pa-

cific ferromanganese nodules and in associated pelagic sediments using the statistical technique of R-mode factor analysis, 2) to demonstrate that the enrichment factors of inter-related elements in ferromanganese nodules relative to associated pelagic sediments are generally very similar, and 3) to discuss briefly possible causes of the observed interelement relationship in nodules and associated pelagic sediments.

SAMPLES AND METHODS

The bulk chemical composition data of abyssal ferromanganese nodules and associated pelagic sediments (for sediments, some acid leachate data were also included) from the equatorial Pacific (28°N ~ 13°S, 117°W ~ 175°E, excluding five sediment cores with high carbonate content), by Calvert and Price (1977), Wahine area (8°20'N, 153°W, near the Dome site A) by Calvert *et al.* (1978) and Dome sites (A = 8°27'N, 150°47'W; B = 11°42'N, 138°24'W; and C = 15°N, 126°W) by Piper *et al.* (1979) were chosen for R-mode factor analysis and enrichment factor calculation. The above three sets of data are all from the same general area. Calvert and Price (1977) and Calvert *et al.* (1978) have performed Q-mode factor analysis on their manganese nodule data. The interelement relationships obtained by Q-mode and R-mode factor analyses are essentially the same. But unlike R-mode factor analysis the multiple-regression coefficient of variables (*i.e.*, the concentrations of various elements) on factors by Q-mode factor analysis is not normalized to one for a perfect correlation; therefore R-mode factor analysis is preferred here for ease of graphic presentation of several results and their comparison.

The computer program for R-mode factor analysis was adopted from the "statistical package for the Social Sciences" (SPSS) by Nie *et al.* (1975). For usual runs, the following statistical information was extracted: means and standard deviations of variables (in the present case, the concentrations of various elements in a set of samples), correlation matrix, communalities, eigen-values and proportion of total and common variance, principal component matrix, and rotated factor matrix (varimax). The SPSS provides a concise definition for each of these terminologies. The eigen-value was cut off at 0.5. Any possible association of a group of elements in a set of given samples can usually be deduced from the coherence of these elements in a three-

Table 1. The correlation coefficients (in %) in ferromanganese nodules and associated sediments from Equatorial Pacific (a), Wahine area (b) and Dome Sites (c)

	Sediment (a)			Nodule (a)			Sediment (b)			Nodule (b)			Sediment (c)			Nodule (c)		
	Al	Fe	Mn	Al	Fe	Mn	Al	Fe	Mn	Al	Fe	Mn	Cs	Fe	(Mn)	Fe	Mn	
Al	100	-42	-52	100	-18	-73	100	35	-31	100	-35	-87	Fe	-24	100	-65	100	-30
Si	72	-83	-85	88	-14	-78	40	6	-57	95	-52	-79	Mn	-14			-30	100
Ti	-26	85	55	-7	73	36	90	29	-49	-1	91	-37	Cu				-77	72
Fe	-42	100	89	-18	100	45	35	100	-44	-35	100	-5	Ni				-70	76
Ca	-73	62	45	-53	44	26	-46	-7	50	62	-40	-53	Co	9	-11	30	76	-2
Mg	14	-12	-43	2	-54	51	-7	3	17	-16	-10	32	Zn	-54	63	86	-44	76
K	86	-53	-55	84	-42	-50	85	32	-53	52	-42	-32	Ba	-50	56	46	-4	31
P	-76	60	56	-19	86	-22	-15	-1	32	12	-12	-18	Hf	50	-7	2	65	-56
Mn	-52	89	100	-73	-45	100	-31	-44	100	-87	-5	100	Sb	-25	59	86	-3	73
CO ₃	-6	-34	-18	-28	69	-2							Th	82	-24	-40	78	-43
C _{org}	-41	85	95	4	-17	3							U	45	19	21	70	-25
As	-31	87	91	-13	83	-27	12	-44	20	-36	81	-1	Sc	-4	-51	-5	25	-63
Ba	21	-31	-8	-45	-58	82	-53	-2	68	-4	-56	25	Cr	94	-35	-48		
Ce	-50	94	95	-19	49	6	47	4	-20	0	88	-41	Cs	100	-24	-57		
Co	-54	87	99	-62	47	31	41	2	31	-35	92	-1	Rb	88	-10	-39		
Cu	-69	37	55	-10	-81	78	-6	-31	80	-30	-48	49	Ta	89	-5	-37		
Mo	-49	85	97	-48	-61	91	-46	-19	79	-69	-23	87	(Cu)	-25	28	77		
Ni	-39	75	88	-36	-80	84	-30	-39	95	-47	-7	48	(Ni)	-30	22	83		
Pb	-51	98	92	-28	76	-20	-3	23	14	-13	91	-23	(Co)	6	-13	44		
Rb	85	-52	-45	68	-42	-45	65	9	-64	40	-1	-45	(Zn)	-53	58	96		
Sr	-41	70	79	-66	77	9	-54	-10	64	31	54	-59	(Mn)	-47	65	100		
Th	0	25	28	45	16	-54	36	-3	-24	12	74	-41	(Fe)	-42	91	68		
Y	-76	44	45	-13	71	-17	-10	20	16	20	66	-54						
Zn	-48	51	28	-11	-59	46	-25	-9	67	-59	-31	80						
Zr	-29	83	74	-18	53	-19	54	23	-17	37	65	-62						
(Mn)*							-35	-46	99									
(Fe)							1	15	-25									

* Elements in parentheses represent the acid leachate data.

dimensional space of the principal component factors 1 to 3. Any pair of elements in a coherent group also should have a reasonably high correlation coefficient in the correlation matrix. Two words of caution concerning the interpretation of factor analysis results are necessary: an apparent correlation could also be caused by systematic error in chemical analysis or be an indirect one, as will be illustrated later. An apparent lack of correlation may also be produced, if the uncertainty in chemical analysis is greater than the natural variability. Therefore, the results of any factor analysis should always be checked for consistency against other relevant information.

The enrichment factor, E'_{Al} , is defined here as the average concentration ratio of element i and the normalizing element Al (C^i/C^{Al}) in ferromanganese nodules compared to this ratio in the associated pelagic sediments. The sea salt contribution in nodules and associated pelagic sediment (especially for Na and SO_4) was subtracted by assuming that Cl in the samples is purely of seawater origin. If the normalizing element is j instead of Al, then

$$E'_j = E'_{Al}/E'_{Alj}$$

and, if $E'_{Al} \approx 1$, then

$$E'_j \approx E'_{Alj}$$

RESULTS AND DISCUSSION

1. R-mode factor analysis

The correlation coefficients of various elements against Al (or Cs), Fe and Mn for three sets of data are presented in Table 1. (The complete correlation matrices will be provided on request by the author). The extracted principal component factors 1 to 3 are plotted (factors 1 vs. 2 and 1 vs. 3) in Fig. 1 for ferromanganese nodules and in Fig. 2 for associated pelagic sediments.

According to Fig. 1, elements in abyssal Pacific ferromanganese nodules can be grossly split into three major phase groups: 1) aluminosilicate group

(Al, Si, K, Rb and probably Sc), 2) Fe oxide group (Fe, Ti, Zr, Hf, Th, U, P, Y, As, Ce, Pb and CO_3), and 3) Mn oxide group (Mn, Mo, Sb, Ni, Cu, Zn, Ba and Mg). The Q-mode factor analysis of North Pacific ferromanganese nodules by Bischoff *et al.* (1981) indicates that Na also belongs to the alu-

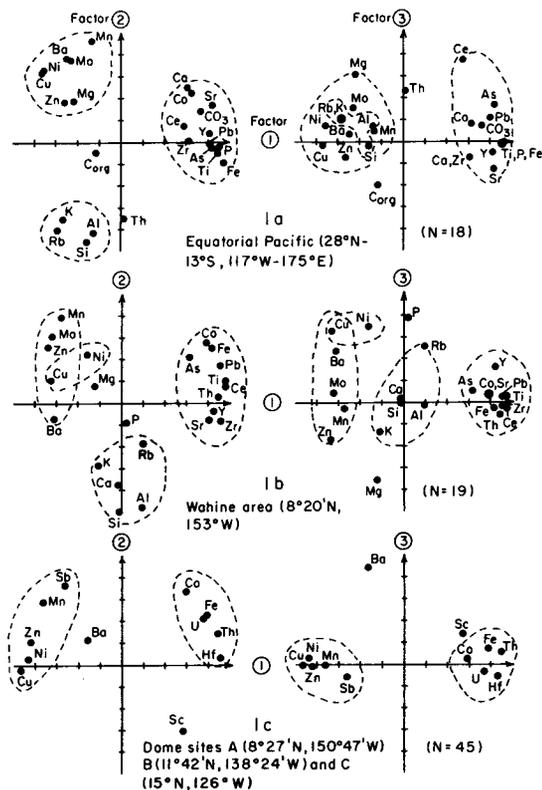


FIG. 1. Plots of the principal component factors 1 vs. 2 and factors 1 vs. 3 for ferromanganese nodules from a) the Equatorial Pacific, b) Wahine area, and c) Dome sites.

sediments (Fig. 2b and 2c, leachate data are in parentheses) even though the percentage of dissolution by acids varies greatly from element to element. (Added note: The correlation matrixes of Tables 4 and 7 by Piper *et al.* (1979) cannot be reproduced by using the raw data given in their Tables 3 and 6. The sign for the correlation coefficient of Co-Fe and Co-Ni pairs in their Table 11 should be reversed.)

In summary, most of the elements, both in abyssal Pacific nodules and associated pelagic clay sediments, are preferentially concentrated in one of the following three major phases, *i.e.*, aluminosilicates (Al, Si, Na, K, Rb, Cs and probably Sc), Fe oxides (Fe, Ti, Zr, Hf, Th, U, P, Y, As, rare earths, Pb, etc.) and Mn oxides (Mn, Co, Ni, Cu, Zn, Ba, Sr, Ca, Mg, Mo, Sb, etc.). In addition, common authigenic minerals in deep sea sediments and nodules also concentrate specific elements, *e.g.*, phosphate minerals (P, Y, Ca, Sr, rare earths), carbonates (Ca, Sr, CO₃) barite (Ba, SO₄) and siliceous ooze (Si). When the Fe content of pelagic sediments is low, aluminosilicates can become the predominant contributor for some of the Fe oxide group elements (Ti, Th, Ta, Cr) in sediments.

The detrital or crystal lattice components of aluminosilicates can contain many kinds of elements, but a significant fraction of alkali elements in aluminosilicates is concentrated by surface adsorption processes (Li, 1981). Fe-oxide group elements exist in seawater as oxyanions (P, As), hydroxide complexes of tri- and tetravalent cations (Ti, Zr, Hf, Th, Y, rare earths) and carbonate complexes (U, Pb), whereas the Mn oxide group elements are mainly mono- and divalent cations, except Mo and Sb which exist as oxyanions in seawater (*e.g.*, Brewer, 1975). While further verification is needed, it is plausible that Mo and Sb in the Mn oxide phase exist as manganese compounds instead of as adsorbed species.

II. Enrichment factor calculations

If Mn oxide group elements are concentrated only in the Mn oxide phases of both nodules and associated sediments through the same enrichment mechanisms, then one would expect that the E_{Al}^i 's of Mn oxide group elements should be similar, or E_{Mn}^i (Mn as normalizing element) should be close to one. This should also apply to Fe oxide and aluminosilicate

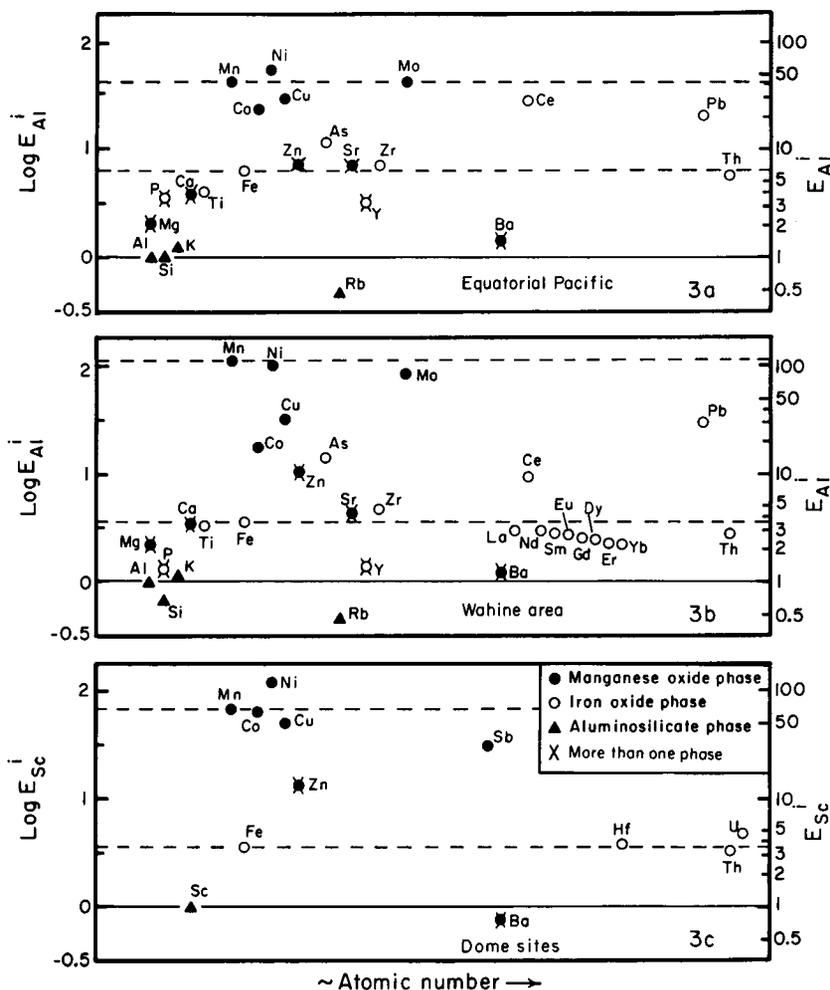


FIG. 3. Enrichment factors of elements in nodules relative to associated sediments (E_{Al}^i) for samples from a) the Equatorial Pacific, b) Wahine area and c) Dome sites.

group elements. Figure 3 shows this to be the case. For example, the E'_{Al} 's of Mn, Co, Ni, Cu, Mo and Sb (Mn oxide group) are high and very similar. The E'_{Al} 's of Fe, Ti, Zr, Hf, Th, U, P, Y, As and rare earth elements except Ce (Fe oxide group) are in medium values and again similar. The E'_{Al} 's of Al, Si, K and Rb (aluminosilicate group) are close to unity. Notice that, in Fig. 3c, Sc instead of Al was used as the normalizing element due to lack of Al data. As will be shown later, E'_{Sc} is close to unity; therefore $E'_{Al} \approx E'_{Sc}$. The rare earth data in Fig. 3b were obtained from Elderfield *et al.* (1981).

The few exceptions to the rule in Fig. 3 are explainable: The E'_{Al} 's of Mg, Ca, Sr, Ba and Zn (Mn oxide group) are much less than E'_{Al} because these elements reside not only in the Mn oxide phase, but also in other dominant phases of the sediments such as aluminosilicates, phosphates, carbonates and barite. The E'_{Al} 's of Pb and Ce (Fe oxide group) are higher than E'_{Al} , suggesting some additional enrichment mechanisms in nodules. For example, the formation of PbO_2 and CeO_2 (Sillen, 1961) in nodules can be postulated. One may reason that, during the extremely slow growth of the mixture of amorphous $FeOOH$ and colloidal δMnO_2 on the top of manganese nodules, any organic matter is oxidized away by aerated seawater, and a high pE environment prevails in the $FeOOH$ - δMnO_2 mixture, facilitating the oxidation of Pb^{+2} to Pb^{+4} and Ce^{+3} to Ce^{+4} . Whereas in sediments the accumulation rate of pelagic clays is relatively fast, the oxidation of organic matter in sediments causes a relatively low pE environment in sediments. In Fig. 3b, the E'_{Al} 's of P and

Y (Fe oxide group) are lower than E'_{Al} , due to the existence of phosphate minerals in Wahine area sediments (Elderfield *et al.*, 1981).

For the purpose of comparison, the E'_{Al} 's of various elements in the world average nodules (using the world average pelagic clays as the reference material) were estimated and given in Fig. 4. Data for world's average nodule composition were taken from Cronan (1976; some missing data were supplemented by his Pacific Ocean data). Additional data are included for rare earths (Piper, 1974), for Li, Be, Ge, Nb and Se (Cronan and Thomas, 1972), for In (Glasby, 1973), and for Na, Cs and S (Glasby *et al.*, 1978). The Na and S data by Glasby *et al.* (1978) are preferred here, since the sea salt contributions can be subtracted using Cl data. The world's average pelagic clay data are mainly from Turekian and Wedepohl (1961). Though better, more recent data are included for the rare earths (Piper, 1974), for Bi (Marowsky and Wedepohl, 1971), and for Au, Pd and Ir (Crocket *et al.*, 1973).

The enrichment pattern of common elements in Figs. 3 and 4 are very similar. In addition, an E'_{Al} of close to one for Be, Sc, Ga in Fig. 4 suggests their association with the aluminosilicate group. Since Na, K, Rb and Cs belong to the aluminosilicate group, one would also expect the association of Li with the same group. However, an E'_{Al} of less than one for alkali elements indicates a deficiency of alkali elements (especially Li) in nodules as compared to sediments. The mineralogical difference of aluminosilicates in nodules (mainly phillipsite, Bischoff *et al.*, 1981, Burns and Burns, 1978) and in sediments (clay

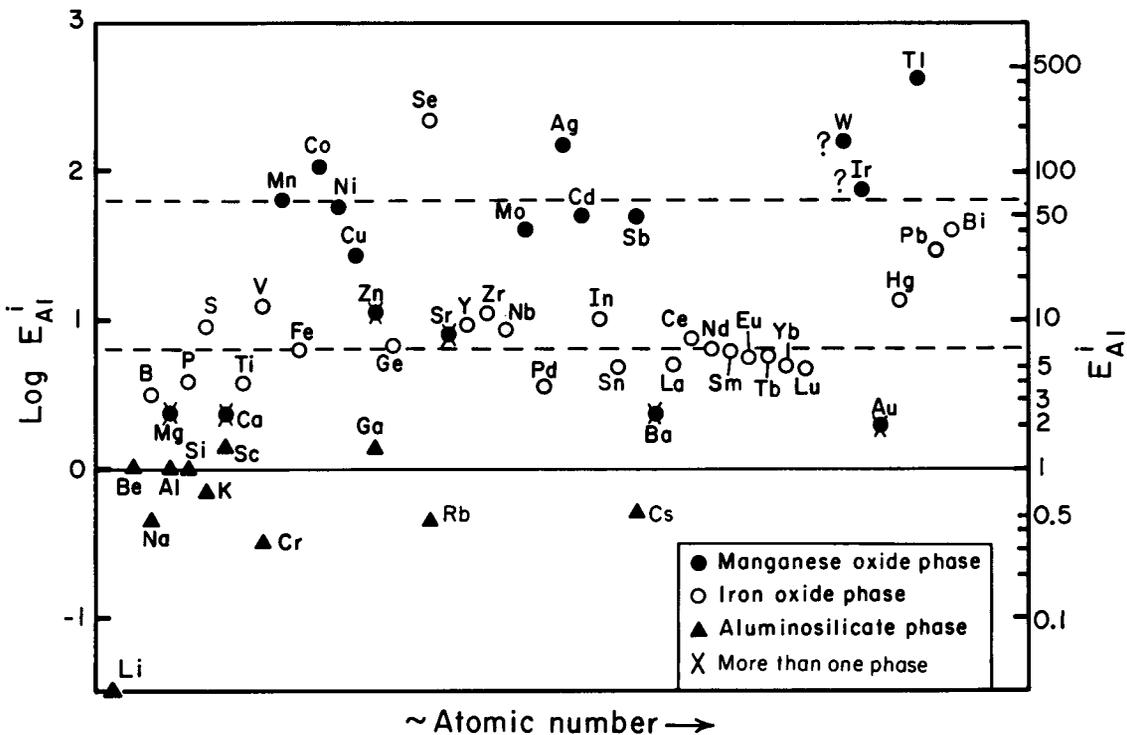


FIG. 4. Enrichment factors of elements in the world's average ferromanganese nodules relative to the world's average pelagic clays (roughly in the increasing order of atomic number).

minerals) may explain the deficiency of alkali elements in nodules, if alkali elements (especially Li) are deficient in phillipsite compared to clay minerals. The E_{Al}^I of less than one (Fig. 4) may be caused by the oxidation of Cr(III) into more soluble CrO_4^{2-} in the highly oxidizing nodule environment and indicates the predominance of Cr in the aluminosilicate phase of sediments.

The similar value of E_{Al}^{Fe} and E_{Al}^I 's of additional elements like B, S, V, Ge, Nb, Pd, In, Sn and Hg in Fig 4 again suggests the association of these elements with the Fe-oxide phase. Adsorption experiments have shown that B (Harder, 1959) and V (Krauskopf, 1956) can be readily adsorbed by fine iron oxide or hydroxide particles in a seawater medium. The results from radiotracer experiments in microcosms simulating the Narragansett Bay environment (Santschi *et al.*, 1980, and unpublished data) also indicate similar rapid removal behavior of Hg, Sn, Th, Pa, Pb, Am(III), Pu(IV), Cr(III) and Fe from the seawater column to sediments. Though Hg exists in seawater as strong $HgCl_4^{2-}$ complex, Hg is not adsorbed by hydrous Fe oxide as chloro-complex (Kinniburgh and Jackson, 1978) but more likely as hydrolyzed $Hg(OH)_2$ due to its very high hydrolysis constant. Pb is probably adsorbed by the Fe oxide phase of sediments as $PbCO_3$ and/or $Pb(OH)_2$ (again needs verification). Se is adsorbed more by ferric oxide or hydroxide than by Mn oxide in seawater medium (Karkar *et al.*, 1968). Fe and Bi are also moderately correlated in nodules (data by Ahrens *et al.*, 1967). But E_{Al}^I 's of Se and Bi are both much higher than E_{Al}^{Fe} , again suggesting some additional enrichment mechanisms for Se and Bi in nodules (possibly as $Fe_2(SeO_3)_3$ and Bi_2O_3). Te is also very much enriched in nodules (Lakin *et al.*, 1963). Considering the geochemical similarity between Se and Te, Te is likely related to the Fe-oxide phase. After subtracting seasalt components, there is still a significant amount of I and Br left in nodules (Cronan and Thomas, 1972). It is likely that I and Br are adsorbed by the iron-oxide phase of nodules as IO_3^- and BrO_3^- species. In short, the additional Fe oxide group elements are again oxyanions or anions (B, S, V, I, Br, Se, Te), hydroxide complexes of tri- and tetravalent cations (Ge, In, Sn, Pa, Am, Pu, Nb, Pd and Bi) except Hg which is chloro-complex in seawater but probably adsorbed as $Hg(OH)_2$.

The E_{Al}^I 's of additional elements like Ag, Cd, W and Ir are close to E_{Al}^{Mn} but E_{Al}^I is greater than E_{Al}^{Mn} (see Fig. 4). The affinity of Ag, Tl and Cd to Mn oxide are well documented (Anderson *et al.*, 1973, for Ag; Vorkresenskaya and Usevich, 1957, for Tl; and Van der Weijden, 1976, for Cd). The fact that E_{Al}^I is greater than E_{Al}^{Mn} may again be caused by the formation of Tl_2O_3 in the highly oxidizing nodule environment.

E_{Al}^{Au} is lower than E_{Al}^{Mn} but is greater than one, suggesting the association of Au with the aluminosilicate phase of the sediments (Glasby *et al.*, 1978) as well as with the Mn-oxide phase. Ag, Au and Cd

form chloro-complexes in seawater (Brewer, 1975), but like Hg, these elements are apparently not adsorbed by Mn oxides as chlorocomplexes. Whether W and Ir really belong to the Mn oxide group (like Mo and Sb) needs to be verified independently.

III. Causes of specific association

The specific association of elements with aluminosilicates, Fe oxides and Mn oxides was also demonstrated by the determination of the distribution coefficients, K_d (= the concentration ratio of elements in solids and seawater at equilibrium). For example, Duursma and Eisma (1974) found that the K_d 's of ^{86}Rb , ^{137}Cs and ^{65}Zn in marine sediments are positively correlated with the cation-exchange capacity or the aluminosilicate content of marine sediments, whereas the K_d 's of ^{59}Fe , ^{106}Ru , ^{95}Zr , ^{147}Pm , ^{144}Ce and ^{210}Pb are independent of cation-exchange capacity and probably are correlated with the amount of iron oxide coating on clay particles, as exemplified by the positive correlation between K_d of ^{106}Ru and 20% HCl extractable Fe in sediments. Takematsu (1979) also found that the K_d 's of Mn(II), Co, Ni, Cu and Zn are the highest in δMnO_2 , followed by hydrous ferric oxide, whereas Na-montmorillonite and ferromanganese-oxide-free red clay have the lowest K_d 's for these transition metals.

The specific association of elements with aluminosilicates, Fe-oxides and Mn-oxides can be explained by fundamental differences in physicochemical properties of these three phases *e.g.*, the pH of zero point of charge (pH_{zpc}) and dielectric constant (ϵ) (Li, 1981). Briefly, according to James and Healy's (1972) adsorption model, the change in the Gibbs free energy during the adsorption of ions on solids (ΔG_{ads}) includes the contributions from the coulombic electrostatic interaction ($\Delta G_{coul.}$), the secondary solvation or hydration ($\Delta G_{solv.}$), and the chemical or non-coulombic interaction ($\Delta G_{chem.}$) at the solid-solution interface, thus,

$$\Delta G_{ads} = \Delta G_{coul.} + \Delta G_{solv.} + \Delta G_{chem.} \quad (1)$$

$\Delta G_{coul.}$ is equal to $Ze\Psi$, where Z is the valency of the adsorbing ion, e the electronic charge, and Ψ the potential at its equilibrium position in the interface. Ψ is, in turn, a function of both RT/e ($pH_{zpc} - pH$) and the ionic strength of the solution. Therefore, at oceanic pH of 8, Ψ is negative for aluminosilicates with $pH_{zpc} \approx 3.3$ to 4.6 for kaolinite and <2.5 for montmorillonite (Parks, 1967) and is also negative for δMnO_2 with $pH_{zpc} \approx 1.3$ to 2.8 (Morgan and Stumm, 1964; Balistrieri and Murray, 1981, 1982). The negative Ψ facilitates the adsorption of positively charged ion species ($\Delta G_{coul.} < 0$) and hinders the adsorption of negatively charged ion species ($\Delta G_{coul.} > 0$). Furthermore, the change in the Gibbs free energy of solvation ($\Delta G_{solv.}$) during the adsorption of hydrated cation on solids is a function of

$$Z^2 e^2 / \gamma [1/\epsilon_{interface} - 1/\epsilon_{water}] \quad (2)$$

where γ = radius of hydrated cation, and $\epsilon_{interface}$ and

ϵ_{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 ϵ_{water} (=78 at 25°C), $\Delta G_{\text{sol.}}$ is always positive and hinders the adsorption of hydrated cations. The dielectric constants of aluminosilicates ($\epsilon \sim 4.8$ to 8, Keller, 1966) are much smaller than that of manganese oxide ($\epsilon \sim 32$, Murray, 1975). Therefore, according to equation (2), $\Delta G_{\text{sol.}}$ is always much greater for aluminosilicates than for manganese oxides, especially for high valent, low ionic radius cations (e.g., transition metals). This can explain why aluminosilicate phases in the ocean strongly adsorb alkali elements but not transition metals, while Mn oxide phases strongly adsorb transition metals.

For Fe-oxide phases, Ψ is probably near zero at an oceanic pH of 8 with $\text{pH}_{\text{zpc}} \approx 7.1$ to 8.3 for $\alpha\text{-FeOOH}$ in NaCl solution and artificial seawater (Hingston *et al.*, 1972; Balistrieri and Murray, 1981). Thus, the $\Delta G_{\text{coul.}}$ term is relatively small for the Fe-oxide phases and is zero for neutral ion species (e.g., hydroxide complexes of many tri- and tetravalent cations). There is no dielectric constant data for hydrous iron oxide but it is likely to be greater than that of aluminosilicates, and the hindrance of adsorption by the secondary solvation should be relatively small. For neutral ion species, $\Delta G_{\text{sol.}}$ is zero. Thus the adsorption of neutrally or negatively charged ions on Fe oxides are largely dominated by the $\Delta G_{\text{chem.}}$ term (e.g., covalent bond formation). The relationship between $\Delta G_{\text{ads.}}$ and the partitioning coefficient in the ocean (the concentration ratio of element in oceanic pelagic clays over seawater) for various elements are discussed elsewhere (Li, 1981).

CONCLUSION

Both in abyssal Pacific ferromanganese nodules and associated pelagic sediments, the elements preferentially incorporated into the Fe-oxide phase are mainly oxyanions or anions (e.g., P, S, V, Se, Te, As, B, Sn, I, and Br), hydroxide complexes of tri- and tetravalent cations (e.g., Ti, Ge, Y, Zr, Nb, Pd, In, rare earths, Hf, Th, Pa, Pu, Am and Bi) carbonate complexes of U and Pb, and chloro-complex of Hg in seawater. The elements associated strongly with the Mn-oxide phase are mono- and divalent cations (e.g., Tl, Ag, Cd, Mg, Ca, Ba, Ra, Co, Ni, Cu and Zn), and oxyanions like Mo, Sb and probably W, which may form manganese compounds. The elements predominant in the aluminosilicate phase are alkali elements and crystal lattice components such as Be, Sc, Ga, Cr, and sometimes Ti, Th, or Ta. In addition, elements are also concentrated by common authigenic minerals in deep-sea deposits such as phosphate minerals (P, Y, Ca, Sr and rare earths), barite (Ba and SO_4), carbonates (Ca, Sr, CO_3) and opal (Si).

The specific association of elements with aluminosilicates, Fe oxides and Mn oxides can be explained by fundamental differences in physicochemical properties of these three major phases.

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REFERENCES

- Ahrens L. H., Willis J. P. and Oosthuizen C. O. (1967) Further observations on the composition of manganese nodules, with particular reference to some of the rarer elements. *Geochim. Cosmochim. Acta* **31**, 2169–2180.
- Anderson B. J., Jenne E. A. and Chao T. T. (1973) The sorption of silver by poorly crystallized manganese oxides. *Geochim. Cosmochim. Acta* **37**, 611–622.
- Balistreri L. S. and Murray J. W. (1981) The surface chemistry of goethite ($\alpha\text{-FeO(OH)}$) in major ion seawater. *Amer. J. Sci* **281**, 788–806.
- Balistreri L. S. and Murray J. W. (1982) The surface chemistry of δMnO_2 in major ion seawater. *Geochim. Cosmochim. Acta* **46**, 1041–1052.
- Banning D. L. (1979) Variations in certain transition elements in the oxides in marine manganese nodules. M. S. Thesis, Dept. Geol., Washington State Univ., Pullman, Washington, 113 pp.
- Bischoff J. L., Heath G. R. and Leinen M. (1979) Geochemistry of deep sea sediments from the Pacific manganese nodule province: DOMES sites A, B, and C. In *Marine Geology and Oceanography of Pacific Manganese Nodule Province* (Eds. J. L. Bischoff and D. Z. Piper.), 397–436, Plenum Publ. Co.
- Bischoff J. L., Piper D. Z. and Leong K. (1981) The aluminosilicate fraction of North Pacific manganese nodules. *Geochim. Cosmochim. Acta* **45**, 2047–2063.
- Bostrom K. and Peterson M. N. A. (1969) The origin of aluminum-poor ferro-manganese sediments in areas of high heat flow on the East Pacific Rise. *Mar. Geol.* **7**, 427–447.
- Brewer P. G. (1975) Minor elements in seawater. In *Chemical Oceanography*, Vol. I, 2nd ed., (Eds. J. P. Riley and G. Skirrow.), Academic Press, New York, 606 pp.
- Burns R. G. (1976) The uptake of cobalt into ferromanganese nodules, soils and synthetic manganese (IV) oxides. *Geochim. Cosmochim. Acta* **40**, 95–102.
- Burns R. G. and Fuerstenau D. W. (1966) Electron-probe determination of inter-element relationships in manganese nodules. *Amer. Mineral.* **51**, 895–902.
- Burns V. M. and Burns R. G. (1978) Post-depositional metal enrichment processes inside manganese nodules from the North Equatorial Pacific. *Earth Planet. Sci. Lett.* **9**, 341–348.
- Callender E. (1973) Geochemistry of ferromanganese crust, manganese carbonate crust, and associated ferromanganese nodules from Green Bay, Lake Michigan. In *Inter-University Program of Research on Ferromanganese Deposits of the Ocean Floor*. Phase I report sponsored by Seabed Assessment Program, NSF, Washington, D. C., 358 pp.
- Calvert S. E. and Price N. B. (1970) Composition of manganese nodules and manganese carbonates from Loch Fyne, Scotland. *Contrib. Mineral. Petrol.* **29**, 215–233.
- Calvert S. E. and Price N. B. (1977) Geochemical variation in ferromanganese nodules and associated sediments from the Pacific Ocean. *Mar. Chem.* **5**, 43–74.
- Calvert S. E., Price N. B., Heath G. R. and Moore T. C. Jr. (1978) Relationship between ferromanganese nodule compositions and sedimentation in a small survey area of the equatorial Pacific. *J. Mar. Res.* **36**, 161–183.
- Carpenter R. H., Robinson G. D. and Hayes W. B. (1978) Partitioning of Mn, Fe, Cu, Zn, Pb, Co and Ni in black coatings on stream boulders in the vicinity of the Magruder mine, Lincoln Co., Georgia. *J. Geochem. Explor.* **10**, 75–89.

- Crocket J. H., MacDougall J. D. and Harriss R. C. (1973) Gold, palladium and iridium in marine sediments. *Geochim. Cosmochim. Acta* **37**, 2547-2556.
- Cronan D. S. (1969/1970) Inter-element associations in some pelagic deposits. *Chem. Geol.* **5**, 99-106.
- Cronan D. S. (1976) Basal metalliferous sediments from the eastern Pacific. *Bull. Geol. Soc. Amer.* **87**, 928-934.
- Cronan D. S. (1976) Manganese nodules and other ferromanganese oxide deposits. In *Chemical Oceanography*, Vol. 5, (Eds. J. P. Riley and C. Chester), Academic Press, New York.
- Cronan D. S. (1977) Deep-sea nodules: distribution and geochemistry. In *Marine Manganese Deposits*. (Ed. G. P. Glasby) 11-44, Elsevier Sci. Publ. Co.
- Cronan D. S. and Thomas R. L. (1972) Geochemistry of ferromanganese oxide concretions and associated deposits in Lake Ontario. *Bull. Geol. Soc. Amer.* **8**, 1493-1502.
- Duursma E. K. and Eisma D. (1974) Theoretical, experimental and field studies concerning reactions of radioisotopes with sediments and suspended particles of the sea, part C: application to field studies. *Netherland J. Sea Res.* **6**, 265-324.
- Elderfield H., Hawkesworth C. J., Greaves M. J. and Calvert S. E. (1981) Rare earth element geochemistry of oceanic ferromanganese nodules and associated sediments. *Geochim. Cosmochim. Acta* **45**, 513-528.
- Gibbs R. J. (1977) Transport phase of transition metals in the Amazon and Yukon rivers. *Bull. Geol. Soc. Amer.* **88**, 829-843.
- Glasby G. P. (1973) Mechanisms of enrichment of the rarer elements in marine manganese nodules. *Mar. Chem.* **1**, 105-125.
- Glasby G. P., Keays R. R. and Rankin P. C. (1978) The distribution of rare earth, precious metal and other trace elements in recent and fossil deep sea manganese nodules. *Geochem. J.* **12**, 229-243.
- Goldberg E. D. (1954) Marine geochemistry I-Chemical scavengers of the sea. *J. Geol.* **62**, 249-265.
- Harder H. (1959) Beitrag zur Geochemie des Bors, Nachdr. Akad. Wiss. Göttingen, II. Math.-Phys. Kl, Teil II. 123.
- Hingston F. J., Posner A. M. and Quirk J. P. (1972) Anion adsorption by goethite and gibbsite. *J. Soil Sci.* **23**, 177-192.
- Horowitz A. (1970) The distribution of Pb, Ag, Tl and Zn in sediments on active oceanic ridges. *Mar. Geol.* **9**, 241-259.
- James R. D. and Healy T. W. (1972) Adsorption of hydrolyzable metal ions at the oxide-water interface III. A thermodynamic model of adsorption. *J. Colloid Interface Sci.* **40**, 65-81.
- Jenne E. A. (1968) Controls on Mn, Fe, Co, Ni, Cu and Zn concentrations in soils and water: the significant role of hydrous Mn and Fe oxides. In *Trace Inorganics in Water* (Ed. R. A. Baker), 337-387, *Advances in Chemistry Series* 73, Amer. Chem. Soc.
- Keller G. V. (1966) Electrical properties of rocks and minerals. In *Handbook of Physical Constants* (Ed. S. P. Clark), Geol. Soc. Amer. Memoir 97, 587 pp.
- Kharkar D. P., Turekian K. K. and Bertine K. K. (1968) Stream supply of dissolved silver, molybdenum, antimony, selenium, chromium, cobalt, rubidium and cesium to the oceans. *Geochim. Cosmochim. Acta* **32**, 285-298.
- Kinniburgh D. G. and Jackson M. L. (1978) Adsorption of Mercury (II) by iron hydrous oxide gel. *Soil Sci. Soc. Amer. J.* **42**, 45-47.
- Krauskopf K. B. (1956) Factors controlling the concentrations of thirteen rare metals in seawater. *Geochim. Cosmochim. Acta* **9**, 1-32.
- Lakin H. W., Thompson C. E. and Davidson D. F. (1963) Tellurium content of marine manganese oxides and other manganese oxides. *Science* **142**, 1568.
- Li Y.-H. (1981) Ultimate removal mechanisms of elements from the ocean. *Geochim. Cosmochim. Acta* **45**, 1659-1664.
- Marowsky G. and Wedepohl K. H. (1971) General trends in the behavior of Cd, Hg, Tl and Bi in some major rock forming processes. *Geochim. Cosmochim. Acta* **35**, 1255-1267.
- Moorby S. A. and Cronan D. S. (1981) The distribution of elements between co-existing phases in some marine ferromanganese-oxide deposits. *Geochim. Cosmochim. Acta* **45**, 1855-1877.
- Morgan J. J. and Stumm W. (1964) Colloid-chemical properties of manganese dioxide. *J. Colloid Sci.* **19**, 347-359.
- Murray J. W. (1975) The interaction of metal ions at the manganese dioxide-solution interface. *Geochim. Cosmochim. Acta* **39**, 505-519.
- Nie N. H., Hull C. H., Jenkins J. C., Steinbrenner K. and Bent D. H. (1975) *Statistical Package for the Social Sciences*, 2nd ed., McGraw-Hill Co., New York 675 pp.
- Nowlan G. A. (1976) Concretionary manganese-iron oxides in streams and their usefulness as a sample medium for geochemical prospecting. *J. Geochem. Explor.* **6**, 193-210.
- Parfitt R. L., Fraser A. R. and Farmer V. C. (1977) Adsorption on hydrous oxides. III: Fulvic and humic acid on goethite gibbsite and imogolite. *J. Soil Sci.* **28**, 289-296.
- Parks G. A. (1967) Aqueous surface chemistry of oxides and complex oxide minerals. Isoelectronic point and zero point of charge. In *Equilibrium Content in Natural Water System* (Ed. R. F. Gould), *Advances in Chemistry Series* 67, Amer. Chem. Soc., 344 pp.
- Piper D. (1974) Rare-earths in ferromanganese nodules and other marine phases. *Geochim. Cosmochim. Acta* **38**, 1007-1022.
- Piper D. Z., Leong K. and Cannon W. F. (1979) Manganese nodules and surface sediment compositions: Dome sites A, B and C. In *Marine Geology and Oceanography of the Pacific Manganese Nodule Province* (Eds. J. L. Bischoff and D. Z. Piper), 437-473, Plenum Publ. Co.
- Santschi P. H., Adler D., Amdurer M., Li Y.-H. and Bell J. J. (1980) Thorium isotopes as analogues for "particle-reactive" pollutants in coastal marine environments. *Earth Planet. Sci. Lett.* **47**, 327-335.
- Sillen L. G. (1961) The physical chemistry of seawater. In *Oceanography* (Ed. M. Sears), Amer. Assoc. Adv. Sci. Publ. 67, 549-581.
- Sorem R. K. and Fewkes R. H. (1979) *Manganese Nodule: Research Data and Methods of Investigation*. IFI/Plenum, New York, 723 pp.
- Takematsu N. (1979) Sorption of transition metals on manganese and iron oxide, and silicate minerals. *J. Oceanogr. Soc. Japan* **35**, 36-42.
- Teraoka H. and Kobayashi J. (1980) Concentrations of 21 metals in the suspended solids collected from the principal 166 rivers and 3 lakes in Japan. *Geochem. J.* **14**, 203-226.
- Tippling E. (1981) The adsorption of aquatic humic substances by iron oxides. *Geochim. Cosmochim. Acta* **45**, 191-199.
- Turekian K. K. and Wedepohl K. H. (1961) Distribution of the elements in some major units of the earth's crust. *Bull. Geol. Soc. Amer.* **72**, 175-192.
- Usui A. (1979) Minerals, metal contents and mechanism of formation of manganese nodules from the central Pacific Basin (GH-76-1 and GH-77-1 areas). In *Minerals, Marine Geology and Oceanography of the Pacific Manganese Nodule Province* (Eds. J. L. Bischoff and D. Z. Piper), 651-699, Plenum Publ. Co.
- Van der Weijden C. H. (1976) Experiments on the uptake of zinc and cadmium by manganese oxides. *Mar. Chem.* **4**, 377-387.
- Voskresenskaya N. T. and Usevich T. D. (1957) The occurrence of thallium in manganese minerals. *Geochemistry*, 710-721.