

Geochemical cycles of elements and human perturbation*

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Abstract—The pollution inputs of various elements are omnipresent in aerosols, snows, rivers and the ocean of the northern hemisphere. The mid-ocean ridges are not important sinks or sources for most of the elements. The settling of fecal pellets is the predominant transport mechanism of most elements (except Mn, Co and Ni) from the surface to deep oceans. Dissolved Mn, Co and Ni are directly incorporated into pelagic clays at the sediment–water interface.

INTRODUCTION

The present work is a preliminary attempt to synthesize various geochemical data and to answer the questions of the relative importance of (1) anthropogenic inputs of various elements as compared to natural sources, (2) mid-ocean ridges (through seawater–basalt interactions) as extra sources or sinks of some elements in the ocean, and (3) zooplankton fecal pellets as the carriers of elements from the surface to deep oceans compared to other possible carriers. Answers to these questions are sought in the following three sections using enrichment factor calculations, R-mode factor analysis and mass balance calculations. The selection of geochemical data from various literature sources may appear somewhat arbitrary. In principle, however, the newest data are always adopted if the new data are quite different from the old data due to the improvement of analytical techniques. If the new data are not greatly different from the old data, the old data are retained.

THE ENRICHMENT FACTORS AND THE INTERELEMENT RELATIONSHIPS IN MARINE PLANKTON, SUSPENDED PARTICLES, AEROSOLS AND POLAR SNOWS

The enrichment factor of element i in a sample, E_{Al}^i , is defined as the concentration ratio of element i to Al (C^i/C^{Al}) in the sample compared to this ratio in a standard material. In this section, average shale (TUREKIAN and WEDEPOHL, 1961) is adopted as the standard material. Average crustal igneous rock (TAYLOR, 1964) is very often used as the standard material (e.g. HERRON *et al.*, 1977; WEISS *et al.*, 1978). Average shale is preferred here, however, since it is more representative of the continental soils (e.g. LANTZY and MACKENZIE, 1979) than is average crustal igneous rock. For example, the concentrations of B, S, Se, As, Sb, Te, I, Hg, Bi are almost about one order of magnitude lower in average crustal igneous rocks than the shale material (LI, 1981). In the calculation of E_{Al}^i values, the sea salt components both in the sample and standard are sub-

tracted by assuming Cl is purely of seawater origin (e.g. the sea salt component of element i in the sample is $C_{sample}^{Cl} \times (C^i/C^{Cl})_{seawater}$). Therefore, an E_{Al}^i value of greater than one indicates sources other than shale or soil particles and sea salts.

The term 'biophile' elements is loosely applied here to a group of elements whose E_{Al}^i values in plankton are about 10 or greater, as shown in Fig. 1A. The sources of plankton data are mainly from MARTIN *et al.* (1976). Additional data for Co, Cr, Ce, Cs, Eu, Hg, Sb, Sc and Se are supplemented by FOWLER (1977) and for V, B and Mo by MOORE and BOSTROM (1978). For common elements the agreement among the above-mentioned three data sources is excellent. As will be shown later, the 'biophile' elements are almost identical to the so-called 'anomalously enriched elements' (AEE) in aerosols (e.g. MAENHAUT and ZOLLER, 1979).

According to the data given by MARTIN and KNAUER (1973) zooplankton give slightly higher E_{Al}^i 's than phytoplankton but the differences are small. Therefore no attempt has been made to separate phyto- and zooplankton in this paper. MOORE and BOSTROM (1978) demonstrated further that E_{Al}^i 's in plankton obtained from various oceans are very similar. For the purpose of comparison, the E_{Al}^i 's in North Atlantic suspended particles (obtained from water depths between 900 and 5000 m by BUAT-MENARD, 1979), North Atlantic aerosols (mainly by BUAT-MENARD, 1979, Cd by DUCE *et al.*, 1976; S by CUONG *et al.*, 1974; and I by MOYERS and DUCE, 1972), Greenland snows (WEISS *et al.*, 1971a, b, 1975 and 1978; HERRON *et al.*, 1977) South Pole aerosols (MAENHAUT and ZOLLER, 1979), and Antarctic snows (BOUTRON and MARTIN, 1980; DELMAS and BOUTRON, 1980; WEISS *et al.*, 1971a, b) are summarized in Figs 1 and 2.

For snow samples from Camp Century and Dye-3 stations, Mn was used as the normalizing element due to the lack of Al data (WEISS *et al.*, 1978). This is justifiable since $E_{Al}^{Mn} \approx 1$ (e.g. Milcent snows, North Atlantic aerosols, Fig. 2A), therefore $E_{Al}^i \approx E_{Mn}^i$. The similarity in the enrichment patterns of various elements among marine plankton, suspended particles (Fig. 1A), aerosols (Figs 1B, 2A and 2B), and polar snows (Figs 2A and 2B) is striking. Equatorial Atlantic aerosols (Fig. 1C) represent mainly the input of soil dust from the Sahara Desert (BUAT-MENARD, 1979) and will be discussed separately.

The 'biophile' elements are very much enriched even in the pre-1900 (or pre-industrial) Greenland snows (Fig. 2A), indicating natural sources other than sea salts and continental soils (e.g. HERRON *et al.*, 1977; WEISS *et al.*, 1978; BOUTRON, 1979). The E_{Al}^i values for Pb, Cu, Zn, Sb and S are about two to three times higher in post-1960 than in pre-1900 Greenland snows (Fig. 2A), suggesting large pollution inputs of these elements (50–75% of the total) in

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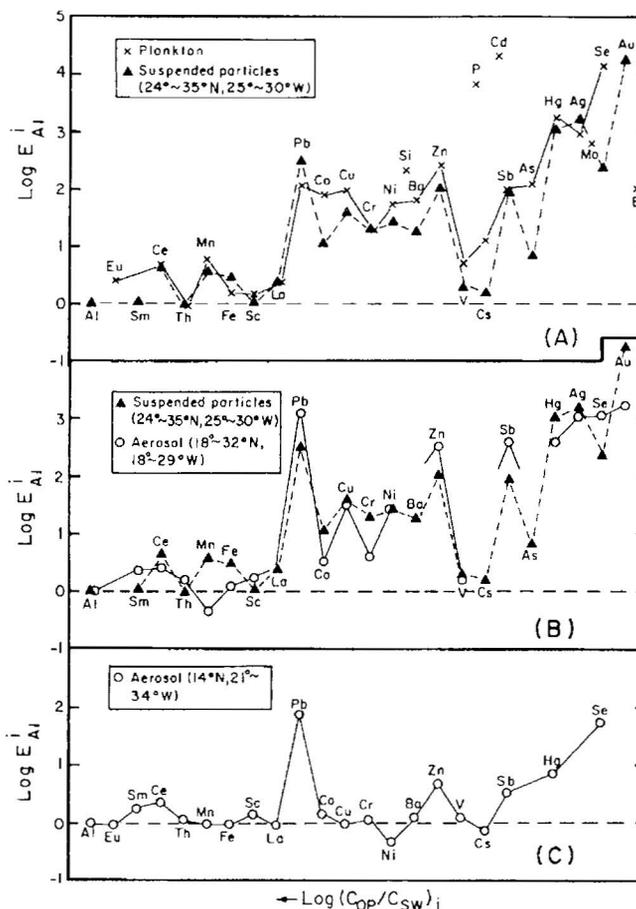


Fig. 1. Enrichment factors of various elements in (A) marine plankton and suspended particles from the North Atlantic, (B) aerosols from the North Atlantic, and (C) aerosols from the equatorial Atlantic. The elements are arranged roughly in decreasing order of C_{op}^i/C_{sw}^i where C_{op}^i and C_{sw}^i are the concentrations of element i in the average oceanic pelagic clay and in seawater, respectively.

addition to natural sources (e.g. HERRON *et al.*, 1977). RAHN and McCAFFREY (1979) suggest the possibility of large fractionation of the 'biophile' elements between aerosols and snows in the Alaskan Arctic (higher enrichment in aerosols than in snows). Therefore, the pollution input components in North Atlantic aerosols may not be quantifiable by sample comparison to pre-1900 Greenland snow. But the pollution component in post-1960 North Atlantic aerosol should be at least as great as that in Greenland snows (50–75%). Interestingly, there is no significant difference in E_{Al}^i values for Hg and Cd between pre-1900 and post-1960 Greenland snows and even North Atlantic aerosols (one exception is Cd from post-1960 snows at the Dye-3 station, probably due to sample contamination as noted by HERRON *et al.*, 1977). The implication is that Hg and Cd have very strong natural sources as compared to any pollution inputs in the northern hemisphere. WEISS *et al.* (1971) reached the same conclusion for Hg by comparing the estimated fluxes of Hg from natural and human sources to the atmosphere.

In Antarctic snows (average of the last 100 yr) and South Pole aerosols collected between 1974, 1975, the E_{Al}^i 's for Pb, Cu, Zn, Cd, Ag and S are surprisingly similar (Fig. 2B), indicating no fractionation between aerosols and snows in the Antarctic. Furthermore, BOUTRON and LORUS (1979), BOUTRON (1980) and DELMAS and BOUTRON (1980) have demonstrated that E_{Al}^i 's for these elements in the Antarctic

snows show no systematic trend from 1881 to 1977. Therefore, they conclude that the background aerosols in the Antarctic region are not significantly influenced by global pollution and the enriched 'biophile' elements and S in aerosols have natural sources other than sea salts and continental soils. The high enrichment of Br in South Pole aerosols, but not in North Atlantic aerosols (Figs 2A and 2B), may suggest that the direct source of Br in South Pole aerosols is gaseous bromine species in the atmosphere instead of sea spray.

In the pre-industrial period, the enrichment of the 'biophile' elements in aerosols and polar snow was supplied from (1) the air-sea interface by the bursting of bubbles (DUCE *et al.*, 1976) and/or by the volatilization of these metals through biological activity (e.g. biomethylation of Hg, Pb, Au, Pd, Pt, Tl, Se, S, Sn, As, etc., as summarized by RIDLEY *et al.*, 1977), (2) volcanic exhalations (e.g. MROZ and ZOLLER, 1975), and (3) volatilization of metals from land vegetation (BEAUFORD *et al.*, 1977) or from surface rocks (GOLDBERG, 1976), etc. The relative importance of various possible sources will be discussed in the next section.

R-mode factor analyses were performed on the chemical composition data of marine plankton (MARTIN *et al.*, 1976), suspended particles and aerosols (BUAT-MENARD, 1979) in order to study the correlation among various elements in these materials and try to elucidate their implications. The

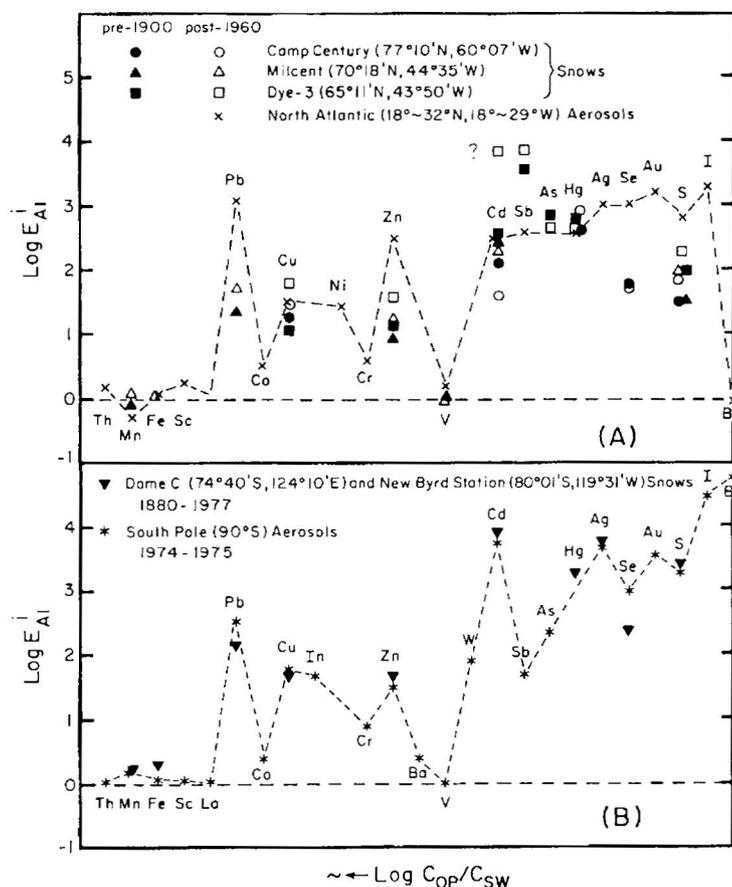


Fig. 2. Enrichment factors of various elements in (A) Greenland snows and North Atlantic aerosols, and (B) Antarctic snows and South Pole aerosols.

computer program for the factor analysis was adopted from SPSS (*Statistical Package for the Social Sciences*; NIE *et al.*, 1975). All of the data were first converted to a logarithmic scale. The eigen-value was cut-off at 0.5. Factors 1-3 of the principal component matrix for various materials are plotted in Fig. 3. The possible grouping of various elements in Fig. 3 (enclosed by dashed lines) was deduced from the coherency of elements, both in the plots of factors 1 vs 2 and factors 1 vs 3 (or factors 2 vs 3). Any pair of elements in one group also should have a high correlation coefficient in the correlation matrix. In interpreting the factor analysis results, one should be aware that an apparent correlation could be caused by systematic error in chemical analysis and an apparent lack of correlation may be produced if the uncertainty in chemical analysis is greater than the natural variability. Therefore, the results of any factor analysis should be checked against other relevant information for consistency.

In both plankton and suspended particles, the aluminosilicate detritus phase (Al, Sc, rare earths, V, Th, Fe and Mn whose E_{Ai} values are near one) and "biophile" elements (e.g. Zn, Pb, K, Ni, Ag, Cu, P for plankton and Hg, Zn, Pb, Sb, Ag, Au, Se for suspended particles) form a coherent group (Figs 3A and 3B), indicating a close genetic link between plankton and suspended particles. In plankton, Mg and Na represent sea salt components, while Si and Ba represent siliceous diatom tests (e.g. KU *et al.*, 1970). The high correlation coefficient between P and Cd confirms the observed correlation between P and Cd in the water column (BOYLE *et al.*, 1976, and MARTIN *et al.*, 1976).

In the marine aerosols from the North Atlantic (Fig. 3C) the aluminosilicate detritus phase (Al, Sc, rare earths, V, Th, Fe and Mn) and 'biophile' elements (Cu, Zn, Ni, Pb, Sb, Ag, Au) become separate groups, even though the enrichment pattern of 'biophile' elements in the aerosols and the suspended particles is very similar (Fig. 1B). Interestingly, aerosol samples from the equatorial Atlantic (probably from the Sahara Desert) are similar to continental soil or shale in composition and the enrichment of Pb, Zn, Sb, Hg and Se is relatively small (Fig. 1C), but the factor analysis (Fig. 3D) is very similar to that from the North Atlantic (Fig. 3C). In Figs 3C and 3D, Na, Cl and Br are sea salt components. As discussed earlier, Pb, Zn, and Cu are mostly pollution inputs in the post-1960 Greenland snows and North Atlantic aerosols. Therefore the grouping of Pb, Cu, Zn, Ni, Sb, Au and Ag in Figs 3C and 3D and the high correlation coefficients between any pair of these elements indicate that the northern and equatorial Atlantic aerosols also contain large pollution components of Ni, Sb, Au and Ag. The fact that the change in Hg concentrations is always independent of other elements (Figs 3C and 3D) is consistent with the earlier suggestion of strong natural Hg sources. Se is strongly correlated with organic carbon in the equatorial Atlantic aerosols.

BOUTRON and LORUIS (1979) also performed R-mode factor analysis on the compositional data of a Greenland snow layer (1973-1974). The results are very similar to that of the North Atlantic aerosols. The grouping of Pb, Cu, Zn and Ag in Greenland snow (Fig. 1 in Boutron's paper) should again represent their dominant human inputs. The

F = the total river water flux = $33 \pm 3 \times 10^{18}$ g/yr (GARRELS and MACKENZIE, 1971);

C_p^i , C_R^i , C_{sh}^i and C_{op}^i are the concentrations of element i in river-suspended particles, filtered river water, shale and oceanic pelagic clays, respectively. $F \cdot \Sigma C_R^i$ = the summation of the dissolved river loadings exclude Ca^{2+} and HCO_3^- which are deposited separately in the ocean as oceanic carbonates, and the recycled sea salt components (by assuming Cl^- is recycled through the atmosphere) $\sim 0.9 \times 10^{15}$ g/yr (LIVINGSTON, 1963).

Dividing eqn (1) by M_T , and substituting various coefficients with known values, one obtains:

$$C_p^i + 1.8 \times 10^3 C_R^i = 0.99 C_{sh}^i + 0.06 C_{op}^i \quad (2)$$

where C^i 's are all in ppm.

Since C_p^i , C_R^i , C_{sh}^i and C_{op}^i are also known, one can compare the balance between the left-hand side (= the total riverine input C_{IN}^i) and the right-hand side (= the total sediment output = C_{OUT}^i) of eqn (2) for various elements, as summarized in Table 1. The average shale (C_{sh}^i) and oceanic pelagic clay (C_{op}^i) data are mainly from TUREKIAN and WEDEPOHL (1961). Exceptions are rare earths (PIPER, 1974), Th and U for pelagic clay (KU, 1966), and Si for shale (WEDEPOHL, 1960). The data for riverine-suspended particles are mainly from MARTIN and MEYBECK (1979) except for Ag (GORDEYEV and LISITSYN, 1978). The agreement between the data sets given by MARTIN and MEYBECK (1979) and by GORDEYEV and LISITSYN (1978) is generally within a factor of two or better. The river water (C_R^i) data are mostly from GOLDBERG *et al.* (1971) except rare earths, Al, Fe (MARTIN and MEYBECK, 1979), U (MANGINI *et al.*, 1979), Th (MOORE, 1967), and Cd (BOYLE *et al.*, 1976). The agreement between the data sets summarized by GOLDBERG *et al.* (1971) and MARTIN and MEYBECK (1979) is usually within a factor of two or better. For some elements, however, they used the same original data sources. For Ca and Sr the 0.06 C_{op}^i term in Table 1 also includes the oceanic carbonates which is about 0.08 C_{oc}^i , where C_{oc}^i is the concentration in the oceanic carbonates. The coefficient 0.08 above is obtained by multiplying the average sedimentation rate of oceanic carbonates (about $0.4 \pm 0.1 \times 10^{-3}$ g/cm² yr in the Pacific for the last 45 Myr, WORSLEY and DAVIES, (1979); a possible different rate in the Atlantic Ocean is ignored presently) by the total area of the ocean and dividing by M_T .

The elements in Table 1 are grouped according to the following criteria.

- Group A: $C_{OUT}/C_{IN} > 0.7$
- subgroup A₁: $C_{op}/C_{sh} < 1.5$
- subgroup A₂: $C_{op}/C_{sh} > 1.5$
- Group B: $C_{OUT}/C_{IN} < 0.7$
- subgroup B₁: $C_{op}/C_{sh} > 1.4$
- subgroup B₂: $C_{op}/C_{sh} < 0.7$

The subgroup A₁ elements are, in general, well balanced ($C_{OUT}/C_{IN} = 0.7 \sim 1.4$) except Li, Sr and As. The high C_{OUT}/C_{IN} ratios for Li, Sr and As (2.6, 1.7 and 1.6, respectively, Table 1) are probably caused by low C_p^i values given by MARTIN and MEYBECK (1979). For example, if the C_p^i values of Li and Sr given by GORDEYEV and LISITSYN (1978) are used, the C_{OUT} and C_{IN} are balanced (see values in parenthesis in Table 1). The high C_{OUT}/C_{IN} ratios could also be caused by additional inputs other than rivers, e.g. mid-ocean ridges (EDMOND *et al.*, 1979a). But one can rule out Sr, since Sr is not enriched in hydrothermal solutions as compared to ambient seawater (EDMOND *et al.*, 1979a).

How to estimate chemical fluxes to and from the mid-ocean ridges is still very much in dispute. For example, WOLERY and SLEEP (1981) argue that the water flux of 140×10^{15} g/yr for axial vents used by WOLERY and SLEEP (1976) and EDMOND *et al.* (1979a) is at least a factor of 6 too high, i.e. 1/6 of this value is on the ridge crest and 5/6 is on the ridge flanks. Because of lower temperatures, the extent of the basalt-seawater interaction should be less in the ridge flanks than in the ridge crest, thus yielding lower hydrothermal inputs than previously suggested. The balance between C_{OUT} and C_{IN} for Ca even suggests that the mid-ocean ridges may not be an important net source for Ca in the ocean.

According to Table 1, the dissolved river inputs of Ca and Sr are mainly deposited in the ocean as carbonates. About one-half of the dissolved Mg river input is deposited in the continental-shelf sediments and the other half could be removed by basalt-seawater interaction in the mid-ocean ridge system. The dissolved river inputs of K and U seem to end up mainly in the continental shelf sediments. The dissolved Si river input is probably deposited as pelagic siliceous oozes.

For the subgroup A₂ elements (Ni, Co, Mn, Ba, Mo and B), the balance between inputs and outputs is again satisfactory ($C_{OUT}/C_{IN} = 0.9 \sim 1.3$): therefore, there is no need to invoke large sources other than rivers to explain the high concentrations in oceanic pelagic clay ($C_{op}/C_{sh} = 2 \sim 10$). The desorption or remobilization of Mn, Co, Ni, Ba and, to a lesser extent, Mo, from the riverine suspended particles during and/or after deposition in estuaries and continental shelves ($C_p^i > C_{sh}^i$) can supply the needed amounts for the deep-sea sediments. A careful study of the Mn geochemical cycle in the Gulf of St Lawrence by YEATS *et al.* (1979) demonstrated that this is the case for Mn. Most of the Mn flux from the mid-ocean ridges (EDMOND *et al.*, 1979a, b) may have been deposited as basal metalliferous sediments near the ridges (e.g. CRONAN, 1976). The average thickness of the basal metalliferous sediments and oceanic sediments are about 10 and 500 m, respectively, and the average concentration of Mn in basal sediments is about 11 times that in average oceanic sediments (roughly the average of carbonaceous and noncarbonaceous sediments, CRONAN, 1976). Therefore, the

Table 1. The mass balance between river inputs [dissolved ($1800 C_p$) and particulate (C_p)] and marine sediments [shale ($0.99 C_{sh}$) and pelagic clay ($0.06 C_{op}$], all in ppm

	$0.99 C_{sh}$	$0.06 C_{op}$	$1800 C_R$	C_p	C_{OUT}/C_{IN}^*	C_{op}/C_{sh}
GROUP A: $C_{OUT}/C_{IN} > 0.7$						
Subgroup A ₁ : $C_{op}/C_{sh} < 1.5$						
Al	79,000	5,000	100	94,000	0.89	1.1
Sc	13	1.1	0.007	18	0.78	1.5
Ti	4,600	280	5	5,600	0.86	1.0
Fe	47,000	3,900	70	48,000	1.1	1.4
Ga	19	1.2	0.2	25	0.80	1.1
Cs	5.0	0.4	0.04	6	0.89	1.2
La	41	2.7	0.1	45	0.96	1.1
Ce	82	6.0	0.14	95	0.93	1.2
Hf	38	2.6	0.07	35	1.1	1.1
Sm	7.4	0.50	0.002	7	1.1	1.1
Eu	1.6	0.11	0.002	1.5	1.1	1.2
Lu	0.60	0.04	0.002	0.5	1.3	1.2
Th	12	0.8	0.08	14	0.90	1.1
V	130	7.2	1.6	170	0.79	0.92
Rb	140	7	2	100	1.4	0.79
Cr	89	5.4	1.8	100	0.93	1.0
Si	273,000	15,000	12,000	285,000	0.97	0.91
Li	65	3.4	5.4	25 (50) ⁺	2.3 (1.2) ⁺	0.86
K	26,000	1,500	4,140	20,000	1.1	0.94
U	3.6	0.16	0.7	3	1.0	0.70
As	13	0.8	3.6	5	1.6	1.0
Mg	14,800	1,200	7,380	11,800	0.83	1.4
Ca	21,900	27,700***	27,000	21,500	1.0	1.3
Sr	300	170***	130	150 (270) ⁺	1.7 (1.2) ⁺	0.60
Subgroup A ₂ : $C_{op}/C_{sh} > 1.5$						
Ni	67	14	0.5	90	0.89	3.1
Co	19	4.4	0.2	20	1.2	3.9
Mn	840	400	13	1,050	1.2	7.9
Ba	570	140	36	600	1.1	4.0
B	99	14	18	70	1.3	2.3
Mo	2.6	1.6	1.1	3	1.0	1.0
F	730	78	180	-	-	1.8
GROUP B: $C_{OUT}/C_{IN} < 0.7$						
Subgroup B ₁ : $C_{op}/C_{sh} > 1.4$						
P	690	90	36	1,150	0.66	2.1
Cu	45	15	13	100	0.53	5.6
Pb	20	4.8	5.4	150	0.16	4.0
Zn	94	9.9	36	350	0.27	1.7
Cd	0.29	0.03	0.12	1	0.29	1.4
Au	0.00099	0.00016	0.0036	0.04	0.026	2.6
Ag	0.069	0.0066	0.54	3	0.021	1.6
Na	9,500	2,400	11,340	7,100	0.65	4.2 (3.0)**
Cl	179	1,260	14,000	-	<0.10	116 (0)**
Br	4.0	4.2	36	5	0.20	18 (-0)**
Subgroup B ₂ : $C_{op}/C_{sh} < 0.7$						
Hg	0.40	0.006	0.13	0.65	0.52	0.25
Sb	1.5	0.06	3.6	2.5	0.25	0.67
S	2,380	78	6,660	-	<0.37	0.54 (0.13)**
I	2.2	0.003	13	-	<0.17	0.023 (-0)**
Se	0.59	0.01	0.36	-	-	0.02
Sn	5.9	0.09	0.07	-	-	0.25
W	1.8	0.06	0.05	-	-	0.56

* $C_{IN}^i = 1800 C_R^i + C_p^i$, $C_{OUT}^i = 0.99 C_{sh}^i + 0.06 C_{op}^i$.

** Corrected for sea salts.

*** Including oceanic carbonates (=0.08 C_{oc}).

+ C_p data from Gordeyev and Lisitsyn (1978).

amount of Mn in the basal metal-rich sediments is only about 24% of that in the overlying oceanic sediments. Also the basal metalliferous sediments can be considered geochemically as a part of the oceanic basalt, since they deposit within or at the surface of the oceanic basalt and are most likely to be subducted along with the oceanic basalt at the plate boundaries. Of course, considering the uncertainty of the data, one can allow about 20% of the Mn and Co

($C_{OUT}/C_{IN} = 1.2$) and 30% of the B ($C_{OUT}/C_{IN} = 1.3$) in the oceanic sediments to be supplied from the mid-ocean ridges. EDMOND *et al.* (1979b) estimated that the mid-ocean ridges alone can supply about one-to-three times the total manganese deposition rate observed in deep-sea sediments today. Apparently their flux calculations for Mn as well as those for other elements are over-estimated (as mentioned before). Since Mo is not enriched in Reykjanes hydrothermal solutions

(BJORNSSON *et al.*, 1972) and Ni is even depleted in hydrothermal solutions from the mid-ocean ridges (EDMOND *et al.*, 1979b) compared to ambient seawater, the mid-ocean ridges also cannot be important sources for Ni and Mo in the deep-sea sediments.

Except for Cl and Na, the Group B elements all belong to the 'biophile' elements. The excess river inputs of Group B elements, defined here as equal to $C_{IN}^i - C_{OUT}^i$ (Table 2), probably can be supplied, (as in the case of marine aerosols) by (1) volcanic gases, volatilization of metals from land vegetation or surface rocks, (2) recycling from the surface ocean through the atmosphere as marine aerosols and back to rivers by rain, and (3) pollution input or, (4) simply caused by bad data. If the excess river inputs are solely caused by the first processes, then in a steady state ocean, excess river inputs to the ocean should be balanced by sinks somewhere other than the ocean sediment reservoirs, e.g. the mid-ocean ridges. The flow rate of seawater through hydrothermal systems at the mid-ocean ridges is estimated, at most, at about 140×10^{15} g/yr (WOLERY and SLEEP, 1976, 1981), as compared to the annual river inflow rate of 3300×10^{15} g/yr (GARRELS and MACKENZIE, 1971). Therefore, even if all of the dissolved P, Cu, Pb, Zn, Cd, Au, Ag, Hg, Sb, Se, Sn and W were taken up by mid-ocean ridges as seawater flowed through the hydrothermal systems, the mid-ocean ridges could take up at most only a few percent to a fraction of one percent of the excess river inputs. According to the data given by BJORNSSON *et al.* (1972), the mid-ocean ridges may even be sources for Br and I. Alternatively, it is plausible that the excess river inputs to the ocean by the first processes could be released from the surface ocean and transported as marine aerosols back to the continents. Therefore, the next question is how efficient is the marine aerosol recycling process.

If one assumes that the excess river input of chlorine ($= C_{IN}^{Cl} - C_{OUT}^{Cl}$) is entirely transported from the

ocean as marine aerosols, then the marine aerosol contribution to the excess river inputs for the Group B elements can be estimated roughly by

$$C_{ma}^i / C_{ma}^{Cl} (C_{IN}^{Cl} - C_{OUT}^{Cl})$$

where C_{ma}^i / C_{ma}^{Cl} is the concentration ratio of element i and chlorine in the marine aerosols.

The results are given in Table 2. North Atlantic aerosols (BUAT-MENARD, 1979) are assumed to be representative of northern hemisphere aerosols. Additional data for W, P and Sn are from RAHN (1976), S from CUONG *et al.* (1974) and I from MOYERS and DUCE (1972).

The marine aerosol contributions can almost entirely explain the excess river inputs of Br, I, Na, Cd and Hg (within a factor of 1.5, Table 2). It is well documented that I can be effectively released from seawater by bubbling during U.V. irradiation (e.g. SETO and DUCE, 1972). The exact chemical forms of the released I are yet unknown. However, LOVELOCK *et al.* (1973) detected appreciable amounts of methyl iodide (CH_3I) over the North Atlantic and suggested a biological origin in the ocean. As shown in the last section, Hg and Cd are the very elements which have strong natural sources for marine aerosols. If the enriched Hg and Cd in marine aerosols are primarily of marine origin, one can conclude that the excess river inputs of Hg and Cd into the ocean are supplied by volcanic exhalation and volatilization from land vegetation or surface rocks, but these elements are mostly redeposited on the continents by transport from the air-sea interface through bubbling and/or biological activity. On the other hand, if Hg and Cd in marine aerosols are mainly supplied from the continents through the atmosphere, then the excess river inputs of Hg and Cd into the ocean have no sink (neither the mid ocean ridges nor atmosphere). Therefore, they should be predominantly pollution inputs (or simply caused by bad data). The conclusion of

Table 2. The excess river inputs ($C_{IN} - C_{OUT}$) of the Group B elements and the marine aerosol contributions to the excess river inputs ($C_{ma}^i / C_{ma}^{Cl} [C_{IN}^{Cl} - C_{OUT}^{Cl}]$), all in ppm unit.

	$C_{IN} - C_{OUT}$	$C_{ma}^i / C_{ma}^{Cl} (C_{IN}^{Cl} - C_{OUT}^{Cl})$
Subgroup B ₁ : $C_{Op} / C_{Sh} > 1.4$		
P	400	5
Cu	53	7
Pb	130	40
Zn	280	50
Cd	0.8	1
Au	0.042	0.003
Ag	3.5	0.12
Na	6,540	9,000
Cl	12,560	12,560
Br	33	28
Subgroup B ₂ : $C_{Op} / C_{Sh} < 0.7$		
Hg	0.37	0.3
Sb	4.6	1.
S	>4,200	2,400
I	>10	12
Se	-	1
Sn	-	0.3
W	-	0.05

SLEMR *et al.* (1981) that gaseous Hg in marine air mostly originates from continental sources tends to support the latter explanation. However, it is still difficult to explain why the anthropogenic inputs of Hg and Cd should greatly affect river concentrations but not marine aerosols.

The excess river inputs of S are about two times, and of P, Pb, Cu, Zn, Sb, Ag and Au at least 4 times, greater than the marine aerosol contributions which, in turn, contain large pollution components. Therefore one can conclude that the excess river inputs of P, Pb, Cu, Zn, Sb, Ag, Au and S are largely caused by pollution and/or bad data.

One may argue that the excess river inputs of these elements are artifacts caused by ignoring some organic-rich sediments (which may be enriched in these elements) in the mass balance calculation (eqn 1). However, the concentrations of Pb, Cu and Zn in average Black Sea sediments (HIRST, 1974) and black shale (VINE and TOURLELOT, 1970) are not greatly different from the average shale (TUREKIAN and WEDEPOHL, 1961), indicating remobilization before or during burial. Therefore, on a mass basis, organic-rich sediments cannot be an important sink for Pb, Cu and Zn as compared to the shale and pelagic clay sediment reservoirs.

THE INTERNAL CYCLES OF ELEMENTS IN THE OCEAN

For convenience, oceanic pelagic clay (C_{op}^i) is used as the standard material for the calculation of E_{Al}^i in this section. The E_{Al}^i 's in zooplankton, fecal pellets obtained from the surface waters off Monaco (FOWLER, 1977; HIGGO *et al.*, 1978) and sediment trap samples from the Sargasso Sea (SPENCER *et al.*, 1978; BREWER *et al.*, 1980) are shown in Fig. 4. Excluding elements related to the aluminosilicate detritus phase (e.g. Eu, Th, Sc and Fe), the E_{Al}^i 's in fecal pellets are always much lower than that in zooplankton (Sb is the exception, probably due to analytical uncertainty or sample contamination), perhaps caused by the dilution effect of ingested inorganic detritus particles which are low in those elements. The E_{Al}^i 's of Cu, Zn, U and I in the sediment trap sample at 5400 m are much lower than that at 1000 m (Fig. 4), indicating the remineralization of these 'biophile' elements during the settling of fecal pellets.

The settling of fecal pellets and fecal aggregates has been suggested as the major transport mechanism of elements from the surface to deep oceans (e.g. CHERRY *et al.*, 1978; BISHOP *et al.*, 1978). The depletion of Mn, Co and Ni ($E_{Al}^i < 1$) in fecal pellets, as well as in the sediment trap samples from the Sargasso Sea (SPENCER *et al.*, 1978), as compared to pelagic clay (Fig. 4), however, indicates that the settling of fecal pellets, as well as manganese-enriched particles (the sediment traps should have collected settling manganese-enriched particles if they do exist), is not the major transport mechanism for Mn, Co and Ni from

the surface to deep oceans and to the sediments. For a series of sediment trap samples in the Atlantic off Barbados (BREWER *et al.*, 1980, site E) the Mn/Al and Co/Al ratios, and therefore their E_{Al}^i 's, increase with depth, but E_{Al}^i 's for Mn and Co are still less than one (0.09 at a water depth of 389 m increasing to 0.15 at 5086 m for Mn and 0.21 at 988 m to 0.35 at 5086 m for Co). COBLER and DYMOND (1980) also have shown that the fluxes of Mn and Ni to the surface sediments near the Galapagos Spreading Center are two to three times greater than the values measured in traps deployed 20 and 100 m above the bottom in the same area. According to MARTIN and KNAUER (1980), an appreciable amount of Mn in the sediment trap samples collected in near-shore California waters is released to the high density NaCl solution (containing 5% formalin) inside the traps. But even after correcting the released Mn back to the samples, the E_{Al}^{Mn} in the sediment trap samples (from water depth of 35–1500 m) is still as low as 0.17–0.11. Therefore, in conclusion, the dissolved Mn, Co and Ni in the deep ocean may be adsorbed directly by pelagic clays at the sediment-water interface.

The flux of Mn from the surface to deep oceans by downwelling (due to the higher concentration in the surface waters than in the deep waters) and particle sinking is estimated to be about 5% (BENDER *et al.*, 1977) to 33% (MARTIN and KNAUER, 1980) of the Mn accumulation rate in pelagic sediments. Therefore, in a steady state ocean, the deep ocean needs Mn sources other than the surface ocean. The most likely sources are the continental margins. As discussed earlier, the remineralized Mn in coastal waters may be partly transported to the surface ocean but largely should be transported to the deep ocean near the continental margins by processes such as benthic nepheloid transport of Mn-enriched particles across the shelves and slopes and redissolution at depth in reducing environments. The mid ocean ridges may also contribute some Mn to the deep ocean.

If one assumes that the settling of fecal pellets is the major transport mechanism of elements (except Mn, Co and Ni) from the surface to the deep ocean and to pelagic clay (e.g. CHERRY *et al.*, 1978), then the redissolution rate of element i into the deep ocean water column from fecal pellets, I_{fp}^i , should be

$$I_{fp}^i = (C_{fp}^i/C_{fp}^{Al}) \cdot C_{op}^{Al} \cdot M - C_{op}^i \cdot M \quad (3a)$$

$$= (E_{Al}^i - 1) \cdot C_{op}^i \cdot M \quad (3b)$$

where

C_{fp}^i/C_{fp}^{Al} = the concentration ratio of elements i and Al in fecal pellets

M = average sedimentation rate of pelagic clay $\approx 0.3 \pm 0.1 \times 10^{-3}$ g/cm²yr (KU *et al.*, 1968).

The first term on the right hand side of eqn (3a) represents the total flux of element i carried down to the deep ocean by fecal pellets and on the second term, the net deposition rate on the ocean floor.

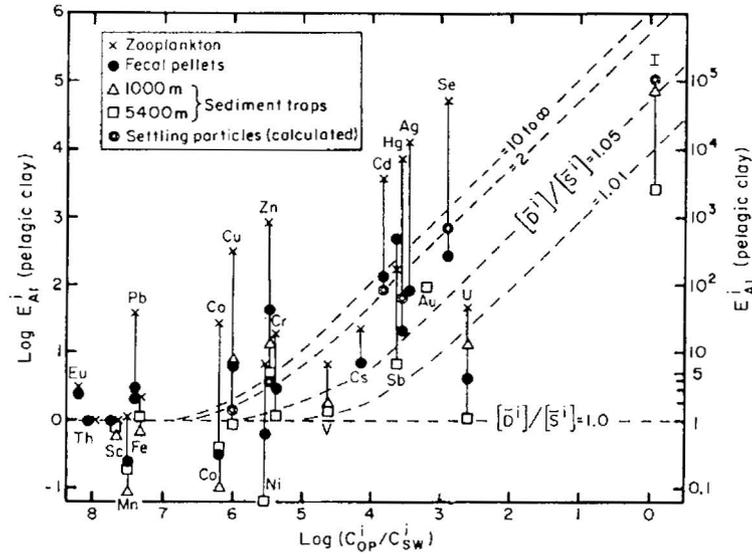


Fig. 4. Plot of the enrichment factors of various elements (pelagic clay as the standard) in zooplankton, fecal pellets and sediment trap samples vs log (C_{op}^i/C_{sw}^i) . The dashed lines represent the enrichment of elements in deep ocean water relative to surface water as functions of log E_{Ai}^i and log C_{op}^i/C_{sw}^i in a steady state ocean.

On the other hand, according to BROECKER's (1971) two-box ocean model, I_{ip}^i also should be equal to $R\{[D^i] - [S^i]\}$ in a steady state ocean where $[D^i]$ and $[S^i]$ are the average concentrations of element i in the deep ocean box (3600 m) and the surface ocean box (200 m), respectively. R is the water exchange rate between the two boxes with an estimated value of about 3 ± 1 m/yr (~ 300 g/cm² yr). Therefore,

$$(E_{Ai}^i - 1) C_{op}^i \cdot M = R\{[D^i] - [S^i]\} \quad (4)$$

Since $C_{sw}^i \approx [D^i]$, (C_{sw}^i = average concentration in seawater) eqn (4) can be rewritten as

$$(E_{Ai}^i - 1) C_{op}^i/C_{sw}^i \cdot M \approx R\{1 - [S^i]/[D^i]\} \quad (5)$$

The interrelationship among E_{Ai}^i , C_{op}^i/C_{sw}^i (distribution coefficient) and $[D^i]/[S^i]$ from eqn (5) is shown by the dashed lines in Fig. 4.

If the data points for fecal pellets fall above the line of $[D^i]/[S^i] = 10$ to infinity in Fig. 4 (e.g. Pb, Cu, Zn), the left-hand side of eq (5) would always be greater than the right-hand side. Therefore the condition of the steady state ocean is violated. In other words, fecal pellets would carry too much of these elements to the deep ocean and cause a steady increase in concentration in the deep ocean. The conclusion is that Pb, Cu and Zn in fecal pellets and the sediment trap samples at 1000 m depth may already contain a large fraction of pollution components, thus causing a violation of the steady state ocean condition.

Similarly, since the E_{Ai}^i values of 'biophile' elements in marine plankton (Figs 2A and 4) and in fine suspended particles (Fig. 2A) mostly fall above the line of $[D^i]/[S^i] = 10$ to infinity, one can rule out the direct settling of marine plankton and fine suspended particles as an important transport mechanism of the

'biophile' elements from the surface ocean to the deep ocean. BUAT-MENARD and CHESSELET (1979) arrive at the same conclusion through the calculation of vertical fluxes of elements associated with small and large particles in the ocean.

Since C_{op}^i/C_{sw}^i values for elements such as rare earths, Th, Sc, Al, etc., are so large ($> 10^7$) (or C_{sw}^i so low), these elements can be easily enriched in the deep ocean water relative to the surface water by slight dissolution from any settling particles as in the case of Al (HYDES, 1979), rare earths (GOLDBERG *et al.*, 1963), Sc (BREWER *et al.*, 1972), etc. The amount of dissolution, however, is limited by solubility and is small compared to the total flux to the sediments. Therefore, it is still safe to use Al as well as Sc, Th, etc., as the normalizing element to derive eqns (3)–(5). In Fig. 4, the Eu and Fe data for fecal pellets also fall above the line of $[D^i]/[S^i] = 10$ to infinity. However, Eu and Fe are not 'biophile' elements, i.e. their regeneration in the water column through biological activity should be small (e.g. E_{Ai}^i 's of Eu and Fe for plankton and fecal pellets are the same). Since there is only one analysis of fecal pellets by FOWLER (1977), slight enrichment of Eu and Fe in fecal pellets as compared to the average pelagic clay may represent only the high side of their natural variability.

The $[D^i]/[S^i]$ values are roughly known for some 'biophile' elements, e.g. I (WONG and BREWER, 1974), Zn, Cu, Cd and Ni (BRULAND, 1980), Hg (MUKHERJI and KESTER, 1978), and Se (MEASURES and BURTON, 1980). Using the known $[D^i]/[S^i]$ and C_{op}^i/C_{sw}^i values for these elements, the E_{Ai}^i values in the settling particles can be predicted from eqn (5). The results are shown in Fig. 4 as double circles. The calculated E_{Ai}^i values for Cd, Hg, Se and I in the settling particles are very similar to those in fecal pellets or sediment trap

samples at 1000 m. This fact further supports the contention that fecal pellets are the main carriers of the 'biophile' elements from the surface to the deep oceans. Even though the fecal pellets and sediment trap samples at 1000 m are enriched in U, the $[D^i]/[S^i]$ value for U should be less than 1.01 (Fig. 4). The field observation by KU *et al.* (1977) confirms this prediction. Similarly, one can predict that the $[D^i]/[S^i]$ ratio for V should be less than 1.05 and for Ag, Cs, and Cr around 1.05 to 2. Equation (5) cannot apply to Ni, since the accumulation of Ni in deep sea sediments is largely by direct adsorption at the sediment-water interface, as discussed earlier, and probably a small fraction by the settling of fecal pellets to account for the small increase in the Ni concentration with depth (BRULAND, 1980). Certainly we need more data to substantiate or disprove many preliminary contentions in this paper.

SUMMARY AND CONCLUSIONS

(1) The enrichment of 'biophile' elements (Pb, Cu, Zn, Cd, Sb, As, Hg, Ag, Au, Se, S, etc.) in pre-1900 Greenland snows indicate their natural sources other than sea salt and continental soil particles.

(2) Enrichment factor calculations and R-mode factor analysis show that post-1960 Greenland snows and North Atlantic aerosols contain large pollution inputs of Pb, Cu, Zn, Ni, Sb, Ag, Au, S and probably Se, while Hg and Cd are mostly from natural sources which over-shadow the pollution input signals.

(3) The balance between the river input rates and the oceanic sedimentation rates for the Group A elements (Table 1) indicates that mid-ocean ridges are not important sinks or sources for these elements.

(4) The high concentrations of Mn, Co, Ni, Ba and Mo (all Group A elements) in oceanic pelagic clays as compared to the average shale are supplied by the desorption or remobilization of these elements from riverine suspended particles during and/or after deposition in estuaries and continental shelves.

(5) The excess river inputs of Hg, Cd, I, Br and Na into the ocean can be balanced by recycling of marine aerosols from the ocean to the continents. The calculated excess river inputs of P, Pb, Cu, Zn, Au, Ag, Sb and S are attributed to pollution inputs and in some cases probably bad data.

(6) The settling of fecal pellets and fecal aggregates is the most important vertical transport mechanism of elements (except Mn, Co and Ni) from the surface to the deep oceans. The direct settling of planktonic detrital materials is shown not to be an important transport mechanism.

(7) The transport of Mn, Co and Ni from coastal environments to the deep ocean may involve benthic nepheloid transport of metal-enriched particles across the continental margins and redissolution. The dissolved Mn, Co and Ni in the deep ocean may have been adsorbed directly by pelagic clays at the sediment-water interface.

(8) Fecal pellets and sediment trap samples at 1000 m depth may contain large pollution components of Pb, Cu and Zn which are probably already causing a steady increase in the concentrations of these elements in the deep ocean.

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