

NOTE

A brief discussion on the mean oceanic residence time of elements

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Abstract—The mean oceanic residence times of elements obtained from deposition rates in deep-sea sediments are more representative than those obtained from river-input rates. The average concentration data of dissolved S, Au, Ag, Se, As, Hg, Sb, Zn, Sn, Cu and Pb in rivers contain large pollution and/or contamination components.

THE MEAN residence time of an element in the open ocean (excluding continental shelf waters) has been estimated either by its river-input rate (Barth 1952; Goldberg *et al.*, 1971):

$$\tau = C_{sw} \cdot V / (C_R \cdot F) \quad (1)$$

or by its deposition rate in deep sea sediments (Goldberg and Arrhenius, 1958):

$$\tau' = C_{sw} \cdot V / (C_{op} \cdot S) \quad (2)$$

where

V = the total mass of ocean water excluding continental shelf waters = 1.3×10^{24} g

F = the annual river water flux to the ocean = 33×10^{18} g/yr

S = the total sedimentation rate of oceanic pelagic clay (= area of ocean \times $0.3 \pm 0.1 \times 10^{-3}$ g/cm² yr, Ku, 1966)

C_{op} = the average concentration of the element in oceanic pelagic clays

C_{sw} and C_R = the average concentration of element in unfiltered sea water and filtered river water, respectively.

Equation (1) implicitly assumes that the river suspended particle inputs are all deposited on estuaries and continental shelves soon after entering the ocean. Therefore the continental shelf waters should not be considered as part of the open ocean. Otherwise, river-suspended particle inputs can no longer be ignored. Furthermore, the total mass of each element in the open ocean ($C_{sw} \cdot V$) will be even harder to estimate if one includes the continental shelf waters, because the concentrations of many elements in unfiltered sea water near shore vary drastically, due to great changes in the composition and concentration of suspended particles there. In Eqn. (2), deposition

of most of the elements in oceanic pelagic carbonates is negligible and is ignored except for Ca and Sr. It will be fruitful to compare τ and τ' for various elements using recently improved data and to explain any differences.

According to Eqns. (1) and (2), τ can be equal to τ' only if $C_R \cdot F = C_{op} \cdot S$ or recasting, only if

$$\log C_{op}/C_{sw} = \log C_R/C_{sw} + \log F/S \quad (3)$$

Figure 1 shows the plot of $\log C_{op}/C_{sw}$ against $\log C_R/C_{sw}$ for various elements for comparison. The C_{op} , C_{sw} and C_R data are mainly from the compilations given by Turekian and Wedepohl (1961), Brewer (1975) and Goldberg *et al.* (1971), respectively, and are tabulated in Table 1. Some values, however, are replaced by more recent data (see footnotes to Table 1). These new data give lower concentration than the older ones (except U).

Except for Si, U, S, I, Au, Ag, Se, As, Hg, Sb, Zn, Sn, Cu and Pb, the correlation between $\log C_{op}/C_{sw}$ and $\log C_R/C_{sw}$ (or between τ and τ') is excellent, but the correlation line does not follow the concordia line (solid line in Fig. 1). Data points falling above the concordia line are caused by neglecting the flux of river suspended particles and/or atmospheric dust that reach to the open ocean in Eqn. (1). As shown by Bewers and Yeats (1977), most of the river suspended particles are deposited in continental margins, but a small fraction does reach the open ocean and contributes a significant amount of particle-associated metals to deep-sea sediments. Elements like Na, Cl, Br and I fall below the concordia line because the output fluxes of these elements from the surface ocean to the atmosphere (as marine aerosols) are ignored in Eqn. (2).

The reason that S, Au, Ag, Se, As, Hg, Sb, Zn, Sn, Cu and Pb fall below the main correlation line (*i.e.* too high river concentration or too low concentration in pelagic clays) can be best explained by large dis-

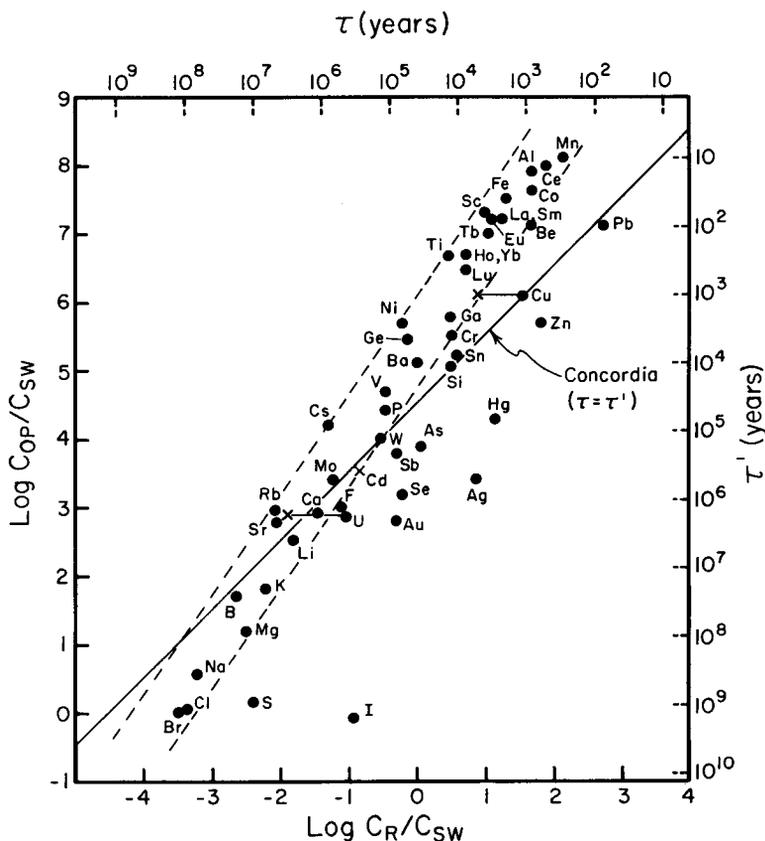


FIG. 1. The plot of $\log C_{op}/C_{sw}$ vs. $\log C_R/C_{sw}$. The crosses represent C_R data from Amazon River.

solved pollution and/or contamination components of these elements in river waters. As it has already been demonstrated in a recent paper (Li, 1981), the total river input rates (including dissolved and suspended particulate forms) for these elements, in addition to P and Cd, are in large excess of the total sediment output rates in continental margins and deep oceans, and these large excesses of river inputs represent mainly pollution inputs and, in some cases, contamination of river samples. By simple mass balance calculations, mid-ocean ridges or the atmosphere as the sinks for these excess river inputs have been ruled out. Originally it was suggested that the excess river inputs of Hg and Cd represent either the recycled components from the surface ocean or pollution inputs (Li, 1981). The most recent work by Fitzgerald (1982), however, confirms the latter to be the case for Hg. The recent discoveries of serious contamination of pre-industrial, polar-snow samples by Pb (Ng and Patterson, 1981), and fallout ^{137}Cs and natural atmospheric ^{210}Pb (Jaworowski *et al.*, 1981) even strongly suggest that the large enrichment or excess of Pb, Cu, Zn, Cd, Hg, Sb, As, Se, Au, Ag, In and S in preindustrial polar snows beyond the contribution from soil dust are also largely of pollution and contamination origin. The apparent high dissolved river-inputs of Si and U (Fig. 1) may be ex-

plained by deposition of Si in deep-sea siliceous ooze and continental margin sediments (DeMaster, 1981) and of U in continental margin sediments (Veeh, 1967; Borole *et al.*, 1982). Interestingly, if one uses the concentration data of Cu, Cd, (Boyle *et al.*, 1982) and U (Moore, 1967) from the Amazon River, these elements fall on the main correlation line (crosses in Fig. 1); these data are either pollution-free or represent the low side of natural river concentration.

Equation (1) also ignores the modification of river fluxes of dissolved trace elements during estuarine mixing through desorption (Boyle, 1976; Hanor and Chan, 1977; Li and Chan, 1979; Van der Weijden *et al.*, 1977), or coagulation and precipitation processes (Holliday and Liss, 1976; Sholkovitz, 1978; Sholkovitz and Copland, 1981). Other possible inputs of some dissolved elements to the open ocean not considered in Eqn. (1) include continental shelf sediments (Li, 1981), deep sea sediments (Sayles, 1979; McDuff and Gieskes, 1976) and the mid-ocean ridges (Edmond *et al.*, 1979).

In summary, except for Na, Cl, Br and I, Eqn. (2) provides a better representation of the mean oceanic residence time of elements than Eqn. (1). However, if one can correct for the pollution and/or contamination components in river water, Eqn. (1) can still provide a useful measure of relative reactivity of ele-

Table 1. The average concentrations of elements in filtered river water (C_R, ppb), seawater (C_{sw}, ppb) and oceanic pelagic clay (C_{op}, ppm)

	C _R	C _{sw}	C _{op}	log C _{op} /C _{sw}	log C _R /C _{sw}
Li	3	180	57	2.5	-1.8
Be	0.01(20)	0.0002(20)	2.6	7.1	1.7
B	10	4440	230	1.7	-2.7
F	100	1300	1300	3	-1.1
Na	6300	10.8x10 ⁶	40000	0.57	-3.2
Mg	4100	12.9x10 ⁵	21000	1.2	-2.5
Al	50(1)	1(8)	84000	7.9	1.7
Si	6500	2000*	2.5x10 ⁵	5.1	0.51
P	20	60	1500	4.4	-0.48
S	3700(2)	9.05x10 ⁵	1300	0.15	-2.4
Cl	7800*	18.8x10 ⁶	21000	0.05	-3.4
K	2300	3.8x10 ⁵	25000	1.8	-2.2
Ca	15000	4.2x10 ⁵	3.2x10 ⁵ **	2.9**	-1.4
Sc	0.004	0.0006	19	7.5	0.82
Ti	3	1	4600	6.7	0.48
V	0.9	2.5	120	4.7	-0.45
Cr	1	0.3	90	5.5	0.52
Mn	7	0.04(9)	6700	8.2	2.2
Fe	40(1)	2	65000	7.5	1.3
Co	0.1	0.002(21)	74	7.6	1.7
Ni	0.3	0.5(10)	230	5.7	-0.22
Cu	7; 1.6(3)	0.2(10)	250	6.1	1.6; 0.9
Zn	20	0.3(10)	170	5.7	1.8
Ga	0.09	0.03	20	5.8	0.47
Ge	0.005(4)	0.007(4)	2	5.5	0.15
As	2	1.8(11)	13	3.9	-0.05
Se	0.06(5)	0.1(12)	0.17	3.2	-0.22
Br	20	67000	70	0.02	-3.5
Rb	1	120	110	3.0	-2.1
Sr	70	8000*	2000**	2.8**	-2.1
Y		0.0013	90	7.8	
Zr		0.03	150	6.7	
Nb		0.01	14	6.2	
Mo	0.6	10	27	3.4	-1.2
Ag	0.3	0.04	0.11	3.4	0.88
Cd	0.01(3)	0.07(10)	0.42	3.8	-0.85
In		0.0001	0.08	5.9	
Sn	0.04(2)	0.01	1.5	5.2	0.60
Sb	0.07(6)	0.15(6)	1	3.8	-0.33
I	7	60	0.05	-0.08	-0.93
Cs	0.02	0.4	6	4.2	-1.3
Ba	20	20*	2300	5.1	0
La	0.05(1)	0.003	45(17)	7.2	1.2
Ce	0.08(1)	0.001	100(17)	8.0	1.9
Pr	0.007(1)	0.0006	9(17)	7.2	1.1
Nd	0.04(1)	0.003	40(17)	7.2	1.1
Sm	0.008(1)	0.0005*	7(17)	7.2	1.2
Eu	0.001(1)	0.0001*	1.5(17)	7.2	1.0
Gd	0.008(1)	0.0007	7.8(17)	7.1	1.1
Tb	0.001(1)	0.0001	1(17)	7.0	1.0
Ho	0.001(1)	0.0002	1(17)	6.7	0.70
Er	0.004(1)	0.0008	2.7(17)	6.5	0.65
Tm	0.001(1)	0.0002	0.4(17)	6.3	0.70
Yb	0.004(1)	0.0008	3(17)	6.6	0.70
Lu	0.001(1)	0.0002	0.5(17)	6.4	0.70
Hf		0.007	4.1	5.8	
Ta		0.002	1*	5.7	
W	0.03	0.1	1	4	-0.52
Re		0.004	0.001	2.4	
Au	0.002	0.004	0.003	2.8	-0.30
Hg	0.07	0.005(13)	0.1	4.3	1.2
Tl		0.01	0.8	4.9	
Pb	1(1)	0.002(14)	80*	7.6	2.7
Bi		4x10 ⁻⁵ (15)	0.53(18)	7.1	
Th	<0.1	6x10 ⁻⁵ (16)	13.4(19)	8.2	
U	0.04; 0.3(7)	3.2	2.6(19)	2.9	-1.9; -1.0

1. Martin & Meybeck (1979) 2. Livingstone (1963) 3. Boyle et al. (1982)
 4. Froelich and Andreae (1980) 5. Measures & Burton (1978) 6. Andreae et al. (1981)
 7. Mangini et al (1979); Borole et al. (1982) 8. Hydes (1979) 9. Klinkhammer & Bender (1980); Martin & Knauer (1980) 10. Boyle (1976), Bruland (1980) 11. Andreae (1977,1979)
 12. Sugimura et al.(1976); Measures & Burton (1980) 13. Matsunaga et al. (1975); Mukherji & Kester (1979) 14. Schaule & Patterson (1981) 15. Lee D.S. (1982) personal communication. Scripps Institution of Oceanography 16. Anderson (1981); Moore (1981) 17. Piper (1974) 18. Marowsky and Wedepohl (1971) 19. Ku (1966) 20. Measures and Edmond (1982)
 21. Knauer et al. (1982)

* Misprinted in the origin tables by Turekian & Wedepohl (1961); Brewer (1975) and Goldberg et al. (1971).

** Concentrations in oceanic pelagic carbonates by Turekian & Wedepohl (1961).

ments in the ocean. Conceptually, it is more meaningful to compare the concentration of any element between filtered river water and filtered sea water

than between filtered river water and unfiltered sea water. Unfortunately good data on filtered sea water is scarce especially for trace elements.

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