

# GEOCHEMICAL MASS BALANCE AMONG LITHOSPHERE, HYDROSPHERE, AND ATMOSPHERE

YUAN-HUI LI

Department of Geological Sciences,  
Harvard University, Cambridge, Mass. 02138

**ABSTRACT.** From  $O^{18}$  mass balance calculation, the total sedimentary mass of  $2.4 \pm 0.4 \times 10^{24}$  g is obtained. A geochemical mass balance model is constructed by using Poldervaart's average crust rock and the constrains from  $O^{18}$ ,  $C^{13}$ , and  $S^{34}$  isotope data. A mathematical model for the distribution of sedimentary mass as a function of age is also given and discussed. The weathering constant,  $w$ , for the last  $700 \times 10^6$  yr is  $4.8 \pm 0.1 \times 10^{-9}$   $yr^{-1}$  which corresponds to a mean residence time of sediment  $(1/w) 210 \pm 5 \times 10^8$  yr.

## INTRODUCTION

In order to account for the present composition and amount of sedimentary mass as well as sea water, Goldschmidt (1933, 1954) suggested that at least  $815 \times 10^{21}$  g of igneous rock is weathered by reacting with  $1400 \times 10^{21}$  g of primary magmatic volatiles (mainly  $H_2O$  and with some  $CO_2$ ,  $HCl$ ,  $H_2$ ,  $H_2S$ ,  $N_2$  et cetera). Rubey (1951) also showed that most of those primary magmatic volatiles should have been supplied continuously from the interior of the Earth, since the amount of  $H_2O$ ,  $C$ ,  $Cl$ ,  $S$ ,  $N_2$ , et cetera in the present sediment, hydrosphere, and atmosphere cannot be accounted for by those released from igneous rocks alone during the weathering.

The purpose of this paper is to present a simple geochemical mass balance between igneous rocks and primary magmatic volatiles on the one hand and the sedimentary mass, hydrosphere, and atmosphere on the other hand. The emphasis is kept on the charge balance and the mass balance of stable isotopes ( $O^{18}$ ,  $C^{13}$ , and  $S^{34}$ ) in the system.

*Chemical weathering and "reverse weathering".*—Chemical weathering bears analogy to an ion exchange or acid titration process, that is, hydrogen ion,  $H^+$ , from magmatic volatiles replaces metal cations in igneous rock and causes the reconstruction of rock materials. Table 1 illustrates this point. The moles of each rock forming minerals for the igneous rock in table 1 are the norms calculated from 100 kg of the average crust rock given by Poldervaart (1955). The iron is partitioned into ferric and ferrous compounds in table 1 according to the  $Fe^{2+}/Fe^{+3}$  ratio in the average crust rock and sedimentary rock given by Poldervaart (1955). The titration capacity is about 0.76 equivalent of  $H^+$  per 100 g of igneous rock.

The "reverse weathering", first proposed by Mackenzie and Garrels (1966), is a general term for the clay mineral-and-salt-forming process. In this process, the metal cations replace  $H^+$  ion as illustrated in table 2. The end components of clay minerals in table 2 are chosen quite arbitrarily and may not exist in sediments, but any clay mineral can be constructed by a proper mixture of those chosen components. The point is to make charge and material balance. Also in order to make the consumption of  $HCl$  minimum, all kaolinite was combined with cations to form other clay minerals.

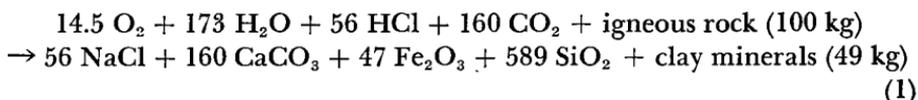
TABLE 1  
A model of chemical weathering

21 H <sub>2</sub> O	+	42 H <sup>+</sup>	+	42 KAlSi <sub>3</sub> O <sub>8</sub>	=	42 K <sup>+</sup>	+	84 SiO <sub>2</sub>	+	21 Al <sub>2</sub> Si <sub>2</sub> O <sub>7</sub> (OH) <sub>4</sub>
47 H <sub>2</sub> O	+	94 H <sup>+</sup>	+	94 NaAlSi <sub>3</sub> O <sub>8</sub>	=	94 Na <sup>+</sup>	+	188 SiO <sub>2</sub>	+	47 Al <sub>2</sub> Si <sub>2</sub> O <sub>7</sub> (OH) <sub>4</sub>
82 H <sub>2</sub> O	+	164 H <sup>+</sup>	+	82 CaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>	=	82 Ca <sup>++</sup>	+	82 Al <sub>2</sub> Si <sub>2</sub> O <sub>7</sub> (OH) <sub>4</sub>	+	78 H <sub>2</sub> O
		156 H <sup>+</sup>	+	78 CaSiO <sub>3</sub>	=	78 Ca <sup>++</sup>	+	78 SiO <sub>2</sub>	+	129 H <sub>2</sub> O
		258 H <sup>+</sup>	+	129 MgSiO <sub>3</sub>	=	129 Mg <sup>++</sup>	+	129 SiO <sub>2</sub>	+	23 H <sub>2</sub> O
		46 H <sup>+</sup>	+	23 FeSiO <sub>3</sub>	=	23 Fe <sup>++</sup>	+	23 SiO <sub>2</sub>	+	29 Fe <sub>2</sub> O <sub>3</sub>
14.5 O <sub>2</sub>			+	58 FeSiO <sub>3</sub>	=			58 SiO <sub>2</sub>	+	18 Fe <sub>2</sub> O <sub>3</sub>
				18 Fe <sub>2</sub> O <sub>3</sub>	=					
				59 SiO <sub>2</sub>	=			59 SiO <sub>2</sub>		
14.5 O <sub>2</sub> + 760 H <sup>+</sup> + (100 kg)igneous rock = ΣM <sup>++</sup> + 619 SiO <sub>2</sub> + 150 Al <sub>2</sub> Si <sub>2</sub> O <sub>7</sub> (OH) <sub>4</sub> + 47 Fe <sub>2</sub> O <sub>3</sub> + 80 H <sub>2</sub> O										

TABLE 2  
A model of "reverse" weathering

180.6 H <sub>2</sub> O	+	25.8 SiO <sub>2</sub>	+	129 Mg <sup>++</sup>	+	25.8 Al <sub>2</sub> Si <sub>2</sub> O <sub>7</sub> (OH) <sub>4</sub>	=	258 H <sup>+</sup>	+	25.8 Mg <sub>5</sub> Al <sub>2</sub> Si <sub>3</sub> O <sub>10</sub> (OH) <sub>8</sub>
32.2 H <sub>2</sub> O	+	4.6 SiO <sub>2</sub>	+	23 Fe <sup>++</sup>	+	4.6 Al <sub>2</sub> Si <sub>2</sub> O <sub>7</sub> (OH) <sub>4</sub>	=	46 H <sup>+</sup>	+	4.6 Fe <sub>3</sub> Al <sub>2</sub> Si <sub>3</sub> O <sub>10</sub> (OH) <sub>8</sub>
			+	42 K <sup>+</sup>	+	63 Al <sub>2</sub> Si <sub>2</sub> O <sub>7</sub> (OH) <sub>4</sub>	=	42 H <sup>+</sup>	+	42 KAl <sub>2</sub> Si <sub>3</sub> O <sub>10</sub> (OH) <sub>2</sub>
			+	38 Na <sup>+</sup>	+	56.6 Al <sub>2</sub> Si <sub>2</sub> O <sub>7</sub> (OH) <sub>4</sub>	=	38 H <sup>+</sup>	+	38 NaAl <sub>3</sub> Si <sub>3</sub> O <sub>10</sub> (OH) <sub>2</sub>
			+	56 Na <sup>+</sup>	+	56 HCl	=	56 H <sup>+</sup>	+	56 NaCl
160 H <sub>2</sub> O	+	160 CO <sub>2</sub>	+	160 Ca <sup>++</sup>			=	320 H <sup>+</sup>	+	160 CaCO <sub>3</sub>
253.2 H <sub>2</sub> O + 30.4 SiO <sub>2</sub> + ΣM <sup>++</sup> + 150 Al <sub>2</sub> Si <sub>2</sub> O <sub>7</sub> (OH) <sub>4</sub> + 56 HCl + 160 CO <sub>2</sub> = 760 H <sup>+</sup> + Σ clay minerals + 56 NaCl + 160 CaCO <sub>3</sub>										

By adding table 1 and 2, the overall reaction is:



where the coefficients are in unit of moles. According to equation (1), by weathering 100 kg of igneous rock, about 113 kg of sediments will be produced. If the total mass of sediments in the present Earth surface is known, it is possible to calculate the total primary magmatic volatiles and  $\text{O}_2$  consumed in the weathering process that produced that mass. Early estimates of the total sedimentary mass ranges from  $0.7 \times 10^{24}$  g to  $1.0 \times 10^{24}$  g (Goldschmidt, 1933, 1954; Conway, 1943; Wickman, 1954; Goldberg and Arrhenius, 1958), and the most recent estimates  $2 \times 10^{24}$  g (Horn and Adams, 1965),  $2.5 \times 10^{24}$  g (Ronov, 1968; Ronov and Yaroshovsky, 1969) and  $2.5 \times 10^{24}$  g (Garrels, 1971; personal commun.). The metamorphic rocks of sedimentary origin but with chemical composition similar to those of igneous rocks are excluded in the estimate on the total sedimentary mass. An  $\text{O}^{18}$  mass balance provides a semi-independent check for their estimates:

*$\text{O}^{18}$  mass balance.*—If all the water in the hydrosphere is ultimately of magmatic origin, one can write the following  $\text{O}^{18}$  mass balance equation:

$$\delta\text{O}_a^{18} \cdot X_a \cdot f_a + \delta\text{O}_b^{18} \cdot X_b \cdot f_b = \delta\text{O}_{a'}^{18} \cdot X_{a'} \cdot f_{a'} \\ + \delta\text{O}_{b'}^{18} \cdot X_{b'} \cdot f_{b'} \quad (2)$$

where  $X_i$  = total mass of component  $i$

$f_i$  = weight fraction of oxygen in  $X_i$

$a$  = igneous rock weathered to make sediment

$a'$  = sediments

$b$  = magmatic water

$b'$  = water in hydrosphere.

Substituting the following data into equation (2):

$$f_a = 0.47 \pm 0.02 \text{ (Mason, 1966)}$$

$$f_{a'} = 0.47 \text{ (from eq 1)}$$

$$f_b = f_{b'} = 0.86 \text{ (water)}$$

$$X_a = X_{a'}, X_b = X_{b'}$$

$$\delta\text{O}_a^{18} = 7.5 \pm 0.5\% \text{ (average of basaltic rock, } \delta\text{O}^{18} = 6\% \text{, and granitic rock, } \delta\text{O}^{18} = 9\% \text{, given by Talyer, 1968)}$$

$$\delta\text{O}_b^{18} = 7.5\% \text{ assuming magmatic water is in equilibrium with magma or igneous rock at high temperature.}$$

$$\delta\text{O}_{a'}^{18} = 17 \pm 1\% \text{, estimated from the relative abundance of carbonate:shale + oceanic clay:sandstone = 15:74:11 (Garrels and Mackenzie, 1971) and } \delta\text{O}^{18} \text{ of those rock types = 25:16:14\% (data compiled from Savin and Epstein, 1970a, b; Garlick, 1969, et cetera)}$$

$\delta O_b^{18} = -0.35 \pm 0.2\%$ , taking into account of average sea water ( $\delta O^{18} = -0.1\%$ , Craig and Gordon, 1965), polar ice ( $\delta O^{18} = -30\%$ ), and  $O_2$  in the atmosphere ( $\delta O^{18} = +23\%$ )

one obtains

$$X_a/X_b = \text{total mass of sediments/total water mass of hydrosphere} \\ = 1.4 \pm 0.2$$

Since the total water mass of hydrosphere (including mainly sea water, interstitial water in the sediments, and polar ice) is about  $1.7 \times 10^{24}$  g (Horn and Adams, 1965), the total mass of sediments should be about  $2.4 \pm 0.4 \times 10^{24}$  g in good agreement with those recent estimates (2 to  $2.5 \times 10^{24}$  g). The total sedimentary mass of  $2.4 \pm 0.4 \times 10^{24}$  g may represent a minimum, since the metamorphosed sediments tend to have low  $\delta O^{18}$  value, and make  $X_a/X_b$  even higher.

Adapting  $2.4 \times 10^{24}$  g as the best estimate of total sedimentary mass, the total consumption of volatiles and  $O_2$  in the weathering process as calculated from equation (1) is:

$$O_2 = 3.1 \times 10^{20} \text{ moles} \\ HCl = 11.9 \times 10^{20} \text{ moles} \\ CO_2 = 34.0 \times 10^{20} \text{ moles} \\ H_2O = 36.8 \times 10^{20} \text{ moles}$$

In addition to  $34.0 \times 10^{20}$  moles of  $CO_2$  that have been used up in the weathering process and ended up as  $CaCO_3$ , some extra  $CO_2$  is needed to account for the organic carbon in the biosphere and sediments. The fraction of primary magmatic  $CO_2$  that ends up as organic carbon can be estimated by  $C^{13}$  isotope mass balance (Wickman, 1955).

*$C^{13}$  mass balance.*—For  $C^{13}$  mass balance, the following relation holds:

$$(\delta C^{13} \text{ of primary magmatic } CO_2) \times 1 \\ = (1 - f) (\delta C^{13} \text{ of carbonate}) + f \times (\delta C^{13} \text{ of organic carbon}) \quad (3)$$

where  $f$  = the fraction of primary magmatic  $CO_2$  ended up as organic carbon.

$\delta C^{13}$  of primary magmatic  $CO_2$  is assumed to be that of kimberlite diamond, that is,  $-5\%$  (Craig, 1953; Wickman, 1955; Vinogradov, Kryptova, and Ustinov, 1965)

$\delta C^{13}$  of carbonate =  $0 \pm 1\%$  (Craig, 1953) and  $\delta C^{13}$  of organic carbon =  $25 \pm 1\%$  (Craig, 1953; Degens, 1969)

Solving equation (3) one obtains:

$$f = 0.20 \pm 0.05$$

which may represent a maximum, since according to new data by Fuex and Baker (1971),  $\delta C^{13}$  of mafic rock (including both noncarbonate and carbonate carbon) ranges from  $-9$  to  $-16\%$ , therefore  $\delta C^{13}$  of primary

magmatic  $\text{CO}_2$  gas should be heavier than the primordial carbon, that is,  $-5\%$ . The "observed"  $f$  varies widely, for example, 0.27 (Rubey, 1951), 0.23 (Borchert, 1951), 0.18 (Ronov, 1968), and 0.13 (Ronov and Yaroshevsky, 1969). If  $f = 0.2 \pm 0.05$  is adopted, the amount of primary magmatic  $\text{CO}_2$  ended up as organic carbon is about  $0.2/(1 - 0.2) \times 34.0 \times 10^{20} = 8.5 \pm 2.5 \times 10^{20}$  moles in comparison with  $7.2 \sim 11.7 \times 10^{20}$  moles which were calculated from the weight percent of organic carbon in the average sediment (0.3 percent, Borchert, 1951; and 0.49 percent, Ronov and Yaroshevsky, 1969) multiplied by the total sedimentary mass. Also, by photosynthesis:  $\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{CH}_2\text{O} + \text{O}_2$ , a total net of  $8.5 \pm 2.5 \times 10^{20}$  moles  $\text{O}_2$  should have been produced. Out of  $8.5 \pm 2.5 \times 10^{20}$  moles of  $\text{O}_2$ ,  $3.1 \times 10^{20}$  moles have been used up in oxidation of ferrous to ferric iron during the weathering process. Except  $0.4 \times 10^{20}$  moles of  $\text{O}_2$  left in the atmosphere today, the rest of  $\text{O}_2$  should have been used up in oxidizing some other reducing compounds such as  $\text{H}_2\text{S}$ ,  $\text{SO}_2$ ,  $\text{H}_2$ ,  $\text{CO}$ , et cetera. In tables 1 and 2, the primary magmatic  $\text{H}_2\text{S}$  and  $\text{SO}_2$  are omitted for the sake of clarity, but in considering the global oxygen budget, sulfur can no longer be neglected.

*S<sup>34</sup> mass balance.*—The primary magmatic sulfur ends up mainly in evaporites ( $\text{CaSO}_4$ ), ocean ( $\text{SO}_4^{=}$ ), and sediments ( $\text{FeS}_2$ ). The fraction in the form of  $\text{CaSO}_4 + \text{SO}_4^{=}$  and  $\text{FeS}_2$  can be estimated again by the relation:

$$(\delta\text{S}^{34} \text{ of primary S}) = (1 - f) \times (\delta\text{S}^{34} \text{ of } \text{CaSO}_4 + \text{SO}_4^{=}) + f \times (\delta\text{S}^{34} \text{ of } \text{FeS}_2) \quad (4)$$

where  $\delta\text{S}^{34}$  of primary sulfur =  $+1\%$  (assuming  $\delta\text{S}^{34}$  of mafic rock as the Earth's primary value)

$$\delta\text{S}^{34} \text{ of } \text{CaSO}_4 + \text{SO}_4^{=} = 17 \pm 2\% \text{ (average)}$$

and

$$\delta\text{S}^{34} \text{ of } \text{FeS}_2 = -12 \pm 5\% \text{ (average)}$$

(data compiled by Holser and Kaplan, 1966). Then,  $f$ , the fraction of primary sulfur in the form of  $\text{FeS}_2$ , is equal to  $0.55 \pm 0.10$  which may represent a minimum since  $\delta\text{S}^{34}$  of granitic rock is quite heavy (average  $\sim 10\%$ ); therefore,  $\delta\text{S}^{34}$  of magmatic sulfur volatile should be lighter than  $+1\%$ .

According to tables 1 to 3 in the paper by Horn and Adam (1965), the sulfur distributed in shale and oceanic clay (mainly  $\text{FeS}_2$ ), in carbonate, evaporite, and sand + graywacke (mainly  $\text{CaSO}_4$ ), and in ocean + interstitial water (mainly  $\text{SO}_4^{=}$ ) are respectively  $1.4 \times 10^{20}$  moles,  $0.5 \times 10^{20}$  moles, and  $0.5 \times 10^{20}$  moles. Therefore, the fraction of sulfur in the form of  $\text{FeS}_2$  is again equal to  $1.4/(1.4 + 0.5 + 0.5) = 0.58$ , in good agreement with the  $\text{S}^{34}$  isotope mass balance. Holser and Kaplan (1966) gave  $f = 0.45$ . The estimated weight percent of sulfur in the average sediments again varies considerably, for example,  $0.49 \pm 0.13$  percent (Holser and Kaplan, 1966), 0.3 percent (Horn and Adams, 1965), and 0.20 percent (Ronov and Yaroshevsky, 1969). The difference depends very much on



TABLE 3  
An improved model of "reverse" weathering

144.2 H <sub>2</sub> O +	20.6 SiO <sub>2</sub> +	103 Mg <sup>++</sup> +	20.6 Al <sub>2</sub> Si <sub>2</sub> O <sub>7</sub> (OH) <sub>1</sub> =	206 H <sup>+</sup> +	20.6 Mg <sub>7</sub> Al <sub>2</sub> Si <sub>8</sub> O <sub>10</sub> (OH) <sub>8</sub>	
24.5 H <sub>2</sub> O +	3.5 SiO <sub>2</sub> +	17.5 Fe <sup>++</sup> +	3.5 (kaolinite)	= 35 H <sup>+</sup> +	3.5 Fe <sub>2</sub> Al <sub>2</sub> Si <sub>3</sub> O <sub>10</sub> (OH) <sub>8</sub>	
		42 K <sup>+</sup> +	63 (kaolinite)	= 42 H <sup>+</sup> +	42 KAl <sub>3</sub> Si <sub>3</sub> O <sub>10</sub> (OH) <sub>2</sub>	+ 63 H <sub>2</sub> O
		42 Na <sup>+</sup> +	63 (kaolinite)	= 42 H <sup>+</sup> +	42 NaAl <sub>3</sub> Si <sub>3</sub> O <sub>10</sub> (OH) <sub>2</sub>	+ 63 H <sub>2</sub> O
		4 Mg <sup>++</sup> +	8 HCl	= 8 H <sup>+</sup> +	4 Mg <sup>++</sup> + 8 Cl <sup>-</sup>	
		48 Na <sup>+</sup> +	48 HCl	= 48 H <sup>+</sup> +	18 NaCl + 30 Na <sup>+</sup> + 30 Cl <sup>-</sup>	
	4 O <sub>2</sub> +	4 Na <sup>+</sup> +	2 H <sub>2</sub> S	= 4 H <sup>+</sup> +	4 Na <sup>+</sup> + 2 SO <sub>4</sub> <sup>=</sup>	
	2.8 O <sub>2</sub> +	5.5 Fe <sup>++</sup> +	11 H <sub>2</sub> S	= 11 H <sup>+</sup> +	5.5 FeS <sub>2</sub>	+ 5.5 H <sub>2</sub> O
	14 O <sub>2</sub> +	7 Ca <sup>++</sup> +	7 H <sub>2</sub> S	= 14 H <sup>+</sup> +	7 CaSO <sub>4</sub>	
175 H <sub>2</sub> O +	22 Mg <sup>++</sup> +	153 Ca <sup>++</sup> +	175 CO <sub>2</sub>	= 350 H <sup>+</sup> +	153 CaCO <sub>3</sub> + 22 MgCO <sub>3</sub>	
43.8 H <sub>2</sub> O			43.8 CO <sub>2</sub>	= 43.8 (CH <sub>2</sub> O) +	43.8 O <sub>2</sub>	
		7.8 O <sub>2</sub> +	15.6 H <sub>2</sub>	= 15.6 H <sub>2</sub> O		

The weight percent of carbonate ( $\text{CaCO}_3 + \text{MgCO}_3$ ) and organic carbon (C) in the sediments calculated from equation (5) are respectively 15 percent and 0.47 percent in good agreement with the values given by Garrels and MacKenzie (1971) for carbonate (15 percent) and by Ronov and Yaroshevsky (1969) for organic carbon (0.49 percent). The weight percent of evaporites ( $\text{NaCl} + \text{CaSO}_4$ ) in the sediments and the weight ratio of  $\text{NaCl}/\text{CaSO}_4$  as calculated from equation (5) are respectively 2.0 percent and one. The ratio of  $\text{NaCl}/\text{CaSO}_4 \approx 1$  is in good agreement with the observed value in the evaporites (Pettijohn, 1957). The weight percent of chlorine and sulfur calculated from equation (5) are respectively 0.57 percent and 0.51 percent in comparison with 0.24 percent and 0.2 percent given by Ronov and Yaroshevsky (1969). Though they differ by a factor of two (due to the choice of different weight percent of evaporites) Cl/S ratio is almost the same. Furthermore, the chemically bonded water in the sediments calculated from equation (5) is 2.9 percent in agreement with 3.9 percent given by Ronov and Yaroshevsky (1969).

For the mass balance of Si in the sediments (in the form of  $\text{SiO}_2$ ), the following relationships hold:

$$\begin{aligned} X_1 + X_2 + X_3 + X_4 &= 1 \\ a_1X_1 + a_2X_2 + a_3X_3 + a_4X_4 &= \bar{a} \end{aligned}$$

where  $X_i$  is weight fraction of rock type  $i$

$a_i$  is weight fraction of  $\text{SiO}_2$  in rock type  $i$

1 = evaporite

2 = carbonate

3 = shale + clay

4 = sandstone

The following data are known:

$$X_1 = 0.02 \quad (\text{present work})$$

$$X_2 = 0.15 \quad (\text{present work})$$

$$a_1 = 0.03$$

$$a_2 = 0.10$$

$$a_3 = 0.55$$

$$a_4 = 0.70$$

$$\bar{a} = 0.49 \quad (= \text{average in the sediment, obtained from eq (5)})$$

Substituting the data into above equation and solving for  $X_3$  and  $X_4$ , one obtains:

$$X_3 = 0.71$$

$$X_4 = 0.12$$

so the relative weight abundance of evaporites:carbonate:shale:sandstone = 2:15:71:12, in general agreement with the estimate (2:15:74:11) by Garrels and Mackenzie (1971).

In summary, the weathering of the imaginary igneous rock, which has a chemical composition of Poldervaart's (1955) average crust rock, can reproduce most of the important features in the sediments observed today.

The weathering of the igneous rock with composition given by Horn and Adams (1965) can produce the following features:

carbonate	= 9 percent (all in weight percent)
organic carbon	= 0.24 percent
evaporite (NaCl + CaSO <sub>4</sub> )	= 3.6 percent
sulfur	= 0.3 percent
chlorine	= 2.1 percent

Apparently, carbonate and organic carbon are only about half the observed values, and chlorine is much too high. Horn and Adams (1965) adopted a chemical composition of marine sediments with very high NaCl content which actually should have been counted as the component of the interstitial water. Therefore, any calculation based on the total chlorine data given by Horn and Adams (1965) is dubious.

The summary of oxygen budget from tables 1 and 3 is as follows (in unit of 10<sup>20</sup> moles):

Net production of photosynthesis	= 9.3 ± 2.5
Free in atmosphere	0.4
Used in oxidation of Fe <sup>+2</sup> to Fe <sup>+3</sup>	3.1
Used in oxidation of primary H <sub>2</sub> S	4.4 ± 0.9
Used in oxidation of primary H <sub>2</sub> , NH <sub>3</sub> , CH <sub>4</sub> , CO, et cetera	1.4 ± 1.9

How important the primary H<sub>2</sub>, NH<sub>3</sub>, CH<sub>4</sub>, CO, et cetera are with regard to the oxygen budget is still uncertain. Within the uncertainty of data, those reducing compounds may not be important at all (a more quantitative treatment will be given in another paper).

#### THE RATE OF DE-GASSING, RECYCLING, AND THE DISTRIBUTION OF SEDIMENTARY MASS AS A FUNCTION OF AGE

The de-gassing rate of primary volatiles is directly related to the accumulation rate of the total sedimentary mass, for example, one possible relationship is an asymptotic equation:

$$M(t) = M(p) (1 - e^{-\lambda t}) / (1 - e^{-\lambda p}) \approx M(p) (1 - e^{-\lambda t}) \quad (6)$$

where:

M(t) = total sedimentary mass as a function of time t

M(p) = total sedimentary mass at present time p

λ = de-gassing constant

p = 4.5 × 10<sup>9</sup> year (that is, t = 0 at the creation of the Earth).

If one assumes that the erosion or recycling rate of sedimentary rock is directly proportional to the amount of sedimentary rock present,

$$\text{that is, } \frac{dN}{dt} = -wN \quad (7)$$

where  $w$  = weathering or recycling constant.

then, one obtains the following theoretical distribution of sedimentary mass as a function of time:

$$N(\tau, t) = M(p) [w(1 - e^{-\lambda\tau}) + \lambda e^{-\lambda\tau}]e^{-w(t-\tau)} \quad (8A)$$

or age:

$$N(t') = M(p) [w(1 - e^{-\lambda(p-t')}) + \lambda e^{-\lambda(p-t')}]e^{-wt'} \quad (8B)$$

where  $N(\tau, t)$  = sedimentary mass formed per unit time at time  $\tau$ , and remaining at time  $t$ ,  $t \geq \tau$ .

=  $N(t')$  = sedimentary mass per unit time with age  $t'$ .

Equation (8B) is obtained by reversing the time axis in equation (8A), that is,

$$t' = \text{time before present} = p - \tau, \text{ and } t = p.$$

(The details of mathematics in this section are given in the appendix) Either  $\lambda \rightarrow \infty$  (that is, all primary volatiles were introduced to the Earth surfaces at the very beginning of the Earth creation)

or  $\lambda = w$ ,

equations (8A) and (8B) reduce to:

$$N(\tau, t) = wM(p)e^{-w(t-\tau)} \quad (9A)$$

$$N(t') = wM(p)e^{-wt'} \quad (9B)$$

(A similar result was given by Gregor, 1968.)

Therefore, for all  $\lambda$  values lying in  $\infty > \lambda > w$ , the distribution of sedimentary mass as a function of age can be represented essentially by the same equations (9A) and (9B). Figures 1A and 1B give the plots of equations (6) and (9B) with  $w = \lambda = 1.16 \times 10^{-9} \text{ yr}^{-1}$ , where  $w = 1.16 \times 10^{-9} \text{ yr}^{-1}$  is the best estimate for fitting the observed gross distribution of sedimentary rock as a function of age as shown by Garrels and Mackenzie (1968).

If the de-gassing rate of primary volatiles has been uniform throughout the Earth's history as suggested by Rubey (1951), then:

$$M(t) = M(p) \cdot t/p \quad (10)$$

and

$$N(t') = M(p) [1 + w(p - t')]e^{-wt'/p} \quad (11)$$

(A similar result is given by Harbauch and Bonham-Carter, 1970, for a computer simulation calculation.) Equations (10) and (11) are also plotted in figures 1A' and 1B with  $w = 1.16 \times 10^{-9} \text{ yr}^{-1}$ . As is clear from figure 1B, equation (11) tends to have more younger sediments than equation (9B), but the difference is too small to determine which de-gassing model is closer to the truth (same conclusion was given by Har-

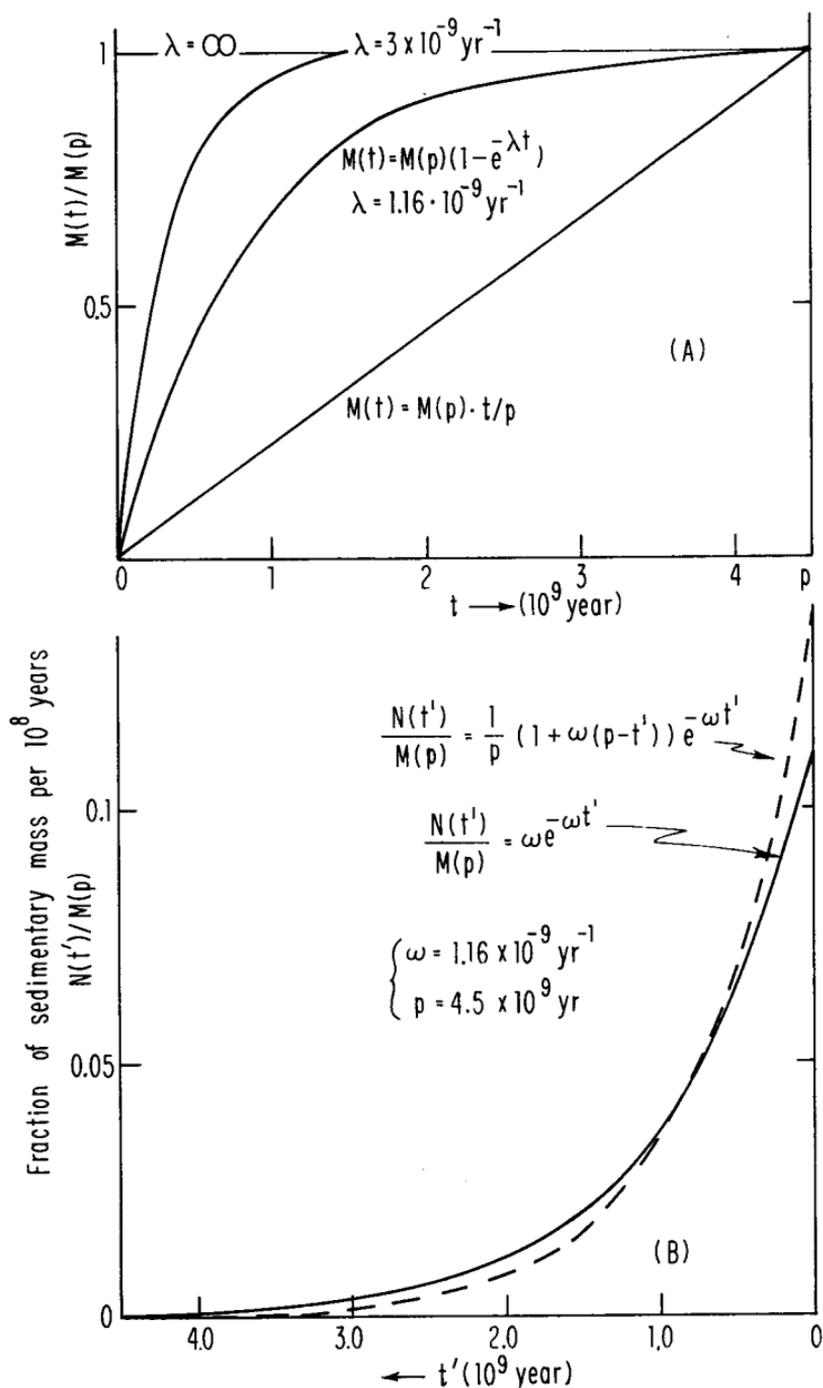


Fig. 1. (A) The fraction of sediments or primary volatiles introduced to the Earth's surface as functions of time and the de-gassing constant,  $\lambda$ .

(B) The fraction of sedimentary mass per  $10^8$  years as function of age.

bauch and Bonham-Carter, 1970). But in considering the general thermal history of the Earth (Birch, 1965), the asymptotic de-gassing model is preferred here.

In the case of  $\lambda = 3 \times 10^{-9} \text{ yr}^{-1}$ , about 95 percent of  $M(p)$  and the primary volatiles would have been introduced to the Earth surface at the first billion years of the Earth's history (fig. 1A). Thereafter we can consider the total mass of sediments is more or less in a steady state, and the later age sediments were formed by recycling of old sediments through the reworking of old sediments and the weathering of fresh igneous rocks which are balanced by the remelting of old sediments (for details of sediment recycling concept see, for example, the paper by Siever, 1968, and the book by Garrels and Mackenzie, 1971).

If after time  $t_1$  the weathering constant changes from  $w_1$  to  $w_2$ , and the sedimentary mass active in the recycling process decreases from  $M_1$  to  $M_2$ , that is a fraction of sedimentary mass  $= 1 - (M_2/M_1)$  becomes non-active; then:

$$N(\tau, t) = \left(1 - \frac{M_2}{M_1}\right) [w_1 M_1 e^{-w_1(t_1 - \tau)}] + \frac{M_2}{M_1} [w_1 M_1 e^{-w_1(t_1 - \tau)}] e^{-w_2(t - t_1)} \quad (13A)$$

$$\text{for } 0 \leq \tau \leq t_1, \text{ and } t > t_1$$

or

$$N(t') = \left(1 - \frac{M_2}{M_1}\right) [w_1 M_1 e^{-w_1(t' - t'_1)}] + \frac{M_2}{M_1} [w_1 M_1 e^{-w_1(t' - t'_1)}] e^{-w_2 t'_1} \quad (13B)$$

$$\text{for } t'_1 \leq t' \leq p, \text{ where } t'_1 = p - t_1$$

and

$$N(\tau, t) = w_2 M_2 e^{-w_2(t - \tau)} \quad (14A)$$

$$\text{for } t_1 \leq \tau \leq t, t > t_1$$

or

$$N(t') = w_2 M_2 e^{-w_2 t'} \quad (14B)$$

$$\text{for } 0 \leq t' \leq t'_1$$

As is clear from equation (14B)  $w_2 M_2$  and  $w_2$  can be obtained directly from the plot of  $\ln N(t')$  versus  $t'$  as shown in Figure 2A. (The data are given by Gregor, 1970). The best estimates are:

$$w_2 M_2 = 7.37 \times 10^{15} \text{ g/yr}$$

$$w_2 = 4.80 \times 10^{-9} \text{ yr}^{-1}$$

$$\text{and } M_2 = 1.53 \times 10^{24} \text{ g}$$

Also  $w_1$  can be obtained graphically from the slope in  $\ln N(t')$  versus  $t'$  plot (see fig. 2A and eq 13B). Within the uncertainty of data,  $w_1$  is equal to  $w_2 = 0.48 \times 10^{-9} \text{ yr}^{-1}$ .  $N(t')$  at  $t'_1 (= 3.5 \times 10^8 \text{ yr})$  is  $3.36 \times 10^{15} \text{ g/yr}$  (Gregor, 1970; also see fig. 2B). Substituting the values of  $w_1 = w_2$ ,  $N(t'_1)$  and  $t'_1$  given above into equation (13B), one obtains:

$$M_1 = 1.97 \times 10^{24} \text{ g}$$

$$\text{and } w_1 M_1 = 9.46 \times 10^{15} \text{ g/yr}$$

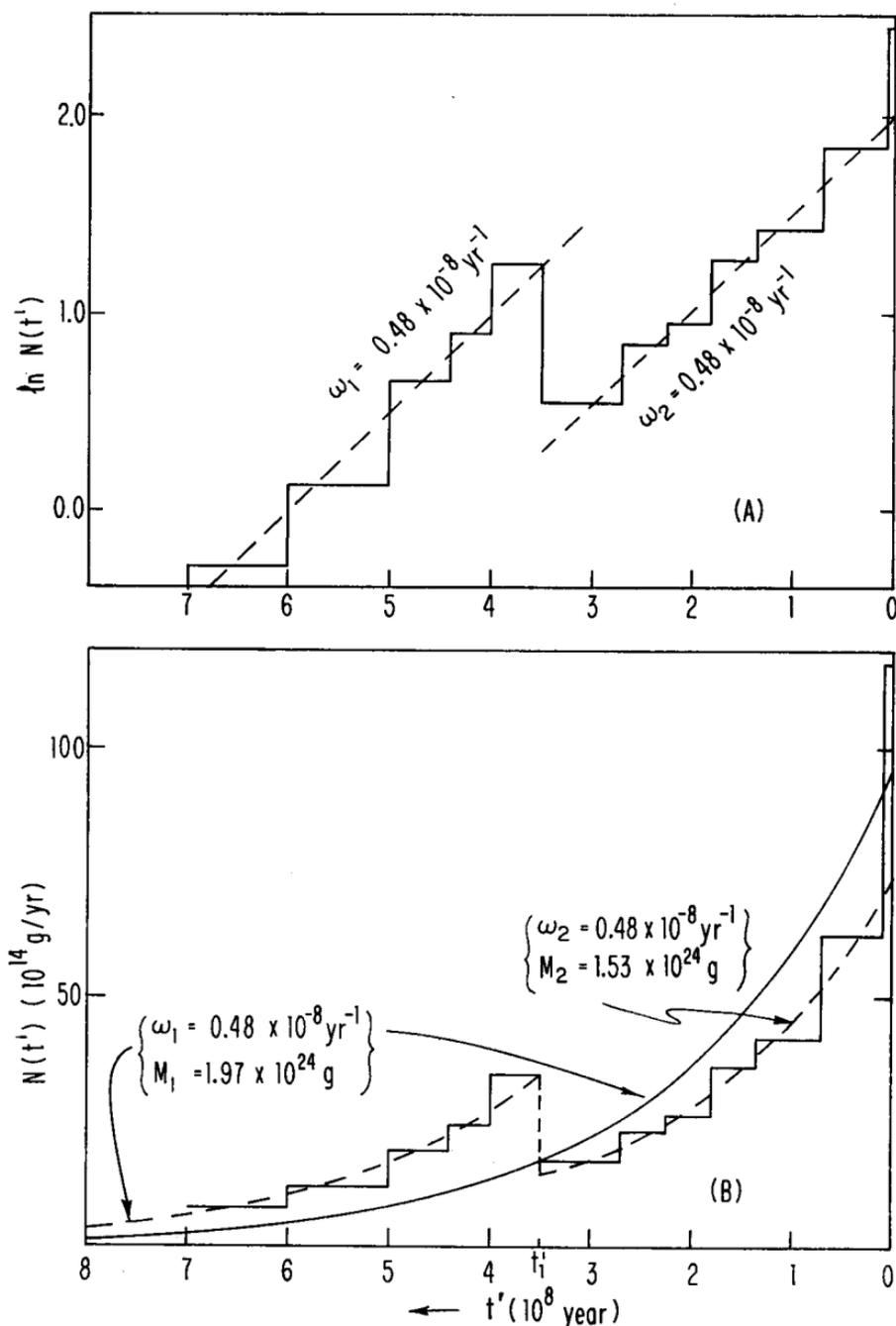


Fig. 2. (A) The plot of  $\ln N(t')$  versus age.  $N(t')$  data from Gregor (1970).

(B) The plot of  $N(t')$  versus age. The dotted curve is the plot of equations (13B) and (14B) with change in  $M$  at  $t'_1$ . The solid curve is the same plot but without the change in  $M$  at  $t'_1$ .

The dotted curves in figure 2B are the plots of equations (13B) and (14B) with the values of  $w_1 = w_2$ ,  $M_1$ , and  $M_2$  given above. The solid curve is the same plot but without change in  $M_1$ , that is,  $M_1 = M_2 = 1.97 \times 10^{24}$  g. The histogram is the "observed" distribution of sediments given by Gregor (1970).  $M_1$  is corresponding to a total sedimentary mass with age between zero and  $7 \times 10^8$  yr plus a small fraction of sediments tailing beyond the age  $7 \times 10^8$  yr (fig. 2B).  $M_1$  is less than the total sedimentary mass observed today (that is,  $M_1 < M(p)$ ), since four other sediment peaks beyond the age  $7 \times 10^8$  yr as shown by Garrels and Mackenzie (1969) are not included in  $M_1$ .

In summary, the discontinuity at  $3.5 \times 10^8$  yr ago in figure 2B was mainly caused by a sudden decrease in the sedimentary mass active in the recycling process ( $M_2 < M_1$ ) with almost no change in the weathering constant ( $w_1 = w_2$ ). The change may be closely related to orogenic activity (for example, Caledonian versus Hercynian). The ratio of the recycling rate  $w_1 M_1 / w_2 M_2$  (and  $M_1 / M_2$ ) is about 1.3 as against the ratio of 4 given by Gregor (1970). The discrepancy is expected, since the binomial equation:

$$N(t') = \frac{M}{2} (e^{-w_a t'} + e^{-w_b t'})$$

used by Gregor (1970) is empirical and has no real physical meaning (or at best ambiguous). This is also so of his calculation. (Garrels and Mackenzie, 1971, also independently reached a similar conclusion.)

If the weathering or recycling constant  $w = 4.8 \pm 10^{-9}$  yr $^{-1}$  for the last  $7 \times 10^8$  yr also applied to the whole geological time and all sedimentary mass in the Earth's crust were active in the recycling process, one would find very little sediment with age beyond 1 b.y. in contradiction with the observed fact. The explanation is that the older sediments have been preferentially preserved by burial under the younger sediments and/or have become relatively non-active in the recycling process due to some special geological conditions, for example, after an intensive orogenic activity and followed by a relatively calm period, the sediments become a part of the stable basement of the continent. Therefore, in the recycling process of sediments, one can distinguish the "long" term effect with  $w = 1.16 \times 10^{-9}$  yr $^{-1}$  and the "short" term effect with  $w = 4.80 \times 10^{-9}$  yr $^{-1}$ .

Taking the sedimentary mass active in the recycling process =  $1.97 \times 10^{24}$  g and  $w = 4.8 \times 10^{-9}$  yr $^{-1}$ , the recycling rate of the old primary volatiles and sediments,  $wM_i$ , (where  $M_i$  = the total mass of component  $i$  active in the recycling process) can be calculated from the data in equation (5) (including the sediments and the interstitial water). The results are given in the table below along with the present recycling rate obtained from average river influx  $R_i$  to the ocean (Livingstone, 1963; and Garrels and Mackenzie, 1966).

i	$wM_1$ $10^{11}$ moles/yr	i	$R_1$ $10^{11}$ moles/yr	$R_1/wM_1$ (dimensionless)
HCl	21	Cl <sup>-</sup>	71.5	3.4
CO <sub>2</sub>	184	HCO <sub>3</sub> <sup>-</sup>	310.	1.7
H <sub>2</sub> S	17	SO <sub>4</sub> <sup>2-</sup>	38.2	2.5
N	trace	NO <sub>3</sub> <sup>-</sup>	2.4	~
Sediments	$95 \times 10^{14}$ g/yr	Solid and dissolved loads*	$93 \times 10^{14}$ g/yr	~1.

\* The total solid and dissolved river loads were obtained by Judson, 1968.

As is clear from the above table, the present recycling rate of sediments is very similar to the average for the precarboniferous period ( $3.5$  to  $7 \times 10^8$  yr ago) and may be slightly higher than the average for the post-carboniferous period ( $0.02 - 3.5 \times 10^8$  yr ago). The high recycling rate of volatiles at present indicates preferential leaching of carbonate and evaporites as suggested by Garrels and Mackenzie (1969). The interesting result is that the present recycling rate of CO<sub>2</sub> (or CaCO<sub>3</sub>) is about twice that of sediments and of H<sub>2</sub>S + HCl (or evaporite) about three times, in good agreement with the relative magnitude of the mass half age for shale + sandstone: carbonate:evaporite = 1:2:3 as given by Garrels and Mackenzie (1969). Most of the water and N<sub>2</sub> are recycled through the atmosphere.

It is also interesting to look into the present situation of marine sediments:

Since the average sedimentation rate of red clay in the deep ocean is about  $0.3 \pm 0.1 \times 10^{-3}$  g/yr/cm<sup>2</sup> (Ku, Broecker, and Opdyke, 1968), the total annual accumulation rate of red clay over the whole ocean would be  $11 \pm 3 \times 10^{14}$  g/yr. Turekian (1965) estimated the total CaCO<sub>3</sub> deposition rate in the ocean =  $12 \pm 3 \times 10^{14}$  g/yr by assuming that the river influx of Ca<sup>++</sup> ends up as CaCO<sub>3</sub> in the ocean. Therefore, the total deposition rate of sediments in the deep ocean is about  $23 \pm 4 \times 10^{14}$  g/yr. On the other hand, according to the ocean floor spreading theory, about  $25 \pm 6 \times 10^{14}$  g of sediments are destroyed annually in the edge of the ocean. The estimate is obtained by multiplying the following data: length of mid-oceanic ridge  $\approx 6.0 \pm 0.4 \times 10^9$  cm,  $2 \times$  average ocean floor spreading rate  $\approx 2 \times (2 \pm 0.5$  cm/yr) (LePichon, 1968), average thickness of deep sea sediments =  $450 \times 10^2$  cm, and density of sediments =  $2.3$  g/cm<sup>3</sup> (Hill, 1957).

As shown above, the deposition and destruction rates of deep sea sediments are the same within the uncertainty of data, so the total mass of deep sea sediments ( $\sim 0.4 \times 10^{24}$  g) is in a steady state. The mean residence time of sediments,  $t_m$  ( $= M_1/(dM_1/dt)$ ), in the ocean is about  $170 \times 10^6$  yr. At steady state the remelting of marine sediments in the edge of the ocean ( $25 \pm 6 \times 10^{14}$  g/yr) should also be balanced out by weathering annually the same amount of fresh igneous rocks which correspond to  $27 \pm 6$  percent of the modern river loads.

## SUMMARY

- The total sedimentary mass of  $2.4 \pm 0.4 \times 10^{24}$  g is obtained from the  $O^{18}$  mass balance calculation.
- The weathering of Poldervaart's (1965) average crust rock can produce a sediment with the following features:
 

carbonate	= 15	(all in wt percent)
organic carbon	= 0.47	
evaporite	= 2	
chlorine	= 0.57	
sulfur	= 0.51	
chemically bonded water	= 2.9	
- In the weathering of 100 g of igneous rock, about 113 g of sediments is produced. The increment is contributed by the primary magmatic volatiles.
- The relative weight abundance of rock types obtained from the model is:
 

evaporite:carbonate:sandstone:shale + clay = 2:15:12:71.
- The total mass of primary magmatic volatiles (in unit of  $10^{20}$  moles) and their major sinks (in molar percent of elements) are:
 

HCl = 11.9,	33 percent in NaCl, 67 percent oceanic $Cl^-$ ,
$CO_2$ = 46.4,	80 percent in carbonates,
	20 percent in organic carbon,
$H_2S$ = 4.2,	55 percent in $FeS_2$ , 35 percent $CaSO_4$ ,
	10 percent $SO_4^{=}$
N = 2.8,	~100 percent in the atmosphere
$H_2O$ = 953,	98 percent in hydrosphere, 2 percent clay minerals

Also, a net of  $9.3 \times 10^{20}$  moles of  $O_2$  has been produced by photosynthesis. The balance of the expenditures is:

0.4 $\times 10^{20}$ moles,	free in atmosphere
3.1 $\times 10^{20}$ moles	used in oxidation of ferrous to ferric iron
5.8 $\times 10^{20}$ moles	used in oxidation of primary volatiles.
- The gross distribution of sedimentary mass as a function of age observed today (Garrels and Mackenzie, 1969) cannot give a definite clue to the de-gassing model of the primary volatiles, but an asymptotic de-gassing model is preferred in this paper in accord with Birch's (1965) thermal history of the Earth.
- The weathering constant,  $w$ , for the last  $700 \times 10^6$  yr is about  $4.8 \pm 0.1 \times 10^{-9}$  yr $^{-1}$  which corresponds to a mean residence time of sediments  $(1/w) = 210 \pm 5 \times 10^6$  yr.
- Older sediments have been preferentially preserved by burial, and all fractions of the sedimentary mass have not been equally active in the recycling process in the past.
- The present recycling rate of carbonate and evaporites are respectively two and three times the value for sandstone + shale.
- The total mass of deep oceanic sediments is more or less in a steady state today. The mean residence time of sediments in the ocean is about  $170 \times 10^6$  yr.

11. About  $27 \pm 6$  percent of the present river loads is the weathering product of fresh igneous rocks.

ACKNOWLEDGMENTS

I am indebted to Drs. W. S. Broecker, R. M. Garrels, R. Siever, and T. J. Shankland for many helpful discussions. I have benefited greatly from their thoughtful and critical reviews of the manuscript. Dr. T. J. Shankland helped in setting up the mathematical model.

Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society.

APPENDIX

The derivation of the age distribution function of sedimentary mass as observed today is as follows: If the erosion or weathering rate of any formation is directly proportional to the mass of that formation, then

$$\frac{dN(\tau, t)}{dt} = -wN(\tau, t) \tag{A1}$$

and the integrated form:

$$N(\tau, t) = N_o(\tau)e^{-w(t-\tau)} \tag{A2}$$

where:

$$N_o(\tau) = N(\tau, \tau) = \text{mass of new sedimentary formation deposited per unit of time at time } \tau.$$

Otherwise, all notations are the same as in the text.  $N_o(\tau)$  can be defined by the boundary condition:

$$\begin{aligned} M(t) &= \int_0^t N(\tau, t) d\tau \\ &= e^{-wt} \int_0^t N_o(\tau) e^{w\tau} d\tau \end{aligned}$$

$$\text{that is, } M(t)e^{wt} = \int_0^t N_o(\tau) e^{w\tau} d\tau \tag{A3}$$

Taking the derivative of equation (A3) with respect to  $t$  then,

$$N_o(t) = wM(t) + \frac{dM(t)}{dt} \tag{A4A}$$

or

$$N_o(\tau) = wM(\tau) + \frac{dM(\tau)}{d\tau} \tag{A4B}$$

put equation (A4B) back into equation (A2):

$$N(\tau, t) = \left[ wM(\tau) + \frac{dM(\tau)}{d\tau} \right] e^{-w(t-\tau)} \tag{A5}$$

If (1)  $M(t) = M(\tau) = M(p) = \text{constant}$

(2)  $M(t) = M(p) \times t/p,$

(3)  $M(t) = (1 - e^{-\lambda t}) \times M(p)$

then, equation (A5) reduces to equations (9A), (11), and (8A), respectively.

## REFERENCES

- Birch, Francis, 1965, Speculation on the Earth's thermal history: *Geol. Soc. America Bull.*, v. 76, p. 133-154.
- Borchert, Hermann, 1951, Zur Geochemie des Kohlenstuffs: *Geochim. et Cosmochim. Acta*, v. 2, p. 62-75.
- Conway, E. J., 1943, Mean geochemical data on relation to oceanic evolution: *Royal Irish Acad. Proc.*, v. 38, sec. B(8), p. 122-159.
- Craig, Harmon, 1953, The geochemistry of the stable carbon isotopes: *Geochim. et Cosmochim. Acta*, v. 3, p. 53-92.
- Craig, Harmon, and Gordon, L. I., 1965, Isotopic oceanography, in *Symposium Marine Geochemistry: Rhode Island Univ., Narragansett Marine Lab., Pub 3*, p. 277-374.
- Degens, E. T., 1969, Biogeochemistry of stable carbon isotopes, in Eglinton, G., and Murphy, M. T. J., *Organic Geochemistry: New York, Springer-Verlag*, p. 304-328.
- Fuex, A. N., and Baker, D. R., 1971, Stable carbon in selected granitic, mafic and ultramafic igneous rocks: *Geophys. Union Trans.*, v. 52, p. 366.
- Garlick, G. D., 1969, The stable isotopes of oxygen, in Wedepohl, K. H., *Handbook of Geochemistry*, v. 2, pt. 1, Chap. 8: New York Springer-Verlag, p. 1-27.
- Garrels, R. M., and Mackenzie, F. T., 1969, Sedimentary rock types: Relative proportions as a function of geological time: *Science*, v. 163, p. 570-571.
- 1971, *The Evolution of Sedimentary Rocks: New York, Norton & Co.*, 500 p.
- Goldberg, E. D., and Arrhenius, G. O. S., 1958, Chemistry of Pacific pelagic sediments: *Geochim. et Cosmochim. Acta*, v. 13, p. 153-212.
- Goldschmidt, V. M., 1933, *Grundlagen der quantitativen Geochemie: Fortschr. Mineralogie, Kristallographie, Petrographie*, v. 17, p. 112-156.
- 1954, *Geochemistry: Oxford, Clarendon Press*, 730 p.
- Gregor, C. B., 1968, The rate of denudation in post-Algonkian time: *Kon. Ned. Akad. Wetensch. Proc.*, v. 71, p. 22-30.
- 1970, Denudation of the continents: *Nature*, v. 228, p. 273-275.
- Harbaugh, J., and Bonham-Carter G., 1970, *Computer simulation in geology: New York, John Wiley & Sons, Inc.*, 575 p.
- Heald, E. F., Naughton, J. J., and Barnes, I. J., 1963, The chemistry of volcanic gases: *Jour. Geophys. Research*, v. 68, p. 545-557.
- Hill, M. N., 1957, Recent geophysical exploration of the ocean floor: *Physics and Chemistry of the Earth*, v. 2, p. 129-163.
- Holland, H. D., 1964, On the chemical evolution of the terrestrial and cytherean atmosphere, in Brancazio, P. J., and Cameron, A. G. W., eds., *The origin and evolution of atmospheres and oceans: New York, John Wiley & Sons*, p. 86-101.
- Holser, W. T., and Kaplan, I. R., 1966, Isotope geochemistry of sedimentary sulfates: *Chem. Geology*, v. 1, p. 93-135.
- Horn, M. K., and Adams, J. A. S., 1965, Computer-derived geochemical balances and element abundances: *Geochim. et Cosmochim. Acta*, v. 25, p. 110-146.
- Judson, S., 1968, Erosion of the land—or what's happening to our continents?: *Am. Scientist*, v. 56, p. 356-374.
- Ku, T. L., Broecker, W. S., and Opdyke, N. 1968, Comparison of sedimentation rates measured by paleomagnetic and the ionium methods of age determination: *Earth and Planetary Sci. Letters*, v. 4, p. 1-16.
- Le Pichon, X., 1968, Sea-floor spreading and continental drift: *Jour. Geophys. Research*, v. 73, p. 3661-3697.
- Livingstone, D. A., 1963, Chemical composition of rivers and lakes, in Fleischer, Michael, ed., *Data of Geochemistry: U.S. Geol. Survey Prof. Paper 440, Chap. G*, p. G1-G64.
- Mackenzie, F. T., and Garrels, R. M., 1966, Chemical mass balance between rivers and oceans: *Am. Jour. Sci.*, v. 264, p. 507-525.
- Mason, B., 1966, *Principles of Geochemistry*, 3rd ed.: New York, John Wiley & Sons, Inc., 329 p.
- Pettijohn, F. J., 1957, *Sedimentary Rocks*, 2d ed.: New York, Harper & Brothers, 718 p.
- Poldervaart, Arie, 1955, Chemistry of the Earth's crust, in Poldervaart, Arie, ed., *Crust of the Earth: Geol. Soc. America Spec. Paper 62*, p. 119-144.

- Ronov, A. B., 1968, Probable changes in the composition of sea water during the course of geological time: *Sedimentology*, v. 10, p. 25.
- Ronov, A. B., and Yaroshevsky, A. A., 1969, Chemical composition of the earth's crust: *Am. Geophys. Union Geophys. Mon.* 13, p. 37-57.
- Rubey, W. W., 1951, Geologic history of sea water: an attempt to state the problem: *Geol. Soc. America Bull.*, v. 62, p. 1111-1147.
- Savin, S. M., and Epstein, S., 1970a, The oxygen and hydrogen isotope geochemistry of clay minerals: *Geochim. et Cosmochim. Acta*, v. 34, p. 25-42.
- 1970b, The oxygen and hydrogen isotope geochemistry of ocean sediments and shales: *Geochim. et Cosmochim. Acta*, v. 34, p. 43-63.
- Siever, R., 1968, Sedimentological consequences of a steady-state ocean-atmosphere: *Sedimentology*, v. 11, p. 5-29.
- Taylor, H. P., 1968, The oxygen isotope geochemistry of igneous rocks: *Contr. Mineralogy and Petrology*, v. 19, p. 1-71.
- Turekian, K. K., 1965, Some aspects of the geochemistry of marine sediments, in Riley, J. P., and Skirron, G., *Chemical oceanography*, v. 2: London and New York, Acad. Press, p. 81-126.
- Vinogradov, A. P., Kryptova, O. I., and Ustinov, V. I., 1965, Possible sources of carbon in diamonds as indicated by the  $C^{13}/C^{12}$  ratios: *Geochem. Internat.*, v. 2, p. 495-503.
- Wickman, F. E., 1954, The total amount of sediments and the composition of the "average igneous rock": *Geochim. et Cosmochim. Acta*, v. 5, p. 97-110.
- 1955, The cycle of carbon and the stable carbon isotopes; *Geochim. et Cosmochim. Acta*, v. 9, p. 136-153.