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CHEMICAL MASS BALANCE BETWEEN RIVERS AND OCEANS

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ABSTRACT. The assumption of constancy of the chemical composition of ocean water requires that the excesses of dissolved constituents carried by streams to the ocean be removed. The chemical mass balance between streams and oceans is an attempt to evaluate this removal process, to see what reactions are necessary to accomplish this removal, and to maintain present ocean water composition.

Postulation of a steady-state model for the ocean leads to the removal of stream-derived dissolved solids as minerals in marine sediments, as dissolved constituents in sediment pore waters, and as materials cycled through the atmosphere. Disposal of the dissolved solids requires synthesis of typical clay minerals from degraded alumino-silicates before burial in sediments, by reactions of the type:

$$\text{X-ray amorphous Al silicate} + SiO_2 + HCO_3^- + \text{cations} = \text{cation Al silicate} + CO_2 + H_2O.$$

Such chemical, if not structural, synthesis implies control of the major ion ratios in sea water and the CO_2 pressure of the atmosphere by equilibria involving alumino-silicates. These "reverse weathering" reactions, by removing HCO_3^- and alkali metals from the oceanic system, prevent the ocean from attaining the composition of a soda lake. Also, chemical synthesis of typical clay minerals in the oceanic system implies that these minerals are in equilibrium, or nearly so, with an aqueous solution of the composition of average ocean water and should not be significantly altered upon entering the ocean as allogenic particles.

INTRODUCTION

Although the ocean receives materials from several sources, the rates of flow of water and dissolved constituents into the ocean from streams far exceeds that from any other source. Postulation of a steady-state oceanic system (Rubey, 1951; Sillén, 1961, 1963; Holland, 1965; Kramer, 1965) requires that these stream-derived constituents be removed as rapidly as they enter the ocean. Garrels and Mackenzie (in press) showed that simple isothermal evaporation, at the P_{CO_2} of the Earth's atmosphere, of waters derived from felsic igneous rocks and isolated from solid weathering products leads to the formation of a soda lake water, high in alkali cations, low in alkaline-earth cations, and with a pH of about 10. The ocean certainly is not a giant soda lake, but the Sierra waters are similar to river waters, which definitely give rise to water of the composition of the ocean. Therefore, the question arises as to why the ocean is not a soda lake.

The purpose of this paper is to present a simple chemical mass balance between streams and oceans. This mass balance is an attempt to evaluate the processes that lead to the removal of stream-derived dissolved constituents from the ocean system and to see what reactions are necessary to accomplish this removal and to maintain constant present ocean water composition.

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SOME PRELIMINARY CONSIDERATIONS

As background for the mass balance between river water and ocean water, we will consider some of the relations between streams and oceans.

Dissolved constituents.—More than 99 percent of the dissolved material in the ocean is accounted for by the constituents Na, Mg, Ca, K, Cl, SO_4, HCO_3, and SiO_2; the same constituents make up more than 99 percent of the total dissolved solids brought in by rivers (table 1). Ocean water is several to many times more concentrated with respect to the major constituents than river water, except for silica, which is much lower in the ocean.

The rates of flow of stream-derived dissolved constituents into the ocean are rapid. The major constituents, except for Na, have residence times in the ocean of less than 10^8 years (Barth, 1952; Goldberg and Arrhenius, 1958), a geologically short time. Livingstone (1963a) has made the most recent study of discharges and dissolved loads of rivers of the world and estimated that 3.9×10^{12} kilograms of dissolved solids are carried to the ocean annually by rivers. This amount of dissolved materials, if precipitated as solids, would approximately equal the total volume of the ocean (1.37×10^{21} liters) in 10^9 years, assuming no net removal of materials from the oceanic system. Also, if the ocean basins were not filled with water and the rivers at their present discharge began to fill them, it would require only 40,000 years for the rivers to fill the ocean basins to their present level. Assuming that the composition of ocean water has remained essentially constant for the past 10^8 years

TABLE 1

Major constituents of river water and sea water

Constituent	River water[1]		Sea water[2]	
	ppm	$\frac{\text{millimoles}}{\text{liter}}$	ppm	$\frac{\text{millimoles}}{\text{liter}}$
Cl^-	7.8	0.220	19,000	535.2
Na^+	6.3	0.274	10,500	456.5
Mg^{++}	4.1	0.171	1,300	54.2
$SO_4^=$	11.2	0.117	2,650	27.6
K^+	2.3	0.059	380	10.0
Ca^{++}	15	0.375	400	9.7
HCO_3^-	58.4	0.958	140	2.3
SiO_2	13.1	0.218	6	0.1
NO_3^-	1	0.016	———	———
Fe	0.67	0.012	———	———
Br^-	———	———	65	0.8
$CO_3^=$	———	———	18	0.3
Sr^{++}	———	———	8	0.1

[1] Livingstone (1963a)

[2] Goldberg (1957)

(Lowenstam, 1961, presents some evidence for constancy of ocean water composition for at least the past 2 x 10^8 years) and that present stream discharge and content are characteristic of the geologic past, the amount of water brought to the ocean by rivers in 10^8 years would be equal to 2400 times the amount now in the ocean. By similar reasoning, the amount of Cl carried to the ocean in 10^8 years would just about equal the amount currently in the ocean, Na would have been "renewed" 1.4 times, Mg 7 times, SO_4 10 times, K 15 times, Ca 81 times, HCO_3 1000 times, and SiO_2 5300 times (table 2). The number, 10^8 years, is not a "magic" number but is used to illustrate that the rates of delivery of dissolved constituents to the ocean by rivers are rapid and that if the ocean suddenly became fresh, it would not take long relative to 10^8 years for it to exceed its present salinity, if all the dissolved solids carried to the ocean by rivers remained in solution.

Suspended material.—Great tonnages of suspended material are carried by rivers to the ocean. If we assume a present average annual world-wide river runoff to the ocean of 3.3 x 10^{16} liters/year (Livingstone, 1963a) and an average suspended-sediment concentration equal to that of the Mississippi River, 250 milligrams/liter (Edwards, Kister, and Scarcia, 1956), we calculate 8.3 x 10^{12} kilograms as the amount of suspended sediment brought to the ocean annually. Kuenen (1950) estimates 32.5 x 10^{12} kilograms. Thus, the world-wide ratio of river suspended load to dissolved load probably is somewhere between 2/1 (Mississippi data) and 8/1 (Kuenen's estimate). Assuming a density of 2.7 grams/cubic centimeter for the suspended particles of rivers and therefore a minimum volume of compacted sediment, the quantity of

Table 2

Number of times river constituents have "passed through" the ocean in 10^8 years assuming present annual world-wide river discharge, mean dissolved constituent concentration of rivers and ocean, and ocean volume of 1.37 x 10^{21} liters

Constituent	Amount delivered by rivers to the ocean annually	Amount in ocean	Amount delivered by rivers to ocean in 10^8 years	Number of times constituents have been "renewed" in 10^8 years
SiO_2	42.6 x 10^{10}kg	0.008 x 10^{18}kg	42.6 x 10^{18}kg	5300
HCO_3^-	190.2 x 10^{10}kg	0.19 x 10^{18}kg	190.2 x 10^{18}kg	1000
Ca^{++}	48.8 x 10^{10}kg	0.6 x 10^{18}kg	48.8 x 10^{18}kg	81
K^+	7.4 x 10^{10}kg	0.5 x 10^{18}kg	7.4 x 10^{18}kg	15
$SO_4^=$	36.7 x 10^{10}kg	3.7 x 10^{18}kg	36.7 x 10^{18}kg	10
Mg^{++}	13.3 x 10^{10}kg	1.9 x 10^{18}kg	13.3 x 10^{18}kg	7
Na^+	20.7 x 10^{10}kg	14.4 x 10^{18}kg	20.7 x 10^{18}kg	1.4
Cl^-	25.4 x 10^{10}kg	26.1 x 10^{18}kg	25.4 x 10^{18}kg	1
H_2O	3,333,000 x 10^{10}kg	1370 x 10^{18}kg	3,333,000 x 10^{18}kg	2400

suspended material delivered to the ocean in 10^9 years would amount to 2 to 9 times the volume of the ocean, if all this material remained in the oceanic system.

Type and reactivity of suspended material.—Unfortunately, complete chemical and mineralogical analyses of the suspended load of modern streams are lacking, but some general conclusions can be made concerning the composition and reactivity of the suspended sediment. This material is dominantly composed of the aluminosilicate minerals: montmorillonite, kaolinite, illite, chlorite, mixed-layer clay, and dioctahedral vermiculite; and of X-ray amorphous aluminosilicates, gibbsite, fine-grained fragments of quartz, feldspar, carbonate, Fe-Ti minerals, rock fragments, and organic matter (compare Powers, 1954; Grim and Johns, 1954; Nelson, 1963; Taggart and Kaiser, 1960; Griffin, 1962; Kennedy, 1963, 1965). It is interesting to note that these same materials, primarily the aluminosilicates, compose the bulk of modern, fine-grained, non-biogenic sediments in the ocean (compare Correns, 1937; Revelle, 1944; Griffin, 1962; Griffin and Goldberg, 1963; Arrhenius, 1963; Biscaye, 1965) and are the major constituents found in ancient shales. The *gross* mineralogical similarity between ancient shales and modern marine argillaceous sediments has led some investigators to conclude that the bulk of the suspended material carried by rivers to the ocean is unreactive and consequently has little effect on oceanic chemistry.

Studies of the distribution patterns of clay minerals in modern stream and nearshore marine sediments (Grim, Dietz, and Bradley, 1949; Favajee, 1951; Grim and Johns, 1954; Powers, 1957, 1959; Nelson, 1963) show progressive changes in the clay mineral types from fresh to saline waters. For example, Grim and Johns (1954) found that illite and chlorite increased at the expense of montmorillonite down the Guadalupe River into the Gulf of Mexico. They interpreted this distribution to be the result of the conversion of montmorillonite to chlorite and illite in the higher salinity environments. The experiments of Whitehouse and McCarter (1958), although not conclusive, lend a certain amount of support to this conclusion. They immersed montmorillonitic material in artificial sea water for periods of up to five years. Analyses of the material showed that montmorillonite was transformed to illitic and chloritic clays. Similar experiments with kaolinite and illite showed that these minerals were unaltered after immersion.

In rebuttal of the above evidence for the reactivity of land-derived clay minerals in the marine environment, Weaver (1959) suggested that the distribution patterns of clay minerals in modern sediments may be due to such physical factors as preferential flocculation, current sorting, effect of various source areas, floods, and periodic variations in the concentration and composition of river detritus. Griffin (1962) presented convincing evidence that the clay mineral distributions in the northeastern Gulf of Mexico are a function of parent rock, stream drainage patterns, and current patterns in the Gulf. Griffin and Goldberg (1963) studied clay mineral distributions in the Pacific Ocean. Their data show that land-derived clay minerals are not markedly altered on entering the Pacific Basin, although K+— and Mg++—uptake by degraded clays may occur. Biscaye (1965) reported that most of the recent deep-sea clay from the Atlantic Ocean is detritus from the continents. and in situ formation of clay minerals is unimportant in the Atlantic Basin. Hurley and others (1963) determined K-Ar ages for K-bearing minerals, principally illite, in pelagic sediments from the North Atlantic. Their age values range from 200 to 400 million years and indicate that the bulk of oceanic illites is detrital.

Recent experimental work (Mackenzie and Garrels, 1965), in which aluminosilicates were placed in low-silica sea water and the pH and silica content of the systems monitored with time, showed that silicate minerals rapidly release silica to sea water. The silica concentrations reached in these experiments were in the order of the average silica content of the ocean (approximately 6 ppm). We concluded that the rates observed indicate that the ocean must be considered as a chemical system with a rapid compositional response to added detrital silicates.

PROCEDURES AND CALCULATIONS

In the steady-state oceanic model, the dissolved constituents carried by streams to the ocean are removed as rapidly as they are added. To simulate this model, we will imagine a hugh batch process in which we allow the rivers to flow for 10^8 years into an ocean of present-day constant composition, maintaining a constant ocean volume by removing

TABLE 3

Amount of dissolved constituents transported to the ocean by rivers in 10^8 years, assuming present mean annual total dissolved load and mean composition of world's rivers

Constituent	Mean composition of river waters of the world		Amount of dissolved constituents brought to the ocean annually, assuming the annual total dissolved load is 390.5 x 10^7 metric tons		Amount of dissolved constituents carried to the ocean in 10^8 years
	ppm	millimoles liter	(x10^{-7} metric tons)	(x10^{-13} moles)	(x10^{-21}mmoles)
HCO_3^-	58.4	0.958	190.2	3.118	3118
Ca^{++}	15	0.375	48.8	1.220	1220
Na^+	6.3	0.274	20.7	0.900	900
Cl^-	7.8	0.220	25.4	0.715	715
SiO_2	13.1	0.218	42.6	0.710	710
Mg^{++}	4.1	0.171	13.3	0.554	554
$SO_4^=$	11.2	0.117	36.7	0.382	382
K^+	2.3	0.059	7.4	0.189	189

only H_2O. If we assume that present stream discharge and content remain constant for 10^8 years, we may calculate the total discharge into the ocean in this period of time of each major stream-derived dissolved constituent (table 3). The river data used in this calculation were taken from Livingstone (1963a), who has made the most recent and comprehensive study of the chemical composition of rivers and lakes. He discusses thoroughly the problems involved in making estimates of the mean dissolved constituent composition of rivers and of the total amount of dissolved material carried to the ocean annually, and we will not pursue these problems further in this paper. His estimates are probably the best to date. Furthermore, our balance is not significantly affected by changes in estimates of the mean world-wide salinity of rivers but only by relatively large changes in the estimates of the mean ratios of dissolved constituents. Table 4 shows that the mean percentage estimates of dissolved constituents in river water as given by several investigators are similar.

We will now dispose of these excesses of dissolved constituents, recognizing that we have simulated a steady-state rate process by integration over 10^8 years of the rates of flow of dissolved constituents into the oceanic system. From the excesses, we have chosen to make the most common minerals observed to precipitate from the ocean, or those reported as most common in marine sediments. Some of the excess material is removed in the pore waters of sediments or through the atmosphere. The balance sheet is shown in table 5. Details of the removal process are given in further sections.

Reactions involving sulfate.—River waters contain 11.2 parts per million $SO_4^=$ derived from (1) oxidation of pyrite and solution of gypsum or anhydrite during rock weathering, (2) sea-spray particles generated at the ocean-atmosphere interface and removed from the atmosphere by rain or as dry fallout, (3) oxidation by photochemical processes in the atmosphere of H_2S formed by the decomposition of organic materials, and (4) industrial activities. About 2.5 parts per million $SO_4^=$ is added to the rivers by atmospheric processes (data in Gorham, 1961; Junge and Werby, 1958); thus 8 to 9 parts per million $SO_4^=$ in rivers is derived from the weathering of rocks, and a negligible amount from human activities in which sulfur-bearing wastes are added directly to the rivers.

Most of the sulfur in sediments is found as gypsum or anhydrite in evaporites and as pyrite in shales and other sedimentary rocks. Unfortunately, the amount of sulfur in the geologic column tied up in pyrite versus that in gypsum or anhydrite is difficult to determine. For the purposes of our balance, we have removed 50 percent of the $SO_4^=$ in making pyrite and 50 percent as $CaSO_4$. The relative proportions used have little effect on the balance; the excess HCO_3^-, generated by forming pyrite, is used up to form $CaCO_3$ by reacting the HCO_3^- with the Ca^{++} left over after making $CaSO_4$.

TABLE 4

Comparison of estimates of the mean composition of river waters of the world

	Salinity, 181 ppm (based on Murray's data, 1887)		Salinity, 137 ppm (based on Clarke's river content data 1924; and Murray's H_2O runoff estimate, 1887)		Salinity, 199 ppm (Conway's, 1942, estimate of Clarke's data)		Salinity, 120 ppm based on Livingstone's data, 1963)	
Constituent	ppm	Percent of total dissolved solids	ppm	Percent of total dissolved solids	ppm	Percent of total dissolved solids	ppm	Percent of total dissolved solids
HCO_3^-	152	58.7	71.5	52.3	104	52.3	58.4	48.7
Ca^{++}	37.1	14.3	20.4	14.9	29.8	14.9	15	12.5
Na^+	6.3	2.4	5.8	4.2	8.4	4.2	6.3	5.3
Cl^-	3.3	1.3	5.7	4.2	8.3	4.2	7.8	6.5
SiO_2	19.5	7.6	11.7	8.6	17.1	8.6	13.1	10.9
Mg^{++}	8.4	3.2	3.4	2.5	5	2.5	4.1	3.4
$SO_4^=$	14.9	5.8	12.1	8.9	17.7	8.9	11.2	9.4
K^+	2.4	0.9	2.1	1.6	3.1	1.6	2.3	1.9
NO_3^-	5.1	2	0.9	0.7	1.3	0.7	1	0.8
Fe	8.6 (Fe + Al)	3.5	2.8 (Fe + Al)	2.0	4 (Fe + Al)	2.0	0.67	0.6
Others	0.7	0.3	0.2	0.1	0.3	0.1	—	—

TABLE 5

Mass balance calculation for removal of river-derived constituents from the ocean

Reaction (balanced in terms of mmoles of constituents used)	Constituent balance (x 10^{-21} mmoles)								HCO_3^-		CO_2		Products	
	$SO_4^=$	Ca^{++}	Cl^-	Na^+	Mg^{++}	K^+	SiO_2	HCO_3^-	Consumed (−)	Evolved (+)	Consumed (−)	Evolved (+)	(x 10^{-21} mmoles)	Percentage of total products formed (mole basis)
Amount of material to be removed from ocean in 10^8 years (x 10^{-21} mmoles)	382	1220	715	900	554	189	710	3118						
$95.5\ FeAl_6Si_6O_{20}(OH)_4 + 191\ SO_4^= + 47.8\ CO_2 + 55.7\ C_6H_{12}O_6 + 238.8\ H_2O = 286.5\ Al_2Si_2O_5(OH)_4 + 95.5\ FeS_2 + 382\ HCO_3^-$	191	1220	715	900	554	189	710	3500		+382	−48		96 Pyrite 287 Kaolinite	3% 8%
$191\ Ca^{++} + 191\ SO_4^= = 191\ CaSO_4$	0	1029	715	900	554	189	710	3500					191 "$CaSO_4$"	5%
$52\ Mg^{++} + 104\ HCO_3^- = 52\ MgCO_3 + 52\ CO_2 + 52\ H_2O$	0	1029	715	900	502	189	710	3396	−104			+52	52 $MgCO_3$ in Magnesian Calcite	2%
$1029\ Ca^{++} + 2058\ HCO_3^- = 1029\ CaCO_3 + 1029\ CO_2 + 1029\ H_2O$	0	0	715	900	502	189	710	1338	−2058			+1029	1029 Calcite and/or Aragonite	29%
$715\ Na^+ + 715\ Cl^- = 715\ NaCl$	0	0	0	185	502	189	710	1338					715 "NaCl"	20%
$71\ H_4SiO_4 = 71\ SiO_{2(s)} + 142\ H_2O$	0	0	0	185	502	189	639	1338					71 "Free" Silica	2%
$138\ Ca_{0.17}Al_{2.33}Si_{3.67}O_{10}(OH)_2 + 46\ Na^+ = 138\ Na_{0.33}Al_{2.33}Si_{3.67}O_{10}(OH)_2 + 23.5\ Ca^{++}$	0	24	0	139	502	189	639	1338					138 Sodic Montmorillonite	4%
$24\ Ca^{++} + 48\ HCO_3^- = 24\ CaCO_3 + 24\ CO_2 + 24\ H_2O$	0	0	0	139	502	189	639	1290	−48			+24	24 Calcite and/or Aragonite	1%
$486.5\ Al_2Si_{2.4}O_{5.8}(OH)_4 + 139\ Na^+ + 361.4\ SiO_2 + 139\ HCO_3^- = 417\ Na_{0.33}Al_{2.33}Si_{3.67}O_{10}(OH)_2 + 139\ CO_2 + 625.5\ H_2O$	0	0	0	0	502	189	278	1151	−139			+139	417 Sodic Montmorillonite	12%
$100.4\ Al_2Si_{2.4}O_{5.8}(OH)_4 + 502\ Mg^{++} + 60.2\ SiO_2 + 1004\ HCO_3^- = 100.4\ Mg_5Al_2Si_3O_{10}(OH)_8 + 1004\ CO_2 + 301.2\ H_2O$	0	0	0	0	0	189	218	147	−1004			+1004	100 Chlorite	3%
$472.5\ Al_2Si_{2.4}O_{5.8}(OH)_4 + 189\ K^+ + 189\ SiO_2 + 189\ HCO_3^- = 378\ K_{0.5}Al_{2.5}Si_{3.5}O_{10}(OH)_2 + 189\ CO_2 + 661.5\ H_2O$	0	0	0	0	0	0	29	−42	−189			+189	378 Illite	11%

Pyrite in marine sediments results from the reduction of $SO_4^=$ and subsequent reactions with mineral phases containing iron (Berner, 1964). Concomitant oxidation of organic materials accompanies the $SO_4^=$ reduction. The source of iron is detrital sediments, primarily clays (Kaplan, Emery, and Rittenberg, 1963). There are several ways to write the $SO_4^=$ reduction reaction:

$$3\ SO_4^= + C_6H_{12}O_6 = 3\ H_2S + 6\ HCO_3^- \tag{1}$$

where $C_6H_{12}O_6$ represents organic compounds, or

$$\begin{aligned} 24\ Fe(OH)_3 + 48\ SO_4^= + 15\ C_6H_{12}O_6 + 6\ CO_2 &= \\ 24\ FeS_2 + 78\ H_2O + 96\ HCO_3^- & \end{aligned} \tag{2}$$

where $Fe(OH)_3$ represents iron obtained from detrital iron-bearing materials and mobilized as ferric hydroxide, and

$$\begin{aligned} 12\ FeAl_6Si_6O_{20}(OH)_4 + 24\ SO_4^= + 6\ CO_2 + 7\ C_6H_{12}O_6 + 30\ H_2O &= \\ 36\ Al_2Si_2O_5(OH)_4 + 12\ FeS_2 + 48\ HCO_3^- & \end{aligned} \tag{3}$$

where $FeAl_6Si_6O_{20}(OH)_4$ represents clay minerals as a source of iron. The important aspect of all three reactions is that two times as much HCO_3^- is released as $SO_4^=$ consumed. This is a crude estimate of the amount of HCO_3^- released during oxidation of organic materials and sulfate reduction, because the actual amount depends on the carbon to hydrogen ratio of the organic compounds involved. For the purpose of the balance, we will use reaction (3) which, using 50 percent of the available $SO_4^=$ in our balance to make pyrite, is written

$$\begin{aligned} 95.5\ FeAl_6Si_6O_{20}(OH)_4 + 191\ SO_4^= + 47.8\ CO_2 + 55.7\ C_6H_{12}O_6 + \\ 238.8\ H_2O = 286.5\ Al_2Si_2O_5(OH)_4 + 95.5\ FeS_2 + 382\ HCO_3^-. \end{aligned}$$

Thus 191 x 10^{21} millimoles of $SO_4^=$ are consumed in making 95.5 x 10^{21} millimoles of pyrite and releasing 382 x 10^{21} millimoles HCO_3^-.

The rest of the $SO_4^=$ is removed as $CaSO_4$. The reaction is

$$Ca^{++} + SO_4^= = CaSO_4$$

and similarly in millimoles of material available in the balance

$$191\ Ca^{++} + 191\ SO_4^= = 191\ CaSO_4.$$

The "$CaSO_4$" formed represents that precipitated in evaporite basins as gypsum or anhydrite, $SO_4^=$ contained in the pore waters of sediments and balanced by Ca^{++}, and $SO_4^=$ and Ca^{++} deposited on the continents by atmospheric processes. At this point in our balance, all the $SO_4^=$ is used up.

Reactions involving carbonate minerals.—Calcium and magnesium are found in modern marine sediments and ancient rocks in several phases. We have removed some of the Ca^{++} in making "$CaSO_4$". The great mass of limestone and dolomite in the geologic column and the large carbonate provinces of the modern seas suggest that most of the rest of the Ca^{++} is removed from the oceanic system in minerals that form carbonate sediments—aragonite, calcite, magnesian calcite, and dolomite. Dolomite is not a major mineral component of modern carbonate sediments. Textural, structural, and geochemical relations suggest that most dolomite in modern and ancient sediments is not precipitated directly from solution. Therefore, for the purposes of the mass balance, we will remove the remaining Ca^{++} as aragonite or calcite and magnesian calcite.

Chave (1954) plotted the $MgCO_3$ content of modern calcareous shelf sediments against number of samples and concluded that the Mg^{++} in shelf sediments is derived mainly from skeletal material. His plot reveals that modern calcareous shelf sediments contain about 5 percent $MgCO_3$ as magnesian calcite, and therefore, an amount of Mg^{++} equal to 5 percent of the Ca^{++} is removed from our balance as magnesian calcite. This percentage represents a maximum for the percentage of $MgCO_3$ tied up in modern calcareous sediments since Turekian (1964) showed that most of the calcium carbonate is now being deposited in the deep sea, and the magnesium concentration of this calcium carbonate is 0.05 to 0.1 percent. The reaction is

$$Mg^{++} + 2\ HCO_3^- = MgCO_3 + CO_2 + H_2O$$

and in millimoles

$$52\ Mg^{++} + 104\ HCO_3^- = 52\ MgCO_3 + 52\ CO_2 + 52\ H_2O.$$

The remaining Ca^{++} is removed as calcite and/or aragonite according to the reaction

$$1029\ Ca^{++} + 2058\ HCO_3^- = 1029\ CaCO_3 + 1029\ CO_2 + 1029\ H_2O.$$

At this stage in the removal of materials, $SO_4^=$ and Ca^{++} have been completely used up, 9 percent of the Mg^{++} has been reacted, 43 percent of the original HCO_3^- is unreacted, and the products are pyrite, "$CaSO_4$", aragonite and/or calcite, and magnesian calcite. Almost half the HCO_3^- remains to be accounted for; even by assuming that dolomite is directly precipitated in the ratio to calcite found in ancient rocks (1/5), we could not reduce the HCO_3^- to less than 30 percent of the original amount.

The important point is that the amount of HCO_3^- carried to the ocean by streams cannot be disposed of by deposition of carbonate sediments. Assuming that all the Ca^{++} is removed with an equivalent amount of HCO_3^- and no Ca^{++} leaves the oceanic system balanced by $SO_4^=$, the most conservative estimate of the bicarbonate excess that can be calculated from the estimates of the mean composition of river waters (table 4) is 15 percent of the original amount transported to the ocean by streams. The following sections are concerned with a mechanism for removal of this HCO_3^- excess and with the possible processes and reactions that lead to the disposal of this excess HCO_3^- and remaining dissolved constituents, in accordance with the volumes of sedimentary rocks in the geologic column and the types of minerals found in marine sediments.

Reactions involving chloride and sodium.—All the Cl^- is removed from the system with an equal amount of Na^+. Part of this "NaCl" leaves the system as halite, part becomes dissolved in the pore waters of sediments, and part goes into the atmosphere. Some Cl^- may be removed in the exchange positions of clay minerals, but we do not have a reasonable estimate of the amount of Cl^- that can be disposed of by this process. Livingstone (1963b) recently recalculated the sodium balance in nature and the sodium age of the ocean. His data show that 65 to 75 percent of the Na^+ carried by rivers to the ocean since post-Alkongian time can be accounted for by deposition of halite in evaporite deposits, as a dissolved constituent in the pore waters of sediments or as material cycled through the atmosphere. He suggests that the rest of the Na^+ is removed in the exchange positions of clay minerals. Our value of 80 percent, obtained by removing equal amounts of Cl^- and Na^+, is in reasonable agreement with Livingstone's.

The NaCl reaction is

$$Na^+ + Cl^- = NaCl$$

and in millimoles

$$715\ Na^+ + 715\ Cl^- = 715\ NaCl.$$

The removal of the remaining Na^+ will be discussed in the next section.

Reactions involving silica and aluminosilicate minerals.—At this stage in the balance, we must remove Mg^{++}, K^+, Na^+, and a large amount of dissolved SiO_2 and HCO_3^- from the system. Bicarbonate and SiO_2 are the clues to this removal. As shown in a previous section, HCO_3^- cannot be disposed of simply by deposition of carbonate minerals. Accumulation of this HCO_3^- would lead to an increase in the alkalinity of the oceans, and ocean water composition would evolve toward that of a soda lake. Also, at the present rate of flow of dissolved SiO_2 into the ocean by streams, the volume of silica, primarily as chert, would be much greater than observed in the geologic column if all the SiO_2 were precipitated chemically or biochemically as "free" silica (silica not bound with alumina and essentially devoid of alkaline-earth or alkali cations). This relationship is developed in detail by Mackenzie and Garrels (in press); figure 1 is adapted from that work.

To resolve the HCO_3^- excess and to be consistent with the volume of "free" silica in the geologic column, we suggest that HCO_3^-, SiO_2, and cations react with degraded aluminosilicates of the suspended load of rivers to form new minerals, according to reactions of the type

$$\text{X-ray amorphous Al silicate} + HCO_3^- + SiO_2 + \text{cations} = \\ \text{cation Al silicate} + CO_2 + H_2O.$$

These reactions may be considered "reverse weathering" reactions in that new minerals are formed from degraded clays and dissolved constituents and CO_2 released; whereas in weathering reactions, degraded

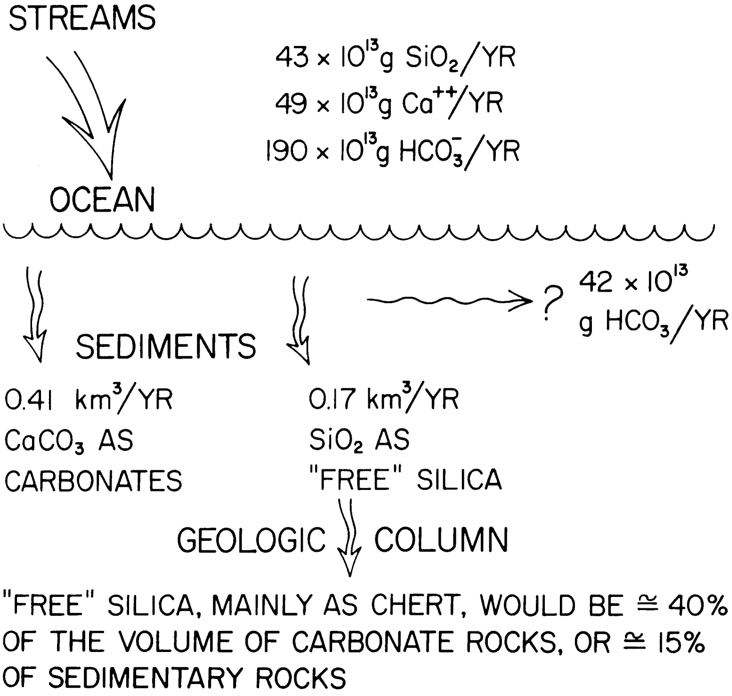

Fig. 1. Silica-bicarbonate balance assuming present stream discharge and content (after Livingstone 1963a), and all Ca^{++} deposited as carbonate minerals. About 1 to 5 percent of the volume of sedimentary rocks is chert. The present rate of delivery of dissolved SiO_2 to the ocean would produce a much greater volume of "free" silica, mainly as chert, than is observed in the geologic column.

products are formed, CO_2 is consumed, and dissolved constituents released. Sillén (1961) and Deffeyes (1963) suggested that reactions involving clays in the oceanic system could be important in determining the pH of the ocean and the CO_2 pressure of the atmosphere. Garrels (1965) emphasized the importance to oceanic chemistry of the above general reaction.

Ion exchange and reconstitution reactions could also account for removal of some of the excess material. Except for the removal of some of the $Na+$ by exchange for other cations on montmorillonite, these reactions could not account for the large excesses of constituents that must be removed from a steady-state oceanic system. Hydrogen ion in the exchange sites of river-derived clays could help to change HCO_3^- to CO_2 but would not help to resolve the SiO_2 balance.

The bulk composition of the degraded aluminosilicates that best fits our model is similar to kaolinite ($Al_2Si_2O_5(OH)_4$) but contains more silica ($Al_2Si_{2.4}O_{5.8}(OH)_4$). This material is compositionally similar to the X-ray amorphous aluminosilicates carried by rivers to the ocean

(Moberly, 1963; Kennedy, 1963, 1965). These "amorphous aluminosilicates" constitute from about 1 to 10 percent of the suspended-sediment load of rivers and consist of structurally disordered alumina, silica, and aluminosilicates.

Some of the SiO_2 initially is removed from the system as "free" silica. Most of this silica is removed from the natural environment by organisms, principally diatoms, and reorganized during diagenesis. The amount of SiO_2 that leaves the system as "free" silica is difficult to determine. Bien, Contois, and Thomas' (1958) data for the Mississippi River and the immediate Gulf of Mexico suggest that during the initial mixing of river water with sea water, biological removal of soluble SiO_2 is not an important process. At chlorosities greater than 8 grams Cl^-/liter, uptake of SiO_2 by organisms increases rapidly (Bien, Contois, and Thomas, 1958, fig. 11). They also point out that removal of soluble SiO_2 from river water as it enters the ocean could be entirely accounted for by inorganic processes. In contrast to this conclusion, Stefánnson and Richard's (1963) data from the Columbia River plume show that inorganic removal of SiO_2 is not an important process in this region of the ocean.

On the basis of the above discussion and because of insufficient knowledge of the amount of stream-derived SiO_2 presently being removed from the ocean as "free" silica, we will dispose of an amount of SiO_2 in our balance that is reasonably consistent with the volume of "free" silica in the geologic column (chert constitutes approximately 1 to 5 percent of the volume of sedimentary rocks). Removal of 10 percent of the SiO_2 from our balance as "free" silica would be consistent with a volume of chert about equal to 2 percent of the volume of sedimentary rocks. The reaction is

$$H_4SiO_4 = SiO_{2(s)} + 2\ H_2O$$

and in millimoles of SiO_2 in our balance

$$71\ H_4SiO_4 = 71\ SiO_{2(s)} + 142\ H_2O.$$

The only reasonable solution to the removal of the remaining Na^+ is by exchange with Ca^{++} on montmorillonites and by synthesis of new sodic montmorillonites from degraded aluminosilicates. Although we recognize that river-borne montmorillonites are not pure Ca-montmorillonites and oceanic montmorillonites are not pure Na-montmorillonites, the exchange positions in the two environments are occupied primarily by Ca^{++} and Na^+ respectively. Therefore, we will use the compositions $Na_{0.33}Al_{2.33}Si_{3.67}O_{10}(OH)_2$ and $Ca_{0.17}Al_{2.33}Si_{3.67}O_{10}(OH)_2$ to represent oceanic and river-borne montmorillonites respectively.

If the suspended load of streams is 32,500 x 10^6 tons/year, and montmorillonite with an exchange capacity of 80 milliequivalents per 100 grams is 10 percent of the load, then about 25 percent of the Na^+

carried by rivers to the ocean can be removed by exchange with Ca^{++}. This is a crude but reasonable estimate. The exchange reaction is

$$\begin{gathered} Ca_{0.17}Al_{2.33}Si_{3.67}O_{10}(OH)_2 + 0.33\ Na^+ = \\ Na_{0.33}Al_{2.33}Si_{3.67}O_{10}(OH)_2 + 0.17\ Ca^{++} \end{gathered}$$

and, in millimoles, using 25 percent of the available Na^+

$$\begin{gathered} 138\ Ca_{0.17}Al_{2.33}Si_{3.67}O_{10}(OH)_2 + 46\ Na^+ = \\ 138\ Na_{0.33}Al_{2.33}Si_{3.67}O_{10}(OH)_2 + 23.5\ Ca^{++}. \end{gathered}$$

The Ca^{++} released is combined with HCO_3^- to form calcite and/or aragonite.

The remaining Na^+ is removed by reacting with degraded aluminosilicates, SiO_2, and HCO_3^- to form sodic montmorillonite, according to the reaction

$$\begin{gathered} 3.5\ Al_2Si_{2.4}O_{5.8}(OH)_4 + Na^+ + 2.6\ SiO_2 + HCO_3^- = \\ 3\ Na_{0.33}Al_{2.33}Si_{3.67}O_{10}(OH)_2 + CO_2 + 4.5\ H_2O \end{gathered}$$

and in millimoles of material available

$$\begin{gathered} 486.5\ Al_2Si_{2.4}O_{5.8}(OH)_4 + 139\ Na^+ + 361.4\ SiO_2 + 139\ HCO_3^- = \\ 417\ Na_{0.33}Al_{2.33}Si_{3.67}O_{10}(OH)_2 + 139\ CO_2 + 625.5\ H_2O. \end{gathered}$$

The remaining Mg^{++} and all the K^+ are disposed of by reaction with degraded aluminosilicates, SiO_2, and HCO_3^- to form chlorite and illite respectively. Both of these minerals are found in abundance in modern and ancient marine sediments. Once more, the phases chosen are considered to be pure, but in the natural environment they are compositionally more complex. The reactions for Mg^{++} and K^+ are

$$\begin{gathered} Al_2Si_{2.4}O_{5.8}(OH)_4 + 5\ Mg^{++} + 0.6\ SiO_2 + 10\ HCO_3^- = \\ Mg_5Al_2Si_3O_{10}(OH)_8 + 10\ CO_2 + 3\ H_2O, \end{gathered}$$

$$\begin{gathered} 2.5\ Al_2Si_{2.4}O_{5.8}(OH)_4 + K^+ + SiO_2 + HCO_3^- = \\ 2\ K_{0.5}Al_{2.5}Si_{3.5}O_{10}(OH)_2 + CO_2 + 3.5\ H_2O; \end{gathered}$$

and in millimoles of material available

$$\begin{gathered} 100.4\ Al_2Si_{2.4}O_{5.8}(OH)_4 + 502\ Mg^{++} + 60.2\ SiO_2 + 1004\ HCO_3^- = \\ 100.4\ Mg_5Al_2Si_3O_{10}(OH)_8 + 1004\ CO_2 + 301.2\ H_2O, \end{gathered}$$

$$\begin{gathered} 472.5\ Al_2Si_{2.4}O_{5.8}(OH)_4 + 189\ K^+ + 189\ SiO_2 + 189\ HCO_3^- = \\ 378\ K_{0.5}Al_{2.5}Si_{3.5}O_{10}(OH)_2 + 189\ CO_2 + 661.5\ H_2O. \end{gathered}$$

In the reactions involving the synthesis of new minerals from degraded aluminosilicates, all the K^+, 90 percent of the Mg^{++}, 90 percent of the SiO_2, 15 percent of the Na^+, and 43 percent of the original HCO_3^- are removed from the system.

It could be argued that we have synthesized pure clay minerals in our balance rather than ones with the actual compositions of those in oceanic sediments. The proportions of K^+, Mg^{++}, Na^+, and SiO_2 in the clay minerals formed in our balance are very similar to the proportions of these constituents found in average shale and average deep-sea argillaceous sediment (fig. 2). The resemblance between our bulk "shale" composition and that of argillaceous sediments suggests that our balance would not be greatly affected by the use of more exact aluminosilicate mineral compositions involving extensive cation substitution.

Assuming (1) degraded aluminosilicates constitute 10 percent of the suspended load of rivers, (2) the suspension to solution load ratio in streams is 5/1, and (3) the relative amounts of shale, sandstone, and carbonates in the geologic column are 0.6, 0.2, 0.2 respectively, the amount of newly formed illite, chlorite, and montmorillonite would compose only about 7 percent of the total mass of sediments at any one time. Such a small amount of authigenic illite would not affect

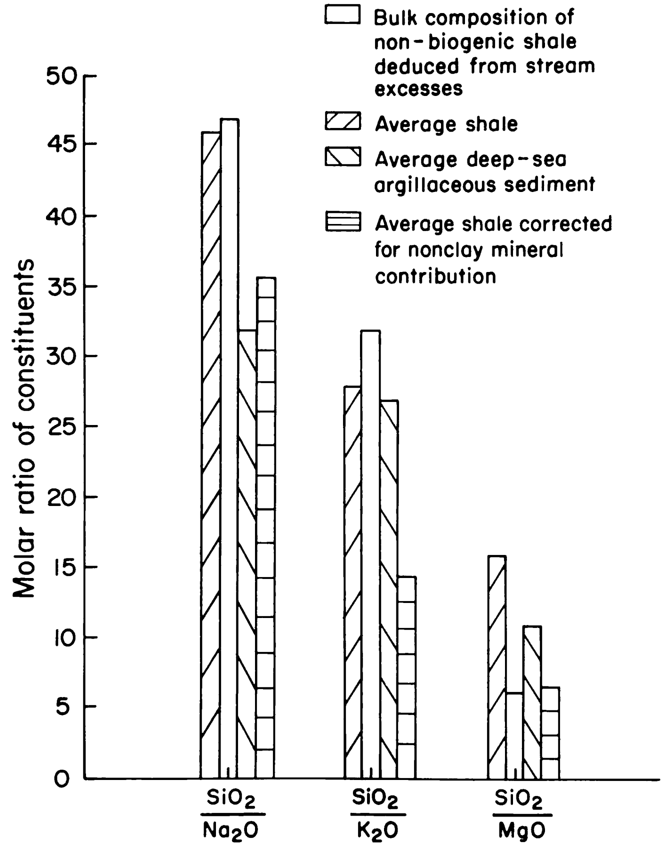

Fig. 2. Bulk composition, expressed as molar ratios, of average shale (Clarke, 1924, p. 34), average deep-sea argillaceous sediment (carbonate, water, and organic C-free basis; Wakeel and Riley, 1961, p. 123), and average shale less nonclay mineral contribution (Shaw and Weaver, 1965, p. 222) compared with the bulk composition of the aluminosilicate minerals ("shale") formed in our balance from stream-derived dissolved constituents and degraded aluminosilicates.

the K-Ar ages of 200 to 400 million years obtained by Hurley and others (1963) from K-bearing minerals in modern marine sediments.

The balance works out well considering the assumption that the average river water analysis represents adequately the dissolved material carried by streams to the ocean. The apparent deficiency of HCO_3^- to form montmorillonite represents the electrical imbalance in the initial excesses of dissolved constituents in which cation equivalents exceed anion equivalents. The final excess in SiO_2 is negligible and could be disposed of by increasing the amount of "free" silica removed from the system or decreasing slightly the silica content of the degraded aluminosilicates.

SUMMARY AND CONCLUSIONS

In recent years several writers (Sillén, 1961, 1963, 1965; Deffeyes, 1963; Garrels, 1965; Holland, 1965; Kramer, 1965; Mackenzie and Garrels, 1965) have discussed the role of silicate reactions in considerations of oceanic chemistry. The mass balance calculation between stream-derived dissolved constituents and a steady-state oceanic system clearly demonstrates the importance of aluminosilicate reactions in the oceanic system and leads to some interesting suggestions and conclusions.

The ocean, when considered over millions of years, is a nearly steady-state system, in which the major constituents carried in by streams are lost at approximately the same rate as they are added. Furthermore, the materials lost by chemical or biochemical precipitation or reaction can be removed as minerals that correspond to those found in sedimentary rocks. However, this removal process requires that typical clay minerals be synthesized compositionally, if not structurally, from degraded aluminosilicates before burial in marine sediments. It is possible that, instead of aluminosilicate clays being synthesized, simple hyroxylated silicates are formed, according to reactions of the type

$$\text{cations} + SiO_2 + HCO_3^- = \text{cation OH silicate} + CO_2.$$

However, we consider this unlikely because simple silicates of this type are not found in abundance in modern or ancient marine sediments.

These "reverse weathering" reactions prevent the alkali metals and bicarbonate from accumulating in the ocean. Consequently, ocean water composition is not simply the result of evaporation of river water, as this would lead to a water of the composition of a soda lake (Garrels and Mackenzie, in press), but is controlled to a large extent by interactions between stream-derived dissolved constituents and suspended sediments. Also, because these reactions involve the release of CO_2 to the atmosphere, it is likely that the long-term carbon dioxide pressure of the atmosphere is maintained by such reactions.

The compositional synthesis of the minerals illite, chlorite, and montmorillonite in the oceanic system implies that these phases are in equilibrium, or nearly so, with an aqueous solution of the composition of average ocean water. Consequently, the reactions involving these minerals probably determine to a large extent the major ionic ratios of ocean water. Also, the minerals illite, chlorite, and montmorillonite carried to the ocean in the suspended load of streams should not be markedly altered chemically or structurally upon entering the ocean, although, a small part of the suspended sediment of rivers, the "amorphous aluminosilicates", does react to form new minerals.

We are well aware that innumerable chemical balance models could be devised and that there are many aspects of our model open to question. However, the fact that the proportions of Mg^{++}, K^{+}, Na^{+}, and SiO_2 in our synthesized clay minerals are in the approximate proportions found in shales, and that the reaction to form typical shale minerals from these excesses simultaneously solves the problems of the HCO_3^- excess and the silica balance cannot be attributed to chance.

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REFERENCES

Arrhenius, G., 1963, Pelagic sediments, *in* Hill, M. N., ed., The Sea, v. 3: New York, Intersci. Pub., p. 655-727.

Barth, T. F. W., 1952, Theoretical petrology: New York, John Wiley and Sons, Inc., 387 p.

Berner, R. A., 1964, Distribution and diagenesis of sulfur in some sediments from the Gulf of California: Marine Geology, v. 1, p. 117-140.

Bien, G. S., Contois, D. E., and Thomas, W. H., 1958, The removal of soluble silica from fresh water entering the sea: Geochim. et Cosmochim. Acta, v. 14, p. 35-54,

Biscaye, P. E., 1965, Mineralogy and sedimentation of recent deep-sea clay in the Atlantic Ocean and adjacent seas and ocean: Geol. Soc. America Bull., v. 76, p. 803-832.

Chave, K. E., 1954, Aspects of the biogeochemistry of magnesium. Pt. 2, Calcareous sediments and rocks: Jour. Geology, v. 62, p. 587-599.

Clarke, F. W., 1924, The data of geochemistry, 5th ed.: U.S. Geol. Survey Bull. 770, 841 p.

Conway, E. J., 1942, Mean geochemical data in relation to oceanic evolution: Roy. Irish Acad. Proc., v. 48, sec. B, p. 119-159.

Correns, C. W., 1937, Die Sedimente des äquatorialen Atlantischen Ozeans: Deutsche Atlantische Exped. auf dem Forschungsschiff- und Vermessungsschiff "Meteor" (1925-1927), Wissenschaftliche Ergebnisse, v. 3, pt. 3, p. 1-42, 135-298.

Deffeyes, K. S., 1963, Role of oceanic carbonate and silicate sedimentation in determining atmospheric carbon dioxide pressure [abs.]: Geol. Soc. America Spec. Paper 76, p. 39-40.

Edwards, M. L., Kister, L. R., and Scarcia, G., 1956, Water resources of the New Orleans area, Louisiana: U.S. Geol. Survey Circ. 374, 41 p.

Favajee, J. C. L., 1951, The origin of the Wadden mud: Wageningen Landbouwhoogeschool Mededel., v. 51, p. 113-141.

Garrels, R. M., 1965, The role of silica in the buffering of natural waters: Science, v. 148, p. 69.

Garrels, R. M., and Mackenzie, F. T., in press, Origin of the composition of some springs and lakes: Am. Chem. Soc., Advances in Chemistry Ser., in press.

Goldberg, E. D., 1957, Biogeochemistry of trace metals, *in* Hedgpeth, J. W., ed., Ecology, v. 1 of Treatise on Marine Ecology and Paleocology: Geol. Soc. America Mem. 67, p. 345-358.

Goldberg, E. D., and Arrhenius, G. O. S., 1958, Chemistry of Pacific pelagic sediments: Geochim. et Cosmochim. Acta, v. 13, p. 153-212.

Gorham, E., 1961, Factors influencing supply of major ions to inland waters with special reference to the atmosphere: Geol. Soc. America Bull., v. 72, p. 795-840.

Griffin, G. M., 1962, Regional clay mineral facies—products of weathering intensity and current distribution in the northeastern Gulf of Mexico: Geol. Soc. America Bull., v. 73, p. 737-768.

Griffin, J. J., and Goldberg, E. D., 1963, Clay-mineral distribution in the Pacific Ocean, *in* Hill, M. N., ed., The Sea, v. 3: New York, Intersci. Pub., p. 728-741.

Grim, R. E., and Johns, W. D., 1954, Clay mineral investigation of sediments in the northern Gulf of Mexico, *in* Swineford, Ada, and Plummer, N. V., eds., Clays and clay minerals: Natl. Research Council Pub. 327, p. 81-103.

Grim, R. E., Dietz, R. S., and Bradley, W. F., 1949, Clay mineral composition of some sediments from the Pacific Ocean off the California coast and the Gulf of California: Geol. Soc. America Bull., v. 60, p. 1785-1808.

Holland, H. D., 1965, The history of ocean water and its effect on the chemistry of the atmosphere: Natl. Acad. Sci. Proc., v. 53, p. 1173-1182.

Hurley, P. M., Heezen, C. B., Pinson, W. H., and Fairbairn, H. W., 1963, K-Ar values in pelagic sediments of the North Atlantic: Geochim. et Cosmochim. Acta, v. 27, p. 393-399.

Junge, C. E., and Werby, R. T., 1958, The concentration of Cl^-, Na^+, Ca^{++}, and $SO_4^=$ in rain water over the U.S.: Jour. Meteorology, v. 15, p. 417-425.

Kaplan, J. R., Emery, K. O., and Rittenberg, S. C., 1963, The distribution and isotopic abundance of sulfur in recent marine sediments off southern Caliornia: Geochim. et Cosmochim. Acta, v. 27, p. 297-332.

Kennedy, V. C., 1963, Base-exchange capacity and clay mineralogy of some modern stream sediments: I.A.S.H. Comm. of Subterranean Waters Pub. 64, p. 95-105.

——— 1965, Mineralogy and cation-exchange capacity of sediments from selected streams: U.S. Geol. Survey Prof. Paper 433-D, 28 p.

Kramer, J. R., 1965, History of sea water. Constant temperature-pressure equilibrium models compared to liquid inclusion analyses: Geochim. et Cosmochim. Acta, v. 29, p. 921-946.

Kuenen, P. H., 1950, Marine Geology: New York, John Wiley and Sons, Inc., 568 p.

Livingstone, D. A., 1963a, 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.

——— 1963b, The sodium cycle and the age of the ocean: Geochim. et Cosmochim. Acta, v. 27, p. 1055-1069.

Lowenstam, H. A., 1961, Mineralogy, O^{18}/O^{16} ratios, and strontium and magnesium contents of recent and fossil brachiopods and their bearing on the history of the oceans: Jour. Geology, v. 69, p. 241-260.

Mackenzie, F. T., and Garrels, R. M., 1965, Silicates-reactivity with sea water: Science, v. 150, p. 57-58.

——— in press, Silica-bicarbonate balance in the ocean and early diagenesis: Jour. Sed. Petrology, in press.

Moberly, R. M., Jr., 1963, Amorphous marine muds from tropically weathered basalt: Am. Jour. Sci., v. 261, p. 767-772.

Murray, Sir John, 1887, On the total annual rainfall on the land of the globe, and the relation of rainfall to the annual discharge of rivers: Scottish Geog. Mag., v. 3, p. 65-77.

Nelson, B. W., 1963, Clay mineral diagenesis in the Rappahannock estuary: an explanation, *in* Bradley, W. F., ed., Clays and clay minerals: Oxford, England, Pergamon Press, New York, The Macmillan Co., p. 210.

Powers, M. C., 1954, Clay diagenesis in the Chesapeake Bay area, *in* Swineford, Ada, and Plummer, N. V., eds., Clays and clay minerals: Natl. Research Council Pub. 327, p. 68-80.

——— 1957, Adjustment of land-derived clays to the marine environment: Jour. Sed. Petrology, v. 27, p. 355-372.

——— 1959, Adjustment of clays to chemical change and the concept of the equivalence level, *in* Swineford, Ada, ed., Clays and clay minerals: Internat. Ser. Mons. Earth Sci., v. 2, p. 309-326.

Revelle, R. R., 1944, Marine bottom samples collected in the Pacific Ocean by the Carnegie on its seventh cruise: Carnegie Inst. Washington Pub. 556, p. 1-180.

Rubey, W. W., 1951, Geologic history of sea water: an attempt to state the problem: Geol. Soc. America Bull., v. 62, p. 1111-1147.

Shaw, D. B., and Weaver, C. E., 1965, The mineralogical composition of shales: Jour. Sed. Petrology, v. 35, p. 213-222.

Sillén, L. G., 1961, The physical chemistry of sea water, *in* Sears, Mary, ed., Oceanography: Am. Assoc. Adv. Sci. Pub. 67, p. 549-581.

——— 1963, How has sea water got its present composition?: Svensk Kemisk Tidsk., v. 75, p. 161-177.

——— in press, Oxidation state of earth's ocean and atmosphere. 1. A model calculation on earlier states. The myth of the "probiotic soup": Arkiv. kemi., in press.

Stefánnson, Unnsteinn, and Richards, F. A., 1963, Processes contributing to the nutrient distributions off the Columbia River and Strait of Juan de Fuca: Limnology and Oceanography, v. 4, p. 394-410.

Taggart, M. S., Jr., and Kaiser, A. D., Jr., 1960, Clay mineralogy of Mississippi River deltaic sediments: Geol. Soc. America Bull., v. 71, p. 521-530.

Turekian, K. K., 1964, The geochemistry of the Atlantic Ocean Basin: New York Acad. Sci. Trans., ser. 2, v. 26, p. 312-320.

Wakeel, S. K., El, and Riley, J. P., 1961, Chemical and mineralogical studies of deep-sea sediments: Geochim. et Cosmochim. Acta, v. 25, p. 110-146.

Weaver, C. E., 1959, The clay petrology of sediments, *in* Swineford, Ada, ed., Clays and clay minerals: Internat. Ser. Mons. Earth Sci., v. 2, p. 154-187.

Whitehouse, U. G., and McCarter, R. S., 1958, Diagenetic modification of clay mineral types in artificial sea water, *in* Swineford, Ada, ed., Clays and clay minerals: Natl. Research Council Pub. 566, p. 81-119.