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CLAY MINERALS AND OCEANIC EVOLUTION

by

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ABSTRACT

A REVIEW of mineralogical and geochemical studies on Recent sediments indicates that the clay fraction of marine sediments is not in isotopic or chemical equilibrium with the oceanic reservoir and will not reflect the chemical environment of deposition. Consideration of the sedimentary geochemistry of the alkali metals suggests that fractionation of these elements, which may be one of the major features of the chemical evolution of ocean water, occurs in the terrestrial weathering environment during the formation of clay minerals and in the subsurface environment during clay mineral diagenesis. It is proposed that during the initial stages of oceanic development the Na/K ratio of ocean water was adjusted to a value of forty to fifty by the extensive diagenesis of the existing natural water. With an increase in oceanic volume and a major change in the hydrologic cycling of natural waters the chemical evolution of alkali metals in ocean water has now become primarily controlled by mixing with continental drainage water.

INTRODUCTION

INTERACTIONS between the lithosphere and hydrosphere involving a transfer of chemical components occur in three principal domains: (1) in the terrestrial weathering environment where atmospheric precipitation reacts with surface materials resulting in weathering and soil formation; (2) in the oceanic environment at and above the sediment–water interface where detrital minerals and chemical precipitates react with ocean water; and (3) in the subsurface environment where interstitial waters react with enclosing rocks in the course of compaction, lithification, and other diagenetic processes.

It is well established from the studies of Barth (1952), Goldberg (1963), and Garrels and Mackenzie (1966) that the constituents in ocean water, with the exception of chloride and the alkali metals, must have residence times in the oceanic reservoir that are short relative to the age of the oceans. In recent years there have been a number of models proposed, based on the assumption of a steady-state oceanic system, which elucidate some of the factors controlling the chemical composition of ocean water (Rubey, 1951; Sillen, 1961,

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1963; Holland, 1965; Kramer, 1965; Nicholls, 1965; Garrels and Mackenzie, 1966). In all the models discussed to date only reactions taking place in the oceanic reservoir have been considered as possible primary factors in regulating the chemical composition of ocean water. Holland (1965) discussed a major difficulty encountered by the equilibrium approach, the observational evidence supporting a detrital origin for most marine sediments, and concluded that the correspondence between equilibrium conditions and the state of the oceans indicates that the equilibrium model is sufficient as a first approximation. Weyl (1966) discussed several non-equilibrium aspects of ocean chemistry concluding that equilibria between ocean water and sediments are not adequate to explain the apparent chemical stability of the oceans, particularly with respect to the carbonate system. Harriss (1966) proposed that biological rather than mineralogical buffering controls oceanic silica concentrations.

An alternate approach to the study of oceanic chemistry is to assume that oceanic sediments are essentially non-reactive, or that the kinetics of silicate–sea water reactions are sufficiently slow that little reaction other than ion exchange and dissolution occurs prior to burial, the composition of ocean water being primarily a function of mixing of parent water types. This assumption seems well justified in light of the mineralogical and geochemical studies by Weaver (1959), Griffin (1962), Biscaye (1965), Hurley *et al.* (1963), and Dasch *et al.* (1966), all of which indicate that marine clays are neither in chemical nor isotopic equilibrium with ocean water and are detrital in origin. It should be noted, however, that Garrels and Mackenzie (1966) calculate that only 7% of the sediment would be required to react with sea water to form authigenic minerals in order to maintain equilibrium. A major difficulty with the proposed equilibrium models would seem to be that the dissolved silica concentrations required for the proposed reactions between aluminosilicates and sea water cannot be maintained in ocean water as a result of silica removal by organisms as proposed by Harriss (1966). The ocean is apparently undersaturated with respect to equilibrium silica concentrations for all the clays except kaolinite (see Mackenzie and Garrels, 1965). Thus, the present lack of any definite geological evidence in support of the equilibrium hypotheses indicates that alternative hypotheses for compositional control of ocean chemistry should be considered.

The approach used in the present paper is to consider, using the available geological observations as a framework, the relative importance of clay mineral reactions with coexisting natural waters in the terrestrial weathering environment, marine environment, and subsurface environment in the chemical evolution of alkali metals in ocean water.

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CHEMICAL CONSIDERATIONS

The ocean basins receive water from a variety of sources including continental drainage, groundwater recharge on the continental shelves and slopes, water extruded from marine sediments during compaction, thermal waters, and metamorphic waters (the latter two terms are taken from White, 1963). Representative alkali metal ratios for various natural water categories are given in Table 1. Due to a lack of adequate data the discussion in this paper will essentially be limited to sodium and potassium. There is a continuum of Na/K ratios in natural waters ranging from continental surface drainage with a median ratio of three to metamorphic waters with Na/K ratios of thirty and higher.

TABLE 1.—REPRESENTATIVE ALKALI METAL RATIOS IN COMMON NATURAL WATERS*

Water type	Na/K	Na/Rb	Na/Cs
Ocean water	28	88×10^3	210×10^5
River water	2.7	4×10^3	1×10^5
Rain water	10		
Groundwaters:			
Shales	6		
Sandstones	3.7		
Limestones	3.6		
Acid igneous rocks	8		
Basic igneous rocks	3.3		
Deep subsurface and metamorphic water	20–50		
Thermal springs	5–15		

* Data from Livingstone (1963), White *et al.* (1963), and Carroll (1962).

In the contemporary hydrologic system the estimated amount of water and dissolved constituents discharged into the ocean from continental drainage exceeds by several orders of magnitude or more that from any other source. Calculations by Garrels and Mackenzie (1966) suggest that all the water presently in the oceans has been through the hydrologic cycle many times, as it would require only 4×10^4 years for rivers to fill the ocean basins to their present levels at present rates of discharge.

Consider the future evolution of alkali metal ratios in ocean water assuming that sediments are non-reactive and that the present hydrologic conditions are maintained. Calculations demonstrate that in 10^6 years the oceanic Na/K ratio would be approximately twenty-five and by 10^7 years from present the Na/K ratio would equal thirteen. It would require approximately 10^9 years for complete equilibration between river and ocean water (Na/K = 2.7). These calculations suggest that under the conditions of the present hydrologic

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cycle the chemical evolution of alkali metals in ocean water is controlled by compositional mixing with river water, whose alkali metal ratios are determined in the terrestrial weathering environment. Since the time required to produce a considerable reduction in the Na/K ratio of ocean is short relative to the age of the ocean two questions arise: (1) how has the ocean obtained its rather high Na/K ratio of twenty-eight?; (2) how stable is the Na/K ratio of ocean water? Under the conditions assumed in the present discussion the ocean would evolve from some initial Na/K ratio to a value approaching equilibrium with the Na/K ratio of river water and would subsequently remain stable. However, several additional factors must be considered as having a possible influence on alkali metal ratios in ocean water. These are: (1) laboratory studies by Carroll and Starkey (1960) and Potts (cited in Keller, 1963) have demonstrated that as river clays come in contact with ocean water, base exchange occurs with the clay minerals releasing calcium and taking up magnesium, sodium, and potassium from ocean water. What effect will ion exchange reactions between detrital clay minerals and sea water have on the Na/K ratio of ocean water? (2) Variation in the composition of the input could have a definite effect on the composition of ocean water. The composition of the input could vary as a result of changes in the terrestrial weathering environment which would alter the composition of continental drainage or by a change in the relative proportions of the sources of ocean water.

Mineral–Water Exchange Reactions in the Oceanic Reservoir

To determine the effect of ion exchange reactions on the Na/K ratio in ocean water the influence of such reactions on the sodium and potassium budgets in the oceans must be calculated. Using the data of Carroll and Starkey (1960) and Potts (see Keller, 1963) the amounts of material involved can be calculated to be approximately 0.4 mg Na/g clay and 0.24 mg K/g clay gained by detrital clay minerals upon contact with ocean water. The total amount of sodium and potassium removed from the oceanic reservoir annually by ion exchange can be calculated by multiplying the total amount of clay entering the oceans by the figures quoted above for removal of alkali metals per unit weight of clay. The total amount of sediment entering the oceans annually is calculated to be 1.5×10^{15} g using annual sedimentation rates for the various oceans as determined by Turekian and Schutz (1965) and Goldberg and Koide (1963). This estimate is similar to that of Garrels and Mackenzie (1966) calculated on the basis of estimates of suspended river sediment transported to the oceans annually. The amount of sodium and potassium entering the ocean annually has been calculated using the data of Livingstone (1963). The amount of recycled sodium and potassium in river water was corrected using the data of Carroll (1962) and Junge and Werby (1958) for the sodium and potassium concentrations in atmospheric precipitation. The results of these calculations are summarized in Table 2.

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It is apparent from the sodium and potassium budget calculations that ion-exchange reactions between detrital clay minerals and ocean water will have no effect on the alkali metal ratios in the oceanic reservoir. The amounts of sodium and potassium involved in ion-exchange processes are several orders of magnitude below the amounts supplied to the oceans by continental drainage. Calculations indicate that even if the amount of clay entering the oceans were increased by an order of magnitude as a result of active tectonism the alkali metal budgets in the oceans would not be affected.

TABLE 2.—ANNUAL SODIUM AND POTASSIUM BUDGET IN THE OCEAN

Na influx from continental waters (corrected for cycling)	1.1×10^{17} mg/yr
Na removed by ion exchange	5.9×10^{14} mg/yr
K influx from continental waters (corrected for cycling)	6.6×10^{16} mg/yr
K removed by ion exchange	3.6×10^{14} mg/yr

Variations in the Hydrologic Input into the Oceans

The composition of surface drainage waters is primarily determined in the terrestrial weathering environment as demonstrated by Feth *et al.* (1964) and Davis (1961). Thus, large-scale changes in the nature of the chemical weathering environment would result in a change in alkali metal ratios in continental drainage and subsequently a change in the evolutionary tendencies of ocean water composition. The degree of chemical variation that can result from differences in the chemical weathering environment can be assessed by comparing the composition of local surface waters from contemporary environmental extremes as, for example, the tropical weathering environment as opposed to the northern latitudes. Data compiled by Livingstone (1963) indicate that rivers in the tropics are characterized by average Na/K ratios of two to four and rivers in the northern latitudes by average Na/K ratios of six to eight. Thus, even under the extreme condition of a uniform global climate the chemical composition of continental drainage water probably would not produce an equilibrium oceanic Na/K ratio higher than approximately eight.

The most plausible explanation for the high Na/K ratio of ocean water seems to involve variation in the input from different water sources. For example, if the relative amounts of water entering the oceans from the deep subsurface environment (brines, thermal waters, metamorphic water) were increased with corresponding decreases in the amount of continental drainage the evolutionary course of the alkali metals would be towards a much higher equilibrium ratio.

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A general diagenetic cycle for natural waters is depicted schematically in Fig. 1. The heavy arrows denote what is essentially the present hydrologic cycle. It is proposed that in the late stages of the evolution of a geosynclinal belt, during periods of active tectonism, large quantities of metamorphic and other deep subsurface water types would be extruded at the surface and mixed with ocean water. If sufficient quantities of water with Na/K ratios of thirty and above were generated during the large-scale diagenesis of

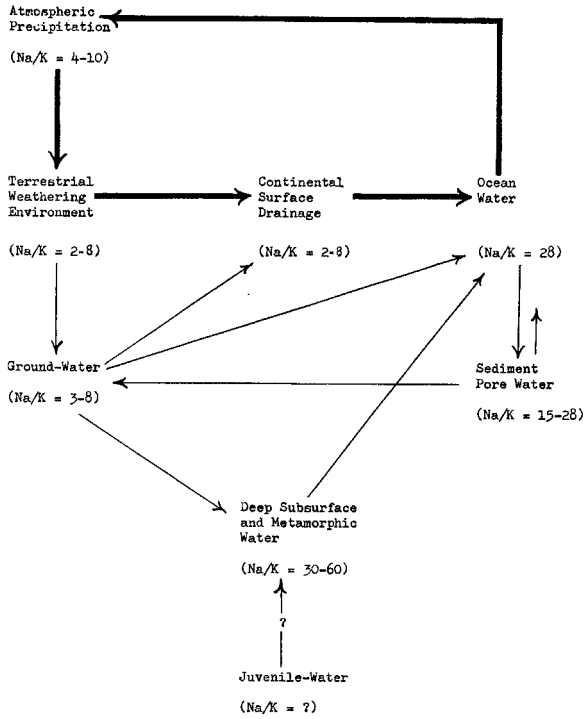


FIG. 1. Diagenetic cycle of natural waters inferred from alkali metal variations.

sedimentary rocks and mixed with ocean water, the Na/K ratio of ocean water would show a rapid increase, the maximum value of the ratio being dependent on the quantity of high Na/K ratio water relative to the total volume of the ocean at the time of mixing. This mechanism probably has caused little or no variation in the composition of ocean water since the late Precambrian, assuming that the volume of the ocean has been essentially constant for the past 5×10^8 years. Calculations indicate that if 10 ml of water with a Na/K ratio of fifty were displaced from every cubic meter of sediment in a geosyncline with dimensions similar to the Appalachian geosyncline the total amount of "tectonic water" produced would be at least

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several orders of magnitude less than the volume of water in the oceanic reservoir. Thus, the large size of the oceanic reservoir is itself an extremely important buffer against variations in oceanic chemistry. The present Na/K ratio in ocean water is probably residual from the early stages of oceanic evolution when the relative proportion of metamorphic water to ocean water may have been quite high due to a smaller oceanic volume and perhaps more extensive metamorphism than has been characteristic of post-Precambrian time.

SUMMARY

It is proposed that the Na/K ratio of ocean water was adjusted to a value of forty to fifty approximately 10^9 years ago by the extensive diagenesis of natural waters. As the oceanic volume approached its present value the input of metamorphic and deep subsurface water became small relative to the quantity of water restricted to the terrestrial weathering and continental drainage portion of the diagenetic cycle, and the frequency and amplitude of perturbations in the alkali metal ratios in ocean water associated with tectonic activity decreased to a level of negligible importance. The compositional evolution of alkali metal ratios in ocean water, for at least the past 5×10^8 years, has been controlled by mixing with continental drainage water. The alkali metal ratios in continental waters are determined by weathering reactions in the soil zone involving the formation of clay minerals. The silicate buffering reactions proposed by Garrels and Mackenzie (1966) should be most effective in the soil zone and subsurface environment as a result of the relatively high dissolved silica concentrations and solid-solution ratios in these environments as compared to the oceanic reservoir.

Hypotheses concerning the chemical evolution of the ocean are abundant and supporting data are scarce. An improved knowledge of the chemical and mineralogical variations in clays as a function of geologic age and setting and experimental studies on the low-temperature solution geochemistry of clay minerals are areas of particular importance for future research.

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