EFFECT OF SEA-WATER ON CLAY MINERALS[1]

by

DOROTHY CARROLL AND HARRY C. STARKEY

U.S. Geological Survey, Washington, D.C.

ABSTRACT

Samples of a montmorillonite, a mixed-layer mineral (mica and montmorillonite) " illite", kaolinite, and halloysite were immersed in 50 ml sea-water for 10 days, and additional samples of the first three were immersed for 150 days. The exchangeable cations were determined both before and after treatment. It was found that Mg^{2+} ions from sea-water moved into the exchange positions in the minerals in preference to Ca^{2+} and Na^+ ions. The H-form of these minerals showed a gradual adjustment to sea-water as measured by change in pH and filling of the exchange positions with cations other than H^+. Kaolinite adjusted very rapidly, but montmorillonite and the mixed-layer mineral were slow. All the minerals reacted to yield appreciable amounts of SiO_2, Al_2O_3, and Fe_2O_3 to the sea-water. The quantities yielded are in the order :

montmorillonite > mixed-layer mineral > " illite " > kaolinite > halloysite

The solubility is considered to be due to direct solution of SiO_2 in the sea-water and to removal of Al_2O_3 from the octahedral layer of the minerals.

When H-clays were titrated with sea-water three distinct kinds of curves were obtained : (a) kaolinite ; (b) mixed-layer mineral, " illite," and halloysite ; and (c) montmorillonite. The curves are similar to those obtained with clay minerals titrated with other alkaline solutions. Kaolinite reacts somewhat like a number of simple acids, but the curves for the other minerals are more complex and are related to the neutralization of H^+ and its replacement in the exchange sites by metallic cations. The exchangeable cations were determined in the minerals after titration, and the results are similar to those obtained after immersing the minerals in sea-water. The volume of sea-water required to reach an end point at about pH 7.6 varies from 11 ml for kaolinite to 135 ml for montmorillonite and is related to the titratable alkalinity of the sea water and to the exchange capacity of the minerals.

INTRODUCTION

Studies of the distribution of clay minerals in near-shore marine environments (Grim, Dietz and Bradley, 1949 ; Grim and Johns, 1954 ; Powers, 1954, 1957) suggest that diagenesis of such minerals may occur when they are transferred from fresh-water to sea-water by river action. The mechanism of any changes that take place is not known, but a first stage must involve reactions of the cations and anions in sea-water with the minerals through exchange. Theoretical consideration of cation exchange indicates that a rearrangement of the cations in the exchange positions will take place. Kelley and Liebig (1934) showed experimentally that a bentonite preferentially adsorbed more magnesium than sodium from sea-water. Hendricks and Ross (1941) suggested that adsorption of magnesium ions was important

---

[1] Publication authorized by the Director, U.S. Geological Survey.

80

in the genesis of glauconite in marine sediments. The relations between the cations in sea-water and those in the exchange positions probably can be explained by the law of mass action. The process is complex because of the different bonding energies of Ca^{2+}, Mg^{2+}, K^+ and Na^+ ions ; the effect of the cations originally in the exchange positions on the clay minerals ; the variation in charge of the exchange positions ; the ionic activity of the sea-water ; and the buffer mechanism of sea-water. This paper describes experiments that give data on the exchangeable cations before and after treatment of clay minerals with natural sea-water. In a later paper the data will be used to show the application of the law of mass action to the reaction of clay minerals with sea-water.

In view of the importance of the marine environment and of the changes that may take place in clay minerals after deposition in the sea, a number of observations was made of the reactions of montmorillonite (A) (Osage, Wyo., A.P.I. standard no. 25b), mixed-layer mineral (B) (Highbridge, Ky., A.P.I. standard no. 42), " illite " (C) (Fithian, Ill., A.P.I. standard no. 35), kaolinite (D) (Bath, S.C., A.P.I. standard no. 5), and halloysite (E) (Tintic, Utah, A.P.I. standard no. 13) when 2 percent suspensions were allowed to remain in contact with sea-water for varying periods of time.

Perusal of the extensive literature describing the relations of clay minerals and various electrolytes together with a knowledge of the crystal structures and chemical composition of these minerals indicate that the reactions to be expected between them and sea-water will be complex and will be different for the structurally different clay minerals. Isomorphous replacement of cations within the clay mineral structures and broken bonds at the edges of the crystals cause the development of negative charges in excess of the positive charges on the particles. The different clay minerals vary in the amount of negative charge developed and hence in their ability to adsorb and exchange cations with those present in a contact solution. In general, the amount of reaction follows the order of total exchange capacity of the minerals, which is : kaolinite < halloysite < "illite" < mixed-layer mineral < montmorillonite.

The quantity of cations in the exchange positions, and their kind, whether mono- or divalent, influences the reactions with solutions. Soil chemists refer to the condition in which all the exchange positions are filled with metal cations as " base saturation", a useful concept when considering exchange reactions. " Base unsaturation " means that H^+ ions take the place of the common metal cations in the exchange positions, and the " percentage base saturation " indicates the proportion of the exchange positions filled with metal cations other than H^+. The presence of H^+ ions in the exchange positions is complicated by the release of aluminum from the octahedral layer as described by Paver and Marshall (1934). Recent work by Low (1955), Aldrich and Buchanan (1958), and Higdon and Marshall (1958) has shown that the aluminum released retards formation of H-clays.

The laws governing replacement of cations on a charged clay mineral surface by those present in a contact solution have been formulated by

Marshall (1954) after extensive experiments to determine the bonding energy of the common metal cations. In general, this bonding energy is in the order: $Ca > Mg > K > H > Na$. However, in certain clay minerals, kaolinite and some Wyoming bentonite, for example, the bonding energy is $Mg > Ca$. Divalent ions with strong bonding energy in contact solutions are able to occupy the exchange positions preferentially to monovalent ions.

Titration of water suspensions of clay minerals in the H-form with alkaline solutions gives neutralization curves that indicate that there are several definite exchange sites on montmorillonite with different capacities for attracting cations. Inflection points occur on these curves where adsorption of cations takes place. The relation between the cations in the contact solution and the adsorption of cations by neutralization of exchange sites on the clay minerals can be explained by the law of mass action (Schofield and Taylor, 1955; Garrels and Christ, 1956). It has long been known (Jarusov, 1937) that in systems containing more than one cation, the cation having the highest mean free bonding energy takes the positions on the clay mineral surface having the highest bonding energy. The positions with less bonding energy are therefore left to be filled with cations of lower bonding energy. Thus Ca^{2+} and Mg^{2+} in a mixed electrolyte are bonded rapidly to the sites of strongest negative charge, leaving monovalent cations, such as Na^+, to fill sites of weaker negative charges.

Another point to be considered about the reaction of clay minerals with sea-water is that small amounts of SiO_2, Al_2O_3, and Fe_2O_3 are dissolved from them by sea-water, but it is not known if this solubility is due to a surface effect as indicated by Nash and Marshall (1956), to the solubility of SiO_2 and Al_2O_3 (the latter is slightly soluble at pH 8.0) at the pH of sea-water (Correns, 1949; Krauskopf, 1956), or to the release of Al_2O_3 from H-clays by a saline solution (Mukherjee, Chatterjee and Ray, 1948). Probably the Cl^- ions in sea-water form a complex with the Al^{3+} ions released from the clay minerals.

Sea-water is an aqueous solution containing a variety of dissolved solids and gases. It is a strong electrolyte with pH ranging from 7.5 to 8.4 depending on the amount of CO_2 present. The composition of sea-water ($Cl = 19\%_0$) is given by Sverdrup, Johnson and Fleming (1946, p. 173) as

Total salinity	34,325 ppm
Na	10,556 ppm
Cl	18,980 ppm
ion ratios	$Na \gg Mg > Ca > K$ (constant with dilution)
Titratable base (alkalinity)	0.00215 eq/l. (the figure varies with CO_2 content, pH, temperature)
pH	7.4 to 8.5 (varies with CO_2 content)

Sea-water is a buffer solution because of the presence of carbonate and borate species. The cation principally affected by buffering action is calcium because of the relation $CaCO_3 \rightleftharpoons CaHCO_3 \rightleftharpoons H_2CO_3$. This series of reactions affects

the availability of Ca^{2+} ions to enter into the exchange positions of clay minerals. Sea-water contains cations in excess of the equivalent anions derived from strong acids (Harvey, 1957, p. 153). This excess base or titration alkalinity is equivalent to that of the bicarbonate, carbonate and borate ions in the water.

ACKNOWLEDGMENT

EXPERIMENTAL PROCEDURE

The effect of sea-water on clay minerals was examined in two ways : (a) by allowing sea-water to remain in contact with the minerals for certain periods of time, and (b) by titrating the H-form of the minerals with sea-water. The sea-water used was collected in the Straits of Florida, 13 June, 1956, by Preston E. Cloud, Jr., who very kindly made it available for experimental purposes. It was stored in polyethylene bottles and at the time of these experiments the pH was 7.6, the alkalinity (Thompson and Anderson, 1940) was 15.0, the titratable alkalinity 0.00164 eq/l., the salinity 35.5‰, and chlorinity 21.5‰ at 25°C.

Each mineral was crushed to pass a 270-mesh sieve ($<53\mu$) and separate portions were used to examine their reactions with sea-water. The H-form of the minerals was at first prepared by pouring a slurry of clay mineral and water through a column of Amberlite IR–120 resin in the H-form [referred to as H-form (a)]. The clay suspensions were originally 1 : 1, clay : water. The suspensions remained in contact with the resin for 15–20 min and then they were washed through the column with distilled water. The ratio of resin exchange capacity to clay exchange capacity was not measured, but 100 g of H-resin was used in the column with about 10 g of clay. The exchange capacity of the resin was considerably greater than that of the mixed-layer mineral, " illite," kaolinite, and halloysite, and adequate to reduce the pH of montmorillonite. However, all the exchangeable cations were not removed. Higdon and Marshall (1958, p. 1205) report that bentonites are almost completely converted to the acidic form with Amberlite IR–120 in 30 min when the ratio of resin exchange capacity to clay exchange capacity is 5. As the treatment with resin did not give the minimum pH expected for some of the minerals, treatment in 1 : 3 HCl (about 3 N) at room temperature (25°C) was used subsequently [mineral then referred to as H-form (b)]. After acid or resin treatment each mineral was washed twice in water and twice in alcohol and allowed to dry at room temperature. The clays were then stored in a desiccator. Some experiments recently made (Carroll and Starkey, in preparation) have shown that treatment of clay minerals with 3 N or stronger HCl at room temperature (25°C) has little effect on the structure if the time is not more than 2–3 hr. Montmorillonites treated with

strong acid are essentially H-clays whereas those treated with dilute acids are H–Al-clays (Coleman and Harward, 1953, p. 6045). Reduction in exchange capacity after acid treatment has been reported by Low (1955, p. 138) and has been found in montmorillonite in these experiments.

Suspensions (2 percent) of each clay mineral were used. The reactions of these suspensions with sea-water were measured by pH (glass electrode), cation exchange capacity, and determination of the exchangeable cations.

A 1 g sample of the natural minerals and a 1 g sample of the same minerals in the H-form were placed in polyethylene beakers with 50 ml sea-water (pH 7.6) and allowed to stand at room temperature (about 25°C) for 10 days. Additional 1 g samples of H-montmorillonite (A), H-mixed layer mineral (B), and " illite " (C), were allowed to stand in 50 ml sea-water for 150 days at room temperature. Exchangeable cations, total exchange capacity, and pH were determined. The exchangeable cations were obtained by leaching the clays (after washing in distilled water to remove any remaining sea-water) with 1 N NH_4Cl at pH 7. Calcium and magnesium were determined by versene titration, and sodium and potassium by flame photometer (Shapiro and Brannock, 1956). The sea-water from above the clays was removed by centrifugation and analyzed for SiO_2, Al_2O_3 and Fe_2O_3 by Leonard Shapiro, U.S. Geological Survey. The amounts of SiO_2, Al_2O_3 and Fe_2O_3 present in the sea-water used were subtracted from the totals found.

Suspensions (2 percent, in distilled water) of the H-form of all the clay minerals were titrated with sea-water to end-points at or near pH 7.6, the pH of the sea-water used. It was found that the best curves were obtained by allowing the suspensions to come to equilibrium with the sea-water for about 8 hr before taking the pH readings. Graphs were constructed that show the pH and the volume of sea-water added.

RESULTS

The pH of Clay–Sea-water Suspensions

The pH of 1 : 5 clay–sea-water suspensions was measured with a pH-meter having a glass electrode. The results are given in Table 1. The pH varied considerably. In the H-form the pH was lower than in the natural form except for mixed-layer mineral (B), kaolinite (D), and halloysite (E), which were apparently H-saturated under natural conditions. Contact with sea-water for 10 days raised the pH of all the minerals. Immersion of the natural minerals in sea-water increased the pH most noticeably in (B), (D) and (E), but the change in (A) and (C) was only slight because both had cations other than H^+ in the exchange positions. Although the ratios of total exchange capacity of the clay minerals to the total milliequivalents of cations available in sea-water are not the same for each mineral, the following observations were made: Change from the H-form after soaking in sea-water was most rapid in kaolinite (D), followed by " illite " (C), and halloysite (E). The pH of the H-form of montmorillonite (A) was about two-thirds that of the natural mineral, indicating either that sufficient time was not allowed for

TABLE 1.—pH OF THE EXPERIMENTAL CLAY MINERALS UNDER VARIOUS CONDITIONS
(1 : 5 clay : water suspensions)

Mineral	Natural Conditions	After Soaking in 50 ml. Sea-water for 10 days	H-form (a)[1]	H-form (a) after Soaking in 50 ml. Sea-water for 10 days
Montmorillonite (A)	8.70	9.22	2.90	5.88
Mixed-layer Mineral (B)	4.50	9.18	3.25	6.87
" Illite " (C)[2]	8.50	9.18	6.80	9.00
Kaolinite (D)	5.18	8.32	5.05	8.35
Halloysite (E)	4.65	8.01	4.70	7.71

[1] Prepared by treatment with H-ion exchange resin.
[2] Contains about 2 percent calcite as impurity.

TABLE 2.—SILICA, ALUMINA AND FERRIC IRON YIELDED BY 1G SAMPLES OF CLAY
MINERALS ON SOAKING IN 50 ML SEA-WATER FOR 10 AND 150 DAYS[1]

Mineral	SiO_2 (mg)	Al_2O_3 (mg)	Fe_2O_3 (mg)	Total (mg)	Percentage of Mineral
Montmorillonite (A)					
10 days	4.0	<1.0	0.3	5.3	0.53
150 days[2]	5.2	2.5	1.4	9.1	0.91
Mixed-layer Mineral (B)					
10 days	1.0	1.0	0.2	2.2	0.22
150 days[2]	3.6	1.4	0.1	5.1	0.51
" Illite " (C)					
10 days	2.0	6.0	0.3	8.3	0.83
150 days[2]	0.5	0.1	<0.002	0.602	0.06
Kaolinite (D)					
10 days	1.0	4.0	0.1	5.1	0.51
Halloysite (E)					
10 days	1.0	1.0	—	2.0	0.20

(Analyst : Leonard Shapiro)
[1] The sea-water was removed from the clay minerals by centrifugation.
[2] The H-form (a) of the mineral was used except for " illite " (C), 150 days where H-form (b) was used.
(These figures are the amounts in the solutions after deduction of the amounts in a sea-water blank. The blank contained SiO_2, 1 mg, Al_2O_3, <1 mg, Fe_2O_3, 0.06mg.)

adjustment to be made or that there were insufficient available cations in 50 ml sea-water. The mixed-layer mineral (B) apparently had more cations in the exchange positions after soaking in sea-water than were in the natural mineral. The rate at which adjustment to sea-water, as shown by pH, takes place is kaolinite (D) = " illite " (C) > halloysite (E) > mixed-layer mineral (B) > montmorillonite (A).

Solubility of Clay Minerals in Sea-water

Small amounts of SiO_2 and Al_2O_3, totalling less than 1 percent of the sample, were removed from these clay minerals. The natural minerals were treated for 10 days in sea-water, and the H-forms of montmorillonite (A), mixed-layer mineral (B), and " illite " (C) were treated for 150 days. Impurities in these minerals are quartz, feldspar, and free alumina. The free alumina present is sufficient to give the small amounts of alumina found by analysis, but some silica has been removed from the tetrahedral layers of the minerals, particularly from the H-forms of montmorillonite (A) and mixed-layer mineral (B) with 150 days treatment (Table 2). Silica was removed preferentially to alumina because at the pH of this sea-water (pH 7.6) alumina is insoluble. However, the effect of a saline solution acting on a desaturated clay mineral is to remove both Al_2O_3 and Fe_2O_3 as shown by Mukherjee et al. (1948) and by Low (1955). As Al^{3+} ions in the clay mineral lattice cannot be replaced by Na^+ ions owing to difference in ionic radii (Al^{3+}, 0.57 Å; Na^+, 0.98 Å), and as Al^{3+} is insoluble at pH 7.6, a complex is probably formed, either with the organic molecules in sea-water or with the chloride ions.

The removal of SiO_2 and Al_2O_3 followed this order: montmorillonite (A) > mixed-layer mineral (B) > " illite " (C) > kaolinite (D) > halloysite (E). A greater quantity of SiO_2 and Al_2O_3 was removed in 150 days than in 10 days. The most stable mineral in these terms is H-" illite " (C). Apparently all the easily soluble SiO_2 and Al_2O_3 were removed by the acid treatment used in obtaining the H-form. The natural " illite " (C) lost more Al_2O_3 (6 mg) than any other mineral but was closely followed by kaolinite (D) with 4 mg.

Cation Exchange Capacity and Exchangeable Cations

The cation exchange capacity, exchangeable cations, and percentage saturation of the exchange positions with cations other than H^+ for the clay minerals are given in Table 3 and in Figs. 1–5.

Montmorillonite (A) (Fig. 1).—The total cation exchange capacity is 89 meq/100 g (average of eight determinations, standard deviation 5). The exchangeable cations are Na^+ 54, Mg^{2+} 15, Ca^{2+} 11 meq/100 g. The H-form has an exchange capacity of 66 meq/100 g, but still has 8 meq Ca^{2+} and 14 meq Mg^{2+}, and is therefore not completely in the H-form. The effect of sea-water on the natural form and on the H-form is to increase the amount of exchangeable Mg^{2+} and to reduce the amount of exchangeable Na^+ in the

TABLE 3.—EXCHANGEABLE Ca^{2+}, Mg^{2+} AND Na^+, TOTAL CATION EXCHANGE CAPACITY AND PERCENT OF EXCHANGE CAPACITY COMPLETED WITH CATIONS OTHER THAN H^+ OF THE EXPERIMENTAL CLAY MINERALS UNDER VARIOUS CONDITIONS IN SEA-WATER

Mineral	Exchangeable Cations (meq/100 g)				Cation Exchange capacity (determined)	Percentage Exchange Positions Filled
	Ca^{2+}	Mg^{2+}	Na^+	Sum		
Montmorillonite (A)						
Natural	11	15	54	80	89	90
Sea-water, 10 days[1]	7	34	16	57	93	61
H-form (a)	8	14	—	22	66	33
Sea-water 10 days[2]	7	27	21	55	91	60
Sea-water 150 days[3]	8	32	21	61	76	80
Mixed-layer Mineral (B)						
Natural	26	7	—	33	33	100
Sea-water 10 days[1]	3	12	2	17	31	55
H-form (a)	3	1	—	4	34	11
Sea-water 10 days[2]	9	8	2	19	21	90
Sea-water 150 days[3]	5	7	5	17	28	61
" Illite " (C)						
Natural	17	3	—	20	20	100
Sea-water 10 days[1]	12	8	—	20	20	100
H-form (a)	10	2	—	12	24	50
Sea-water 10 days[2]	9	8	2	19	21	90
Sea-water 150 days[3]	8	8	—	16	28	57
Kaolinite (D)						
Natural	0.5	0.4	—	0.9	5	18
Sea-water 10 days[1]	0.9	1.7	—	2.6	8	32
H-form (a)	0.9	—	—	0.9	13	7
Sea-water 10 days[2]	1.4	1.7	—	3.1	16	19
Halloysite (E)						
Natural	1.8	1.7	0.6	4.1	11	37
Sea-water 10 days[1]	2.7	7.1	0.5	10.3	47	22
H-form (a)	1.8	0.8	—	2.6	42	6
Sea-water 10 days[2]	4.1	5.4	0.6	10.1	31	32

[1] Natural mineral soaked in 50 ml sea-water.
[2] H-form (a) soaked in 50 ml sea-water.
[3] H-form (b) soaked in 50 ml sea-water.
" Illite " (C) contained about 2 percent calcite as impurity ; the figures given above have been corrected for Ca due to calcite.

natural form from 54 to 16 meq/100 g. After the H-form soaked for 10 days and for 150 days in 50 ml sea-water, exchangeable Ca^{2+} was 7 and 8, exchangeable Mg^{2+} was 27 and 32, and exchangeable Na^+ was 21 meq/100 g. No exchangeable K^+ could be detected. Complete replacement of H^+ by Ca^{2+}, Mg^{2+} and Na^+ was not attained in the time the montmorillonite was

7

treated, but as the exchange capacity is high, possibly 50 ml sea-water could not supply additional cations, although there is an abundance of Na^+ ions in this volume of sea-water.

Mixed-layer mineral (*B*) (Fig. 2).—This mineral consists of montmorillonite interlayered with hydrous mica. It has a total cation exchange capacity of 33 meq/100 g (average of seven determinations, standard deviation, 0.45). The principal exchange cation is Ca^{2+}, and there is no Na^+ or K^+. In the H-form Ca^{2+} is 3 and Mg^{2+} is 1 meq/100 g. Sea-water increases the Mg^{2+}
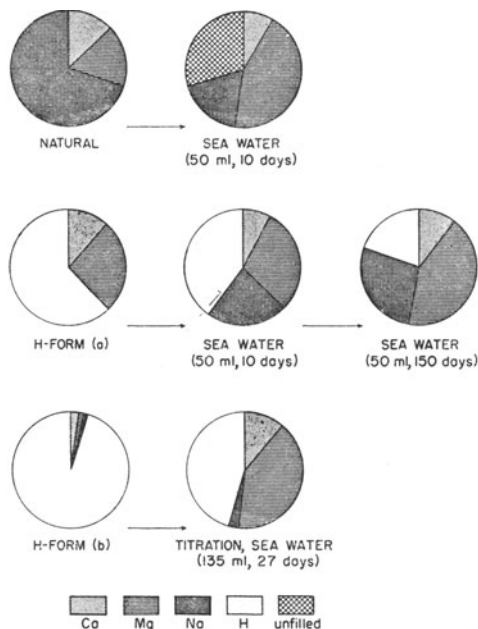
FIGURE 1.—Exchangeable cations in montmorillonite (A) on treatment with sea-water. The diagrams represent the percentage of exchangeable Ca^{2+}, Mg^{2+}, and Na^+ ions as determined (Tables 3 and 4). H^+ ions are assumed to difference from the total exchange capacity of the H-form montmorillonite. The notation " unfilled " for montmorillonite in sea-water indicates that cations did not completely fill the available positions. H-form (a), montmorillonite treated with H-ion exchange resin ; H-form (b), montmorillonite treated with HCl (1 + 3) at 25°C.

from 7 in the natural form to 12 meq/100 g in 10 days. Sea-water increases Ca^{2+}, Mg^{2+}, and Na^+ in the exchange positions after the H-mineral has been in contact with it for 10 and 150 days.

" *Illite* " (*C*) (Fig. 3).—This " illite " from Fithian has an exchange capacity of 20 meq/100 g (standard deviation 0.55), but contains about 2 percent calcite so that high figures are obtained for exchangeable Ca^{2+} as calcite is soluble in the 1 N NH_4Cl solution used for leaching the samples. The corrected figures are given in Table 3. Exchangeable Mg^{2+} increases on soaking the " illite " in sea-water. There is no exchangeable Na^+ or K^+ in

the natural mineral, but 2 meq Na⁺ per 100 g were found after treatment in sea-water for 10 days.

Kaolinite (D) (Fig. 4).—The total exchange capacity of this kaolinite is 5 meq/100 g (average of eight determinations, standard deviation 2),[1] but only 0.9 meq of combined Ca^{2+} and Mg^{2+} are present per 100 g. After treatment in sea-water for 10 days the exchangeable Ca^{2+} increased to 0.9, and the exchangeable Mg^{2+} increased to 1.7 meq/100 g. In the H-form the
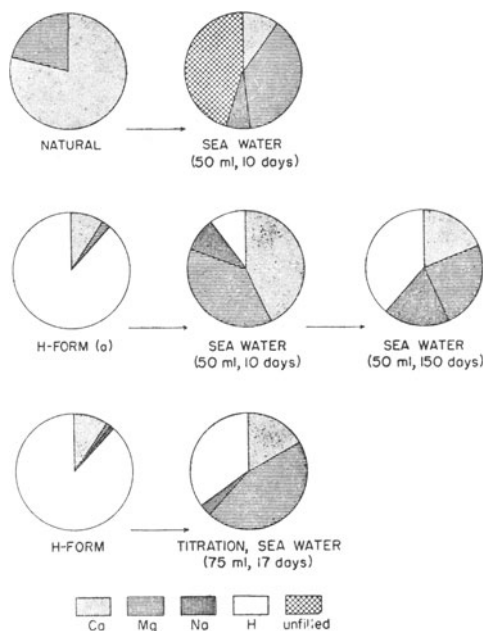

FIGURE 2.—Exchangeable cations in mixed-layer mineral (B) on treatment with sea-water. The diagrams represent the percentage of exchangeable Ca^{2+}, Mg^{2+} and Na⁺ ions as determined (Tables 3 and 4). H⁺ ions are assumed by difference from the total exchange capacity of the H-form mixed-layer mineral. The notation " un-filled " for mixed-layer mineral in sea-water indicates that cations did not com-pletely fill the available exchange positions. H-form (a), mixed-layer mineral treated with H-ion exchange resin ; H-form (b), mixed-layer mineral treated with HCl (1 + 3) at 25°C.

exchangeable Ca^{2+} was not removed, and the amount increased after sea-water treatment. The natural kaolinite contains exchangeable H⁺ and is, therefore, undersaturated in metal cations in the exchange positions. Treat-ment in sea-water decreases the undersaturation from 82 to 68 percent (Table 3) in the natural mineral and from 93 to 81 percent in the H-kaolinite.

[1] Determination on various samples with different methods of grinding ; range of determinations is 2.4–8.0 meq/100 g.

Halloysite (E) (Fig. 5).—The natural halloysite in the air-dry condition has an exchange capacity of 11 meq/100 g. The sum of the exchangeable Ca^{2+}, Mg^{2+} and Na^+ is 4.1 meq/100 g, indicating that the exchange positions are filled only to the extent of 37 percent. The natural mineral after sea-water treatment has an exchange capacity of 47 meq/100 g. This high figure, together with those for the H-form and H-form treated with sea-water, seems
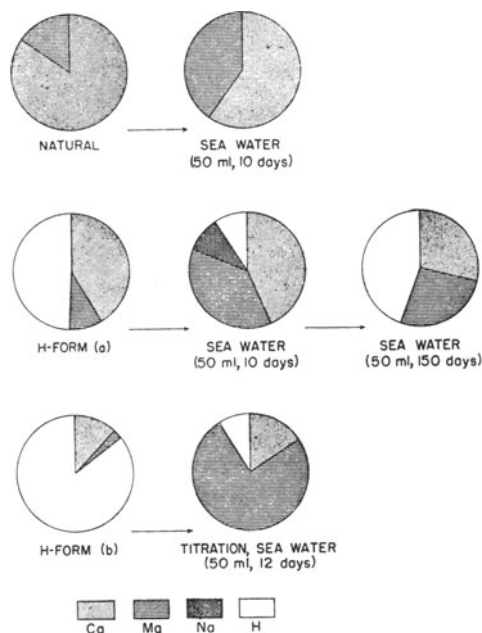

FIGURE 3.—Exchangeable cations in " illite " (C) on treatment with sea-water. The diagrams represent the percentage of exchangeable Ca^{2+}, Mg^{2+} and Na^+ ions as determined (Tables 3 and 4). H^+ ions are assumed by difference from the total exchange capacity of the H-form " illite ". H-form (a), " illite " treated with H-ion exchange resin ; H-form (b), " illite " treated with HCl (1 + 3) at 25°C.

to be due to activation of the mineral by attack on both silica tetrahedral and alumina octahedral layers. The natural halloysite after soaking in seawater for 10 days shows an increase of Ca^{2+} and Mg^{2+} ions in the exchange positions, and the sum of the cations is raised from 4.1 to 10.3 meq/100 g. Table 3 shows that the H-form has the same amount of exchangeable Ca^{2+} as the natural mineral, but after sea-water treatment for 10 days, Ca^{2+} is raised to 4.1 and Mg^{2+} to 5.4 meq/100 g. The figure for Na^+ is unchanged, and the sum of the cations, 10.1, is practically identical with that for the natural mineral treated in sea-water. It seems that there is a limit to the kind and quantity of cations that can be adsorbed by the exchange positions.

The results may be summarized as follows :

(1) The total exchange capacity of these minerals after sea-water treatment is about the same as in the natural minerals. The H-forms of kaolinite (D) and halloysite (E) have an increased exchange capacity that may be caused by activation (as in the treatment of commercial clays with acid to increase their exchange capacity). The natural form of halloysite (E) shows an increased exchange capacity after sea-water treatment and may possibly have changed from the $2H_2O$ to the $4H_2O$ form. The latter has a range of exchange capacity from 40 to 50 meq/100 g.
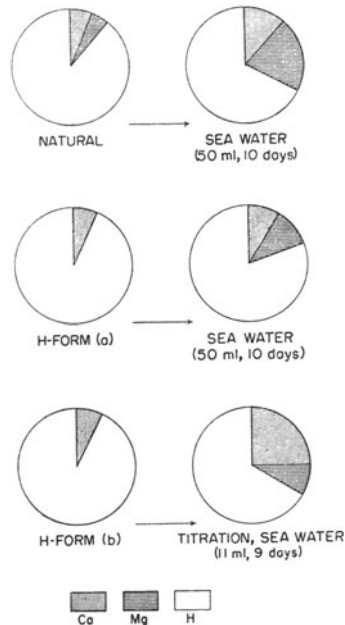

FIGURE 4.—Exchangeable cations in kaolinite (D) on treatment with sea-water. The diagrams represent the percentage of exchangeable Ca^{2+} and Mg^{2+} ions as determined (Tables 3 and 4). It is assumed that H^+ ions are present in the natural mineral as the pH is low. H-form (a), kaolinite treated with H-ion exchange resin ; H-form (b), kaolinite treated with HCl (1 + 3) at 25°C.

(2) The exchangeable cations are rearranged by the uptake of cations from sea-water. Magnesium becomes the dominant cation in the exchange positions. This confirms the results of Kelley and Liebig (1934).

(3) The replacement of H^+ in the exchange positions in the minerals was not complete. Stability was reached after 10 days for montmorillonite (A), mixed-layer mineral (B), and " illite " (C). It is noteworthy that for kaolinite (D) and halloysite (E) both the natural and H-forms gave similar sums of cations and it is possible that these figures are the maximum to be expected for these minerals. The replacement of H^+ in the exchange positions was not complete, but no determinations of alumina liberated by acid treatment were made.

(4) Exchangeable K$^+$ was less than 2 meq/100 g and could not be recorded by the method used. Previous experience with clay minerals has shown that the K$^+$ ion is not important as an exchangeable cation in any of these minerals. In " illite " the K$^+$ ion binds the silicate layers together and is not exchangeable. It is possible that some potassium was fixed in " illite " and in the mixed-layer mineral, but analyses were not made to show this.

Titration of H-clays with Sea-water

The results of titrations of 2 percent suspensions of H-clays with sea-water in equilibrium with atmospheric CO$_2$ are shown in Table 4 and Figs. 6 and 7.
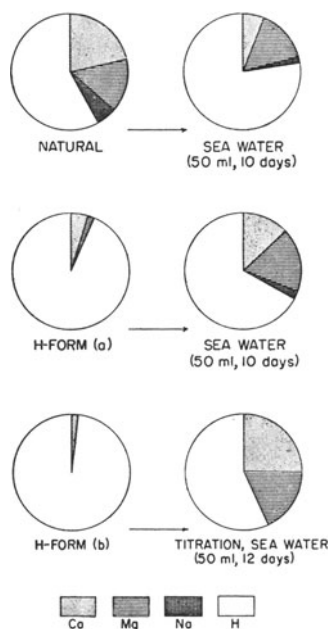

FIGURE 5.—Exchangeable cations in halloysite (E) on treatment with sea-water. The diagrams represent the percentage of exchangeable Ca^{2+}, Mg^{2+} and Na$^+$ as determined (Tables 3 and 4). It is assumed that H$^+$ ions are present in the natural mineral as the pH is low. H-form (a), halloysite treated with H-ion exchange resin; H-form (b), halloysite treated with HCl (1 + 3) at 25°C.

The titration curves are similar to those described by Marshall (1954) for titration of H-clays with dilute alkaline solutions. The titration curves for volume of sea-water plotted against pH of the suspensions fall into three groups.

(1) Kaolinite (D) has a simple curve (Fig. 6) with a marked inflection point at pH 4.8 after the addition of 3 ml sea-water. The curve then slopes steeply to pH 6.7 (5 ml sea-water), and gradually until pH 7.4 is reached (11 ml sea-water). Further additions of sea-water do not increase the pH.

TABLE 4.—ADSORPTION OF EXCHANGEABLE CATIONS BY H-FORM CLAY MINERALS
UPON TITRATION WITH SEA-WATER
(pH 7.6 ; titratable alkalinity, 0.0016)

Mineral	Exchangeable Cations (meq/100 g)				Percent Exchange Positions Filled with Cations other than H+
	Ca+2	Mg+2	Na+	Sum	
Montmorillonite (A)					
H-form (b)	1.8	1.5	0.3	3.6	4.0
After titration	9.6	36.5	2.2	48.3	54.3
Mixed-layer Mineral (B)					
H-form (b)	3.0	0.5	0.2	3.7	11.2
After titration	12.7	17.6	—	30.3	91.8
" Illite " (C)					
H-form (b)	2.4	0.5	—	2.9	14.5
After titration	3.2	16.0	—	19.2	90.0
Kaolinite (D)					
H-form (b)	1.2	—	—	1.2	25.0
After titration	3.9	1.8	—	5.7	100.0+
Halloysite (E)					
H-form (b)	0.6	—	—	0.6	4.5
After titration	7.7	5.6	—	14.3	46.1[1]

[1] Halloysite (E) seems to be activated by acid treatment and by immersion in sea-water. Drying of samples was not standardized before determining the exchange capacity.

(2) " Illite " (C) has a titration curve with two marked inflection points, the first after the addition of 10 ml sea-water (pH 4.65), and the second at pH 7.1 with the addition of 40 ml sea-water (Fig. 7). The curve then slopes rapidly to an end point at pH 7.6 with 50 ml sea-water.

Halloysite (D) has a titration curve very similar to that of " illite " (C) (Fig. 7) with two marked inflection points. The curve is steep between pH 3.5 and pH 6.9 (30 ml sea-water). The second inflection occurs after the addition of 50 ml sea-water, and the pH rises from 6.9 to 7.5. Further additions of sea-water do not increase the pH.

Mixed-layer mineral (B) has a titration curve intermediate in character between those of halloysite (D) and montmorillonite (A) (Fig. 7). The first and strongest inflection occurs after the addition of 25 ml sea-water (pH 5.4) and the curve rises steeply to pH 6.6 (40 ml sea-water), after which the slope is gradual to pH 6.85 (50 ml sea-water). A marked inflection occurs with 55 ml sea-water (pH 7.2). With additional sea-water the pH is gradually raised to an end point at pH 7.4 with 80 ml sea-water.

(3) Montmorillonite (A) has a complex titration curve (Fig. 7) with several small inflections—at pH 3.1 (10 ml sea-water), pH 3.4 (25 ml sea-water),

at pH 3.8 (45 ml sea-water), and pH 6.7 (90 ml sea-water), after which it flattens and the slope is gradual to the end point at pH 7.6 (135 ml sea-water). It is apparent that the principal reaction takes place between pH 4.0 (60 ml sea-water) and pH 6.15 (80 ml sea-water).

These titrations were made by allowing at least 8 hr to elapse between the addition of sea-water and the pH reading used in the graphs. A set of titrations for these same clays was also made during one day, but larger volumes of sea water had to be used to raise the pH of the suspensions, the curves were flatter, and the inflections were less marked. The final pH readings were below that of the sea-water (pH 7.6). It is noticeable, however, that montmorillonite (A) and kaolinite (D) required about the same quantity of sea-
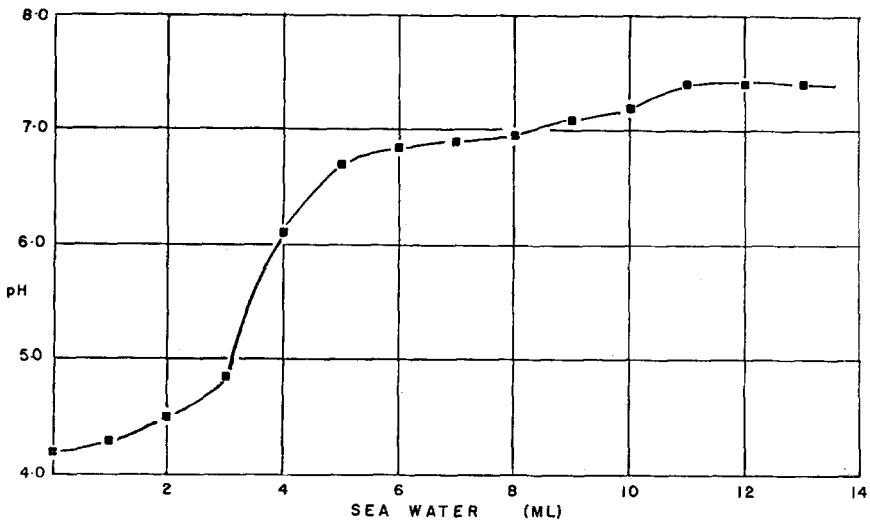

FIGURE 6.—Titration of a 2 percent suspension in distilled water of the H-form (a) of kaolinite (D) with natural sea-water (salinity 35.5‰; chlorinity 21.5‰; titratable alkalinity, 0.0016; and pH 7.6).

water to reach the end point in both the rapid and the prolonged titrations. The volume of sea-water required to reach an end point near pH 7.6 in the titration of the different minerals is kaolinite (D) 11 ml, " illite " (C) 50 ml, halloysite (E) 50 ml, mixed-layer mineral (B) 75 ml, and montmorillonite (A) 135 ml. The volume of sea-water is roughly proportional to the exchange capacity of the minerals.

DISCUSSION

The results of these experiments indicate that the reactions of clay minerals with sea-water are similar to those described for clay minerals reacting with dilute alkaline solutions. Figs. 1 to 5 show that magnesium and calcium enter the exchange positions in preference to sodium even though the quantity
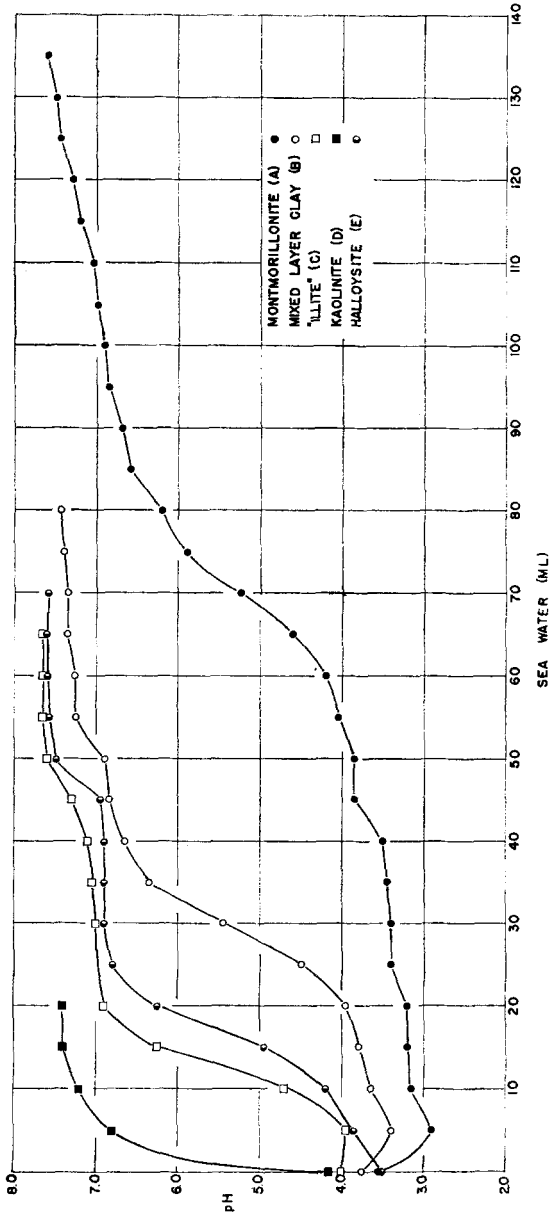
FIGURE 7.—Titration of 2 percent suspensions in distilled water of the H-form (a) of montmorillonite (A), mixed-layer mineral (B), "illite" (C), kaolinite (D), and halloysite (E) with natural sea-water (salinity 35.5‰; chlorinity, 21.5‰; titratable alkalinity, 0.0016; and pH 7.6).

of sodium available in sea-water is much greater than that of magnesium or calcium. In montmorillonite (A), mixed-layer mineral (B), and " illite " (C), magnesium is the dominant cation in the exchange positions after immersion in sea-water, but in kaolinite (D) and halloysite (E), which are structurally simpler, calcium and magnesium are nearly equal.

The clay minerals are multifunctional in their ionization. The rearrangement of the cations in the exchange positions as a result of reactions in sea-water (a polyelectrolyte) seems to follow Jarusov's (1937, p. 301) law. The cations with the higher free bonding energy occupy the exchange sites on the mineral surfaces with the highest bonding energy, leaving the cations with the lower free bonding energy to occupy the less attractive sites. The replacing power of Na^+ ions in sea-water is reduced by the presence of Ca^{2+} and Mg^{2+} ions that have higher bonding energy. This is evident from the titration curves of Figs. 6 and 7. Much larger volumes of sea-water are required to increase the pH of the clay suspensions than the composition of the sea-water would seem to warrant. The volume of sea-water used contains ample Na^+ ions to fill the exchange positions, but it is unable to do so in the presence of Ca^{2+} and Mg^{2+}.

The sea-water used contained the following quantities of cations, expressed as meq/ml: Na^+, 0.450; K^+, 0.012; Ca^{2+}, 0.026; Mg^{2+}, 0.125. Sea-water, however, contains anions as well as cations, and the total effect of the anions may be a reduction of the ability of metallic cations to replace the H^+ ions of the H-form minerals because they may not be completely dissociated, for example, Ca^{2+} and HCO_3^-. The titratable alkalinity of the sea-water, 0.00164 eq/l., provides the anions to neutralize the H^+ ions in the exchange positions of the H-form clay minerals. After neutralization the cations in sea-water can enter the exchange positions vacated by H^+ ions. The concentration of Ca^{2+} ions in sea-water is less than that of Mg^{2+} ions and in addition Ca^{2+} ions form part of the buffer mechanism, so that calcium is probably less available than an equivalent quantity of magnesium. In the natural form of these clay minerals (Figs. 1–5) Mg^{2+} ions replaced Ca^{2+} ions and Na^+ ions upon treatment in sea-water. Hence Mg^{2+} ions have a greater bonding energy than Ca^{2+} ions, in agreement with Marshall (1954) except for illite in which he found the bonding $Ca^{2+} > Mg^{2+}$. However, when the H-forms of the experimental minerals are considered it is seen (Figs. 1–5) that Ca^{2+} ions are not removed as readily as Mg^{2+} ions and Na^+ ions by acid treatment. The minerals are therefore partially saturated with Ca^{2+} and Mg^{2+} before the treatment in sea-water. In montmorillonite (A) Mg^{2+} and Na^+ enter the exchange positions and there is little change in the amount of Ca^{2+} ions (Fig. 1). In the mixed-layer mineral (B) Ca^{2+} ions remain after acid treatment, but Ca^{2+} ions together with Mg^{2+} and Na^+ enter the exchange positions on treatment in sea-water (Fig. 2). Calcium ions are strongly held by H-" illite " (C) (Fig. 3) and Mg^{2+} ions alone replace H^+ ions except for a little Na^+ in one sample. No Na^+ ions occur in the exchange positions of the natural mineral. The H-forms of kaolinite (D) take Ca^{2+} ions equally or preferentially into the exchange positions (Fig. 4). This is contrary to

Marshall's (1954) results, where Mg > Ca. Halloysite (E) behaves in a similar manner to kaolinite (D). Both minerals have low total exchange capacities and Ca^{2+} ions are difficult to remove. It must be presumed that in sea-water both kaolinite and halloysite have stronger bonding energies for Ca^{2+} ions than for Mg^{2+} ions.

In considering the reactions of these minerals with sea-water it was found that the total exchange capacity was approximately the same before as after treatment with sea-water. Table 5 shows that the exchange positions

TABLE 5.—COMPARISON OF SUMS OF EXCHANGEABLE CATIONS IN H-FORM MINERALS AFTER SOAKING IN 50 ML SEA-WATER FOR 10 DAYS AND AFTER TITRATION WITH SEA-WATER

Mineral	10 Days in Sea-water, Sum of Cations (meq/100 g)	Sea-water (ml)	Exchange positions filled with Cations other than H$^+$ (%)	Titration with Sea-water, Sum of Cations (meq/100 g)	Sea-water[1] (ml)	Exchange positions filled with Cations other than H$^+$ (%)
Montmorillonite (A)	55	50	63	48	135	55
Mixed-layer mineral (B)	19	50	57	30.3	75	92
" Illite " (C)	19	50	95	19.2	50	95
Kaolinite (D)	3.1	50	38	5.7	11	71
Halloysite (E)	10.1	50	100	14.3	50	100+[2]

[1] Volume of sea-water used to titrate to pH near 7.6.

[2] Halloysite apparently becomes activated in sea-water, and the total exchange capacity may increase (see Table 3).

of montmorillonite (A), mixed-layer mineral (B), and kaolinite (D) were not filled with cations after soaking the clay in 50 ml sea-water for 10 days. The exchange positions were filled in " illite " (C) and halloysite (E). Titration with sea-water almost filled the exchange positions in mixed-layer mineral (B) in addition to filling the positions in " illite " (C) and halloysite (E). Although the exchange capacity of kaolinite (D) is low the exchange positions were only 71 percent filled. Calculations of the amount of free bases in the volume of sea-water used for the titrations (Table 6) shows that there is sufficient available to fill 90 percent of the exchange positions in montmorillonite (A), 80 percent in mixed-layer mineral (B), 84 percent in " illite " (C), 70 percent in kaolinite (D) and over 100 percent in halloysite (E). The agreement with the titration figures is quite good for mixed-layer mineral (B), " illite " (C), kaolinite (D), and halloysite (E). However, there may be a time factor or hysteresis involved in the filling of the exchange positions in montmorillonite (A) because, although sufficient bases are available to

TABLE 6.—VOLUME OF SEA-WATER REQUIRED TO SUPPLY TOTAL EXCHANGEABLE BASES
DETERMINED IN THE CLAY MINERALS AFTER TITRATION
(Sea-water $=$ 0.00/6 meq " free " bases per ml)

Mineral	Exchangeable Cations in 0.5 g Sample after Titration (meq)	Sea-water for Titration (ml)	" Free" Bases in Sea-water (meq)	Difference
Montmorillonite (A)	0.241	135	0.216	+0.025
Mixed-layer mineral (B)	0.151	75	0.120	+0.031
" Illite " (C)	0.095	50	0.080	+0.015
Kaolinite (D)	0.025	11	0.017	+0.008
Halloysite (E)	0.071	50	0.080	+0.009

fill 90 percent of the exchange positions, only 55 percent were filled. Calcium and magnesium ions are more active in filling the exchange sites than Na^+ ions, and they therefore occupy those positions with higher bonding energy, leaving the less attractive sites to Na^+ ions that have lower bonding energy. No analyses were made to see if K^+ ions were fixed in any of the minerals; no K^+ ions were present in the exchange positions either before or after sea-water treatment. It is possible that Al^{3+} ions from the octahedral layers in montmorillonite (A) have been moved by acid treatment to the exchange positions and that Al^{3+} ions cannot be replaced by Ca^{2+}, Mg^{2+}, or Na^+ ions. Figures for sum of cations in Table 3 suggest that there is a limiting factor for replacement of cations in both montmorillonite (A) and mixed-layer mineral (B) but not in the other minerals used in these experiments.

As the forms of the titration curves (Figs. 6 and 7) are similar to those obtained for alkaline titrations of clay minerals (Marshall, 1954), the exchange reactions can be examined by the law of mass action as described by Garrels and Christ (1956) for beidellite and " illite " using the data obtained by Marshall and Bergman (1942). The number and kind of exchange sites are reflected in the titration curves by equivalence points or inflections. At these points the H^+ ions in the exchange positions of the H-form clay minerals are replaced by cations from sea-water. The first large inflection in these curves is caused by the filling of the C^--sites, that is, the interlayer positions, and the second by the filling of the E^--sites or edge positions. Garrels and Christ (1956) have shown that the H-form of beidellite can be considered as two clay acids. The strength of the bonding of the H^+ ion is uniform in each acid (exchange site), but the exchange constants for the two acids (exchange sites) are different. The magnitude of the exchange reactions measured in moles or milliequivalents of cations is greater for the C^--sites than it is for the E^--sites. The H^+ ion is more strongly held in the E^--sites (edges of mineral plates with charges due to unsatisfied valences), than in the C^--sites (interlayer positions with charge due to isomorphous replacements within the octahedral or tetrahedral layer, or both). Blackmon

(1958, pp. 742–743) has confirmed the fact that the H^+ ion is more strongly bound to the E^--sites than to the C^--sites. Hydrogen appears to have a " preference " for the E^--sites whereas potassium, ammonium and sodium " prefer " the C^--sites. Sodium replaces H^+ ions with more difficulty than do either K^+ or NH_4^+ ions. This difficulty of replacement of H^+ by Na^+ ions in montmorillonite in our experiments may be reflected in the failure to attain base saturation after the most favorable sites are filled with Ca^{2+} and Mg^{2+} ions.

The titration curve of kaolinite (D) shown in Fig. 6 and the information given about the amount of exchangeable cations in Fig. 4 suggests that there are two kinds of exchange sites. One exchange site is readily filled with Ca^{2+} and Mg^{2+} ions. In the other exchange site the H^+ ions are tightly held and are not readily replaceable with other cations. Mitra and Rajogopalan (1952) obtained a similar type of titration curve for kaolinite and they suggest that it is caused by the difference in bonding energy of the two different surfaces of kaolinite, the O^- ions of the silica tetrahedra on one surface and the OH^- ions of the alumina octahedra on the opposite surface.

CONCLUSIONS

Clay minerals react with the cations in sea-water through the same kinds of exchange mechanisms that have been found experimentally for electrolytes such as NaOH and KOH. The replaceability of H^+ ions in the H-form of the clay minerals examined follows the order $Ca^{2+} > Mg^{2+} > Na^+ > K^+$, but Mg^{2+} commonly makes up a larger proportion of the cations in the exchange positions than Ca^{2+} because there is more magnesium than calcium in sea-water and, in addition, calcium is tied up in the buffer mechanism of sea-water. It is thought that Ca^{2+} ions have greater bonding energy than Mg^{2+} ions because if this were not so then there would not be any Ca^{2+} ions in the exchange positions in the presence of excess Mg^{2+} ions that are more readily available than the Ca^{2+} ions. The proportion of Mg^{2+} to Ca^{2+} in sea-water is 3 to 1. The volume of sea-water required to titrate 2 percent suspensions of clay minerals to end points near the pH of sea-water is related to the titratable alkalinity of the sea-water. The three distinct kinds of titration curves obtained for these clay minerals are due to structural differences which cause differences in the exchange sites. Inflections on the titration curves are due to replacement of the H^+ ions by metallic cations. Plateaus in the titration curves at about pH 7, particularly marked for halloysite and " illite " (Fig. 7), may represent precipitation of Al_2O_3 from Al^{3+} released by acid into the exchange positions. The small amounts of silica gradually dissolved from the clay minerals by sea-water could provide the source of the increased silica content of near bottom water found at all South Pacific stations investigated by Goldberg and Arrhenius (1958, p. 169). They report " . . . a flow of dissolved silica from the bottom sediments back into the ocean."

REFERENCES

Aldrich, D. G. and Buchanan, J. R. (1958) Anomalies in techniques for preparing H-bentonites : *Soil Sci. Soc. Amer., Proc.*, v. 22, pp. 281–285.

Blackmon, P. D. (1958) Neutralization curves and the formulation of monovalent cation exchange properties of clay minerals : *Amer. J. Sci.*, v. 256, pp. 733–743.

Coleman, N. T. and Harward, M. E. (1953) The heats of neutralization of acid clays and cation exchange resins : *J. Amer. Chem. Soc.*, v. 75, pp. 6045–6046.

Correns, C. W. (1949) *Einführung in die Mineralogie* : Springer, Berlin, 414 pp.

Garrels, R. M. and Christ, C. L. (1956) Application of cation-exchange reactions to the beidellite of the Putnam silt loam soil : *Amer. J. Sci.*, v. 254, pp. 372–379.

Goldberg, E. D. and Arrhenius, G. O. S. (1958) Chemistry of Pacific pelagic sediments : *Geochim. Cosmochim. Acta*, v. 13, pp. 153–212.

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 : *Bull. Geol. Soc. Amer.*, v. 60, pp. 1785–1808.

Grim, R. E. and Johns, W. D. (1954) Clay mineral investigation of sediments in the northern Gulf of Mexico : in *Clays and Clay Minerals*, Natl. Acad. Sci.—Natl. Res. Council, pub. 327, pp. 81–103.

Harvey, H. W. (1957) *The Chemistry and Fertility of Sea Waters* (2nd Ed.) : Cambridge University Press, 234 pp.

Hendricks, S. B. and Ross, C. S. (1941) Chemical composition and genesis of glauconite and celadonite : *Amer. Min.*, v. 26, pp. 683–708.

Higdon, W. T. and Marshall C. E. (1958) Electrochemical properties in relation to two methods of preparation of colloidal clays : *J. Phys. Chem.*, v. 62, pp. 1204–1209.

Jarusov, S. S. (1937) On the mobility of exchangeable cations in the soil : *Soil Sci.*, v. 43, pp. 285–303.

Kelley, W. P. and Liebig, G. F., Jr. (1934) Base exchange in relation to composition of clay with special reference to effect of sea water : *Bull Amer. Assoc. Petrol. Geol.*, v. 18, pp. 358–367.

Krauskopf, K. B. (1956) Dissolution and precipitation of silica at low temperatures : *Geochim. Cosmochim. Acta*, v. 10, pp. 1–26.

Low, P. F. (1955) The role of aluminum in the titration of bentonite : *Soil Sci. Soc. Amer., Proc.*, v. 19, pp. 135–139.

Marshall, C. E. (1954) Multifunctional ionization as illustrated by the clay minerals : in *Clays and Clay Minerals*, Natl. Acad. Sci.—Natl. Res. Council, pub. 327, pp. 364–385.

Marshall, C. E. and Bergman, W. E. (1942) The electrochemical properties of mineral membranes. II. Measurement of potassium-ion activities in colloidal clays : *J. Phys. Chem.*, v. 46, pp. 52–61.

Mitra, R. P. and Rajogopalan, K. S. (1952) Origin of the base exchange capacity of clays and significance of its upper limiting value : *Soil Sci.*, v. 73, pp. 349–360.

Mukherjee, J. N., Chatterjee, B. and Ray, A. (1948) Liberation of H^+, Al^{+3}, and Fe^{+3} ions from pure clay minerals on repeated salt treatment and desaturations : *J. Colloid Sci.*, v. 3, pp. 437–446.

Nash, V. E. and Marshall, C. E. (1956) The surface reactions of silicate minerals, Part II, Reactions of feldspar surfaces with salt solutions : *Univ. Missouri Coll. Agric. Research Bull.* 614, 36 pp.

Paver, H. and Marshall, C. E. (1934) The role of aluminium in the reactions of the clays : *J. Soc. Chemical Industry*, v. 53, pp. 750–760.

Powers, M. C. (1954) Clay diagenesis in the Chesapeake Bay area : in *Clays and Clay Minerals*, Natl. Acad. Sci.—Natl. Res. Council, pub. 327, pp. 68–80.

Powers, M. C. (1957) Adjustment of land derived clays to the marine environment : *J. Sed. Petrology*, v. 27, pp. 355–372.

Schofield, R. K. and Taylor, A. W. (1955) Measurements of the activities of bases in soils : *J. Soil Sci.*, v. 6, pp. 137–146.

Shapiro, Leonard and Brannock, W. W. (1956) Rapid analysis of silicate rocks : *U.S. Geol. Survey. Bull.* 1036–C, 56 pp.

Sverdrup, H. U., Johnson, M. W. and Fleming, R. N. (1946) *The Oceans : Their Physics, Chemistry and General Biology* : Prentice-Hall, New York, 1087 pp.

Thompson, T. G. and Anderson, D. H. (1940) The determination of the alkalinity of sea water : *J. Marine Res.* v. 3, pp. 224–229.