

## REACTIVITY OF CLAY MINERALS WITH ACIDS AND ALKALIES\*

DOROTHY CARROLL† and HARRY C. STARKEY

U.S. Geological Survey, Menlo Park, Calif. 94025 and Denver, Colo. 80225

(Received 16 April 1971)

**Abstract**—One-g samples of a montmorillonite, a metabentonite, an illite, two kaolinites, and three halloysites were treated with 50 ml of hydrochloric acid (6.45 N, 1:1), acetic acid (4.5 N, 1:3), sodium hydroxide (2.8 N), sodium chloride solution (pH 6.10; Na = 3.5%; Cl = 21.5%), and natural sea water (pH 7.85; Na = 35.5%; Cl = 21.5%) for a 10-day period in stoppered plastic vials. The supernatant solutions were removed from the clay minerals and analyzed for SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, CaO, MgO, Na<sub>2</sub>O, and K<sub>2</sub>O. All the solutions removed some SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and Fe<sub>2</sub>O<sub>3</sub> from the samples, but the quantities were small. Sodium hydroxide attacked the kaolin group minerals more strongly than it did montmorillonite, metabentonite, or illite. Halloysite was more strongly attacked by hydrochloric acid than was any of the other experimental minerals. Hydrochloric acid removed iron oxide coatings from soil clay minerals, but acetic acid did not remove them completely. The samples most strongly attacked by HCl and NaOH were examined by X-ray diffraction. Acid treatment did not destroy the structure of the clays, but the halloysite structure was partially destroyed. Sodium hydroxide attacked the halloysite structure, as shown by chemical analysis and X-ray diffraction. These experiments show that treatment in dilute acids has no harmful effect in the preparation of clays for X-ray diffraction. Acetic acid is preferred to hydrochloric acid for this purpose. Hydrochloric acid cleans clay minerals by removing free iron oxide from the surface; acetic acid is less effective.

### INTRODUCTION

INSOLUBLE residues of limestones and dolomites containing clay minerals are commonly prepared by treatment in hydrochloric, acetic, or formic acids or by ion exchange resins in the H-form (Ray *et al.*, 1957). Acids and ion-exchange resins are also used to prepare the H-form of clay minerals for studies of exchange reactions and for titration with bases (Aldrich and Buchanan, 1958). Nutting (1943) found that acids remove alkali metals, alkaline earths, iron, and aluminum from clay minerals and that alkalis remove silica. The first effect of acids is to remove the exchangeable cations, thereby producing H-clays. The alumina octahedral layer of a clay mineral is then attacked, and later the silica tetrahedral layer. Alkalis first attack the tetrahedral layer. If the attack is prolonged and severe the mineral structure is destroyed, but 75–85 per cent of the total alumina must be removed from montmorillonite before the structure is completely destroyed (Grim, 1953, p. 298). The kaolinite structure resists prolonged treatment in concentrated sulfuric acid (Murray, 1951). One of the most noticeable effects of acid

treatment is the solution of aluminum from the octahedral layer (Paver and Marshall, 1934). This aluminum has been called "exchangeable aluminum" because it is released from H-clays and is presumed to occupy the exchange positions in minerals such as montmorillonite and may be partly present as free alumina (Foster, 1953) and partly released from the octahedral layer. The presence of this alumina makes it difficult to use H-form clay minerals in titration studies or to keep H-clays for experimental purposes (Aldrich and Buchanan, 1958).

This paper describes the results of treating eight clay-mineral samples with acids and alkalis for 10 days at room temperature (about 25°C). The acids used were hydrochloric and acetic, 6.45 N and 4.5 N, respectively. The alkalis used were sodium hydroxide (2.8 N), a 3.5% solution of sodium chloride (0.6 N), and natural sea water (pH 7.85). The sea water was collected in the Florida Straits and was given to the authors for experimental purposes by Preston E. Cloud, Jr. The salt solution was included in the experiments because Mukherjee *et al.* (1947, 1948) had reported that silica, alumina, and iron were removed from the H-forms of clay minerals by leaching with a salt solution. Sea water was used so that the effects of a simple electrolyte and a polyelectrolyte could be compared, and also the removal of SiO<sub>2</sub> and

\*Publication authorized by the Director, U.S. Geological Survey.

†Deceased, January 30, 1970.

Al<sub>2</sub>O<sub>3</sub> from clay minerals by sea water could be assessed.

The effect of the various solutions on clay minerals was examined by chemical analysis of the solutions after they had been in contact with the minerals. X-ray diffraction studies were made of those minerals that were shown by chemical analysis to have lost considerable amounts of silica and alumina.

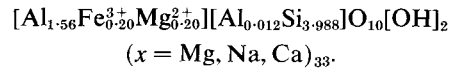
**EXPERIMENTAL CLAY MINERALS**

The clay minerals used in these experiments can be described structurally as in Table 1. Chemical analyses of them are in Table 2.

*Montmorillonite (A)*

Calculation of the standard formula by the method of Ross and Hendricks (1945, pp. 41-42) indicates that the amounts of free SiO<sub>2</sub> and free Al<sub>2</sub>O<sub>3</sub> are negligible. However, Table 2 shows that some quartz is present. Some of the MgO is in the exchangeable form. It is probably not correct to place all the Fe<sub>2</sub>O<sub>3</sub> given in Table 1 in the octa-

hedral unit, inasmuch as some is present as free ferric oxide. The formula calculated is



This is almost identical with that for a montmorillonite from Upton, Wyoming, given by Foster (1951, p. 724). The total exchange for montmorillonite (A) is 87 me/100 g. The exchange capacity of the Upton montmorillonite is given as 86 me/100 g.

*Metabentonite (B)*

The metabentonite from High Bridge, Kentucky (API no. 24), consists of a mixed-layer structure of illite and montmorillonite, with illite predominating (Bradley, 1945); it has been termed a potash bentonite.

*Illite (C)*

The illite from Fithian, Illinois (API No. 35), is

Table 1. Structural description of experimental clay minerals

Mineral	Layer lattice		
	1:1	1:1, poorly crystalline	2:1 Interstratified
Am. Petroleum Inst. standards; API Project 49 (1949)			
Montmorillonite (A)			x
Metabentonite (B)			x
Illite (C)			x
Kaolinite (D)	x		
Halloysite (E)	x		
Iron oxide-coated clays separated from soils			
Kaolinite (F)		x	
Halloysite (G)		x	
Halloysite (H)		x	

Description of samples

- (A) Montmorillonite, Osage, Wyoming. API std. 25b.
- (B) Metabentonite, Highbridge, Kentucky. API std. 42.
- (C) "Illite", Fithian, Illinois. API std. 35.
- (D) Kaolinite, Bath, South Carolina. API std. 5.
- (E) Halloysite, Tintic, Utah. API std. 13.
- (F) Kaolinite, Y-3, clay fraction separated from old red residual soil on colluvial material on County Road 796 near Oak Grove Church, 4.2 miles NNW of Waynesboro, Augusta County, Virginia.
- (G) Halloysite, 1-2, clay fraction separated from Chacha clay on Mariana limestone, about 2.5 miles southeast of Agana, Guam (depth, 6-8 in.).
- (H) Halloysite, 6-2, clay fraction separated from Atate clay on volcanic tuff and conglomerate, about 2.5 miles south of center of Talafofo village, Guam (depth, 2-10 in.).

Table 2. Chemical composition (in per cent) of experimental clay minerals

	(A) Montmorillonite	(B) Metabentonite	(C) Illite	(D) Kaolinite	(E) Halloysite	(F) Kaolinite	(G) Halloysite	(H) Halloysite
SiO <sub>2</sub>	58.4	54.0	56.1	43.7	46.1	39.8	33.6	35.6
Al <sub>2</sub> O <sub>3</sub>	19.6	19.7	19.0	38.2	34.8	31.2	30.2	28.0
Fe <sub>2</sub> O <sub>3</sub>	4.0	1.8	5.5	0.26	0.04	11.0	13.4	70.8
MgO	2.0	3.5	1.6	<0.05	<0.05	0.32	0.45	0.52
CaO	1.1	1.4	2.1	<0.05	<0.05	0.14	0.26	0.07
Na <sub>2</sub> O	2.0	0.10	0.56	0.05	0.04	0.18	0.08	0.04
K <sub>2</sub> O	0.46	7.4	4.6	0.11	0.03	0.77	0.06	0.10
H <sub>2</sub> O	10.4	9.9	7.3	14.4	18.0	15.1	18.1	19.1
TiO <sub>2</sub>	0.16	0.26	0.93	1.4	0.01	0.94	0.73	0.74
P <sub>2</sub> O <sub>5</sub>	0.06	0.09	0.22	0.08	0.28	0.36	0.64	0.18
MnO	0.04	0.00	0.07	0.00	0.00	0.02	0.03	0.06
CO <sub>2</sub>	0.36	0.14	1.2	<0.05	<0.05	0.11	0.17	0.15
Sum	99	98	99	98	99	100	98	95

Total iron shown as Fe<sub>2</sub>O<sub>3</sub>. H<sub>2</sub>O is total water in air-dried sample. Sample (B) contains some sulfur; samples (G), (H) contain appreciable organic matter.

a mixture of 1 Md and 2M micas with montmorillonite (Yoder and Eugster, 1955, pp. 249–250). The sample used also contained small amounts of quartz, calcite, and pyrite.

#### *Kaolinite (D)*

There is an excess of 1.1%  $Al_2O_3$  after calculation of normative kaolinite from the analysis in Table 1. Table 2 shows that some quartz is present and that excess  $Al_2O_3$  determined chemically is more than that calculated. There are about 2 per cent of constituents that are not part of the kaolinite.

#### *Halloysite (E)*

Calculation of normative halloysite from the analysis in Table 1 shows that there is an excess of 5.1%  $SiO_2$ . The amount of quartz found by centrifugation (Table 3) is 6.1 per cent. There is no excess alumina, and the figure for free alumina in Table 2 apparently represents attack by acid. Other impurities in the sample amount to 0.55 per cent.

#### *Kaolinite (F)*

The impurities in this sample are 7.3% goethite, 3.0% excess  $SiO_2$ , and nearly 3% other impurities. The sample, therefore, contains about 87% kaolinite. The excess  $SiO_2$  is present as quartz (Table 3), which is exceedingly fine grained and difficult to remove by centrifugation.

#### *Halloysite (G)*

This sample of soil clay contains organic matter which is responsible for the low chemical total in Table 2. Calculation of normative halloysite shows that there is 0.7% excess  $Al_2O_3$ , about 8% goethite (+hematite), and 2.4% other impurities. The original sample contains 89% halloysite.

#### *Halloysite (H)*

This soil clay also contains an appreciable amount of organic matter. It contains 2.6% excess  $SiO_2$ , and both quartz and feldspar are present (Table 3). There is 6.6% goethite (+hematite) and about 1.8% other impurities. This sample contains about the same amount of halloysite as (G).

Samples (F), (G), and (H) are reddish-brown soil clays that are coated with adhering goethite and hematite. They are shown, by X-ray diffraction, to be poorly crystalline. These samples were included in the experiments because they are characteristic of strongly weathered soils and are the type of clay minerals that are being transported from deeply weathered land surfaces to be deposited in marine sediments.

All the samples are contaminated with extraneous material. Organic matter is present in halloysites (G) and (H) from Guam and sulfur is present, presumably as pyrite, in metabentonite (B). Carbon dioxide occurs in all the samples, showing that small amounts of calcite and possibly also of dolomite are contaminants. Table 3 shows the impurities (contaminants) in the standard minerals that were estimated by chemical and X-ray analysis.

### EXPERIMENTAL PROCEDURE

Samples of the standard clay minerals, montmorillonite (A), mixed-layer mineral (B), illite (C), kaolinite (D), and halloysite (E), were ground with a pestle in a mortar to pass a 270-mesh (0.053 mm) sieve, dried in an oven at 80°C for several hours, and stored in a desiccator. Kaolinite (F) and halloysites (G) and (H) were separated from the soils in which they occurred by repeated dispersion in distilled water in an end-over-end shaker. The

Table 3. Contaminants and exchangeable cations in experimental clay minerals

Mineral	Free $SiO_2$	Free $Al_2O_3$	Free $Fe_2O_3$	Exchangeable cations				Mineral impurities identified by X-ray diffraction
				CaO	MgO	$Na_2O$	$K_2O$	
Montmorillonite (A)	1.0	1.7	0.2	0.31	0.30	1.70	—	Feldspar, quartz
Metabentonite (B)	1.1	*9.3	0.5	0.73	0.13	—	—	Feldspar, quartz
Illite (C)	0.8	*4.4	0.6	1.68	0.05	—	—	Quartz, calcite
Kaolinite (D)	0.6	1.9	0.1	0.01	tr.	—	—	Quartz
Halloysite (E)	6.1	*5.3	tr.	0.04	0.03	—	—	Quartz
Kaolinite (F)	0.1	n.d.	11.0	n.d.	n.d.	n.d.	n.d.	Quartz, goethite, hematite
Halloysite (G)	tr.	n.d.	13.4	n.d.	n.d.	n.d.	n.d.	Quartz, goethite, hematite
Halloysite (H)	tr.	n.d.	10.8	n.d.	n.d.	n.d.	n.d.	Quartz, feldspar, hematite, goethite

\*The high figure for free alumina may indicate attack of the octahedral layer by acid.

Analyses (in per cent) by Dorothy Carroll, H. C. Starkey, and J. C. Hathaway, tr. — trace; n.d. — not determined; —, not present. Free  $SiO_2$  = quartz.

silt was removed by centrifugation, and the clay fraction ( $< 2 \mu$ ) was dried at room temperature.

Five 1-g samples of each of the eight clay minerals were weighed out in polyethylene vials (40 vials in all). Five 40- to 50-ml lots of HCl (1:1, 6.45 N), acetic acid (1:3, 4.5 N), NaOH (2.8 N), NaCl (35‰, 0.6 N), and natural sea water (salinity 35.5‰, chlorinity 21.5‰, pH 7.85) were added to the appropriate vials which were then stoppered tightly and allowed to stand at room temperature (about 25°C) for 10 days. The contents of each vial was mixed each day by shaking, and after 10 days the solutions were separated from the clay minerals by centrifugation. The clay minerals were washed once with distilled water, and this was added to the solution removed from each clay. Each clay mineral sample was then washed twice more with distilled water and transferred to an evaporating dish and allowed to dry at room temperature.

The solutions were made up to volumes that would contain less than 25 mg of  $\text{SiO}_2 + \text{Al}_2\text{O}_3$  in a 50-ml aliquot so that they could be analyzed by the rapid methods of Shapiro and Brannock (1962) for  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ , CaO, MgO,  $\text{Na}_2\text{O}$ , and  $\text{K}_2\text{O}$ . In order to obtain a sharp end-point, it was necessary to precipitate the  $\text{R}_2\text{O}_3$  group before determining MgO and CaO by versene titration. Blanks were made for each solution and figures for the blanks were deducted from those obtained by analysis of the supernatant solutions.

Exchangeable cations were removed from the original clay minerals by leaching with 1 N  $\text{NH}_4\text{Cl}$  adjusted to pH 7 with  $\text{NH}_4\text{OH}$ . Exchangeable calcium and magnesium were determined in the leachate by versene titration, and exchangeable sodium and potassium were determined by flame photometer (Table 3). The free silica present as quartz and feldspar was removed from a weighed sample of each clay by repeated centrifugation at high speed. The quantity was weighed and the material examined by X-ray diffraction (Table 3). The free alumina was determined by treating the minerals with dilute cold hydrochloric acid (0.08 N) for about 2 hr and then precipitating the  $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$  with  $\text{NH}_4\text{OH}$ . The precipitate was dried and weighed. The  $\text{Fe}_2\text{O}_3$  present was determined colorimetrically with KCNS and deduced from the total weight of the precipitate to give  $\text{Al}_2\text{O}_3$  by difference. Free iron oxide in samples (A), (B), (C), (D), and (E) was removed by treatment with dithionate at 40°C (Deb, 1950) and determined colorimetrically with KCNS. The free iron in samples (F), (G), and (H) given in Table 3 is from the analyses in Table 2, as all the iron in these clays is considered to be free iron oxides coating the clay particles.

## RESULTS

### *Chemical analyses of supernatants*

The amounts of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ , CaO, MgO,  $\text{Na}_2\text{O}$ , and  $\text{K}_2\text{O}$  dissolved from the experimental clay minerals by treatment in 50 ml of various solutions at about 25°C are given, in Table 4, as concentrations and atomic proportions in the supernatants. Table 4 shows that measurable amounts of chemical elements are dissolved from the clay minerals by the various reagents used. However, the percentages removed are very small, as shown in Table 5. The well-crystallized clay minerals, montmorillonite, metabentonite, illite, and kaolinite, are only slightly affected by the acids and alkalies at the pH values stated. The HCl (1:1) removed ferric oxide impurities, magnesium and calcium (part of which may be exchangeable cations), and some silica and alumina. Sodium hydroxide removed some silica and alumina, but was less effective in removing the other constituents than HCl. Sodium chloride removed CaO and MgO, but the effect on silica and alumina was negligible. Sea water removed a small amount of silica, the largest amount being from montmorillonite, as had been previously noted (Mackenzie and Garrels, 1965, p. 58). HCl and NaOH removed a much greater percentage of constituents from poorly crystalline clays and halloysite than from the well-crystallized clays, but HAc, NaCl, and sea water removed similar amounts from all the clays.

A summary of the results of the experiments follows:

### *Montmorillonite (A)*

The structure is that of a 2:1-layer silicate with silica tetrahedra exposed on the outer surfaces of the finely divided platy mineral and on the upper and lower boundaries of the water interlayer. The alumina tetrahedra are sandwiched between the two silica layers, and only the edges of this layer are exposed. All the solutions removed silica, the order of removal by the reagents being  $\text{NaOH} \gg \text{NaCl} > \text{HCl} = \text{HAc} = \text{sea water}$  (Table 4). For  $\text{Al}_2\text{O}_3$  the order of removal was  $\text{HCl} > \text{NaOH} > \text{HAc} > \text{NaCl} > \text{sea water}$ . HCl was the most effective reagent in removing  $\text{Fe}_2\text{O}_3$ . The small amounts of the remaining constituents determined were exchangeable cations (Table 3). The exposed  $\text{SiO}_2$  tetrahedra were attacked by the reagents releasing the Si originally in tetrahedral coordination. NaOH may have removed the silica layer, but the other reagents effected only a partial removal.

### *Metabentonite (B)*

Because this mineral is a mixture of illite and montmorillonite, the results of the experiment with this mineral cannot be assessed fully. However,

Table 4. Analyses of supernatants of the reaction of 1 g of clay minerals with 50 ml of various solutions for 10 days at 25°C

	HCl 6.45 N		HAc 4.5 N		NaOH 2.8 N		NaCl Na, 35.5/100		Sea water Na, 35.5/100	
	ppm	a.p.	ppm	a.p.	ppm	a.p.	ppm	a.p.	ppm	a.p.
<b>Montmorillonite (A)</b>										
SiO <sub>2</sub>	80	1.333	120	2.00	580	9.666	200	3.333	80	1.333
Al <sub>2</sub> O <sub>3</sub>	240	2.353	<20	<0.196	200	1.960	380	3.725	<20	<0.196
Fe <sub>2</sub> O <sub>3</sub>	100	0.625	10	0.062	8	0.050	16	0.100	6	0.037
CaO	11	0.196	24	0.428	20	0.357	58	1.035	n.d.	—
MgO	71	1.775	144	3.600	nil	—	36	0.900	n.d.	—
Na <sub>2</sub> O	7	0.113	116	1.871	n.d.	—	n.d.	—	n.d.	—
K <sub>2</sub> O	nil	—	nil	—	nil	—	nil	—	n.d.	—
<b>Metabentonite (B)</b>										
SiO <sub>2</sub>	80	1.333	60	1.000	240	4.000	40	0.666	20	0.333
Al <sub>2</sub> O <sub>3</sub>	300	2.941	40	0.392	280	2.745	<20	<0.196	20	0.196
Fe <sub>2</sub> O <sub>3</sub>	220	1.375	40	0.25	10	0.062	4	0.025	4	0.025
CaO	56	1.000	77	1.375	99	1.768	119	2.125	n.d.	—
MgO	60	1.500	31	0.775	6	0.150	32	0.800	n.d.	—
Na <sub>2</sub> O	nil	—	nil	—	n.d.	—	n.d.	—	n.d.	—
K <sub>2</sub> O	2	0.021	nil	—	tr.	tr.	nil	—	n.d.	—
<b>Illite (C)</b>										
SiO <sub>2</sub>	40	0.666	80	1.333	160	2.666	60	1.000	40	0.666
Al <sub>2</sub> O <sub>3</sub>	380	3.725	160	1.568	180	1.765	140	1.372	120	1.176
Fe <sub>2</sub> O <sub>3</sub>	340	2.125	60	0.375	12	0.075	14	0.087	6	0.037
CaO	21	0.375	356	6.357	76	1.357	104	1.857	n.d.	—
MgO	266	6.650	76	1.900	4	0.100	14	0.350	n.d.	—
Na <sub>2</sub> O	nil	—	tr.	tr.	n.d.	—	n.d.	—	n.d.	—
K <sub>2</sub> O	tr.	—	nil	—	nil	—	nil	—	n.d.	—
<b>Kaolinite (D)</b>										
SiO <sub>2</sub>	60	1.000	100	1.666	1120	18.666	40	0.666	20	0.333
Al <sub>2</sub> O <sub>3</sub>	960	9.412	480	4.706	580	5.686	40	0.392	80	0.784
Fe <sub>2</sub> O <sub>3</sub>	14	0.087	4	0.025	nil	nil	2	0.012	2	0.012
<b>Halloysite (E)</b>										
SiO <sub>2</sub>	80	1.333	160	2.666	1700	28.333	60	1.000	20	0.333
Al <sub>2</sub> O <sub>3</sub>	3800	37.255	460	4.510	1820	17.843	80	0.784	20	0.196
Fe <sub>2</sub> O <sub>3</sub>	n.d.*	—	n.d.*	—	n.d.*	—	n.d.*	—	n.d.*	—
<b>Kaolinite (F)</b>										
SiO <sub>2</sub>	60	1.000	60	1.000	2200	36.666	40	0.666	<20	<0.333
Al <sub>2</sub> O <sub>3</sub>	860	8.431	100	0.980	2000	19.608	40	0.392	20	0.196
Fe <sub>2</sub> O <sub>3</sub>	2000	12.500	20	0.125	4	0.025	4	0.025	2	0.012
<b>Halloysite (G)</b>										
SiO <sub>2</sub>	60	1.000	80	1.333	1880	31.333	20	0.333	<20	<0.333
Al <sub>2</sub> O <sub>3</sub>	1480	14.510	160	1.568	1840	18.040	60	0.588	<20	<0.196
Fe <sub>2</sub> O <sub>3</sub>	2380	14.875	20	0.125	4	0.025	4	0.025	4	0.025
<b>Halloysite (H)</b>										
SiO <sub>2</sub>	100	1.666	120	2.000	10	0.166	40	0.666	<20	<0.333
Al <sub>2</sub> O <sub>3</sub>	1340	13.137	280	2.745	1920	18.823	<20	<0.196	<20	<0.196
Fe <sub>2</sub> O <sub>3</sub>	1980	12.375	4	0.025	1720	10.750	6	0.037	10	0.062

Analysts: Leonard Shapiro and Dorothy Carroll. ppm—parts per million; a.p.—atomic proportions; tr.—trace; n.d.—not determined; n.d.\*—not determined, because sample appeared colorless; —, not applicable. Because of the limitations in the usefulness of chemical methods, Na<sub>2</sub>O was not determined in the supernatants of NaOH, NaCl, or sea water, nor were CaO, MgO, Na<sub>2</sub>O, K<sub>2</sub>O determined in sea water. Blanks were made for each solution used in this experiment and the figures given represent the analyses of the supernatants minus the blank determinations.

Table 5. Average loss (in per cent) of total constituents of experimental clay minerals

Clay minerals	HCl 6.45 N	HAc 4.5 N	NaOH 2.8 N	NaCl Na, 35‰	Sea water Na, 35.5‰
A-D (well-crystallized)	0.08	0.04	0.09	0.03	0.01
E (halloysite)	0.39	0.06	0.35	0.01	0.004
F-H (poorly crystallized)	0.34	0.03	0.38	0.007	0.004

the structure as a whole is less attacked by these reagents than is pure montmorillonite. The results may show that the montmorillonite component is attacked whereas the illite component is not.

#### *Illite (C)*

The illite structure seems to be less subject to attack than that of montmorillonite. As the illite structure is bonded together by  $K^+$  ions, there is no interlayer space. Small amounts of  $SiO_2$  were dissolved by all the reagents. More than twice as much  $Al_2O_3$  was removed by HCl than by NaOH, but HCl also removed iron (determined as  $Fe_2O_3$ ) which was in the octahedral layer isomorphously replacing  $Al_2O_3$ .

#### *Kaolinite (D)*

As kaolinite has a 1:1-layer structure, one of its plane faces consists of silica tetrahedra and the other of alumina octahedra. The structure of well-crystallized kaolinite is uncharged and the exchange capacity is negligible (Table 3). Kaolinite (D) contains very little iron (Table 2). In a solution the two layers are equally exposed to reaction. Table 4 shows that the silica layer is only slightly attacked by all the reagents except NaOH. The alumina layer is attacked strongly by both acids and NaOH, but only very slightly by NaCl and sea water.

#### *Halloysite (E)*

The structure of halloysite is similar to that of kaolinite, except that it contains interlayer water between the kaolinite-like layers. The X-ray diffractogram of the experimental halloysite (Fig. 2) shows that the sample was dehydrated and corresponds to metahalloysite in the accepted nomenclature (Brindley, 1966, p. 30). The reaction of halloysite (E) is similar to that of kaolinite (D), although the amount of both silica and alumina dissolved from this halloysite is greater for HCl and NaOH. This suggests that halloysite is not as structurally stable as kaolinite. Halloysite regains its interlayer water in sea water (Carroll and Starkey, 1960, p. 87) and expands, but this change evidently has little effect on its reactivity (Table 4).

The iron-coated soil clays—kaolinite (F), and halloysites (G) and (H)—show reactions similar to kaolinite (D) and halloysite (E). Ferric oxide is

readily removed by HCl but not by HAc. These clays are poorly crystallized and may be disordered structurally, as shown in the X-ray diffractogram of halloysite (G), Fig. 3. The poor crystallinity was confirmed by electron micrographs taken by John C. Hathaway.

#### *X-ray examination of clay minerals*

HCl and NaOH dissolved larger amounts of  $SiO_2$  and  $Al_2O_3$  from kaolinite (D) and halloysites (E) and (G) than from the other clay minerals. X-ray diffractograms made of these three clay minerals before and after treatment are shown in Figs. 1–3.

These diffractograms do not show any structural changes in these minerals after treatment in HCl; but Fig. 2 shows that in halloysite (E) there was an increase in intensity of the X-ray spacings due to quartz (this sample in its natural state contains 5–6 per cent quartz as an impurity). This indicates that some halloysite was dissolved, which increased the relative amount of quartz in the sample.

The X-ray diffractogram of kaolinite (D), after its treatment in NaOH, is similar to that of the untreated sample (Fig. 1). The NaOH solution attacked halloysite (E) (Fig. 2) more strongly than did the HCl; accordingly, the amount of quartz, as evidenced by the increased peak heights, is greater. The NaOH-treatment of halloysite (G) almost completely destroyed its structure (Fig. 3). Halloysite (G) and also (H) (not illustrated) have disordered structures in their natural condition. Such structures are more readily attacked than those similar to the well-crystallized structure of halloysite (E). Removal of  $SiO_2$  and  $Al_2O_3$  from halloysite (G) causes a relative increase of the iron oxides in the sample and therefore a high background is given with  $CuK_\alpha$  radiation.

#### DISCUSSION

These experiments have examined four kinds of reaction of clay minerals (as 2 per cent suspensions) with various reagents that can be grouped as follows: (1) strong acids (HCl) and strong bases (NaOH); (2) weak acid (acetic acid,  $CH_3COOH$ ); (3) a strong salt (NaCl); and (4) average sea water (salinity 35.5‰, chlorinity 21.5‰, pH 7.85).

The suspensions of the clay minerals were

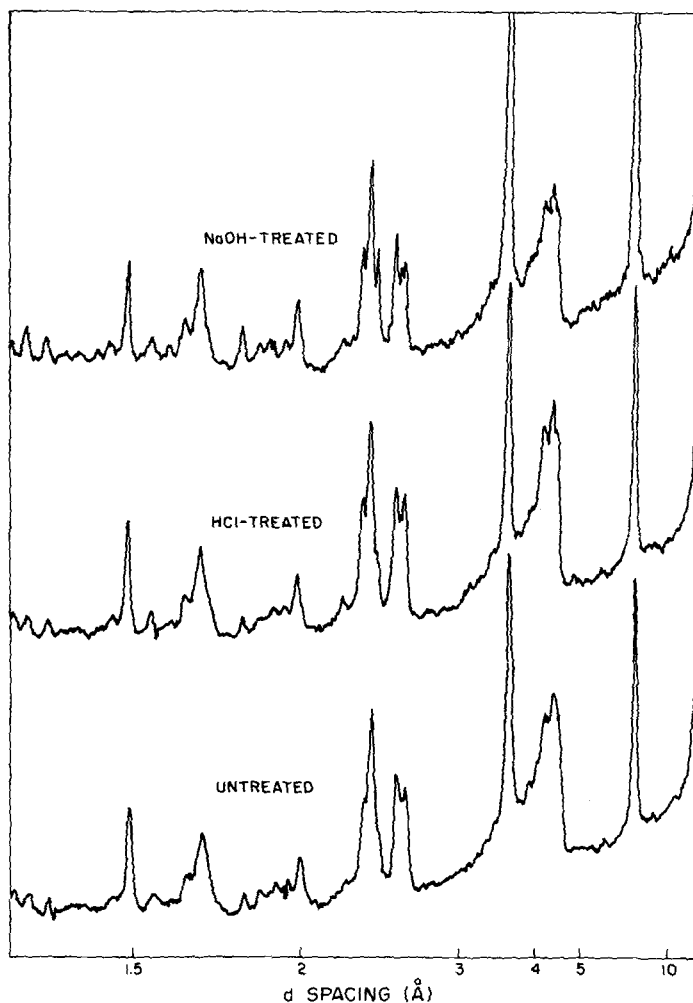


Fig. 1. X-ray diffractograms of kaolinite (D), untreated and after treatment in HCl and NaOH ( $CuK_{\alpha}$  radiation).

reacted with the four types of solutions for 10 days in a closed system. Probably none of these reactions reached equilibrium in this time, but the reaction of sea water with clay minerals other than montmorillonite may have been about 50 per cent complete (Mackenzie and Garrels, 1965, p. 57).

In the first section of the experiment (1) the clay mineral is dissolved incongruently by reaction with a strong acid (HCl) and base (NaOH). In solution the ions become completely ionized and are free to react with the silica and alumina layers of the minerals. The amounts of silica and alumina removed are given in Table 4. Kaolinite and halloysite have 1:1-layer structures in which each layer would seem to be equally vulnerable to the reagents, but generally a greater amount of alumina

is removed than silica and stability of the structure is attacked through the alumina layer. In montmorillonite and illite (2:1-layer silicates), the silica layer is more exposed than the alumina layer, but HCl removes about as much alumina as does NaOH, and the structure is primarily attacked through the alumina layer.

In (2) the acetic acid used has a low concentration (1:3), and as it is a weak acid it is not completely dissociated. It has only a slight effect on the clay minerals: although an equal quantity of silica was removed from montmorillonite (A), metabentonite (B), and illite (C) as with HCl, very little alumina was removed even from the 1:1-layer clays, kaolinite (D) and halloysite (E).

In (3) the NaCl solution contains a higher con-



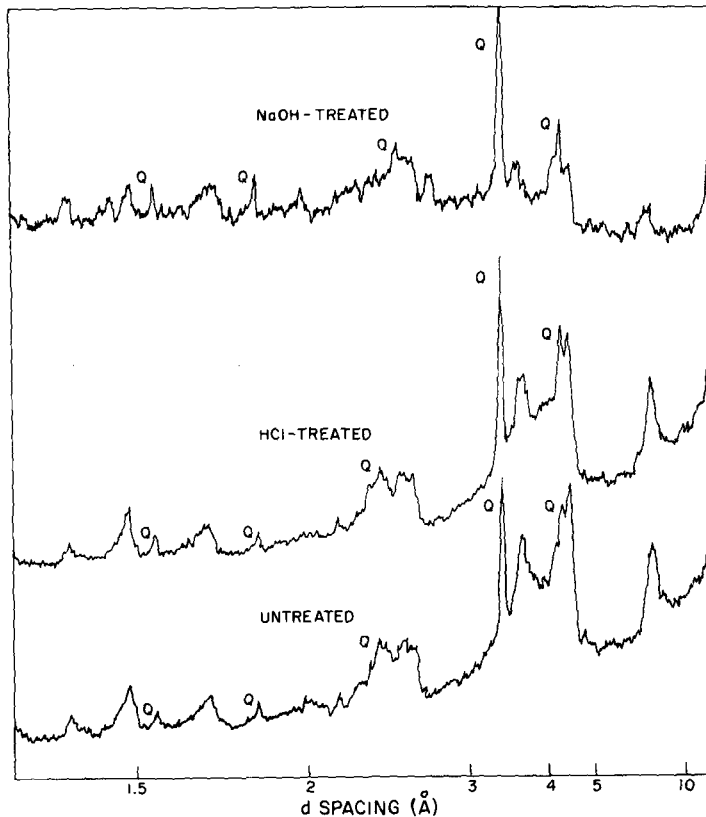


Fig. 2. X-ray diffractograms of halloysite (E), untreated and after treatment in HCl and NaOH ( $\text{CuK}\alpha$  radiation).

centration of the  $\text{Na}^+$  ion than sea water (0.6 equivalent as against 0.46 equivalent), but almost the same concentration of the  $\text{Cl}^-$  ion (0.6 equivalent as against 0.535 equivalent). The  $\text{Na}^+$  ion is completely dissociated in NaCl and 99 per cent dissociated in sea water (Garrels and Thompson, 1962, p. 57). The analyses of the NaCl supernatant may show the effect of the anion,  $\text{Cl}^-$ . Mukherjee *et al.* (1947, 1948) showed that salt solutions liberated  $\text{H}^+$ ,  $\text{Al}^{3+}$ , and  $\text{Fe}^{3+}$  ions from H-clays in an open system. Apparently the prior acid treatment removed some silica, and so alumina became available for reaction with the salt solution. Both alumina and iron may have reacted to form aluminum chloride and iron chloride, respectively. Nash and Marshall (1956, a and b) similarly showed that salt solutions would react with feldspar surfaces after acid treatment of these surfaces.

Sea water (4) is a polyelectrolyte with a complex chemistry (Garrels and Thompson, 1962, p. 63). It has been observed that silica is released from certain silicate minerals by reaction with sea water (Carroll and Starkey, 1960; Mackenzie and Garrels,

1965; Siever *et al.*, 1965), that the dissolved silica in sea water acts as a buffer controlling the pH as well as the concentration of the chief ions in sea water (Sillén, 1961), and that the amount of silica in sea water is controlled by the silicate minerals (Mackenzie *et al.*, 1967) which are added to the oceans by erosion of the land and by atmospheric winds (Griffin *et al.*, 1968). When detrital clay minerals and fresh water are added to oceans or are dropped by winds, the sea water gradually adjusts to its normal composition, in which it contains about 1 ppm  $\text{SiO}_2$ . After mixing, the silicate particles are widely dispersed until they are flocculated and deposited on the sea floor. The silicates (clays) have been added to a closed basin, just as they were in the experiment described. In the marine environment, the  $\text{Na}^+$  ion is almost completely free (Garrels and Thompson, 1962, p. 63) and it can therefore react as does the  $\text{Na}^+$  ion in a solution, except that it is present with other ions and its chemical activity depends partly on the buffering action of  $\text{CO}_2$  in the sea water.

In experiments with the reaction of various salt

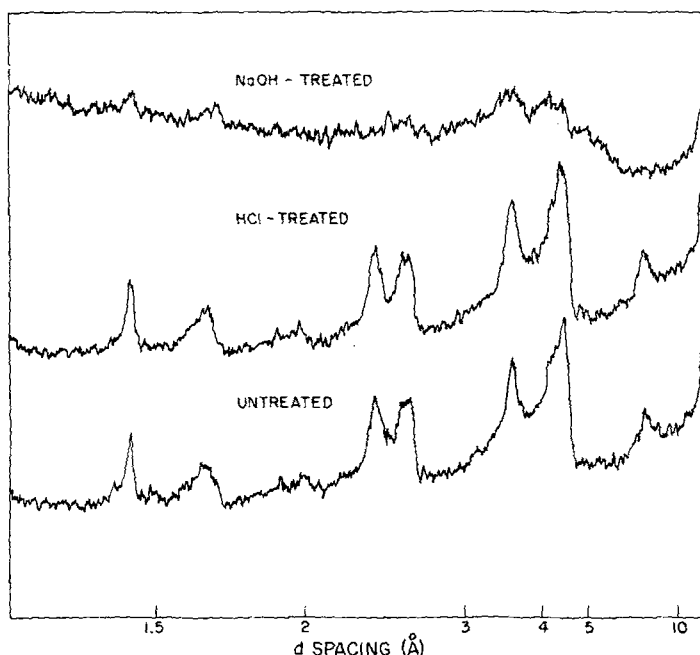
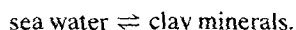


Fig. 3. X-ray diffractograms of halloysite (G), untreated and after treatment in HCl and NaOH ( $\text{CuK}_\alpha$  radiation).

solutions with feldspar surfaces. Nash and Marshall (1956, a and b) found that if the feldspar surface had been mildly attacked by  $\text{H}^+$  ions, a zone of lattice flexibility was produced in which cation exchange occurs with cations in contact with the surface. Only the  $\text{H}^+$  ion is small enough to penetrate the feldspar lattice and thereby cause a breakdown in the normal lattice relations. Attack by the  $\text{H}^+$  ion release  $\text{SiO}_2$  but no  $\text{Al}_2\text{O}_3$ . The amount of  $\text{SiO}_2$  released from feldspar is about the same as that for quartz (solubility 6 ppm). An equilibrium may be reached between the thin zone of lattice adjustment (about 2–3 unit cells thick; Nash and Marshall, 1956b, p. 35) from which silica is removed and a salt solution or sea water independent of the pH. In sea water an equilibrium may be reached when no further chemical reaction takes place with added clay minerals:



Mackenzie and Garrels (1965, p. 57) suggest that in their experiment this may take about 6 months as judged by the release of silica, although more than 50 per cent of the silica was released in 10 days from the silicates they examined. However, montmorillonite released more silica than did kaolinite, illite, muscovite, or chlorite. This difference is probably related to the different types of

crystal lattice of the minerals and to the strength of the bonding of the layers. The layers of all these minerals, except montmorillonite, are strongly bonded, whereas the structure of montmorillonite (Fig. 4) generally shows isomorphous replacement in the octahedral layers which results in exchangeable ions in the interlayer region to preserve electrical neutrality.

#### CONCLUSIONS

The pH of the reagents used in these experiments ranged from less than 1 to over 12, thereby covering the solubility ranges for silica, alumina, and ferric oxide. During the experiments the pH of the sodium hydroxide and the pH of sea water were lowered slightly by the absorption of  $\text{CO}_2$  (Carroll, 1960), but the amount of  $\text{CO}_2$  absorbed by these solutions in the stoppered vials was insufficient to affect the reactions. The analyses of the supernatants are those to be expected with HCl and NaOH and 2 per cent suspensions of clay minerals. The reactions to acetic acid, though varying with the kind of clay mineral, are noticeably weaker than to HCl. Acetic acid is to be preferred in preparing for X-ray examination insoluble residues containing clay such as occur in many impure limestones and other materials. The acid treatment shows that the arrangement of the silica and alumina layers in clay minerals influences the

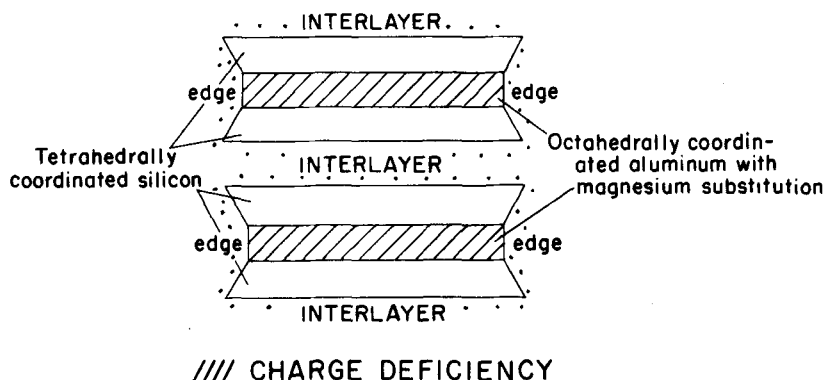


Fig. 4. Schematic montmorillonite layer structure (after Fommer, 1963).

removal of silica and alumina. The reactivity of both HCl and HAc is in the order: montmorillonite (A) > metabentonite (B) > kaolinite (D) > halloysite (E) = illite (C). Adhering iron oxide prevented the attack of HAc on the other three kaolinite and halloysite group minerals (F, G, H). The kaolin minerals were attacked more strongly by NaOH than were montmorillonite, metabentonite, or illite. Small quantities of SiO<sub>2</sub> were removed from all the minerals by NaCl solution and by sea water. Alumina was also removed from the clay minerals by these reagents. The mechanism of release of alumina is not known, but it may be a complexing of alumina with the Cl<sup>-</sup> ions of the solutions if the alumina is moved from the octahedral sheet to exchange positions in the minerals, as it is with acid treatment.

*Acknowledgements*—We thank Leonard Shapiro for making many of the chemical analyses and for helpful advice in many ways, W. W. Brannock for chemical advice, critical reviews, and suggestions, and R. M. Garrels and R. O. Fournier for critical reviews.

#### REFERENCES

- Aldrich, D. G. and Buchanan, J. R. (1958) Anomalies in techniques for preparing H-bentonites: *Soil Sci. Soc. Am. Proc.* **22**, 281–285.
- Bradley, W. F. (1945) Diagnostic criteria for clay minerals: *Am. Mineralogist* **30**, 704–713.
- Brindley, G. W. (1966) Discussions and recommendations concerning the nomenclature of clay minerals and related phyllosilicates: *Clays and Clay Minerals* **14**, 27–34.
- Carroll, Dorothy (1960) Carbon dioxide and alumina in the potentiometric titration of H-montmorillonite: *U.S. Geol. Survey Prof. Paper* **400-B**, B436–438.
- Carroll, Dorothy and Starkey, H. C. (1960) Effect of sea water on clay minerals: *Clays and Clay Minerals* **7**, 80–101.
- Deb, B. C. (1950) The estimation of free iron oxides in soils and clays and their removal: *J. Soil Sci.* **1**, 212–220.
- Foster, M. D. (1951) Geochemical studies of clay minerals—I. The importance of the exchangeable magnesium and cation-exchange capacity in the study of montmorillonitic clays: *Am. Mineralogist* **36**, 717–730.
- Foster, M. D. (1953) Geochemical studies of clay minerals—III. The determination of free silica and free alumina in montmorillonites: *Geochim. et Cosmochim. Acta* **3**, 143–154.
- Garrels, R. M. and Thompson, M. E. (1962) A chemical model for sea water at 25°C and one atmosphere total pressure: *Am. J. Sci.* **260**, 57–66.
- Griffin, J. J., Windom, Herbert and Goldberg, E. D. (1968) The distribution of clay minerals in the World Ocean. *Deep-Sea Res.* **15**, 433–459.
- Grim, R. E. (1953) *Clay Mineralogy*. McGraw-Hill, New York, 384 pp.
- Mackenzie, F. T. and Garrels, R. M. (1965) Silicates—Reactivity with sea water. *Science* **150**, 57–58.
- Mackenzie, F. T., Garrels, R. M., Bricker, O. P. and Bickley, Frances (1967) Silica in sea water: control by silica minerals: *Science* **155**, 1404–1405.
- Mikherjee, J. N., Chatterjee, B. and Banerjee, B. M. (1947) Liberation of hydrogen, aluminum, and ferric ions from hydrogen clays by neutral salts: *J. Colloid Sci.* **2**, 247–256.
- Mukherjee, J. N., Catterjee, B. and Ray, A. (1948) Liberation of hydrogen, aluminum, and ferric ions from pure clay minerals on repeated salt treatment and desaturation: *J. Colloid Sci.* **3**, 437–445.
- Murray, H. H. (1951) *The structure of kaolinite and its relation to acid treatment*. Ph.D. thesis, University of Illinois, Urbana, Illinois.
- Nash, V. E. and Marshall, C. E. (1956a) The surface reactions of silicate minerals—I. The reactions of feldspar surfaces with acidic solutions: *University Missouri, Coll. Agr. Expt. Sta. Res. Bull.* **613**, 36 pp.
- Nash, V. E. and Marshall, C. E. (1956b) The surface reactions of silicate minerals—II. Reactions of feldspar surfaces with salt solutions: *University Missouri, Coll. Agr. Expt. Sta. Res. Bull.* **614**, 36 pp.

- Nutting, P. G. (1943) The action of some aqueous solutions on clays of the montmorillonite group: *U.S. Geol. Survey Prof. Paper* **197-F**, 219–235.
- Paver, H. and Marshall, C. E. (1934) The role of aluminum in the reactions of the clays: *Chem. Indus.* pp. 750–760.
- Pommer, A. M. (1963) Relation between dual acidity and structure of H-montmorillonite: *U.S. Geol. Survey Prof. Paper* **386-C**, 23 pp.
- Ray, Satyabrata, Gault, H. R. and Dodd, C. G. (1957) The separation of clay minerals from carbonate rocks: *Am. Mineralogist* **42**, 681–686.
- Ross, C. S. and Hendricks, S. B. (1945) Minerals of the montmorillonite group, their origin and relation to soils and clays: *U.S. Geol. Survey Prof. Paper* **205-B**, 23–79.
- Shapiro, Leonard and Brannock, W. W. (1962) Rapid analysis of silicate, carbonate, and phosphate rocks: *U.S. Geol. Survey Bull.* **1144-A**, 56 pp.
- Siever, Raymond, Beck, K. C. and Berner, R. A. (1965) Composition of interstitial waters of modern sediments: *J. Geology* **73**, 39–73.
- Sillén, L. G. (1961) The physical chemistry of sea water: in M. Sears, Ed., *Oceanography. Am. Assoc. Adv. Sci. Publ.* **67**, 549–581.
- Yoder, H. S., Jr. and Eugster, H. P. (1955) Synthetic and natural muscovites: *Geochim. et Cosmochim. Acta* **8**, 225–280.

**Résumé**—Des échantillons d'un gramme d'une montmorillonite, d'une métabentonite, d'une illite, de deux kaolinites et de trois halloysites ont été traités avec 50 ml d'acide chlorhydrique (6,45N 1:1), d'acide acétique (4,5N 1:3), de soude (2,8N), d'une solution de chlorure de sodium (pH 6,10; Na = 35%<sub>00</sub>; Cl = 21,5%<sub>00</sub>) et d'eau de mer naturelle (pH 7,85; Na 35,5%<sub>00</sub>; Cl = 21,5%<sub>00</sub>), pendant une période de 10 jours dans des fioles de plastique bouchées. Les solutions surnageantes ont été séparées des minéraux argileux et l'on en a déterminé par analyse les teneurs en SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, CaO, MgO, Na<sub>2</sub>O, K<sub>2</sub>O et Fe<sub>2</sub>O<sub>3</sub>. Toutes les solutions extraient des échantillons une certaine quantité de SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> et Fe<sub>2</sub>O<sub>3</sub>, mais les quantités sont petites. L'attaque par l'hydroxyde de sodium des minéraux du groupe du kaolin est plus intense que celle de la montmorillonite, de la métabentonite ou de l'illite. L'halloysite a été attaquée par l'acide chlorhydrique plus fortement que n'importe quel autre des minéraux étudiés. L'acide chlorhydrique fait disparaître les oxydes de fer de recouvrement des minéraux argileux du sol, mais l'action de l'acide acétique n'est pas complète. Les échantillons les plus fortement attaqués par HCl et NaOH ont été examinés par diffraction X. Le traitement acide ne détruit pas la structure des argiles, mais la structure de l'halloysite a été partiellement détruite. L'hydroxyde de sodium attaque la structure de l'halloysite comme le montrent l'analyse chimique et la diffraction X. Ces expériences montrent que le traitement par les acides dilués n'a pas d'effet nuisible dans la préparation des argiles pour la diffraction X. Pour cet usage, on préfère l'acide acétique à l'acide chlorhydrique. L'acide chlorhydrique nettoie les minéraux argileux en faisant disparaître de la surface l'oxyde de fer libre; l'acide acétique est moins efficace.

**Kurzreferat**—Eingrammproben von Montmorillonit, einem Metabentonit, einem Illit, zwei Kaoliniten und drei Halloysiten wurden mit 50 ml Salzsäure (6,45N, 1:1), Essigsäure (4,5N, 1:4), Natriumhydroxyd (2,8N), Natriumchloridlösung (pH 6,10; Na = 35%<sub>00</sub>; Cl = 21,5%<sub>00</sub>) und natürlichem Meerwasser (pH 7,85; Na = 35,5%<sub>00</sub>; Cl = 21,5%<sub>00</sub>) über einen Zeitraum von 10 Tagen in zugestopften Kunststoff-Phiolen behandelt. Die überstehenden Lösungen wurden von den Tonmineralen entfernt und auf SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, CaO, MgO, Na<sub>2</sub>O und K<sub>2</sub>O analysiert. Alle die Lösungen entfernten etwas SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> und Fe<sub>2</sub>O<sub>3</sub> aus den Proben, doch handelte es sich um mengenmässig kleine Beträge. Natriumhydroxyd griff die Minerale der Kaolingroup stärker an als den Montmorillonit, Metabentonit oder Illit. Der Halloysit wurde durch Salzsäure stärker angegriffen als irgendeines der anderen Versuchsminerale. Salzsäure entfernte Eisenoxydbeläge von Eodentonmineralen, jedoch wurden dieselben durch Essigsäure nicht vollständig entfernt. Die am stärksten von HCl und NaOH angegriffenen Proben wurden durch Röntgenbeugung untersucht. Die Säurebehandlung zerstörte das Gefüge der Tone nicht, während die Halloysitstruktur teilweise zerstört wurde. Wie aus der chemischen Analyse und der Röntgenbeugung ersichtlich, wurde die Halloysitstruktur durch Natriumhydroxyd angegriffen. Diese Versuche zeigen, dass eine Behandlung mit verdünnten Säuren keine schädliche Wirkung bei der Vorbereitung der Tone für Röntgenbeugung ausübt. Essigsäure wird für diesen Zweck gegenüber Salzsäure vorgezogen. Die Salzsäure säubert Tonminerale durch Entfernung des freien Eisenoxys von der Oberfläche; Essigsäure ist in dieser Hinsicht weniger wirksam.

**Резюме**—Обработке 50 мл растворов HCl (6,45 N; 1:1), уксусной кислоты (4,5 N; 1:3), NaOH (2,8 N), NaCl (pH 6,10; Na = 35%<sub>00</sub>; Cl = 21,5%<sub>00</sub>) и морской водой (pH 7,85; Na = 35,5%<sub>00</sub>; Cl = 21,5%<sub>00</sub>) в течение 10 дней в закрытых пластиковых бутылочках были подвергнуты по 1 г. монтмориллонита, метабентонита, иллита, двух каолинитов и трех галлуазитов. Раствор над осадком подвергался анализу на SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, CaO, MgO, Na<sub>2</sub>O, K<sub>2</sub>O. Во всех растворах обнаружены извлеченные из глинистых минералов SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> и Fe<sub>2</sub>O<sub>3</sub>, но в небольших количествах. NaOH воздействовал на минералы каолиновой группы сильнее, чем на монт-

мориллонит, метаботенит или иллит. На галлуазит HCl оказывала более сильное действие, чем на другие глинистые минералы. HCl удаляла пленки окислов с почвенных глинистых минералов, а уксусная кислота не оказывала на них никакого воздействия. Образцы, испытавшие наиболее сильное воздействие HCl и NaOH, были изучены рентгеновским методом. Оказалось, что кислотная обработка не разрушила структуры глин, но структура галлуазита испытала некоторое изменение. NaOH вызвал изменение структуры галлуазита как следует из данных химических анализов и из рентгеновских дифракционных картин. Эксперименты показали, что обработка разбавленными кислотами не оказывает вредного влияния на приготовление глин для рентгеновского анализа. Уксусная кислота для этого более пригодна, чем соляная. HCl очищает глинистые минералы, удаляя с их поверхности окислы железа; уксусная кислота менее эффективна.