

AN ABSTRACT OF THE THESIS OF

DUMITRU DUMITRU CARSTEA for the Ph.D. in SOILS
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Title FORMATION AND STABILITY OF Al, Fe, AND Mg INTER-
LAYERS IN MONTMORILLONITE AND VERMICULITE

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The effects of pH and time on the formation of hydroxy-Al, Fe, and Mg interlayer were compared for montmorillonite and vermiculite.

The stability of interlayers was evaluated by sequentially increasing the severity of dissolution treatments and by subjecting the interlayers to an HCl treatment. The interlayer formation and stability were evaluated by X-ray diffraction analysis and CEC measurements.

In montmorillonite, aluminum interlayers were formed at all pH levels. Systems equilibrated in acid media exhibited the greatest degree of interlayering and the resulting material showed the essential X-ray diffraction characteristics of chlorite. However, the amount of interlayers decreased after six months and one year. Those interlayers formed in alkaline media exhibited increased interlayering after one year. Boiling Na_2CO_3 and particularly boiling NaOH generally removed part of interlayers. This removal was more pronounced for neutral and alkaline media than for acid media. The

interlayer formed in alkaline conditions showed the highest stability to HCl treatment, whereas that formed in acid medium was the least stable.

In vermiculite, aluminum interlayers were also greater for acid than for alkaline media. In contrast to montmorillonite, the amount of interlayer in vermiculite in acid media increased with time. For alkaline media there was some increase in the interlayering after six months followed by decrease after one year. As the severity of dissolution treatments increased the degree of collapse increased. However, chloritic components, in addition to dominant collapsible components, were evident after NaOH treatment for systems formed at intermediate pH levels. The stability to the HCl treatment decreased toward alkaline media.

Moderate amounts of iron interlayers were formed in montmorillonite at all pH levels. The interlayers did not inhibit expansion on solvation but the systems exhibited moderate resistance to collapse. Diffraction patterns were characterized by diffuse peaks and plateaus suggesting mixed layer systems. Some reorganization or decrease of interlayers occurred after equilibration for one year. The interlayers were partially removed by dissolution treatments. Interlayers formed at intermediate pH values were, presumably, more stable than those formed in other media. Iron interlayers from all media exhibited a high stability to the HCl treatments.

Iron interlayers in vermiculite were favored by alkaline environments. Formation was greatest after ten days and less after six months or one year. Iron removal and particularly boiling NaOH treatments resulted in resolution of collapsible and non-collapsible components. In the latter case, definite chlorite lines were observed. The interlayer from alkaline media exhibited somewhat higher stability to sequential treatments than those from other media. The HCl treatments removed more interlayer from acid media than from alkaline media.

Magnesium interlayers in montmorillonite and vermiculite were formed only in alkaline environments ($\text{pH} > 10$). After ten days, in both systems, the degree of interlayers formation decreased as the pH increased. The montmorillonite system showed only a slight dissolution of interlayers after 6 months and one year, whereas a strong interlayer decrease was observed for the vermiculite system. The interlayered montmorillonite formed at an initial pH of 11 became nearly amorphous to X-ray diffraction following a 6-month period. The boiling NaOH treatment produced a partial resolution of the montmorillonite system into collapsible and non-collapsible components. In vermiculite, the second dithionite-citrate removed most of the interlayers and induced a high degree of collapse and a high CEC. The boiling NaOH treatment resolved a small 14 \AA component in addition to a dominant 10 \AA component after K-saturation. The

interlayers in montmorillonite showed a high stability to HCl treatments. In contrast, most of the magnesium interlayers in vermiculite were removed by the HCl treatments.

In conclusion, the hydroxy-Al, Fe, and Mg interlayers in montmorillonite showed a higher degree of formation and exhibited a higher stability to sequential and HCl treatments than the interlayers formed in vermiculite. Reasons were given in order to explain these behavioral differences.

FORMATION AND STABILITY OF Al, Fe, AND Mg INTERLAYERS
IN MONTMORILLONITE AND VERMICULITE

by

DUMITRU DUMITRU CARSTEA

A THESIS

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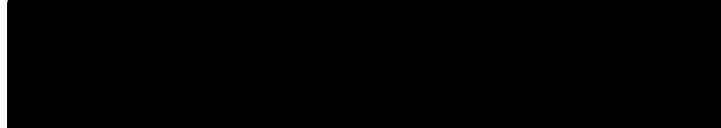
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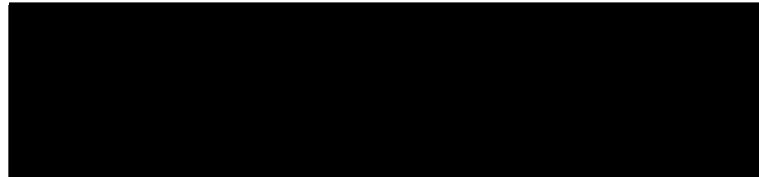
APPROVED:



Professor of Soils
In Charge of Major



Head of Department of Soils



Dean of Graduate School

Date thesis is presented January 12, 1967

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FORMATION AND STABILITY OF Al, Fe, AND Mg INTERLAYERS IN MONTMORILLONITE AND VERMICULITE

INTRODUCTION

Early efforts in the investigation of soil clays were directed toward identification and characterization of the major clay mineral groups such as 1:1 kaolinites, 2:1 smectites¹ and vermiculites, and 2:2 chlorites.

The expansible 2:1 layer silicates such as smectites and vermiculites are composed of negatively charged layers which are balanced predominantly by calcium, magnesium, or sodium counter ions. The 2:1 lattice is composed of an octahedral layer which is coordinated to two tetrahedral layers. The negative charge is the result of isomorphous substitution in tetrahedral and/or octahedral sheets. The C axis of these minerals varies commonly from 10 Å to 21 Å or higher depending upon the charge density, location of charge, kinds of interlayer cations, vapor pressure, and kind of solvating agent employed. Norrish (1954) reported a basal spacing of 40 Å for montmorillonite in water, and Garrett and Walker (1962) measured spacings of several hundred Angstroms for vermiculite crystals treated with n-alkyl-ammonium ions.

¹The term smectite was proposed by MacEwan, Douglas M. C. (1961) to designate the group of montmorillonite minerals.

Chlorite is thought to be a macroscopic or microscopic metamorphic mineral. According to this viewpoint, hydrothermal processes are responsible for the crystallization of chlorites. The members of the classical chlorite group of layer silicates were considered to be trioctahedral (Grim, 1953); that is, magnesium and ferrous iron occupy the available octahedral positions in both mica-like $[(\text{Al}_2\text{Si}_6)\text{Mg}_6\text{O}_{20}(\text{OH})_4]^{2-}$ and brucite-like $[(\text{Al}_2\text{Mg}_4)(\text{OH})_{12}]^{2+}$ layers. The excess negative charge originating from isomorphous substitution of Al^{3+} for Si^{4+} in the tetrahedral layer is balanced by a positively charged brucite-like interlayer. The excess positive charge in the brucite layer originates from isomorphous substitution of Al^{3+} for Mg^{2+} . The average formula of a trioctahedral chlorite-- $(\text{Al}_2\text{Si}_6)\text{Mg}_6\text{O}_{20}(\text{OH})_4 \cdot (\text{Al}_2\text{Mg}_4)(\text{OH})_{12}$ --reflects its structural characteristic. The hydrogen bond also plays an important role in chlorite minerals in addition to the ionic bond. The designation of chlorite as 2:2 layer silicate originates from the alternation of octahedrally and tetrahedrally coordinated sheets. The basal spacing of chlorites is about 14 \AA and it does not change position on solvation, K saturation, and heating to 550°C .

Recently, natural 14 \AA layer silicates with properties intermediate between typical chlorite and vermiculite or montmorillonite were found to be common in soils. These chloritic intergrades have been described under names such as "dioctahedral analogue of

vermiculite" (Brown, 1953, 1954), "dioctahedral vermiculite" (Rich and Obenshain, 1955), "vermiculite-type clay" (Hathaway, 1955), "interstratified chlorite-vermiculite" (Dixon and Seay, 1957; Jackson et al., 1954), "intergradient chlorite-expansible layer silicates" (Dixon and Jackson, 1962), "chloritized montmorillonite" or "chloritized vermiculite" (Sawhney, 1958), "chlorite-like" mineral (Klages and White, 1957), "interlayered 3-layer clay" (Weed and Nelson, 1962), "chlorite-vermiculite-montmorillonite intergrade" (Dixon and Jackson, 1959), "swelling chlorite" (Stephen and MacEwan, 1951), etc. Their characteristic property in all cases was resistance to collapse, i. e., they collapsed with difficulty; they may or may not show resistance to expansion.

The degradation of chlorite by weathering processes has been suggested as a mechanism by which the chloritic intergrades are formed. The typical trioctahedral chlorites are particularly unstable under acid conditions of soils. The replacement of OH^- from the brucite interlayer by H_2O was proposed by Droste (1956) as a mechanism of chlorite degradation.

The formation of hydroxy Al, Fe, and Mg interlayers in the expansible 2:1 minerals is another mechanism which has been proposed for the genesis of chloritic-intergrades. The mechanism of hydroxy-interlayer formation has been called "partial chloritization" (MacEwan, 1949), "alumination" (Tamura et al., 1959), and

"chloritization" (Sawhney, 1960). The interlayer precipitation of various hydroxy polymers has been reported for montmorillonite (Tamura, 1958), dioctahedral vermiculite (Brown, 1953; Rich and Obenshain, 1955), and vermiculite (Tamura, 1956; Sawhney, 1960). The processes which lead to the formation of chloritic intergrades seem to be confined to "open" environments (Jackson, 1963). The degree of the interlayer filling with hydroxy Al, Fe, or Mg is presumed to depend upon the nature of parent material, type of biological complex, and physico-chemical processes.

The presence of chloritic intergrades in soils is important in soil fertility. For example, soil physico-chemical processes which involve fixation of nutrients such as potassium, ammonium, or phosphorus are influenced to a large extent by the presence of hydroxy interlayers. The formation of different hydroxy interlayers is closely related to the genesis and development of soils which occur under various sets of natural conditions. The formation of magnesium interlayer is presumably but one mechanism which helps in explaining the high buffering capacity of the oceans and associated sediments.

Two main approaches have been used in the study of the intergrade minerals. One approach is that of identification and characterization of the soil constituents as they occur in situ. It has been concluded that the processes which favor the formation of the

chloritic intergrades constitute a general feature of soil formation. The interlayers formed in well drained soils have been shown to be more stable than those from poorly drained soils (Sawhney, 1958, 1960). The amount of chloritization was found to increase toward the soil surface (Jeffries et al., 1953; Tamura, 1956). Hydroxy interlayer formation is therefore related to the degree of weathering of soils. The role of aluminum in acid soils has received a great deal of attention whereas little attention has been given to other cations such as iron and magnesium. The occurrence and conditions of interlayer formation in alkaline environment is still a problem to be solved.

The second approach is that of preparing synthetic counterparts of chloritic intergrades in the laboratory. Both montmorillonite and vermiculite have been used for the synthetic preparation of hydroxy-Al, Fe, and Mg interlayers. It was concluded in a previous study (Carstea, 1965) that pH, salt concentration, time and kind of minerals are among the essential factors involved in interlayer formation.

In the present study, the second approach has been adopted. This was preferred over the first because the synthetic systems may serve as models for naturally occurring materials. Soil systems are complex and contain both crystalline and amorphous phases. Both hydroxy-interlayering and interstratification are common in

soil and it is very difficult to differentiate between them. Finally, there is difficulty in getting the interlayers out by chemical treatments without an alteration of the basic matrix, especially when the latter is poorly crystallized. The problem involved starting with purified known samples, studying the conditions of hydroxy inter-layer formation, the properties of the intergrades, and then testing stability of different interlayers to removal treatments.

The objectives of this study can be briefly stated as follows:

1. To determine the conditions and degree of hydroxy inter-layer formation with respect to:
 - a. Kind of cations: Al^{3+} , Fe^{3+} , and Mg^{2+}
 - b. Differences between montmorillonite and vermiculite
 - c. Acidity
 - d. Time
2. To determine the stability of the different hydroxy-inter-layered systems when subjected to sequential dissolution treatments of increasing severity.

In addition to providing needed information on formation and properties of chloritic intergrades, the results of the study have implications on methods and criteria for clay minerals identification.

EXPERIMENTAL MATERIALS

Sources and Name of Clay Minerals

Standard samples of montmorillonite and vermiculite were used for the experimental work involving formation and stability of different hydroxy interlayers. A standard chlorite was used for comparison. The samples used were:

1. Montmorillonite 11, Santa Rita, New Mexico,

From Ward's Natural Science Establishment, Inc.

Rochester, New York²

2. African Vermiculite

From Perlite Company

Portland, Oregon

3. Prochlorite 6, Chester, Vermont,

From Ward's Natural Science Establishment, Inc.

Rochester, New York

Pretreatments, Dispersion, and Fractionation of Montmorillonite

Dry chunks of montmorillonite were ground in a Wiley mill to pass a 40-mesh sieve. The less than 40-mesh material was then

² Trade names and company names are included for the benefit of the reader, and do not infer any endorsement or preferential treatment of the products.

dispersed using Jackson's boiling Na_2CO_3 treatment (1956, p. 73) with the modification that Na_2CO_3 was added as a liquid and not as a solid. The separation and concentration of material with less than 2μ effective spherical diameter was obtained by a centrifugation method described by Jackson (1956, p. 101-164).

Pretreatments, Dispersion, and Fractionation of Vermiculite

Problem

Vermiculite seldom occurs in nature in a pure state. It is more often associated with chlorite and/or biotite and occurs as random or regular interstratifications (Barshad, 1948; Walker, 1949; Norrish and Radoslovich, 1957; Midgley and Midgley, 1960; Harward and Carstea³). Such materials have been called hydro-biotites. Preliminary X-ray analyses of the natural flakes of African vermiculite used in this study indicated the presence of some impurities (Table 1). The diffraction maxima of 25.2 and 12.6 Å for Ca-saturated samples indicate the first and second orders of a regular interstratification of mica and vermiculite units. The 14 Å peak suggests some discrete vermiculite although incomplete collapse on K-saturation indicates the presence of some hydroxy interlayers (chloritic

³ Unpublished data, Soils Department, Oregon State University, Corvallis, Oregon.

Table I. Properties of various size fractions of natural African vermiculite.

Size Fractions	C. E. C. me/100g	Basal Spacings (Å)*				
		X-ray Pretreatments				
		Ca	Ca Solv.	K	K 300° C	K 550° C
Natural flakes	64.5	25.2	24.52	25.2	28.47	<u>10.04</u>
		14.7	14.29	<u>11.0</u>	<u>10.35</u>	7.27
		12.6	<u>11.72</u>	7.2	7.27	
		11.9				
Medium, coarse and very coarse sand (2000 - 250μ)	80.9	23.73	25.22	<u>10.67</u>	<u>10.39</u>	<u>10.02</u>
		14.24	14.29			
		<u>12.20</u>	<u>11.8</u>			
Fine sand (250 - 100μ)	83.4	24.52	23.86	24.52	<u>10.39</u>	<u>10.11</u>
		14.34	14.24	<u>10.72</u>		
		<u>12.34</u>	<u>11.84</u>			
Very fine sand (100 - 50μ)	90.4	25.37	24.94	<u>10.57</u>	<u>10.37</u>	<u>10.16</u>
		<u>14.52</u>	14.11	7.31	7.32	7.27
		<u>12.41</u>	<u>12.17</u>			
Silt (50 - 2μ)	101.2	25.96	25.22	<u>10.47</u>	<u>10.20</u>	<u>10.13</u>
		<u>14.57</u>	<u>14.29</u>	7.34	7.27	7.30
		12.62	12.62			
Clay (<2μ)	90.4	<u>14.72</u>	26.75	11.87	11.35	11.94
		12.48	<u>15.49</u>	10.59	<u>10.47</u>	<u>10.18</u>
			13.06			
Coarse clay (2 - 0.2μ)	63.1	<u>14.48</u>	14.02-	11.04	<u>10.39</u>	12.00
			15.44	10.23		<u>10.04</u>
Fine clay (<0.2μ)	N. D. **	26.27	26.75	<u>10.54</u>	<u>10.37</u>	<u>10.16</u>
		14.06	13.18	7.25	7.25	7.31
		<u>12.51</u>				

*Where two or more peaks were observed, the more prominent one is underlined.

**N. D. = not determined.

intergrade). There is also a possibility of kaolinite as indicated by the 7 Å line. It, therefore, was necessary to purify the material and obtain a sample typical of vermiculite.

Separation of Silt Size Fraction

Preliminary experiments were conducted to select the appropriate size fraction for vermiculite. Portions of 20g of natural vermiculite were suspended in 400 ml of 2 percent Na_2CO_3 and ground in an Osterizer blender for about two minutes. Mackenzie and Milne (1953) reported that prolonged dry grinding degraded the structure of biotite and, to a less extent, of vermiculite. Consequently, wet grinding over short periods of time was preferred over dry grinding. The ground sample was then dispersed using boiling Na_2CO_3 (Jackson, 1956).

The separation of various size fractions (Table I) was accomplished by using the wet sieve method in conjunction with centrifugation (Jackson, 1956, p. 101-164). The selection of the silt fraction for further experimental work was accomplished on the basis of: (1) higher cation exchange capacity, (2) higher intensity and sharpness of 14 Å peak characteristic of discrete vermiculite, and (3) common occurrence of vermiculite in the silt fraction of soils. A chemical treatment was required in order to obtain a sample typical of vermiculite. This treatment is described in the next section.

Alteration of Mica-Vermiculite Mixture to Vermiculite

The silt fraction was mainly a mixture of vermiculite and interstratified mica-vermiculite. The sample contained 3.70 percent potassium. If all potassium is attributed to mica, presumably biotite, the approximate composition of the sample was 60 percent vermiculite and 40 percent mica.

It has been shown that continued treatment with salt solutions will remove the interlayer potassium from micas. Among the most common salts used to accomplish the alteration of hydro-biotite to vermiculite are MgCl_2 (Carter et al., 1963; Barshad, 1948) and NaCl (Mortland and Lawton, 1961; Rich, 1960; Rich and Cook, 1963; Carstea, 1965). Molten lithium nitrate (White, 1956), and Na tetraphenylboron (Scott et al., 1960; DeMumbrum, 1963) have been used to remove potassium from muscovite.

In the present study, NaCl was selected and preliminary experiments were conducted to establish the conditions of alteration. Specifically, 3g samples of the sodium saturated silt size of natural vermiculite were treated with 3000 ml of 5 N NaCl and digested in a water bath at approximately 80°C for periods up to 18 days. The NaCl solution was changed every day. A reflux condenser was provided to prevent evaporation during digestion. Subsamples of material were analyzed by X-ray diffraction after 3, 5, 7, 10, and 18

days to determine the degree of conversion. The peaks associated with the mica component decreased in intensity after three and five days and disappeared completely after 7, 10, and 18 days. Data obtained after 7, 10, and 18 days are given in Table II. A decrease in exchange capacity and decrease in collapse (larger basal spacings) after K saturation were observed after 18 days of digestion. These changes were presumably due to fixation of hydroxy-aluminum polymers in the interlayer space. Previous studies (Rich and Cook, 1963) indicated that NaCl attacked the crystalline structure of minerals with liberation of Al^{3+} ions from octahedral layers. It appeared that alteration for 18 days had a destructive effect upon vermiculite. Consequently, the seven-day period of alteration was finally selected for the preparation of the experimental material.

The presence of the 7.2-7.4 Å diffraction peak in vermiculite suggests the presence of kaolin. A sample was treated for differential dissolution of kaolin by heating to 400° C for four hours and then boiled in NaOH for 2.5 minutes (Dixon and Jackson, 1959). The resulting X-ray diffraction patterns indicated that 7 Å peak had been removed but the intensity of the 14 Å peak characteristic of vermiculite was considerably reduced. It was reasoned that the presence of the 7 Å component would not seriously interfere with the subsequent interpretations on the formation of hydroxy interlayers. Therefore,

the treatment for removal of kaolin was considered to be too severe and it was avoided.

Table II. Alteration of the silt fraction of a mica-vermiculite mixture to vermiculite by digestion with 5 N NaCl for different periods of time.

Length of Treatment (days)	C. E. C. (me/100g)	Total K %	Basal spacings (Å) [*]	
			X-ray Pretreatments	
			Casat'd	Ksat'd
0	101	3.70	25.96 <u>14.57</u> 12.62	<u>10.47</u> 7.34
7	152	0.31	14.6	<u>10.37</u> 7.31
10	159	N.D. **	14.5	<u>10.47</u> 7.31
18	144	N.D.	14.5	11.07 <u>10.27</u> 7.28

*Where two or more peaks were observed, the more prominent one is underlined.

**N.D. = not determined.

Pretreatments, Dispersion, and Fractionation of Chlorite

Dry chunks of chlorite were ground in an Osterizer blender in a way similar to that of vermiculite. The silt and clay size fractions were obtained by wet sieving method and centrifugation following boiling in 2 percent Na_2CO_3 . Unlike vermiculite, no structural differences were noted between the two size fractions. Cation exchange

capacities of these fractions increased with a decrease in particle size. This is explained by the increasing area of edges with a decrease in particle size. Only results with silt size fractions are reported here.

Calcium Saturation

The sediments of the selected size fractions of each of the minerals were calcium saturated by five washings (Rich, 1960) with $\frac{1}{2}$ N CaCl_2 . The soluble salts were removed by two washings with distilled water followed by two washings with 99 percent methanol until there was no positive test for chloride using AgNO_3 . The materials were dried at 65°C , ground by mortar and pestle, stored in bottles, and used as stock material for subsequent experiments.

GENERAL METHODS

X-ray Diffraction Techniques

X-ray Equipment

X-ray diffraction patterns were obtained by means of a Norelco X-ray diffractometer equipped with a Geiger-Mueller tube and a Brown recorder. Nickel-filtered Cu K-alpha radiation generated at 50 kilovolts and 37 milliamperes was used. A system of divergent and scatter slits with $1/4^\circ$ angular aperture and a 0.006-inch receiving slit were found to be most adequate for optimum peak height and resolution. It is known that the higher orders of randomly mixed systems give poorly defined and, more often, nondistinct X-ray diffraction peaks. It was, therefore, considered that the bulk of necessary information could be obtained from the 001 basal spacings. The 001 basal reflection is the most sensitive to the changes produced by fixation or removal of different hydroxy interlayers. Consequently, and in view of the large number of samples to be analyzed, the X-ray patterns were run from 1 degree 2θ to 14 degrees 2θ . The scanning speed was one degree 2θ per minute. The rate meter and time constant settings were varied to meet the need for resolution and detail for each particular pattern.

Calcium Saturation and Solvation

Subsamples were analyzed by X-ray diffraction after specified periods of time during formation of interlayers and after each removal treatment. These samples were saturated with calcium by four washings with 1 N CaCl_2 . Two water and two methanol washings were used to remove the excess salt. A small amount of the Ca-saturated clay was then removed from the centrifuge tube with a micro-spatula and thinly spread on petrographic micro-slides (Theisen and Harward, 1962). The slides were first air-dried and then dried at 65°C for two hours. They were placed in a desiccator containing drierite until analyzed by X-ray diffraction. Manual scanning of the diffraction patterns was used in selection of the better of duplicate slides. Following the X-ray diffraction analysis, the slides were solvated by condensation of ethylene glycol vapor (Kunze, 1955).

Potassium Saturation and Heat Treatment

Other subsamples were K-saturated by washing four times with 1 N KCl. Three washings with distilled water were used to remove the excess salt. Duplicate slides were prepared in a manner similar to Ca slides. After the irradiation of the selected K-saturated slide, it was successively heated in a muffle furnace at 300°C and 500°C

for two hours with additional X-ray diffraction analyses recorded after each heating period.

Cation Exchange Capacity Determination

A procedure for exchangeable calcium extraction as described by Rich (1961) was followed with a slight modification. The difficulty in determining calcium in the presence of excess magnesium salts led to the substitution of sodium for magnesium as the replacing cation. The calcium saturated material, free of soluble salts, was dried and weighed in a centrifuge tube. It was then equilibrated with 20 ml of 1 N NaCl. The samples were shaken for 16 hours, centrifuged, and the supernatant filtrated into 100 ml volumetric flasks. A second extraction for 20 minutes was performed to insure a complete removal of the exchangeable calcium. The solution was then brought to volume. An aliquot was titrated with cyclohexanediamine tetraacetic acid (CyDTA) using calcein as an indicator (Carlson and Johnson, 1961). The CyDTA was standardized against standard grade CaCO_3 dissolved in HCl and titrated in the presence of 1 N NaCl. Determinations of cation exchange capacities, as reported under specific methods of the following chapters, were made on duplicate samples and the results were based on the weights of the sample dried from alcohol at 65° C.

X-ray diffraction analyses and determinations of exchange capacities were performed on the selected size fractions of the purified experimental materials prior to interlayer formation (Table III). Montmorillonite formed a duo-interlayer with ethylene glycol and expanded to 17.3 \AA , whereas vermiculite formed only a single-sheet complex. Potassium-saturated montmorillonite exhibited a 11.9 \AA basal spacing which indicates some hydration occurred. Heating to 300° C and 550° C removed the water of hydration and produced a closure of the crystal lattice to about 10 \AA . On the other hand, potassium-saturated vermiculite collapsed to 10 \AA even in the absence of heat and did not show any sign of hydration. Chlorite did not exhibit any change in basal spacings after solvation or potassium saturation and heat treatments. The properties of the experimental material were typical of the three minerals. They represent the reference to which the interlayered systems were compared.

Table III. Properties of montmorillonite, vermiculite and chlorite used in study of interlayers.

Materials	Basal Spacings (\AA)				C. E. C. (me/100g)
	Ca solv	K	K 300° C	K 550° C	
Montmorillonite (2μ)	17.3	11.9	10.1	9.9	108
Vermiculite (50 to 2μ)	15.2	10.3	10.2	10.1	152
Chlorite (50 to 2μ)	14.2	14.2	14.2	14.2	1

The hydration effects of divalent cations, particularly calcium and magnesium, upon the basal spacings of montmorillonite and vermiculite have been known for some time. However, the hydration effects of potassium upon the basal spacings were not appreciated at the time this study was initiated, and therefore no attempts were made to control the relative humidity during X-ray analysis. Sayegh et al. (1965) recently reported that the basal spacings of the K-saturated montmorillonites change with different relative humidities. Unlike montmorillonite, the K-saturated vermiculites show very little hydration effects and do not exhibit the 11-12 Å spacing. The reader, therefore, needs to be aware of the hydration problem before he proceeds to interpret the interlayer data. For example, peaks between 11.9 and 12.1 Å recorded for K-saturated and interlayered montmorillonite may not necessarily indicate the presence of interlayers. Similar spacings were recorded for K-montmorillonite prior to interlayer formation when no attempts to control the relative humidity were made. In order to avoid any ambiguity during interpretation of X-ray data, only K-saturated diffraction patterns after heating to 300° C and 550° C will be shown for montmorillonite.

FORMATION OF HYDROXY- Al , Fe , AND Mg INTERLAYERS IN MONTMORILLONITE AND VERMICULITE

General

Hydrolysis and polymerization of aluminum and iron are believed to be involved in the formation of chloritic intergrade minerals in soils. The importance of iron in interlayer formation probably has been under-emphasized since almost any occurrence of chloritic intergrades in soils has been considered to contain aluminum hydroxy interlayers. Brown (1953) reported a mineral in some English soils which gave a 14 \AA peak upon glycerol solvation and could not be collapsed to 10 \AA after leaching with either ammonium or potassium solutions. The thermal stability of the mineral was intermediate between vermiculite and chlorite. The 060 lines indicated that the mineral in question and the illite in the parent material were dioctahedral. He speculated that the interlayer ion present was aluminum in a non-exchangeable form. The type of structure and related properties led Brown to designate this chloritic intergrade as the dioctahedral analogue of vermiculite. Jeffries et al. (1953) and Rolfe and Jeffries (1953) also reported the occurrence of minerals possessing properties similar to those described by Brown in the soils of the Appalachian Piedmont and central New York. These minerals were designated as "hydrated mica," "mica intermediate"

or "chlorite" depending on the behavior after K saturation and heating. Definite evidence has been obtained for the occurrence of intergrade minerals in soils of various regions of the United States (Rich and Obenshain, 1955; Klages and White, 1957; Tamura, 1956, 1957, 1958; Sawhney, 1958; Tamura and Swanson, 1954; Weed and Nelson, 1962; Hathaway, 1955; Singleton, 1966; and many others). The occurrence of a "dioctahedral clay vermiculite" in a Spanish soil from a semi-arid climate has also been reported (Martin Vivaldi and Camazano, 1961).

There also has been a considerable amount of work dealing with synthetic hydroxy-Al interlayers in montmorillonite and vermiculite. Sawhney (1958, 1960) produced synthetic aluminum interlayers in montmorillonite and vermiculite by washing with an AlCl_3 -NaOH solution of pH 5.0. In other experiments he treated standard clay minerals with 1 N AlCl_3 and then raised the pH to 5.0. Slaughter and Milne (1960) prepared aluminum hydroxide-montmorillonite complexes using aluminum nitrate and sodium hydroxide solutions. Although the aluminum hydroxide complex was fairly stable against collapse, the expansion of the lattice occurred upon either water or ethylene glycol treatment. Methods, basically similar to those just mentioned, have been employed by other investigators who studied various aspects of the formation and stability of hydroxy-Al interlayers in standard clay minerals (Rich, 1960; Shen

and Rich, 1962; Carstea and Harward, 1963; Barnishel and Rich, 1963; Hsu and Bates, 1964a; Barnishel, 1965). Another approach to the formation of aluminum interlayer involved drying an appropriate amount of Al-saturated clay with or without addition of salts (Rich and Obenshain, 1955; Coleman et al., 1960; Carter et al., 1963; Carstea, 1965).

Despite the large number of papers written on this subject, some aspects related to formation and stability of Al-interlayer are not completely understood. For example, the formation of Al-interlayer in acid conditions has been particularly emphasized while less attention has been given to the formation of interlayers in neutral and alkaline conditions. Data on the formation of aluminum interlayers in montmorillonite as contrasted to vermiculite over a long period of time are not yet available.

The role of iron in hydroxy-interlayer formation has been probably under-emphasized. Theoretically, iron can co-precipitate with aluminum to form chloritic minerals (Brydon et al., 1961). Norrish and Taylor (1961) reported that about 15 percent of iron in a natural soil goethite was substituted by aluminum. There are several reasons which could explain the under-emphasis of iron with respect to formation of hydroxy-iron interlayers. Among these only two will be briefly discussed below:

1. The lack of sufficient chemical data on extracts from

treatments for interlayer removal is a main reason which explains the present status of knowledge about iron interlayers. Wherever these chemical data were obtained, iron in addition to aluminum or magnesium was found to be a component of the hydroxy interlayer (Tamura, 1956; Weed and Nelson, 1962; Singleton, 1966).

2. The use of the same chelating reagents, namely, citrate for both cleaning procedures and interlayer removal, is another factor which contributed to the present underestimation as to the role of iron in interlayer formation. Sodium citrate, often used in cleaning or removal treatments, does not exhibit an absolute specificity for either aluminum or iron. Sawhney (1960) removed synthetic aluminum interlayers from montmorillonite and vermiculite by using sodium citrate. Tamura (1956) extracted 6.23 percent Al_2O_3 and 9.39 percent Fe_2O_3 from the coarse clay fraction of the Paxton soil which was thought to contain aluminum interlayer by using the dithionite-citrate procedure. Following this treatment, the 14 Å component showed a decrease in basal spacing upon K saturation. The dithionite-citrate treatment removed 3.01 percent Al_2O_3 and 11.1 percent Fe_2O_3 from a 14 Å intergrade mineral of Holyoke loam (Tamura, 1958). These examples indicate that sodium citrate is effective to varying degrees in removing both aluminum and iron interlayers. The iron removal treatment by using buffered dithionite-citrate may also remove appreciable amounts of Al.

A number of investigators have mentioned the possibility of iron fixation in the interlayer space of the expansible clay minerals (Brown, 1954; Tamura, 1956; Dixon and Jackson, 1959; Sawhney, 1960). Singleton (1966) and Weed and Nelson (1962) found that hydroxy iron was indeed a significant component of the chloritic intergrades in some soils from Oregon and North Carolina, respectively. Rich and Obenshain (1955) considered the possibility of iron in addition to aluminum forming interlayers in a chloritic intergrade of a Red Yellow Podzolic soil. However, they were unsuccessful in synthesizing such an interlayer by subjecting a Fe-saturated vermiculite to several drying and wetting cycles. Carstea and Harward (1963) were successful in forming synthetic hydroxy-iron interlayer in montmorillonite by using either a titration or drying method. Iron interlayer in montmorillonite was also synthetically formed by Coleman et al. (1964). Carstea (1965) also reported the formation of hydroxy-iron interlayer in vermiculite.

Hydroxy-Mg interlayer formation and occurrence in soils has received relatively little attention. From the standpoint of solubility products of magnesium hydroxide, formation of chloritic intergrades with magnesium in interlayer space would be expected to occur in soils (Bryden et al., 1961). These interlayers are more likely to occur in saline and alkaline soils and also in sediments derived from basic igneous rocks with imperfect drainage. According to

Jackson (1959), the association of hydroxy-Mg interlayers with montmorillonite led to the formation of secondary chlorite in the Dark Magnesium Clay soils of Hawaii and a Grumosol (Ladybrook series) of Queensland, Australia. Later, Jackson (1960, 1962, 1964) reiterated the hypothesis concerning the formation of magnesium interlayers in expansible clay minerals. Singleton (1966, p. 76) determined magnesium in chemical extracts from interlayer removal treatments. He concluded that a chloritic intergrade mineral from the Lookout soil series of Oregon contained hydroxy-Mg, in addition to Fe and Al.

The precipitation of $\text{Mg}(\text{OH})_2$ between layers of montmorillonite was successfully accomplished by Caillère and Hénin (1949), Youell (1951, 1960), Slaughter and Milne (1960), and Carstea and Harward (1963). Carstea (1965) prepared hydroxy magnesium interlayer in vermiculite. Different people have added various bases in conjunction with MgCl_2 in order to prepare hydroxy-magnesium interlayers. Carstea and Harward (1963) studied the influence of pH, salt concentration, and drying upon hydroxy-Mg interlayer formation. Unlike aluminum and ferric iron interlayers, magnesium interlayer was produced only in alkaline environments.

Experimental Methods

Formation of Interlayers

A titration method (Carstea, 1965) was used for the preparation of various interlayers. The method is essentially similar to that of Slaughter and Milne (1960). In addition to the constant amount of Al, Fe, and Mg chloride, different amounts of NaOH were added to clay suspensions to give a wide range of hydroxyl:cation ratio and also a wide pH range. This ratio (on a milliequivalent basis) will be designated as $\frac{\text{OH}}{\text{cation}}$ solution ratio throughout this study. The samples were studied after different periods of equilibration of up to one year.

Study of Interlayer Formation

Among other factors, pH is recognized to be important with respect to intergrade mineral formation. Decrease in solution pH during synthetic interlayer preparation has been interpreted as being indicative of hydrolysis and subsequent formation of basic polymers. The pH values were, therefore, recorded after one minute, ten days, six months, and one year by using a Beckman model G pH meter. The readings were taken when the needle was stabilized. The time required to obtain the readings was short for

acid samples, and it increased for samples from alkaline conditions.

The cation exchange capacities (CEC) are reduced by fixation of hydroxy-Al polymers in the interlayer space of expansible clay minerals. The more completely the interlayer space is filled with hydroxy polymers, the more the CEC is reduced. Therefore, the exchange capacity measurements give a good indication of the degree of hydroxy interlayer formation. Conversely, one expects an increase in CEC when the interlayers are removed and the sites are rendered free for exchange. Exchange capacity measurements were made on the interlayered samples equilibrated for six months and one year. These values are compared with the exchange capacity data of the untreated clay minerals. They are correlated with X-ray measurements to obtain information about interlayer formation or dissolution. The strong influence of time factor upon hydroxy interlayer formation was not fully known when the study was initiated. X-ray measurements revealed that significant changes in basal spacings occurred between ten days and six months. It is now apparent that the exchange capacity data after ten days would have been helpful in supporting the X-ray measurements.

Finally, X-ray diffraction patterns were recorded after ten days, six months, and one year. The fixation of hydroxy-Al, Fe, or Mg in the interlayer space of montmorillonite or vermiculite prevents these minerals from exhibiting their characteristic basal

spacings following various treatments (Table III). The presence of hydroxy interlayers first restricts the collapse of basal spacings. As the amount and stability of hydroxy interlayers increase, the resistance to collapse also increases. If the amount of interlayer is sufficient, the expansion on solvation may also be affected. In the case where expansion on solvation does not occur and the lattice does not collapse on heating, the mineral exhibits the properties of chlorite.

Results

Hydroxy-Al Interlayer in Montmorillonite

The effects of pH and time on the formation of synthetic hydroxy-Al interlayer in montmorillonite are shown in Figure 1. This figure gives only the X-ray diffraction patterns of the interlayered montmorillonite after Ca-saturation plus solvation and K-saturation plus 300° C. An almost constant basal spacing of about 15 Å was measured for the unsolvated Ca-saturated samples. The basal spacings after K-saturation varied as a function of the atmospheric relative humidity. Finally, the X-ray diffraction patterns recorded after K-saturation plus 550° C, generally, did not provide any significant information over the 300° C heating treatment. For these reasons, data obtained after Ca- and K-saturation treatments

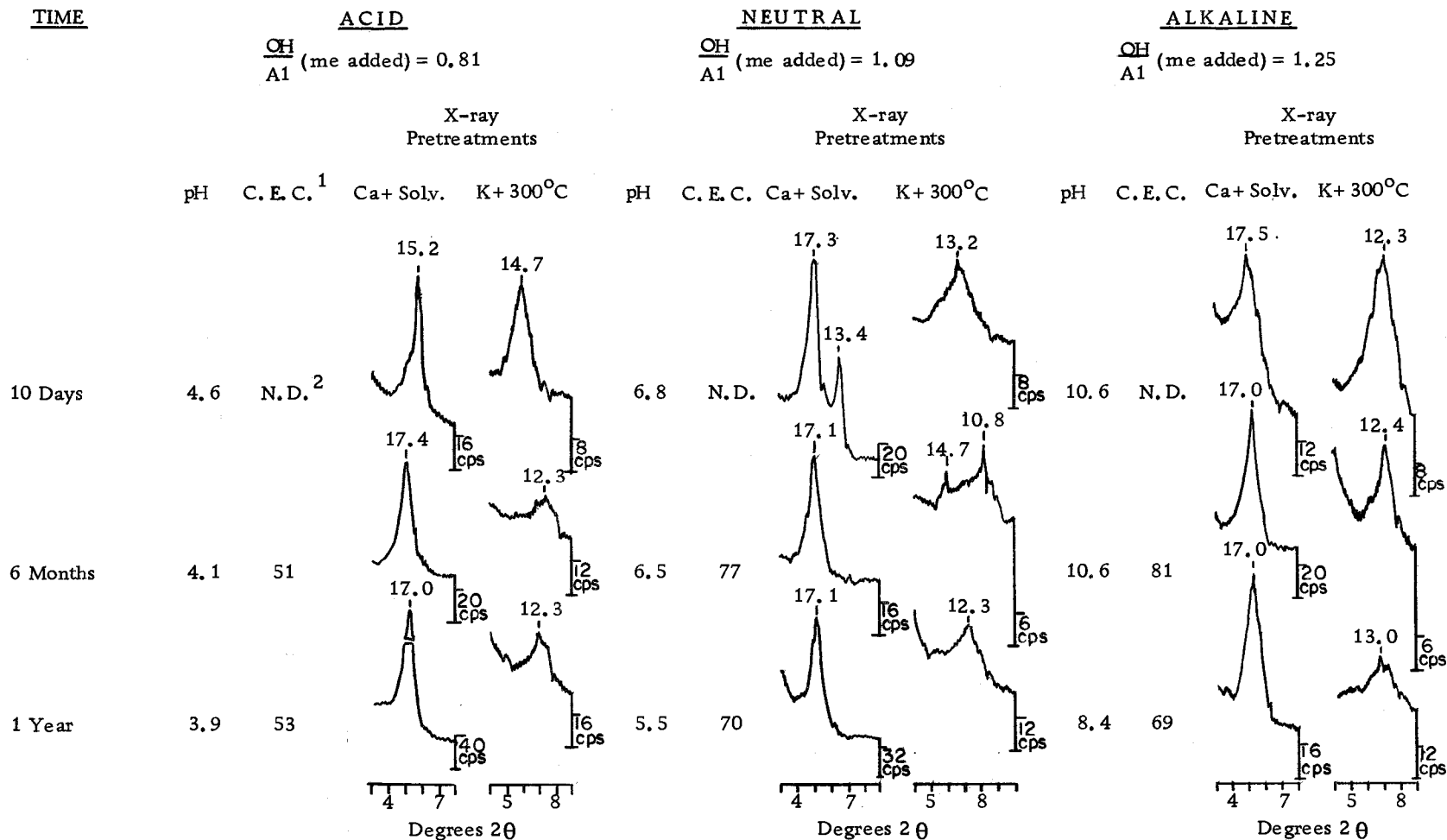


Figure 1. Influence of time and acidity on the formation of hydroxy-Al interlayer in montmorillonite.

as well as after potassium plus 550° C are not shown here. The amount and stability of interlayer, as used throughout this study, were estimated by comparing the basal spacings and CEC of chloritic intergrades with similar properties of typical montmorillonite and vermiculite.

The resulting material from acid medium after ten days of equilibration exhibited the essential characteristics of chlorite (see Table III). Solvation with ethylene glycol produced practically no expansion of the lattice and the 14 Å peak persisted after heating to 300° C and even to 550° C (not shown). The interlayer exhibited only a partial stability with time. After an equilibration for six months, the material regained its full expansion on solvation, but it exhibited only a partial collapse after K saturation plus heat. The CEC of the interlayered sample represented about 50 percent of the original CEC of montmorillonite and indicated that almost half of the exchangeable sites were satisfied or blocked by the positively charged aluminum polymers. No further visible changes in the basal spacings and exchange capacity were recorded after one-year equilibration. The degradation of interlayer with time, particularly after six months, requires a brief comment. Based on findings reported by Barnishel and Rich (1963) and Barnishel (1965), it is speculated that gibbsite and/or amorphous $\text{Al}(\text{OH})_3$ were formed from hydroxy-Al polymers. The new products presumably precipitated external to

the crystal lattice. As a result of this interlayer depletion, some of the once-blocked negative sites became available for exchange. Furthermore, the material responded relative easily to different treatments during X-ray investigation. The dissolution of interlayer with time was accompanied by decreases in pH values.

A moderate amount of interlayer was produced in neutral conditions after ten days. The X-ray diffraction patterns indicated the presence of a dominant expandable phase in addition to a small non-expandable phase. The interlayered material exhibited a fairly high resistance to collapse after 300° C heating. However, after six months of equilibration, all the material expanded on solvation to about 17 Å. The chloritic intergrade collapsed upon heating with less difficulty. This behavior again suggested that some aluminum polymers moved out from the interlayer space. One-year equilibration produced no further changes as far as the expansion on solvation was concerned. Yet, the collapse upon heating and CEC indicated that some hydroxy interlayer was formed during the intervening period. The decrease in pH between six months and one year is related to formation of gibbsite, perhaps, in addition to formation of interlayers.

The amount of interlayer formed in alkaline conditions after ten days was lower than the amount produced in other media. The expansion on solvation of the resulting material was similar to that

of a typical montmorillonite. Still, the partial collapse after K-saturation plus 300°C indicated the presence of a chloritic intergrade. The basal spacings showed practically no changes after six months. However, the resistance to collapse after K-saturation (not shown) and K-saturation plus 300°C increased slightly after one year as compared to six months. The increase in basal spacings with time, along with a decrease in CEC again suggested some interlayer formation. As in the case of intermediate conditions, a significant decrease in pH occurred. This could be related to formation of gibbsite in addition to formation of interlayers.

Hydroxy-Al Interlayer in Vermiculite

Figure 2 shows the formation of aluminum interlayers in vermiculite with respect to time and acidity. Only the X-ray diffraction patterns recorded after K-saturation and K-saturation plus 300°C are given here, since solvation with ethylene glycol produced no expansion beyond 15 \AA and heating to 550°C always collapsed the lattice in the vicinity of 10 \AA .

A moderate to high amount of aluminum interlayer was produced in acid medium after ten days of reaction as indicated by the resistance to collapse following K-saturation. The relative low thermal stability of interlayer was revealed by heating to 300°C which collapsed the crystal lattice to a marked extent. The basal

TIME

ACID

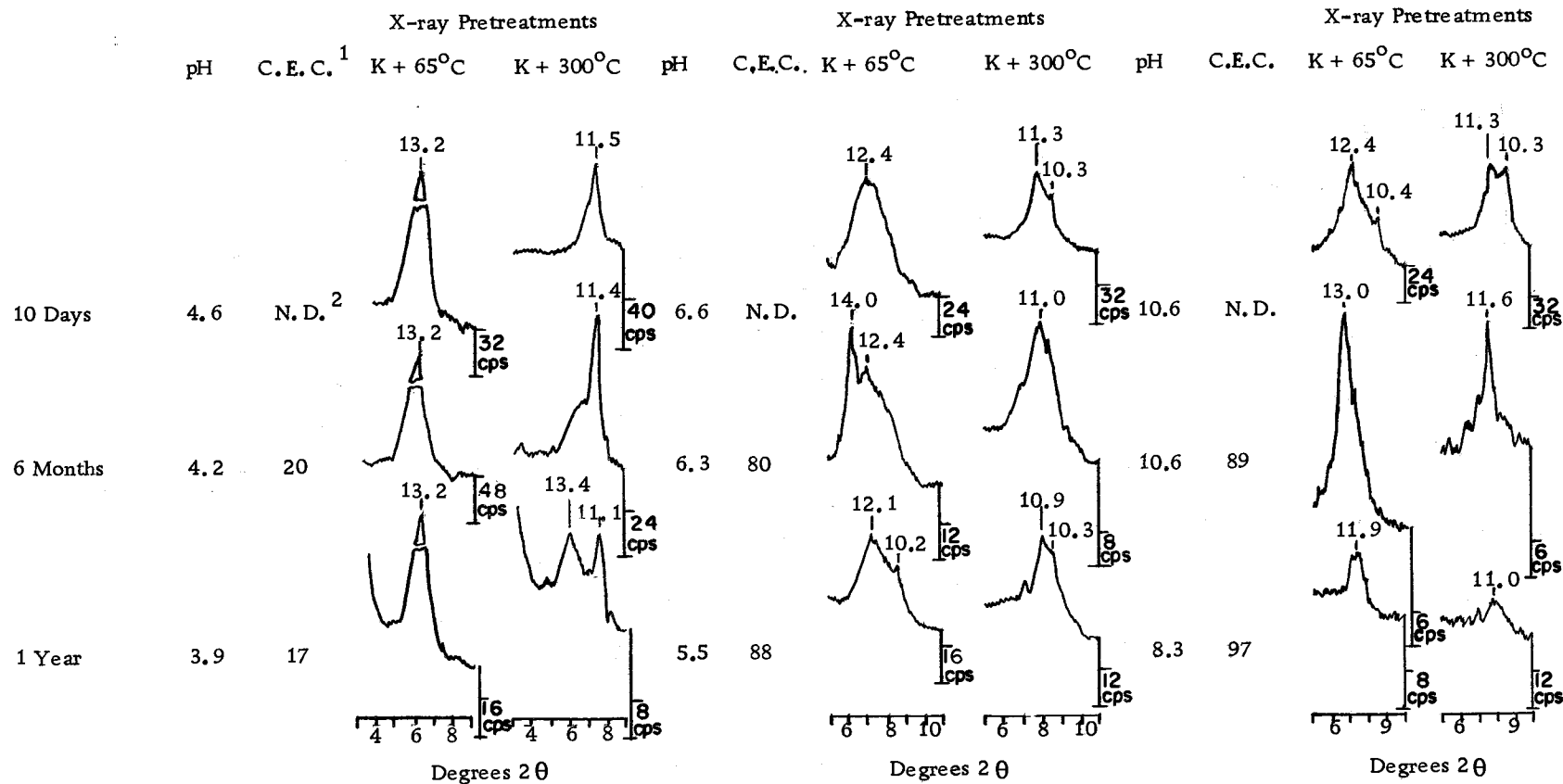
NEUTRAL

ALKALINE

$\frac{OH}{Al}$ (me added) = 0.81

$\frac{OH}{Al}$ (me added) = 1.00

$\frac{OH}{Al}$ (me added) = 1.25



¹ C.E.C. = cation exchange capacity, me/100 g.

² N.D. = not determined

Figure 2. Influence of time and acidity on the formation of hydroxy-Al interlayer in vermiculite.

spacings of the K-saturated material showed no visible changes after six months and one year. However, heating to 300°C clearly indicated that some interlayer has been formed with time particularly after one year. As a matter of fact, more than half of the interlayered material displayed a high resistance to collapse upon heating to 300°C as indicated by the 13.4 \AA peak. Like montmorillonite, the formation of interlayer with time in vermiculite occurred with a decrease in pH values. The exchange capacity of chloritic intergrade represented about 13 percent of the original CEC of vermiculite. In this respect, the hydroxy-Al interlayer in vermiculite was more effective in reducing the CEC than the interlayer formed in montmorillonite. The low CEC (20 meq/100 g) of the interlayered material, measured after six months, seems to be at variance when compared to a relatively low thermal stability of the interlayer. This discrepancy is only apparent if one takes into account the physical distribution of aluminum polymers in the interlayer space.

Data of this study suggest that the first polymers were presumably fixed in the very proximity of the external edges. As a result of this steric arrangement of polymers, the penetration of exchangeable cations toward the negative sites was almost completely blocked. This situation resulted in a low CEC in spite of the presence of exchange sites which did not have adsorbed polymers. On the other hand, the sparse

distribution of islands of polymers in the interlayer space, primarily close to the edges, was presumably the reason for the relatively lower thermal stability than one may expect from the CEC value.

The initial amount of interlayer formed in vermiculite in neutral conditions was lower than in acid medium. The amount of interlayer increased after six months as indicated by an increase in basal spacings, particularly after K-saturation plus 65° C. The interlayer then showed a decrease after one year, as compared to six months, as indicated by lattice collapse. The pH showed only a slight decrease during the first six months when some interlayer was formed. However, a significant decrease in pH was recorded after the next six months, even though a dissolution of interlayer took place.

Still less interlayer was initially formed in alkaline conditions than in acid medium as indicated by the degree of collapse. The amount of interlayer increased after six months and then decreased after one year as revealed by changes in basal spacings. The pattern of pH changes was quite similar to that observed for the system from neutral conditions.

Hydroxy-Fe Interlayer in Montmorillonite

The results with synthetic hydroxy-Fe interlayers in montmorillonite are given in Figure 3. The iron interlayers did not

TIME

ACID

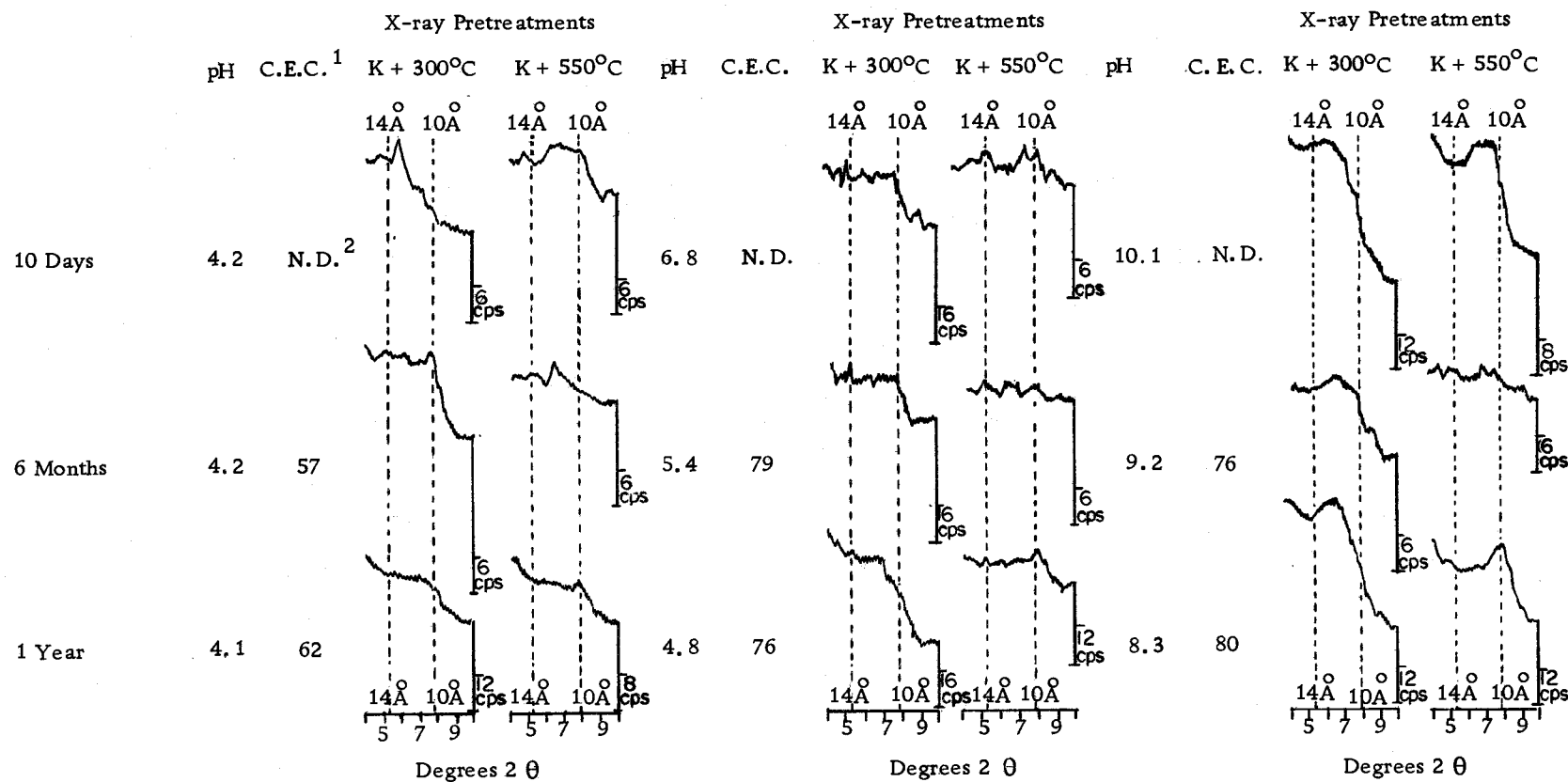
$$\frac{\text{OH}}{\text{Fe}} (\text{me added}) = 0.88$$

NEUTRAL

$$\frac{\text{OH}}{\text{Fe}} (\text{me added}) = 1.00$$

ALKALINE

$$\frac{\text{OH}}{\text{Fe}} (\text{me added}) = 1.25$$



¹ C.E.C. = cation exchange capacity, me/100 g.

² N.D. = not determined

Figure 3. Influence of time and acidity on the formation of hydroxy-Fe interlayer in montmorillonite.

prevent a normal expansion on solvation of the clay matrix and, consequently, the X-ray patterns following solvation are not shown. The diffraction patterns of the Fe-interlayered material showed high backgrounds and broad peaks with a strong tendency to form plateaus. The scattering effects due to Fe fluorescence and the relatively poor crystallinity of iron interlayers themselves account, at least in part, for the appearance of the above features. The same features have been reported by Carstea and Harward (1963) and by Coleman et al. (1964). Coleman et al. (1964) speculated that iron interlayer was preferentially deposited on the edges and terminal surfaces, whereas hydroxy-Al interlayer was primarily deposited in the interplanar space. The broadness of X-ray diffraction peaks renders the interpretation of the results quite difficult, regardless of the causes which may determine it.

A moderate amount of hydroxy-iron interlayer was formed in all conditions of acidity after ten days. The material formed in acid medium exhibited a relatively high resistance to collapse after heat to 300° C and 550° C. After six months, some dissolution of interlayer took place as inferred from the appearance of a 10 Å shoulder after heating to 300° C. The 550° C heat treatment also suggested a slight dissolution of interlayer after one-year equilibration. The pH remained almost constant during the entire period of reaction.

The iron interlayer formed in neutral conditions showed

practically no change after six months compared to that present initially. It is rather difficult to make a precise assessment as to the formation or dissolution of interlayer after one year when compared to either six months or ten days. On one hand, heating to 300°C suggested that some interlayer was formed; on the other hand, the degree of collapse after heating to 550°C suggested some dissolution of iron interlayer. The pH values showed equal decreases of 0.6 pH units after six months and one year.

It is probable that more iron interlayer was formed in alkaline environment than in acid medium. This trend appears to be in contrast with aluminum interlayer which decreased in amount toward alkaline environment. Some dissolution of interlayer took place after one year as compared to ten days and six months. This is indicated by the degree of collapse of the chloritic intergrade following heating treatments. Again, the pH values showed decreases of 0.9 pH units after six months and one year.

Hydroxy-Fe Interlayer in Vermiculite

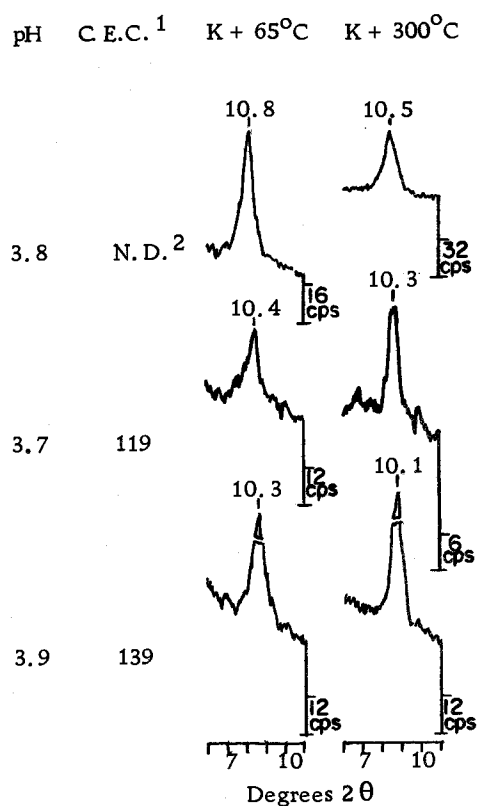
The influence of pH and time on the formation of iron interlayer in vermiculite are shown in Figure 4. In contrast to montmorillonite, the diffraction patterns of iron interlayered vermiculite exhibited relatively sharp and definite peaks. The data show: (1) decrease in the amount of interlayer with time which was more apparent for

TIME

ACID

$\frac{\text{OH}}{\text{Fe}}$ (me added) = 0.88

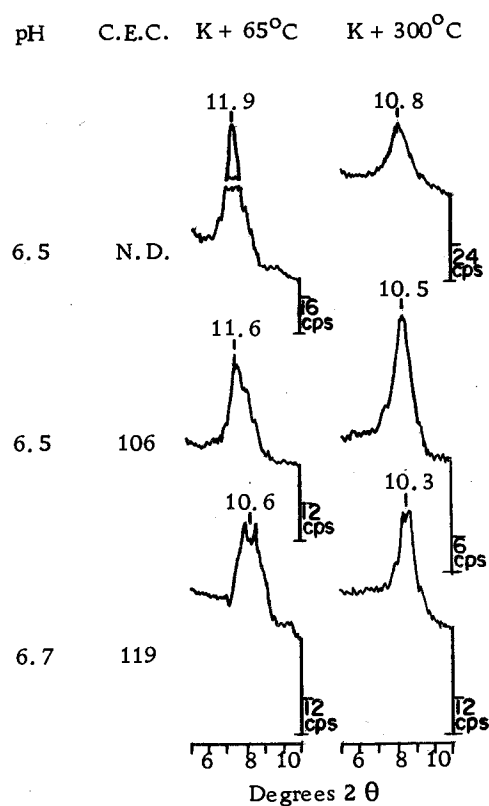
X-ray Pretreatments



NEUTRAL

$\frac{\text{OH}}{\text{Fe}}$ (me added) = 1.00

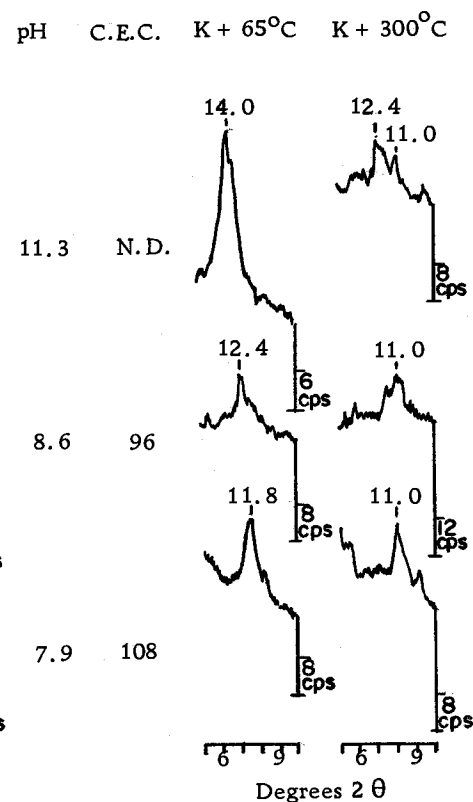
X-ray Pretreatments



ALKALINE

$\frac{\text{OH}}{\text{Fe}}$ (me added) = 1.25

X-ray Pretreatments



¹ C.E.C. = cation exchange capacity, me/100 g.

² N.D. = not determined

Figure 4. Influence of time and acidity on the formation of hydroxy-Fe interlayer in vermiculite.

alkaline conditions; (2) increase in interlayer formation by decreasing acidity (raising pH); (3) less interlayer formation in vermiculite than montmorillonite.

Hydroxy-Mg Interlayer in Montmorillonite

Previous studies by Carstea and Harward (1963) have shown that unlike aluminum and iron interlayers which formed to various extents in both acid and alkaline conditions, magnesium interlayer began to form only at pH of about 10 or higher. Consequently, in this study only alkaline media were investigated. Figure 5 gives the diffraction patterns and exchange capacity data recorded as a function of time and alkalinity for magnesium interlayered montmorillonite. With sufficient addition of NaOH to give a pH of 10.6 (after ten days), there was a reduction in the degree of expansion on solvation and a very high resistance to collapse after heating to 300° C and even after heating to 550° C (not shown). After six months, all of the sample expanded to 17 Å and it showed only a partial resistance to collapse after heating to 300° C. No significant changes in either basal spacings or CEC were observed after one-year equilibration as compared to six months. Based on findings reported by Slaughter and Milne(1960) and by analogy with Al and Fe interlayers, it is speculated that $Mg(OH)_2$ was formed from hydroxy-Mg interlayer and deposited external to the clay interplanar surfaces. The precipitation of

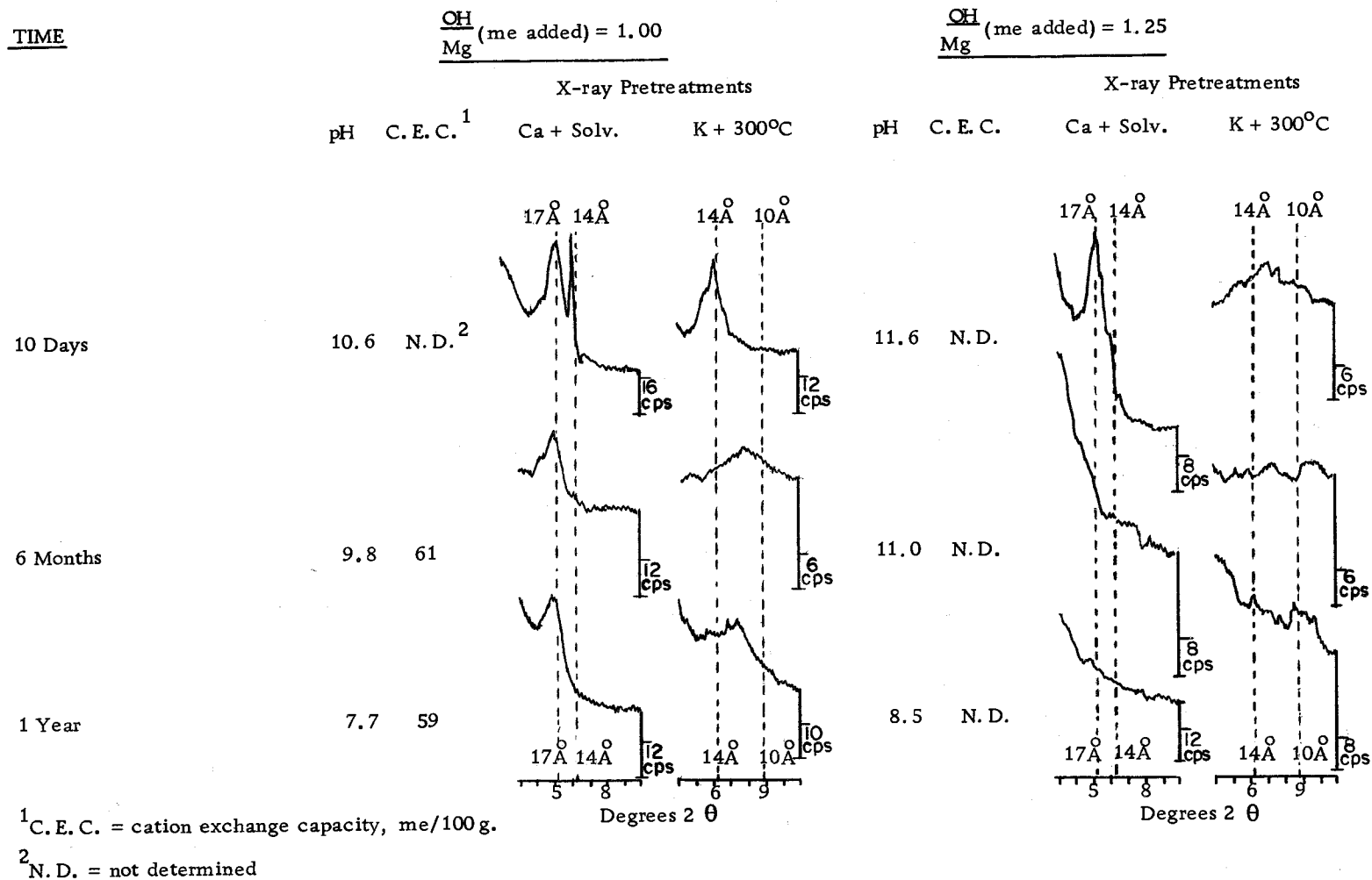


Figure 5. Influence of time and acidity on the formation of hydroxy-Mg interlayer in montmorillonite.

$\text{Mg}(\text{OH})_2$ was, therefore, reflected in a decrease in the amount of interlayer with time. The pH decreased with time, particularly between six months and one year.

Less interlayer was formed at the higher pH (11.6) after ten days. However, the crystalline structure of clay matrix was almost completely destroyed after six months and one year. The material was nearly amorphous to X-ray diffraction. The decrease in pH followed a pattern similar to that observed for Mg-interlayered montmorillonite which had an initial pH of 10.6; that is, the significant decrease occurred between six months and one year.

Hydroxy-Mg Interlayer in Vermiculite

Like magnesium interlayers in montmorillonite, the Mg-hydroxy interlayer in vermiculite was formed only in alkaline conditions (Figure 6). At pH 9.7 (after ten days) the chloritic intergrade exhibited a high resistance to collapse, particularly after K-saturation without heat. Some dissolution of interlayer took place after six months as indicated by the 11.8 \AA shoulder for K + 65°C and by collapse after K-saturation plus 300°C . In spite of the persistence of 14 \AA peak after K-saturation, the CEC was relatively high. This suggests that the density of interlayer islands in the interplanar space was relatively low and, consequently, only a small part of the negative sites were neutralized by the interlayer. After one year,

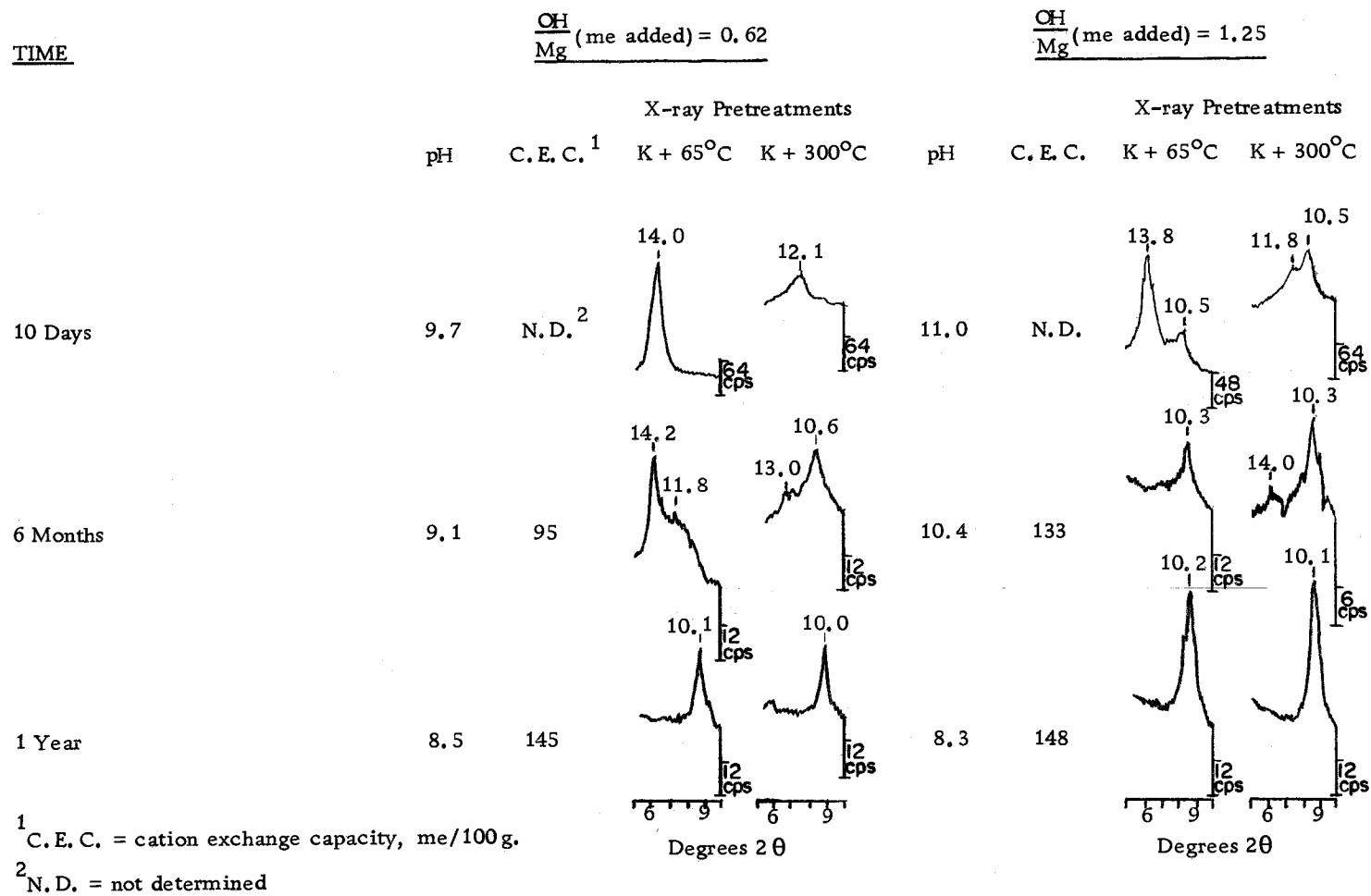


Figure 6. Influence of time and acidity on the formation of hydroxy-Mg interlayer in vermiculite.

practically no interlayer was left in vermiculite as indicated by the ease of collapse to 10 \AA . The pH values showed equal decreases after six months and one year. The amount of interlayer formed at pH 11.0 (after ten days) was lower than at pH 9.7. The interlayer showed a marked decrease after six months and further, a slight decrease after one year. The pH also decreased with time, particularly during the equilibration between six months and one year.

STABILITY OF HYDROXY-AL, Fe, AND Mg INTERLAYERS
IN MONTMORILLONITE AND VERMICULITE
TO SEQUENTIAL TREATMENTS

Problem

Since the discovery of the crystallinity of the fine-grained inorganic material in soils, efforts have been made to segregate and concentrate these minerals for further studies. The separation of crystalline from amorphous soil colloids without alteration of the crystalline structure itself is a challenging problem to soil scientists. The destruction of organic and inorganic binding materials is regarded as a prerequisite to dispersion and segregation of size fractions. There is a great variability among the soil investigators with respect to kind of reagents used for dispersion prior to size separation. Among others, these reagents include NH_4OH , NaOH , cold or boiling Na_2CO_3 , $\text{Na}_2(\text{PO}_3)_6$ and $\text{Na}_4\text{P}_2\text{O}_7$. These reagents are supposed to remove some of the amorphous coatings of aluminum and silicon oxides, to Na-saturate the colloid, and to promote dispersion.

There is also a considerable variability among investigators with respect to procedures which are used for removal of free iron oxides. Some of the reagents which have been proposed for removal of free iron compounds include hydrogen sulphide and oxalic acid

(Drosdoff and Truog, 1935), tartrates (Dion, 1944), dithionites (Deb, 1950; Mackenzie, 1954), and dithionite-citrate (Aguilera and Jackson, 1953; Jackson, 1956; Mehra and Jackson, 1960). These methods were initially designed to selectively remove the "free" iron oxides, namely, the iron which is not a part of the crystal lattice of silicate clays. Iron removal treatments, however, removed aluminum oxides in addition to iron oxides as reported by some investigators (Mackenzie, 1954; Tamura, 1956; Singleton, 1966; and others). Aguilera and Jackson (1953) stated that any method designed for iron removal has some destructive effects upon the layer silicates as indicated by a loss or gain in exchange capacity. However, the iron removal treatments facilitate dispersion, decrease X-ray absorption, and improve the orientation of material on microslides. Harward and Theisen (1962) and Harward et al. (1962) showed that X-ray diffraction patterns of three Oregon soils revealed more expansion and collapse after various dispersion and iron removal treatments than the samples which were dispersed in water. They interpreted these behavioral changes of clays as due to a partial removal of poorly crystalline hydroxy interlayers in addition to the removal of amorphous coatings. Changes in basal spacings following different chemical pretreatments were also reported by other investigators (Singleton, 1966; Beutelspacher, 1964; Pawluk, 1962). Sharp diffraction peaks obtained after some chemical

treatments may not reflect the true mineral suite which occurs in the natural environment.

The stability of both natural and synthetic hydroxy interlayers is of great practical and theoretical importance. Different studies on the interlayer stability have provided information about the weathering intensity and about the nature and properties of chloritic intergrades.

The methods used for interlayer removal vary widely from investigator to investigator. Brown (1953) succeeded in collapsing a natural 14 \AA clay mineral to 10 \AA by boiling it in KOH-KCl solution for five hours. Rich and Obenshain (1955) used either 1 N KCl-0.1 N HCl solution or 1 N NH_4F to remove the aluminum interlayer from a chloritic intergrade. They further stated that prolonged boiling in the NH_4F solution had a destructive effect upon the crystal structure of clay minerals. Recently, Rich (1965) proposed the use of a solvent composed of 0.4 N NH_4F , 0.1 N HCl, N NH_4Cl for removal of hydroxy-Al interlayers. He reported that this solvent does not have an adverse effect upon dioctahedral mica and vermiculite matrices.

Tamura (1956, 1957, 1958) considered the use of 1 N NH_4F to be too severe and, consequently, he avoided it. He used instead sodium citrate or dithionite-citrate to remove different hydroxy interlayers. An interlayer vermiculite from the Paxton soil

collapsed with less difficulty after a dithionite-citrate treatment (Tamura, 1956). On the other hand, the dithionite-citrate treatment did not alter the basal spacings of a 14 \AA chloritic intergrade formed in a montmorillonite matrix (Tamura, 1957). However, this interlayer was removed by a three-hour extraction with sodium citrate (pH 7.3). Tamura concluded that the interlayer formed in montmorillonite was more stable to dithionite-citrate treatment than the interlayer formed in vermiculite. Tamura's findings indicated that neutral sodium citrate was effective to various degrees in removing interlayer Al and Fe. The effectiveness in interlayer removal was probably dependent upon the amount, kind, and crystallinity of interlayers and kind of clay matrix. Sawhney (1958, 1960) also employed sodium citrate to remove natural and synthetic aluminum interlayers. No differences in stability were observed between aluminum interlayers in montmorillonite and vermiculite. Hydrochloric acid treatment has been successfully used by Caillère and Hénin (1949) to remove synthetic magnesium interlayers formed in montmorillonite. Likewise, Shen and Rich (1962) removed hydroxy-Al interlayer from a montmorillonite by repeated HCl washings. Coleman and Thomas (1964) removed most of the synthetic hydroxy iron interlayer from a montmorillonite system by leaching with 1 N KCl and titration with NaOH. Rich (1960) used NaCl and NaOH to remove hydroxy-aluminum interlayer formed in a vermiculite. Dixon and

Jackson (1959, 1962) preheated samples at 400° C for four hours and then boiled these samples in 0.5 N NaOH for 2.5 minutes in order to remove interlayers from the intergrade minerals.

Hashimoto and Jackson (1958) suggested procedures for differential dissolution of the various amorphous colloids associated with silicate minerals.

It is apparent that a number of different treatments may be used for the removal of hydroxy interlayers. Any treatment which results in the displacement, chelation, or formation of a more stable phase may be expected to have some effect upon removal of the hydroxy polymers from interplanar surfaces. In view of this, and because of implications to methodology, it was decided to use some of the chemical treatments more commonly employed in dispersion and segregation procedures for soil analysis. Further, the treatments were selected to provide a sequence of increasing severity in order to evaluate differences in stability.

Experimental Methods

Preparation of Samples for Sequential Treatments

Subsamples of clay size montmorillonite and silt size vermiculite which had been aged for six months under different conditions of acidity were withdrawn from the reacting Erlenmeyer flasks.

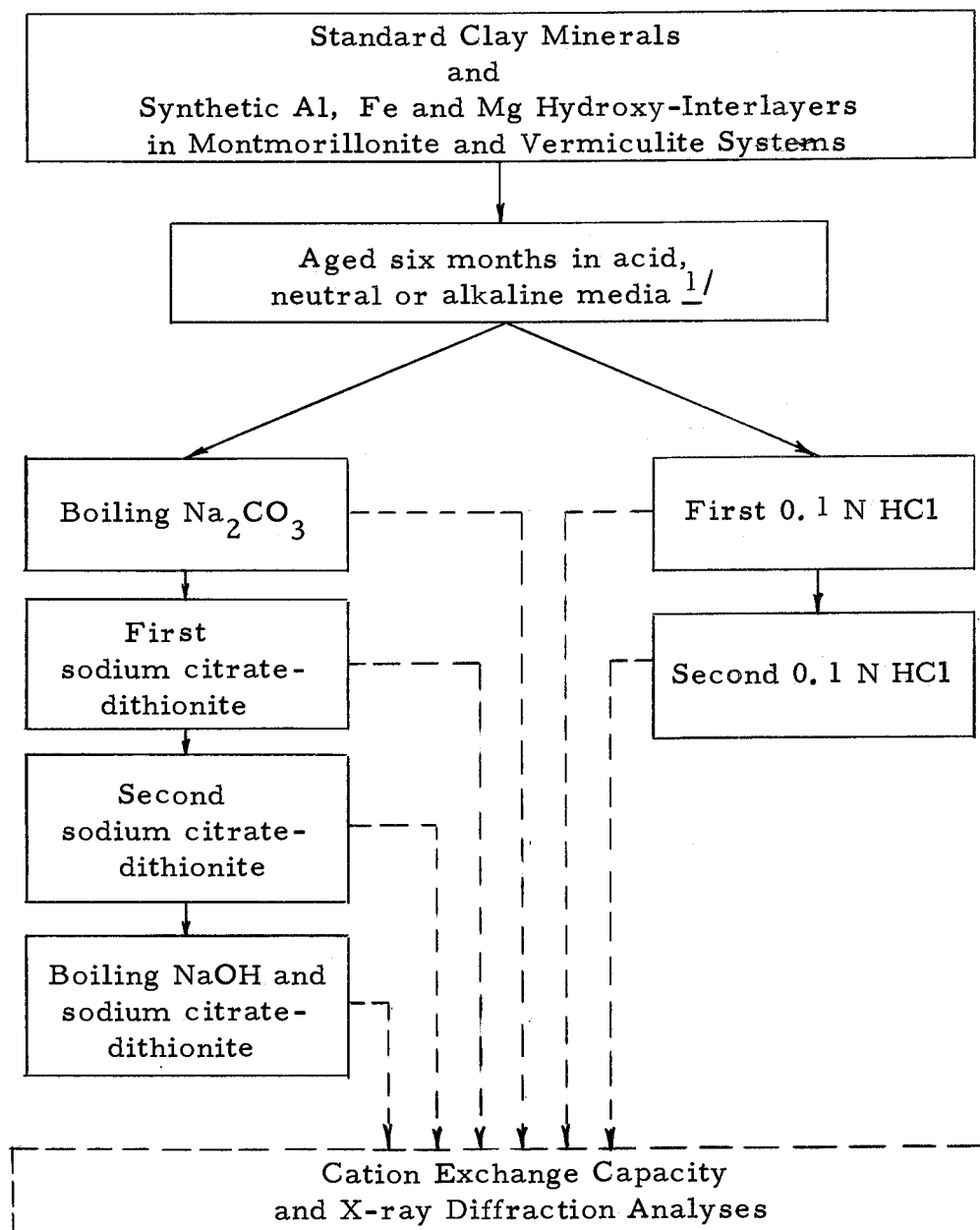
These samples were then subjected to a series of progressive dissolution treatments designed to test the stability of different synthetic interlayers (left branch of Figure 7). Standard clay minerals were similarly treated in order to assess the extent to which the clay matrices were affected by the selected treatments.

Boiling 2 Percent Sodium Carbonate

The boiling Na_2CO_3 treatment was essentially as described by Jackson (1956, p. 73). Sodium saturated samples were transferred to stainless steel beakers and boiled for five minutes in 2 percent Na_2CO_3 solution. The residue was washed twice with cold 2 percent Na_2CO_3 and twice with distilled water. A small subsample was withdrawn for exchange capacity and X-ray analyses.

Buffered Sodium Citrate-Dithionite

Following boiling sodium carbonate, the samples were treated for removal of free iron oxides (Jackson, 1956, p. 57). Forty ml of 0.3M sodium citrate buffered at pH 7.3 with 5 ml of M NaHCO_3 were added to the clay samples in 50 ml plastic centrifuge cups. About eight to ten cups were placed in a stainless steel beaker containing boiling water. One gram of $\text{Na}_2\text{S}_2\text{O}_4$ (sodium dithionite) was added to each sample and the suspension was stirred constantly for one minute. After 15 minutes of reaction, the samples were



^{1/} Standard clay minerals were not aged prior to sequential or HCl treatments.

Figure 7. Flow chart indicating the various treatments received by samples during the stability studies.

centrifuged and washed twice with 0.3 M sodium citrate and two times with a 2:1 acetone-water mixture. Subsamples were withdrawn for X-ray and exchange capacity determinations. The free iron removal treatment was repeated and subsamples again taken.

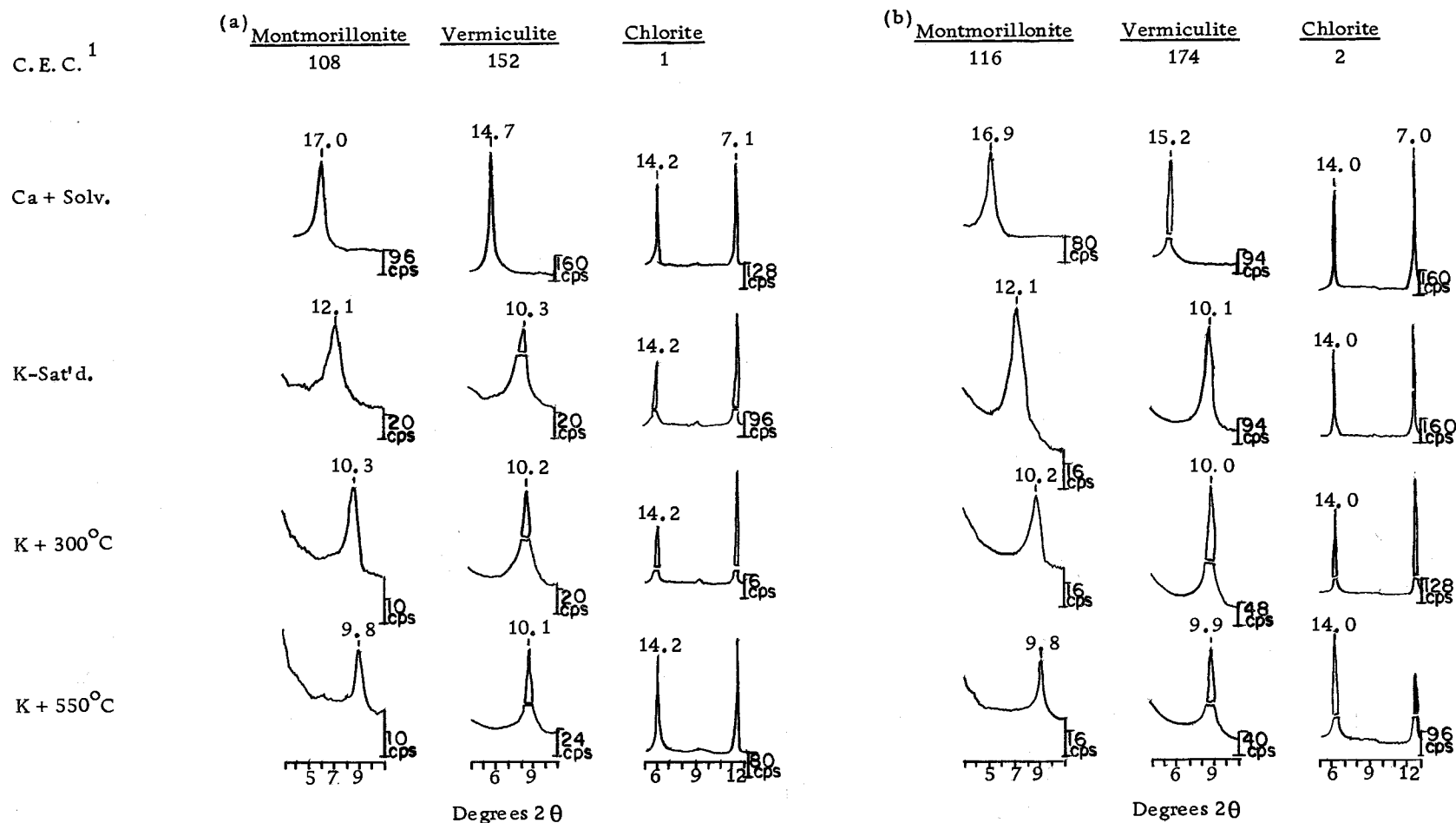
Boiling Sodium Hydroxide

This treatment was made according to the procedure outlined by Hashimoto and Jackson (1958). A ratio of 0.1 g solid to 100 ml of solution was maintained throughout the study. The sequence included another dithionite-citrate treatment following NaOH as recommended by the above authors.

Results

Standard Clay Minerals

Figure 8 gives the X-ray diffraction patterns and exchange capacity data for the standard clay minerals, without synthetic interlayers, before and after the sequential treatments. The data given for the treated samples (part b) were recorded after the full sequence of all dissolution treatments. The X-ray diffraction patterns showed practically no difference between samples which were and were not subjected to sequential treatments. However, the cation exchange capacity of all minerals increased following the dissolution



¹C.E.C. = cation exchange capacity, me/100 g.

Figure 8. Comparison of effects of sequential treatments on properties of standard clays: (a) as initially used in experimental work (prior to interlayer formation); (b) same as (a) but with sequential dissolution treatments.

treatments. It was, therefore, concluded that the selected treatments had no adverse effect upon the crystalline structure of the standard clay minerals used in this study.

Hydroxy-Al Interlayer in Montmorillonite

The amounts of interlayers initially present may complicate the interpretation related to stability. Some assumptions are therefore made in order to simplify the interpretation. The amounts of reagents used should be sufficient to get the interlayer out, even though the amounts of interlayer present are different, if they have equal stability. In other words, the concentrations of reagents are such that removal is independent of amount of interlayer present and dissolution is dependent only on the nature of the interlayer material.

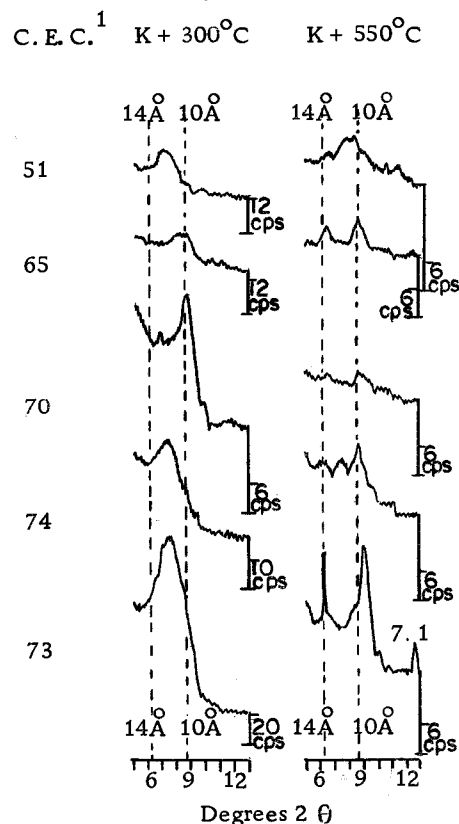
The stability of hydroxy-Al interlayers in montmorillonite with respect to sequential treatments is shown in Figure 9. Boiling Na_2CO_3 removed more interlayer from the alkaline sample than from the other samples as indicated by the degree of collapse following heat treatments. The amount of interlayer removed by the first dithionite-citrate treatment was less for material formed in neutral than in acid media. The interlayered samples also showed a differential response to the second dithionite-citrate treatment. The occurrence of a 14 \AA reflection, indicative of a chloritic

SEQUENTIAL
TREATMENTS

ACID

$$\frac{\text{OH}}{\text{Al}} (\text{me added}) = 0.81$$

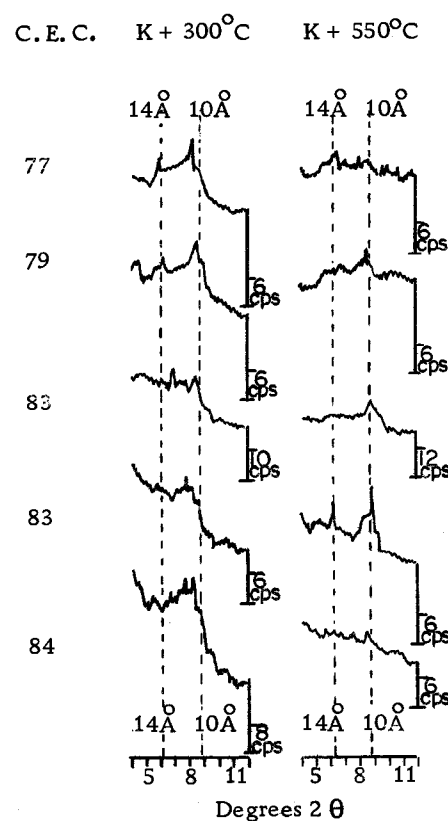
X-ray Pretreatments



NEUTRAL

$$\frac{\text{OH}}{\text{Al}} (\text{me added}) = 1.09$$

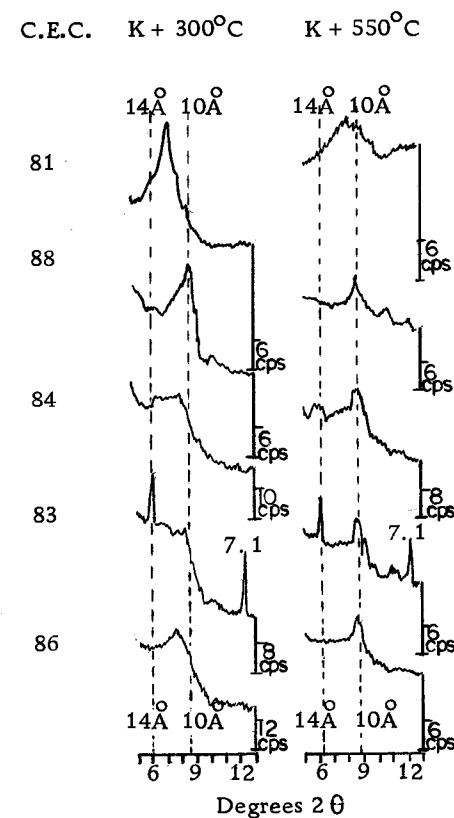
X-ray Pretreatments



ALKALINE

$$\frac{\text{OH}}{\text{Al}} (\text{me added}) = 1.25$$

X-ray Pretreatments



¹ C.E.C. = cation exchange capacity, me/100 g.

² Check = interlayered material after 6 months equilibration and prior to removal treatments

Figure 9. Stability of hydroxy-Al interlayer in montmorillonite with respect to sequential treatments.

component, in addition to a 10 \AA line following the second dithionite-citrate treatment was recorded. The intensity of the former increased from acid toward alkaline conditions. Further, the 14 \AA line was not recorded after the boiling NaOH treatment for neutral and alkaline systems, but it was quite evident for the acid system. The occurrence of the 14 \AA reflection in aluminum systems as well as in iron and magnesium systems is of particular interest and it will be discussed in detail in a special subsection.

When the data for the "check" samples are compared to those after the full sequence of dissolution treatments, one may reach the conclusions that (1) aluminum interlayer exhibited a fairly high stability regardless of conditions of formation and (2) the stability of interlayer was in the order acid > neutral > alkaline conditions.

Hydroxy-Al Interlayer in Vermiculite

In contrast to montmorillonite, most of the hydroxy-Al interlayer in vermiculite was removed by the sequential treatments (Figure 10). Generally, the removal of interlayer increased as the sequential treatments also increased in severity. However, not all interlayer was removed even by the most severe treatments regardless of initial conditions of formation.

All the interlayered samples responded more readily to potassium treatment after boiling Na_2CO_3 treatment. However, the

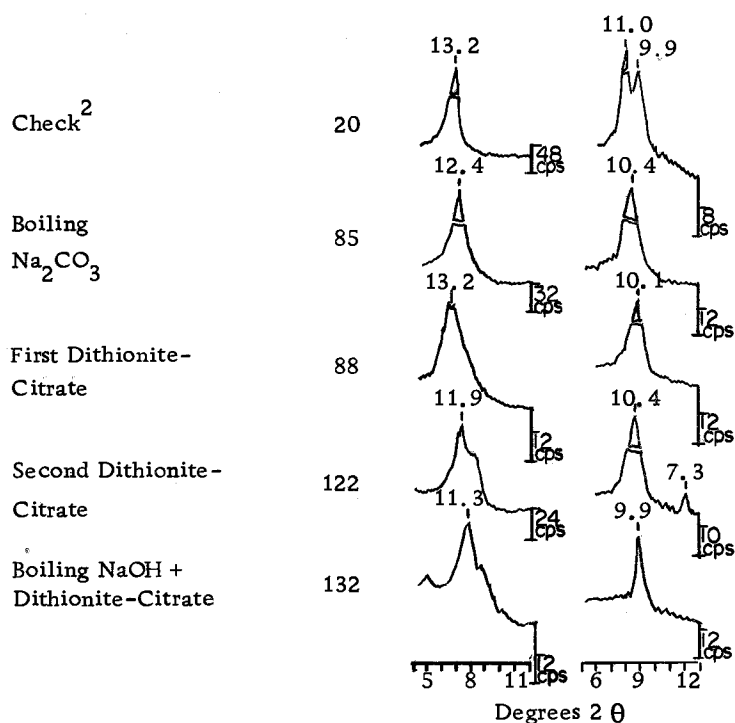
SEQUENTIAL
TREATMENTS

ACID

$$\frac{\text{OH}}{\text{Al}} \text{ (me added)} = 0.81$$

X-ray Pretreatments

C.E.C.¹ K + 65°C K + 550°C

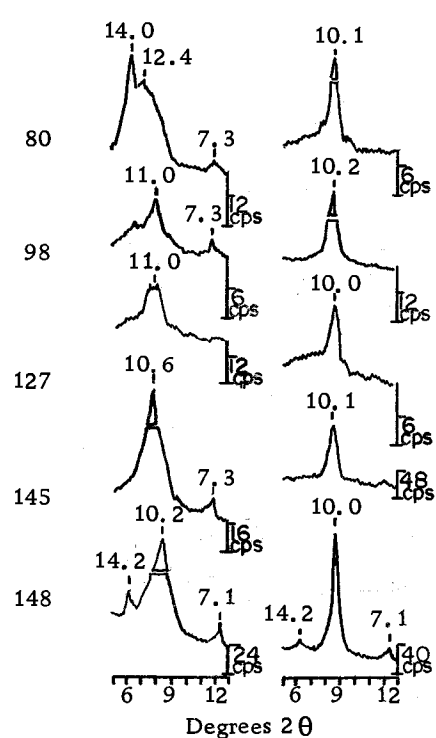


NEUTRAL

$$\frac{\text{OH}}{\text{Al}} \text{ (me added)} = 1.00$$

X-ray Pretreatments

C.E.C. K + 65°C K + 500°C

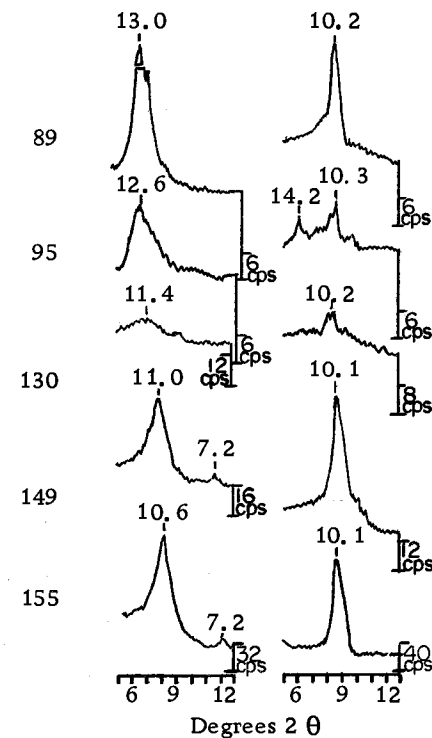


ALKALINE

$$\frac{\text{OH}}{\text{Al}} \text{ (me added)} = 1.25$$

X-ray Pretreatments

C.E.C. K + 65°C K + 550°C



¹ C.E.C. = cation exchange capacity, me/100 g.

² Check = interlayered material after 6 months equilibration and prior to removal treatments

Figure 10. Stability of hydroxy-Al interlayer in vermiculite with respect to sequential treatments.

alkaline sample showed a decrease in collapse after $K + 550^{\circ} \text{C}$. The effect of the boiling Na_2CO_3 treatment on CEC is of interest. The increase in CEC was much greater for interlayers formed in acid media than in neutral or alkaline conditions. The effect on CEC was greater than upon the lattice spacings. As previously pointed out, formation of interlayers at the edges of the interlayer planes effectively blocks interior exchange sites. The marked increase in CEC by the boiling Na_2CO_3 treatment of systems equilibrated in the acid media is consistent with the removal of the edge polymers. It is apparent that one cannot use CEC alone as a direct measure of the amounts of interlayer material removed.

The dithionite-citrate treatments removed more interlayer from the neutral and alkaline samples than from the acid system as indicated by increases in CEC and degree of lattice collapse. After an increase in basal spacing following the first dithionite-citrate treatment, the acid sample showed a relatively high degree of collapse and a large increase in CEC after the second dithionite-citrate treatment. Finally, the NaOH treatment removed very small amounts of interlayer in the order acid > neutral > alkaline systems.

The overall evidence indicates that the interlayer formed in acid conditions showed the highest stability to sequential treatments while that formed in alkaline conditions was the least stable.

Hydroxy-Fe Interlayer in Montmorillonite

Figure 11 shows that hydroxy-Fe interlayers formed in montmorillonite under various conditions of acidity were removed to various extents by the sequential treatments.

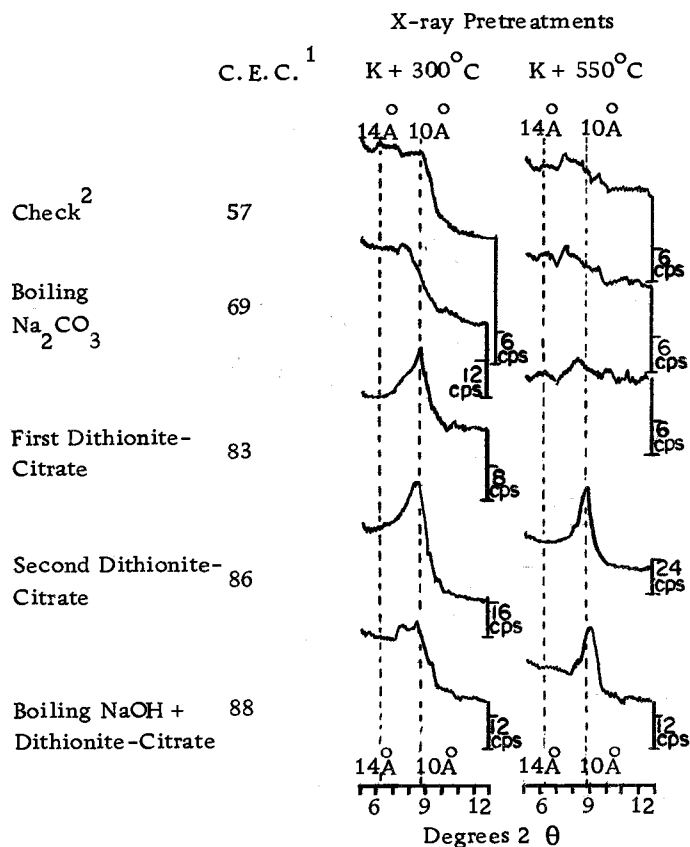
Only small changes in the basal spacings of the interlayered samples occurred after boiling Na_2CO_3 although the CEC of the acid sample showed an increase of 12 me. In contrast, the dithionite-citrate treatments were quite effective in facilitating lattice collapse and provided information with respect to the differential interlayer stability. The interlayer formed in neutral conditions apparently exhibited a higher stability than the counterparts from acid or alkaline media. The boiling NaOH produced either a broadening of peaks toward higher spacings, as illustrated by the acid and neutral samples after K plus 300°C , or an increase in the degree of collapse, as illustrated by the neutral sample following K plus 550°C . The adverse effects of the boiling NaOH treatment is of concern and the reasons are not understood.

On the basis of behavioral differences between the samples upon dissolution treatments, one may reach the conclusion that the interlayers formed in neutral and alkaline conditions exhibited more stability than the interlayer formed in acid media.

SEQUENTIAL
TREATMENTS

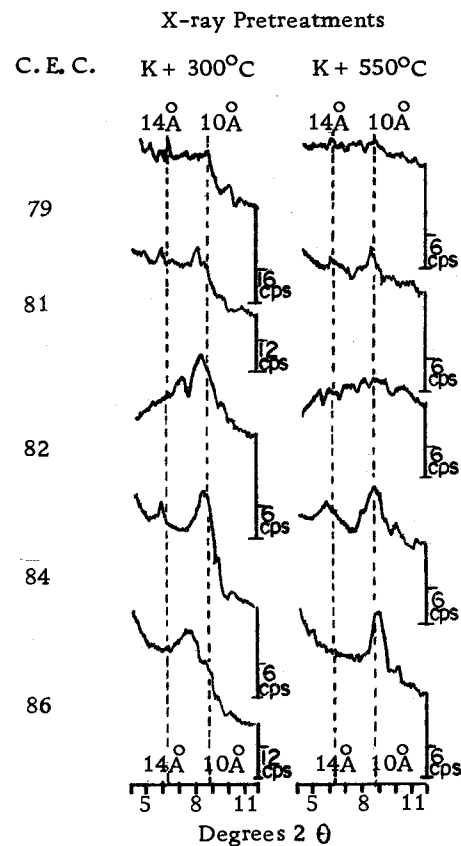
ACID

$$\frac{\text{OH}}{\text{Fe}} (\text{me added}) = 0.88$$



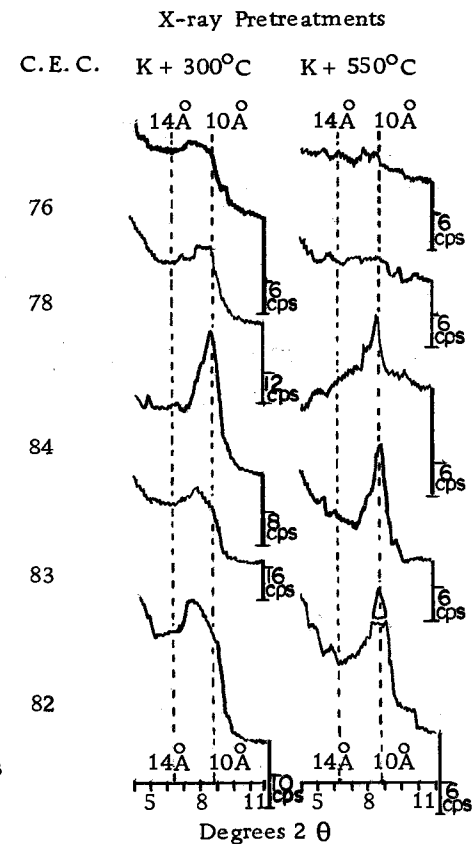
NEUTRAL

$$\frac{\text{OH}}{\text{Fe}} (\text{me added}) = 1.00$$



ALKALINE

$$\frac{\text{OH}}{\text{Fe}} (\text{me added}) = 1.25$$



¹ C. E. C. = cation exchange capacity, me/100 g.

² Check = interlayered material after 6 months equilibration and prior to removal treatments

Figure 11. Stability of hydroxy-Fe interlayer in montmorillonite with respect to sequential treatments.

Hydroxy-Fe Interlayer in Vermiculite

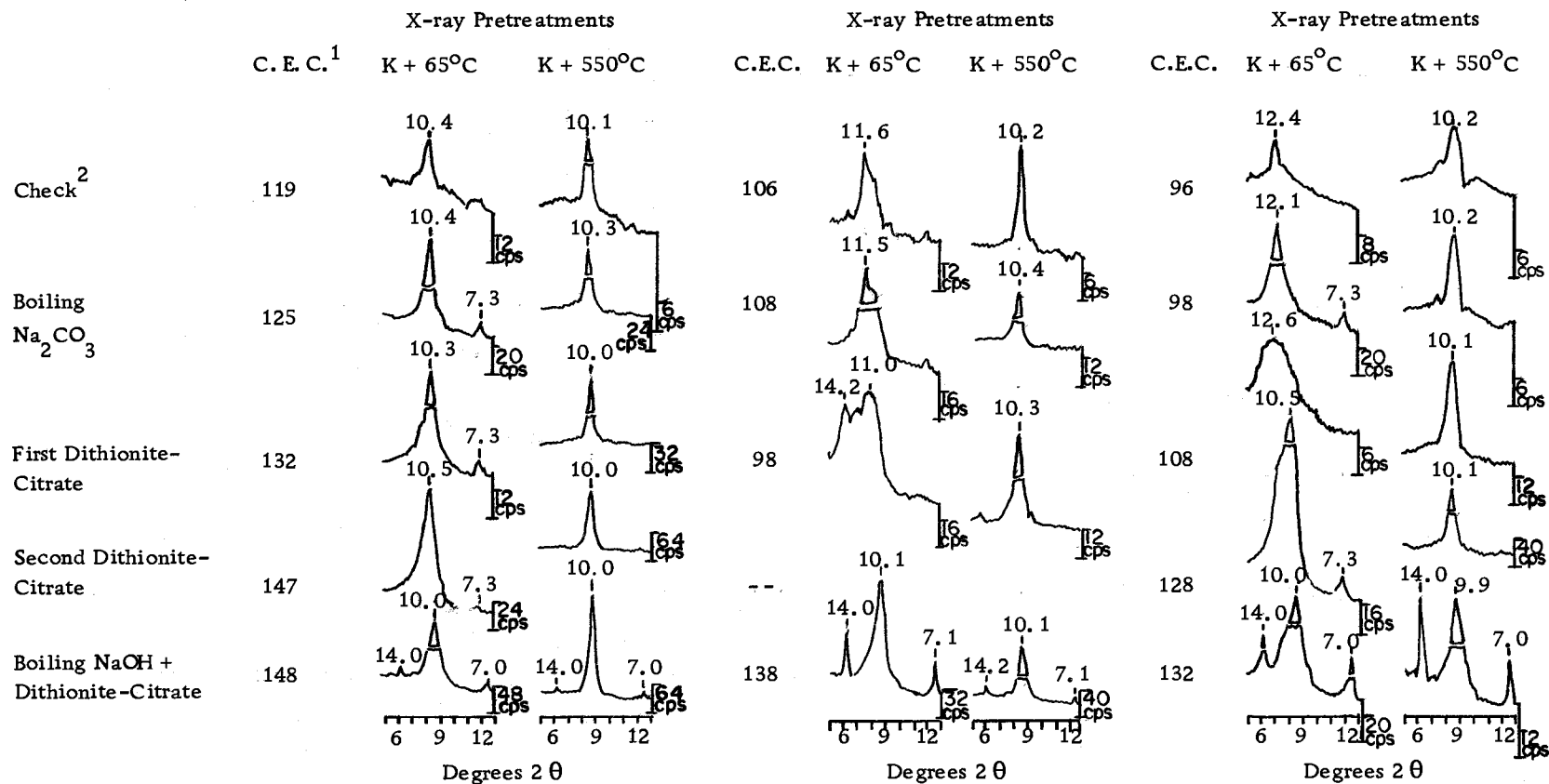
The X-ray diffraction patterns and exchange capacity data of the iron interlayered vermiculite samples subjected to sequential treatments are shown in Figure 12. Boiling Na_2CO_3 had but minor influence upon the basal spacings of interlayered samples. The first dithionite-citrate treatment apparently removed some interlayer which was formed in acid conditions. However, it produced a broadening of peaks toward higher basal spacings for the neutral and alkaline samples as shown by the K plus 65°C treatment. In addition to an increase in basal spacing, the neutral sample showed a decrease in CEC. Unlike other samples, the one from the neutral medium was not subjected to the second dithionite-citrate treatment. This should be taken into account in the interpretation of both X-ray and CEC data. The second dithionite-citrate treatment removed some interlayer formed in acid and alkaline media as indicated by the increases in CEC, degree of lattice collapse and sharpness of X-ray diffraction peaks. The boiling NaOH treatment apparently removed no additional interlayer formed in acid and alkaline conditions, but it removed a considerable amount of interlayer from the neutral sample. This is also suggested by the changes in CEC. However, the 14 \AA reflection occurred after boiling NaOH in all systems. Except for the neutral sample which showed indication of a 14 \AA peak before the NaOH

SEQUENTIAL
TREATMENTS

ACID
 $\frac{\text{OH}}{\text{Fe}}$ (me added) = 0.88

NEUTRAL
 $\frac{\text{OH}}{\text{Fe}}$ (me added) = 1.00

ALKALINE
 $\frac{\text{OH}}{\text{Fe}}$ (me added) = 1.25



¹ C.E.C. = cation exchange capacity, me/100 g.

² Check = interlayered material after 6 months equilibration and prior to removal treatments

Figure 12. Stability of hydroxy-Fe interlayer in vermiculite with respect to sequential treatments.

treatment, there were no clear indications of this peak for the other samples. It is concluded that the stability of iron interlayers formed in different degrees of acidity was in the order alkaline \geq neutral \geq acid conditions.

Hydroxy-Mg Interlayer in Montmorillonite

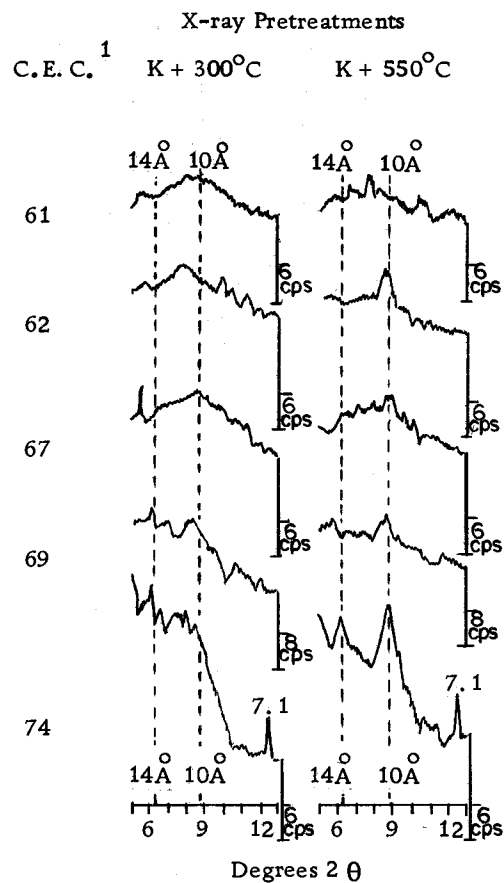
The hydroxy-Mg interlayer in montmorillonite exhibited a fairly high stability to sequential dissolution treatments (Figure 13). Except for the boiling NaOH treatment, all the other treatments produced only minor changes in basal spacings and cation exchange capacity of the interlayered material. A 14 \AA line was recorded after the boiling NaOH treatment.

Hydroxy-Mg Interlayer in Vermiculite

Boiling Na_2CO_3 and the first dithionite-citrate treatments removed only small amounts of hydroxy-Mg interlayer from the system $\frac{\text{OH}}{\text{Mg}} = 0.62$ (Figure 14). This removal was indicated by the increase in CEC and also by the increase in the 10 \AA peak at the expense of the 14 \AA peak. The second dithionite-citrate treatment was almost completely effective in removing the hydroxy-Mg interlayer. Following this treatment, the material exhibited a high degree of collapse as indicated by the sharp and symmetrical 10 \AA peaks and by a high CEC. The boiling NaOH treatment collapsed the lattice of

SEQUENTIAL
TREATMENTS

$$\frac{\text{OH}}{\text{Mg}} (\text{me added}) = 1.00$$



Check²

Boiling
 Na_2CO_3

First Dithionite-
Citrate

Second Dithionite-
Citrate

Boiling NaOH +
Dithionite-Citrate

¹ C.E. C. = cation exchange capacity, me/100g.

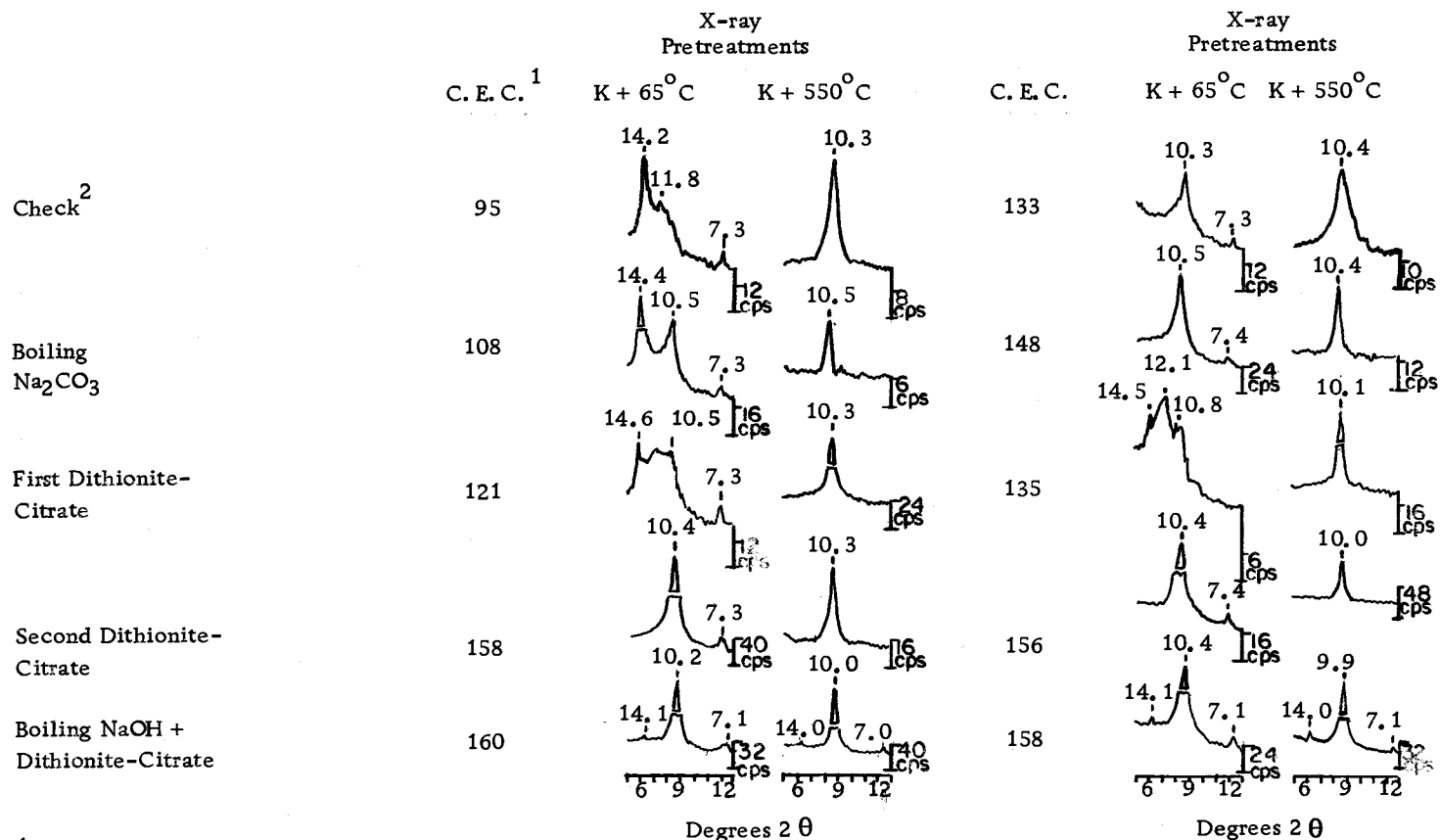
² Check = interlayered material after 6 months
equilibration and prior to removal
treatments

Figure 13. Stability of hydroxy-Mg interlayer in montmorillonite with respect to sequential treatments.

SEQUENTIAL
TREATMENTS

$$\frac{\text{OH}}{\text{Mg}} \text{ (me added)} = 0.62$$

$$\frac{\text{OH}}{\text{Mg}} \text{ (me added)} = 1.25$$



¹ C.E.C. = cation exchange capacity, me/100 g.

² Check = interlayered material after 6 months equilibration and prior to removal treatments

Figure 14. Stability of hydroxy-Mg interlayer in vermiculite with respect to sequential treatments.

the interlayered material to about 10 Å spacings. Further, the 14 Å reflection was recorded after the last treatment.

After six months of equilibration, very little interlayer remained in the sample with a ratio of $\frac{\text{OH}}{\text{Mg}}$ (me added) = 1.25. An increase in basal spacing and a decrease in CEC were recorded after the first dithionite-citrate treatment and K plus 65° C. However, the second dithionite-citrate treatment again permitted collapse of the lattice to 10 Å and appreciably increased the CEC. The 14 Å line was again observed.

STABILITY OF HYDROXY-AL, Fe, AND Mg INTERLAYERS
IN MONTMORILLONITE AND VERMICULITE TO
0.1 N HCl TREATMENT

Problem

Hydrochloric acid treatment is commonly used in soil laboratories for removal of carbonates (Jackson et al., 1950), dispersion of some allophane-type minerals (DeMumbrum and Chesters, 1964), removal of synthetic and natural interlayers (Caillere and Hénin, 1949; Shen and Rich, 1962; Rich and Obenshain, 1955), differentiation of chlorite from kaolinite (Brindley and Youell, 1957), and in conjunction with free iron removal (Deb, 1950; Kilmer, 1960; Mackenzie, 1957). H-saturated clays have been used for surface area measurement of soil colloids (Mehra and Jackson, 1959) and in titration experiments (Coleman and Thomas, 1964; Schwertmann and Jackson, 1963, 1964; and many others). In view of the multiple uses of acid treatment and, particularly in view of the different effects of HCl upon the solubility of chlorite, intergrades, and other clay minerals, it was considered appropriate to test the stability of the synthetic Al, Fe, and Mg interlayers with respect to HCl treatments.

Experimental Methods

Portions of about 0.5 g samples of the interlayered clays which had been equilibrated for six months were treated with 40 ml of cold

0.1 N HCl. The stoppered plastic cups were shaken for 20 minutes, centrifuged, and the excess acid was poured off. Following two washings with distilled water, subsamples were Ca and K saturated for X-ray diffraction analysis and exchange capacity measurements. The HCl treatment was repeated and subsamples were again analyzed as above.

Results

Standard Clay Minerals

The effects of 0.1 N HCl upon the properties of standard clay minerals used in this study are recorded in Figure 15. "Check" represents the samples which were not subjected to HCl treatment and serves for comparison.

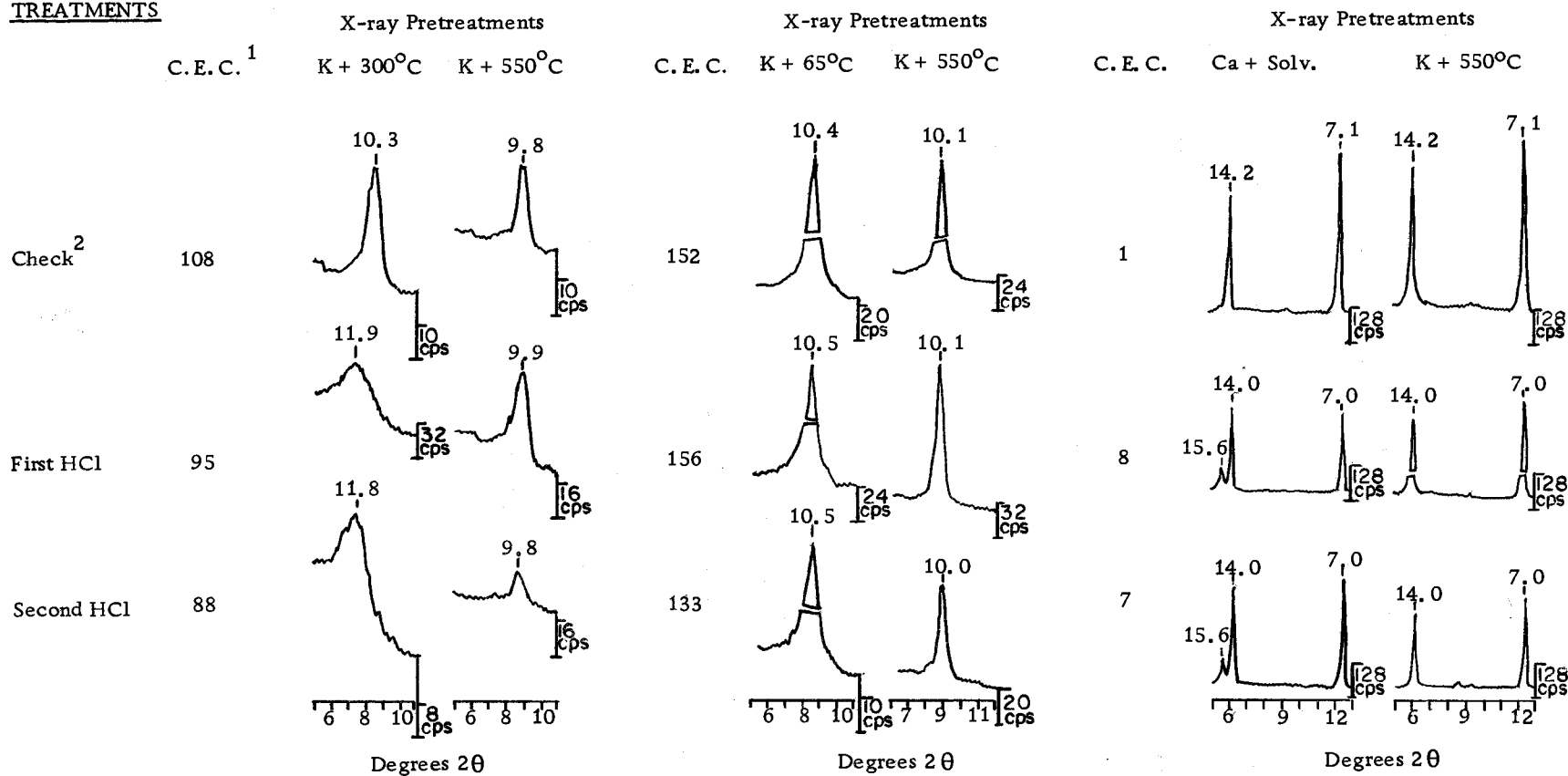
Montmorillonite exhibited decreases in both collapse and exchange capacity after the first and second acid treatments. The hydronium ions presumably attacked the crystalline network and released structural aluminum from the octahedral layer. The charged hydroxy-Al polymers resulting through hydrolysis and polymerization of trivalent aluminum, were then sorbed by montmorillonite to form hydroxy-interlayers. Mathers et al. (1955) also reported a decrease in exchange capacity of acid-treated montmorillonite, but they found no shift in the position of X-ray diffraction peaks.

SEQUENTIAL
TREATMENTS

MONTMORILLONITE

VERMICULITE

CHLORITE



¹C.E.C. = cation exchange capacity, me/100 g.

²Check = standard minerals prior to interlayer formation and without HCl treatment

Figure 15. Stability of standard clay minerals with respect to 0.1 NHCl treatment.

Acid treatment produced practically no changes in basal spacings of vermiculite. However, a decrease in exchange capacity was observed after the second acid treatment.

Finally, chlorite showed a partial degradation of the brucite interlayer after acid treatment. This degradation is indicated by the occurrence of a small 15.6 \AA peak on solvation and by an increase in exchange capacity.

Hydroxy-Al Interlayer in Montmorillonite

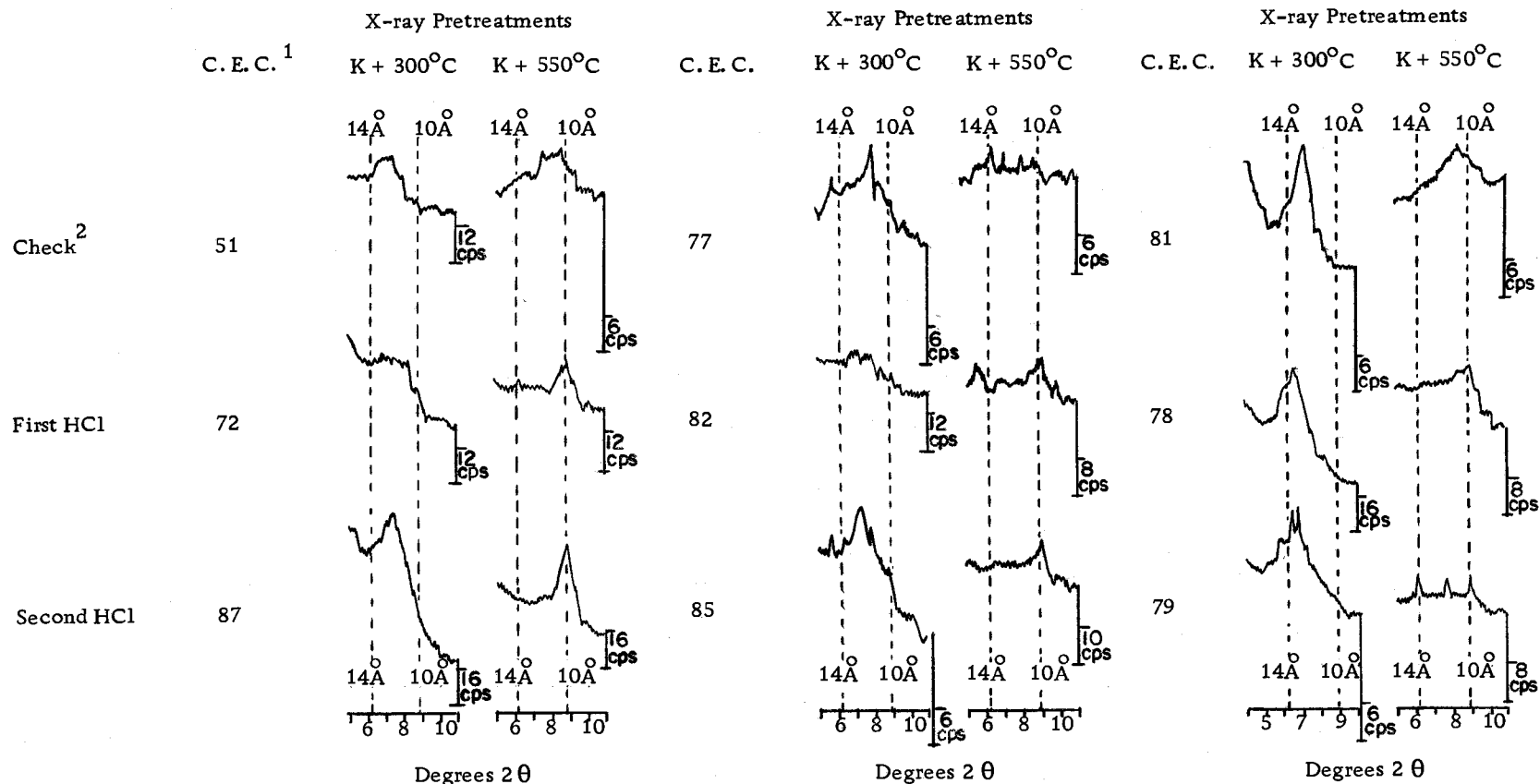
The effects of 0.1 N HCl upon hydroxy-Al interlayer in montmorillonite are shown in Figure 16. The patterns designated as "check" were recorded for the interlayered material which has been aged for six months and has not been subjected to HCl treatment. The HCl treatments had the greatest effect on the acid system, as indicated by increases in lattice collapse and cation exchange capacity. There was also some removal of interlayer from the neutral system. In the case of the alkaline system, there is no evidence of any interlayer removal and, in fact, it appears that stability has been increased. It is, therefore, concluded that aluminum interlayer formed in alkaline conditions showed the highest stability to HCl treatments, whereas that formed in acid medium was the least stable.

SEQUENTIAL
TREATMENTS

ACID
 $\frac{\text{OH}}{\text{Al}}$ (me added) = 0.81

NEUTRAL
 $\frac{\text{OH}}{\text{Al}}$ (me added) = 1.09

ALKALINE
 $\frac{\text{OH}}{\text{Al}}$ (me added) = 1.25



¹ C.E.C. = cation exchange capacity, me/100 g.

² Check = interlayered material after 6 months equilibration and prior to removal treatments

Figure 16. Stability of hydroxy-Al interlayer in montmorillonite with respect to 0.1 NHCl treatment.

Hydroxy-Al Interlayer in Vermiculite

As in the case of montmorillonite, not all the interlayer in vermiculite was removed by the two HCl treatments (Figure 17). The first HCl treatment removed some of the interlayers formed under alkaline and, to a lesser extent, under neutral conditions. On the other hand, the interlayer formed in acid medium remained practically unaffected by the treatment. The second HCl treatment removed small amounts of interlayer regardless of conditions of formation. It is, therefore, concluded that the stability of aluminum interlayer in vermiculite was in the order acid > neutral > alkaline systems.

Hydroxy-Fe Interlayer in Montmorillonite

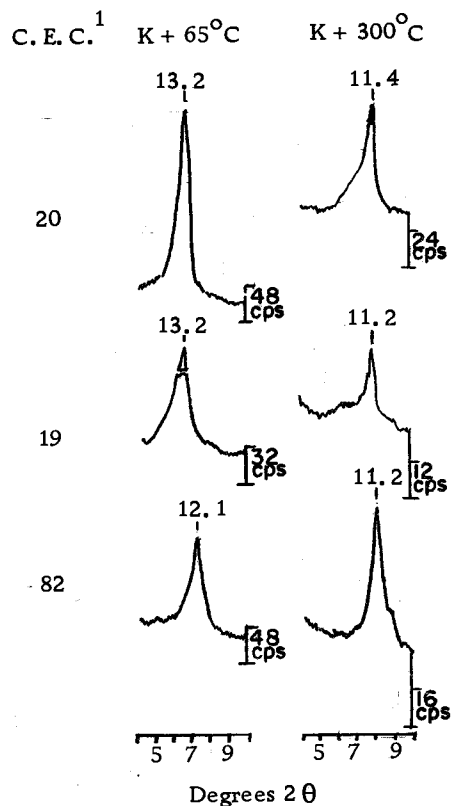
The diffraction maxima of iron interlayered systems were broad and diffuse (Figure 18). These features suggest the presence of poorly organized interlayer or mixed layer systems. The poor patterns could also result from iron fluorescence which produced high background scatter to the extent that diffraction maxima were masked. There was little, if any, improvement of diffraction patterns due to HCl treatments. It is, therefore, difficult to make any interpretation as to relative stability of the iron interlayers to HCl. A removal of the most labile or poorly organized hydroxy

SEQUENTIAL
TREATMENTS

ACID

$\frac{\text{OH}}{\text{Al}}$ (me added) = 0.81

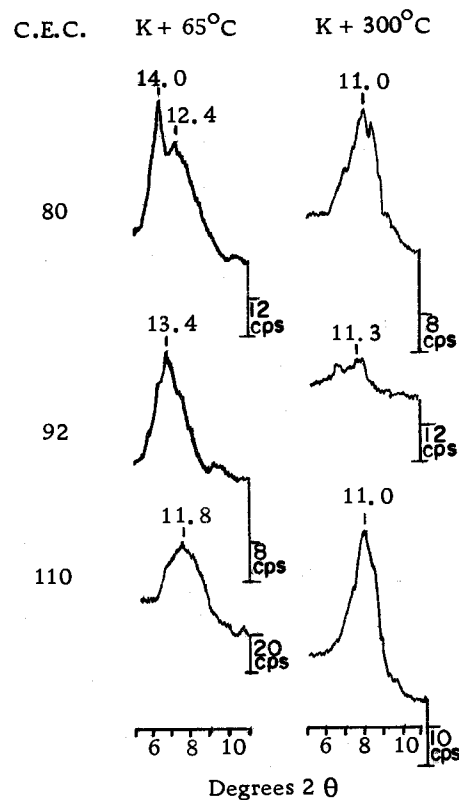
X-ray Pretreatments



NEUTRAL

$\frac{\text{OH}}{\text{Al}}$ (me added) = 1.00

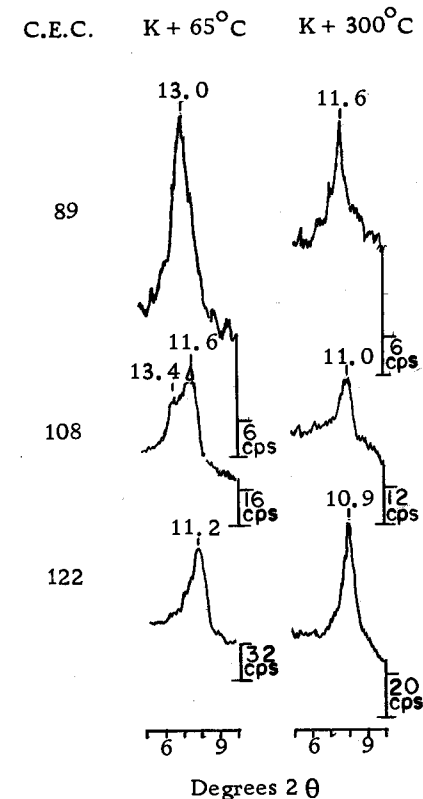
X-ray Pretreatments



ALKALINE

$\frac{\text{OH}}{\text{Al}}$ (me added) = 1.25

X-ray Pretreatments



¹ C.E.C. = cation exchange capacity, me/100 g.

² Check = interlayered material after 6 months equilibration and prior to removal treatments

Figure 17. Stability of hydroxy-Al interlayer in vermiculite with respect to 0.1 NHCl treatment.

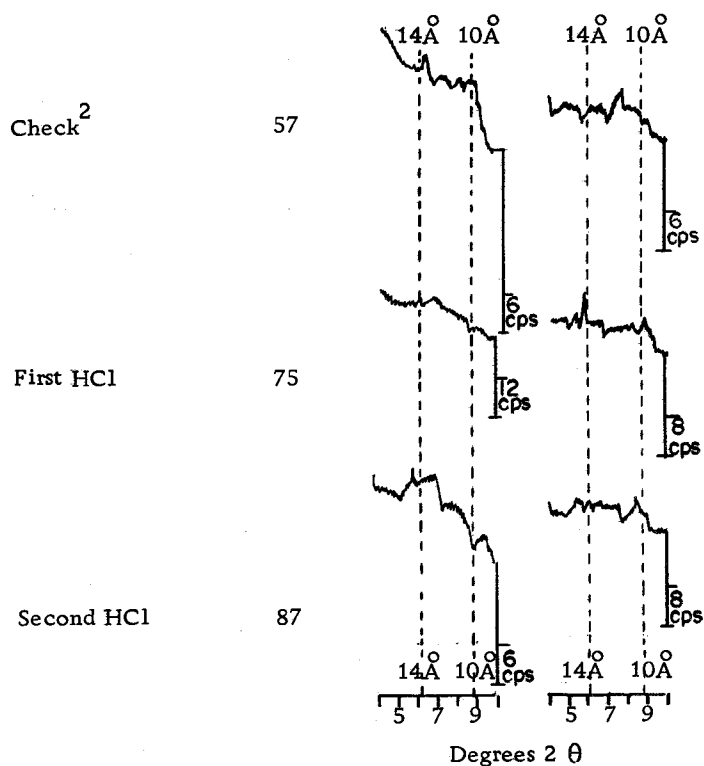
SEQUENTIAL
TREATMENTS

ACID

$$\frac{\text{OH}}{\text{Fe}} (\text{me added}) = 0.88$$

X-ray Pretreatments

C. E. C.¹ K + 300°C K + 550°C

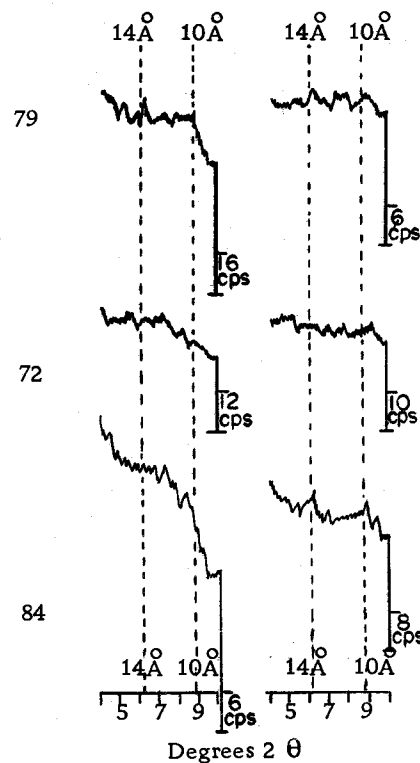


NEUTRAL

$$\frac{\text{OH}}{\text{Fe}} (\text{me added}) = 1.00$$

X-ray Pretreatments

C. E. C. K + 300°C K + 550°C

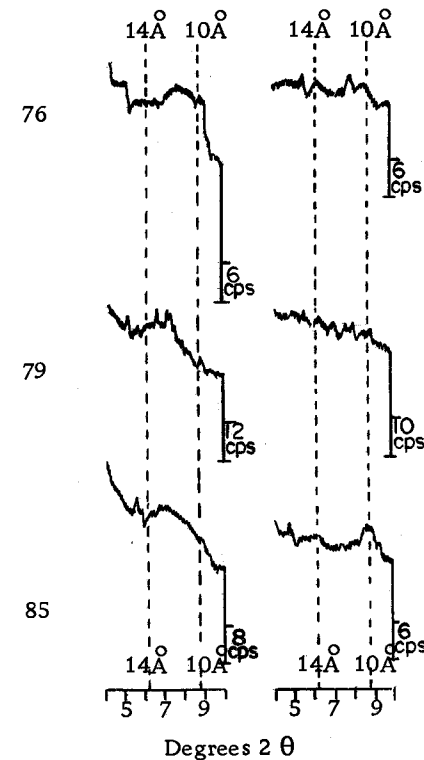


ALKALINE

$$\frac{\text{OH}}{\text{Fe}} (\text{me added}) = 1.25$$

X-ray Pretreatments

C. E. C. K + 300°C K + 550°C



¹ C. E. C. = cation exchange capacity, me/100 g.

² Check = interlayered material after 6 months equilibration and prior to removal treatments

Figure 18. Stability of hydroxy-Fe interlayer in montmorillonite with respect to 0.1 NHCl treatment.

interlayer in addition to amorphous coatings may explain the increase in CEC for the acid sample.

Hydroxy-Fe Interlayer in Vermiculite

The first HCl treatment produced rather opposite effects when used for removal of different Fe interlayers (Figure 19). A decrease in CEC from 119 to 98 me/100g and an increase in basal spacing after K-saturation from 10.4 Å to 11.2 Å indicated a formation of interlayer in the sample from acid conditions. On the other hand, a small amount of interlayer was removed from the sample equilibrated in alkaline conditions. Finally, the interlayer formed in neutral conditions was, for all practical purposes, unaffected by the first HCl treatment. The second HCl treatment removed not only the newly formed interlayer from the acid sample and also some iron interlayer present in the "check" sample. Additional interlayer was removed by the second HCl treatment from the chloritic intergrades resulting from neutral and alkaline conditions. In comparison to the check, the sequence of two HCl treatments removed only small amounts of interlayer formed in acid, neutral, and alkaline conditions. It was concluded that the stability of iron interlayers in vermiculite was in the order alkaline > neutral > acid systems.

SEQUENTIAL
TREATMENTS

ACID

$$\frac{\text{OH}}{\text{Fe}} (\text{me added}) = 0.88$$

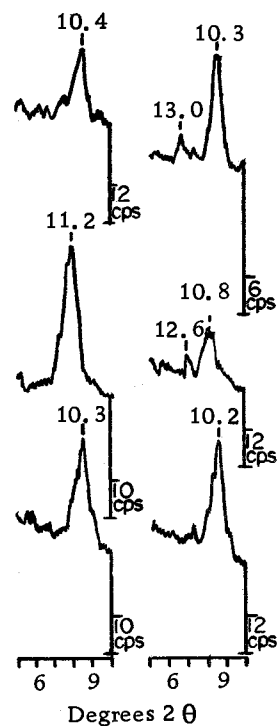
X-ray Pretreatments

C.E.C.¹

K + 65°C K + 300°C

Check²

119



First HCl

98

Second HCl

135

NEUTRAL

$$\frac{\text{OH}}{\text{Fe}} (\text{me added}) = 1.00$$

X-ray Pretreatments

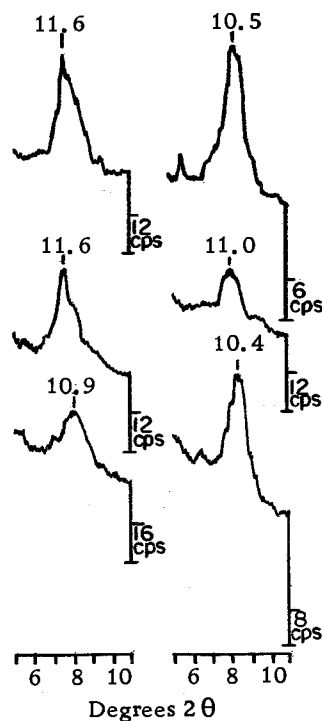
C.E.C.

K + 65°C K + 300°C

106

104

117



ALKALINE

$$\frac{\text{OH}}{\text{Fe}} (\text{me added}) = 1.25$$

X-ray Pretreatments

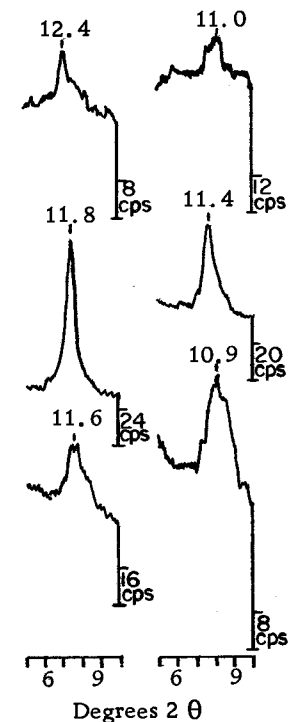
C.E.C.

K + 65°C K + 300°C

96

101

106



¹ C.E.C. = cation exchange capacity, me/100 g.

² Check = interlayered material after 6 months equilibration and prior to removal treatments

Figure 19. Stability of hydroxy-Fe interlayer in vermiculite with respect to 0.1 NHCl treatment.

Hydroxy-Mg Interlayer in Montmorillonite

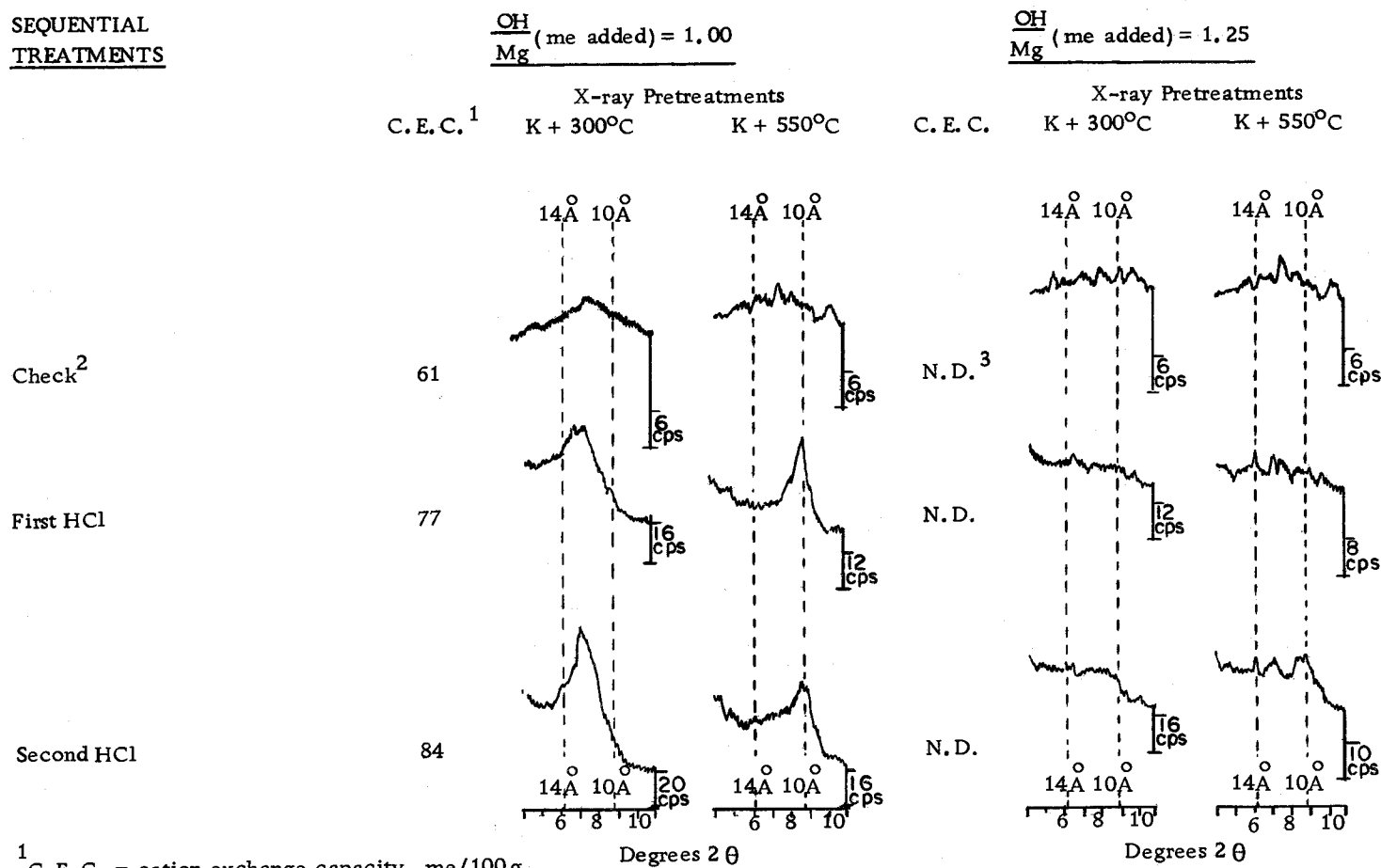
The first HCl treatment removed only a part of the Mg hydroxy interlayer from the sample with an initial solution ratio of $\frac{\text{OH}}{\text{Mg}} = 1.00$ as indicated by CEC and degree of collapse (Figure 20). The second HCl treatment resulted in a further increase in CEC but little change as far as the basal spacings were concerned. It was, therefore, concluded that the magnesium interlayer exhibited a fairly high stability to HCl.

The sample with an initial solution ratio of $\frac{\text{OH}}{\text{Mg}} = 1.25$ showed practically no changes after HCl treatments. It is believed that the structure of montmorillonite has been destroyed following equilibration for six months at high pH. The data presented earlier on formation pointed toward the same interpretation.

Hydroxy-Mg Interlayer in Vermiculite

Practically all the synthetic magnesium interlayer was removed by the two HCl treatments from an interlayered vermiculite with an initial solution ratio of $\frac{\text{OH}}{\text{Mg}} = 0.62$ (Figure 21). This removal of interlayer is clearly indicated by increases in collapse and CEC following acid treatments. The interlayered sample with an initial solution ratio of $\frac{\text{OH}}{\text{Mg}} = 1.25$ exhibited a slight increase in basal spacings and a decrease in CEC after the first HCl treatment which

SEQUENTIAL
TREATMENTS



¹ C.E.C. = cation exchange capacity, me/100g.

² Check = interlayered material after 6 months equilibration and prior to removal treatments.

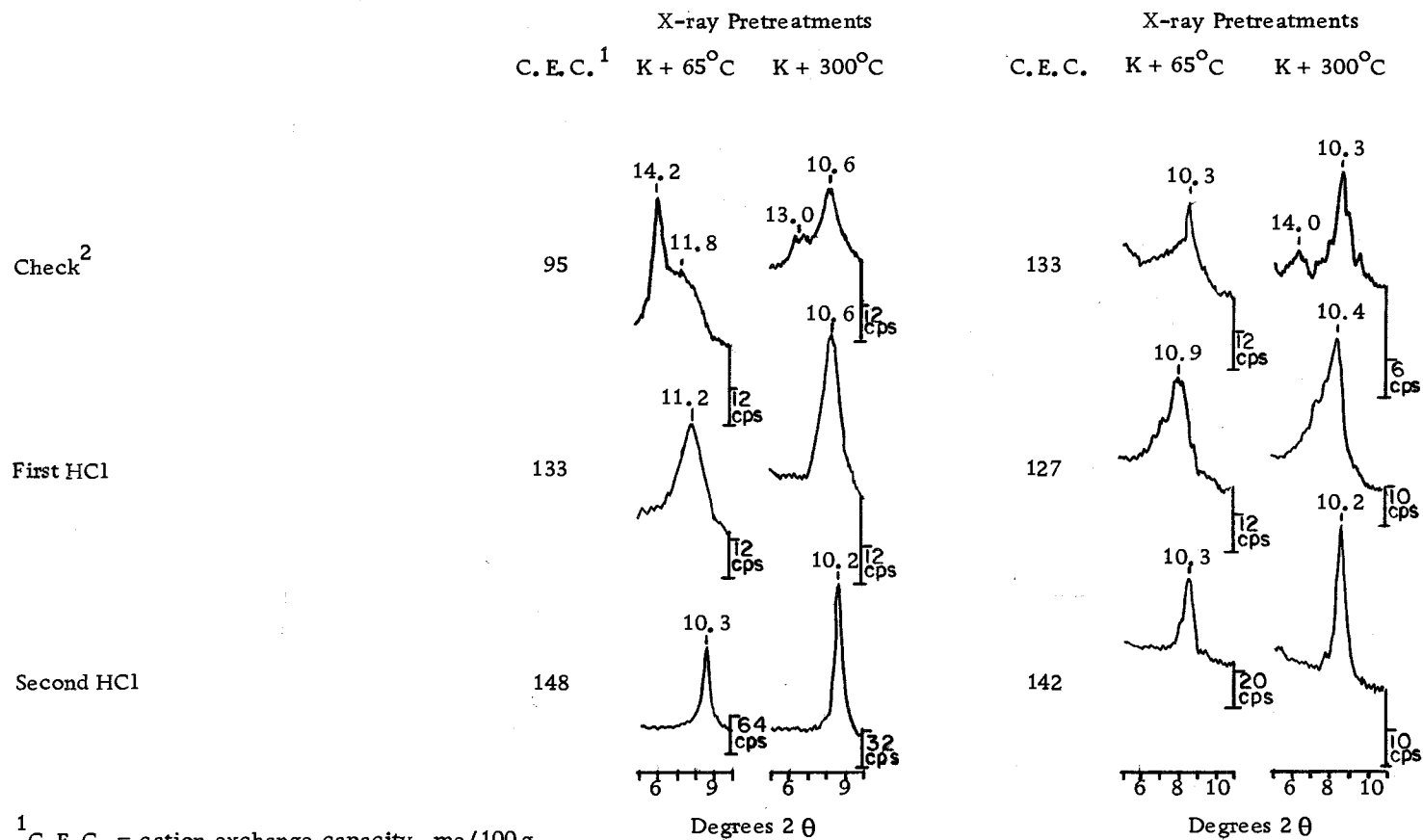
³ N.D. = not determined

Figure 20. Stability of hydroxy-Mg interlayer in montmorillonite with respect to 0.1NHCl treatment.

SEQUENTIAL
TREATMENTS

$$\frac{\text{OH}}{\text{Mg}} (\text{me added}) = 0.62$$

$$\frac{\text{OH}}{\text{Mg}} (\text{me added}) = 1.25$$



¹ C. E. C. = cation exchange capacity, me/100 g.

² Check = interlayered material after 6 months equilibration and prior to removal treatments

Figure 21. Stability of hydroxy-Mg interlayer in vermiculite with respect to 0.1 NHCl treatment.

indicated some interlayer formation. The conditions of pH in 0.1 N HCl were such as to favor the formation of interlayer, presumably originating from the solution of $\text{Mg}(\text{OH})_2$ located outside of the crystal lattice with subsequent adsorption in the interlayer space. The next HCl treatment produced increases in collapse and CEC indicating that removal of interlayer took place.

DISCUSSION

Formation of Interlayers

Influence of pH

The formation of hydroxy-Al, Fe and Mg interlayers was strongly dependent upon pH, time and type of mineral.

The pH was the essential determining factor for the interlayer formation and the pH values recorded after different periods of time are listed, for convenience, in Tables IV, V and VI. It can be readily seen that the pH values were not constant and, except in a few instances, the systems exhibited decreases in pH with time. These decreases were attributed to H^+ accumulation in solution and to a corresponding depletion of the hydroxyls as hydrolysis reactions proceeded (Ragland and Coleman, 1960).

Data of this study show that the pH changes are not a good measure of the formation of hydroxy interlayers. A few examples will be given below in order to illustrate this statement.

1. Hydrolysis of aluminum salt to polymers which were subsequently fixed in the interlayer space of clay minerals was accompanied by decreases in pH.
2. Hydrolysis of adsorbed aluminum polymers to aluminum hydroxide which was subsequently desorbed from the interlayer space

was also accompanied by decreases in pH.

3. Hydrolysis of salt directly to hydroxide without interlayer adsorption being involved was also accompanied by decreases in pH.

Therefore, decreases in pH values indicate the net result of all of these reactions.

Table IV. Formation and dissolution of hydroxy-Al interlayers in montmorillonite and vermiculite with respect to time and acidity.

Acidity	Time	pH		Formation	
		M	V	Montmorillonite	Vermiculite
acid	10 days	4.6	4.6	high formation	moderate formation
	6 months	4.1	4.2	moderate decrease	slight formation
	1 year	3.9	3.9	slight decrease	slight formation
neutral	10 days	6.8	6.6	moderate formation	low formation
	6 months	6.5	6.3	moderate decrease	moderate formation
	1 year	5.5	5.5	slight formation	moderate decrease
alkaline	10 days	10.6	10.6	low formation	low formation
	6 months	10.6	10.6	no change	moderate formation
	1 year	8.4	8.3	slight formation	moderate decrease

M stands for montmorillonite

V stands for vermiculite

Table V. Formation and dissolution of hydroxy-Fe interlayers in montmorillonite and vermiculite with respect to time and acidity.

Acidity	Time	pH		Formation	
		M	V	Montmorillonite	Vermiculite
acid	10 days	4.2	3.8	moderate formation	very low formation
	6 months	4.2	3.7	very slight decrease	slight decrease
	1 year	4.1	3.9	very slight decrease	slight decrease
neutral	10 days	6.8	6.5	moderate formation	low formation
	6 months	5.4	6.5	slight formation	slight formation
	1 year	4.8	6.7	slight decrease	slight decrease
alkaline	10 days	10.1	11.3	moderate formation	moderate formation
	6 months	9.2	8.6	very slight decrease	moderate decrease
	1 year	8.3	7.9	slight decrease	slight decrease

M stands for montmorillonite

V stands for vermiculite

Table VI. Formation and dissolution of hydroxy-Mg interlayers in montmorillonite and vermiculite with respect to time and acidity.

Acidity	Time	pH		Formation	
		M	V	Montmorillonite	Vermiculite
pH 10.0 (after 1 minute)	10 days	10.6	9.7	high-moderate formation	moderate-high formation
	6 months	9.8	9.1	moderate decrease	slight decrease
	1 year	7.7	8.5	no change	high decrease
pH 11.0 (after 1 minute)	10 days	11.6	11.0	moderate formation	moderate formation
	6 months	11.0	10.4	nearly amorphous material	high decrease
	1 year	8.5	8.3	nearly amorphous material	very slight decrease

M stands for montmorillonite

V stands for vermiculite

The initial (10 days) formation of different hydroxy interlayers in montmorillonite and vermiculite systems equilibrated in three kinds of media is of particular interest. The aluminum interlayers were formed in both minerals in acid, neutral and alkaline conditions (Table IV). The amounts of interlayers in montmorillonite and vermiculite were highest in acid media and they decreased with increasing pH. The interlayered montmorillonite resulting from equilibration in acid media, like the natural chlorite, showed no expansion and exhibited practically no collapse after K treatment and heating to 300° C and 550° C. Further, more interlayers were formed in montmorillonite than in vermiculite under all conditions of acidity.

The formation of interlayers depended, among other factors, upon kind and amount of ionic species at a certain pH, size and charge of resulting polymers and upon fixation and distribution of polymers. DeMumbrum and Jackson (1957) reported that at pH 2 the $\frac{\text{Al}^{3+}}{\text{Al OH}^{2+}} = 10^3$ for AlCl_3 , while at pH 5 this ratio was found to be 1. These data show that at low pH values Al^{3+} ions are predominant. Al^{3+} becomes equal to AlOH^{2+} only at pH 5. The hydroxy aluminum ions will undergo polymerization with a subsequent formation of a 6-Al-ion ring-like unit or multiples of such units. Brossett et al. (1954) proposed a structure of a polymer with a composition $\text{Al}_6(\text{OH})_{15}^{3+}$. Later, Hsu and Rich (1960) and Hsu and

Bates (1964b) proposed, by analogy to the structure of gibbsite, a polymer with a composition $\text{Al}_6(\text{OH})_{12}^{6+}$. The charged polymers are attracted and fixed by ionic and hydrogen bonds between layers of expandable clay minerals. This fixation produces, in turn, alteration of expansion, collapse and thermal stability of minerals.

Data of the present study indicated that hydroxy-Al polymers formed in acid media entered the montmorillonite and vermiculite and redistributed themselves in the interspace at a higher rate than hydroxy-Al polymers formed in other media. These results seem to be consistent with the findings reported by Hsu and Bates (1964b) who reported that the size and charge of polymers increased from acid toward alkaline conditions. Further they stated that the time required to reach equilibrium during aluminum fixation increased with increasing pH.

Special attention is drawn to the fact that the role of $\text{Al}(\text{OH})_3$ which may have been precipitated in the neutral and alkaline systems was not fully assessed. It is felt that, at least in part, the aluminum interlayers formed in neutral and alkaline conditions consisted of $\text{Al}(\text{OH})_3$ in addition to basic polymers. Jackson (1962, 1963) reported that amorphous aluminum precipitate carried a positive charge which made possible its attachment to the negative sites in the interlayer space. Slaughter and Milne (1960) stated that aluminum hydroxide was precipitated outside of the clay and

subsequently adsorbed in the interlayer through hydrogen bonding.

Moderate amounts of iron interlayers were formed in montmorillonite at all pH levels (Table V). The diffraction patterns were characterized by diffuse peaks and plateaus suggesting mixed layer systems. The interlayers did not inhibit expansion on solvation but the systems exhibited moderate resistance to collapse. Unlike montmorillonite, the iron interlayers in vermiculite were strongly influenced by the conditions of acidity; the amounts of interlayers increased as the pH increased (acidity decreased). Like aluminum interlayers, more iron interlayers were formed in montmorillonite than in vermiculite.

The reactions of hydrolysis and polymerization of the iron salts resemble those of aluminum salts (McGeorge, 1924; Lutz, 1938; Lamb and Jacques, 1938; Hedstrom, 1953; Whittig and Page, 1961; Page and Whittig, 1961; Coleman et al., 1964; Thomas and Coleman, 1964). In contrast to aluminum, Fe^{3+} equals FeOH^{2+} at pH as low as 2 with a predominance of the latter with increase in pH (DeMumbrum and Jackson, 1957). Hydroxy-iron polymers were also prepared and studied (Hedstrom, 1953). In the present study, iron interlayers were formed in montmorillonite and vermiculite at all levels of acidity. In montmorillonite, presumably, more iron interlayer was formed in alkaline environment than in acid medium. Further, iron interlayers were slightly less effective in reducing the

CEC than the aluminum interlayers. This seems to agree with findings reported by Coleman et al. (1964). In contrast to montmorillonite, the exchange capacity and basal spacings indicated that more iron interlayer was produced in vermiculite systems equilibrated in alkaline media than in acid media. Obviously, the nature of the original silicate lattice has a profound effect on the formation and stability of interlayers. This point will be discussed in detail in a subsequent section.

A reddish-brown precipitate, presumably iron hydroxide, was observed in the montmorillonite and vermiculite systems equilibrated in neutral and particularly in alkaline media. Coleman and Thomas (1964) and Thomas and Coleman (1964) reported that ferric hydrous oxides interacted with the negative sites of montmorillonite and produced a reduction of CEC and an alteration of its basal spacings. As in the case of aluminum hydroxide, the role of iron hydroxide with respect to interlayer formation was not evaluated in this study.

Magnesium interlayers were produced in montmorillonite and vermiculite only in alkaline media at a pH of about 10 or higher (Table VI). The amounts of interlayers of both systems decreased with increasing pH. More interlayers were formed in the montmorillonite system than in vermiculite system at a pH of about 10. Further, this interlayered montmorillonite exhibited only a partial expansion on solvation and showed a high resistance to collapse

following heat to 300° C and 550° C. At higher pH, the differences between the two minerals with respect to interlayer formation were less pronounced.

Influence of Time and Type of Clay Mineral

Time and type of clay mineral are considered important factors with respect to crystallization, formation and orientation of bonds, precipitation or dissolution, diffusion of ions and other surface phenomena. Previous studies have indicated differences with respect to formation and stability of interlayers between montmorillonite and vermiculite (Carstea, 1965). These differences which occurred also during the present study can be explained, at least in part, by the differences in electro-chemical and physical properties of the minerals involved. The structure of vermiculite differs from that of a montmorillonite in both source and amount of charge. The electrical field is of special importance with respect to expansion and contraction of the crystal lattice. The strength of the electrical field influences the diffusion rate of both cations and positively charged polymers, the degree of hydrolysis of the adsorbed ions, the repulsion of anions, etc. Montmorillonite has a smaller amount of charge than vermiculite. The charge in montmorillonite originates mainly in the octahedral layer, whereas in vermiculite, the charge originates mainly in the tetrahedral layer. According to Coulomb's

law, the interlayer cation will be held almost four times more strongly by the tetrahedral charge than by the octahedral charge. Hsu and Bates (1964a) obtained experimental evidence that OH-Al polymers were more tightly held by vermiculite than by montmorillonite. Schwertmann and Jackson (1964) and Jackson (1960, 1962) concluded that hydroxy-aluminum polymers were more rapidly formed in vermiculite than in montmorillonite. Schwertmann and Jackson (1964) further stated that the hydroxy-Al polymers in vermiculite had a greater stability to H-resin treatment and to exchange in KCl than the interlayers in montmorillonite.

Differences between montmorillonite and vermiculite with respect to interlayer formation as a function of time were observed in the present study. Table IV summarizes the results with aluminum interlayers. The terminology used in this table, as well as in Tables V and VI was selected in such a way as to reflect the formation or dissolution of different interlayers during the intervening period. For example, the data obtained after six months were compared with those recorded after ten days while the data recorded after one year were compared with those after six months. The differences between montmorillonite and vermiculite, as far as the interlayer formation was concerned, were more evident in this study over a one year period. It can be readily seen from Table IV that after a six-month period, the formation of hydroxy-Al interlayers in the two minerals

followed nearly an opposite path. In acid and neutral media, a depletion of interlayer was recorded for montmorillonite whereas a slow formation of interlayer took place in the vermiculite system. In alkaline medium, the aluminum interlayers in montmorillonite showed no visible changes whereas in vermiculite, the formation of interlayer was still an active process. After the lapse of another six months, the pattern was almost unchanged for the acid systems. However, for the neutral and alkaline systems, a slight formation of interlayer was noted for montmorillonite and a moderate dissolution of interlayer was recorded for vermiculite.

An attempt will be made to explain the changes described above. The hydroxyls necessary for building the interlayers may be either supplied to the system by an addition of NaOH or they may be formed through hydrolysis. In the present study both sources of hydroxyls were present, but in different proportions. For example, in acid media, more hydroxyls were presumably formed through hydrolysis than in alkaline media. Further, more hydroxyls were added as NaOH in alkaline media than in acid media. Due to the reasons which have been already discussed, vermiculite is expected to have a greater effectiveness in suppressing the hydrolysis of Al^{3+} , Fe^{3+} and Mg^{2+} than montmorillonite. Similarly, the repulsion of OH^- would be greater for vermiculite than montmorillonite. Therefore, the clay minerals acting as anions will repel the hydroxyls

and they will adsorb the cations with various degrees of strength. The strength of adsorption will, in turn, influence the hydrolysis in place, polymerization of basic ions and the precipitation of the appropriate hydroxide. Barnishel and Rich (1963), Barnishel (1965) and Hsu and Bates (1964a) reported that the amount of hydroxy-Al interlayers formed in acid conditions decreased over time. They also found that gibbsite was precipitated outside the montmorillonite and vermiculite lattices. The data of this study are consistent with that point of view. These data also suggest that dissolution of interlayers and precipitation of hydroxide took place in neutral and alkaline conditions in addition to acid medium. This seems to be more evident for the aluminum vermiculite system than for the aluminum montmorillonite system.

Table V summarizes the results with iron interlayers. Both montmorillonite and vermiculite iron systems showed slight decreases in the amount of interlayer over a one-year period. By analogy to aluminum interlayers it is presumed that the dissolution of iron interlayers is accompanied by the formation of iron hydroxide outside the crystalline lattices. It may be pointed out here that the X-ray diffraction patterns of iron systems reflected a poor degree of orientation and crystallization of interlayer in the interspace. The iron montmorillonite system exhibited broad peaks which had a strong tendency to form plateaus. In addition to a poor crystallinity

of iron interlayer, the heavily coated iron montmorillonite produced a strong X-ray fluorescence which may be a contributing factor to the diffuse peaks. It has been reported that iron was adsorbed by clay minerals, particularly by montmorillonite, in excess of their exchange capacity (Lutz, 1939; DeMumbrum and Jackson, 1957; Thomas and Coleman, 1964). Whittig and Page (1961) and Page and Whittig (1961) suggested that iron was adsorbed as monovalent or divalent complex ions in addition to iron hydroxide. Data of this study showed that iron interlayered vermiculite systems exhibited relatively distinct peaks which were comparable to those recorded for the aluminum systems. This suggests a higher degree of orientation and crystallization of the iron interlayers in vermiculite than in montmorillonite. Mackenzie (1957) reported that ferric hydroxide precipitated by NH_4OH at pH 5.0 remained amorphous for a long period of time, while the ferric hydroxide at pH 10.0 crystallized to goethite. Gastuche et al. (1964) reported that hematite crystallized rapidly in a dialized medium from ferric gels prepared at pH as low as 4.5, whereas above pH 8.0 goethite started to crystallize in addition to hematite.

Magnesium interlayer in vermiculite experienced a decrease over a one year period. A decrease in the amount of interlayer was also recorded by the montmorillonite system with an initial pH of 10.0. The decrease was not evident for the interlayers formed at an

initial pH of 11.0 since the montmorillonite itself became almost amorphous after six months of equilibration. The decrease in magnesium interlayers is presumed to be related to the formation of magnesium hydroxide outside of crystalline lattices.

Stability of Interlayers

Stability to Sequential Treatments

Table VII gives the stability of hydroxy-Al, Fe, and Mg interlayers in montmorillonite and vermiculite. It may be recalled that the stability of interlayers was evaluated by subjecting the interlayered samples, equilibrated at different pH values, to a sequence of treatments increasing in severity. The stability of hydroxy-Al interlayers decreased from acid toward alkaline conditions for both montmorillonite and vermiculite systems. Unlike aluminum interlayers, the stability of iron interlayers in montmorillonite increased from acid toward alkaline conditions. The iron interlayers in vermiculite showed an equal stability to removal regardless of conditions of interlayer formation. The stability of magnesium interlayers in vermiculite followed a pattern similar to aluminum interlayers, that is, it decreased with increasing pH.

The hydroxy-Al, Fe, and Mg interlayers in montmorillonite exhibited a higher stability than the interlayers in vermiculite.

These results are consistent with the findings reported by Tamura (1956, 1957) who reported that a natural hydroxy interlayer, primarily aluminum, in a montmorillonite matrix (1957) was more stable to the dithionite-citrate treatment than the interlayer formed in a vermiculite matrix (1956). Later, Sawhney (1960), although he did not state so, found no differences between montmorillonite and vermiculite with respect to stability of synthetic aluminum interlayers to the citrate treatment.

Table VII. Stability to sequential treatments for hydroxy-Al, Fe, and Mg interlayers formed after 6 months in different conditions of acidity.

Type of interlayer	Type of mineral	Stability of interlayers across acidity
Aluminum	Montmorillonite	acid > neutral > alkaline
	✓ Vermiculite	acid > neutral > alkaline
Iron (Ferric)	Montmorillonite	acid < alkaline ≤ neutral
	✓ Vermiculite	acid ≤ neutral ≤ alkaline
Magnesium	Montmorillonite	$\frac{\text{OH}}{\text{Mg}} = 1.00$ (Fairly stable)
	✓ Vermiculite	$\frac{\text{OH}}{\text{Mg}} = 0.62 \geq \frac{\text{OH}}{\text{Mg}} = 1.25$

Stability to HCl Treatment

Table VIII summarizes the stability of different interlayers with respect to HCl treatments. It may be noted that the stability to HCl of aluminum interlayers in montmorillonite decreased toward

acid conditions of formation, while the stability of interlayers in vermiculite increased in the same direction. Shen and Rich (1962) reported that $\text{Al}(\text{OH})_3$ which precipitated from the hydroxy-Al interlayer in montmorillonite was practically not affected by five washings with 0.2 N HCl. They further stated that the hydroxy-Al interlayers themselves were removed by the HCl treatment and the original CEC of montmorillonite was fully restored. The results of the present study dealing with aluminum interlayers in montmorillonite are consistent with the above point of view. However, the differences between montmorillonite and vermiculite with respect to stability of interlayer to HCl are rather difficult to explain. Although the mechanism of aluminum interlayer formation in these two minerals may be quite similar, nevertheless the degrees of crystallization and orientation of interlayer in the interspace may be different. The degree of crystallization of aluminum hydroxide was found to be important with respect to its solubility in HCl (Hsu and Bates, 1964a). They reported that the solubility in acid decreased with an increase in the degree of crystallinity. The above discussion also applies to iron and magnesium systems which revealed behavioral differences as a function of type of mineral used.

The directions of increasing stability of the iron interlayers to HCl were just opposite to those observed for the aluminum systems. Generally, the stability of iron interlayers in montmorillonite

increased from acid to alkaline media, while the stability of iron interlayers in vermiculite decreased from alkaline toward acid conditions.

Table VIII. Stability to HCl treatments for hydroxy-Al, Fe, and Mg interlayers formed after 6 months in different conditions of acidity.

Type of interlayer	Type of mineral	Stability of interlayers across acidity
Aluminum	Montmorillonite	acid < neutral < alkaline
	✓ Vermiculite	acid > neutral > alkaline
Iron (Ferric)	Montmorillonite	acid ≥ neutral ≥ alkaline
	✓ Vermiculite	acid < neutral < alkaline
Magnesium	Montmorillonite	$\frac{\text{OH}}{\text{Mg}} = 1.00 \leq \frac{\text{OH}}{\text{Mg}} = 1.25$
	✓ Vermiculite	$\frac{\text{OH}}{\text{Mg}} = 0.62 < \frac{\text{OH}}{\text{Mg}} = 1.25$

Finally, magnesium interlayers in montmorillonite were relatively stable to the HCl treatment and the stability decreased with increasing pH. In contrast, stability of magnesium interlayers in vermiculite increased with increasing pH.

Degree of Interlayer Removal by Chemical Treatments

An estimate of the degrees of interlayer removal by the sequential and acid treatments is shown in Table IX. It may be recalled that the removal treatments were used in an effort to assess the interlayer

stability. Without exception, the degree of interlayer removal was much higher for vermiculite than for montmorillonite. Aluminum and magnesium interlayers in vermiculite were highly removed by either sequential or HCl treatments. Their counterparts in montmorillonite were only slightly or very slightly removed. The differences between the two minerals were also quite evident for iron interlayers.

Table IX. The degree of interlayer removal by chemical treatments regardless of conditions of formation.

Type of interlayer	Type of mineral	Degree of removal by	
		Sequential treatments	Acid treatments
Aluminum	Montmorillonite	slight	very slight
	^ Vermiculite	strong	strong
Iron (Ferric)	Montmorillonite	slight	very slight
	^ Vermiculite	moderate	slight
Magnesium	Montmorillonite	very slight	very slight
	^ Vermiculite	strong	strong

It may be recalled that the results with stability of interlayers revealed wide differences in behavior which were particularly related to the type of clay mineral and kind of chemical treatment. The use of the chemical treatments, undoubtedly, has implications on methods and criteria for clay minerals identification. The

chemical treatments used in this study are more commonly employed, alone or in combination, in dispersion and segregation procedures for soil analysis. Some investigators avoided the use of chemical treatments during dispersion and segregation of samples for mineralogical analysis and used water instead as a dispersing medium (Harward et al., 1962; Singleton, 1966). Some of the treatments directed at one component may affect the other because of the chemical and mineralogical similarity. Treatments too severe may destroy or remove the silicate clay and other minerals in addition to amorphous materials. On the other hand, a treatment too mild may fall short of the desired results. The suite of minerals identified in soil samples or sediments may depend upon the chemical pretreatments received by the samples (Harward et al., 1962). The selection of chemical treatments will rest ultimately upon the investigator so as to fulfill the objectives of his investigation. Further research is undoubtedly necessary on this line.

Occurrence of 14 Å Lines in Relation to Removal Treatments

The occurrence of 14 Å lines in different interlayered systems after sequential treatments has been repeatedly mentioned in the Results section. No attempt has been made there to explain this occurrence. However, it is appropriate that a brief explanation of the origin of these lines, which are characteristic of chlorite, is in

order at this time. There are two points of view with respect to the origin of the 14 \AA lines. One point of view considers that the 14 \AA component was initially present in the interlayered sample and that the specific treatment permitted its resolution. The other point of view is that the chlorite was created as a result of chemical treatments themselves (Harward et al., 1962).

There is evidence in the present study to support the first point of view. Data from Figures 8, 9 and 12 will be used to illustrate this point. The standard clay minerals, without artificial interlayers, were not adversely affected by any of the sequential treatments (Figure 8, part b). On the contrary, some improvements of the X-ray diffraction patterns and an increase in the CEC values were recorded for all three minerals following the sequential treatments. Figures 9 and 12 provided a clear evidence that the 14 \AA lines occurred only in interlayered systems. The intermediate position of the X-ray diffraction peaks of the interlayered materials indicated the formation of randomly interstratified systems. Figure 9 shows a random montmorillonite-chlorite line interstratification whereas Figure 12 illustrates a random vermiculite-chlorite like interstratification.

The presence of amorphous and poorly crystalline materials was an important contributing factor to the low peak background ratios. The specific interaction of these materials with the X-ray

beam made the detection of the two components difficult. The sequential treatments progressively removed the amorphous material and the labile forms of interlayers and markedly increased the intensity of the diffraction peaks. This improvement was also accompanied by the appearance of a small 14 \AA peak which, generally, increased in intensity with the severity of treatments (Figure 9). The resolution of the mixed systems into collapsible (montmorillonite or vermiculite) and non-collapsible (Al-polymer montmorillonite or Fe-polymer vermiculite) components was particularly apparent after the second dithionite-citrate and NaOH treatments. The resolution of the existing components is also supported by (1) the progressive increase in CEC values following sequential treatments, (2) the lattice collapse with a simultaneous occurrence of the 14 \AA peaks, and (3) the direct relationship between the intensity of 14 \AA lines and the amount of interlayer prior to sequential treatments.

It is concluded that the treatments facilitated the resolution of the components already present in the system. Heating of interlayered samples to 400°C for 4 hours in conjunction with NaOH treatment, as proposed by Hashimoto and Jackson (1958), is required for removal of the most stable chlorite-like component. However, Singleton (1966) indicated that this treatment should be used with caution for natural systems because there is always a possibility of destroying the matrix minerals in addition to interlayers.

Formation versus Stability of Hydroxy Interlayers in
Montmorillonite and Vermiculite

It is quite apparent from the result of this study that the formation of interlayers in expandable clay minerals should be looked upon as a dynamic process which exhibited significant changes with time. Aluminum montmorillonite system equilibrated in acid media for ten days exhibited the greatest degree of interlayering. However, a dissolution of interlayer was noted following six months or one year. Unlike montmorillonite, the aluminum interlayer formation in vermiculite from acid medium showed an increase with time. Two arbitrary terms will be defined below in order to facilitate the understanding of differences between formation and stability of interlayers. The term "natural stability" is defined as the stability of different interlayers with time. The amounts of interlayer were measured by X-ray diffraction and CEC and together, they provided a good estimate of this stability. The capacity of various interlayered systems to respond to the chemical dissolution treatments was defined here as an "artificial" stability. Aluminum interlayers in vermiculite from acid conditions exhibited a greater "natural" stability but a lesser "artificial" stability than their counterparts in montmorillonite. At the same time, iron and magnesium interlayers in montmorillonite, generally, showed higher degrees of

interlayer formation and higher "natural" and "artificial" stability than similar interlayers formed in vermiculite. If one recognized that more hydroxy-Al, Fe, and Mg interlayers were initially formed in montmorillonite than in vermiculite, then a direct relationship between formation and stability is quite evident (Table IX). Thus, the stability of interlayers to chemical treatments or the "artificial" stability, as defined earlier, was always higher for montmorillonite systems than for vermiculite systems.

Chloritic intergrade minerals have been formed in natural soils from vermiculite (Dixon and Jackson, 1962; Sawhney, 1960; Brown, 1953; Rich, 1960; Jackson, 1959), beidellite (Singleton, 1966), montmorillonite (Singleton, 1966; Tamura, 1957, 1958; Dixon and Jackson, 1959), and chlorite (Droste, 1956). The formation of chloritic intergrade from one or the other mineral would depend upon the intensity and duration of the weathering forces, mineralogical nature of the parent material, acidity of medium and species of exchangeable ions. The degree of formation will vary in intensity as a function of time and changes in the forming environment. The size fraction plays, presumably, but a minor role with respect to the preferential formation of interlayers. The larger size will allow lesser formation of interlayers, at least initially, than the smaller size fractions for the reasons already discussed in the body of the thesis.

SUMMARY AND CONCLUSIONS

General

The effects of pH and time on the formation of hydroxy-Al, Fe, and Mg interlayers were compared for montmorillonite and vermiculite. The stability of interlayers was evaluated by sequentially increasing the severity of dissolution treatments, which included (1) boiling 2% sodium carbonate, (2) buffered sodium citrate-dithionite which was repeated once, and (3) boiling sodium hydroxide. The stability of interlayers to HCl treatments was also investigated. The formation and stability of interlayers were evaluated by X-ray diffraction analysis and cation exchange capacity measurements after various periods of time and after each treatment of the sequence. A natural chlorite was used for comparison.

Generally, more hydroxy-Al, Fe, and Mg interlayers were initially produced in montmorillonite than in vermiculite. At the same time, the interlayers in montmorillonite always exhibited higher stability to either sequential or HCl treatments than the interlayers in vermiculite. The stability was about in direct relationship to the initial amount of interlayer.

The formation of different interlayers was strongly dependent upon pH, time and type of clay mineral. The pH changes were not a good measure of hydroxy interlayer formation. However, it is

believed that differences between the three kinds of media with respect to interlayer formation were a result of kind and amount of ionic species, size and charge of resulting polymers and fixation and redistribution of polymers in a particular medium. Time and type of clay mineral are considered important factors with respect to crystallization, formation and orientation of bonds, precipitation or dissolution, diffusion of ions and other surface phenomena.

Aluminum Interlayers

In montmorillonite, aluminum interlayers were formed at all pH levels. Systems equilibrated in acid media exhibited the greatest degree of interlayering. For those formed in an acid media, the resistance to expansion and collapse was greater after ten days than after six months or one year, suggesting decrease of interlayering with time. The synthetic material, resulting after ten days of equilibration, like the natural chlorite, did not show any expansion and exhibited practically no collapse after K treatment and heating to 300°C and 550°C . Those interlayers formed in alkaline media exhibited increased interlayering after one year equilibration. Boiling Na_2CO_3 , and particularly boiling NaOH generally removed part of the interlayers. This removal was more pronounced for neutral and alkaline media than for acid media. Interlayered samples from neutral and particularly from alkaline media which

received the dithionite-citrate dissolution treatments exhibited mixed layer systems and the appearance of a 14 \AA component after heating. Interlayer formed in alkaline conditions showed the highest stability to HCl treatment, whereas that formed in acid media was the least stable.

In vermiculite, aluminum interlayers were also greater for acid than for alkaline media. In contrast to montmorillonite, the interlayer formation in vermiculite in acid media increased with time. For alkaline media there was some increase in the interlayering after six months followed by dissolution after one year. As the severity of dissolution treatments increased the degree of collapse increased. However, chloritic components in addition to dominant collapsible components were evident after NaOH treatment for systems formed at intermediate pH levels. A mixed system persisted after the NaOH treatment in the interlayered sample from acid media. Unlike montmorillonite, the stability of interlayers to the HCl treatment was in the order acid > neutral > alkaline systems.

Iron Interlayers

Moderate amounts of iron interlayers were formed in montmorillonite at all pH levels. The interlayers did not inhibit expansion on solvation but the systems exhibited moderate resistance

to collapse. Diffraction patterns were characterized by diffuse peaks and plateaus suggesting mixed layer systems. Some reorganization or dissolution occurred after equilibration for one year. The interlayers were partially removed by dissolution treatments, the degree of removal increasing with severity of treatment. However, some interlayers persisted after the most severe treatment. Interlayers formed at intermediate pH values were, presumably, more stable than those formed in other media. The interlayer formed in acid media was somewhat more stable to the HCl treatment than the interlayer formed in alkaline media.

Iron interlayer formation in vermiculite was favored by alkaline environments. Formation was greatest after ten days and less after six months or one year. Samples receiving minimal treatments for removal exhibited intermediate spacings suggesting mixed layer systems. Iron removal and particularly boiling NaOH treatments resolved the mixed systems into collapsible and non-collapsible components. In the latter case, definite chlorite lines were observed. The stability of iron interlayers in vermiculite was in the order alkaline > neutral > acid systems. The HCl treatment removed more interlayer from acid media than from alkaline media.

Magnesium Interlayers

Magnesium interlayers were formed in montmorillonite only in alkaline conditions at $\text{pH} > 10$. The interlayered montmorillonite resulting at $\text{pH} 10$ exhibited only a partial expansion on solvation and showed a high resistance to collapse following 300°C or even 550°C . Some decrease of interlayer occurred after one year. The interlayered material formed at an initial pH of 11.0 was nearly amorphous to X-ray diffraction following a 6-month period. Except for the boiling NaOH treatment, all the treatments produced only minor changes in basal spacings and cation exchange capacity of the interlayered material. Heating to 550°C following NaOH treatment partially resolved the mixed system into collapsible and non-collapsible components. The interlayer showed a high stability to HCl treatments.

Moderate amounts of magnesium interlayers were formed in vermiculite and, like montmorillonite, the interlayers formed only in alkaline media. The interlayer formation decreased with increasing pH . A strong dissolution of interlayers took place with time. The rate of interlayer dissolution increased as the pH increased. Boiling Na_2CO_3 and the first dithionite-citrate treatments removed only small amounts of interlayers. The second dithionite-citrate treatment, however, removed most of the interlayer and

induced a high degree of collapse and a high CEC. The boiling NaOH treatment resolved a 14 Å component in addition to a dominant 10 Å component. Unlike montmorillonite, most of the magnesium interlayers were removed by the HCl treatments.

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