

AN ABSTRACT OF THE THESIS OF

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Title NATURE OF INTERLAYER MATERIAL IN SILICATE CLAYS OF

SELECTED OREGON SOILS

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A study was conducted to investigate the nature of hydroxy interlayers in the chlorite-like intergrade clays of three Oregon soils with respect to kind, amount, stability, and conditions of formation.

The clays of the Hembre, Wren, and Lookout soils, selected to represent weathering products originating from basaltic materials under humid, subhumid, and semi-arid climatic conditions respectively, were subjected to a series of progressive treatments designed to effect a differential dissolution of the materials intimately associated with them. The treatments, chosen to represent a range of increasing severity of dissolution, were (1) distilled water plus mechanical stirring, (2) boiling 2% sodium carbonate, (3) buffered sodium citrate-dithionite, (4) boiling sodium hydroxide, and (5) preheating to 400 °C for 4 hours plus boiling sodium hydroxide.

Extracts from the various steps of the dissolution procedure were chemically analyzed in order to identify the materials removed from the clays. X-ray diffraction analysis and cation exchange

capacity determinations were made on the clays after each step, and any differences noted in the measured values were attributed to the removal of hydroxy interlayers from the clays.

Hydroxy interlayers were found to occur more in the Hembre and Wren soils than in the Lookout soil, with the most stable interlayers occurring in the Wren. Soil reaction was one of the major differences between these soils. The pH values of the Hembre and Wren ranged between 4.5 and 5.0, while that of the Lookout soil was near neutral at the surface and 8.3 in the zone of calcium carbonate accumulation. It appeared from the data, that the parent material of the Wren soil had reached a more advanced stage of weathering than that of the other soils.

The data from the Hembre clays showed that hydroxy interlayers formed to the greatest extent in the surface horizon and decreased with depth. Such interlayers occurred in the A and B horizons of the Wren clays in about equal amounts, but less in the C horizon. The zone of clay enrichment in the B horizon of the Wren soil suggests a downward movement of clay in the profile. Consequently, it is conceivable that some of the interlayer hydroxides formed in the A horizon would ultimately have reached the B horizon. There appeared to be as much interlayering in the C horizon clays of the Lookout soil as in the upper horizons. This seems to contradict the idea that interlayering develops most in the upper horizons where weathering is greatest. The apparent anomaly is resolved, however, if the lithologic discontinuity in the profile is taken into consideration. Evidence indicates that the present C horizon of the Lookout soil may have been a surface soil at one time.

Chemical analysis of the treatment extracts suggests that iron and magnesium as well as aluminum probably occupy the interlayer positions of the clays studied. A part of the magnesium was presumed to have been residuum from brucite interlayers of degraded chlorite.

The results indicated that intergrade clays may have formed both from chloritization, and from chlorite degradation. The high amount of chlorite in the Hembre parent materials together with the acid environmental conditions probably led to some chlorite breakdown. Somewhat similar conditions existed in the Wren soil. There is, however, a high amount of biotite in the parent materials of the Wren soil that could readily weather to an intergrade by being altered to smectite or vermiculite and undergoing subsequent chloritization. The intergrades in the Lookout soil clays apparently formed from chloritization of smectites in as much as no chlorite was observed in the parent materials.

NATURE OF INTERLAYER MATERIAL IN SILICATE CLAYS
OF SELECTED OREGON SOILS

by

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NATURE OF INTERLAYER MATERIAL IN SILICATE CLAYS OF SELECTED OREGON SOILS

INTRODUCTION

The existence of major clay groups such as 1:1 kaolins, 2:1 smectites and vermiculites, and 2:2 chlorites were recognized quite early in the investigation of clay minerals. As studies progressed and techniques became more refined, results indicated that the clay mineral suites of most soils were quite complex. The complexities resulted from differences in degree of crystallinity, interstratification, and occurrence of intergrades. Many soil clays with anomalous characteristics have since been described. Such clays were reported as having properties intergradient between those of the 2:1 expansible minerals and those of 2:2 chlorite. The behavioral characteristics of chlorite as compared to those of the expansible minerals are best understood if the structural differences of the two are taken into consideration.

Two ionic coordination groups are the basic units of which layer silicates are formed. Silicon ions each surrounded by four, equally spaced oxygen ions in tetrahedral coordination make up the first group. Each silica tetrahedron shares three of its oxygen ions with three adjacent tetrahedra. The tetrahedrons thus connected form a sheet with the unshared apical oxygen of each tetrahedron all pointing in the same direction. To a certain extent, Al^{+3} can substitute for Si^{+4} which results in one excess negative charge in the sheet for every substitution. The second group is formed of either aluminum,

magnesium, or iron ions in octahedral coordination with six oxygen or hydroxyl ions. Adjacent octahedra share oxygen or hydroxyl ions forming an octahedral sheet. Octahedral sheets formed with trivalent ions have a cation in two out of every three octahedral positions with one remaining empty, while those formed from divalent ions have a cation in every octahedral position. The sheets are referred to as dioctahedral and trioctahedral respectively.

Layer silicates consist of tetrahedral silica sheets attached to octahedral hydroxyl sheets with each apical oxygen of the tetrahedral sheet replacing one hydroxyl ion of the octahedral sheet. Different combinations of these two general units, the tetrahedral and octahedral sheets, yield various types of layer silicates. When one tetrahedral sheet is condensed on each side of an octahedral sheet, the resulting structure with a two-to-one ratio is designated as a 2:1 layer silicate. The formulas which represent the classical unsubstituted end members of the 2:1 layer silicates are $\text{Si}_8\text{Al}_4\text{O}_{20}(\text{OH})_4$ for dioctahedral pyrophyllite, and $\text{Si}_8(\text{Mg},\text{Fe})_6\text{O}_{20}(\text{OH})_4$ for trioctahedral talc. The unsubstituted minerals, however, rarely occur in nature; rather, those with varying degrees of substitution prevail. Muscovite and biotite, for example, represent mica minerals in which there is a high degree of substitution of aluminum for silicon in the tetrahedral sheet. The formula for dioctahedral muscovite is $\text{K}_2(\text{Al}_2\text{Si}_6)\text{Al}_4\text{O}_{20}(\text{OH})_4$, and that for trioctahedral biotite is $\text{K}_2(\text{Al}_2\text{Si}_6)(\text{Mg},\text{Fe})_6\text{O}_{20}(\text{OH})_4$. The two potassium ions shown in both formulas furnish the positive charges necessary to offset the un-

balanced condition resulting from the tetrahedral substitution of two Al^{+3} for two Si^{+4} . Tetrahedral substitutions in the mica unit may range between (Al Si_7) and Al_4Si_4 . Other 2:1 layer silicates such as smectites and vermiculites result from different degrees of isomorphous substitution in both the tetrahedral and octahedral sheets, with calcium, magnesium, or sodium acting as the predominant counter ions. The various 2:1 layer silicates have expandible C axis dimensions that range from less than 10 \AA to 18 \AA and greater, depending upon the degree of substitution, the location of substitution, the species of counter ion, and the degree of interlayer solvation.

The classical structure of chlorite is described by Grim (1953) as having alternate mica-like and brucite-like layers. The brucite-like layer takes the place of the potassium counter ions between the mica units. It has the general composition of $(\text{Mg,Al})_6(\text{OH})_{12}$. The unbalanced charges of the mica layer are balanced by an excess charge in the brucite layer as a result of Al^{+3} being substituted for Mg^{+2} . The formula for trioctahedral chlorite can be expressed as

$(\text{Al}_2\text{Mg}_4)(\text{OH})_{12} \cdot (\text{Al}_2\text{Si}_6)\text{Mg}_6\text{O}_{20}(\text{OH})_4$ where the hydroxide term before the dot represents the positively charged brucite-like interlayer which neutralizes the negative charge of the mica-like layer. As a consequence of the two alternating layers in chlorite, it has been designated as a 2:1:1 layer silicate, or more commonly as a 2:2 layer silicate. Such minerals, because of the brucite-like interlayer, have a fixed C axis dimension of about 14 \AA .

Layer silicates that deviate from the classical in that their structures are intermediate between 2:1 and 2:2 minerals appear to be

quite common in soil clays. Under certain environmental conditions, hydroxy precipitates of either aluminum, magnesium, or iron may occur in the interlayer spaces of 2:1 minerals giving them a chlorite-like structure. On the other hand, true chlorites may, through degradation processes lose certain interlayer constituents and become chlorite-like minerals. In either case, the heterogeneous scattering of interlayer islands prevents the mineral from exhibiting C axis dimensions that are characteristic for either the 2:1 or 2:2 minerals. Specific surface and cation exchange capacity measurements of such partially interlayered minerals are also intermediate between the 2:1 and 2:2 types.

Interlayer hydroxy materials are of interest because of their effect on soil fertility and plant nutrition. Soil physicochemical processes involving fixation of nutrient elements such as potassium, ammonium, and phosphorous are greatly influenced by the presence of hydroxy interlayers. Also, the formation of intergrade minerals appears to be closely associated with normal pedogenic processes that occur under certain environmental conditions.

The occurrence of chloritic intergrades seems to be fairly common in acid soils of Oregon. Variations in the amount and stability of interlayer materials have been noted. Although the formation, structure, and occurrence of chloritic intergrades have received a great deal of attention in the past several years, a number of questions still remain:

1. What role, if any, does iron play in interlayer formation?
- A great deal of attention has been paid to the role of aluminum, but

relatively little has been given to iron.

2. Most investigations of interlayers have been conducted with acid soils. What are the relationships in alkaline soils?

3. Certain studies have related weathering sequences and drainage to interlayer occurrence, but more information is needed on the broad effects of climate, vegetation, and parent material.

With the above in mind, a study was conducted to learn more about the nature of intergrade clays, and the conditions under which they form in situ. Soils from different climatic areas of Oregon were chosen for the study in order to appraise the effect of climate and associated factors on the properties and mechanism of intergrade formation. An attempt was made to select only soils originating from basalt in order to eliminate the variable of parent material.

The objectives of the study were as follows:

1. To investigate the nature of interlayer materials in silicate clays with respect to
 - a. kinds of interlayer material
 - b. amounts of interlayer present
 - c. stability of interlayer materials
2. To determine conditions under which natural interlayer materials develop.

LITERATURE REVIEW

General

Soil clays that contain minerals intergradient between the 2:1 and 2:2 layer silicates have been described as chlorite-vermiculite-montmorillonite intergrade (Dixon and Jackson, 1959), dioctahedral analogue of vermiculite (Brown, 1954), vermiculite-chlorite (Bryant and Dixon, 1964), chloritized vermiculite (Sawhney, 1958), chlorite-like (Klages and White, 1957), "chlorite" (Brown and Ingram, 1954), and "swelling chlorite" (Stephen and MacEwan, 1951).

Minerals such as those described exhibit properties that are intermediate between those of the expansible clays and chlorite. The presence of scattered brucite-like or gibbsite-like hydroxy interlayers between the mica units of the mineral account for their unusual behavioral characteristics. Usually they do not completely expand upon solvation but tend to retain a 14 \AA (001) spacing. They may show some collapse when potassium saturated but not to the same extent as the expansible minerals. When potassium saturated and subjected to temperatures between 300 and 500 °C, they will exhibit some collapse, indicating that the hydroxy interlayers decompose in that temperature range. Because of this characteristic, the relative stability of intergrade materials has been related to their heat resistance to collapse. True chlorites can be identified and separated from "chlorite-like" interlayered minerals because they have temperature stability above 550 °C (Jackson, 1959).

The extent of hydroxy interlayering has been related to the active surface area of the mineral. The more completely the interlayer spaces are filled with hydroxy polymers, the more the active surface area is reduced, the surface being restricted primarily to the outer faces of the mineral when completely interlayered. Cation exchange capacity measurements, being closely related to total active surface, likewise give a good indication of the degree of hydroxy interlayering.

Chlorite-like expansible minerals revert to normal montmorillonite or vermiculite behavior when stripped of the interlayer hydroxides by chemical dissolution.

Occurrence of Intergrade Clay

Various workers in the last ten to fifteen years have described soil clays that exhibit properties unlike any of the previously described specimens. Grim and Johns (1954) found a type of montmorillonite that was common to bay and gulf environments in sediments of the Northern Gulf of Mexico that was unique in that it exhibited properties common to both montmorillonite and chlorite. X-ray diffraction of the clay showed characteristic chlorite lines, but the intensities of the higher orders relative to the first order were lower than would be expected for a true chlorite. They believed that this was indicative of an interlayer population considerably deficient in brucite as compared to material definitely called chlorite. They assumed that this material could represent incipient chloritization by aggradation of montmorillonite or by degradation of chlorite in the source area by the removal of magnesium. They suggested that the

interlayer region consisted of occasional "islands" of brucite scattered laterally at random over otherwise hydrated montmorillonite surfaces. The islands occurred with sufficient frequency to keep the silicate layers strongly together and prevent glycolation and subsequent expansion, or to prevent complete collapse upon moderate thermal treatment. They were also of the opinion that the clays which Stephen and MacEwan (1951) designated as "swelling chlorites" were probably similar to the gulf clays.

Brown (1954) found a dioctahedral mineral in soils from north-western England containing aluminum which he called the dioctahedral analogue of vermiculite. It has a characteristic 14 \AA chlorite line that did not expand when treated with glycerol and CaCl_2 . Unlike chlorite, when heated to 400°C it showed partial collapse with a broad line from 14 \AA to 10 \AA . Stephen (1952 a,b) also found chlorite-vermiculite-like clays in soils from the Malvern Hills of Worcestershire, England. He postulated that they originated from biotites and chlorites by a process of "vermiculitization".

Tamura (1957) described a mineral found in Connecticut soils with a stable 14 \AA spacing that exhibited a behavior between that of vermiculite and chlorite. Sawhney (1958, 1960) also worked with Connecticut soils and identified an intergrade clay from a Charlton silt loam soil as a vermiculite when the interlayer materials were removed. He suggested that the formation of such intergrades was essentially a "chloritization" of the expanding 2:1 type layer silicates. By studying the clays from soils of the Hollis-Charlton-Sutton-Leicester drainage catena, he found that hydroxy interlayer

formation was related to the degree of weathering to which the soils had been subjected. He noted that well drained soils exhibited interlayer materials which were more stable than poorly drained ones. He also observed that the interlayer material in the surface minerals was more stable than that found in the subsoil. Jeffries, Rolfe, and Kunze (1953), and Tamura (1956) report respectively that chloritization increases toward the surface of profiles, and that surface soils had more chlorite-like minerals than deeper horizons.

Brown and Ingram (1954) studied sediments from the Neuse River of North Carolina and described a clay which they called "chlorite" and which resembled the clay from England that Brown (1954) described. It differed, however, in that it showed signs of collapse at 300 °C whereas the English counterpart collapsed at 400 °C. They noted that the downstream clay suite changed from that found upstream, and they suggested a sequence of diagenesis whereby kaolinite and montmorillonite altered to degraded kaolinite and amorphous material, and these in turn were converted to mixed layer aggregates and "chlorite".

Intergrade clays have been observed in many acid, podzolic soils of the eastern United States. Chlorite-like minerals have also been studied in surface soils of Pennsylvania (Jeffries, Rolfe, and Kunze, 1953), and central New York (Rolfe and Jeffries, 1953) that were considered to have originated from "chloritized" micas. Intergradient chlorite-vermiculites have been found to occur in acid Red-Yellow Podzolic soils of Virginia (Rich and Obenshain, 1955); in Gray Brown Podzolic soils of Kentucky (Dixon and Seay, 1957); Gray Brown Podzolic soils of Indiana (Klages and White, 1957); coastal plains, piedmonts,

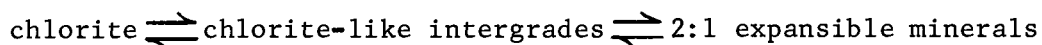
and mountain soils of North Carolina (Rolfe, 1954; Weed and Nelson, 1962), Virginia, New Jersey, and Wisconsin (Hathaway, 1955); Red-Yellow Podzolic soils from the Alabama Piedmont (Bryant and Dixon, 1964); and Reddish-Brown Lateritic soils of Mississippi (Glenn and Nash, 1964). Dioctahedral vermiculites with interlayer alumina, and dioctahedral chlorites have also been observed in highly weathered red loams of Victoria, Australia (Jones, Milne, and Attiwill, 1964).

Theories of Intergrade Formation

Silicate clays are the product of many interacting factors such as the nature of the primary minerals found in the parent materials, the type of biological complex associated with soil development, and the physical and chemical environmental conditions under which the formation processes take place. Under any set of conditions, the degree of development is dependent upon the period of time in which the parent rocks have been under the influence of weathering forces.

Chloritic intergrades are considered to originate from 2:2 or 2:1 layer silicates. Chlorite, a 2:2 mineral completely interlayered with brucite, may become a chloritic intergrade through partial degradation and subsequent replacement of portions of the brucite layer with exchangeable cations. Moreover, expansible 2:1 minerals may become chlorite-like intergrades when environmental conditions favor the hydrolysis of exchangeable aluminum, magnesium, or iron ions to non-exchangeable brucite-like hydroxy polymers. Consequently, the degree of hydroxy interlayering in layer silicates can range from completely interlayered chlorites on the one hand to

2:1 expansible minerals void of hydroxy interlayers on the other. The transitory nature of such interlayer materials can be expressed in the following equilibrium reaction between layer silicates that contain different degrees of hydroxy interlayering:

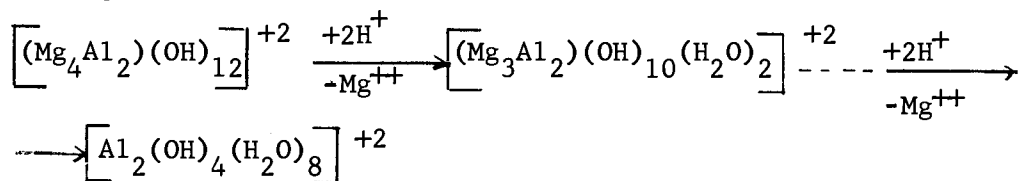


Mechanism of Chlorite Degradation

Jackson and Sherman (1953) indicated that micaceous parent materials might undergo a transformation from the primary micas through 2:2 chlorite and/or 2:1 vermiculite to montmorillonitic or kaolinitic clays. The chlorite and/or vermiculite stage of the weathering sequence is the period of pedogenesis when intergrade clays develop. The loss of magnesium from the brucite interlayer leads to a chlorite-like intergrade. Drost (1956), and Honeyborne (1951) also indicated that chlorite is readily weathered to a 2:1 mineral. Drost postulated that protons react with hydroxyl radicals and gradually hydrate the brucite sheet. As a result of the hydration, the OH ions that surround magnesium ions change to H₂O. Complete hydration of the magnesium ions forms a mineral that may be called vermiculite.

Stephen (1952 a,b) suggested that as weathering proceeds in certain soils formed from biotite in Malvern Hills, Worchestershire, England, the chlorite minerals of the unweathered parent rock are converted into a vermiculitic material. The vermiculite product may be formed either through mixed layer mica-vermiculite stage or mixed layer mica-chlorite and chlorite-vermiculite. Since weathering in this case takes place at fairly low pH values, there is a considerable concentration of hydrogen ions. These may penetrate into the brucite

layer and replace magnesium ions by an exchange process. The ultimate effect being that the hydrogen ions may add to the hydroxyl groups forming H_2O molecules. The net effect would be to convert two hydroxyl groups into neutral water molecules for each magnesium ion replaced, leaving the charge on the layer unchanged. The process could go through such stages as:



When the last stage is reached, all the magnesium will have been removed and the residue would consist of isolated $Al(OH)_2$ groups linked with water molecules. Eventually, the brucite layer is completely disintegrated and an aluminum vermiculite remains in which the aluminum ions should be mobile and exchangeable.

Murry and Leininger (1956) and Harrison and Murry (1959) studied soils of different degrees of maturity that had developed from glacial till of Indiana. They found that montmorillonite was the most abundant clay mineral in the highly weathered portion of the profile, and illite and chlorite most abundant in the unweathered portion. Chemical and mineralogical analyses indicated that the montmorillonite developed from illite and chlorite. They suggested that the initial mechanism in the transformation was the oxidation of ferrous iron in the mica layers of the illite and chlorite. There is a possibility, however, that this may not always apply to illite because of the low iron content in some illite minerals (Harrison and Murry, 1959). The structure of the mineral is slightly disrupted when the iron is

oxidized, and the layer charge is also changed. The bonds between the sheets are weakened thus allowing penetration of water and hydronium ions into the interlayer position and the removal of potassium from illite, and iron, magnesium, and hydroxyl ions from chlorite.

Mechanism of Chloritization

Evidence indicates that a large portion of intergrade minerals in the soil originate from the precursors, montmorillonite and vermiculite. Synthesis occurs when environmental conditions favor high quantities of aluminum or magnesium in the weathering complex. These ions readily hydrolyze to form positively charged hydroxides that act as counter ions on the exchange sites of expanding clays. As these complex ions accrue on the interfacial surfaces, they tend to condense into a polymeric network which makes subsequent exchange difficult (Jackson, 1963). Continued polymerization could result in the formation of discrete gibbsitic or brucitic layers between the crystal units of the clay. Theoretically, any negatively charged 2:1 layer silicate could be transformed into a 2:2 mineral with properties similar to chlorite.

Jackson (1962) indicated that the silica layer of the clay crystal may serve sterically as a template for nucleating gibbsite-like crystal units during interlayer polymerization in addition to serving as a negative surface for sorbing the positive aluminohydroxy units. Interlayer precipitation of aluminum hydroxide gel in expansible layer silicates tends to occur preferentially to precipitation of a separate free gibbsite phase (Jackson, 1963). This has been called an "antigibbsitic effect" (Jackson, 1962). According to

this concept, positive charged aluminum polymers at pH values below the isoelectric pH (4.8) of the gibbsite molecule would respond to charges on the exchange sites of montmorillonite and vermiculite minerals, entering their interlayer positions to form chlorite-like structures and prevent gibbsite nucleation. At pH values above the isoelectric pH, the gibbsite molecule would be negative and tend to be repulsed from the interlayer positions permitting nucleation of a crystalline gibbsite phase (Glenn and Nash, 1964). On the other hand, Jackson (1963) has shown that the isoelectric pH of amorphous gel of aluminum hydroxide is 8.3, much greater than that of crystalline gibbsite. Up to pH 8.3, amorphous aluminum hydroxides possess a positive charge that can attach to the negative sites in the interlayer spaces of layer silicates. This reaction would explain the presence of hydroxy aluminum interlayers in some montmorillonitic clays from alkaline soils of arid regions. Frink and Peech (1962) found that the time necessary to reach the solubility product of gibbsite was much longer in a clay or soil suspension than in an aqueous solution having the same pH values. They attributed the phenomena to the relatively large amount of adsorbed aluminum as compared to that in solution.

The matrix of many chlorite-like materials from soils has been identified as vermiculite. It is expected that chlorite-like structures would readily form in vermiculite because of the similarity of chlorite and vermiculite with respect to degree of isomorphous substitution. The fact that more hydroxy interlayer development has been noted in the coarser clay fraction of soils suggests that the

interlayer structures may be preferentially developed in vermiculite rather than montmorillonite. Dixon and Jackson (1962) attributed more interlayer development in vermiculite to its higher charge. Hsu and Bates (1964) in their studies of synthetic aluminum hydroxy formation in vermiculite concluded that vermiculite functions as an anion which has a very strong affinity for aluminum hydroxy polymers.

On the other hand, recent laboratory studies by Carstea (1965) have shown that it is much easier to form stable chlorite-like materials in montmorillonite than it is in vermiculite. He suggested that vermiculite, because of its higher charge, has less tendency to fix hydroxy interlayers than does montmorillonite. It is interesting to note in the discussion above, that Dixon and Jackson used the same argument to explain the existence of such interlayers in vermiculite. Carstea, however, postulated that in vermiculite the counter ions would be held so firmly by the charges originating in the tetrahedral layer that hydrolysis of the ions would be hindered. Pawluk's study (1962) of clay minerals from podzolized soils of Alberta, Canada also minimizes the argument that hydroxy interlayers are mostly in vermiculite because of their frequent occurrence in the coarse clay fraction. He found that the hydroxy aluminum interlayers bound fine sized montmorillonite into aggregates of coarse clay size that exhibited stable $14 \overset{\circ}{\text{\AA}}$ (001) spacing. When the interlayers were removed, the mineral reverted back to montmorillonite of fine clay size. Jackson (1962) implied that hydroxy interlayers form in montmorillonite as well as vermiculite but, in as much as montmorillonite is composed of smaller size particles than vermiculite, its higher

surface area is more subject to the attack of weathering acids. Thus, the tendency for montmorillonite to become interlayered in acid weathering environment seems to be countered by the rapid decomposition of the crystal.

Jones, Milne, and Attiwill (1964), Dixon and Jackson (1962), Sawhney (1960), Brown (1954), Rich (1960), and Jackson (1959) have all determined that chlorite-like intergrade minerals have originated from vermiculite. Tamura (1957, 1958), Dixon and Jackson (1959), and Grim and Johns (1954) have identified montmorillonite as a precursor to chlorite-like intergrades.

The process of interlayer formation has been referred to as "partial chloritization" (MacEwan, 1949), and as "alumination" (Tamura, Hanna, and Shearin, 1959). Sawhney (1960) indicated that chloritization in soils is analogous to diagenesis of chlorite sediments. The cationic environment of sediments produces brucite interlayers as contrasted to gibbsite interlayers in soil clays.

Nature of the Interlayer

It has been postulated that the interlayer material is composed of a polymeric hexaluminumhydroxyhydronium cation, $\text{Al}_6(\text{OH})_{12}(\text{-OH}_2)^{+6}_{12}$ with an OH/Al ratio of two, written as $\text{Al}(\text{OH})_2^+$ or $\text{Al}_6(\text{OH})_{12}^{+6}$ in older literature (Jackson, 1962; Hsu and Rich, 1960). This represents a one unit surface coverage of 100 \AA^2 and is equal to 16.6 \AA^2 surface coverage per unit positive charge. Bradley (1945) stated that the interlayer surface area of clay associated with each exchange site was of the order of 50 to 100 \AA^2 . Klages and White (1957) suggested a

general formula for the interlayer material to be $\left[\text{Al}(\text{OH})_x (\text{H}_2\text{O})_{3-x} \right]^{(3-x)+}$ where x varies with the soil pH.

Although aluminum has received the most attention, there is a possibility that other ions may be important in interlayer structures. Iron could co-precipitate with aluminum, especially under conditions of good drainage (Jackson, 1960). The fact that wetness and gleying "cleaned up" the interlayered 2:1 minerals suggests that iron may be involved (Jackson, 1962). It is implied that under anaerobic conditions, iron in the interlayer as $\text{Fe}(\text{OH})_2^+$ would be reduced to the ferrous state thus losing its capacity to be retained as a positively charged interlayer hydroxide. From the standpoint of the solubility products of magnesium, iron, and aluminum, interlayers could be expected to form from hydroxides of iron and magnesium as well as from aluminum. Precipitation of magnesium hydroxides would be expected to take place in alkaline environments, and iron and aluminum hydroxides in acid and mildly alkaline environments (Brydon, Clark, and Osborne, 1961). Hydroxy aluminum interlayer formation has been shown to cause a decrease in solution pH as a result of hydrogen ions being liberated during hydrolysis (Ragland and Coleman, 1960).

Considerable organic matter may also occupy the interlayer position. Brown (1954) noted that following H_2O_2 treatment, the (001) spacing responded more readily to differential cation treatment. He postulated that collapse of the structure by heat may be due to dehydration of the absorbed organic matter rather than dehydration of the adsorbed metallic ions.

Effect on Properties

Dixon and Jackson (1962) noted an increase in cation exchange capacity (CEC) after removing interlayers from the clay. They found that a removal of 1% Al_2O_3 increased the CEC 20 me. per 100 g. when the interlayer aluminum hydroxide had the general structure of $\text{Al}(\text{OH})_2^+$. This is equivalent to 26.5 mg. of aluminum per 1 me. of CEC. Sawhney (1960) noted an increase of 30 to 40% in CEC, and Tamura (1956) indicated an increase of over 100% when aluminum interlayers or free iron oxides were removed from various soils. Deb (1950), and Mitchell and Mackenzie (1954) also reported increases in CEC after interlayer removal.

Shen and Rich (1962) found a decrease in CEC of 1 me. per 24.6 mg. of aluminum fixed when they introduced synthetic interlayers into montmorillonite. Barnhisel and Rich (1963) noted that cation exchange capacity decreased from 72 to 2 me. per 100 g. by interlayers formed in montmorillonite.

Dixon and Jackson (1962) noted that the CEC values of Red-Yellow Podzolic soils from Kentucky and Virginia, and Gray-Brown Podzolic soils from Wisconsin suggest that one-third to one-half of their clay mineral components were 2:1 expanding clays. Specific surface values, however, indicated only one-fourth of the materials were expansible. The reduction in glycerol retention relative to exchange capacity by aluminous interlayers probably indicates a concentration of hydroxy-aluminum islands near the edges of the crystal plates, thus blocking entry of the large glycerol molecules yet admitting the

smaller exchangeable cations.

Oregon researchers have indicated that the presence of intergrade clay in soil samples may lead to erroneous results in clay characterization studies. They found that it was possible in some cases to make more than one interpretation of X-ray diffraction data depending on assumptions made with regard to the effect of various pretreatments on interlayer materials that might have different degrees of stability. It could be assumed that interlayer material was initially present but was removed or changed by a given treatment such that lattice collapse was facilitated or, it could be postulated that another method resulted in interlayer formation and thus prevented collapse or made collapse difficult (Harward and Theisen, 1962).

Synthesis of Intergrades

Numerous workers have been successful in synthesizing intergrade minerals in the laboratory. Their efforts have contributed a great deal of information toward a better understanding of the natural "chloritization" process.

Interlayer formation has been shown to be dependent upon controlled pH and proper OH/M ratio (where M indicates the interlayer cation). Rich (1960) formed aluminum interlayers in vermiculite at pH 5.70. Hsu and Rich (1960) developed aluminum layers in a synthetic cation exchanger at a pH of 5.2 with OH/Al molar ratios of 0.296, 1.185, and 2.37. Barnhisel and Rich (1963) successfully introduced aluminum interlayers into montmorillonite using OH/Al ratios of 1.5,

2.25, and 3.00. After six months, the interlayers that were formed at a ratio of 1.5 were the only stable ones. Those formed with higher ratios were converted into separate gibbsite phases. Shen and Rich (1962) noted that minimum cation exchange capacity occurred in montmorillonite when aluminum interlayers were introduced at an OH/Al ratio of about 2.0, and a pH of 3.4. Sawhney (1960) formed interlayers in both montmorillonite and vermiculite in the presence of AlCl_3 titrated to pH 5.0 with 1.0N NaOH.

Carstea (1965) formed aluminum interlayers in both acid and alkaline media, but those that were produced at a pH of 4.6 when the OH/Al ratio was less than 1.0 most closely resembled chlorite. Slaughter and Milne (1960) produced a gibbsite-montmorillonite complex by simultaneous dropwise addition of aluminum nitrate and sodium hydroxide solutions to a 0.2% clay suspension.

Magnesium interlayers have been synthesized in montmorillonite and vermiculite under alkaline conditions at a pH of about 10.0 (Carstea, 1965). Slaughter and Milne (1960) prepared a montmorillonite-brucite complex by using a thick suspension of montmorillonite (2% to 10%) in solutions of 1.0 to 2.0N MgCl_2 . Magnesium hydroxide was precipitated in the interlayer position most effectively by the addition of lithium hydroxide.

The idea of iron being involved in interlayer formation has received little consideration although Dion (1944) concluded from his work that ferric oxide which he introduced into montmorillonite reduced the cation exchange capacity by chemical action rather than by physical obstruction. He postulated that some $\text{Fe}(\text{OH})_2^+$ was fixed

(non-exchangeable) on the negatively charged sites. Carstea (1965) formed iron interlayers in both acid and alkaline media. Initial interlayer formation began at pH 3.1 with an OH/Al ratio of 0.75, and continued up to pH 11.8 with an OH/Al ratio of 2.25. At no time did the iron interlayer prevent the solvated clay from expanding, but in all cases, the clay was blocked from collapsing.

Rhodes (1957) showed the existence of a plutonium polymer taken up by the soil at pH values between 2.0 and 9.0. The polymer carried a positive charge that enabled it to be readily adsorbed by the soil. He noted that the chemistry of plutonium suggested a polymer consisting of plutonium hydroxide.

Intergrade clays have also been synthesized with zinc, nickel, and cobalt as the nuclei of the interlayer material (quoted by Carstea, 1965).

Removal of Interlayers

Treatments used to separate silicate clay minerals from non-crystalline inorganic colloidal material must be very delicately balanced. Any treatment directed at one component may affect the other because of the similarity of their chemical constituents. A treatment too severe will not only remove the non-crystalline materials, but might destroy the silicate clay as well (Mathers, Weed, and Coleman, 1955). On the other hand, a treatment too mild may fail to produce the desired results.

Rich and Obenshain (1955) boiled clay in either 1.0N KCl plus 0.1N HCl for 48 hours, or in KCl plus 1.0N NH_4F (pH 7.0) for 5 minutes

in order to remove interlayered aluminum. Tamura (1956, 1957) considered the KCl and NH_4F to be too severe. He used a milder method to expand a 14 Å mineral by treating it with 1.0N citrate (pH 7.3). He also effected partial collapse of a 14 Å mineral by treatment with sodium dithionite-citrate reagent, and complete collapse by subsequent KOH plus KCl treatment with no apparent decomposition of the silicate mineral. Brown (1953) also facilitated collapse of a 14 Å mineral by removing the interlayer with KOH and KCl.

Hashimoto and Jackson (1960) suggested a system for differential dissolution of the various inorganic colloids associated with silicate clay. Sodium citrate-dithionite reagent was used to remove the free iron; boiling 2.5 minutes in 0.5N NaOH removed aluminum and silicon of allophane, gibbsite, and amorphous SiO_2 and Al_2O_3 ; and heating for 4.0 hours at 400 °C plus boiling for 2.5 minutes in 0.5N NaOH finally removed the more resistant interlayer aluminum.

The work of other investigators on different clays indicates the methods used by Hashimoto and Jackson may be less specific for particular components than was proposed. Saunders (1959) showed that neutral citrate-dithionite reagent was not specific for iron. It was found that between 0.32 and 2.20% aluminum was removed by the treatment. Tamura (1956) showed that two dithionite-citrate treatments removed 9.39% Fe_2O_3 and 6.23% Al_2O_3 from a natural intergrade clay. Harward and Theisen (1962) and Harward, Theisen, and Evans (1962) indicated that various dispersion methods and iron removal treatments caused different degrees of expansion and collapse on each of three different soils believed to contain hydroxy interlayer materials.

Weed and Nelson (1962) heated a North Carolina soil clay to 400 °C for two hours and then treated it with 1.0N sodium citrate (pH 2.0) for the removal of interlayer iron. Both the heat treatment and the sodium citrate treatment were made after the free iron had been previously removed. The amount of iron removed by the final treatments, and the degree of collapse of the clay, suggested that iron, in addition to aluminum, was a constituent of the interlayer material.

The fact that interlayer materials may be as different chemically and stability-wise as the innumerable conditions under which they are formed makes it impossible to say precisely how a specific treatment will affect clay minerals.

MATERIALS AND METHODS

Materials

Three soils were selected for this study to represent weathering products originating from basaltic materials under humid, subhumid, and semi-arid climatic conditions. Although there are questions as to the degree in which truly residual soils exist in Oregon, the sites were selected so as to minimize the possibility that foreign material had been mixed with the predominantly basaltic colluvium. Three horizons of each soil were analyzed, one to represent each major horizon.

The Hembre soil series, classified as an Andic Haplumbrept, came from a cool humid zone in the Coast Range mountains of Tillamook County, Oregon at an elevation of about 1500 feet. The average July temperature is 64 °F, and the average January temperature is 38 °F, with an annual precipitation of about 100 inches. The soil is well drained, has good permeability, and rapid surface runoff. The principal plants that occur on this soil are brackenfern, alder, vine maple, huckleberry, and hemlock. A profile description^{1/} of the Hembre series follows:

<u>Horizon</u>	<u>Depth</u>	<u>Description</u>
A ₁	0-7"	Very dark brown (10YR 2/2) loam; strong, very fine granular structure, very friable, nonsticky, non-plastic; common large shot; abundant interstitial pores; abundant roots; many charcoal fragments; clear smooth boundary.

^{1/} Profile description by C. Bowlsby and R. Parsons, Oct. 1, 1962.

- A₃ 7-13" Very dark brown (10YR 2/2) loam; strong, fine granular structure; friable, nonsticky, nonplastic; common medium shot; abundant interstitial pores; abundant roots; common charcoal flakes; clear, smooth boundary.
- B₁ 13-20" Dark reddish brown (5YR 3/3) fine gravelly loam; weak, fine subangular blocky, breaking to strong fine granular structure; friable (smaller peds are moderately firm), nonsticky, nonplastic; few fine shot; abundant interstitial pores, abundant roots; clear wavy boundary.
- B₂₁ 20-34" Dark reddish brown (5YR 3/4) fine gravelly loam; weak, fine subangular, breaking to moderate very fine subangular blocky structure; friable (smaller peds are moderately firm), nonsticky, nonplastic; abundant interstitial pores; many roots; clear wavy boundary.
- B₂₂ 34-46" Dark reddish brown (5YR 3/4) fine gravelly loam; nearly massive, breaking to moderate very fine subangular blocky structure; friable (smaller peds are moderately firm), nonsticky, nonplastic; some iron segregations; a few transparent waxy bridges between peds; common roots; abrupt wavy boundary.
- B₃ 46-64" Variegated dark reddish brown (5YR 3/4), yellowish red (5YR 4/6), and dark brown (10YR 3/4) fine gravelly loam; massive; friable, nonsticky, nonplastic; few roots; 60% angular weathered basalt fragments; gradual wavy boundary.
- C&R 64-70+ 95% basalt saprolite, 5% variegated as above, loam.

Samples of the Hembre soil were selected from the A₁, B₂₁, and C&R horizons.

The Wren Series selected for this study is a Reddish Brown Lateritic soil classified as a Cumulic Andic Umbrihumult. The sample was collected from the McDonald Forest located in Benton County, Oregon at an elevation of 1000 feet. The climate is transitional between humid and subhumid with an annual precipitation of about 40 to 45 inches. The average July temperature is about 67 °F and the

January average is near 40 °F. The winters are very moist and the summers are dry. The frost free season is about 191 days. The soil which developed from basalt residuum or colluvium is well drained with moderate permeability and slow runoff. The sample area had been logged, and the secondary vegetation included grass, blackberry, poison-oak, fern, young douglas-fir, hazel nut, madrone, bigleaf maple, dogwood, and thimbleberry. A profile description of the soil follows ^{2/} :

<u>Horizon</u>	<u>Depth</u>	<u>Description</u>
A ₁	0-4"	Dark reddish brown (5YR 3/3 dry, 5YR 2/2 moist), clay loam, strong medium to very fine granular structure, very friable, slightly sticky, slightly plastic, common fine spherical pellets (shot) in the top inch. Few below, roots abundant, pH 6.0 (chlorphenol red), lower boundary smooth and clear.
A ₃	4-9"	Dark reddish brown (5YR 3/2 dry, 5YR 2/2 moist), clay loam, strong medium subangular blocky breaking to moderate fine and very fine subangular blocky, breaking to moderate fine granular structure, friable, slightly sticky, slightly plastic, few fine spherical pellets, roots abundant, lower boundary smooth and clear.
B ₁	9-14"	Reddish brown (4YR 4/3 dry, dark reddish brown 4YR 3/3 moist), clay, strong fine and very fine angular blocky structure, friable, plastic, sticky, thin continuous clay flows, roots common, a few old root channels filled with material from above, pH 5.8 (chlorphenol red), lower boundary smooth and clear.
B ₂₁	14-21"	Reddish brown (2.5YR 4/4 dry, dark reddish brown 2.5YR 3/4 moist), clay, moderate fine and very fine angular blocky structure, friable, plastic, sticky, thin continuous clay flows, roots common, pH 5.6 (chlorphenol red), lower boundary smooth and gradual.

^{2/} Profile description by E. G. Knox, November 5, 1955.

- B₂₂ 21-29" Reddish brown (2.5YR 4/4) dry, dark reddish brown (2.5YR 3/4) moist, clay, moderate fine angular blocky structure, friable, sticky, plastic, thin continuous clay flows, roots common, pH 5.4 (chlorphenol red), lower boundary smooth and gradual.
- B₃ 29-44" Red (2.5YR 4/6) dry, dark reddish brown (2.5YR 3/4) moist, clay, moderate medium and fine angular blocky structure, friable, sticky, plastic, thin continuous clay flows, few black (MnO₂) splotches, few basalt fragments, roots few, pH 5.4 (chlorphenol red), lower boundary smooth and gradual.
- B₃Dr 44-52" Red (2.5YR 4/8) dry, dark red (2.5YR 3/6) moist, clay moderate medium and fine angular blocky structure, friable, slightly plastic, slightly sticky, common thin patchy clay flows, abundant basalt fragments (about 50% by volume), pH 5.4 (chlorphenol red).

Samples of the Wren soil were selected from the A₁, B₂₁, and B₃Dr horizons.

The Lookout soils occur in the Brown soil zone and are classified as Mollic Durargids. They are found at elevations of about 2,800 to 3,600 feet in a semi-arid climate with an average annual precipitation of 8 to 12 inches, with warm dry summers and cold moist winters. Average January temperature is 26 to 30 °F and the average July temperature is 64 to 68 °F, with a frost free season from 100 to 130 days. They have formed in colluvium from weathered basalt and andesite on nearly level to gently sloping footslopes. The native vegetation consists mainly of bunchgrasses. In places, the A horizon is influenced by admixtures of loess and/or volcanic ash and pumice. These soils are well drained, runoff is medium to rapid, permeability is slow through the B₂ horizon, and very slow through the C horizon. The sample was collected in Union County, Oregon. A modal series description follows:

<u>Horizon</u>	<u>Depth</u>	<u>Description</u> ^{3/}
A ₁₁	0-4"	Light brownish gray (10YR 6/2) stony silt loam, dark grayish brown (10YR 3/2) when moist; weak to moderate thin platy breaking to weak fine granular structure; slightly hard, friable, slightly sticky and slightly plastic; abundant roots many fine interstitial pores; pH 6.4 to 6.8; clear smooth boundary.
A ₁₂	4-9"	Grayish brown (10YR 5/2) stony silt loam, dark grayish brown (10YR 3/2) when moist; weak coarse prismatic breaking to weak coarse subangular blocky structure; slightly hard, friable, slightly sticky and slightly plastic; plentiful roots; many fine tubular pores; pH 6.6 to 7.0; clear smooth boundary.
B ₁	9-13"	Dark brown (10YR 3/3) when moist, stony light silty clay loam, commonly coated light gray (10YR 6/1) when dry with very fine sand or silt that may be volcanic ash; weak medium prismatic breaking readily to moderate fine subangular blocky structure; hard, firm, slightly sticky and slightly plastic; plentiful roots; many fine tubular pores; thin patchy clay films on peds and in pores; pH 6.8 to 7.2; abrupt smooth boundary.
B ₂₁	13-16"	Dark grayish brown (10YR 4/2) when moist, cobbly silty clay; strong medium to fine prismatic breaking to strong fine blocky structure; very hard, very firm, very sticky, very plastic; plentiful roots; common very fine tubular pores; thick continuous clay films on peds and in pores; pH 7.0 to 7.4; clear smooth boundary.
B ₂₂	16-19"	Dark brown (10YR 4/3) when moist, cobbly silty clay; strong medium to fine prismatic breaking to strong fine blocky structure; very hard, very firm, very sticky and very plastic; plentiful roots; common very fine tubular pores; thick continuous clay films on peds and in pores; slightly darker brown than interior of peds; pH 7.2 to 7.4; abrupt smooth boundary.

^{3/} Description taken from established series description by W. M. Johnson, May, 1961.

- B_{3ca} 19-24" Pale brown (10YR 6/3) silty clay loam, dark brown (10YR 4/3) when moist; moderate fine subangular blocky structure; hard, firm, sticky, and plastic; few roots; common fine tubular pores; moderately thick nearly continuous clay films on peds and in pores; common segregated and disseminated lime; pH 7.8 to 8.4; clear smooth boundary.
- C_{ca} 24-29" Light yellowish brown (10YR 6/4) loam, dark yellowish brown (10YR 4/4) when moist; massive; hard, firm to friable slightly sticky and slightly plastic; few roots; common fine tubular pores; strongly calcareous with disseminated lime; pH 8.2 to 8.5; abrupt smooth boundary.
- C_m 29-45+ Very pale brown (10YR 7/3), dark brown (10YR 3/3) when moist; indurated silica-cemented pan containing seams and segregations of lime; extremely firm and extremely hard. The pan has some cemented basaltic cobbles and gravels.

Samples of the Lookout soil were selected from the A₁₁, B₂₁, and C_{ca} horizons. Table I contains chemical and physical data for each of the three soils as actually sampled and used in this study.

Methods

General

In order to determine the chemical nature, quantity, and stability of the interlayer materials in the soil clays, samples of the clays were subjected to a series of progressive treatments designed to effect a differential dissolution of materials intimately associated with them.

Some of the treatments used here are normally made prior to separation of the clay fraction in soil mineralogical analysis. Such procedures could result in differential dispersion and separation of soil components and complicate interpretation of the data. Since the

TABLE I. MECHANICAL ANALYSIS, pH, ORGANIC MATTER, CATION EXCHANGE CAPACITY, EXTRACTABLE CATIONS, AND PERCENT BASE SATURATION DATA FOR THE HEMBRE, WREN, AND LOOKOUT SOILS.*

Horizon	Inches Depth	Percent			pH 1:1	% O.M.	C.E.C. me/100g	Extractable Cations me/100g				Percent Base Sat.
		Sand	Silt	Clay				Ca	Mg	Na	K	
(Hembre)												
#A ₁	0-7	60.2	27.2	12.6	5.0	29.0	56.8	1.5	2.3	0.43	0.60	8.5
A ₃	7-13	63.6	26.1	10.3	4.8	24.1	51.8	0.2	0.5	0.43	0.23	2.6
B ₁	13-20	60.2	32.4	7.4	5.1	14.6	46.8	0.2	0.2	0.37	0.10	1.9
#B ₂₁	20-34	63.5	31.0	5.5	5.2	6.9	44.7	0.2	0.5	0.32	0.08	2.5
B ₂₂	34-46	75.2	22.0	2.8	4.9	2.8	54.9	0.2	0.9	0.35	0.02	2.7
B ₃	46-64	71.4	27.5	1.1	5.0	1.5	60.0	1.8	3.7	0.39	0.08	10.0
#C&R	64-70	80.8	18.0	1.2	5.0	1.6	62.6	2.8	5.7	0.39	0.08	14.3
(Wren)												
#A ₁	0-4	13.8	44.2	42.0	5.7	9.3	34.6	14.5	4.8	0.10	2.50	63.0
A ₃	4-9	11.8	43.8	44.4	5.5	7.6	32.2	11.7	4.3	0.10	1.50	55.0
B ₁	9-14	12.2	43.7	44.1	5.3	6.4	29.6	9.1	4.5	0.10	0.90	49.0
#B ₂₁	14-21	11.2	39.2	49.6	4.9	2.9	24.7	6.1	4.0	0.10	0.60	44.0
B ₂₂	21-29	11.4	35.8	52.8	4.8	1.6	22.6	6.0	3.5	0.10	0.50	45.0
B ₃	29-44	12.4	33.8	53.8	4.8	1.0	28.5	6.2	4.2	0.10	0.30	38.0
#B ₃ Dr	44-52	38.8	24.4	36.8	4.5	0.5	31.0	6.2	4.2	0.30	0.10	35.0
(Lookout)												
#A ₁₁	0-4	25.8	53.2	21.0	6.6	2.3	29.1	10.4	5.3	1.60	1.22	63.6
A ₁₂	4-9	24.6	51.1	24.3	6.6	1.7	29.2	9.6	4.8	0.66	1.66	57.2
#B ₂₁	9-14	11.7	32.9	55.4	7.5	1.2	60.0	21.9	15.3	8.03	1.90	78.5
B ₂₂	14-17	11.6	33.5	54.9	8.2	0.9	58.6	31.0	17.9	9.35	1.74	100.0
B _{3ca}	17-19	8.0	34.7	57.3	8.1	1.0	62.4	46.0	17.5	10.23	1.70	100.0
#C _{1ca}	19-24	34.2	43.8	22.0	8.3	1.7	69.4	55.0	16.5	11.00	1.66	100.0

* Analyses performed by Oregon State University Soil Testing Laboratory: Exchange properties determined with ammonium acetate at pH 7.

Soil Horizons used in this study.

primary emphasis here is on the nature of hydroxy interlayers in the clay fraction, the treatments were sequentially imposed on equivalent clay fractions of less than 2.0 micron size which had been separated by water dispersion after the removal of organic matter by H_2O_2 . Differences associated with treatments thus can be properly interpreted in light of changes in the same clay fraction. The treatments imposed were chosen to represent a range of increasing severity of dissolution. Extracts from the various steps of the dissolution procedure were chemically analyzed to determine the amount of aluminum, iron, magnesium, and silicon removed. X-ray diffraction analysis and cation exchange capacity determinations were made on the clays from each treatment in order to evaluate the degree of change incurred as a result of the removal of various materials (see Figure 1).

Pretreatment of Soils

The soil samples were placed in a revolving grinder that crushed the aggregates and sieved the less than two millimeter fraction. Bulk samples of the sieved soil were placed in beakers and treated with dilute HCl to remove the carbonates. The HCl treatment was continued until effervescence was no longer evident.

Organic matter was removed by oxidation with 30% hydrogen peroxide (Kilmer and Alexander, 1949). The H_2O_2 was added to the samples and stirred intermittently for ten minutes. The treatment was repeated until strong reaction had subsided, then the samples were allowed to digest. After 24 hours, a final application was made and the samples were slowly heated for thirty minutes in a steam bath to complete the reaction. When cool, they were transferred to 250 ml

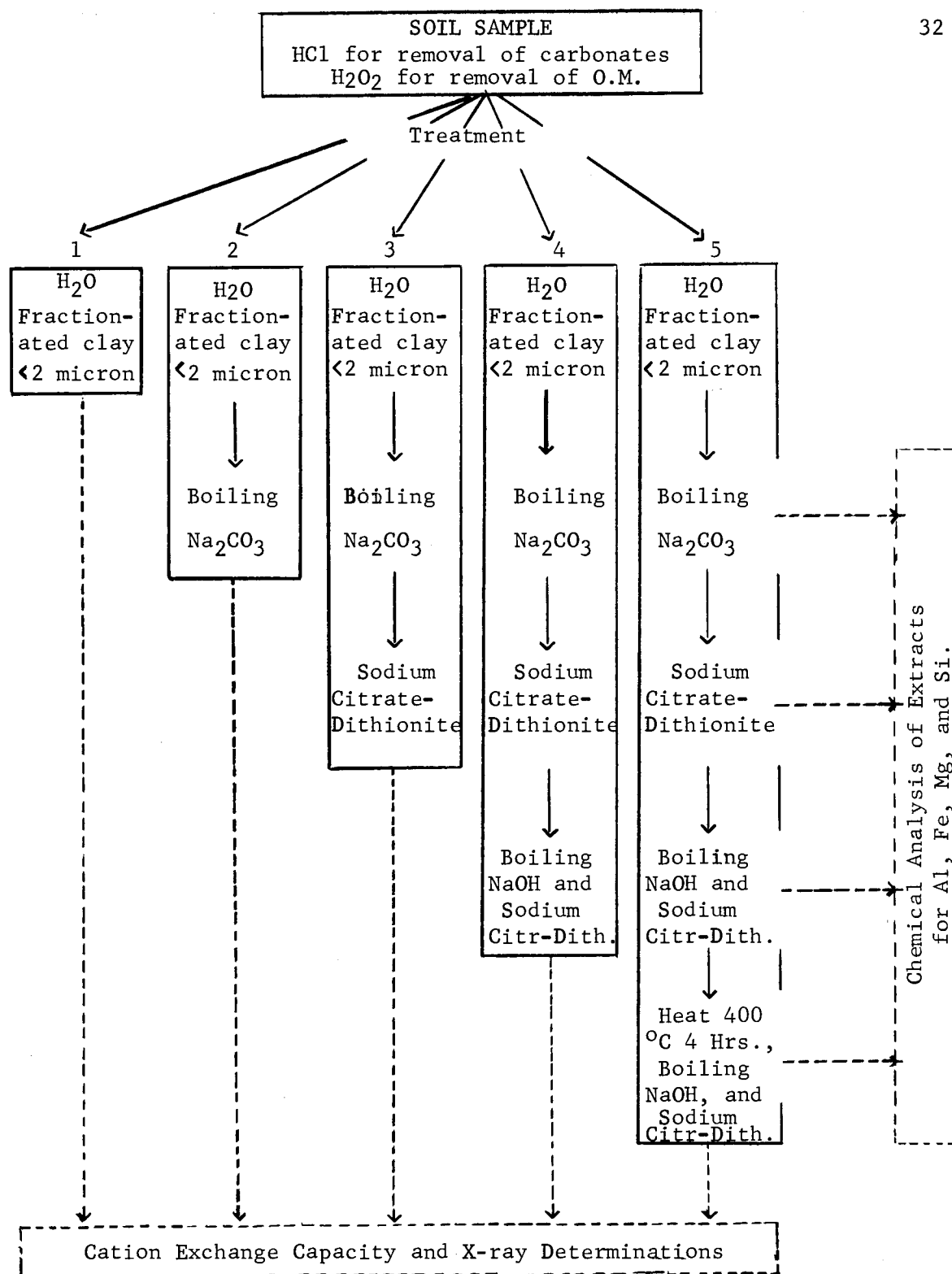


Figure 1. Flow chart indicating the various treatments that each soil sample received.

polyethylene centrifuge cups, washed with distilled water, and centrifuged to remove soluble salts.

Dispersion and Fractionation

The samples were dispersed in distilled water with a mechanical stirrer for thirty minutes. Water alone was used as the dispersing agent because it was desirable to fractionate the sample with the least possible chemical change in the clay fraction. The less than two micron clay was separated according to centrifugation procedures outlined by Jackson (pp 101-160, 1956).

Differential Dissolution Treatments

Five two gram aliquots of the less than two micron clay (see initial procedure of each treatment in Figure 1), were placed in 50 ml. polyethylene centrifuge tubes and treated as follows:

Boiling 2% sodium carbonate. The boiling Na_2CO_3 treatment was intended to remove amorphous coatings of aluminum and silicon oxides. There is some evidence that it may also remove some of the more labile or poorly crystallized hydroxy interlayer material. Treatments two through five contained a boiling Na_2CO_3 treatment essentially as described by Jackson (p. 73, 1956). The clay was placed in a stainless steel beaker and boiled for five minutes in the 2% Na_2CO_3 solution. The residue was washed once with cold 2% Na_2CO_3 solution. The combined extracts were saved for analysis.

Buffered sodium citrate-dithionite. The sodium citrate-dithionite-bicarbonate treatment was intended to accomplish the removal of amorphous coatings and crystals of iron oxides. Some of these iron materials may be present on interlayer surfaces. The treatment

may not be entirely selective, and it is recognized that some hydroxy aluminum may also be removed, presumably due to the chelating action of the citrate. Treatments 3, 4, and 5 also contained procedures for the removal of free iron oxides as outlined by Jackson (p. 57, 1956). The procedure was repeated twice with the clays from the Hembre and Wren soils which contained more iron, and once for the clay from the Lookout soil. The supernatants for each soil were combined and saved for analysis.

Boiling sodium hydroxide. This treatment was intended to accomplish the dissolution of allophane and free alumina and silica. Boiling in 2% Na_2CO_3 has been shown to remove amorphous cementing materials consisting of finely divided films of SiO_2 and Al_2O_3 ; however, the dissolution of the more resistant amorphous components is incomplete. The work of Hashimoto and Jackson (1958) indicates that this latter material may be removed by a boiling NaOH treatment. This procedure was therefore a part of treatments 4 and 5. The extracts were saved for analysis.

Following the sodium hydroxide treatment, one iron removal treatment identical to that described in the section "Buffered sodium citrate-dithionite" was then made. The purpose was to remove any iron that may have been chemically or sterically bound by the allophane or free alumina and silica. The extract was saved for analysis.

Preheating and dissolution in NaOH. Although some of the above treatments seem to be quite vigorous, there is some evidence that the more resistant interlayer hydroxides may remain. Dixon and Jackson (1959) have indicated that the removal of this material may be

facilitated by dehydroxylation and dissolution with boiling NaOH. This method was therefore applied to treatment 5. The procedure consisted of the following steps:

1. The sample was washed in benzene and transferred to a pyrex beaker. The clay was evaporated to dryness and placed in a muffle furnace and heated to 400°C for four hours to dehydroxylate the interlayer hydroxides.

2. After heating, the clay was treated with boiling NaOH as outlined above, to remove the aluminum from the interlayer spaces.

3. A final iron removal treatment as outlined above was made to remove any iron that may have been released from the interlayer spaces. The extracts were saved for analysis.

Preparation of Clay for X-ray Diffraction Analysis

Magnesium saturated clay. Following the differential treatment procedures, a portion of the clay from each treatment was saturated with magnesium by washing four times with 1.0N MgCl_2 . Two water and two methanol washings were used to remove the excess salt. A small amount of the clay was thinly spread on petrographic micro-slides with a micro-spatula according to a procedure by Theisen and Harward (1962). The slides were air dried, followed by oven drying at 65°C for two hours. Duplicate slides were placed in a desiccator containing a saturated solution of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with a relative humidity of about 55%. The desiccator was evacuated and the slides equilibrated for at least forty-eight hours prior to analysis. Following the X-ray diffraction analysis, one of the duplicates was solvated with ethylene glycol according to a procedure described by Kunze (1955), and the

other duplicate was solvated with glycerol according to Brown and Farrow (1956). The solvated slides were then analyzed by X-ray diffraction.

Potassium saturated clay. Another portion of clay from each treatment was saturated with potassium by washing four times with 1.0N KCl. Three washings with distilled water were used to remove the excess KCl salt. Duplicate slides were prepared in the same manner as the Mg saturated ones. The slides were air dried then placed in an oven and dried at 65 °C for two hours. They were placed in a desiccator containing anhydrous CaCl_2 until analyzed by X-ray. The duplicate slides were manually scanned on the X-ray machine and the one that gave the better pattern was used for the analysis. After X-ray diffraction analysis, the slide was successively heated in a muffle furnace at 300 and 550 °C for two hours with additional X-ray diffraction analyses recorded after each heating period.

X-ray Equipment

Diffraction patterns were made with a General Electric XRD-3 diffraction spectrometer equipped with a Geiger-Mueller tube and a Leeds and Northrup Speedomax recorder. Nickel-filtered Cu K-alpha radiation generated at 50 kilovolts and 16 milliamperes was used. A system composed of a 1° beam slit, a high resolution Soller collimator slit, and a 0.05° detector slit gave optimum peak height and resolution. The scanning speed was 2 degrees 2 θ per minute and the patterns were run from 2° 2 θ to 14° 2 θ except as specified. The rate meter and time constant settings were varied to meet the need for resolution and detail of each sample.

Cation Exchange Capacity Determination

CEC of the clay from each of the treatments was determined essentially as described by Frink and Peech (1963) where sodium was used as the saturating ion and calcium as the replacing ion. The sodium saturated clay was shaken for at least sixteen hours (Rich, 1961) in 1.0N CaCl_2 solution to effect a replacement of the sodium. A second extraction similar to the first was performed for ten minutes to insure complete removal of the exchangeable sodium. Sodium in the combined extracts was determined with a Perkin-Elmer atomic absorption spectrophotometer (Perkin-Elmer Corp., 1964).

Chemical Analysis of Extracts

Aluminum was determined in the various extracts by the aluminon method as described by Hsu (1963) with slight modification. One drop of thio-glycolic acid was added prior to color development to reduce any ferric iron to ferrous iron and thus eliminate its effect on the color of the aluminum-aluminon complex (Robertson, 1950).

Silicon was determined colorimetrically using an ammonium molybdate method slightly modified from that described in the U. S. Salinity Laboratory Manual (p. 143, 1954). Since phosphorous reacts with molybdate similar to silicon, two milliliters of 10% citric acid was added to eliminate any possible phosphorous interference. The citric acid destroys the phosphomolybdic complex immediately whereas the silicon complex is not affected for several minutes (Metson, 1956).

Iron was determined colorimetrically using Tiron reagent to develop the color as described by Jackson (p. 291, 1958). Analyses of blank Na_2CO_3 and NaOH treatments indicated no iron was brought into

solution from the stainless steel beakers.

Magnesium was determined with a Perkin-Elmer atomic absorption spectrophotometer. In the procedure, certain samples developed a cloudy condition that caused concern as to whether correct values were being determined. Samples of the questionable extracts were treated with known amounts of magnesium, and recovery studies were made. The results indicated that approximately 95 to 97% of the magnesium present was being determined.

Petrographic Analysis of Soil Minerals

Samples of soils treated for removal of organic matter, carbonates, and free iron oxides were dispersed and wet sieved in order to fractionate the sand sized particles. Permanent slide mounts of the mineral grains of the very fine sand fraction (50 to 100 micron) were made by fixing the grains in Canada Balsam on petrographic slides according to the procedure outlined by Jackson (p. 490, 1956). A mineral grain count was made for the three horizons of each soil used in the study with the aid of a petrographic microscope.

RESULTS AND DISCUSSION

The presence or absence of hydroxy interlayers in 2:1 layer silicates can be inferred from X-ray diffraction data. Clays that fail to show normal expansion and/or collapse when subjected to X-ray diffraction analysis techniques are suspected of containing such interlayers. In this study, clay samples from the various treatments were Mg saturated and analyzed by X-ray diffraction before and after solvation with glycerol and with ethylene glycol to determine expansibility, and other samples were similarly analyzed after K saturation to determine collapsibility. The degree of resistance to collapse of the K saturated samples when heated to 65, 300, and 550 °C also gave indication as to the stability of the interlayer material.

Cation exchange capacity (CEC) measurements of the various clays, determined after each treatment, gave further evidence of the existence of hydroxy interlayers. The occurrence of such interlayer material in a clay generally reduces the total CEC of the clay by neutralizing some of the negative sites, and by sterically blocking others. The CEC of such clay is normally increased when the interlayered materials are removed. The composition of the interlayer hydroxides was inferred by considering the material extracted by each dissolution treatment in conjunction with the changes which occurred in the clay as reflected by X-ray diffraction data and CEC measurements. The clay from treatment 1, which had been subjected only to distilled water and mechanical stirring, was used as a basis to compare the effect of subsequent treatments.

A chemical analysis of each treatment extract showed the amount of aluminum, iron, silicon, and magnesium removed. The amount of each element removed was calculated as a percentage of the original weight of the clay at the start of the dissolution procedures. The percentages were converted to molecular values by dividing the percent by the molecular weight of the appropriate element. The molecular value thus represents the moles of element removed from 100 g. of clay.

The results of X-ray diffraction analyses, CEC measurements, and chemical analyses are presented for each soil in the following sections.

Hembre Soil

X-ray Diffraction Analyses

The data obtained from samples receiving treatment 1, most closely represented the properties of the clay minerals as they existed in situ. A comparison of the diffraction patterns of Hembre samples which received this minimal treatment (figures 2, 3, and 4) reveals the presence of 2:1 type clay minerals whose properties are intermediate between the smectites or vermiculites on one extreme, and chlorite on the other. This is indicated by resistance to expansion and collapse without retaining a stable 14 \AA spacing. Comparison of Mg saturated samples with those treated with glycerol or ethylene glycol shows there was no significant change in basal spacing due to solvation except in the case of the C horizon sample, which expanded to 15.5 \AA with ethylene glycol (treatment 1, figure 4). Some collapse occurred upon K saturation, especially after heating,

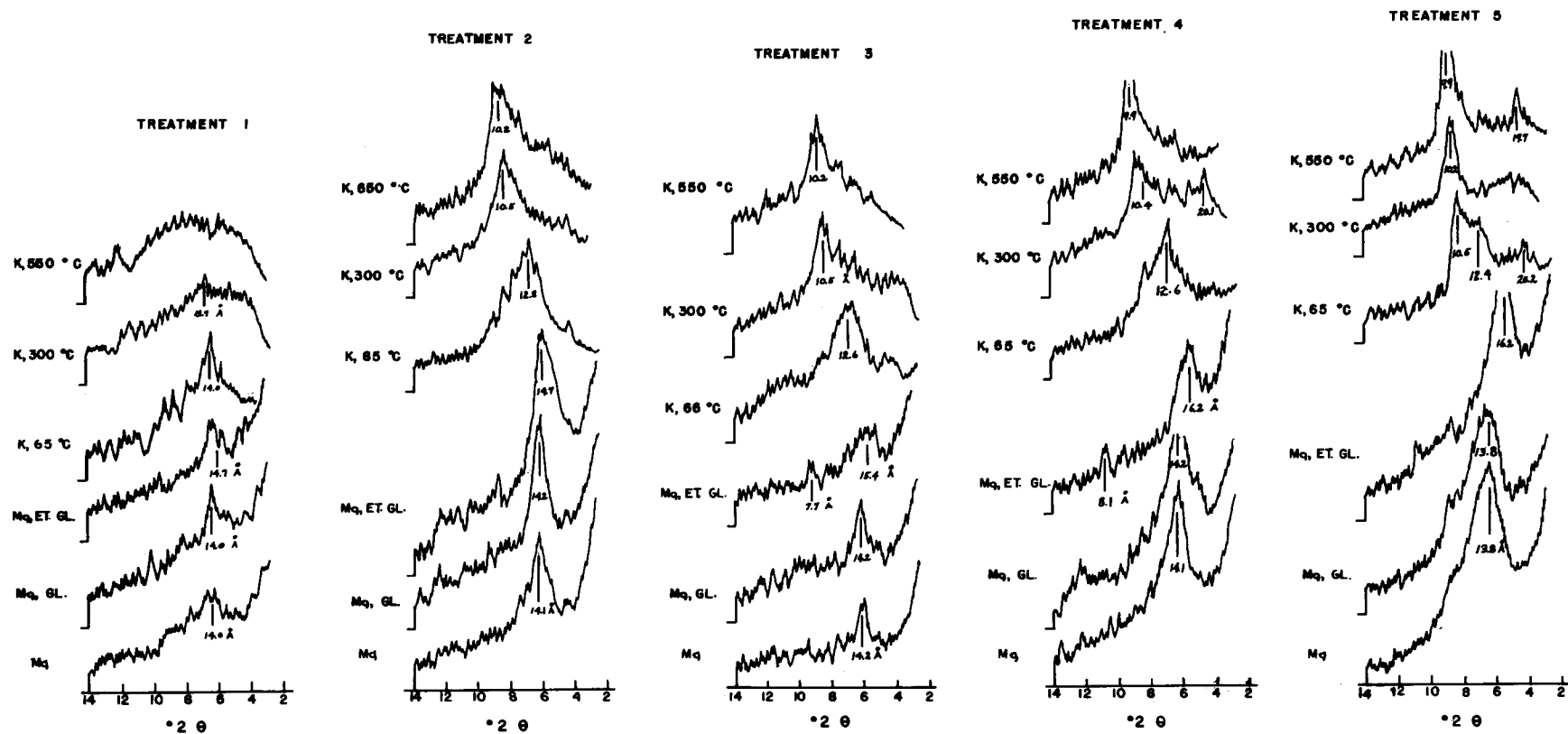


Figure 2. X-ray diffraction patterns of less than two micron clay from the Hembre A horizon after different dissolution treatments (see Methods, page 29).

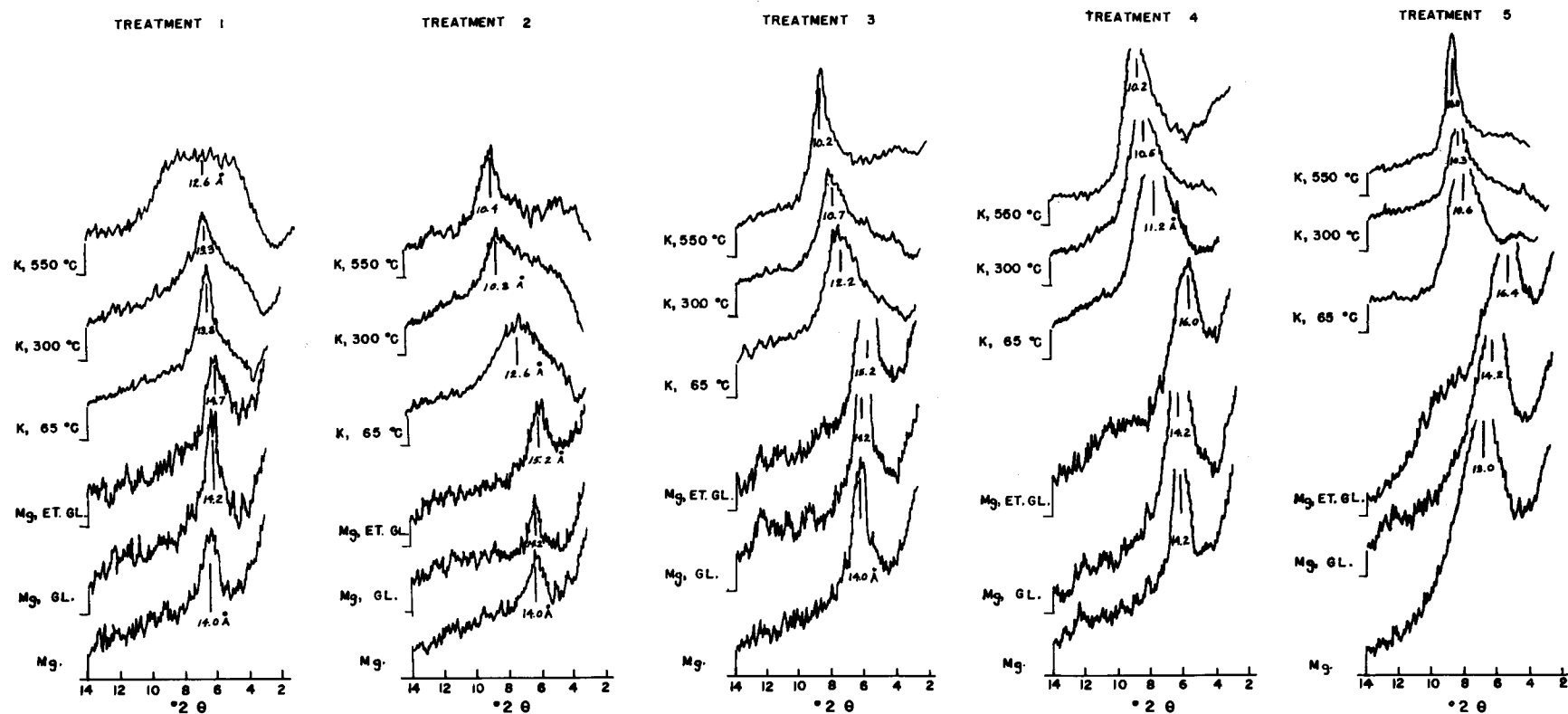


Figure 3. X-ray diffraction patterns of less than two micron clay from the Hembre B horizon after different dissolution treatments (see Methods, page 29).

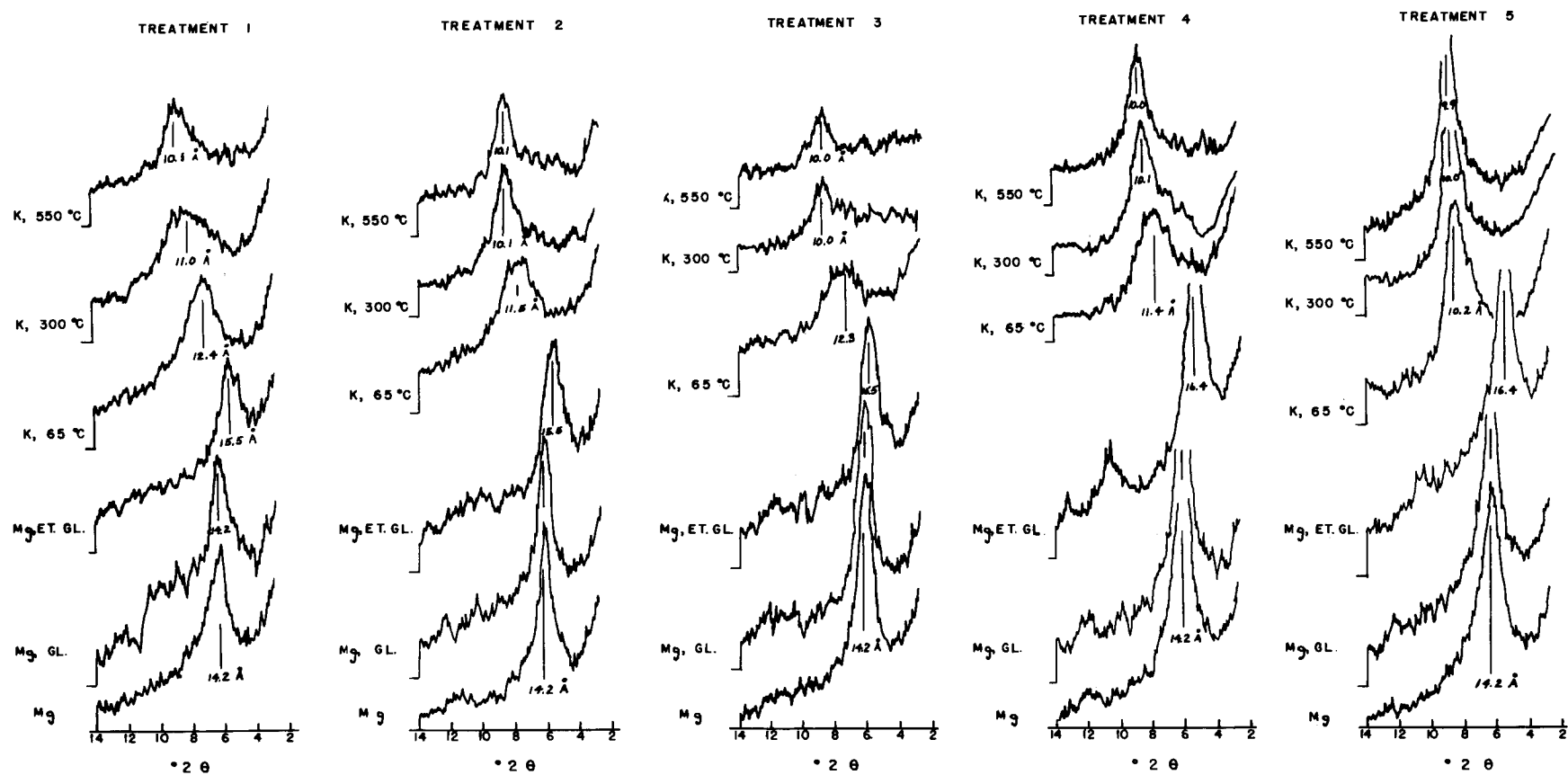


Figure 4. X-ray diffraction patterns of less than two micron clay from the Hembre C horizon after different dissolution treatments (see Methods, page 29).

but complete collapse to 9.7 to 10 Å was not observed. In many cases the diffraction maxima were broad and diffuse, suggesting the presence of poorly organized or mixed layer systems. These phenomena are similar to those which have been ascribed to the presence of hydroxy materials on the interlayer surfaces of the clay minerals. Accordingly, they have been called "intergrade", or "hydroxy-interlayered" clays.

The data reveal differences in properties of expansion and collapse for the different horizons (trmt 1, fig. 2 vs. fig. 3 vs. fig. 4). The diffraction maxima for the A horizon are generally less intense and more diffuse (broad) than lower horizons. As depth in the profile increases, the degree of collapse increases (basal spacing decreases) with K saturation and heating. The C horizon sample exhibited some expansion on solvation with ethylene glycol, although a basal spacing corresponding to a regular 2-layer organic complex was not obtained. Expansion was not observed for A and B horizon samples. These data suggest a greater degree and stability of hydroxy interlayers in the upper horizons. This is in agreement with the results of Sawhney (1958, 1960) in Connecticut.

Assuming that the above phenomena are due to the presence of some kind of material on the interlayer surfaces, it is next logical to further define its nature and stability. The data in figures 2, 3, and 4, are arranged according to increasing severity of treatment for removal of interlayer materials reading from left to right, and may be regarded as a two-way table of severity of dissolution treatment vs. depth in the profile. Generally, the degree of expansion and

collapse increased as pretreatments increased and they also increased with depth of horizons in the profile. The A horizon clay (figure 2) did not exhibit complete collapse on K saturation and heating even after having received the maximum treatment (treatment 5); some components still were contributing to diffraction on the low angle side of the 10 \AA peak. On the other hand, the C horizon sample (figure 4) exhibited essentially the same lattice spacings after treatment 4 as it did for treatment 5. However, treatment 5 did appear to increase the sharpness and intensities of the peaks over that of treatment 4.

The diffraction patterns for the Hembre samples did not reveal the presence of any crystalline clays other than the 2:1 "intergrade" described above. It is of interest to consider the nature of the 2:1 matrix in these samples. After treatment to remove the hydroxy interlayer materials, solvation with ethylene glycol resulted in expansion which approached the spacing for the 2-layer organic complex. On the other hand, glycerol solvation did not increase the basal spacing. Harward and Brindley (1965) using synthetic clays and vapor techniques have shown that montmorillonite will form the 2-layer 17 to 18 \AA complexes with either ethylene glycol or glycerol. Beidellite, on the other hand, forms the 1-layer complex (14 \AA) with glycerol and the 2-layer complex (17 \AA) with ethylene glycol. The data here would therefore suggest that the 2:1 matrix in the Hembre samples is beidellite. Further work is needed to verify this however. Since these studies were completed, it has been found that variation in techniques of handling the samples for solvation by condensation

from the vapor phase may result in different amounts of expansion, especially with glycerol.^{4/} In view of the critical nature of the placement of samples in the solvation containers there may be some ambiguity in the interpretation of these data. Nevertheless, it is clear that the 2:1 matrix in the Hembre samples belongs to the smectite group, and not to the vermiculites since expansion to 16.4 Å did occur with ethylene glycol.

Cation Exchange Capacity Measurements

CEC measurements were substantially increased in the clays of all horizons of the Hembre soil when they were subjected to certain treatments for the removal of hydroxy interlayers (table II). The initial values, as determined on the clays from treatment 1, were progressively increased by treatments 2 and 3, but the more drastic procedures of treatments 4 and 5 failed to produce any further significant change. Boiling Na_2CO_3 (treatment 2) apparently removed some of the more labile or poorly crystallized hydroxy interlayer material in addition to amorphous coatings of aluminum and silicon oxides which might have been present. These data are in agreement with the X-ray diffraction data which also indicated that some interlayer hydroxides were apparently removed at this stage of the dissolution procedures (trmt. 1 vs. trmt. 2, figures 2, 3, and 4). The additional increase in CEC as a result of buffered sodium citrate-dithionite (treatment 3)

^{4/} Personal communication. M. Harward and D. D. Carstea. Oregon State University, Corvallis, Oregon.

indicated that at least a portion of the material removed came from the interlayer positions of the clay. X-ray diffraction data also substantiate this view (trmt. 2 vs. trmt. 3, figures 2, 3, 4). A chemical analysis of the extract of treatment 3, discussed in the next section, shows that iron was the major constituent removed by

TABLE II. THE EFFECT OF DIFFERENT DISSOLUTION TREATMENTS ON THE CATION EXCHANGE CAPACITY OF CLAYS FROM THE HEMBRE SOIL.

<u>Horizon</u>	<u>Cation Exchange Capacity (me./100g.)</u>				
	<u>Treatments <u>1/</u></u>				
	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>
A	57	94	131	133	132
B	44	92	132	138	135
C	95	129	154	156	140

1/ Treatments as shown in Methods Section page 32.

this treatment. Treatment 5 caused a notable decrease in the CEC of the C horizon clay. This decrease could possibly be attributed to a slight reduction in the total surface area of the clay as a result of some irreversible dehydration that may have occurred during the preheating step of this treatment. In several instances when preparing glass slides for X-ray diffraction analysis, it was noted that certain clays from treatment 5 contained a small amount of gritty material that was not evident before the preheat treatment. This seems to indicate that some irreversible aggregation had occurred.

Chemical Analyses of Extracts

Table III lists the data obtained from chemical analyses of the treatment extracts of the Hembre soil clays. Treatment 1 is not listed in the table since distilled water and mechanical stirring had

no apparent effect on the clay constituents.

TABLE III. ALUMINUM, IRON, SILICON, AND MAGNESIUM REMOVED FROM THE HEMBRE SOIL CLAYS BY DIFFERENT DISSOLUTION TREATMENTS, EXPRESSED AS A PERCENTAGE OF ORIGINAL WEIGHT OF THE CLAY, AND IN MILLIMOLES PER 100 GRAMS OF CLAY.

Horizon	Trmt ^{1/}	Al		Fe		Si		Mg	
		%	mmoles	%	mmoles	%	mmoles	%	mmoles
A	2	0.32	12	0.06	1	0.14	5	0.04	2
	3	0.05	2	4.33	78	0.67	24	0.28	12
	4	1.06	39	0.48	9	2.77	99	0.28	12
	5	0.81	30	0.48	9	2.20	78	0.39	16
B	2	0.43	16	0.01	T ^{2/}	0.06	2	0.01	T
	3	0.06	2	4.77	85	0.48	17	0.31	13
	4	1.08	40	0.45	8	1.72	61	0.20	8
	5	0.58	22	0.95	17	1.36	48	0.46	19
C	2	0.46	17	0.02	T	0.44	16	0.02	1
	3	0.06	2	2.27	41	0.16	6	0.38	16
	4	1.30	48	0.30	5	3.07	109	0.43	18
	5	0.64	24	0.39	7	2.61	93	0.64	26

^{1/} Treatments listed in Methods Section page 32.

^{2/} Trace amount

The clay from each horizon when treated with boiling Na_2CO_3 (treatment 2) yielded primarily aluminum, with lesser amounts of silicon, iron, and magnesium. It is obvious from the X-ray diffraction data (trmt. 1 vs. trmt. 2, figures 2, 3, 4) and from CEC values (table II) that at least a portion of the aluminum removed by the treatment came from interlayer positions. The aluminum removed from the clay of the A horizon was equivalent to 7.3 mg. (about 1 me.) per 1 me. increase in CEC. These data imply that the aluminum removed carried a unit positive charge of approximately 3. This suggests that the aluminum was less polymerized than that reported by Dixon and Jackson (1962). They reported an increase in CEC of 1 me. per 26.5 mg.

of aluminum removed from the hydroxy interlayered clays which they were studying. The interlayer aluminum removed from the Hembre clay by the boiling Na_2CO_3 apparently was less stable than that reported by Dixon and Jackson since they had to preheat the clay to 400°C for four hours then treat it with boiling NaOH in order to remove the hydroxy interlayer. On the other hand, it is conceivable that the small amount of aluminum removed from the Hembre clay might have been polymerized near the edges of the interlayer spaces such that it sterically blocked other exchange sites near the center of the micelle. A hydroxy polymer in this more vulnerable position might have been more easily removed by the Na_2CO_3 treatment. The CEC of the B horizon clay was increased 1 me. per 11.3 mg. of aluminum removed and that of the C horizon was increased 1 me. per 15.9 mg. of aluminum removed by the boiling Na_2CO_3 treatment. This would suggest that polymerization increased with depth; however, from this data it is impossible to separate the aluminum removed from the interlayer positions from that removed from other sources.

Treatment 3 (buffered sodium citrate-dithionite) removed from 20 to 40 times more iron than aluminum, and from 3 to 6 times more iron than magnesium from the clay. The aluminum removed by this treatment was insufficient to account for the increase in CEC values even if it all came from the interlayer positions. Consequently, it is logical to assume that iron and possibly magnesium also occupy the hydroxy interlayer complex in these clays. A question exists, however, whether magnesium would form as a hydroxy interlayer under the acid conditions which this soil developed. Carstea (1965) was able to

synthesize magnesium interlayers in montmorillonite and vermiculite only at a pH of about 9.7 and higher. However, magnesium hydroxy interlayers could be present if the intergrade developed from the degradation of chlorite.

Treatments 4 and 5 removed a relatively large amount of silicon and aluminum in a ratio of about 2:1 to 3:1. This could represent the dissolution of allophane or even the breakdown of some clay lattice in as much as these two treatments did not materially change the CEC values.

Wren Soil

X-ray Diffraction Analyses

The data from the Wren soil clays that received treatment 1 (figures 5, 6, 7) are considered to be indicative of the soil clays in situ. The data show that two main diffraction peaks are evident with basal spacings of approximately 14 and 7 Å. The 14 Å peak is somewhat broad and diffuse indicating poor organization and crystallinity. The 14 Å peak was unaffected by solvation with either glycerol or ethylene glycol. K saturation resulted in some collapse but these effects were not marked; rather, the diffraction bands became more broad and diffuse. It appears that the 14 Å component is an intergrade in which some interlayer material is having strong effect on resistance to expansion and collapse.

The diffraction maximum at 7.3 to 7.4 Å is somewhat stronger than the 14 Å peak although still broader than would be expected for well crystallized clays. This peak could represent a distinct mineral phase different from that giving the 14 Å maximum. A possibility

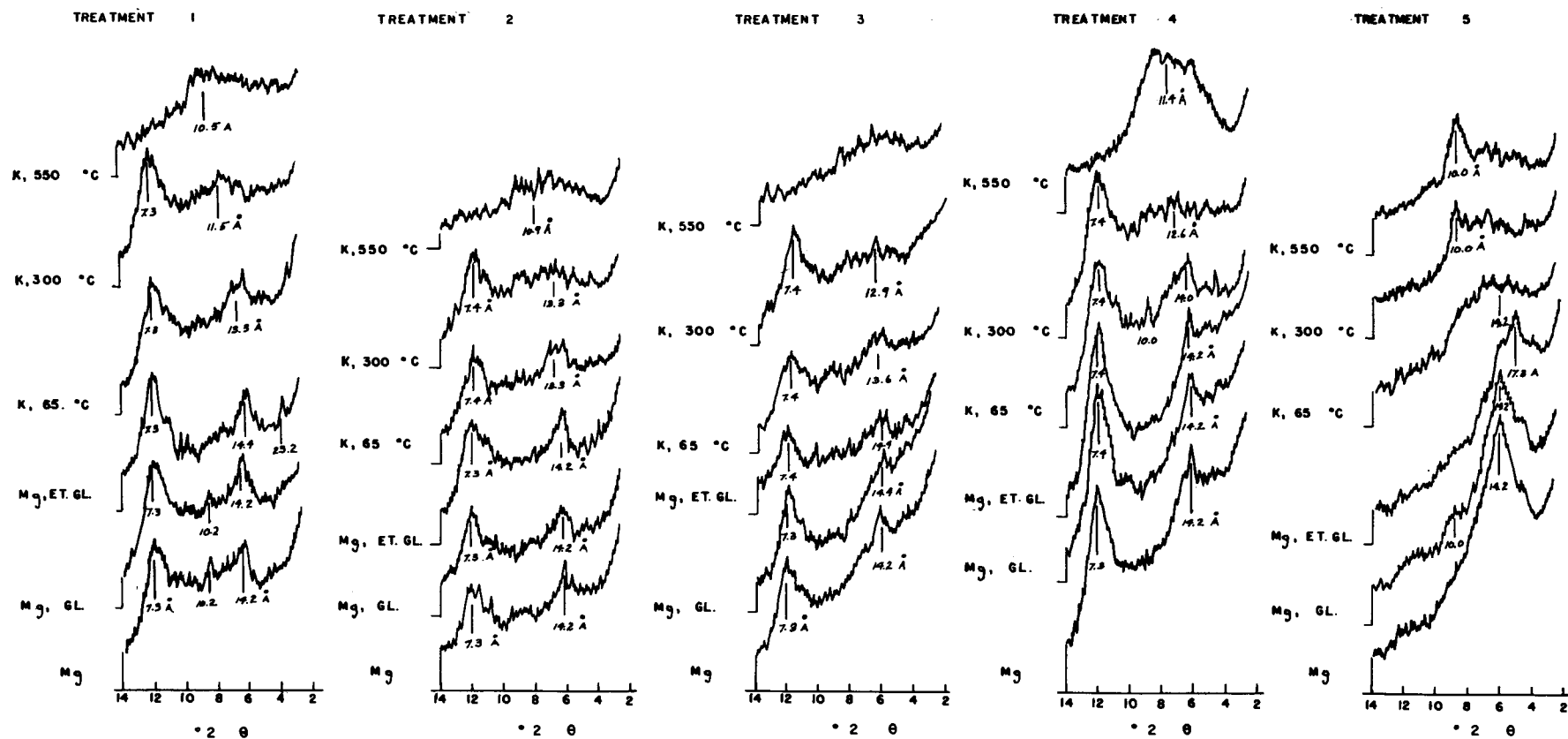


Figure 5. X-ray diffraction patterns of less than two micron clay from the Wren A horizon after different dissolution treatments (see Methods, page 29).

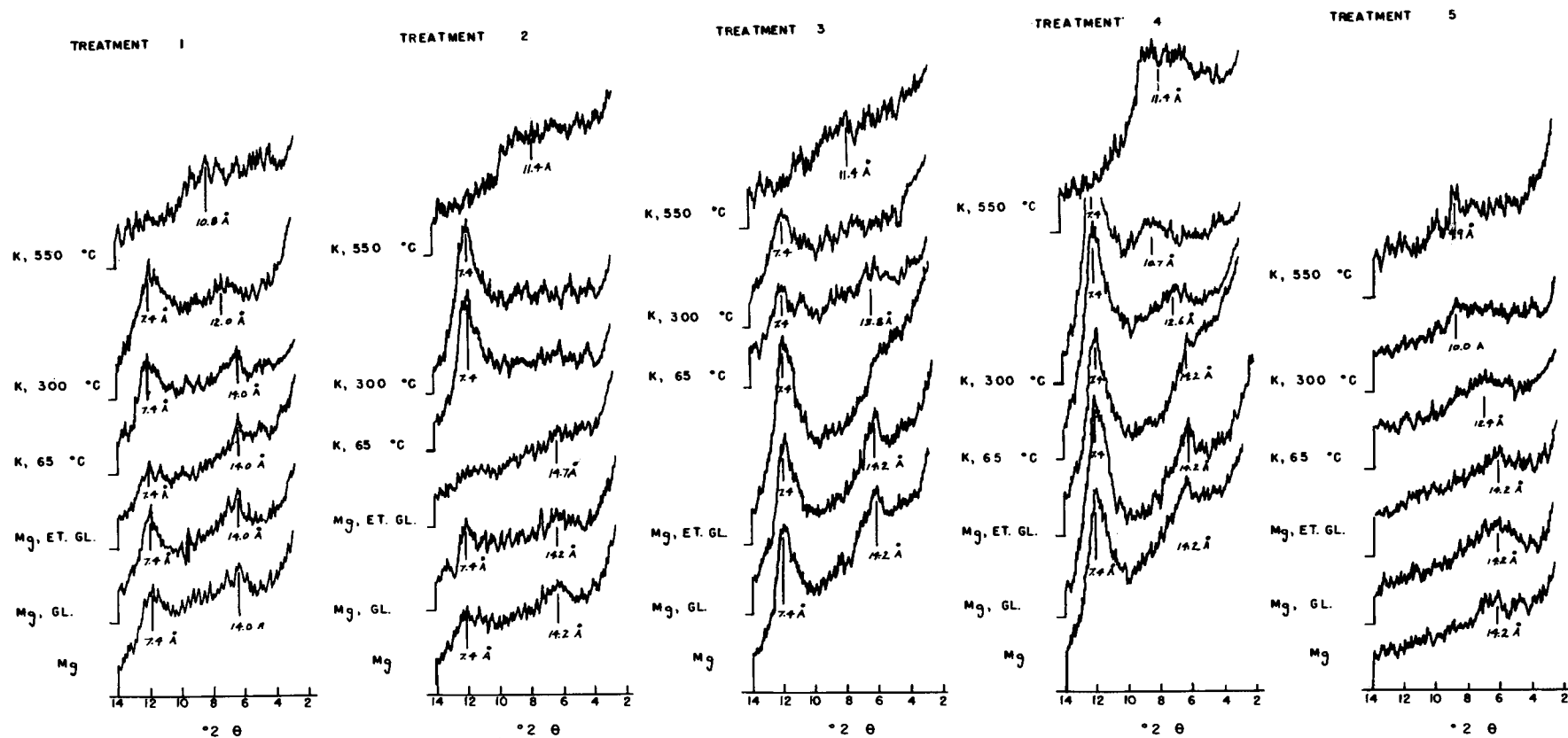


Figure 6. X-ray diffraction patterns of less than two micron clay from the Wren B horizon after different dissolution treatments (see Methods, page 29).

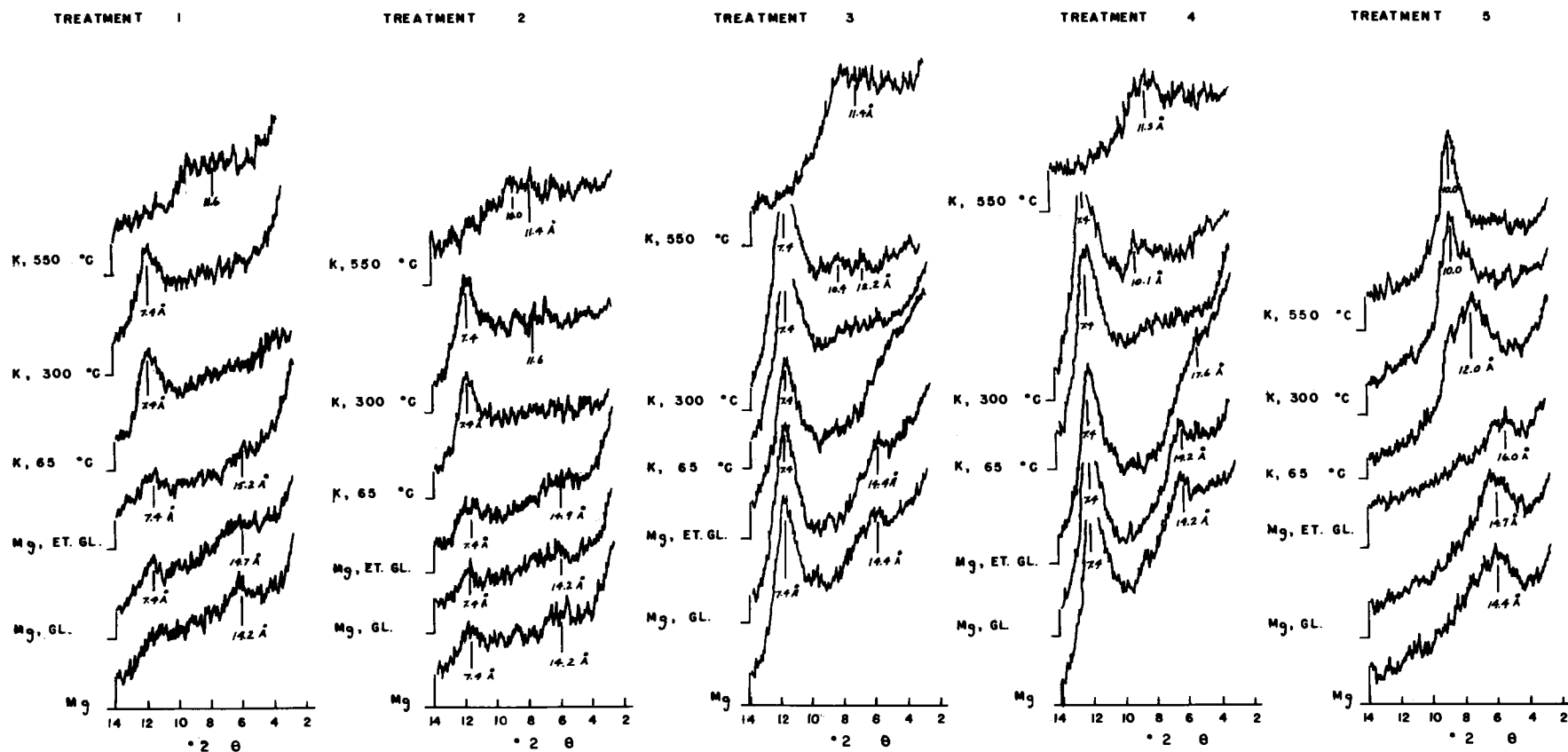


Figure 7. X-ray diffraction patterns of less than two micron clay from the Wren C horizon after different dissolution treatments (see Methods, page 29).

exists, however, that it could be a second order of the 14 \AA peak, or it could be an iron rich chlorite which would exhibit strong (002) and weak (001) peaks. In the latter case, however, some reinforcement of the 14 \AA line would be expected on heating at 550°C . The fact that the 7.3 to 7.4 \AA lines were unaffected by K saturation or heating to 300°C in the same manner as the 14 \AA line, suggests that they are not second order reflections. The 550°C heat treatment is not definitive since both the second order chlorite line and first order kaolinite line would be destroyed at this temperature. It thus appears that the Wren soil contains at least two clay components, a 2:1 intergrade and a kaolin mineral. The spacing of 7.3 to 7.4 \AA rather than 7.2 \AA reported for well crystallized kaolinite, along with the broadness of the peak suggests disordered kaolinite similar to that reported from Provins (France) by Von Engelhardt and Goldschmidt in 1954 (Brown p. 113, 1961). The 7.3 to 7.4 \AA peak might also be attributed to metahalloysite (partially dehydrated halloysite). However, in as much as solvation with ethylene glycol had no effect on the clay, together with the fact that it's crystallinity was destroyed at 400°C makes this theory less probable.

There was a marked decrease in diffraction peaks of Mg saturated samples with increasing depth in the profile (fig. 7, treatment 1). This could be due to a decrease in crystallinity, and/or the presence of amorphous coatings and cementing agents which would interfere with the orientation of particles, and contribute to random scatter. The 7 \AA component was accentuated by K saturation. This has frequently been observed in soils of western Oregon but the reason for it is not

understood (Harward and Theisen, 1962).

The nature of the 2:1 intergrade was of most importance in this study. Considering the effects of treatments for dissolution of interlayer materials, the components of the intergrade exhibited a considerable amount of stability. In the case of the A horizon clays (figure 5), treatment with boiling Na_2CO_3 (treatment 2), iron removal (treatment 3), and boiling NaOH (treatment 4) did not result in any marked differences in properties of expansion or collapse. There were some changes in the clay properties as a result of the 400°C heating and subsequent dissolution in boiling NaOH (treatment 5). Ethylene glycol gave a 17.3 \AA peak with a shoulder corresponding to approximately 14 \AA . There was also greater collapse on K saturation as indicated by a maxima at 10 \AA after heating, but there was still some incompletely collapsed material as indicated by broad, diffuse peaks and high background on the low angle side of the 10 \AA lines. It therefore appears that all of the interlayer material was still not removed even after the maximum treatment. This makes interpretation as to the nature of the 2:1 matrix difficult. The 17.3 \AA peak after ethylene glycol treatment must be interpreted as smectite. Whether it is montmorillonite or beidellite is more difficult to tell. There is some suggestion of slight expansion with glycerol as indicated by the shoulder on the low angle side of the 14 \AA peak. This would indicate montmorillonite although expansion was greater with ethylene glycol. The residual 14 \AA component after solvation would be due to vermiculite or lack of expansion due to interlayer material still present. Typical vermiculite would be expected to show stronger

collapse on K saturation.

X-ray diffraction patterns of B and C horizon clays from treatment 1 (figures 6, 7) are similar to those of the A horizon, in that there was no marked change in the position of peaks after K saturation, and no distinct 10 \AA lines after heating. There were some differences, however, between the surface horizon and the B and C horizons after treatment 3 was imposed. The ethylene glycol solvated clays of the lower horizons show broadened peaks and a high plateau on the low angle side of the 14 \AA peak which indicates some expansion that was not observed in the A horizon clay. Apparently the hydroxy interlayer complex is less stable in the lower horizons.

Treatment 5, which consisted of preheating the clay to 400°C for 4 hours, then treatment with boiling NaOH apparently was sufficiently severe to completely destroy the crystallinity of the kaolin mineral and cause partial destruction of the 14 \AA mineral. This would suggest that both the 1:1 and 2:1 components may have been poorly crystallized. A well crystallized kaolinite would have withstood temperatures to about 550°C before dehydration and loss of crystallinity.

Cation Exchange Capacity Measurements

The CEC values of the Wren clays were progressively increased by each of the successive dissolution treatments (table IV). The unusually high increase observed after treatment 5 was attributed to the fact that the 2:1 member of the clay suite was the only component remaining after the treatment, as revealed by X-ray diffraction data (treatment 5, figures 5, 6, 7). On the other hand, the CEC values of the clays from the first four treatments represented the combined

values of both the 1:1 and 2:1 components of the clay suite (trmts. 1-4, figures 5, 6, 7). Thus, the measured values of clays from treatments 1 through 4 were essentially diluted by the presence of the lower capacity 1:1 mineral.

TABLE IV. THE EFFECT OF DIFFERENT DISSOLUTION TREATMENTS ON THE CATION EXCHANGE CAPACITY OF CLAYS FROM THE WREN SOIL.

Horizon	Cation Exchange Capacity (me./100g.)									
	Measured values					Adjusted values ^{2/}				
	Treatments ^{1/}					Treatments				
	1	2	3	4	5	1	2	3	4	5
A	42	44	49	60	99	74	78	88	110	99
B	37	39	44	59	127	64	68	78	108	127
C	36	38	49	59	104	62	66	88	108	104

^{1/} Treatments as shown in Methods Section page 32.

^{2/} Adjusted values represent the CEC of the expansible member only. Values based on assumptions that the clay suite consists of 50% 1:1 intergrade and 50% kaolinite minerals, and that kaolinite contributed 10 me. per 100 g. to the measured values.

In order to evaluate the effect of removal of interlayer materials on cation exchange capacity values, it was necessary to consider only the 2:1 component of the clay suite. The measured values were, therefore, adjusted to reflect only the 2:1 component. In making the adjustment, it was necessary to make two assumptions that may be questionable. First, from the X-ray data (figures 5, 6, 7) it was inferred that the clay suite was composed of approximately 50% 1:1 and 50% 2:1 clay minerals; and second, that the CEC value of the clay from treatment 5 represented only the 2:1 component. The values for the clays of the first four treatments were then adjusted to represent the 2:1 clay by assuming the kaolinite member contributed 10 me. per 100 g.

to the original measurements. In spite of the possibility that the adjusted values may not represent the absolute conditions, it is felt they do reflect reliable trends. It appeared that in the clays from the A and C horizons, a progressive increase in CEC resulted from the successive treatments to a maximum after treatment 4 (boiling NaOH). Treatment 5 seemed to cause a decrease in the value of the A horizon clay and little or no change in the C horizon. Presumably, the decrease could have resulted from some irreversible dehydration as mentioned previously. X-ray data (trmt. 5, figure 5) shows a slight 10 \AA^0 peak for the Mg saturated, glycerol solvated sample which may represent the portion of the clay that experienced irreversible collapse. The CEC values for the clays of the B horizon increased to a maximum after treatment 5.

Chemical Analyses of Extracts

An interpretation of the chemical data from the extracts of the Wren clays was confounded by the fact that the kaolinitic member of the clay suite was apparently destroyed by treatment 5 as revealed by X-ray diffraction data (figures 5, 6, 7). The question arose as to whether the mineral remained as an amorphous constituent of the clay suite, or whether it represented part of the material extracted by treatment 5.

Table V shows that treatment 2 (boiling Na_2CO_3) removed mostly aluminum and silicon from the Wren clays. When these data are considered in conjunction with CEC measurements (table IV), it is seen that in the A horizon the treatment removed 33.7 mg. aluminum per 1 me. increase in CEC. Evidently the aluminum which was removed

represented coatings from the clay particles, or highly polymerized interlayer hydroxy compounds. An even higher amount of aluminum was removed from the B and C horizons, representing 127 to 135 mg. aluminum removed per 1 me. increase in CEC. The large amount of silicon removed by this treatment probably represents dissolved silicon oxides.

TABLE V. ALUMINUM, IRON, SILICON, AND MAGNESIUM REMOVED FROM THE WREN SOIL CLAYS BY DIFFERENT DISSOLUTION TREATMENTS, EXPRESSED AS A PERCENTAGE OF ORIGINAL WEIGHT OF THE CLAY, AND IN MILLIMOLES PER 100 GRAMS OF CLAY.

Horizon	Trmt ^{1/}	Al		Fe		Si		Mg	
		%	mmoles	%	mmoles	%	mmoles	%	mmoles
A	2	0.22	8	0.02	T ^{2/}	1.00	36	0.04	2
	3	T	T	6.32	113	0.40	14	0.35	14
	4	1.54	57	0.31	5	3.64	130	0.25	10
	5	3.70	137	0.82	15	5.70	203	0.22	9
B	2	0.61	23	0.00	0	2.85	102	0.04	2
	3	T	T	6.90	124	0.54	19	0.33	14
	4	1.66	62	0.21	4	7.85	280	0.24	10
	5	2.04	76	0.65	12	7.78	277	0.22	9
C	2	0.52	19	0.00	0	1.14	41	0.03	1
	3	T	T	6.71	120	0.27	10	0.21	9
	4	1.48	55	0.20	4	5.23	186	0.15	6
	5	2.17	80	0.69	12	6.58	234	0.16	7

^{1/} Treatments listed in Methods Section page 32.

^{2/} Trace amount

Sodium citrate-dithionite (treatment 3) removed iron in rather large amounts, silicon and magnesium in a lesser amount, and only a trace of aluminum. The properties of collapse and expansion were not greatly affected by the removal of these materials (treatment 3, figures 5, 6, 7), however, the CEC was increased (table IV). It would appear that some of the exchange sites were exposed by the treatment,

and yet sufficient islands of interlayer materials remained to block expansion and collapse. In view of the large amount of iron removed, and the fact that the CEC was increased, one comes to the assumption that at least a part of the interlayer material consisted of iron.

Treatment 4 (boiling NaOH) removed a relatively high amount of aluminum and silicon in a Si:Al ratio of about 3:1 to 4:1. It is possible that dissolved allophane could have contributed to the aluminum and silicon removed. The treatment did not materially affect the expanding and collapsing properties of the A horizon; however, it did increase the CEC considerably. The clays of the B horizon, and especially those of the C horizon, did show noticable signs of expansion and/or collapse after the boiling NaOH treatment; consequently, some aluminum and iron evidently was removed from the interlayer positions. In spite of the relatively high amount of aluminum and silicon removed by treatment 4, which should have accounted for the majority of the more resistant amorphous components, an even greater amount of these elements was removed by treatment 5. The ratio of silicon to aluminum removed was from about 1:1 to 3:1. The destruction of the kaolinitic component (trmt. 4 vs. trmt. 5, figures 5, 6, 7) probably accounts for a large portion of the materials removed. It is possible that some aluminum and iron came from the interlayer positions because some change of properties were observed (trmt. 5, fig. 5,6,7). Each of the treatments removed some magnesium from the clay. Although the data obtained do not provide information on what the source was, it is possible that it represents the dissolution of remnants of brucite interlayers from degraded chlorite.

Lookout Soil

X-ray Diffraction Analyses

The data obtained for the Lookout soil strongly indicated a discontinuity in the soil profile. The morphological characteristics also suggested that the A horizon and possibly the B horizon may have been influenced by admixtures of loess and/or volcanic ash and pumice. It is therefore necessary to discuss the data individually for the separate horizons.

The natural state of the A horizon clays should be most closely represented by the data from treatment 1 (figure 8). The Mg saturated sample exhibited a micaceous (illitic) 10 \AA peak, plus a very broad peak or plateau with center at 14.7 \AA . These data suggest some interstratification of illitic and other 2:1 components. There was some expansion of the 14 \AA component on solvation with glycerol as indicated by a shift of the broad peak, and still further shift with ethylene glycol centering at about 17.6 \AA . The 10 \AA peak was noticeably enhanced when the clay was K saturated. The enhancement seemed to occur at the expense of the 14.7 \AA mineral. This would indicate that the minerals in this horizon have a tendency to fix potassium. Dissolution treatments 2 through 4 had no marked influence on expansion and collapse. Treatment 5 resulted in some decrease in the intensity of the 14 \AA component relative to the 10 \AA mineral, suggesting that some dissolution of crystal lattice may have occurred. It thus appears that the clay suite of the A horizon consists of illite interstratified with smectite. There is reason to believe from the X-ray diffraction

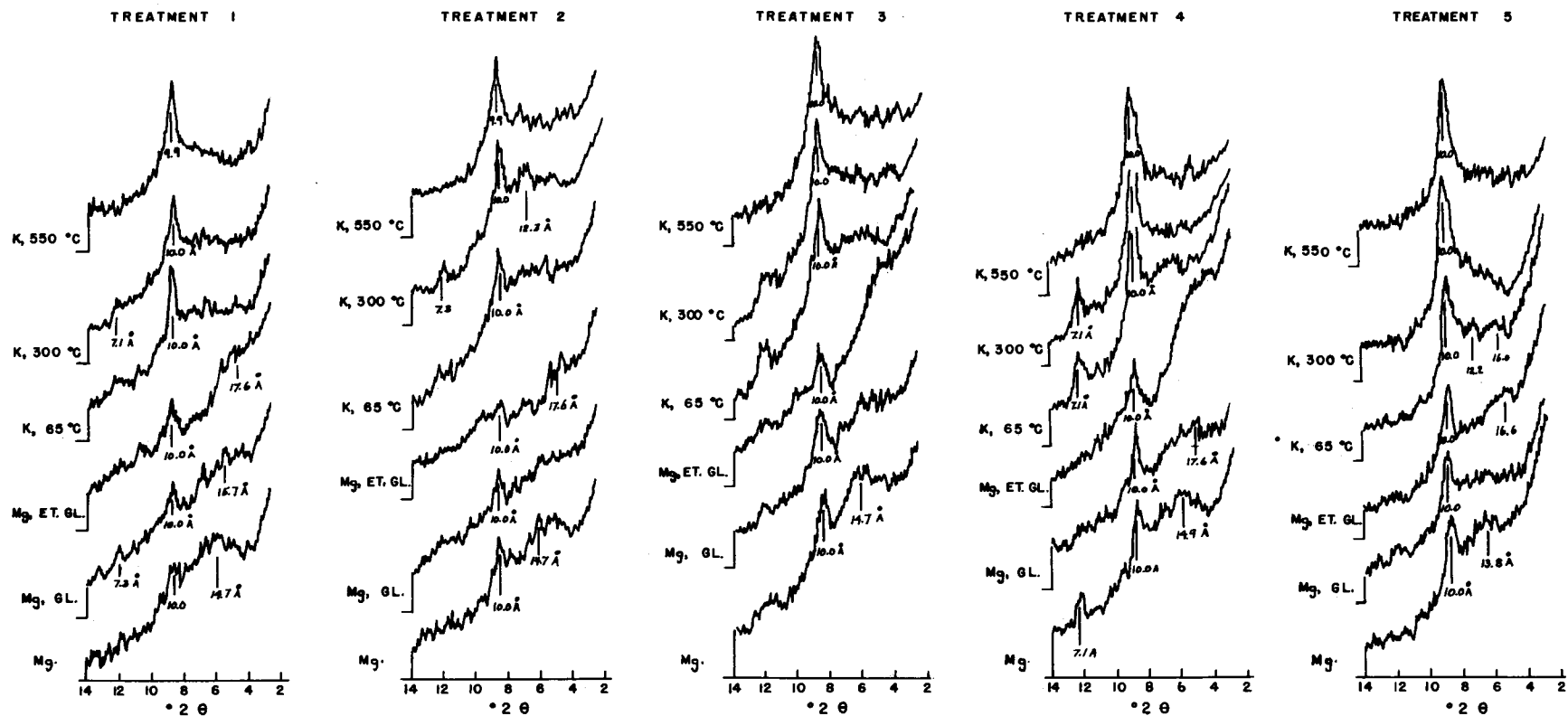


Figure 8. X-ray diffraction patterns of less than two micron clay from the Lookout A horizon after different dissolution treatments (see Methods, page 29).

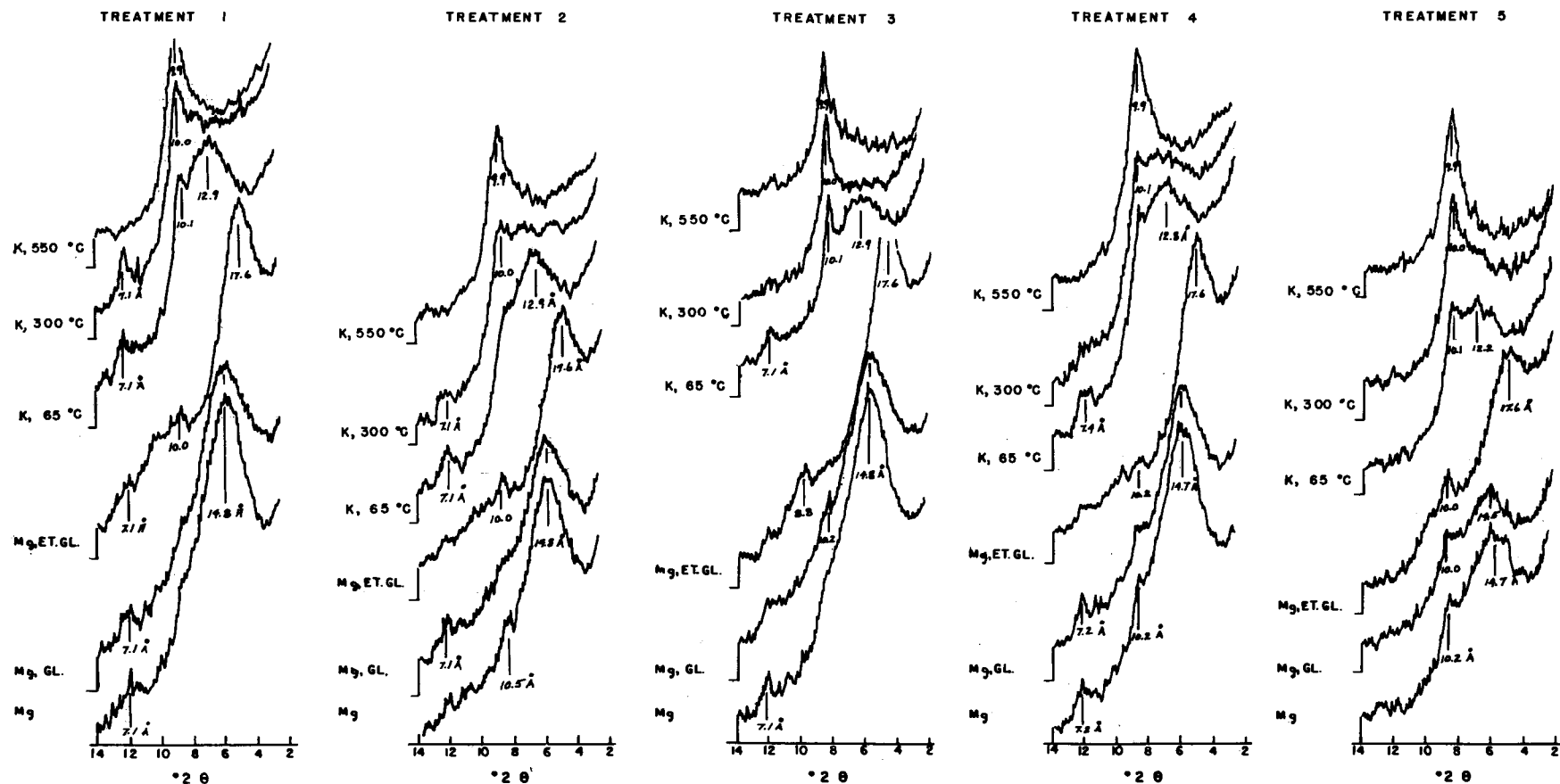


Figure 9. X-ray diffraction patterns of less than two micron clay from the Lookout B horizon after different dissolution treatments (see Methods, page 29).

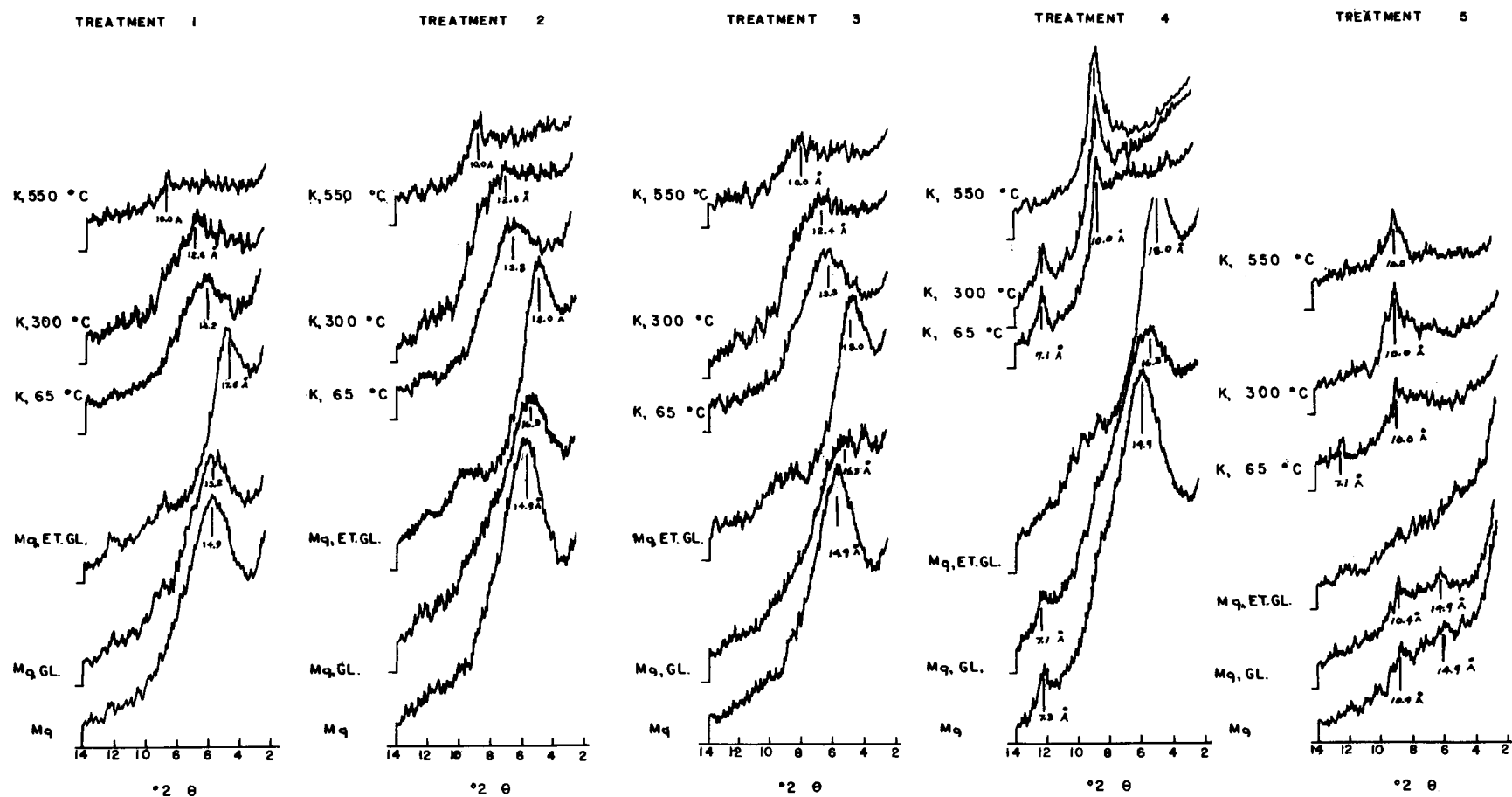


Figure 10. X-ray diffraction patterns of less than two micron clay from the Lookout C horizon after different dissolution treatments (see Methods, page 29).

data that some hydroxy interlayers are present (figure 8). In most cases, a high plateau is present on the low angle side of the 10 \AA^0 peak, which apparently results from incomplete collapse of the mineral. The low angle background was decreased in relation to the 10 \AA^0 peak as successive dissolution treatments were imposed on the clay.

The dominant clay of the B horizon gave a broad 14.8 \AA^0 reflection which sloped off to a smaller 10 \AA^0 peak, suggesting some inter-stratification (treatment 1, figure 9). Mg saturation and solvation with glycerol failed to expand the 14 \AA^0 component; however, ethylene glycol caused expansion to 17.6 \AA^0 . This would suggest a mineral of the smectite group with a strong indication that it is beidellite. K saturation resulted in a marked increase in the 10 \AA^0 peak in addition to a peak at 12.9 suggesting the possibility of some vermiculite, although a distinct 14 \AA^0 line was not evident after solvation with ethylene glycol. The 14 \AA^0 peak, however, could have been masked by the large 17.6 \AA^0 line on one side, and the smaller 10 \AA^0 line on the other so that it may not have been resolved.

A smaller 7.1 to 7.2 \AA^0 line in many patterns of the B horizon clay (figure 9) was unaffected by solvation or K saturation, suggesting the probability of some kaolinite. It is difficult to imagine, however, that kaolinite would form under the alkaline environmental conditions of this soil, but it must be remembered that a discontinuity exists in the profile.

Treatments 2 through 4 failed to cause any marked differences in the clay as reflected by X-ray diffraction data (figure 9). Treatment 5 caused a broadening of the 14 \AA^0 peak with some reduction in intensity

relative to the 10 \AA peak, suggesting some breakdown of the 14 \AA mineral crystal lattice. The broad diffuse plateau on the low angle side of the 10 \AA peak of the K saturated and heated sample, even after treatment 5, indicated incomplete collapse, and suggested the presence of some stable hydroxy interlayers. Treatment 5 also removed the 7 \AA component like it did to the kaolinitic member of the Wren clay.

The clay in the C horizon appeared to be quite similar to that in the B horizon although the peaks are broader, suggesting poor crystallinity or possible interstratification with smaller amounts of illite -- the illite peaks become more evident in the solvated samples. The mineral giving the 14 \AA peak (figure 10) is identified as smectite, although unlike the clay of the B horizon since some expansion was noted when the Mg saturated samples were solvated with glycerol. This would suggest that the smectite may be in part a montmorillonitic mineral. Even though the mineral expanded on solvation, there was definite resistance to collapse. Apparently hydroxy interlayers are present in the clay but are bonded only to one interface of the micelle, as is often the case with interlayered montmorillonite. Because of its swelling characteristics when moist, the interlayers can attach to only one side of the widely separated sheets.

Treatments 2 and 3 caused some collapse of the 14 \AA component upon K saturation, while treatment 4 caused a further collapse to 10 \AA (figure 10). A high plateau on the low angle side of the 10 \AA peak of the K saturated samples indicated that some hydroxy interlayering was still preventing a complete collapse of the mineral. Treatment 5 evidently

caused some destruction of the 14 \AA mineral as evidenced by a marked reduction and broadening of the 14 \AA peak in relation to the 10 \AA line. The plateau on the low angle side of the 10 \AA peak was still present, even after the maximum treatment, indicating that residual interlayers were still present.

Cation Exchange Capacity Measurements

The CEC of the Lookout soil clays generally was increased by the various dissolution treatments (table VI). The greatest change in CEC values occurred in the A horizon clay, while the least change occurred in the C horizon. The highest CEC values were approximately the same for all horizons -- reaching the maximum in the A and C horizons after treatment 5, and in the B horizon after treatment 4.

TABLE VI. THE EFFECT OF DIFFERENT DISSOLUTION TREATMENTS ON THE CATION EXCHANGE CAPACITY OF CLAYS FROM THE LOOKOUT SOIL.

<u>Horizon</u>	<u>Cation Exchange Capacity (me./100g)</u>				
	<u>Treatments ^{1/}</u>				
	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>
A	48	55	56	64	95
B	74	69	79	86	82
C	85	73	76	78	94

^{1/} Treatments as shown in Methods Section page 32.

For an unexplained reason, treatment 2 (boiling Na_2CO_3) caused a decrease in the CEC value of both the B and C horizon clays, although subsequent treatments ultimately raised the values above the original measurements. These data seem to substantiate the X-ray diffraction data, that hydroxy interlayers are present in the clays of the Lookout soil. Further, from the CEC measurements, it would seem that the most

interlayering occurs in the A horizon clays.

Chemical Analyses of Extracts

From the chemical data it is evident that there is very little easily removed aluminum in these clays (table VII). Boiling Na_2CO_3 (treatment 2) and sodium citrate-dithionite (treatment 3) removed only a trace of aluminum. Also, comparatively little iron was removed by the iron removal treatment (treatment 3). Sodium carbonate did, however, remove a considerable quantity of silicon. Treatments

TABLE VII. ALUMINUM, IRON, SILICON, AND MAGNESIUM REMOVED FROM THE LOOKOUT SOIL CLAYS BY DIFFERENT DISSOLUTION TREATMENTS, EXPRESSED AS A PERCENTAGE OF ORIGINAL WEIGHT OF THE CLAY, AND IN MILLIMOLES PER 100 GRAMS OF CLAY.

Horizon	Trmt ^{1/}	Al		Fe		Si		Mg	
		%	mmoles	%	mmoles	%	mmoles	%	mmoles
A	2	0.03	1	0.00	0	2.61	93	0.02	1
	3	0.00	0	0.70	13	0.03	1	0.11	5
	4	1.37	51	0.05	1	6.70	239	0.10	4
	5	2.68	99	0.46	8	6.64	237	0.16	7
B	2	T ^{2/}	T	0.00	0	0.66	24	0.01	T
	3	T	T	0.41	7	0.12	4	0.18	7
	4	0.76	28	0.00	0	2.05	73	0.11	5
	5	1.55	57	0.19	3	3.04	108	0.14	6
C	2	0.01	T	0.02	T	1.99	71	0.08	3
	3	T	T	0.43	8	0.00	0	0.42	17
	4	0.81	30	0.06	1	4.01	143	0.33	14
	5	1.24	50	0.37	7	3.94	140	0.25	10

^{1/} Treatments listed in Methods Section page 32.

^{2/} Trace amount

4 and 5 removed considerable aluminum and silicon from the sample.

This would seem to indicate that some allophane and/or free alumina, as well as the more stable hydroxy interlayer materials were present in the clays. The dissolution treatments removed more magnesium

than iron, suggesting the possibility that under the alkaline environment of this soil, some magnesium hydroxy interlayers may have developed. The amount of magnesium removed increased with depth.

Petrographic Analyses of the Very Fine Sand

A petrographic study of the very fine sand fraction showed quite a wide variation between the minerals of the Hembre, Wren, and Lookout soils (table VIII).

The data shows the dominant mineral in the Hembre is chlorite and that the A, B, and C horizons contain 33.7, 79.0, and 66.8 percent respectively. The lower percentage of chlorite in the A horizon may have been due to the weathering of some of the chlorite into the chlorite-like intergrades identified previously, or it may have been caused by the addition of volcanic ash to the surface soil which would automatically lower the percentage composition of chlorite. The high amount of altered glass in the A horizon suggests a surface deposition of volcanic origin.

The minerals identified in the Wren soil were predominantly biotite and altered glass. The ratio of these two minerals in the surface horizon compared to the ratios in the lower horizons is quite different. The minerals in the B and C horizons are quite uniform. The relatively higher amount of chlorite in the A horizon over that in the lower horizons suggests that there might have been some mixing or movement of soil parent materials.

The minerals in the Lookout soil are nearly the same in the A and B horizons. These horizons contain 62.6 and 77.6 percent feldspar

TABLE VIII. PETROGRAPHIC ANALYSIS OF THE VERY FINE SAND FRACTION (50 TO 100 MICRON) FROM THE
HEMBRE, WREN, AND LOOKOUT SOILS.^{1/}

Soil	Horizon	Mineral Content ^{2/}											
		Chl. %	Alt. Gl. %	Br. Gl. %	Cl. Gl. %	Pyrx. %	Amph. %	Qtz. %	Feld. %	Alt. Fels. %	Mag. %	Bio. %	Misc. %
Hembre	A	33.7	44.4	3.0	----	4.9	----	0.4	0.4	----	0.4	7.5	4.9
"	B	79.0	9.4	4.4	----	0.9	----	1.3	0.9	----	----	3.8	0.3
"	C	66.8	8.9	22.0	----	0.6	----	----	1.1	----	----	0.6	----
Wren	A	13.0	20.0	----	----	3.7	0.3	----	9.0	----	----	54.0	----
"	B	2.0	56.2	----	----	0.9	----	----	6.9	----	----	34.0	----
"	C	0.3	56.3	----	----	1.6	----	----	7.8	----	----	33.8	----
Lookout	A	----	----	----	16.5	0.5	7.5	0.5	62.6	7.5	2.2	0.7	----
"	B	----	----	----	4.7	0.2	7.7	----	77.6	6.6	0.4	2.8	----
"	C	----	----	----	2.4	----	1.8	----	16.2	79.6	----	----	----

^{1/} Petrographic analysis made by L. Lackey, Graduate Student, Geology Department, University of Wyo.

^{2/} Chl. = Chlorite

Alt. Gl.= Altered glass changing to chlorite

Br. Gl. = Brown volcanic glass (unaltered)

Cl. Gl. = Clear glass (unaltered)

Pyrx. = Pyroxene

Amph. = Amphibole

Qtz. = Quartz

Feld. = Feldspar

Alt.Fels= Altered felsic grains. Possibly to clay and chlorite

Mag. = Magnetite

Bio. = Biotite

Misc. = Rounded bodies (unidentified)

respectively, whereas the C horizon contains only 16.2 percent. On the other hand, the C horizon contains 79.6 percent altered felsic grains that may be changing to chlorite and chlorite-like minerals, while the A and B horizons contain only 7.5 and 6.6 percent respectively. It is evident that a discontinuity exists in the profile as a result of admixtures of loess and/or volcanic ash and pumice deposited in the A and B horizons.

SUMMARY AND CONCLUSIONS

The three soils chosen in this study to represent soils formed under high, medium, and low rainfall zones were the Hembre, Wren, and Lookout soils respectively. Clays from the major horizons of each soil were subjected to a series of dissolution treatments of increasing severity for the removal of hydroxy interlayers. Extracts from the various steps of the dissolution procedure were chemically analyzed in order to identify the materials removed. X-ray diffraction analysis and CEC determinations were made on the clays after each step of the dissolution procedure and compared to similar measurements made on the clays receiving a minimal treatment. Differences between the measurements were attributed to the removal of hydroxy interlayers from the clays. A summarization of the data is reported for each clay in the following paragraphs.

Hembre

X-ray diffraction analysis revealed that the clays receiving minimal pretreatment displayed expanding and collapsing properties intermediate between smectites on the one hand and chlorite on the other. As the severity of the dissolution treatments increased, the degree of expansion and collapse also increased. The A horizon clay, however, did not exhibit complete collapse on K saturation and heating, even after the maximum treatment had been imposed. As depth in the profile increased, the degree of collapse increased, suggesting that hydroxy interlayers were most evident in the surface

and decreased with depth.

The CEC values of the clays receiving the minimal treatment were increased by the boiling Na_2CO_3 treatment, and further increased by sodium citrate-dithionite. Subsequent treatments involving dissolution with NaOH failed to produce any further significant increase. The maximal treatment, of preheating and dissolution with NaOH, caused a reduction of CEC in clays of the C horizon over those treated with NaOH without preheating. The decrease in CEC is presumed to have resulted from some irreversible dehydration incurred during the preheat treatment.

Chemical analysis of the extracts from treatments which influenced CEC values most indicated that both aluminum and iron probably occupied interlayer positions. There was also a notable amount of magnesium removed which could have been residuum from the brucite interlayers of degraded chlorite. The ratio of silicon and aluminum removed from the more resistant materials by the NaOH treatments varied between 1.5:1 to 3:1.

Wren

X-ray data of the Wren soil clays disclosed two components in the clay suite; one, a disordered kaolinite or metahalloysite, and the other a chlorite-like intergrade. The hydroxy interlayers of the A horizon clay appeared to be very stable, and the stability decreased with depth in the profile. Peak intensity also decreased with depth, suggesting less crystallinity, or the presence of amorphous coatings. The matrix of the intergrade was determined to be smectite. Pre-

heating and treatment with NaOH (treatment 5) destroyed the 7 Å component of the clay suite and decreased the 14 Å component, again indicating poor crystallinity.

Cation exchange measurements were considered in terms of the 14 Å component only, in order to evaluate the effect of hydroxy interlayer removal on the measured values. CEC maximums were obtained in the clays of the A and C horizons only after treatment with boiling NaOH (treatment 4), and those of the B horizon, only after preheating and treatment with NaOH (treatment 5). These data further testify to the stability of the interlayers in the Wren soil.

Chemical analysis of the extracts revealed that aluminum, iron, and possibly magnesium could have occupied the interlayer positions. Extremely high amounts of aluminum and silicon were removed by the total treatments. Treatment 4 (boiling NaOH) apparently removed considerable allophane or free alumina and silica, while treatment 5 removed the kaolinitic component of the clay suite. The ratio of silicon to aluminum removed by treatment 4 was about 2:1 in all horizons, while that removed by treatment 5 was in the ratios of 1:1, 2:1, and 3:1 for the A, B, and C horizons respectively.

Lookout

X-ray diffraction data of the Lookout clays disclosed an illitic mineral in association with a 14 Å intergrade. The intergrade appeared to be similar to those which have been termed "swelling chlorite" in that the mineral showed resistance to collapse with K saturation and heat, but was expanded to 17.6 Å by solvation with

ethylene glycol. Thus, interlayering was found to occur in all horizons with about equal intensity. After removal of the interlayers, the matrix was determined to be smectite.

CEC values were increased in the Lookout clays as a result of hydroxy interlayer removal. The greatest increase occurred in the A horizon and the least in the C horizon; however, the maximum values attained were about the same in all horizons. Maximum values were obtained after treatment 5 in the A and C horizons, and after treatment 4 in the B horizon.

Chemical analysis of the extracts showed there was very little aluminum or iron removed by the Na_2CO_3 and sodium citrate-dithionite treatments. Treatments 4 and 5 involving NaOH, however, removed considerable aluminum and silicon, which suggests the occurrence of allophane and/or free alumina and silica in addition to hydroxy interlayer materials. On a mole basis, more magnesium was removed from the Lookout soil than iron. There is the possibility that under the alkaline environmental conditions of this soil that hydroxy magnesium interlayers do occur. Although the Lookout soil seemed to contain less hydroxy interlayering than the other soils investigated, the interlayers which were present appeared to have considerable stability, in as much as the more severe treatments were required to remove them.

Conditions Under Which Hydroxy Interlayering Developed

Hydroxy interlayers were found to occur more in the Hembre and Wren soils than in the Lookout soils, with the most stable interlayers occurring in the Wren. Soil reaction was one of the major differences

between these soils. The pH values of the Hembre and Wren ranged between 4.5 and 5.0, while that of the Lookout soil was near neutral at the surface and 8.3 in the zone of calcium carbonate accumulation. More iron and aluminum hydroxy interlayers would be expected to occur in the Hembre and Wren clays in as much as the charged hydroxy polymers which constitute the interlayer materials occur only under acid conditions. Carstea (1965) in preparing synthetic hydroxy interlayers in montmorillonite found that the most stable aluminum interlayers were formed at pH 4.6 while iron hydroxy interlayers were formed at even lower pH values. Lithologic intergrades formed from the breakdown of chlorite also develop under acid conditions. Nevertheless, hydroxy interlayers were found to be present in the alkaline Lookout soil clays. The chlorite-like intergrades of the Lookout soil were of the swelling type, whereas, those found in the Hembre and Wren soils were of the type that showed resistance to expansion when solvated.

The data from the Hembre clays definitely showed that hydroxy interlayers formed to the greatest extent in the surface horizon and decreased with depth. Hydroxy interlayers occurred in the A and B horizons of the Wren clays in about equal amounts, but less in the C horizon. It appears from this and morphological data that the Wren soil has weathered rather deeply. The B horizon has a definite zone of clay enrichment which presumably formed as a result of downward movement of clay. Thus if interlayer hydroxides were developed in the A horizon where weathering was most intense, it is conceivable that they would ultimately have reached the B horizon.

Results of this study show that a linear relationship cannot

be drawn between the relative degree of weathering of these soils and present climatic conditions. The Wren soil, for example, which was chosen to represent moderate weathering conditions, is a mature soil with a well developed argillic horizon, while the Hembre soil, chosen from an area of intense weathering, is a young soil classified as an Inceptisol.

A lithologic discontinuity in the profile of the Lookout soil made comparison of one horizon with another difficult. Interlayering occurred in all horizons, although not to the same extent as in the other soils. On the basis of the X-ray data, there appeared to be as much interlayering in the C horizon as in the upper horizons. This seems to contradict the idea that interlayering develops most in the upper horizons where weathering is greatest. The apparent anomaly is resolved, if the discontinuity in the profile is taken into consideration. Apparently the upper horizons have been subjected to a great deal of aeolian influence, and under the circumstances, it is possible that the present C horizon may in the past, have been exposed as a surface soil. The presence of 1.7 percent organic matter in the C horizon as compared to 0.9 percent in the B₂₂, and 1.7 percent in the A₁₂ (table I) seems to substantiate this idea.

Results of this study indicate that intergrades may have formed both from chloritization, and from chlorite degradation. The high amount of chlorite in the Hembre parent materials together with the acid environmental conditions, no doubt led to some chlorite breakdown. Somewhat similar conditions existed in the Wren soil. There is, however, a high amount of biotite in the Wren soil that could

readily weather to an intergrade by altering to smectite and subsequently undergoing chloritization. The intergrades in the Lookout soil apparently formed from chloritization of smectites, in as much as no chlorite was observed in the very fine sand fraction.

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