

ALTERATION OF DI-OCTAHEDRAL MICAS IN SOILS

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by

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INTRODUCTION

A comprehensive knowledge of the development of a soil is dependent in part upon an understanding of the changes which the soil minerals undergo from the time they are exposed to weathering as part of the parent rock until they are transformed into fine material. Thus far, attention of soil scientists in weathering studies of a particular soil has been directed chiefly to the accumulation of clay or colloidal material at different depths and to changes in the gross chemical composition of the soil material in the various horizons. Changes in the individual mineral constituents have received little attention, especially those changes which take place in the deeper parts of the profile, that is, below the B horizon, usually the layer of clay accumulation.

Diocahedral micas, among which muscovite is an important member, are important primary minerals found in soil parent material. They show great compositional variation and can form under a wide range of physical and chemical conditions. The ubiquitous occurrence of these micas makes them of considerable importance in studies of rock weathering and soil formation. Despite this more common occurrence, there is relatively much less information on weathering and alteration of dioctahedral micas than trioctahedral micas.

Micas are influential on the clay fraction of soils in at least three ways. First, micas weather to clay size in relatively unaltered form. Second, micas are altered during the weathering processes, and these altered forms of mica occur in the clay fraction. Third, micas

may weather to ionic components, which undergo reorganization with other ions to form kaolinite or other minerals. Perhaps of greatest importance to soils are the alteration products accompanying the weathering of dioctahedral micas. For example, many of the mica weathering products exhibit a high cation exchange capacity, which is reflected in the properties of the soil in which the weathered products occur. The property of cation exchange is of great fundamental and practical importance in soils investigations, as well as in other fields concerned with the study and use of clay materials.

This investigation is concerned with some of the changes that take place in the dioctahedral mica group of minerals during weathering in certain Virginia soils. It deals with the occurrence of muscovite and paragonite type micas in soils, with the nature of their alteration products, and with artificial weathering studies designed to give insight into the mechanisms of mica alteration in soils.

LITERATURE REVIEW

Characteristics of Dioctahedral Micas

The basic structural unit of the micas is a layer structure composed of two sheets of Si tetrahedra between which is a sheet of cations in octahedral coordination with O^{--} and OH^- ions. The O^{--} ion, comprising the apex of each tetrahedron in the Si sheets, points toward the center of the unit and is shared in octahedral coordination with the adjacent cations of the central sheet. Some of the Si^{++++} ions in the tetrahedral layer are replaced by Al^{+++} ions and the resultant charge deficiency is balanced by cations, e.g., K^+ , Na^+ , outside the sheet. These cations occur between unit layers where they fit into the holes formed by the six member O^{--} rings of the tetrahedral layer.

Dioctahedral micas are those micas in which only two-thirds of the possible octahedral positions are filled, primarily with Al^{+++} ions. Micas in which all the octahedral positions are filled, primarily by Mg^{++} and Fe^{++} ions, are trioctahedral. Of the two types, the dioctahedral type occurs more frequently and is of greater importance from the soils standpoint. Muscovite is the most common dioctahedral mica, occurring over a wide range of geological conditions. A diagrammatic sketch of muscovite is shown in figure 1.

The fundamental features of the muscovite structure were first presented by Jackson and West (1930, 1933). Only recently have other detailed analyses of muscovite been made (Radoslovich, 1960). Hendricks and Jefferson (1939), later Levinson (1953), and others have demonstrated extensive polymorphism among the micas. Polymorphism occurs be-

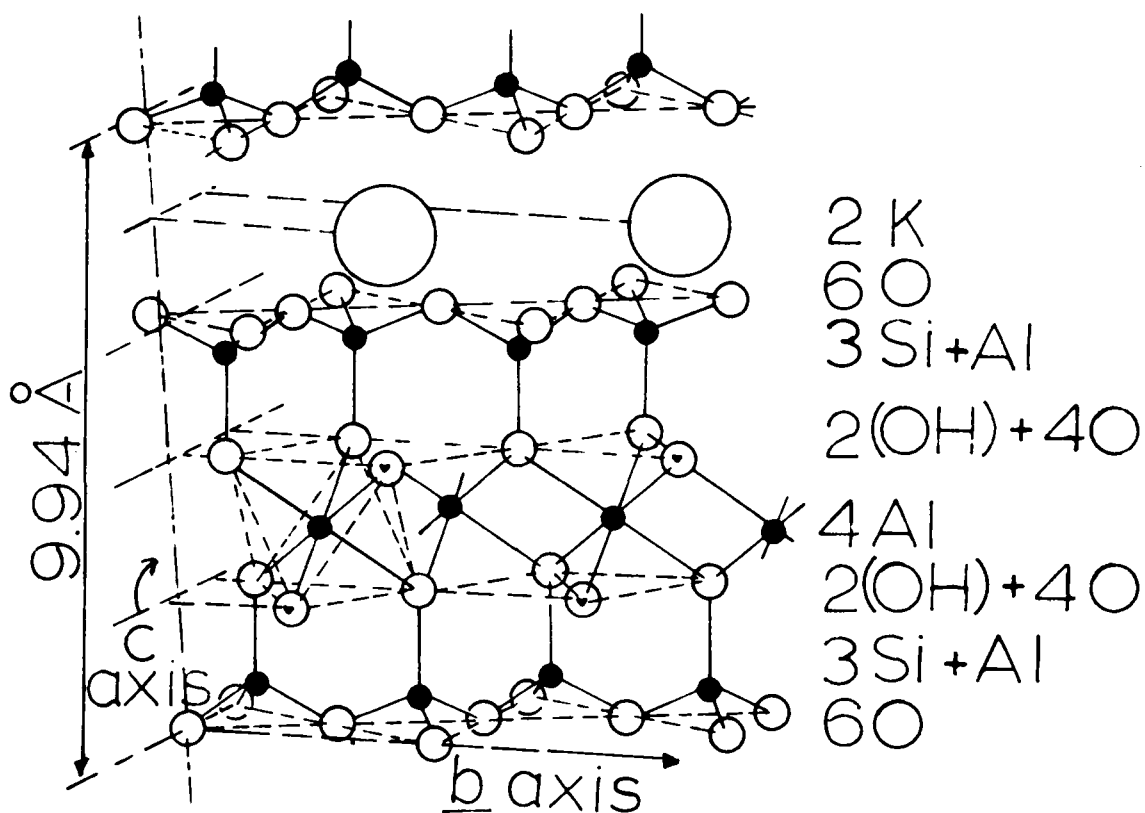


Fig. 1. Structure of muscovite, $K_2Al_4(Si_6Al_2)O_{20}(OH)_4$.
 Pyrophyllite layers with one aluminum substituted for one
 out of four silicons in each tetrahedral layer, linked
 together by potassium ions in twelvefold coordination with
 oxygen. (After Berry and Mason, 1959).

cause the atomic arrangement of the fundamental unit cell has monoclinic symmetry whereas the surface of the unit cell has hexagonal or pseudohexagonal symmetry. Smith and Yoder (1956), in a detailed discussion of mica polymorphism, both theoretically and experimentally, predicted that six simple polymorphs should be observed: $1M$, $2M_1$, $2M_2$, $3T$, $2O$, and $6H$. For muscovite, only the $1M$, $2M_1$, and $3T$ polymorphs have been found definitely; the $2O$ and $6H$ polymorphs have not been found in either natural or synthetic products. Radoslovich (1959) suggested that the reason for this lies in the ditrigonal rather than hexagonal symmetry of the actual layer surfaces of micas. Such surfaces can fit together most readily in ways which correspond to no rotation, or to rotations which are multiples of 120° . Those polymorphs, which correspond to rotations between layers and are multiples of 60° ($2O$, $2M_2$, and $6H$), should only be observed in micas showing little or no distortion. Yoder (1959) stated that the composition of the mica plays the dominant role in determining the polymorphic structure. He stated that this is especially true for dioctahedral micas, which enhance the departure from the hexagonal character of the (Al, Si) sheets due to the difference in Al-O and Si-O bond lengths.

Closely related to muscovite is the mica, paragonite, the Na analogue. Paragonite as a rock forming mineral occurs always in small flakes (Eugster, in Abelson, 1954). It seems to be impossible to distinguish optically these flakes from fine-grained muscovite (Schaller and Stevens, 1941), and they are therefore included in the group "white micas."

The validity of paragonite as a distinct mineral species has been definitely established only in recent years (Schaller and Stevens, 1941). The viewpoint of earlier workers was expressed by McCormick (1934), who concluded that "paragonite as a distinct mineral has not been found in nature, indicating that it probably is an unstable molecule of the mica group." However, investigations (Eugster and Yoder, in Abelson, 1955) into the occurrence of paragonite in nature revealed that in some areas this mineral is one of the major rock-forming silicates. The environment in which paragonite was found varied from that of fine-grained sediments, phyllites, muscovite-biotite gneisses, staurolite-albite schists, muscovite-garnet schists, and kyanite-staurolite schists to that of paragonite-kyanite lenses within quartz veins. Thus, it was concluded that the occurrence of paragonite is less restricted than was previously assumed.

Synthetic preparations of paragonite have been helpful in the positive identification of the mineral. Gruner (1942) synthesized paragonite by heating $\text{Al}(\text{OH})_3$, silicic acid, and NaCl with 0.1 N HCl solution at 400°C . for seven days in a gold-lined bomb. He believed that paragonite is uncommon because Na^+ ions are so small that they will not fit readily into the K^+ positions of the micas. Morey and Chen (1955) formed paragonite by hydrothermally treating albite.

Studies at the Carnegie Institution of Washington (Eugster and Yoder, in Abelson, 1954, 1955; Yoder, 1959) indicated that the stability field of paragonite closely resembles that of muscovite. Paragonite polymorphs were synthesized that paralleled the muscovite polymorphs.

On the basis of these laboratory syntheses, it was concluded that the two micas should occur simultaneously, provided the chemical composition requirements for Na and K were met. Investigation of many fine-grained schists by x-ray methods revealed that muscovite and paragonite almost always occur simultaneously. Most specimens labeled paragonite are mixtures of muscovite and paragonite, a conclusion reached following analysis of some 100 low-grade metamorphic schists containing white mica (Eugster, in Abelson, 1954). Only two specimens of pure paragonite were obtainable by the author. These samples were from Italy and Switzerland, and were supplied through the courtesy of the U.S. National Museum.

Weathering of Dioctahedral Micas

Views regarding weathering of micas appear to be founded chiefly on examinations of decomposing rocks and alteration of mica in deposits. The synthesis and decomposition of mica under laboratory conditions has attracted considerable interest in recent years. Comparatively few investigations deal directly with the weathering of mica in soil. Although it is not to be expected, of course, that the weathering of mica in soil is necessarily comparable in nature or extent to that operating under other conditions, one may reasonably infer that the alterations which take place in mica under either natural or artificial conditions are indicative of what may be expected to take place in the soil.

Muscovite-secondary muscovite relationships

Considerable difference of opinion exists as to the alterability of the dioctahedral mica muscovite. Muscovite is one of the most stable minerals in weathering, even though it is believed by some to weather to clay minerals.

The general opinion maintained for many years regarding muscovite alteration was expressed by Clarke (1924):

Muscovite, under ordinary conditions, is one of the least alterable of minerals. The feldspar of a granite may be completely kaolinized, while the embedded plates of mica retain their brilliancy almost unchanged.

Thoulet (1913) listed muscovite among those minerals most indestructible in his "order of destruction." Goldich (1938) proposed a "mineral stability series" in which muscovite was the most resistant of the aluminosilicates to decomposition. Pettijohn (1941) noted that muscovite was reported more commonly from older rocks than from younger ones, and on the basis of a "persistence index" rated muscovite as one of the most persistent. Muscovite was considered exceptionally stable also on the basis of a "weathering potential index" devised by Reiche (1945). This extreme stability of muscovite was questioned by Denison, Fry, and Gile (1929), who observed that muscovite and biotite did not differ appreciably in their rates of decomposition. The position was then taken that, insofar as origin is concerned, two kinds of muscovite were being recognized: primary muscovite and secondary muscovite. Clarke (1924), Merrill (1906), Van Hise (1904), and others considered secondary muscovite to be an alteration product of the potash feldspars. But these writers did not state that this alteration takes place under

normal conditions of weathering, or whether secondary muscovite differs from primary muscovite in readiness of alteration. Investigations of china clays by Hickling (1908) and Galpin (1912) indicated that secondary muscovite may be formed in the atmospheric weathering of granites to clays. Hickling's work went farther in suggesting that the secondary muscovite thus formed is much more readily altered than the primary. He pointed out that in decomposing granite, feldspar is altered only to secondary muscovite. In the further decomposition of the rock to china clay, however, he noted that secondary muscovite passes into kaolinite, while much of the primary mica persists without obvious alteration. Of course, china clays differ widely from soils in their nature and perhaps in their origin. Consequently, such transformations can be assumed to hold for soils only as they are borne out by investigations of mineral alteration under soil conditions.

Ross and Kerr (1931) examined, chemically, materials like those described by Hickling as secondary mica, as well as those described as sericite by Stelle (1907), and concluded that they were not micas, but similar to kaolinite in composition except for the lower water content. X-ray studies of the same materials by Ross and Kerr indicated that the secondary mica had a kaolinitic structure, suggesting that the feldspar weathered directly to kaolinite without an intermediate stage of mica.

The nomenclature of secondary muscovites is somewhat confounded by the plethora of names used to describe the materials. Sericite is perhaps the most common field term used to describe fine-grained mica.

Winchell (1951) defined sericite as "a fine scaly or fibrous kind of muscovite, confined to white mica that is secondary." Other names ascribed to secondary muscovites include illite, sarospatakite, potash bentonite, pinite, mariposite, hydromica, and glimmerton. The characteristic features of all secondary muscovites are a decrease in K content and an increase in water, or H_3O^+ , content compared to primary muscovite.

Mackenzie (1955) showed a relationship among the various secondary muscovites in the following scheme:

INCREASING HYDRATION AND DECREASING K^+ CONTENT

Series I (after Grim, Bradley, and Brown, 1951)

Muscovite---Hydromuscovite---Illite---Al-illidromica

- Mica intermediate
- Bravaisite
- Sarospatakite

Hydrous Mica

Series II (after Mackenzie, 1955)

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graph LR
    Muscovite --- Hydromuscovite
    Hydromuscovite --- Illite
    Illite --- Mica_intermediate[Mica intermediate]
    Illite --- Al_Andreattite[Al-Andreattite]
    Illite --- Mica_smectite[Mica-smectite interstratified minerals]
  
```

Muscovite --- Hydromuscovite --- Illite --- Mica intermediate

Muscovite --- Hydromuscovite --- Illite --- Al-Andreattite

Muscovite --- Hydromuscovite --- Illite --- Mica-smectite interstratified minerals

Hydrous Mica

The term "illite" was first used by Grim, Bray, and Bradley (1937) to describe any clay mica, but Mackenzie's scheme restricts it to include micas having approximately 6-8% K_2O . "Hydromuscovite" was used by Bram-

mall, Leech, and Bannister (1937) to describe a mica with only a small amount of K^+ replaced by H_3O^+ , while Andreatta (1949) applied the term "Al-illidromica" to dioctahedral minerals with large amounts of K^+ replaced by H_3O^+ . "Bravaisite" and "sarospatakite" were proposed to describe those minerals which contain layers of the mica type and layers of the smectite (montmorillonite) type interstratified. The term "hydrous mica" is broad in significance and was used to include all members between the ends of the arrows in the scheme.

In an excellent review of synthetic and natural muscovites, Yoder and Eugster (1955) concluded that many of the mineral names for secondary muscovites were unnecessary, that most of the minerals were straightforward varieties of muscovite with only minor variations in composition. They did make an important distinction between illite and hydromica. Illite was considered a field term only (as originally intended by Grim) and should not be used when the muscovite polymorph can be identified and specified. In contrast, hydromica denoted a particular type of substitution in the mica as inferred by Ganguly (1951), and by Brown and Morrish (1951). These workers independently proposed that H_3O^+ , the hydronium ion, which has a radius approximately that of K^+ , substitutes for K^+ .

Due to the similarity in structures of muscovite and paragonite, one would expect hydration and subsequent alteration of the two micas to proceed similarly. The amount of published information on 'secondary paragonite' is meager compared to the amount available on muscovites, however. Bannister (1943) reported the occurrence of a Na-containing

mica and proposed the name "brammallite." In a recent paper by Erdelyi, Koblenz, and Tolnay (1958), the term "hydroparagonite" was introduced as the Na analogue to hydromuscovite. They also classified the mineral described under the name "brammallite" by Bannister as hydroparagonite and not as sodium-illite. Hydroparagonite has been recognized officially as a mineral species by the European mineralogist Strunz (1957) (Dr. J. Erdelyi, personal communication).

Weathering of dioctahedral micas in soils

The few studies with emphasis on alteration of muscovite micas in soils have approached the problem primarily from the standpoint of weathering sequences. Fieldes and Swindale (1954) suggested that most soil micas of the muscovite type are likely to be less stable than muscovite itself due to varying degrees of substitution in the micas found in soil parent material. They visualized three important steps in the weathering of mica in soils:

- a) Mica--Unweathered primary mica, including muscovite, with basal spacing of approximately 10 \AA^1 .
- b) Illite--The first order basal spacing is still 10 \AA ., but hydroxyl has increased and K decreased with increase in exchange capacity.
- c) Clay-vermiculite--These minerals expand, which differentiates them from mica and illite, essentially non-expanding minerals.

¹ The letter 'A' will be used to represent the symbol of the Angstrom unit, \AA .

At early weathering stages in which H^+ ions are dominant, clay-vermiculite can be a stable phase of expanded micaceous clay.

Walker (1950) noted a stepwise breakdown of the trioctahedral mica, biotite, to trioctahedral vermiculite, but no comparable alteration seemed to occur with dioctahedral mica. Earlier, Walker (1949) had observed that the final product of weathering for both muscovite and biotite was kaolinite and thus predicted similar weathering of the two types of minerals.

Other workers, however, have observed numerous occurrences of materials with a vermiculitic nature which have weathered from muscovite. Accordingly, these materials have been grouped under the name 'dioctahedral vermiculite.' Brown (1953) identified a mineral found in soil clays from northwest England as a dioctahedral analogue of vermiculite, which seemed to be derived from a dioctahedral mica. Other occurrences of dioctahedral vermiculite have been noted in the Shenandoah Valley of Virginia (Hathaway, 1955), in the Piedmont of Virginia (Rich, 1954, 1958; Rich and Obenshain, 1955), and in several hundred soil samples of the southeastern United States (Rich, unpublished data). In all of these studies, the origin of the dioctahedral character of vermiculite was attributed to dioctahedral mica. Jackson (1959) indicated that the dioctahedral type of vermiculite is more common in soil clays than the trioctahedral type.

In a study of residual kaolins in the southern Appalachian region, Sand (1956) pointed out that mica formed by weathering of feldspar

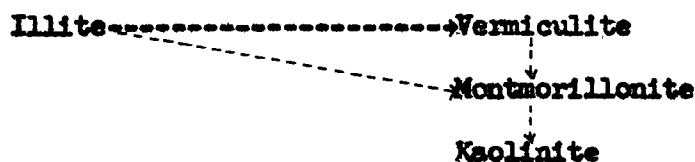
altered to vermicular kaolinite. No evidence was obtained that suggested vermiculite as an intermediate stage in the mica to kaolinite transition.

The formation of secondary chlorite from mica during weathering was cited by Jeffries, Rolfe, and Kunze (1953) in the following sequence:

Mica---mica intermediate---chlorite intermediate---chlorite---kaolin

Secondary chlorite refers to the chlorite formed by interlayering mica with positively charged Al, Fe⁽⁺⁺⁺⁾, and/or Mg hydroxides. The Al-hydroxy interlayer is thought to be the most common type in acid soil clays. Chlorite-vermiculite intergradational material formed from mica was found in a Gray-Brown Podzolic soil of Indiana (Klages and White, 1957). A similar end product of mica weathering in Pennsylvania soils was listed by Johnson and Jeffries (1957). In a study of three mica-containing soils of New York, Rolfe and Jeffries (1953) placed chlorite as the initial stage of the weathering sequence rather than the end point. It seems likely that the stability of apparently similar chlorite-like minerals in soils may differ considerably.

The alteration of dioctahedral mica to montmorillonitic minerals has been observed only rarely. Thorp, Cady, and Gamble (1959) pictured the following sequence in the Miami soil:



Droste and Tharin (1958) observed a mixed layer illite-montmorillonite

mineral formed from well-crystallized illite. Murray and Leininger (1956) attributed the greater abundance of montmorillonite in loess than till to greater amounts of finer mica particles in loess. Studies by Weaver (1958) on an Ordovician shale indicated that montmorillonite is derived from muscovite.

Laboratory investigations of mica alteration

Artificial weathering of muscovite micas in the laboratory has given promising results toward understanding the mechanisms involved in alteration. The high stability of muscovite is illustrated by the work of Starik and Litvina (1958), who leached muscovite with hot concentrated HCl for 15 hours without removing any K. DeMumbrum (1959) noted that digestion of fresh mica proceeded only very slowly when treated with hydrofluoric acid. No doubt the number of laboratory investigations conducted on muscovite is small due to its high resistance to alteration.

Warshaw (1960) treated natural and synthetic illites hydrothermally at temperatures above 250°C. and at pressures above 10,000 lb./in². A sample of Pithian illite was converted partially to vermiculite at temperatures below 400°C. and then to mica plus chlorite from 400 to 550°C. It was concluded that differences in properties between illites and well-crystallized micas are a function of composition as well as of the temperature of formation.

However, less drastic methods have been employed with success in altering micaceous minerals. By means of an artificial leaching tech-

nique, Dekeyser et al. (1958) found that micas exhibit mechanical exfoliation in water at 100°C. and undergo chemical decomposition in water, charged with CO₂ or H₂S, at room temperature. Muscovite was more stable than biotite in all cases.

Gaines and Rutkowski (1957) treated muscovite with 0.1 N HCl and 0.1 N KCl and measured the amounts of Al and Si extracted. They concluded that acids attack the octahedral layer most readily, whereas basic solutions attack primarily the tetrahedral layers.

In studies of the reaction of molten LiNO₃ with a muscovite, White (1956) found that Li replaced a large portion of the inter-layer K. He also found that a portion of the Li was not exchangeable. The nonexchangeable Li⁺ ions apparently migrated into the vacant octahedral positions. When Ba-saturated and glycerol-solvated, the treated material gave an (001) spacing of 17.8 Å, the basal spacing for glycerol-solvated montmorillonite.

The precipitation of K from micas with sodium tetraphenylboron (NaPh₄B) has attracted attention in recent years. However, its efficiency as a replacing agent is questionable. After long periods of repeated extractions, DeMumbrum (1959) was not able to reduce the K level of muscovite below 6.7% K₂O. Scott, Hunziker, and Hanway (1960) removed all the K in vermiculite and 47% of the K in illite, but only 12% of the K in muscovite. Later work by Scott and Reed (1960) suggested more complete removal of K from micaceous minerals with boiling NaPh₄B solutions, but no data were presented as to the amount of K removed from muscovite micas.

The muscovite structure may also be broken down by grinding at room temperature. The effect of grinding has been studied previously in detail by Mackenzie and Milne (1953). They concluded that the muscovite structure is nearly destroyed in eight to nine hours of grinding in an agate mortar, and that recrystallization then takes place with the growth of hydrous mica (illite). Their conclusions were questioned by Yoder and Eugster (1955), who attributed the results to incomplete grinding, and not to resynthesis upon grinding.

Grim and Bradley (1948) heated illite at 600°C. and 800°C. for one hour each, and allowed the material to remain in the atmosphere for varying periods of time. The DTA curves of the materials left standing indicated to them that the dehydrated illite had absorbed water and OH⁻ ions. Their interpretation tends to support the conclusion of Mackenzie and Milne (1953) that illite was formed from grinding of muscovite, since their grinding product had similar water sorption characteristics. However, no DTA curves were made of the materials immediately after heating and it is likely that all the water had not been driven out by heating for only one hour. Roy (1949) indicated that less than 20% of the OH⁻ content of muscovite is removed by heating at 600°C. for one hour.

Mechanisms of mica weathering

Explanation of the chemistry of weathering muscovite mica beyond secondary mica have not always been satisfactory. Nevertheless, several constructive efforts have been made to elucidate the weathering process, and a brief summary of the conclusions reached from these

efforts seems worthwhile.

Fieldes and Swindale (1954) proposed several hypotheses regarding micaceous weathering:

- 1) Hydrogen ions are required to remove interlayer K from mica to form illite and expanding micas. High pH favors accumulation of vermiculite.
- 2) When both H^+ and Ca^{++} ions are in appreciable concentration, the H^+ ion is effective in making interlayer surfaces accessible to Ca^{++} which, in turn, assists the development of a fully expanded montmorillonite. Under these conditions the weathering sequence is:

$$\begin{array}{ccccccc} H^+ & & H^+ & & & & Ca^{++} \\ \text{Mica} & \text{-----} & \text{Illite} & \text{-----} & \text{Vermiculite} & \text{-----} & \text{Montmorillonite} \end{array}$$
- 3) Under acid leaching, the high concentration of H^+ ion accelerates weathering of mica to clay-vermiculite but with low concentration of alkaline earth cations, montmorillonite is slow to form.
- 4) Continued weathering under acid conditions is capable of degrading either vermiculite or montmorillonite to kaolin.

Jackson et al. (1952) interpreted their observations as an indication that micas weather along a given K plane (see figure 1) faster than the initiation of weathering of another such plane. They proposed four chemical weathering reactions which effect weathering of micas: 1) Depotassication; 2) Hydroxylation; 3) Dealumination; 4) Desilication. Depotassication simply means the release of K^+ ion from between mica crystal layers by H_2O and other cations. Hydro-

xylation is the association of H^+ ion with the apical $O^=$, which is shared mutually by tetrahedral and octahedral layers, thus rendering the H^+ ion "nonexchangeable." Dealumination is, in effect, the substitution of Si for Al in the tetrahedral layer. This reaction would generally be in acid solution and the Al would appear as an exchangeable cation or some hydrolyzed form. Desilication refers to the chemical weathering process of Si removal, with particular reference to its removal from three-layer silicates to form kaolinite and gibbsite.

Most of the work to date has pictured the mica alteration mechanism as ion exchange primarily. Gardiner and Shorey (1917) found that muscovite liberated K upon soaking in $(NH_4)_2 SO_4$ solutions at room temperature. Kelley and Jenny (1936) found that the amount of ion exchange depended on the fineness to which the sample had been ground, and suggested that the K^+ ions on cleavage planes were exchanged for cations in solution. Jackson and Truog (1939) were able to liberate K from a muscovite sample by soaking it in NH_4OAc solution after wet grinding for three days. Schachtschabel (1940), using ground muscovite, found that equilibrium was reached slowly, and suggested that ions from solution could slowly penetrate the K planes within the mica particles and induce ion exchange inside as well as on the external surfaces of the particles. Garrels and Howard (1959) viewed the loss of K as occurring through straightforward $H^+ - K^+$ exchange. An important substitution may be that of hydronium, H_3O^+ , for K^+ (Brown and Norrish, 1951), which has

been mentioned earlier.

Whether exchange is limited to external surfaces or can take place with "internal" K^+ ions as suggested by Schachtschabel has not yet been clearly decided. Barshad (1950) measured the c-axis spacing in muscovite particles of 5-50 μ and less than 0.5 μ sizes, and found no change whether the sample was dry, saturated with water, or saturated with glycerol. But paragonite, which contains Na^+ instead of K^+ as the interlayer cation, showed a c-axis expansion in water. Perkins (1949) also stated that no tendency to swell was observed with his ground mica samples. Gaines (1957) noted little or no penetration of cleavage planes by neutral aqueous salt solutions after treatment for several days. Ion exchange of surface ions occurred rapidly, usually in a few minutes.

Mortland (1958) suggested that the rate of K release from micas is a diffusion controlled process. Walker (1959) indicated that the movement of divalent ions in vermiculite is diffusion controlled. If the rate of appearance of available K is governed by diffusion, then the mechanism of K removal from mica is more dependent on factors affecting diffusion processes than those affecting the law of mass action. Such factors would include type of diffusion, geometry of the diffusion zones, diffusion coefficients, and relative concentration of ions in the weathering solution.

It is believed by some that a mechanism other than ion exchange is needed to account for the differences between dioctahedral and trioctahedral micas in susceptibility to alteration. Bassett

(1960) suggested hydroxyl orientation as a factor influencing mica alteration. Using infrared absorption techniques on both dioctahedral and trioctahedral mica specimens, he concluded that in the phlogopite structure (trioctahedral) the OH^- ion is oriented perpendicular to the cleavage plane, thus placing the H^+ end, or the proton, in juxtaposition with the K^+ ion. In the muscovite structure (dioctahedral), the OH^- ion is inclined to the plane of cleavage, thus placing the proton farther from the K^+ ion and the negative or O^- end of the dipole closer to the K^+ ion. This difference in the environment of the K^+ ions is postulated to account for the fact that most trioctahedral micas alter by ion exchange, whereas the dioctahedral micas do not, at least in the initial stages of weathering.

MATERIALS AND GENERAL METHODS

Materials--In a study of this kind, monomineralic specimens are preferred since many difficulties arise when trying to evaluate a single mineral component in a multicomponent mixture. Therefore, an attempt was made to obtain fresh dioctahedral mica specimens which had not undergone weathering to any appreciable extent so that the weathering products formed could be attributed to the mica component only. However, it was soon observed that the influence of atmospheric weathering reaches great depths and it is practically impossible to obtain samples of unweathered mica using conventional sampling means. Nevertheless, reasonably fresh mica samples were obtained from several exposures in the Virginia Piedmont. Two of the samples collected were phyllites. One sample was taken from a railway exposure near Lynchburg in Campbell County, the other from a roadbank near Orange in Orange County. Two other samples studied were soil micas taken from soil parent material in Orange County and Prince William County. Soils above the mica-containing rock also were sampled in order to obtain a continuous weathering sequence from the fresh material to the soil surface. Further description of the materials sampled will be given under 'Results' in connection with the experimental data associated with each sample.

General Methods

Initial treatment and dispersion of sample--The massive mica samples were first lightly ground in an agate mortar, then were further broken

down with alternate manual grinding and mixing in a Waring blender. Grinding was kept to a minimum in an effort to avoid breakdown or alteration of the original mica structure. Soil samples were pulverized to pass a 2 mm. sieve prior to dispersion and fractionation. Dispersion was accomplished using NH_4OH or Na_2CO_3 to adjust the dispersant to pH 10. Ammonium hydroxide was used in those cases where Na analyses were critical and it was desired to keep the samples free of extraneous Na.

Particle size fractionation--The samples were fractionated into the following particle size ranges: $50 - 20\mu$, $20 - 5\mu$, $5 - 2\mu$, $< 2\mu$, and in certain cases, $< 0.2\mu$. The $> 2\mu$ size ranges were separated by sedimentation methods, following essentially the procedure outlined by Jackson (1956). The $< 2\mu$ fraction was separated by centrifugation using an International No. 2 centrifuge. Sedimentation and centrifugation times were determined from the nomographs of Tanner and Jackson (1947).

Removal of free Fe oxides--Free Fe oxides were removed from samples containing appreciable amounts by the method of Aguilera and Jackson (1953).

Cation saturation of sample--Following free Fe removal, each sample was Ca-saturated by washing it 5 times with N CaCl_2 solution. Washing was accomplished by mixing the CaCl_2 solution thoroughly with the sample and centrifuging the resultant suspension. Excess salts were then removed with one wash of H_2O followed by 100% methanol washes until the supernatant liquid was Cl^- free as indicated by no precipitation when a few drops of a 0.5 N AgNO_3 solution were added. The Ca-saturated

samples were dried in a vacuum desiccator and stored in closed vials for further study.

Cation-exchange capacity determination--The method proposed by Rich (1961) was employed, in which 20 mg. of Ca-saturated sample was transferred to a 15 ml. centrifuge tube, 5 ml. N MgOAc added, and the tube stoppered and shaken on a mechanical shaker for 18 hours. The suspension was centrifuged and the supernatant extract was analyzed immediately for Ca with the flame photometer. Results are reported on an oven-dry (110°C.) sample basis.

Preparation of sample for mineralogical analysis--When feasible, the sample used in the determination of CEC was also used for x-ray diffraction analysis. The Mg-saturated sample was transferred to a small centrifuge tube, 1 ml. of 10% glycerol solution (in water) was mixed well with the clay, and the suspension centrifuged. Excess glycerol was allowed to drain thoroughly, then the sample was dispersed well with 1 ml. of H_2O and poured on a glass slide to dry. Slides of K-saturated samples were prepared by suspending approximately 25 mg. of sample in H_2O and allowing the suspension to dry on glass slides. In some cases, a 'spatulation' technique was employed usefully. In this technique, the sample is transferred to a slide and spread into a thin layer with a spatula. This method tended to give better orientation of the (001) spacings.

X-ray diffraction studies--X-ray diffraction patterns were obtained with a General Electric XRD-3 instrument using Ni-filtered Cu radiation. The radiation was generated at 35 KV and 23 ma. The slits

used were 0.4° , MR, and 0.2° for the beam, Soller, and detector slits, respectively, except for a few instances where the HR Soller slit was required. Intensities were recorded logarithmically.

The (060) reflections were measured using an orientation technique devised by Rich (1957). The sample was preheated at 550°C. to destroy kaolinite, which has a reflection at 1.49 Å., and may interfere with the (060) for muscovite at 1.50 Å.

Determination of total K and Na--Total K and Na analyses were made according to the semimicrochemical method of Corey and Jackson (1953), in which K and Na are determined by flame photometry following HF decomposition. Percentages of K and Na are reported on the basis of a sample dried at 110°C. for at least 4 hours.

RESULTS

One of the primary interests of this investigation was the relationship between weathering of mica and changes in the CEC. The interpretation and discussion of results will be emphasized from this standpoint.

During the course of the investigation, however, other interesting observations were made that deserve attention. One significant finding was the occurrence of paragonite in certain soils and parent materials. Results pertinent to this finding will be reported first. Data on the natural weathering of paragonite-muscovite micas will be followed by results of artificial weathering studies, with emphasis on loss of K and Na, increase in CEC, and expansion properties.

It was pointed out in the literature review that muscovite can exhibit several polymorphic forms. Thus it was desirable to establish the particular mica polymorph encountered in this investigation. Randomly oriented powder samples were used to obtain the (hkl) spacings of the experimental micas. A comparison of the results with calculated spacings for 2M muscovite and a natural 2M muscovite is given in table 1. The d spacings which distinguish the 2M polymorph from the 1M and 3T polymorphs are indicated by an asterisk(*). All the micas possessed the 2M structure primarily, which was expected since Yoder and Eugster (1955) and others have demonstrated that the 2M polymorph is the most common one, especially in sedimentary rocks. Candler phyllite and Nason soil--Samples of phyllite were collected from an exposure on the Norfolk and Western Railway located approxi-

TABLE 1. Comparison of x-ray powder data of experimental micas with published x-ray powder data for 2M muscovite.

Calculated d (Jackson & West, 1933)	Natural 2M (Smith & Yoder, 1956)	Candler phyllite	Loudoun phyllite	Mica OR	Mica PW
9.96 A.	10.04 A.	**14.4 10.1 A.	10.1 A.	10.1 A.	10.1 A.
4.98	5.02	** 7.19 5.00	5.00	5.00	5.00
*4.51	4.48	***4.84 --	***4.90 4.50	4.52	--
4.48	4.46	4.48	--	--	--
*4.40	4.39	--	--	--	4.43
*4.295	4.30	4.30	4.30	4.30	4.30
4.117	4.11	4.08	4.11	--	4.08
*3.965	3.97	3.94	3.95	--	--
3.865	3.89	--	--	--	--
*3.735	3.74	3.73 **3.58	3.73	3.76	--
*3.480	3.50	--	3.50	3.50	--
3.340	3.35	3.32 ***3.22	3.34 ***3.25	3.34	3.33
*3.200	3.21	--	3.20	3.21	3.20
2.987	3.00	2.97	2.95	--	2.99

Continued on next page

TABLE 1 (Continued)

Calculated d (Jackson & West, 1933)	Natural 2M (Smith & Yoder, 1956)	Candler phyllite	Loudoun phyllite	Mica OR	Mica PW
2.862	2.87	2.87	2.89	2.89	2.86
*2.785	2.80	2.81	2.77	2.82	2.79
2.592	2.59	2.60	2.60	2.60	2.60
2.580	2.580	--	--	--	2.58
2.562	2.56	2.56	2.55	--	--
*2.490	2.51	2.492	2.490	2.510	2.499
*2.458	2.458	--	2.453	--	2.459
2.441	2.446	--	--	--	--
*2.387	2.396	--	***2.434 2.396	2.408	2.396
2.380	2.380	--	--	--	--
2.260	2.247	2.279	2.261	2.247	--
2.142	2.149	--	2.149	2.149	--
*2.136	2.132	2.135	2.135	2.135	2.135
2.002	2.010	1.995	1.996	2.012	2.000
1.660	1.670	***1.935 1.671	***1.951 1.671	1.674	1.668
1.500	1.499	1.495	1.495	1.508	1.517

*Characteristic 2M reflections

**Chlorite basal spacings

***Paragonite basal spacings

mately one mile east of Lynchburg at the U.S. Highway 460 overpass. An excellent vertical exposure more than 50 feet deep occurs at this location. Samples were taken at 10, 20, 30, and 50 foot depths along a given plane of bedding, which dips from vertical to approximately 65° NW. The depths of sampling were chosen on the basis of color differences in the phyllite, which changes from blue-gray at 50 feet to gray-brown near the surface. The phyllite was also highly fissile and lustrous.

The material sampled is commonly called Wissahickon schist, a name introduced by Jonas (1927), who correlated rocks of this area with rocks of the Wissahickon formation in Pennsylvania. The geologic formation at the site sampled has been more specifically identified by Brown (1958) as the Candler formation, the oldest and widespread formation of the Evington group. According to Brown, the Candler formation is continuously exposed from Patrick County at the North Carolina line northeastward into northern Orange County where it passes beneath Triassic beds. This sample will be referred to as Candler phyllite throughout this thesis.

The soil above the phyllite was sampled by genetic horizon to a depth of 34 inches. It was classified as a member of the Mason series grading toward the Manteo series.

Mineralogy of Candler phyllite--The mineralogical character of Candler phyllite, as indicated by x-ray diffraction, is shown in figure 2. The x-ray pattern was obtained from a raw sample of Candler phyllite ground to pass a 100-mesh sieve. Particularly significant was the

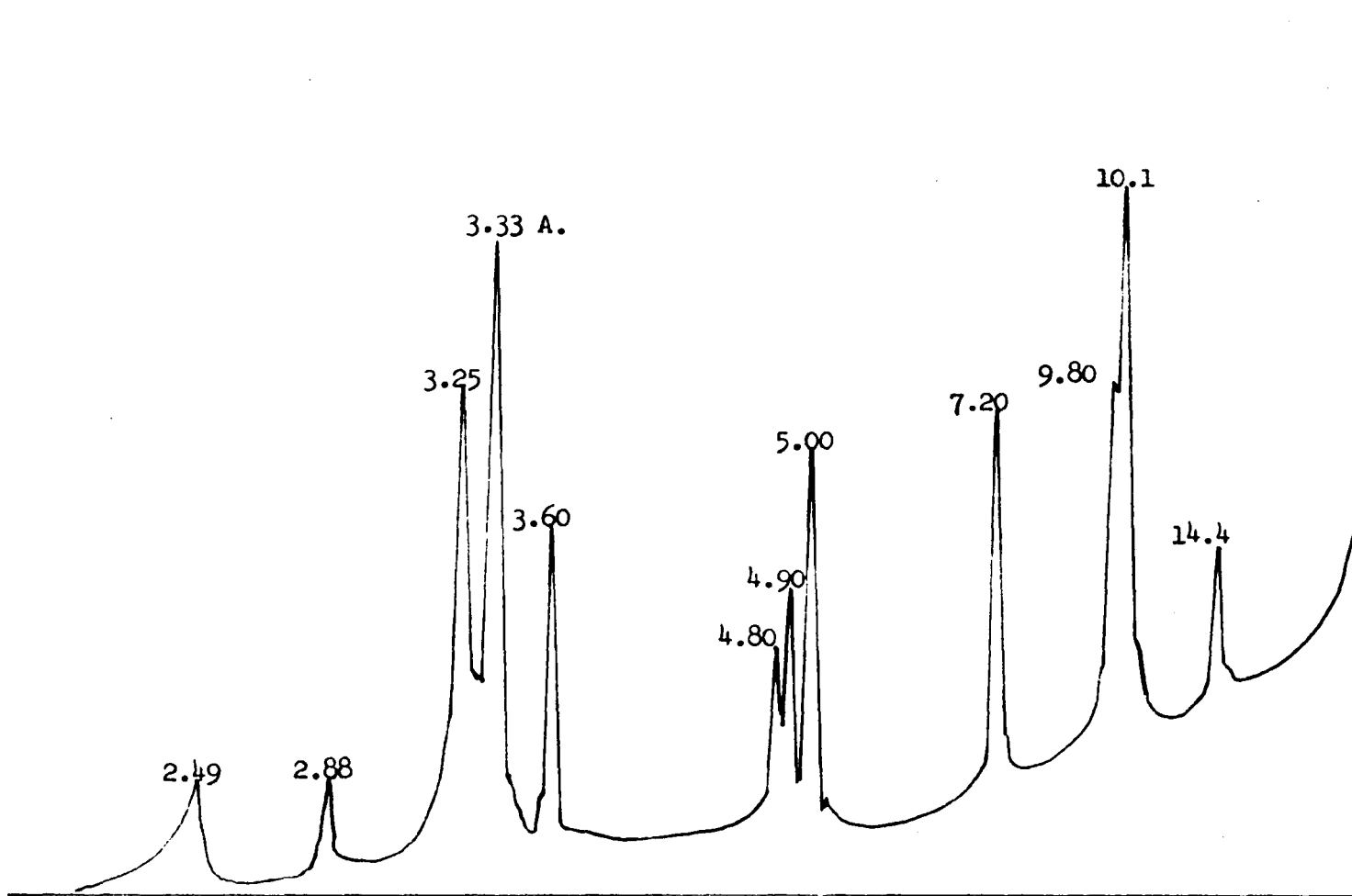


Fig. 2. Smoothed x-ray diffraction trace of Candler phyllite(<100 mesh) prior to any laboratory treatment.

occurrence of paragonite (9.60 Å.) in association with muscovite (10.0 Å.). Paragonite is believed to be a rather rare mineral species, judging from the small number of published findings of it. Chlorite (14.4 Å.) and kaolinite (7.2 Å.) were other minerals present in significant amounts. Chlorite is distinguishable by the sharp peaks of the 14.4 Å. spacing and the higher order spacings which are sub-multiples of 14.4 Å. Kaolinite was distinguished from chlorite by expanding the kaolinite to 14.0 Å., using the KQAc method of Andrew, Jackson, and Wada (1960). The 14.0 Å. peak of expanded kaolinite and the 14.4 Å. peak of chlorite produced a doublet, which permitted the recognition of the two minerals.

Weathering of Candler phyllite and overlying Nason soil--The mineral assemblage of the least weathered material was similar to that of the 100-mesh material. The only significant change with depth in the mineralogical content of the phyllite was the loss of chlorite and formation of vermiculite, as shown in figure 3. The weathering of mica is indicated by the decreased peak intensities. A first order spacing of 9.70 - 9.80 Å. was obtained for paragonite, which normally has a 9.60 Å. spacing. Random interstratification of muscovite and paragonite probably accounts for the higher spacing obtained in this sample, because the higher order spacings are regular sub-multiples of 10.0 Å. and 9.60 Å., respectively. The higher order peaks also are distinctly separate and thus afford an excellent means of identification. Attempts to separate the micas by means of heavy liquid separation were unsuccessful. It was concluded that the paragonite and muscovite occurred as an intimate mixture of very small crystals

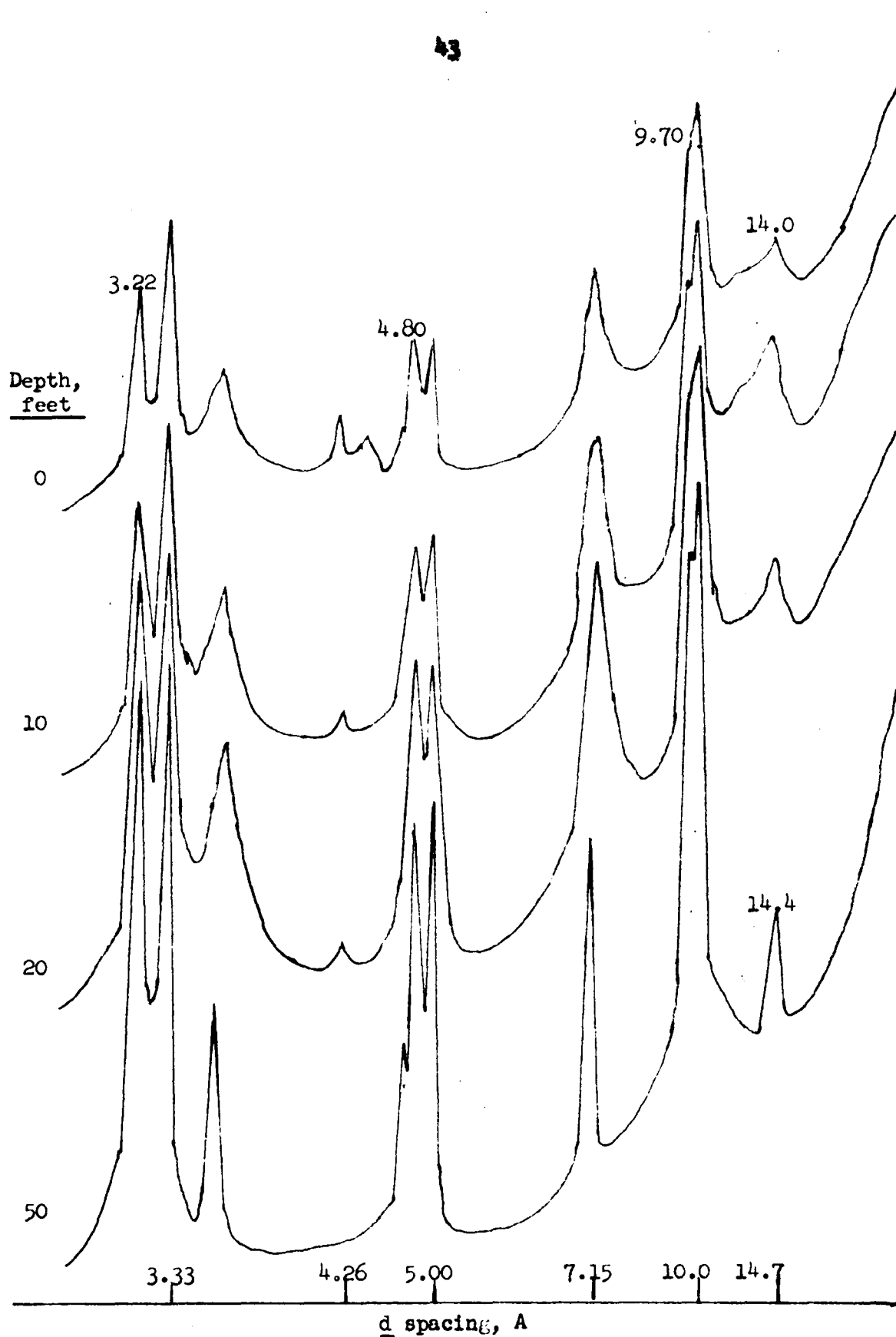


Fig. 3. Weathering of Candler phyllite ($< 2/\mu$) as a function of depth, as indicated by smoothed x-ray diffraction traces of Mg-saturated and glycerol-solvated samples.

of the two minerals.

The weathering of Na-mica compared to K-mica is indicated by the Na and K analyses, and the Na/K molar ratio, given in table 2. A Na/K ratio of unity indicates that Na and K are removed in equal amounts on a molar (or equivalent) basis. A Na/K ratio greater than one would indicate greater loss of K, whereas a Na/K ratio less than one would indicate greater loss of Na. The relatively constant ratio near one suggests that Na-mica and K-mica weather similarly. Furthermore, it lends support to the belief that the micas are interstratified and removal of one layer may leave the adjacent layers more susceptible to weathering.

As weathering intensity increased, the chlorite disappeared while vermiculite and quartz remained quite pronounced. The origin of vermiculite is attributed to the mica component rather than to chlorite, as might be suspected. The fact that vermiculite continued to increase as the surface was approached, whereas chlorite had disappeared within the 30-50 foot depth, makes it seem unlikely that chlorite was the source material for the vermiculite. The distinction of chlorite from vermiculite is indicated by the sharp-peaked regular orders for chlorite in the Mg-saturated specimen and confirmed by the persistence of the 14.4 Å. spacing upon K saturation and heating at 550°C. (figure 4). The latter test also distinguishes the second-order reflection of chlorite from kaolinite, which is destroyed upon heating at 550°C. The larger 4.26 Å. peak of the surface sample most likely is due to a greater proportion of quartz relative to other

TABLE 2. Contents of Na and K in Candler phyllite
($< 2 \phi$) as a function of depth.

Depth, feet	Na		K		Na + K	$\frac{\text{Na}}{\text{K}}$ (molar)
	%	me./100g.	%	me./100g.	me/100g.	
0	1.55	67.4	2.75	70.4	138	0.95
10	1.65	71.7	2.85	73.0	145	0.98
20	1.70	73.8	3.05	78.1	152	0.95
30	2.30	100.0	3.80	97.3	197	1.03
50	2.55	111.0	4.05	104.0	215	1.07

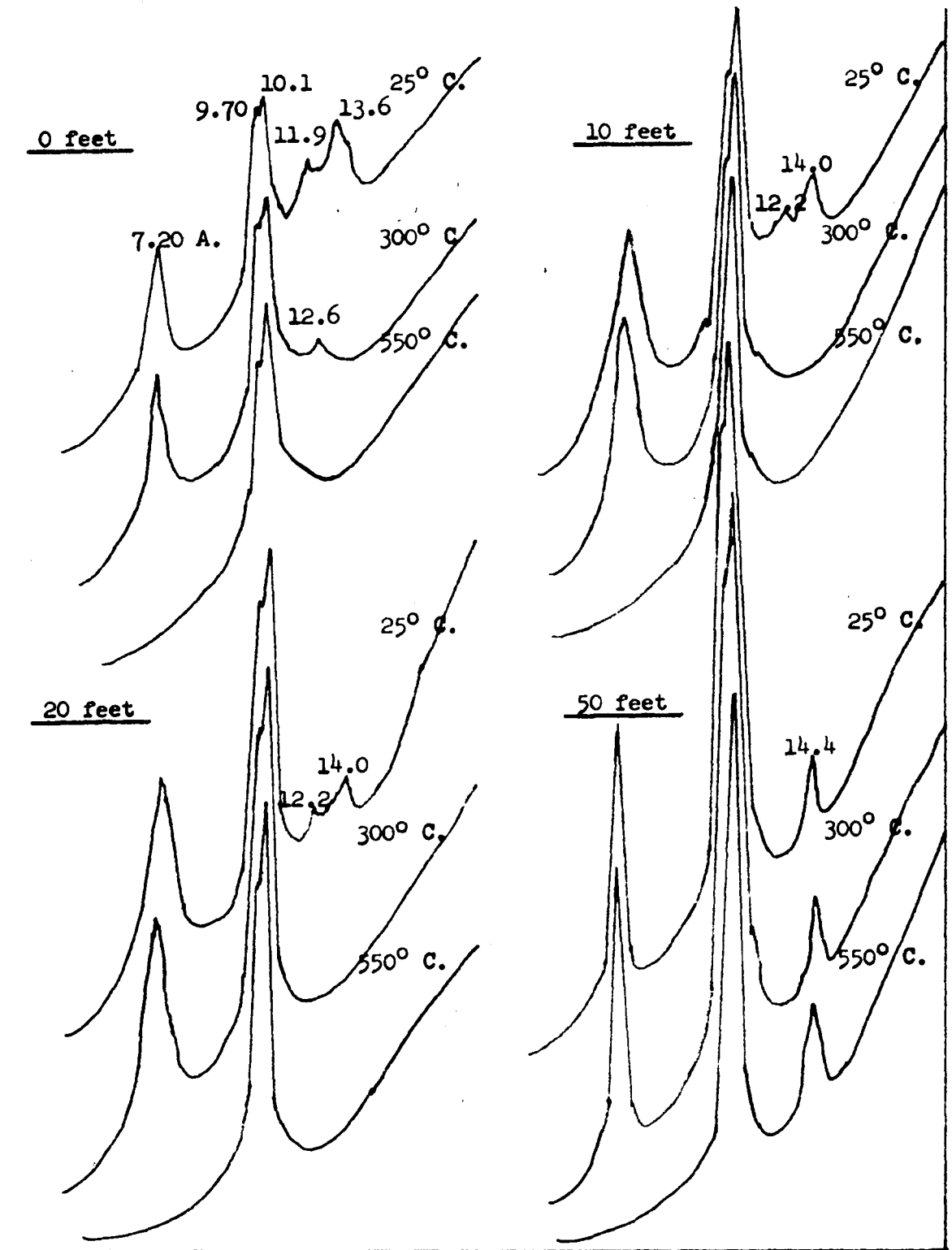


Fig. 4. Effect of K-saturation and heating on Candler phyllite (< 2 μ), as shown by smoothed x-ray diffraction traces.

minerals, which have weathered more.

As the surface was approached, the stability of the 10-14 Å. material increased, as indicated by its resistance to collapse upon K saturation and heat treatment (figure 4). Such effects have been attributed to interlayers composed principally of hydroxy-Al groups (Rich and Obenshain, 1955).

The occurrence of kaolinite at the 50-foot depth suggests that kaolinite is one of the first alteration products of mica. Apparently the transition takes place relatively early in weathering because it was impossible to obtain mica samples free from kaolinite even at the 50-foot depth. This idea is supported by the work of Sand (1956), who observed kaolinite in fresh mica deposits and concluded that kaolin minerals are formed directly from muscovite.

Weathering sequences according to particle size and depth in the Nason soil are shown in figures 5, 6, 7, and 8. Quartz was more abundant in the coarse fraction but mica was more abundant in the finer fractions. The clay ($< 2 \mu$) fraction contained appreciable amounts of vermiculite which contracted with difficulty, as shown in figure 9. The material was affected little by K saturation but collapsed on heat treatment at 550°C. Glycerol did not expand the mineral beyond 14.4 Å. The peak at approximately 25 Å. was probably due to regular interstratification of alternate mica and vermiculite layers. Potassium saturation and heating collapsed this component also.

The changes in mica as affected by depth were small. The only noticeable differences were higher proportions of quartz and kaolinite

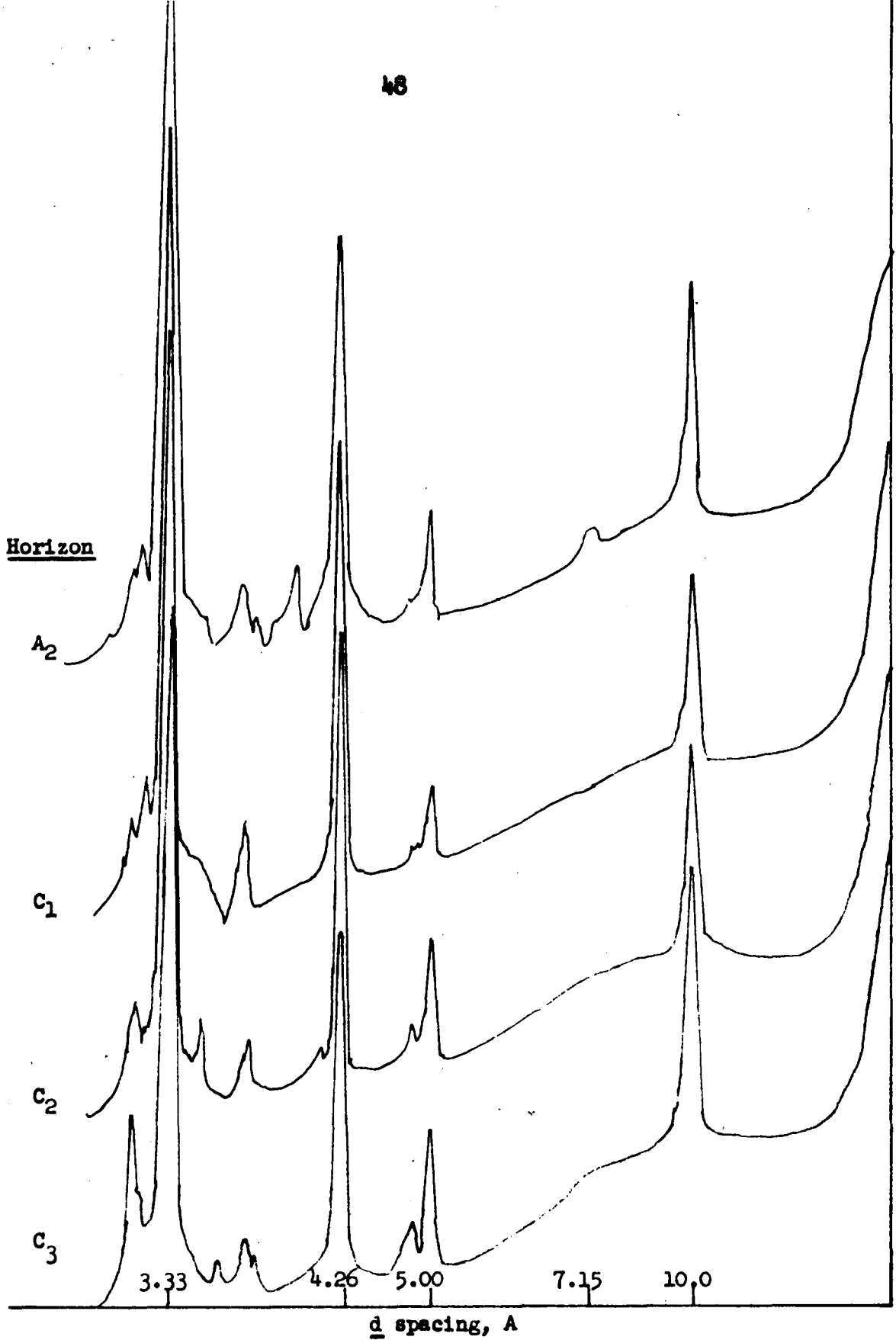


Fig. 5. Characteristics of 50 - 20 μ fraction of Nason soil at various depths, as shown by smoothed x-ray diffraction traces.

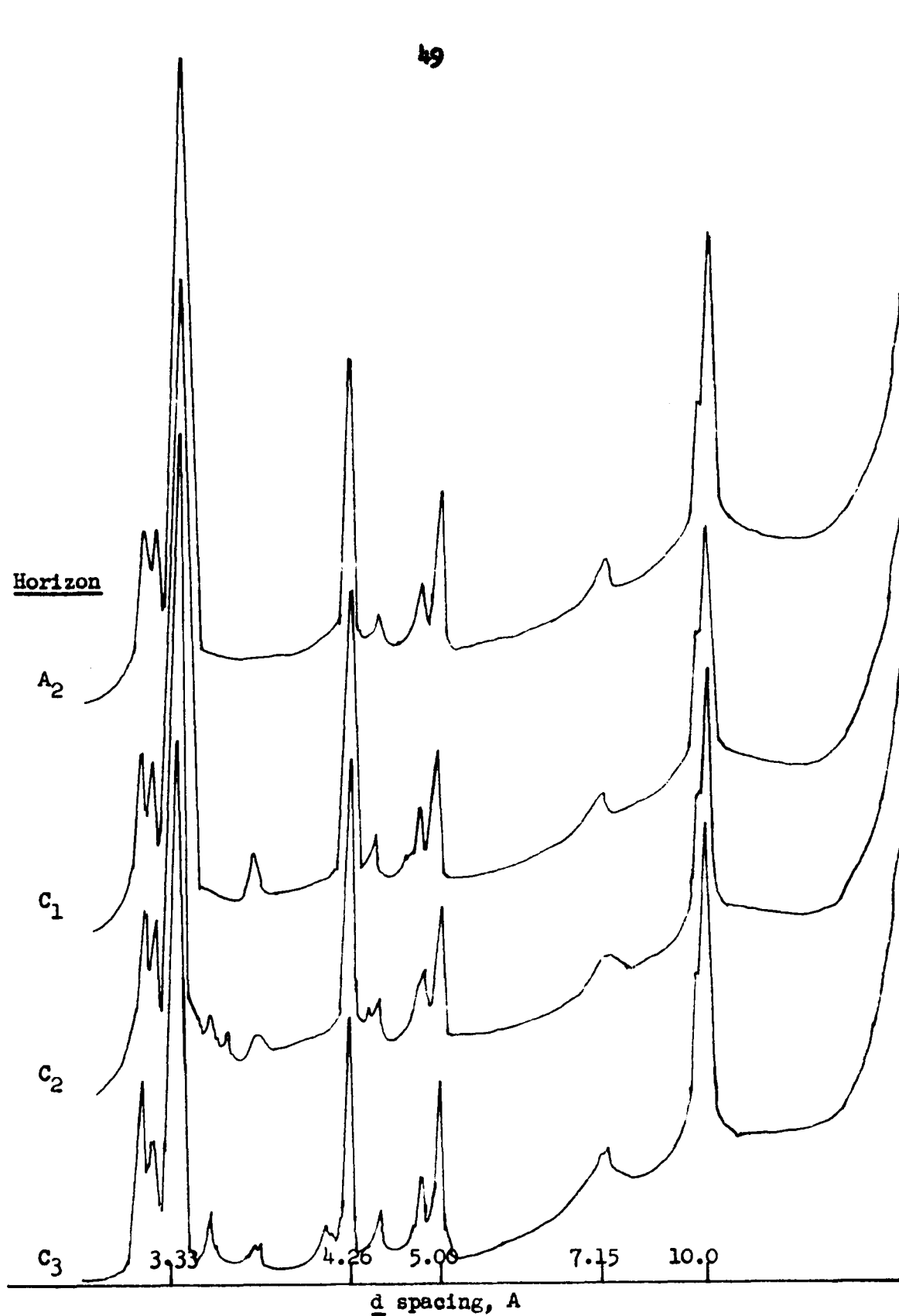


Fig.6. Characteristics of 20 - 5 μ fraction of Nason soil at various depths, as indicated by smoothed x-ray diffraction traces.

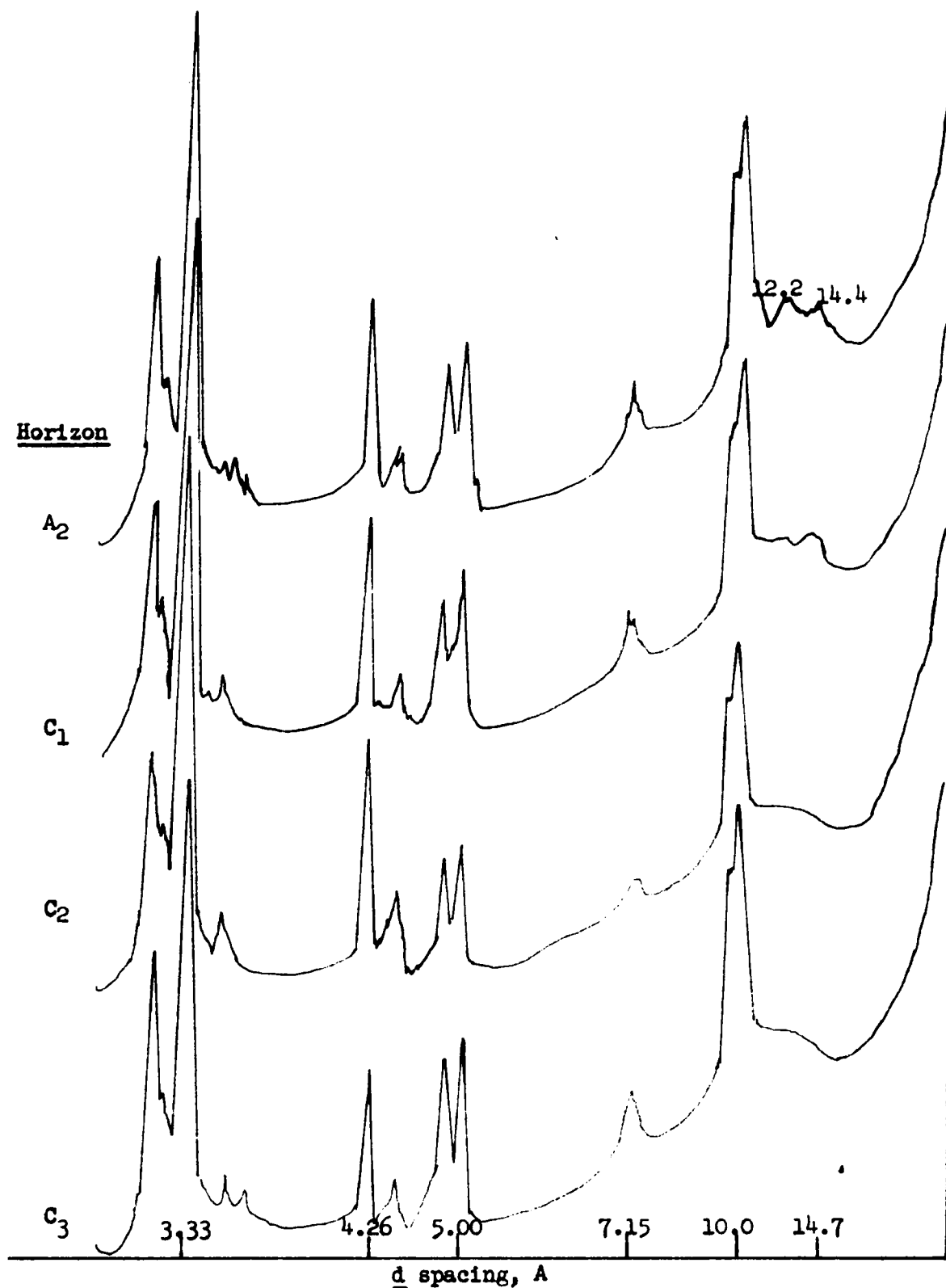


Fig. 7. Variation in weathering with depth of 5 - 2 μ fraction of Nason soil, as shown by smoothed x-ray diffraction traces of Mg-saturated and glycerol-solvated samples.

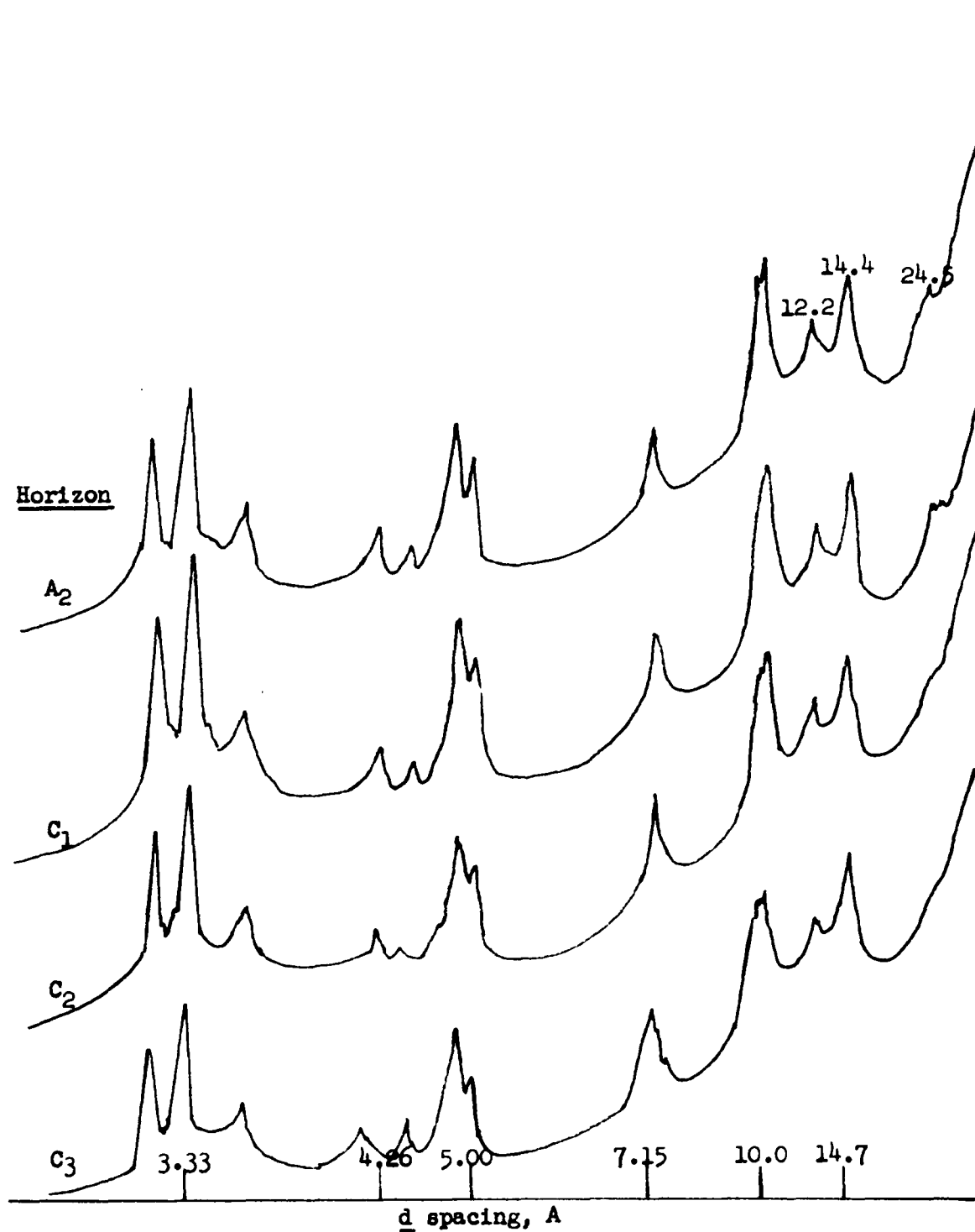


Fig. 8. Mica weathering as a function of depth in the <2 μ fraction of Nason soil, as indicated by smoothed x-ray diffraction traces of Mg-saturated and glycerol-solvated samples.

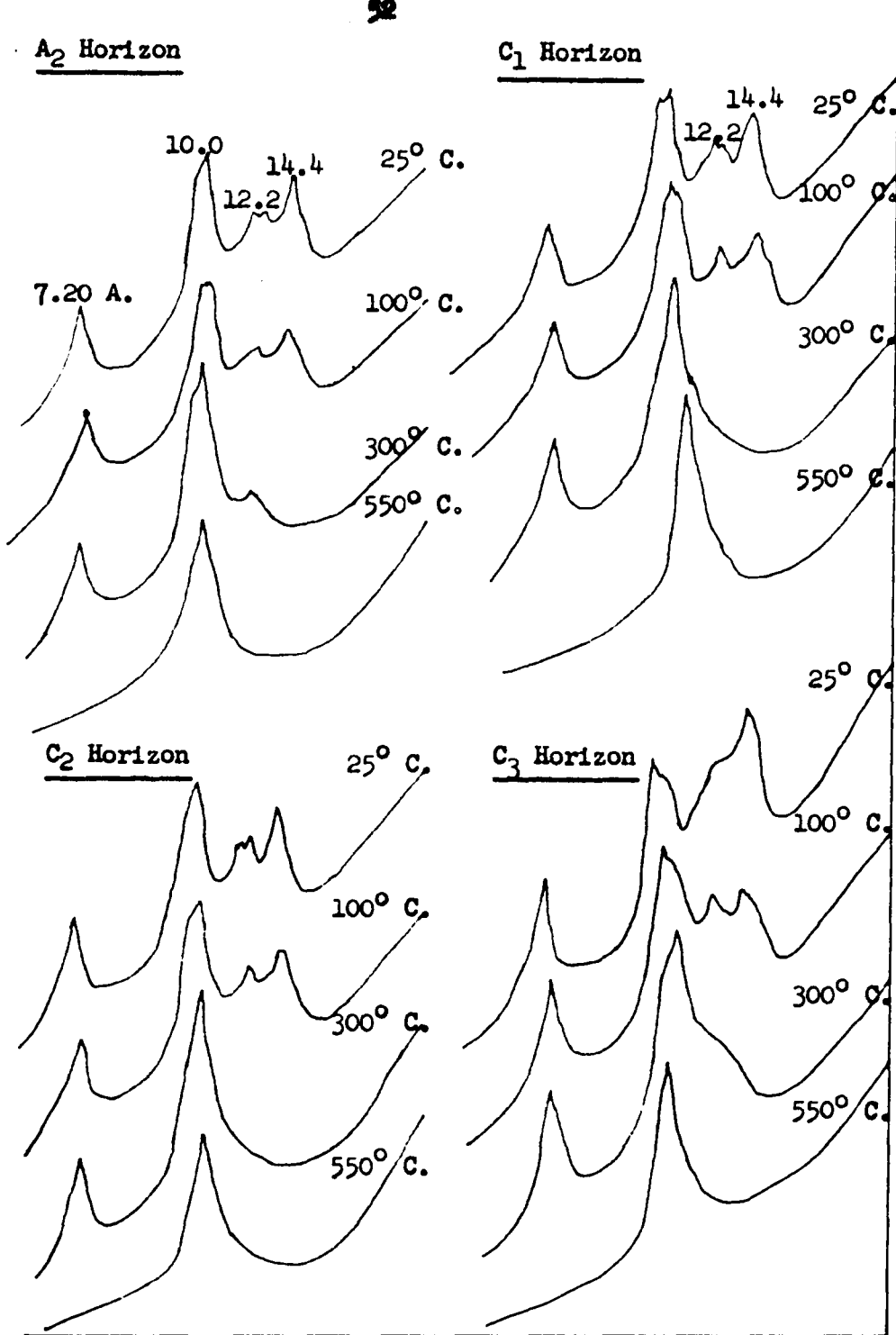


Fig. 9. Effect of K-saturation and heating on $<2\mu$ fraction of Nason soil, as shown by smoothed x-ray diffraction traces.

nearer the surface, and increased amounts of interlayered material in vermiculite in the surface horizons.

The influence of weathering on the Na-K relationship in the mica of $< 2\mu$ particle size is shown in table 3. Although there was variation in the amounts of Na and K throughout the profile, the Na/K molar ratio remained relatively constant, near unity. This constancy did not hold for the coarser fractions, which contained considerably more K than Na. This suggests that Na-mica is confined to a smaller particle size than K-mica, which is in agreement with the observations of Rosenfeld (1956). This finding is also borne out by the x-ray diffraction results (figures 5 through 8), in which the paragonite spacings increased in intensity relative to the muscovite spacings with decreasing particle size. It should be pointed out, however, that direct correlation of basal spacing with composition is not possible due to the ternary nature of the paragonite solid solution (Rosenfeld *et al.*, 1959).

Loudoun phyllite and Manteo soil-- A phyllite was sampled from a road-bank located southeast of Orange on Virginia Highway 612, 3.3 miles from the intersection of Highways 638, 647, and 688, and approximately 250 yards east of the junction of Highways 631 and 632. The material closely resembled the fresh material sampled near Lynchburg in color, luster, and fissility. The phyllite has been designated as the Loudoun formation on the Geologic Map of Virginia (Stose, 1928). The use of the name Loudoun was criticized by Brown (1958), who suggested that it should be abandoned. However, to distinguish this sample from the

TABLE 3. Contents of Na and K, as a function of depth, of Mason soil ($< 2 \mu$), overlying Candler phyllite.

Horizon	Depth, inches	%	Na me./100g.	%	K me./100g.	Na + K me./100g.	$\frac{Na}{K}$ (molar)
A ₁	0-6	1.40	60.7	2.45	62.7	123	0.97
B ₁	6-11	1.47	63.8	2.57	65.8	130	0.97
B ₂	11-15	1.35	58.6	2.35	60.2	120	0.97
B ₃	15-18	1.32	57.3	2.25	57.6	115	0.99
C ₁	18-24	1.30	56.4	2.22	56.9	113	0.99
C ₂	24-30	1.34	58.2	2.17	55.6	114	1.04
C ₃	30-34	1.45	62.9	2.35	60.2	123	1.04

Candler phyllite near Lynchburg, it will be referred to as Loudoun phyllite throughout this thesis.

The soil above the phyllite was sampled by genetic horizon to a depth of 36 inches and designated as Manteo.

Weathering of Loudoun phyllite and overlying Manteo soil--Weathering sequences of Loudoun phyllite and Manteo soil, as a function of particle size and depth, are shown in figures 10, 11, 12, and 13. The mineral assemblage of the phyllite ($> 2\mu$) consisted of muscovite, paragonite, kaolinite and quartz. With decreasing particle size, kaolinite increased and quartz decreased. In the $< 2\mu$ fraction, a regular interstratification was noted, as revealed by the high spacing reflection at 32.7 A. and the higher order reflections at 16.8 A. and 8.2 A., which are approximate submultiples of the 32.7 A. reflection. Most of the higher order spacings were weak, or even indistinguishable, which is to be expected according to Brown and MacEwan (1951). The nature of the interstratified material is questionable. The spacings satisfy those for interstratified montmorillonite (~ 18 A.) and vermiculite (~ 14.4 A.), even though there is no other evidence of montmorillonite in the Loudoun phyllite or its weathering products. It could be that a montmorillonite-like material is formed in the fine particle-sized material, but either decomposes or reverts to vermiculite upon weathering.

The mineralogical composition of the Manteo soil was essentially the same as that of the Mason soil. Also, the Na and K contents of the $< 2\mu$ fraction of Manteo soil (table 4) were in the same range of

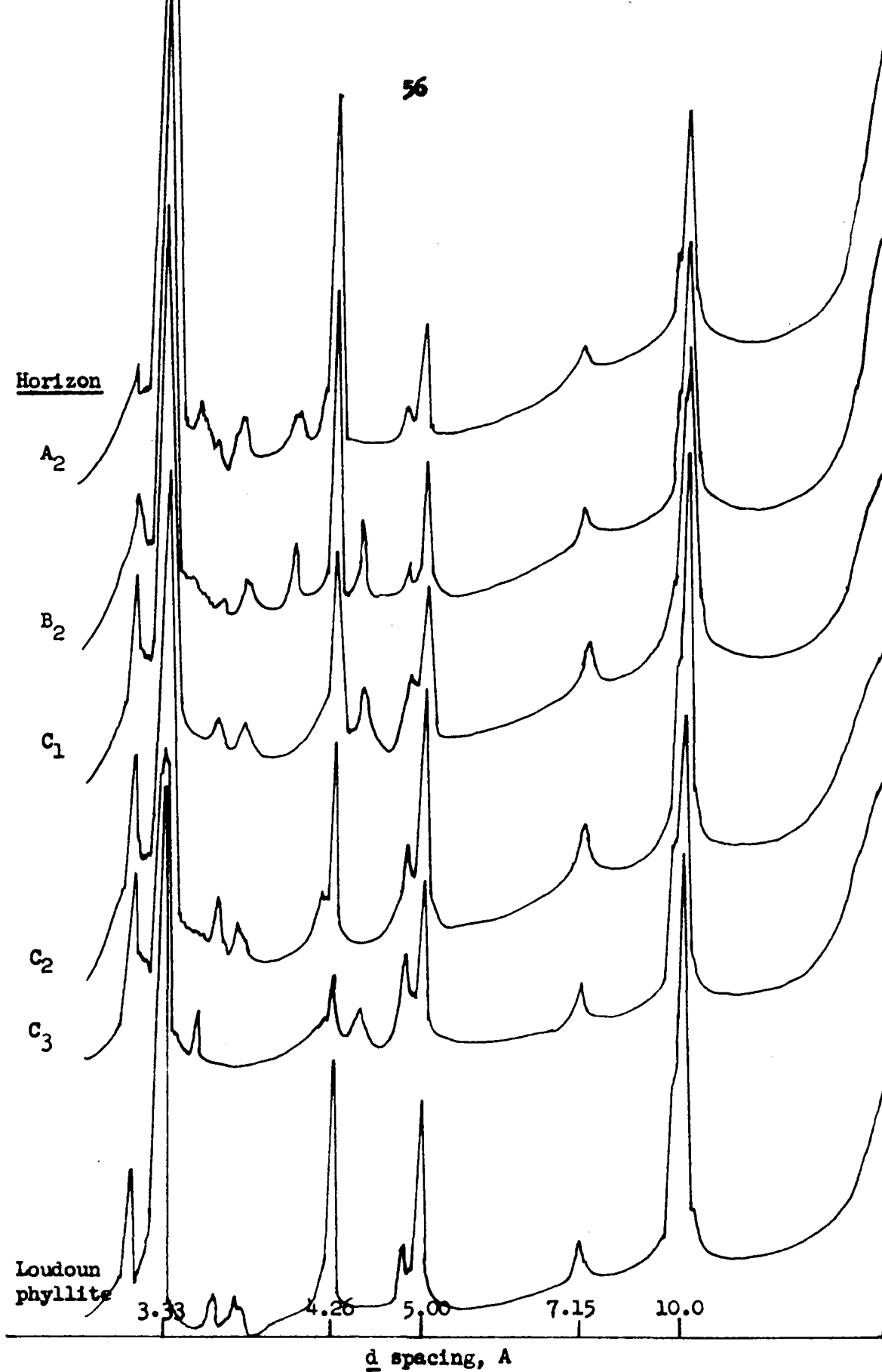


Fig. 10. Weathering sequence as a function of depth in the 50 - 20/ μ fraction of Loudoun phyllite and Manteo soil, as denoted by smoothed x-ray diffraction traces.

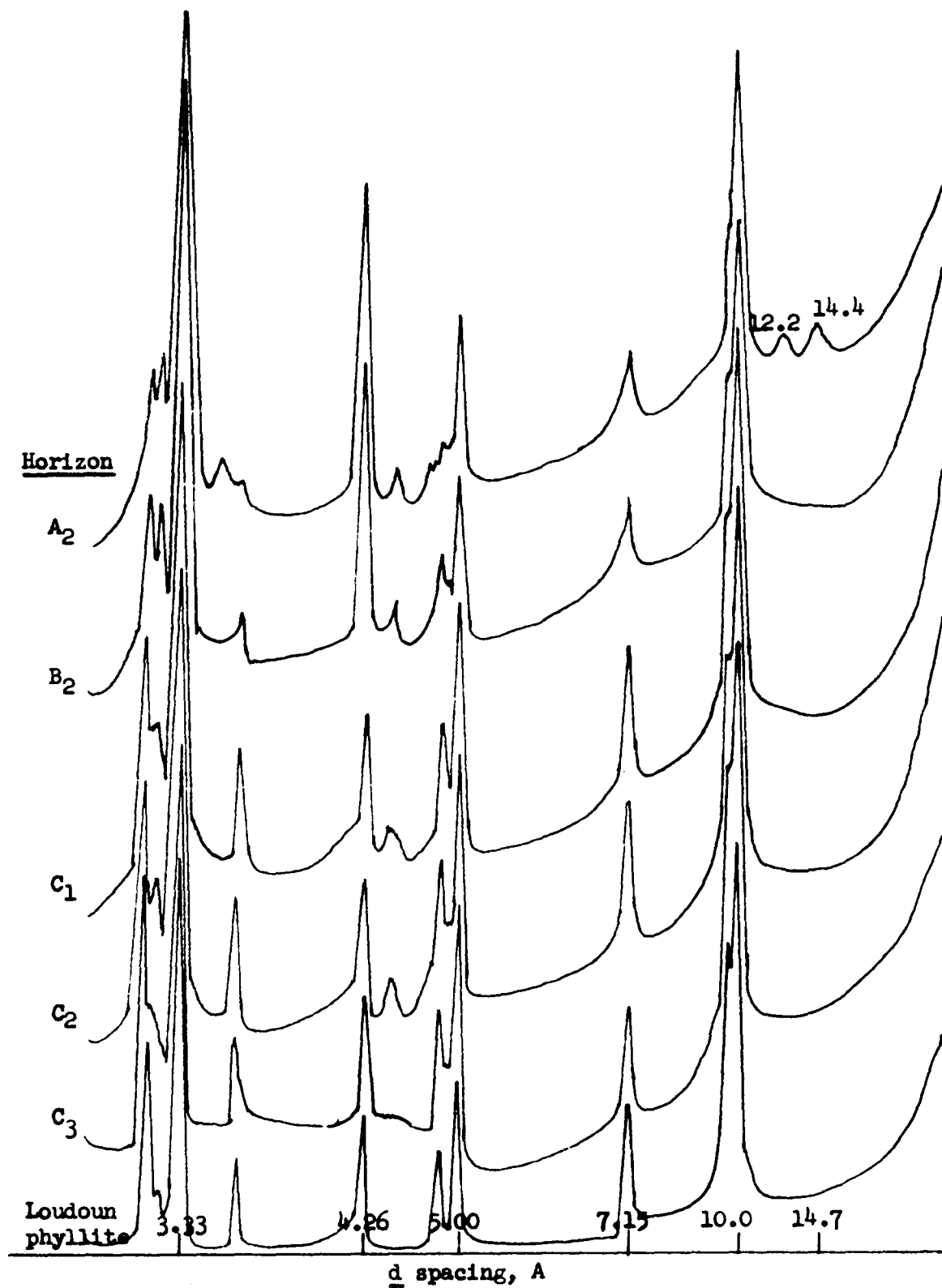


Fig. 11. Weathering sequence as a function of depth in the 20 - 5 μ fraction of Loudoun phyllite and Manteo soil, as indicated by smoothed x-ray diffraction traces.

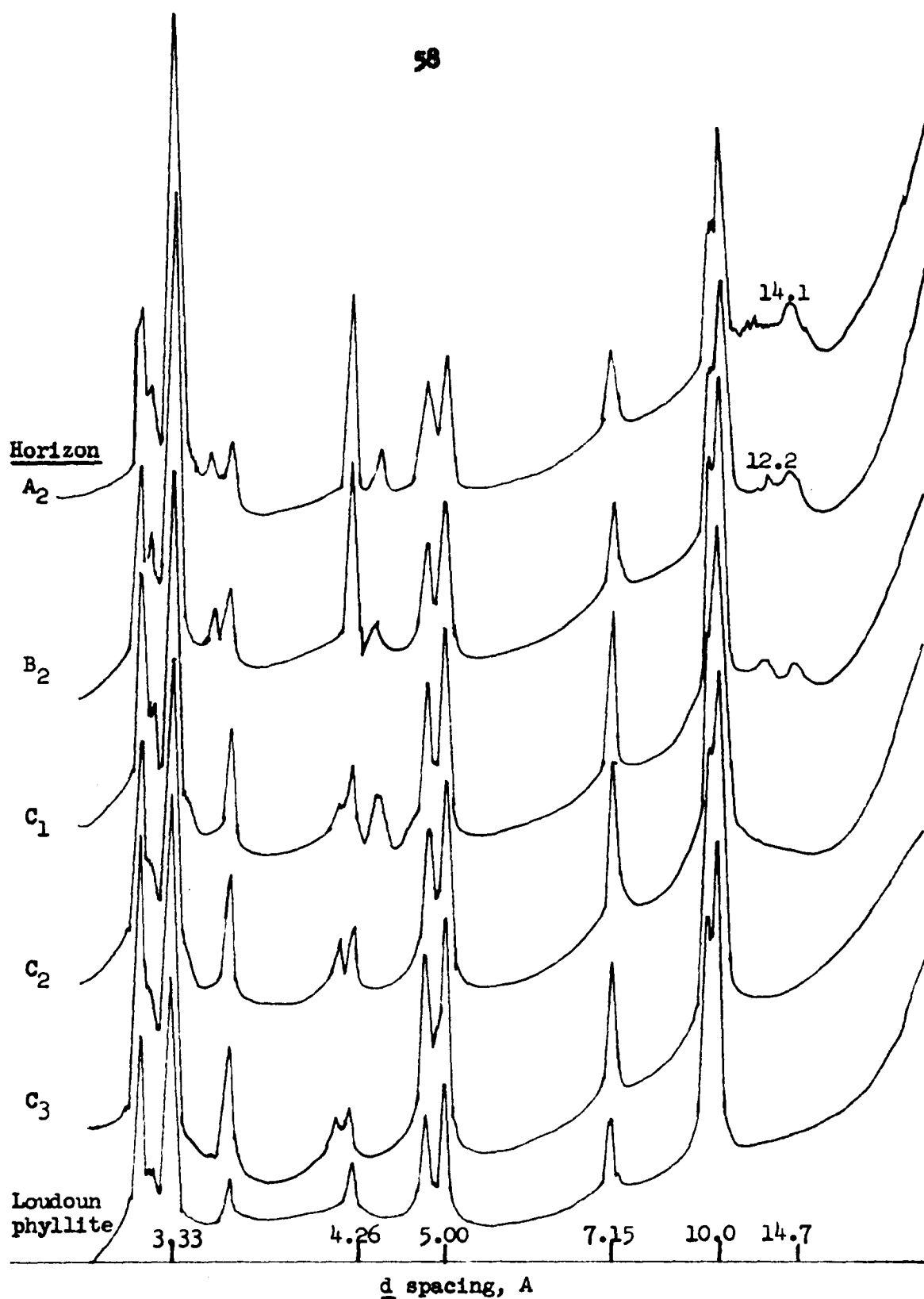


Fig. 12. Weathering sequence as a function of depth in the 5 - 2/u fraction of Loudoun phyllite and Manteo soil, as shown by smoothed x-ray diffraction traces of Mg-saturated and glycerol-solvated samples.

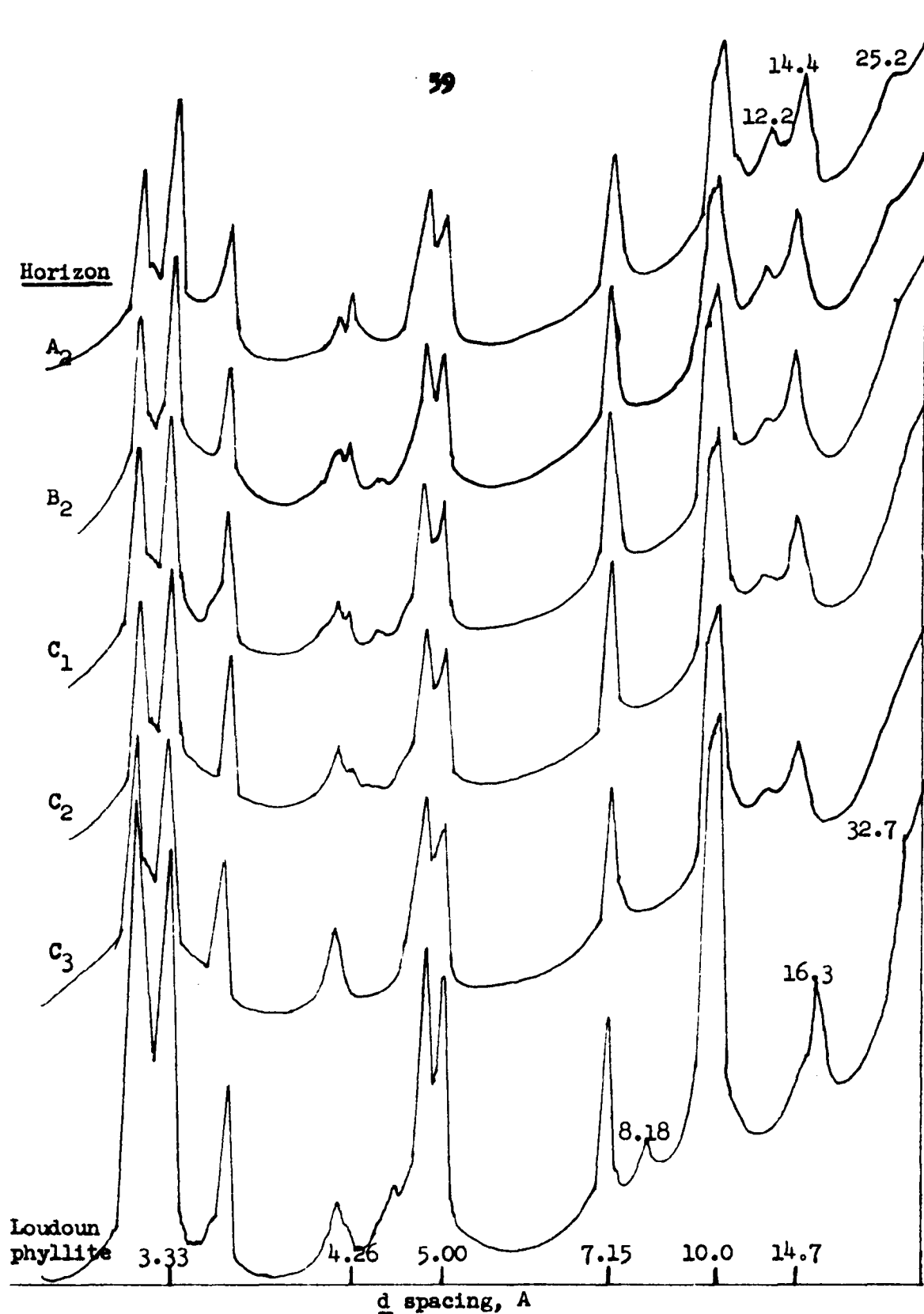


Fig. 13. Mica weathering as a function of depth in the $< 2\mu$ fraction of Loudoun phyllite and Manteo soil, as indicated by smoothed x-ray diffraction traces of Mg-saturated and glycerol-solvated samples.

TABLE 4. Contents of Na and K, as a function of depth, of Manteo soil ($< 2 \mu$) and underlying Loudoun phyllite.

Horizon	Depth inches	Na		K		Na + K	$\frac{\text{Na}}{\text{K}}$ (molar)
		%	me./100g.	%	me./100 g.	me./100g.	
A ₂	0-4	1.22	53.0	2.50	64.0	117	0.83
B ₂	4-18	1.18	51.2	2.30	58.9	110	0.87
C ₁	18-24	1.32	57.3	2.27	58.2	116	0.98
C ₂	24-30	1.52	66.0	2.62	67.2	133	0.98
C ₃	30-36	1.63	70.7	2.62	67.2	138	1.05
Loudoun phyllite	36	2.75	119	3.20	82.0	201	1.45

magnitude as those of Mason. However, the parent rock contained 40 me./100 g. less K than the least weathered sample of Candler phyllite. The noticeable differences in the Manteo soil compared to the Mason soil were a greater abundance of kaolinite in all particle size ranges, the appearance of 12.2 Å. and 14.4 Å. components in the larger particle sizes, and a smaller Na/K molar ratio in the upper horizons. These differences suggest an advanced degree of weathering in the Manteo soil. Potassium saturation and heating of the interlayered vermiculite in the $< 2\mu$ fraction effected collapse similarly in both soils (figures 9 and 14).

Laboratory weathering of Loudoun phyllite--Laboratory experiments were conducted in an effort to weather dioctahedral mica artificially and compare the artificially weathered products with those occurring under natural conditions. Particular attention was given to the relationship between loss of K, or K and Na, and increase in CEC. As stated earlier, it is desirable to have as experimental material a specimen free of impurities in order to associate the products formed during treatment with the source material. Since both phyllite specimens contained kaolinite, free Fe oxides, and other materials extraneous to the mica, it was necessary to remove these impurities from the rock sample. The NaOH dissolution technique of Hashimoto and Jackson (1960) was employed to remove kaolinite, interlayered material, and amorphous silica. Free Fe oxides were subsequently removed according to the method of Aguilera and Jackson (1953). The effects of NaOH treatment and free Fe removal on Loudoun phyllite are shown in figure 15.

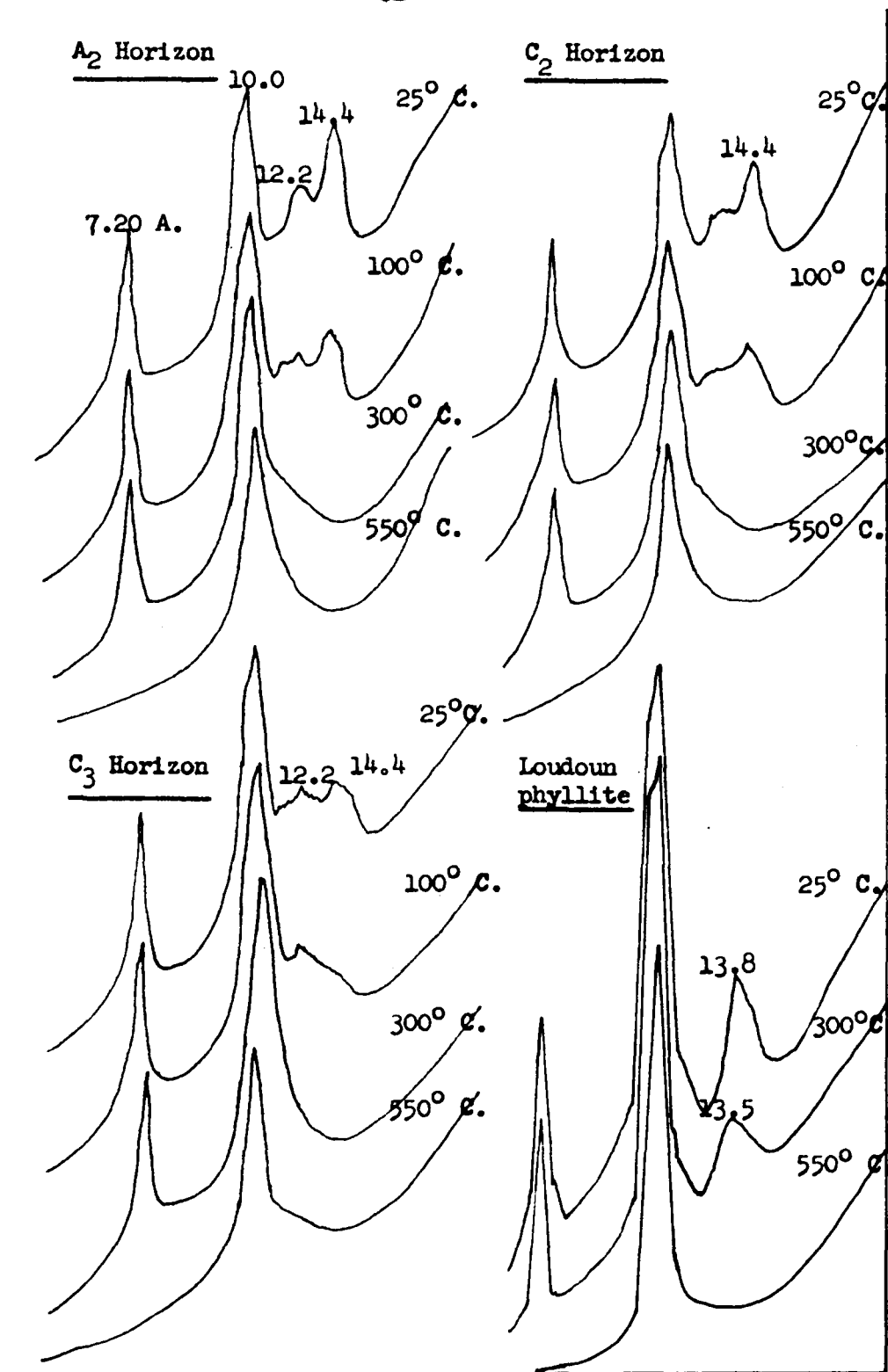


Fig. 14. Effect of K-saturation and heating on the <2/u fraction of Loudoun phyllite and Manteo soil, as shown by smoothed x-ray diffraction traces.

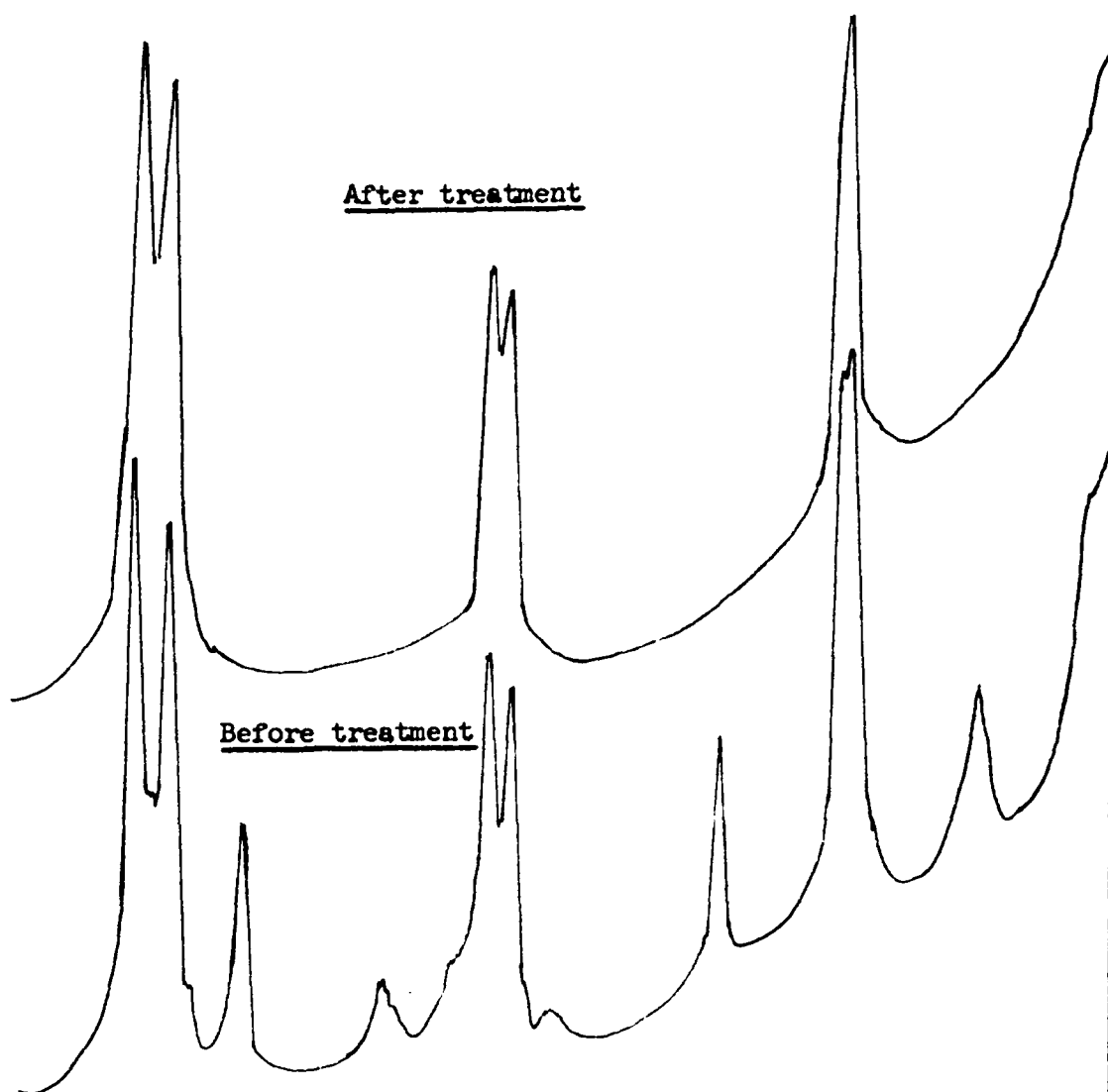
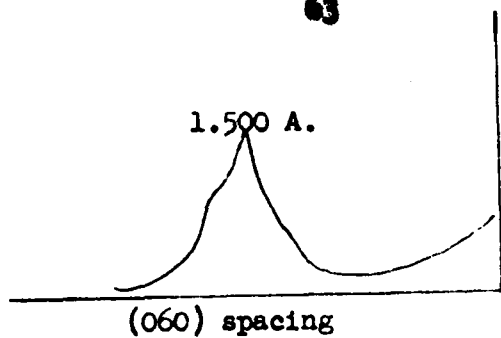


Fig. 15. Smoothed x-ray diffraction traces of Loudoun phyllite ($<2\mu$), showing effect of NaOH treatment and free Fe-oxide removal. Inset shows (060) spacing.

The treatments appeared to have an insignificant destructive effect on the mica. The dioctahedral nature of the mica is evidenced by the (060) spacing of 1.500 Å. Trioctahedral micas give an (060) spacing near 1.53 Å.

Two types of experiments were carried out on Loudoun phyllite. One treatment consisted of boiling the sample in various salt solutions, the other treatment was with a molten salt, namely LiNO_3 . A brief description of the method used in each case will be given preceding the results.

Boiling treatments

Method--Approximately 1 g. of pretreated, $< 2\mu$ -size material was placed in a 6-liter flask containing 5 liters of the appropriate salt solution and heated to boiling on an electric hotplate. A reflux condenser was inserted through the rubber stopper closing the flask in order to prevent evaporation during boiling. The salts and their concentrations used were 5 N NaCl , 5 N MgCl_2 , 0.2 N HOAc , and 0.001 N HCl . Aliquots of the boiling suspension were taken at the intervals indicated and 5 liters of fresh replacing solution was added.

Results--The effect of boiling 5 N NaCl , pH 5.2, on the mica structure is shown by the x-ray diffraction traces in figure 16. Slight expansion was noted after 2 days treatment. At 8 days, a material resembling a regularly interstratified 50-50 mixture of mica and vermiculite was formed, as indicated by the 25.2 Å. and 12.6 Å. spacings, respectively. Continued boiling to 30 days destroyed the crystal structure of the mineral.

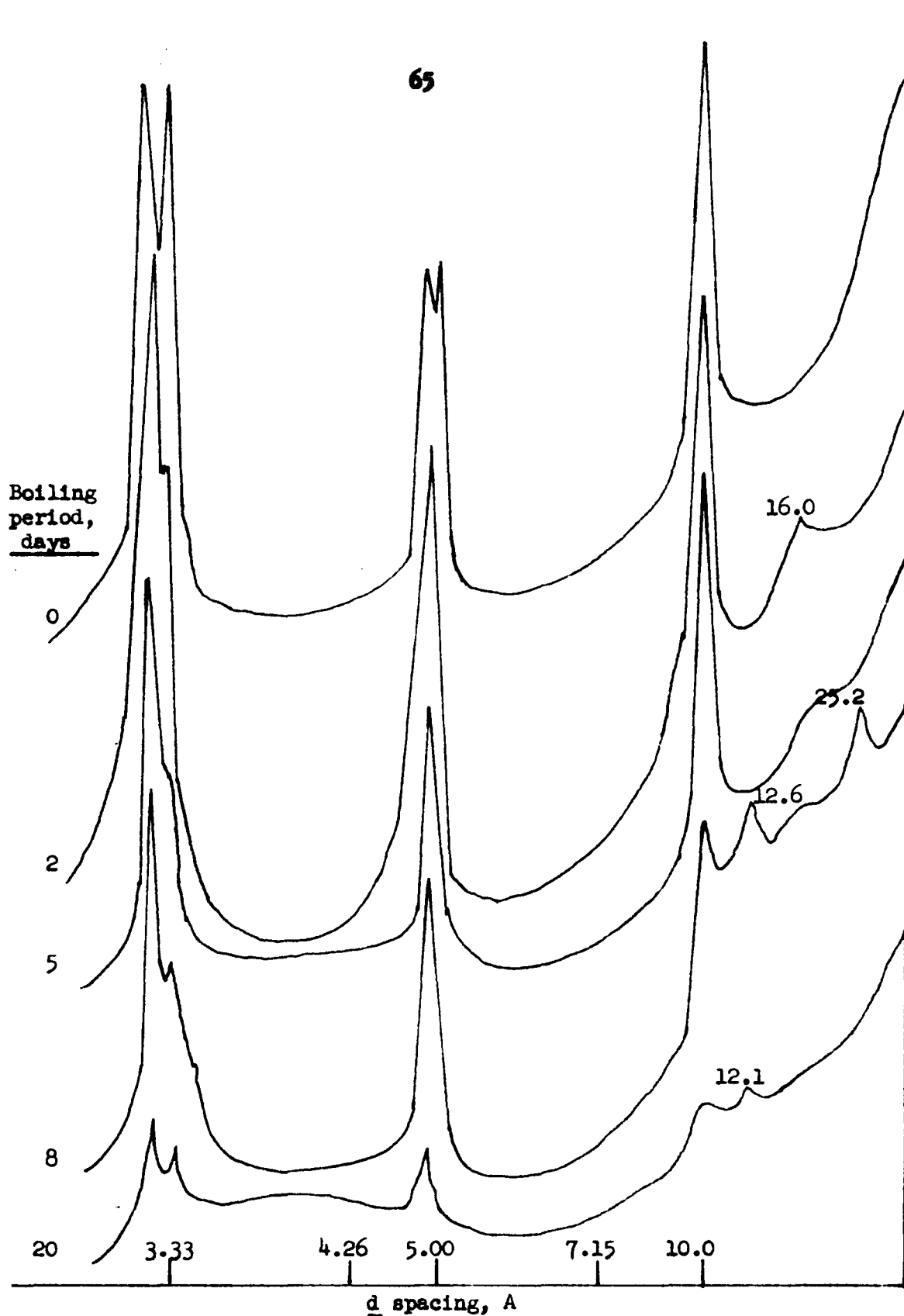


Fig. 16. Expansion of Loudoun phyllite ($< 2\mu$) following boiling 5 N NaCl treatment, as indicated by smoothed x-ray diffraction traces of Mg-saturated and glycerol-solvated samples.

Examination of table 5 reveals that considerably more K than Na was lost through NaCl boiling. Especially noticeable is the fact that the increase in CEC was non-stoichiometric with the loss of Na and K. Apparently the exchange sites were blocked by positively charged Al-hydroxy groups that formed as Al was released during breakdown of the mineral. That charged Al-hydroxy groups exist and balance unsatisfied negative charges has been demonstrated in studies like those of Hsu and Rich (1960), and Shen and Rich (1961). Furthermore, salts actually speed the Al-hydrolysis reaction (Rich, 1960).

It was thought that the use of boiling NaCl solution on a Na-containing mineral gave a distorted picture of the relative rates of Na and K release from the mica due to the equilibrium existing between Na in the sample and that in solution, thus restricting its removal. To eliminate this effect, a boiling 5 N MgCl₂ solution, pH 4.8, was employed. Magnesium chloride was chosen also because its effectiveness in altering hydrobiotite to vermiculite was illustrated by Barshad (1949). Unfortunately, an aliquot was not taken until after 10 days, by which time the mica had been almost completely altered (figure 17). The expanded materials formed were similar to those produced with NaCl, but the mica-vermiculite mixture formed from MgCl₂ treatment produced more prominent peaks and was slightly more resistant to collapse with heat treatment (figure 18). However, there were insignificant differences in K and Na losses, and CEC gain (table 6). This suggests that the 'weathering' action of the Na and Mg salts was essentially the same.

TABLE 5. Effect of boiling 5 N NaCl on K content, Na content, and CEC of Loudoun phyllite ($< 2\mu$).

Boiling period, days	K	Na	K Na	CEC
	me./100 g.			
0	86.2	93.8	180	5.8
5	31.3	81.8	112	19.0
20	23.0	71.4	94	26.2
30	23.0	69.5	93	30.7

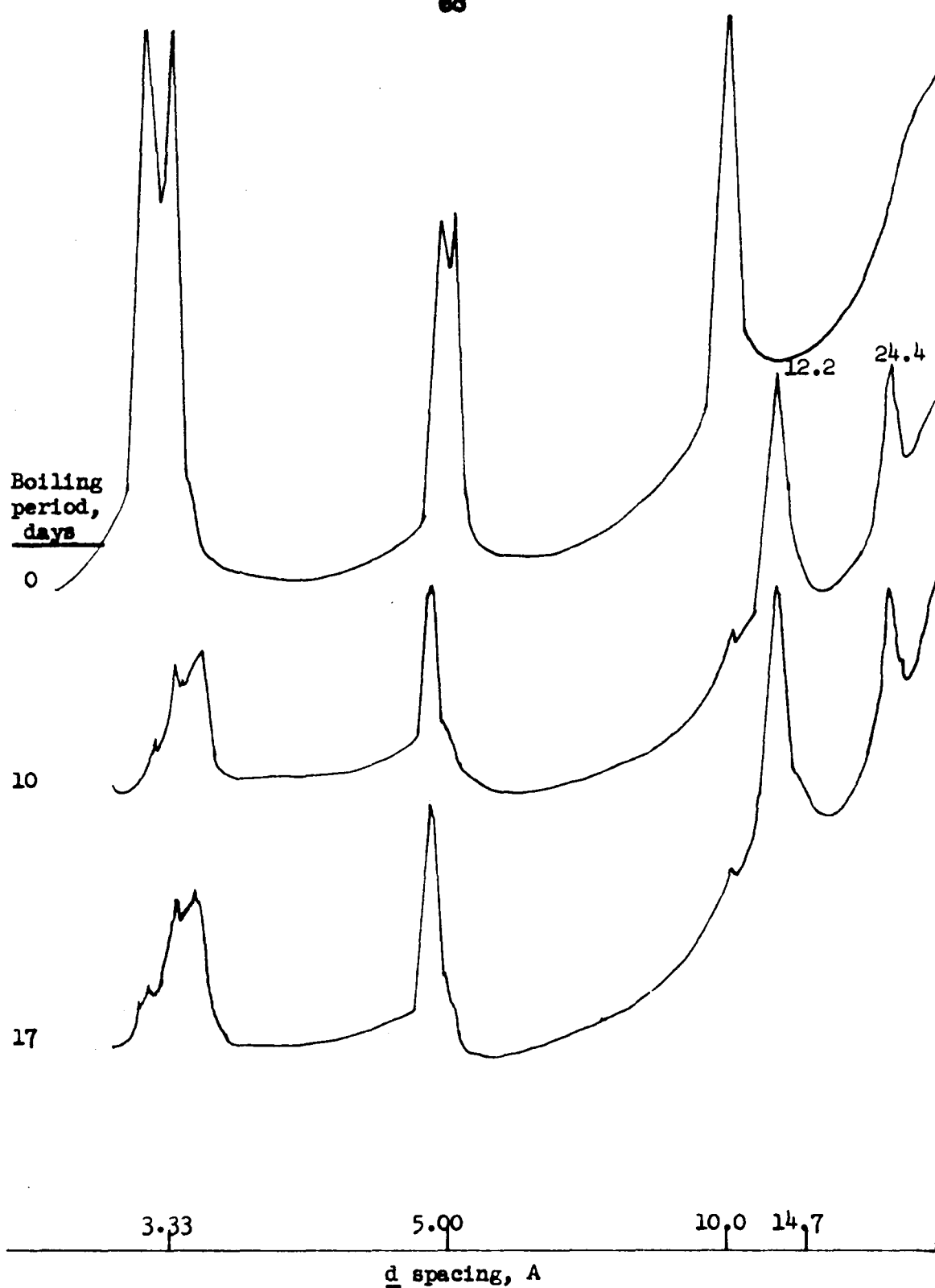


Fig. 17. Expansion of Loudoun phyllite (<2/μ) following boiling 5 N MgCl₂ treatment, as indicated by smoothed x-ray diffraction traces of Mg-saturated and glycerol-solvated samples.

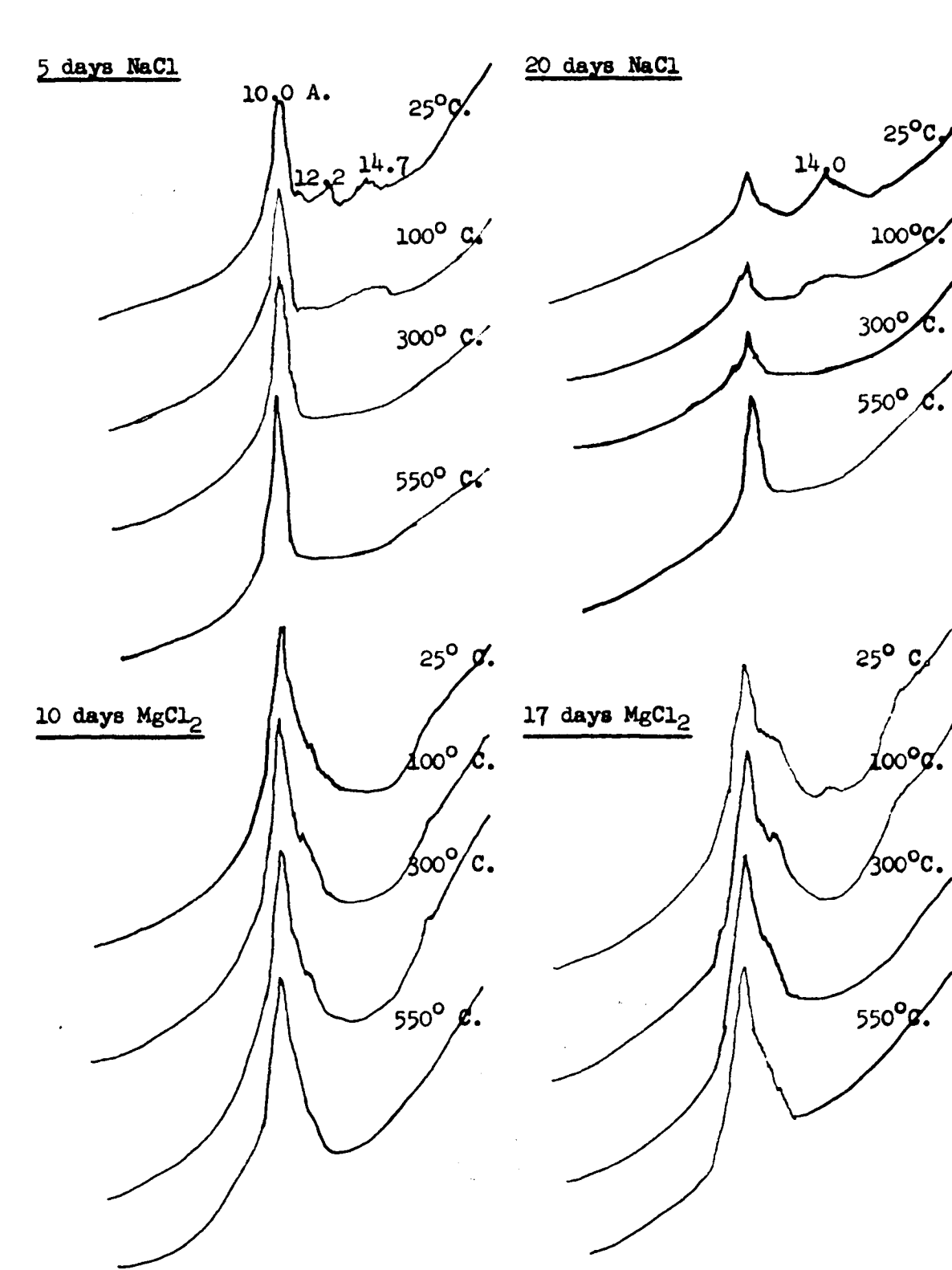


Fig. 18. Effect of K-saturation and heating on Loudoun phyllite (<2/u) following NaCl and MgCl₂ boiling treatments, as shown by smoothed x-ray diffraction traces.

TABLE 6. Effect of boiling 5 N MgCl_2 on K content, Na content, and CEC of Loudoun phyllite ($\leq 2\mu$).

Boiling period, days	K	Na	K + Na	CEC
	----- me./100 g. -----			
0	86.2	93.8	180	5.8
10	30.7	71.3	102	26.5
17	27.6	64.2	92	32.6

Both NaCl and MgCl₂ are strongly ionized salts. To observe the effect of a weak acid, a boiling treatment with 0.2 N HOAc, pH 3.0, was carried out. The results, as shown in table 7, were quite different from those obtained with boiling salt solutions. Acetic acid removed approximately 44 me. Na/100 g., whereas NaCl and MgCl₂ removed approximately 24 me./100 g. and 30 me./100 g., respectively. Also slightly less K was replaced with HOAc than with NaCl and MgCl₂. A striking difference in cation exchange behavior was noted. A net increase of only 7 me./100 g. of exchange sites was obtained despite the large amounts of Na and K removed. The likely explanation is that the HOAc solution was buffered at a lower pH than the salt solutions, and the lower pH(greater acidity) brought into solution more Al⁺⁺⁺, which subsequently reacted to form hydroxy-Al polymeric groups. Although the CEC increased only slightly, considerable expansion occurred, as indicated in figure 19. Furthermore, the material formed was resistant to collapse, particularly after the 30-day treatment (figure 20). The difficult contraction indicates a more stable Al interlayer configuration as a result of HOAc treatment.

The dilute weak acid treatment produced such different results from the other treatments that it was decided to see what effect dilute strong acid would have on expansion and cation exchange properties. A boiling 0.001 N HCl solution produced neither expansion nor an increase in CEC after 30 days treatment. However, the treatment, surprisingly, did produce cristobalite, the high temperature SiO₂ polymorph. Cristobalite also was found occurring naturally

TABLE 7. Effect of boiling 0.2 N HOAc on K content, Na content, and CEC of Loudoun phyllite ($< 2 \mu$).

Boiling period, days	K	Na	K + Na	CEC
	----- me./100 g. -----			
0	86.2	93.8	180	5.8
5	86.0	84.4	170	5.8
10	65.6	79.2	145	5.9
15	43.0	73.1	116	6.0
20	31.5	65.2	97	7.0
30	30.7	49.4	80	12.8

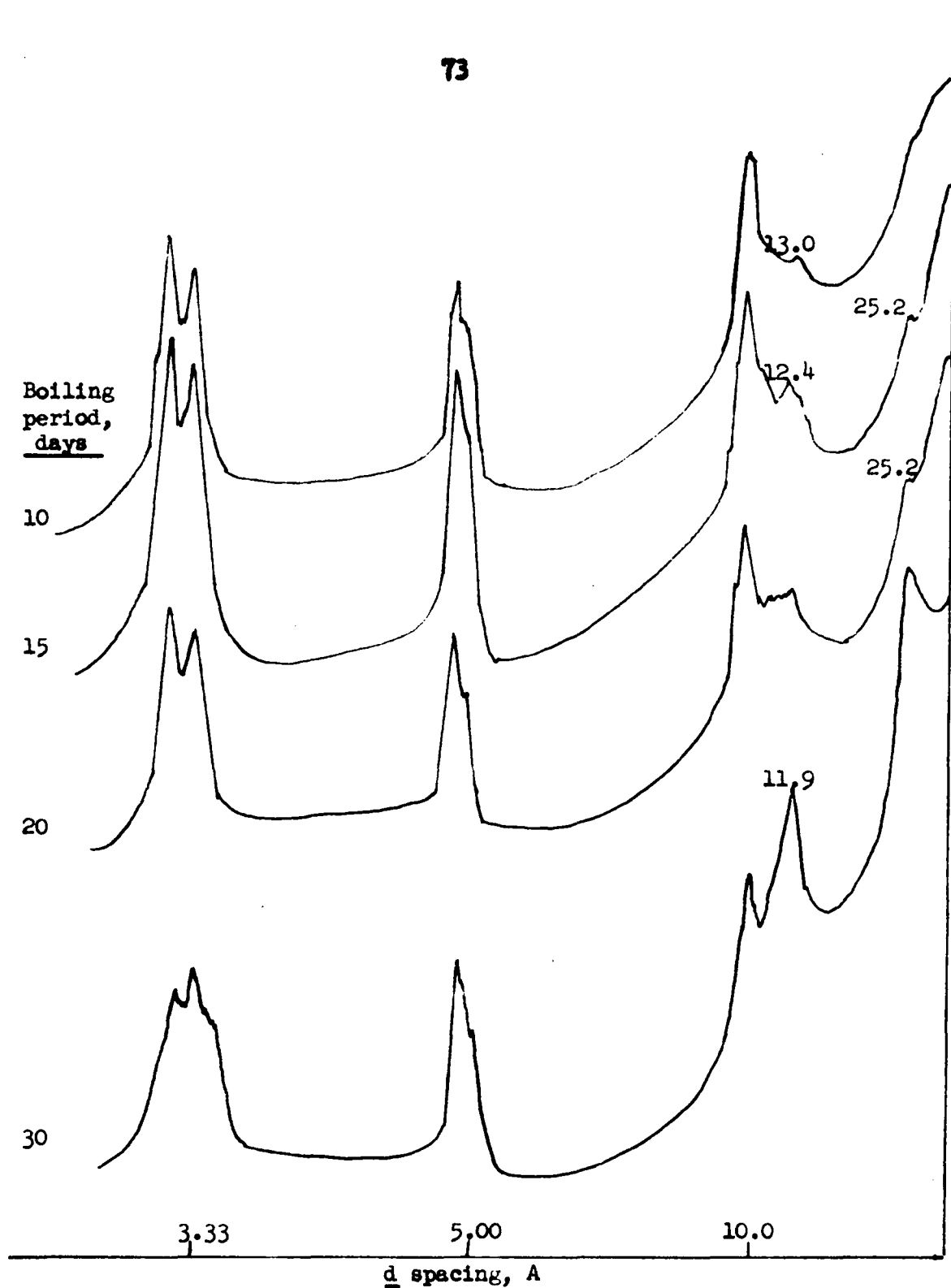


Fig. 19. Expansion of Loudoun phyllite (<2/u) following boiling 0.2 N HOAc treatment, as indicated by smoothed x-ray diffraction traces of Mg-saturated and glycerol-solvated samples.

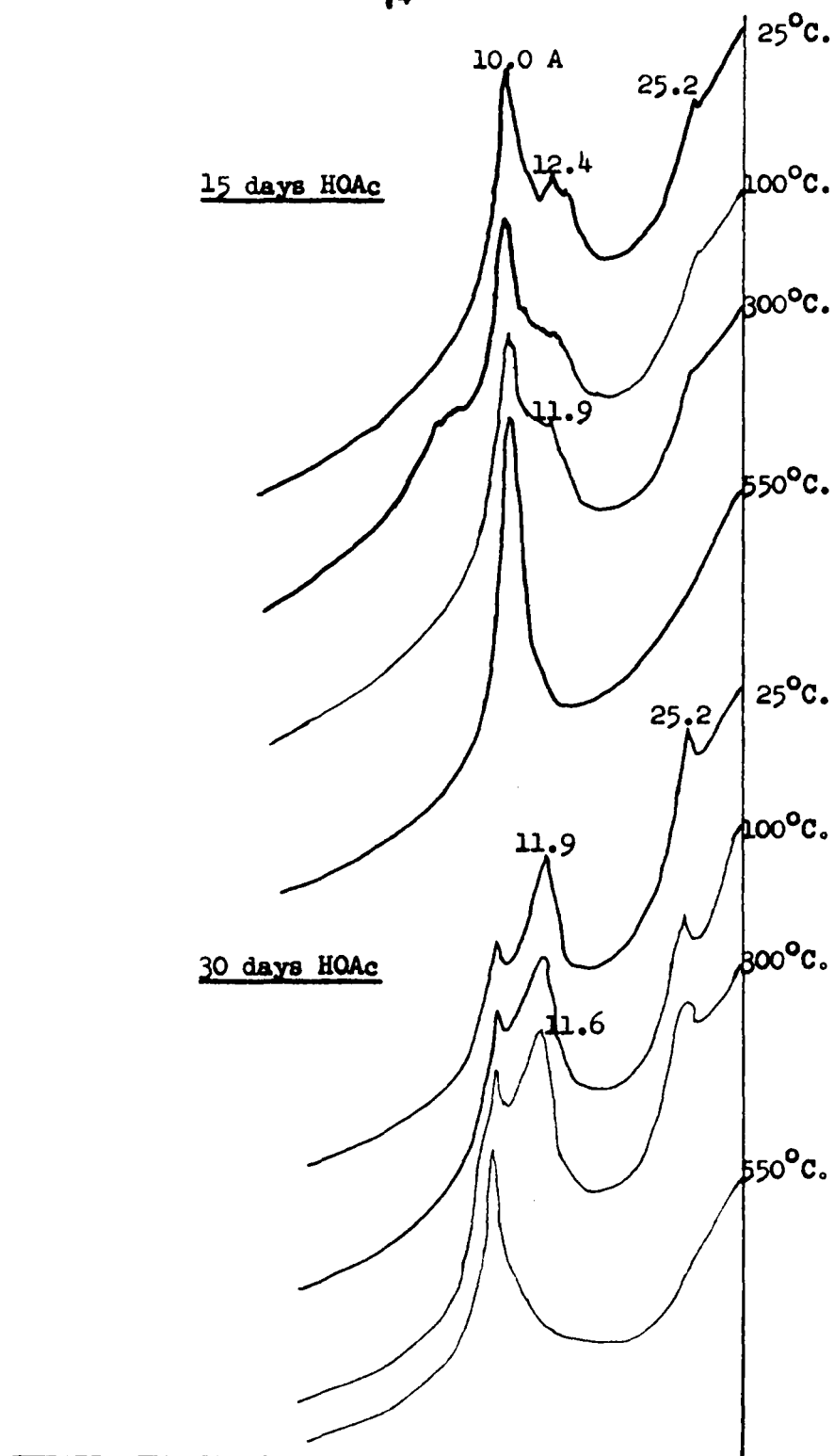


Fig. 20. Effect of K-saturation and heating on Loudoun phyllite ($< 2\mu$) following boiling HOAc treatment, as shown by smoothed x-ray diffraction traces.

in the $0.2\mu - 0.1\mu$ fraction. A comparison of the x-ray patterns revealed a close similarity between the natural and synthetic products (figure 21). The formation of cristobalite is attributed to gelation of amorphous silica. Although cristobalite normally is formed at very high temperatures ($1470^{\circ}\text{C} - 1713^{\circ}\text{C}.$), it may form at much lower temperatures when crystallization takes place rapidly (Berry and Mason, 1959). Also the presence of foreign ions, particularly Na^+ , and fine grain size probably account for this occurrence of cristobalite because these factors are known to enhance the catalysis of cristobalite crystallization under metastable conditions (Berry and Mason, 1959).

Molten LiNO_3 treatment

Method--A method similar to that used by White (1956) was employed. A 0.5 g. sample was dry-mixed with 50 g. of solid LiNO_3 in each of several platinum crucibles. The crucibles and their contents were heated at $300^{\circ}\text{C}.$ for varying periods of time. After cooling, the solidified melt was dissolved in water, then the remaining sample was washed twice with water to remove excess salt. Total Li was determined flame photometrically following HF digestion. Other techniques and determinations used have been described previously under "General Methods."

Results--The effect of molten LiNO_3 on the chemical composition of Loudoun phyllite is indicated in table 8. The treatment removed K more effectively than Na, which indicates that the K-containing layers are more easily penetrated than the Na-containing layers.

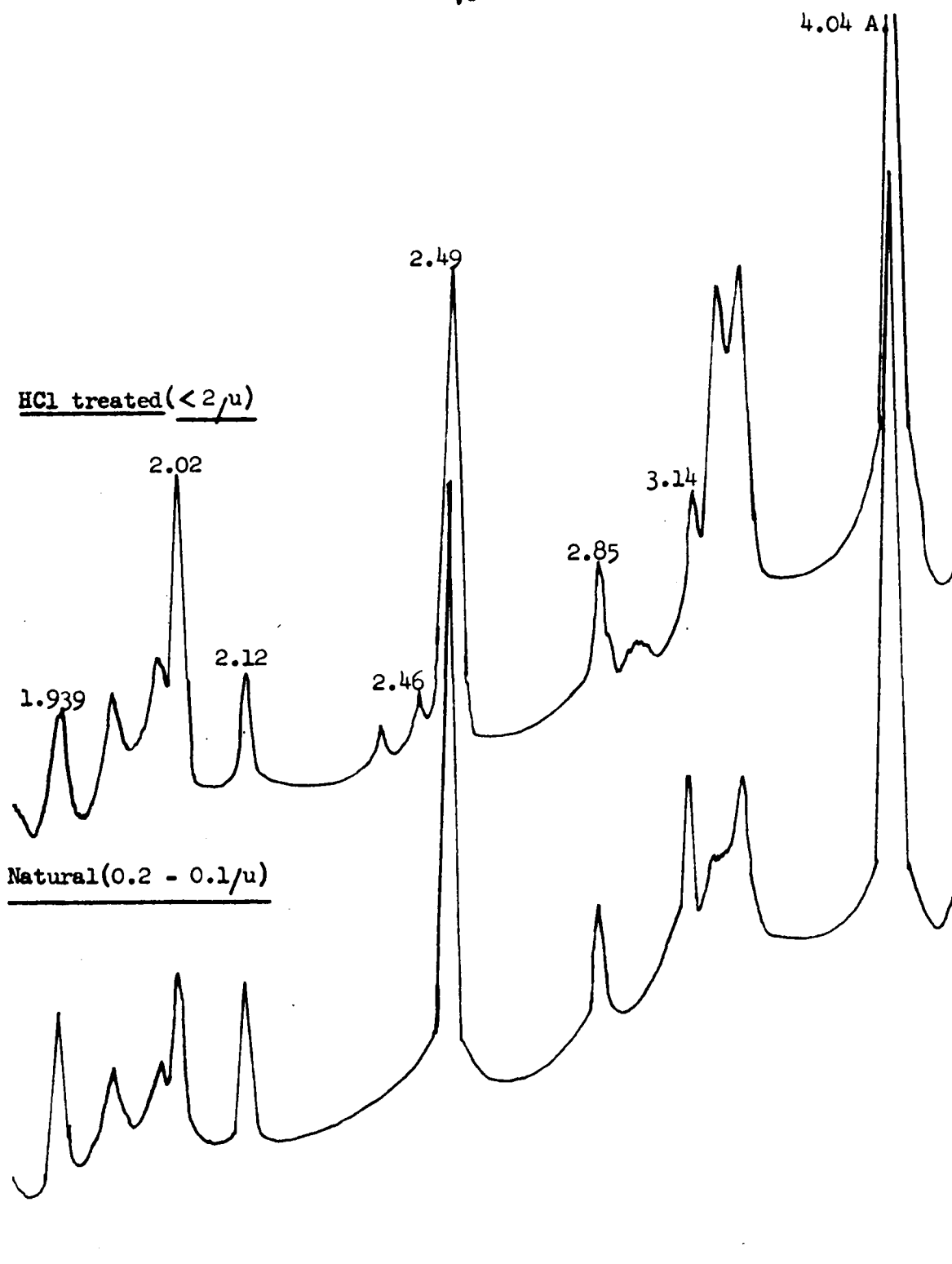


Fig. 21. Occurrence of cristobalite, as identified by x-ray diffraction data.

TABLE 8. Chemical composition of Loudoun phyllite ($< 2\mu$) as affected by molten LiNO_3 (1:100 ratio) at 300°C .

Reaction time	K	Na	Li	CEC	Layer Charge ($\Sigma\text{K, Na, CEC}$)	Total Charge ($\Sigma\text{K, Na, Li, CEC}$)
-----me./100 g.-----						
0	86.2	93.8	4.08	5.82	186	190
$\frac{1}{2}$ hr.	67.0	80.0	24.4	21.4	168	193
1 hr.	57.5	77.9	30.4	26.7	162	193
2 hrs.	50.4	75.0	31.0	32.2	158	189
6 hrs.	39.0	72.4	41.3	39.4	151	192
12 hrs.	32.6	71.8	42.4	45.3	150	192
1 day	28.8	66.9	45.6	53.7	149	194
2 days	23.4	64.6	47.0	60.8	149	196
3 days	21.4	58.7	49.5	66.8	147	196
4 days	19.5	57.7	60.6	71.0	148	209
5 days	18.2	57.7	66.7	73.7	148	216
6 days	15.9	56.0	95.5	79.6	152	247

The difference in interlayer accessibility apparently is due to differences in the ionic sizes of K^+ and Na^+ . The K^+ ion has an ionic diameter of 2.66 Å., which is slightly larger than the 'hole' of approximately 2.55 Å. diameter formed by the hexagonal rings of O^{--} ions of the tetrahedral layers above and below. Thus the tetrahedral layers are held apart slightly by the K^+ ion. On the other hand, the smaller diameter of the Na^+ ion, 1.94 Å., permits the tetrahedral layers to close completely around it. As a result, a greater energy would be required to initiate expansion along Na-containing layers than K-containing layers.

The relationship between changes in chemical composition and CEC is shown in figure 22. The rapid changes occurring initially probably indicate reaction with the finer particle-sized material. White (1958) observed a stoichiometric relationship between the amount of Li migrating into the lattice and the increase in CEC. However, in this study, total increase in CEC seemed to be correlated more closely with the loss of K. If K^+ and/or Na^+ are replaced by cation exchange or the negative charge on the layer decreased internally by penetration of Li into the structure, the summation of me. of Na^+ , K^+ , Li^+ , and CEC should be constant. A relatively constant sum of approximately 192 me. was maintained through 3 days treatment, but a sharp rise to 247 me. was noted after the 6-day period. This latter figure of 247 me. approaches the total charge of muscovite, approximately 250 me./100 g., as calculated from the theoretical formula of muscovite. It is interesting to note that the experimentally determined CEC (80me./100 g.) is in good agreement with the

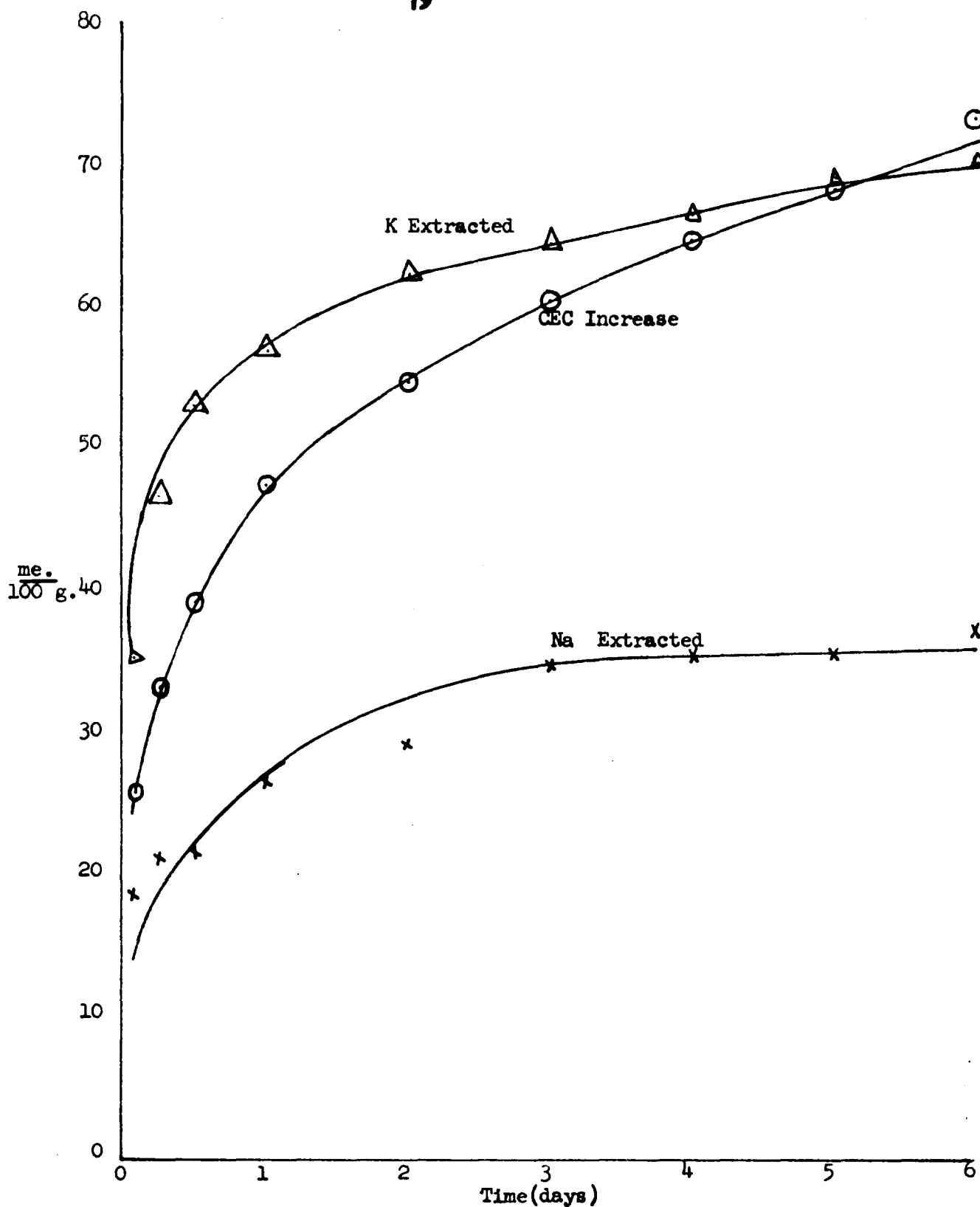


Fig. 22. Variation in K, Na, and CEC with reaction time in the treatment of Loudoun phyllite (<2/u) with molten LiNO_3 (100:1 ratio).

difference $250 - (\sum K^+, Li^+, Na^+)$, or 83 me./100 g.

Expansion of the Li-treated samples after various reaction times is shown in figure 23. Expansion occurred rapidly, which was to be expected according to the rapid initial losses of K^+ and Na^+ , and decrease in layer charge (table 8). The layer charge was computed by summation of K^+ , Na^+ , and CEC. This summation was based on the assumption that all the Li migrated to octahedral positions. A relatively constant layer charge was reached after about 6 hours. This agrees with the finding of White (1958), who attributed the leveling-off in layer charge to attainment of a critical K content in the melt. The magnitude of layer charge is an important factor in the interlamellar expansion of micaceous minerals. Earlier studies, e.g., Barshad (1954), seemed to indicate that a crystal lattice with a layer charge greater than 150 me./100 g. will remain contracted at 10 Å. However, significant expansion was observed in Loudoun phyllite when the layer charge was 172 me./100 g. More recent work by Barshad (1960) indicated that a vermiculite with a charge of approximately 200 me./100 g. expanded quite readily.

A specimen-type muscovite from Ontario, Canada, was also treated with $LiNO_3$ for periods up to 48 hours. The results are given in table 9. The high initial CEC is believed to be caused by excessive grinding during fractionation of the sample. Mackenzie and Milne (1953) increased the CEC of a muscovite to almost 30 me./100 g. by grinding for only one hour.

The low initial charge of 187 me./100 g. for the Ontario mus-

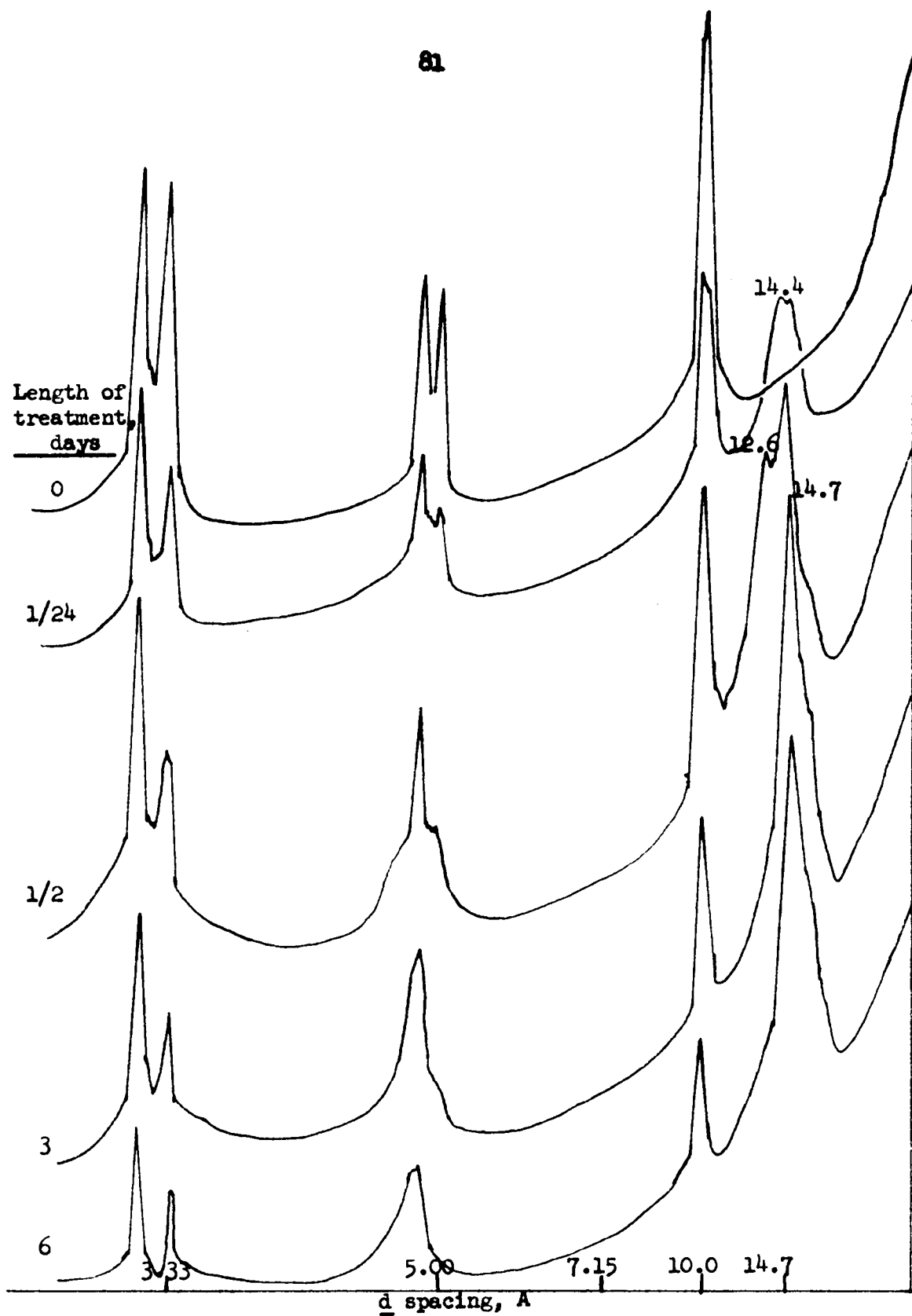


Fig. 23. Influence of molten LiNO_3 (100:1 ratio) on expansion of Loudoun phyllite (<2 μ), as shown by smoothed x-ray diffraction traces of Mg-saturated and glycerol-solvated samples.

TABLE 9. Chemical composition of an Ontario muscovite (2-0.2 μ) as affected by molten LiNO_3 (1:100 ratio) at 300°C.

Reaction time, hours	K	Li	CEC	Layer charge ($\Sigma\text{K, CEC}$)	Total charge ($\Sigma\text{K, Li, CEC}$)
-----me./100g.-----					
0	150	7.8	37.1	187	195
1	37.0	35.0	145	182	217
5	32.3	57.8	150	182	240
24	16.5	90.5	165	182	272
48	15.8	110	170	186	296

covite is noticeable, since it represents a marked discrepancy from the theoretical value for well-crystallized muscovite. Low-charged micas have been observed, however, as in the case of high-silica micas (Schaller, 1950). Total charge increased to the unusually high value of 296 me./100 g. It is difficult to account for this high figure. It is possible that in the separation of the 2 - 0.2 μ fraction, some of the K was replaced by Na from the Na₂CO₃ dispersing solution. Also, an increase in total charge would occur upon the substitution of Li⁺ for K⁺ due to the difference in atomic weights of Li (6.94) and K (39.1). Even if Li⁺ replaced all the K⁺, though, the total charge would be only 273 me./100 g. Furthermore, if all the vacant octahedral positions in a dioctahedral mica were filled, it would appear that the structure would be neutral. Since it isn't, perhaps the negative charge on the tetrahedral layer cannot be balanced by Li⁺ in the octahedral layer.

Differences in expansion of the Loudoun phyllite and Ontario muscovite were noted, as shown in figures 23 and 24. The Loudoun phyllite did not expand beyond 14.7 Å., which is indicative of a vermiculite-like material. Muscovite expanded to 18.4 Å., which is a characteristic spacing of montmorillonite. This difference seems to point up the fact that soil micas and specimen-type micas are quite different from an alteration standpoint. The fact that the LiNO₃ treatment produced a vermiculite-like material further indicates that vermiculite as a weathering product of dioctahedral mica is probable. Both the phyllite and muscovite collapsed readily upon

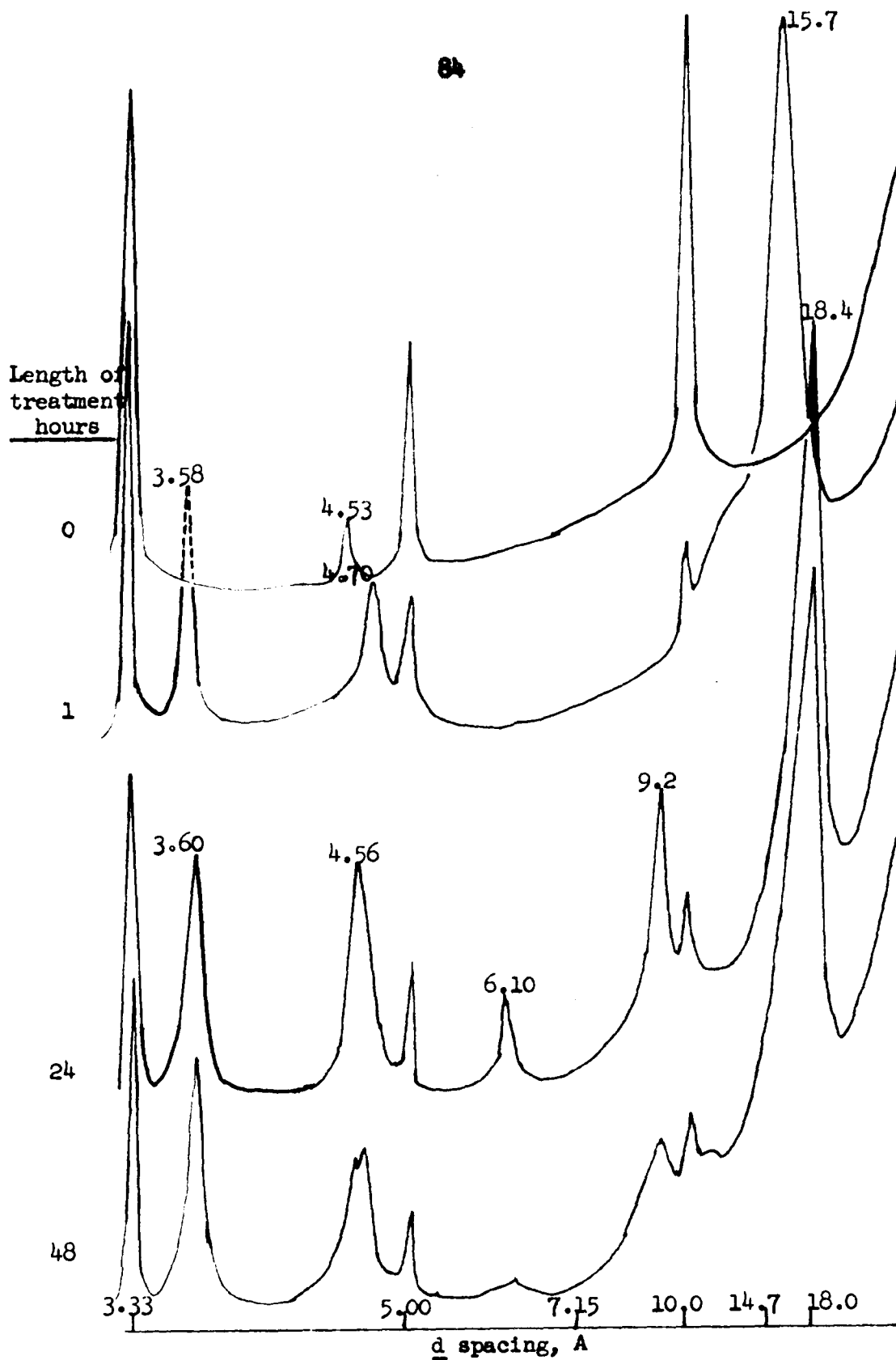


Fig. 24. Influence of molten LiNO_3 (100:1 ratio) on expansion of an Ontario muscovite (2 - 0.2 μ), as shown by smoothed x-ray diffraction traces of Mg-saturated and glycerol-solvated samples.

K saturation and heating, as exemplified by two samples of Li-treated muscovite in figure 25.

As in the case of Loudoun phyllite, the increase in CEC of the muscovite, 133 me./100 g., approximated the decrease in K content, 134 me./100 g. The equivalence between K extracted and CEC increase, concomitant with the expansion of the mica, suggests that the mechanism involved in the LiNO_3 treatment consists of Li^+ replacing K^+ , then entering the lattice and reducing the charge on the lattice, which renders it expandable.

Laboratory weathering of mica from Orange County-- Laboratory studies were conducted on the micaceous parent material (C_3 horizon) of a Tatum soil sampled prior to the beginning of this investigation. The sampling site was located two miles east of Orange on Virginia Highway 637 and one-half mile west of Highway 612 in an old hardwood forest. This sample will be referred to as Mica OR throughout this presentation. A description of some of the chemical, physical, and mineralogical properties of the entire soil profile has been given by Rich and Obenshain (1955).

The 5 - 2 μ fraction of Mica OR was used in most of the laboratory treatments. The dioctahedral character of the mica and its appearance following NaOH treatment and free Fe oxide removal are shown in figure 26. The mica peaks are noticeably sharper as a result of the removal of free Fe and extraneous materials. After the pretreatment, the mica contained 134 me. K/100 g. (5.23%), 12.1 me.

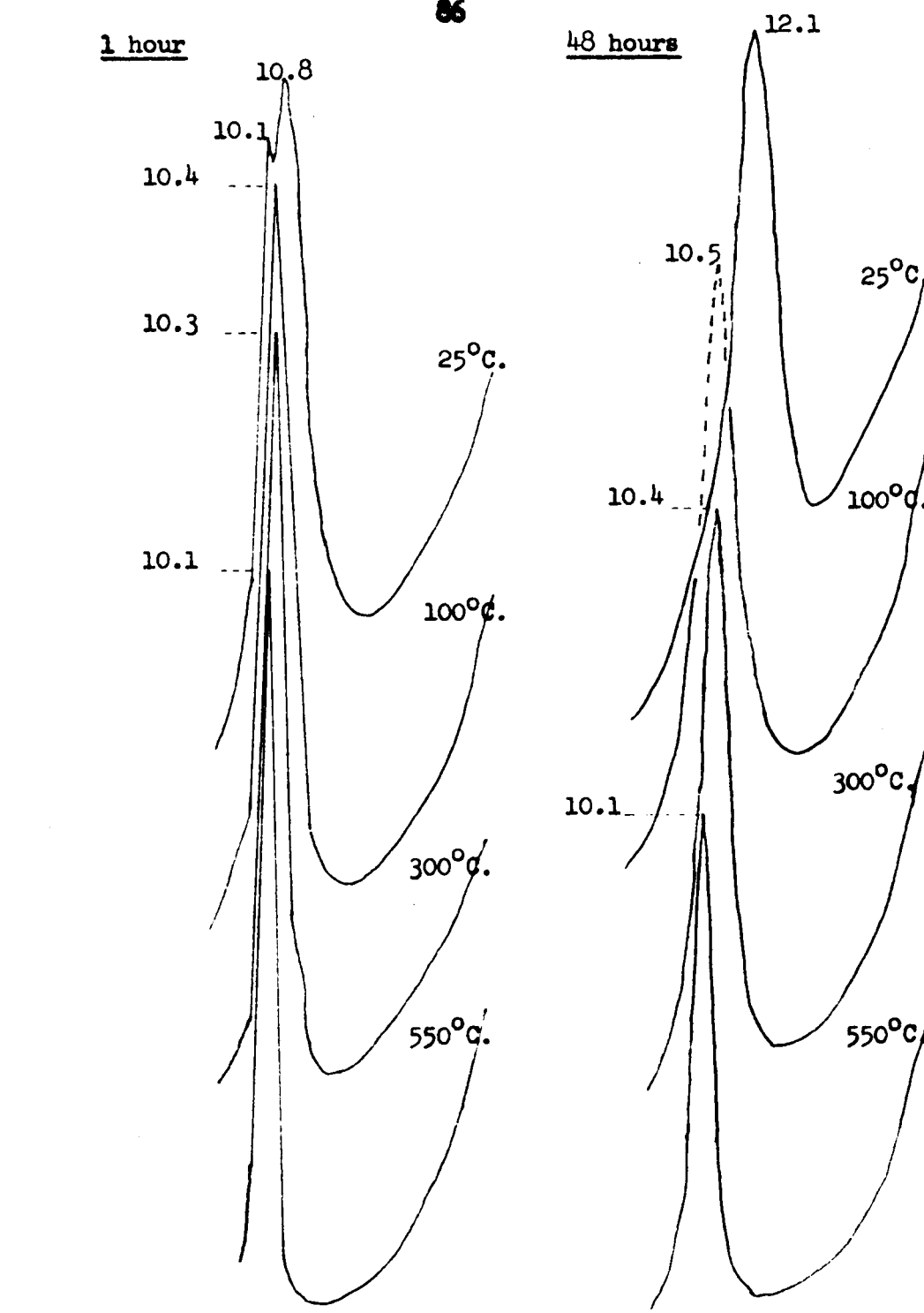


Fig. 25. Effect of K-saturation and heating on an Ontario muscovite(2 - 0.2/u) following molten LiNO_3 treatment, as indicated by smoothed x-ray diffraction traces.

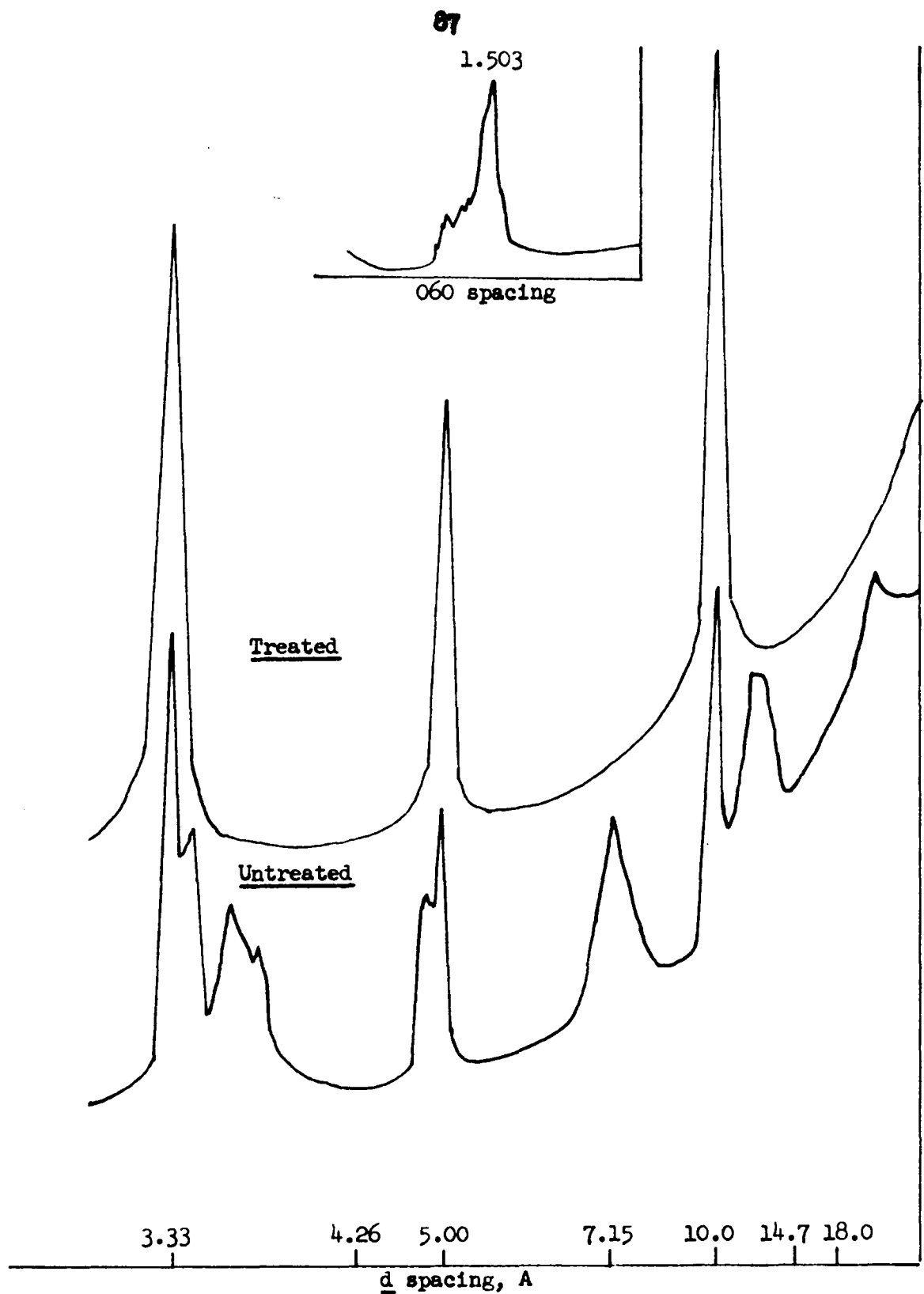


Fig. 26. Smoothed x-ray diffraction traces of Mica OR(5 - 2/u), showing effect of NaOH treatment and free Fe-oxide removal. Inset shows (060) spacing.

Na/100 g. (0.28%), and had a CEC of 9.2 me./100 g.

Boiling treatments were carried out in a similar manner to those conducted on Loudoun phyllite. An important exception was the more frequent changing of boiling solutions. The solution was changed daily to keep the solution as fresh and reactive as possible. Rich (personal communication) observed that 10 ppm of K in solution was sufficient to block exchange.

It will be recalled that a 0.2 N HOAc solution removed Na and K effectively but produced a negligible effect on the CEC. To note the effect of a more concentrated HOAc solution, a 1 g. sample of Mica OR was boiled in 5 liters of a N HOAc solution for 8 days. The amount of K extracted in comparison with the increase in CEC is given in table 10. It is noted that the CEC did not increase stoichiometrically with the loss of K. This apparent loss of charge may be accounted for in two ways: 1) Blocking of exchange sites, presumably by Al^{+++} or hydroxy-Al groups; 2) Internal reduction or compensation of charge. Rich (1960) indicated that hydroxy-Al may be an effective blocking agent in vermiculite. In an acidic solution of HOAc (pH 2.4), the formation of hydroxy groups is probably small. However, Al^{+++} may be released from the mineral and satisfy the negative charge, since Al^{+++} is strongly attracted to the exchange sites and is difficult to replace by other ions.

A mechanism that accounts for the reduction of charge within the lattice would seem applicable in this case. Jackson et al. (1952) proposed that the H^+ ion may become associated with the apical oxygen

TABLE 10. Effect of boiling N HOAc on K and Na content and CEC of Mica OR (5-2 μ).

Boiling period, days	K	Na	CEC	$\frac{\text{CEC gain}}{\text{K+Na loss}}$
-----me./100g.-----				
0	134	9.6	9.2	--
2	118	7.3	23.3	0.77
4	112	7.5	24.5	0.64
6	102	7.0	33.0	0.69
8	100	6.4	36.0	0.72

of the tetrahedral sheet, forming OH^- from O^{--} , and thus reduce the negative charge. This reaction may have taken place during the HQAc treatment since large amounts of H^+ ions were present and in an active state as a result of boiling. However, no experimental evidence can be offered to support the proposed mechanism.

Accompanying the increase in CEC was expansion of the mica structure, as indicated in figure 27. In general, weak variable spacings were produced. After 8 days, a pronounced 12.2 Å spacing appeared, suggesting a mica-vermiculite type interstratification. Potassium saturation and heating to 300°C. contracted the material (figure 28). The patterns tend to confirm the conclusion that blockage of exchange sites by interlayer hydroxy-Al groups was small but not negligible. The appearance of a small kaolinite peak after 8 days is attributed to kaolinite that was masked by amorphous material, which later was removed upon HQAc boiling.

A boiling treatment using 1 N Na-citrate (pH 7.6) was then employed to compare the products formed previously upon acid treatment with those formed upon slightly alkaline treatment. Determinations of Na were made to check for contamination from Na-citrate. Sodium citrate was chosen also because it is a complexer of Al, and thus should give insight into the proposition that hydroxy-Al groups were formed during the previous boiling treatments. The effectiveness of Na-citrate in complexing Al has been utilized in the removal of Al-interlayers from clays (Tamura, 1958).

The effect of the Na-citrate treatment on loss of K and increase

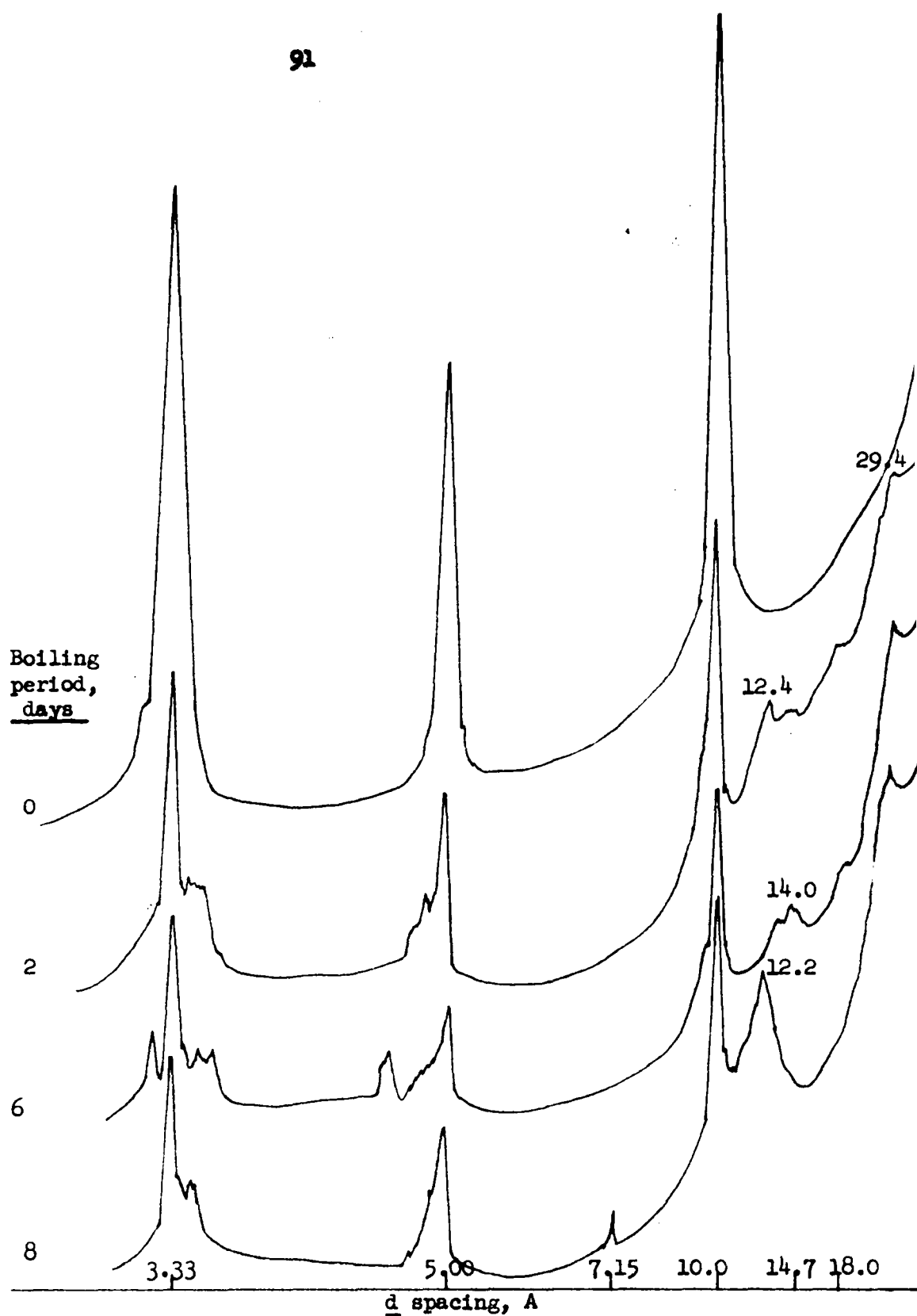


Fig. 27. Effect of N HOAc boiling treatment on Mica OR(5 - 2/u), as indicated by smoothed x-ray diffraction traces of Mg-saturated and glycerol-solvated samples.

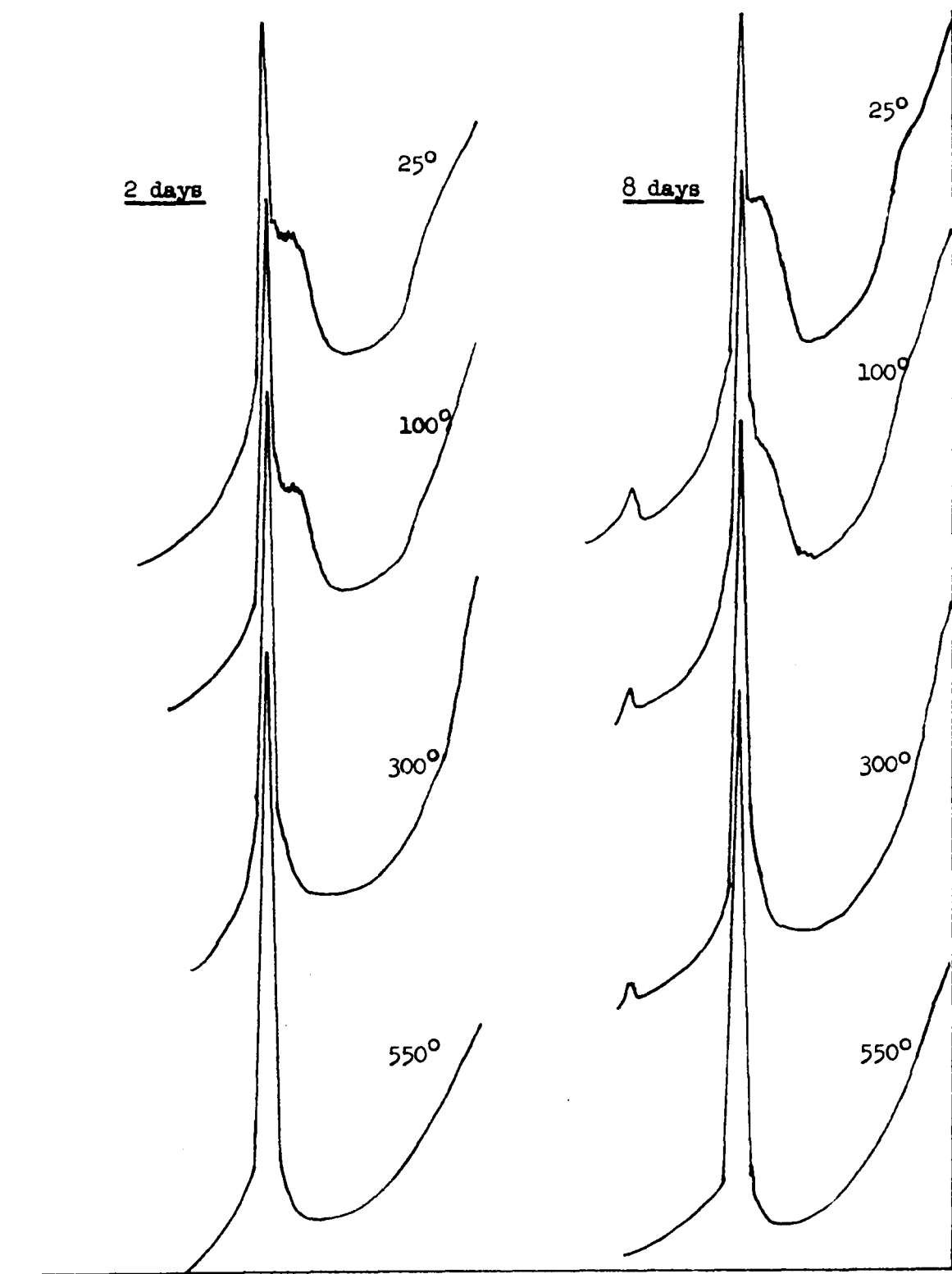


Fig. 28. Effect of K-saturation and heating on Mica OR(5 - 2/u) following HOAc boiling treatment, as shown by smoothed x-ray diffraction traces.

in CEC is shown in table 11. Whereas previous treatments removed increments of K in excess of the CEC gain, Na-citrate produced a greater CEC increase than could be accounted for by K removal. The explanation offered for this unexpected occurrence is that amorphous material, possessing no CEC, was present initially, causing the initial K content to be lower than it would have been had the sample been pure mica. As the amorphous material was removed during boiling, the percentage of K measured in the aliquot was high relative to the initial value. That amorphous materials were removed through boiling is indicated by the increase in size and intensity of the x-ray diffraction peaks after treatment compared to those before treatment.

Expansion occurred readily as a result of the Na-citrate treatment, as shown in figure 29. A vermiculitic component and a mica-vermiculite interstratification are indicated by the 14.4 Å. and 12.2 Å. spacings, respectively. The amount of interstratified material increased with time of treatment. However, the expanded material collapsed as easily after 16 days treatment as with 2 days treatment (figure 30).

An important factor in chemical reactions, e.g., weathering, is particle size. To observe the particle size effect in the boiling treatment, a sample of Mica OR, $< 2\mu$ particle size, was boiled in N Na-citrate for 8 days and observed for changes. Following NaOH treatment and free Fe removal, the sample contained 64.8 me. K/100 g. (2.53%), 68.7 me. Na/100 g. (1.58%), and had a CEC of 10.0 me./100 g. A comment on the high Na content is required. Analysis of an untreated

TABLE 11. Effect of boiling $\frac{N}{Na}$ -citrate on K and Na content and CEC of Mica OR(5-2 $\frac{11}{11}$).

Boiling period, days	K	Na	CEC	$\frac{\text{CEC gain}}{\text{K+Na loss}}$
- - - - - me./100 g. - - - - -				
0	134	9.6	9.2	--
2	112	10.4	32.5	1.06
4	102	8.8	47.3	1.19
6	96.0	11.3	52.5	1.14
8	93.2	9.2	56.5	1.16
10	91.5	10.8	58.4	1.16
12	88.8	9.6	63.5	1.18
14	88.3	9.6	65.7	1.23
16	88.0	12.1	69.0	1.30

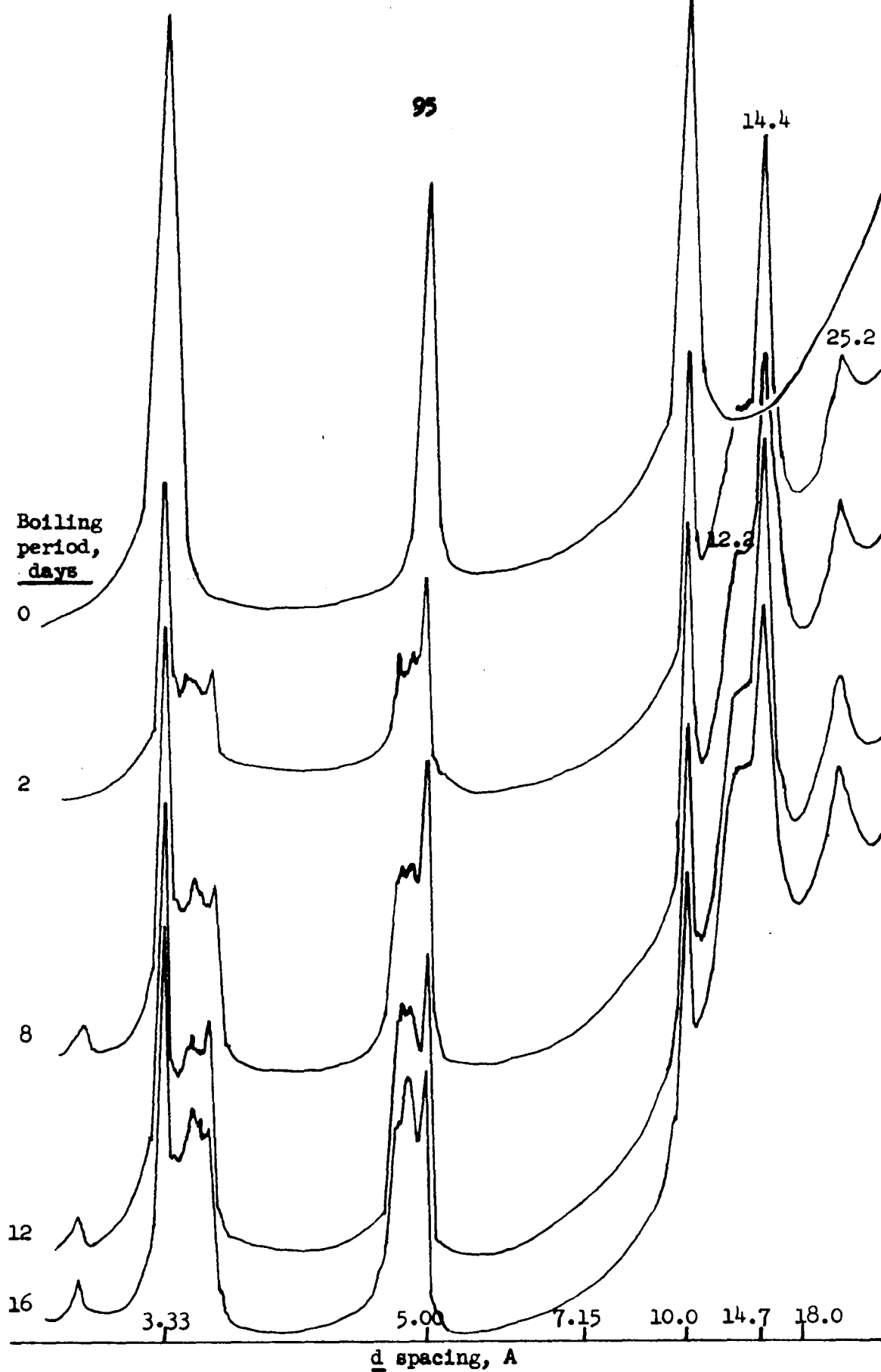


Fig. 29. Influence of boiling Na-citrate on Mica OR(5 - 2/u), as shown by smoothed x-ray diffraction traces of Mg-saturated and glycerol-solvated samples.

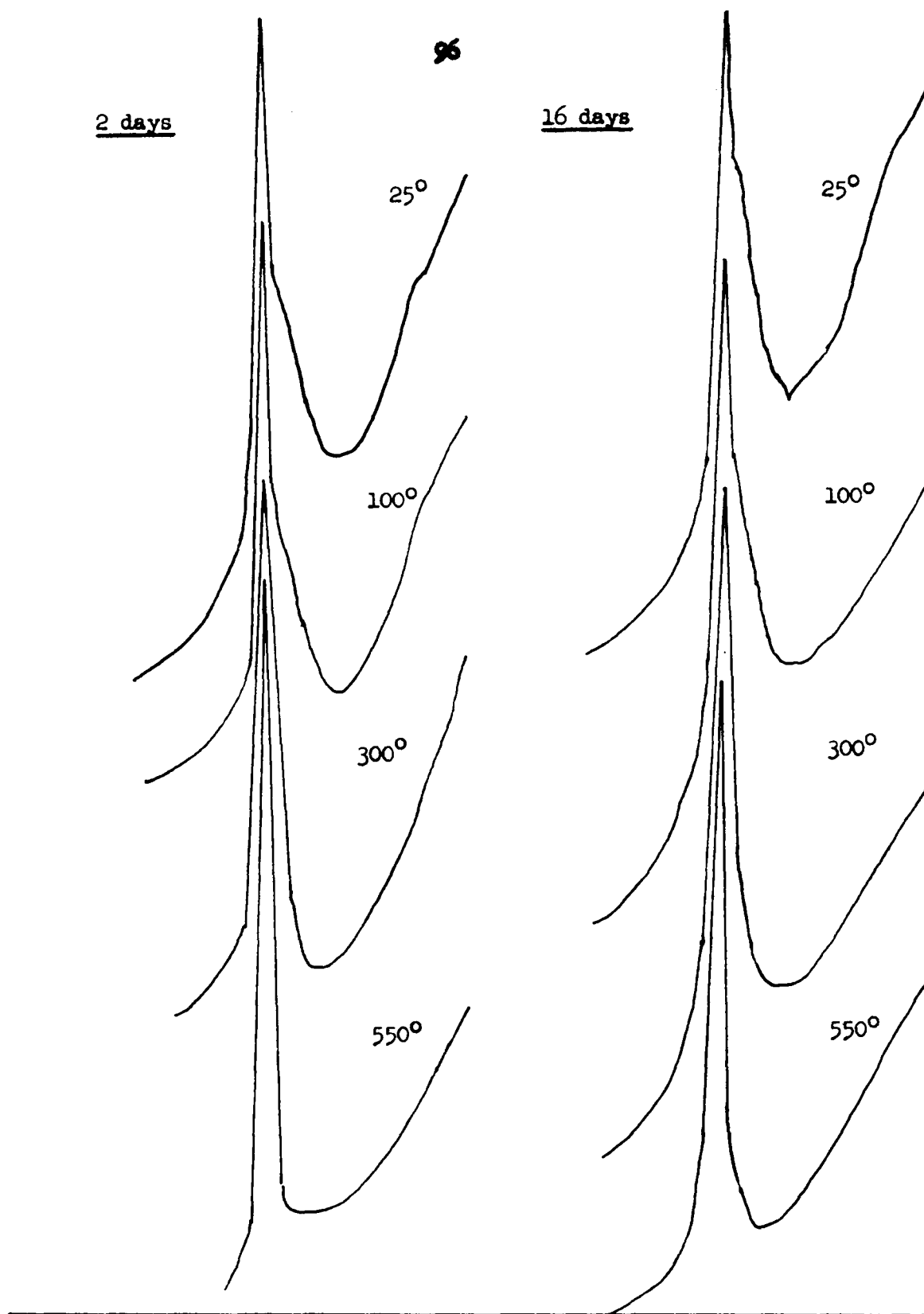


Fig. 30. Effect of K-saturation and heating on Mica OR(5 - 2/u) following Na-citrate boiling treatment, as shown by smoothed x-ray diffraction traces.

sample of $< 2\mu$ material indicated a Na content of 0.22%. Therefore, the Na apparently was incorporated into the sample during the pre-treatment. Ordinarily the free Fe was removed following heating and NaOH treatment. In this particular case, Fe was removed prior to heating, the purpose in mind being that more complete removal of kaolinite and interlayer materials should occur on Fe-free samples. Since the sample contained vermiculite, it is likely that the Na added through Na-dithionite and Na-bicarbonate in the Fe removal procedure was trapped in the vermiculite during heating.

Figure 31 shows that almost all the mica expanded to 14.2 Å. after 8 days treatment. Of interest is the increase in CEC accompanying the expansion (table 12). A gain of almost 100 me./100 g. was accomplished although only about 73 me. K+Na/100 g. was released. The only explanation offered is that enough amorphous material was present to account for the discrepancy. The removal of amorphous material is indicated in the K-saturated and heated samples (figure 32). After 8 days, the peaks were larger and sharper than after 4 days, and collapse occurred much more readily.

On the basis of CEC data and expansion characteristics, it is concluded that Na-citrate reacted differently with the micaceous material than did HOAc. The Na-citrate alteration process is pictured as one in which Na^+ ions replace K^+ ions in the interlayer position, followed by expansion of the mica structure. Expansion was easier with Na-citrate due to the greater hydrateability of Na^+ than H^+ (or H_3O^+), and the absence of interlayer blocking material.

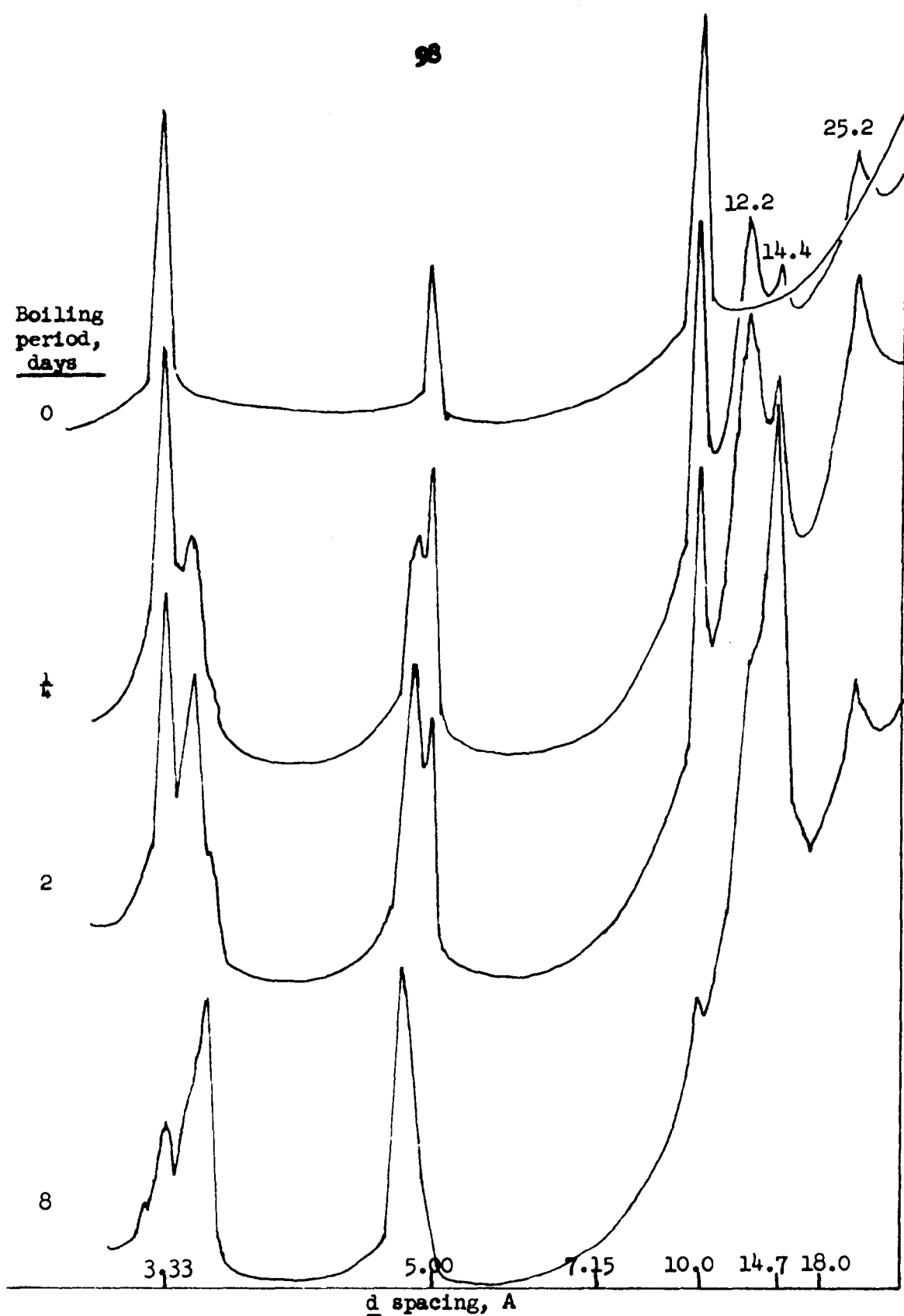


Fig. 31. Expansion of <2 μ fraction of Mica OR as a result of boiling N Na-citrate treatment, as shown by smoothed x-ray diffraction traces of Mg-saturated and glycerol-solvated samples.

TABLE 12. Effect of boiling $\underline{\text{N}}$ Na-citrate on K content and CEC of Mica OR ($< 2\mu$).

Boiling period, days	K	Na	CEC	CEC gain
				K + Na loss
		me./100 g.		
0	64.7	68.7	10.0	--
$\frac{1}{4}$	--	--	49.6	--
$\frac{1}{2}$	48.6	50.4	52.3	1.23
2	--	--	54.5	--
4	35.7	38.7	88.4	1.33
6	33.3	33.2	100	1.35
8	31.5	28.6	108	1.33

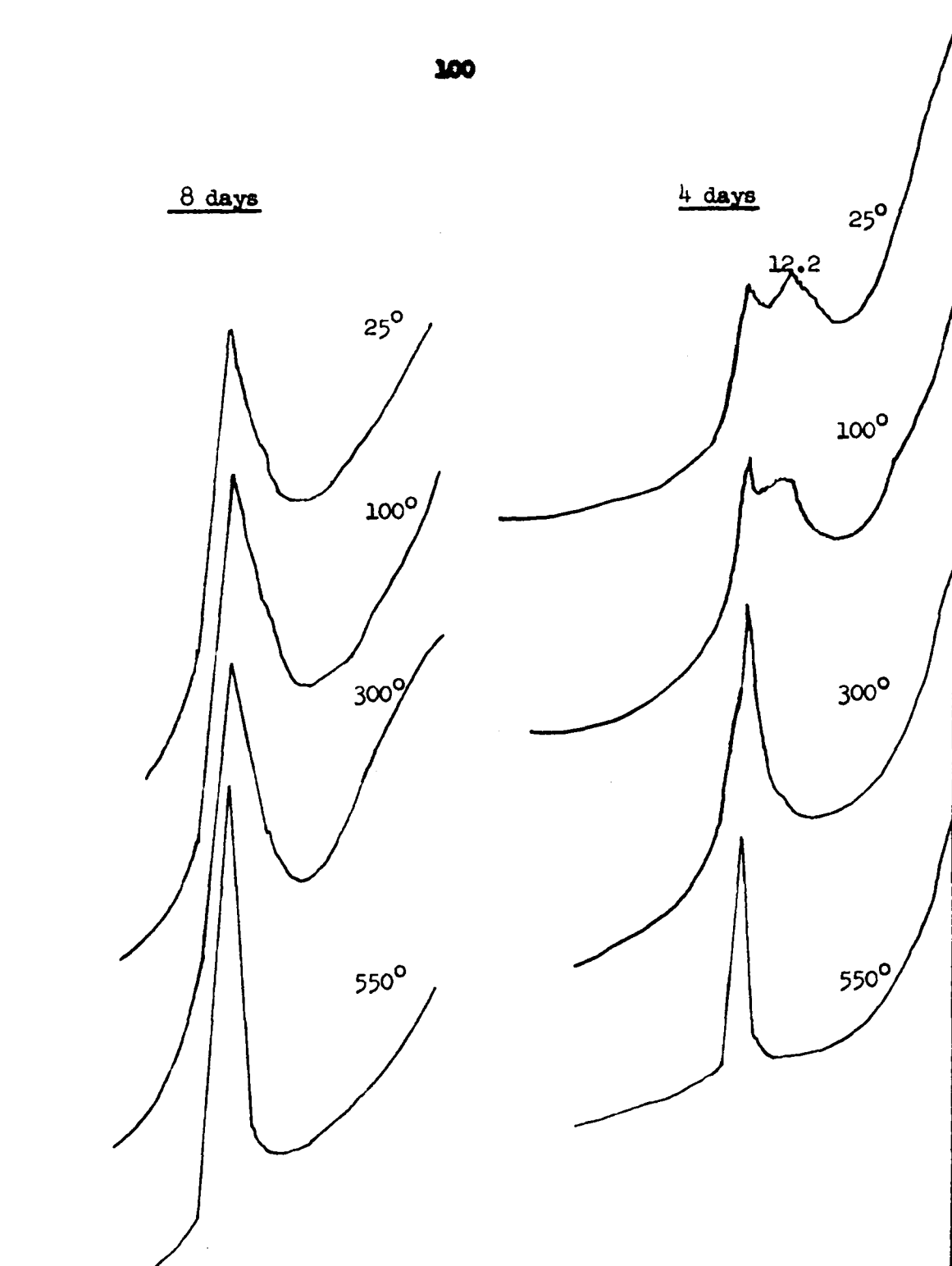


Fig. 32. Effect of K-saturation and heating on Mica OR(<2/u) following Na-citrate boiling treatment, as indicated by smoothed x-ray diffraction traces.

The absence of interlayered material, which is known to inhibit expansion as well as restrict contraction, is indicated by the high CEC of the treated material and unrestricted collapse upon K saturation. Removal of the interlayered material, which normally contains Al, was effected by complexing the Al with citrate.

An interesting feature of the products formed by the boiling treatments, particularly Na-citrate, is their similarity to the naturally weathered products formed in soils. The weathering sequence in the clay fraction of Tatum soil overlying Mica OR is shown in figure 33. The most weathered material near the surface in the $2 - 0.2\mu$ fraction of Tatum is analogous to the $5 - 2\mu$ fraction of Mica OR treated 16 days with Na-citrate. Likewise, the $0.2 - 0.08\mu$ fraction of Tatum resembles the $< 2\mu$ fraction of Mica OR treated 8 days with Na-citrate.

Hydrochloric acid treatment

Method-- A sample of Mica OR ($5 - 2\mu$) was treated with 10% HCl in a manner similar to the acid-dissolution technique employed by Osthaus (1956). A 1.0 g. sample was placed in 200 ml. of 10% HCl in a polystyrene bottle. The suspension was stirred constantly and heated at approximately 80°C. in a water bath on a steam hotplate. Aliquots were taken at various time periods and analyzed for Al, Fe, and Si. Aluminum was determined according to the method of Jones and Thurman (1957), Fe by the orthophenanthroline method described by Jackson (1956), and Si by the semimicrochemical method following Na_2CO_3 fusion of the sample (Jackson, 1956). Potassium removed was determined by

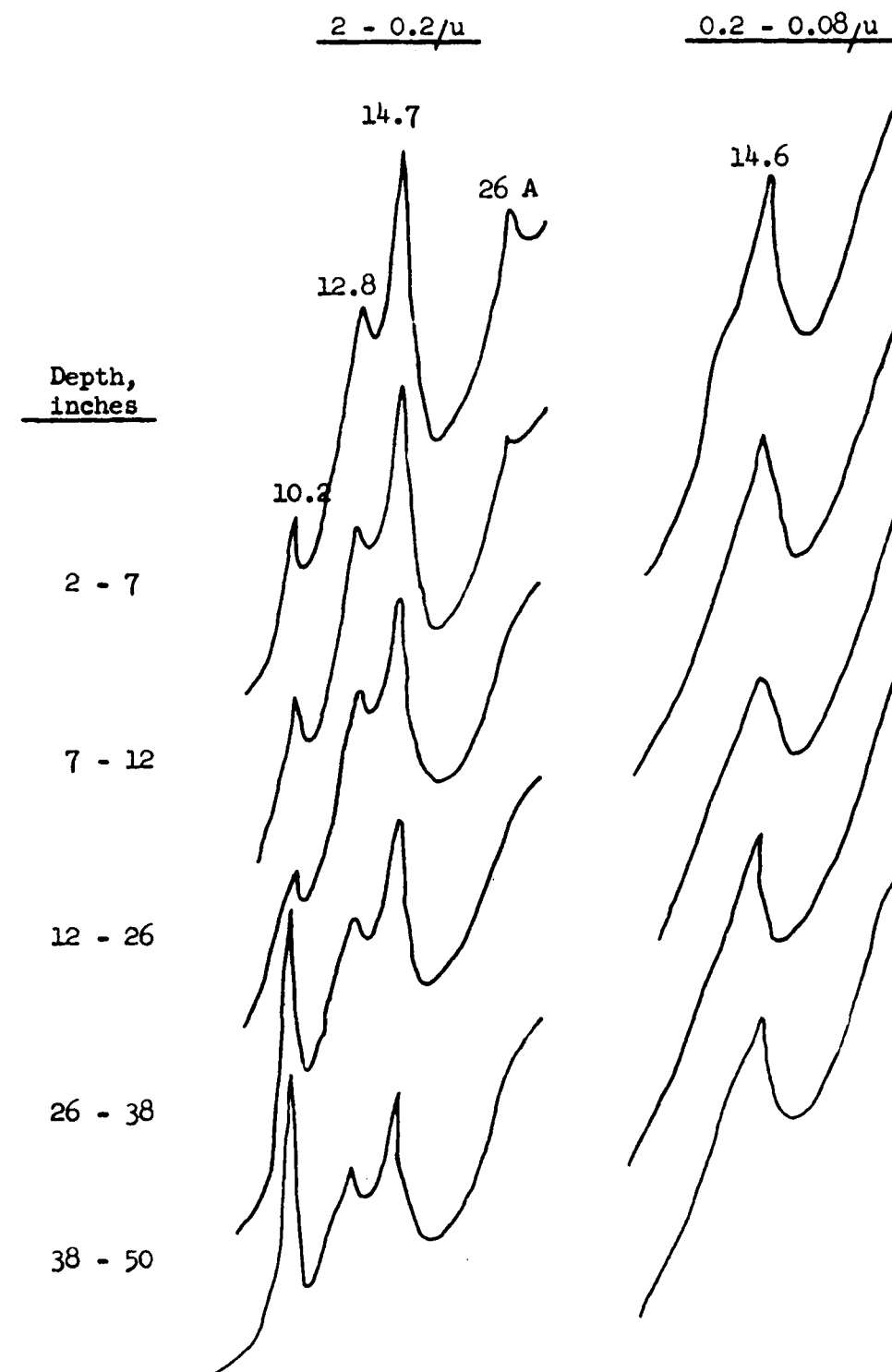


Fig. 33. Mica weathering in the clay fraction of Tatum soil, as revealed by smoothed x-ray diffraction traces of Mg-saturated and glycerol-solvated samples.

difference between K contents of the sample before and after treatment.

Results--The amounts of Al, Fe, and Si dissolved by 10% HCl are shown in table 13. Osthaus (1956), working with $<0.2\mu$ material, obtained acid-dissolution curves by plotting the logarithm of the percentage of the undissolved ion versus time. However, in this case, where $5 - 2\mu$ material was used, only very small amounts of the ions were dissolved relative to the total composition. Thus, the percentages of the undissolved ions in the final residue were not changed significantly from the original material. Therefore, the results could not be plotted like those of Osthaus. The Al and Si results were similar to those obtained by Gaines and Rutkowski (1957). They treated a sample of Ruby muscovite (100-200 mesh) with 0.1 N HCl at 25°C. and obtained a Si/Al ratio of 0.30 - 0.37 up to 24 hours treatment.

On the basis of the limited results obtained, it seems likely that acid attack occurs primarily at the edges of the particles, where the octahedral layer is exposed, and it is this layer which is attacked primarily. This conclusion was also reached by Osthaus (1956). On the basis of the coordination principles of Pauling (1960), one would expect the octahedral layer with 6-coordination to be less stable than the tetrahedral layer with 4-coordination and, thus, dissolve more readily.

The effect of 10% HCl on the mica structure is shown in figure 34. In the period up to 4 hours, a weak 18.6 Å. spacing was produced.

TABLE 13. Effect of 10% HCl on dissolution of certain elements and CEC of Mica OR (5 - 2 μ).

Length of treatment, hours	Total amount removed				$\frac{Si}{Al}$ (molar)	CEC
	Al	Si	Fe	K		
	- - - - μ g./g. - - - me./100g.					me./100g.
$\frac{1}{2}$	738	545	100	--	0.72	11.5
1	1613	563	230	--	0.33	13.0
4	3033	1100	431	--	0.35	11.7
8	4873	1440	1451	--	0.29	10.7
24	9300	5550	1831	--	0.58	10.0
36	15940	12500	1871	10	0.76	10.0

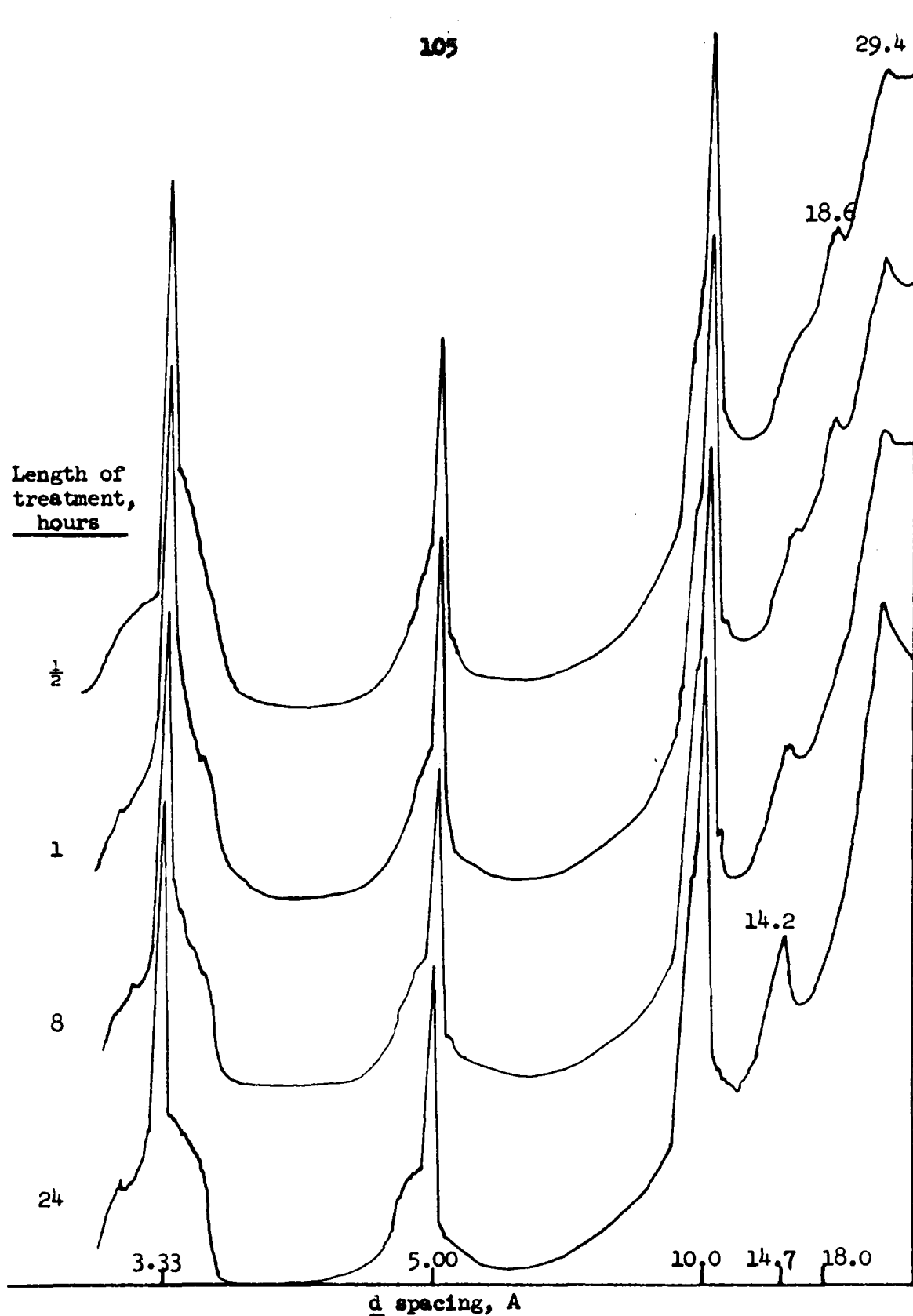


Fig. 34. Influence of hot 10% HCl treatment on expansion of Mica OR (5 - 2/u), as shown by smoothed x-ray diffraction traces of Mg-saturated and glycerol-solvated samples.

This spacing was replaced with one near 14 Å. upon further treatment. Despite the limited expansion and loss of 10 me. K/100 g., there was no increase in CEC (table 13).

To evaluate the permanent effect of the HCl treatment on expansion and CEC, the HCl-treated sample was subjected to Na-citrate boiling. Striking increases in expansion and CEC properties were observed, as shown in figure 35 and table 14. In fact, the increase in CEC was more rapid in the HCl-treated sample than in the previous sample boiled in Na-citrate (table 11). Also the loss of K proceeded more rapidly. Apparently the HCl treatment removed amorphous material, thus permitting greater reactivity between the boiling solution and mica surfaces. The effectiveness of HCl + KCl for removing interlayer material was shown by Rich and Obenshain (1955). Of great significance is the equivalence between loss of K and increase in CEC (table 14). It was suggested earlier that amorphous material could account for the non-equivalence by affecting the weight basis in calculation. This suggestion seems to be borne out in the combined HCl and Na-citrate treatments. Furthermore, it is tempting to postulate that the relationship between K loss and CEC increase is stoichiometric. Non-equivalence results when impurities, amorphous material, etc., become mixed with the mica, making it difficult to isolate the mica component for precise studies.

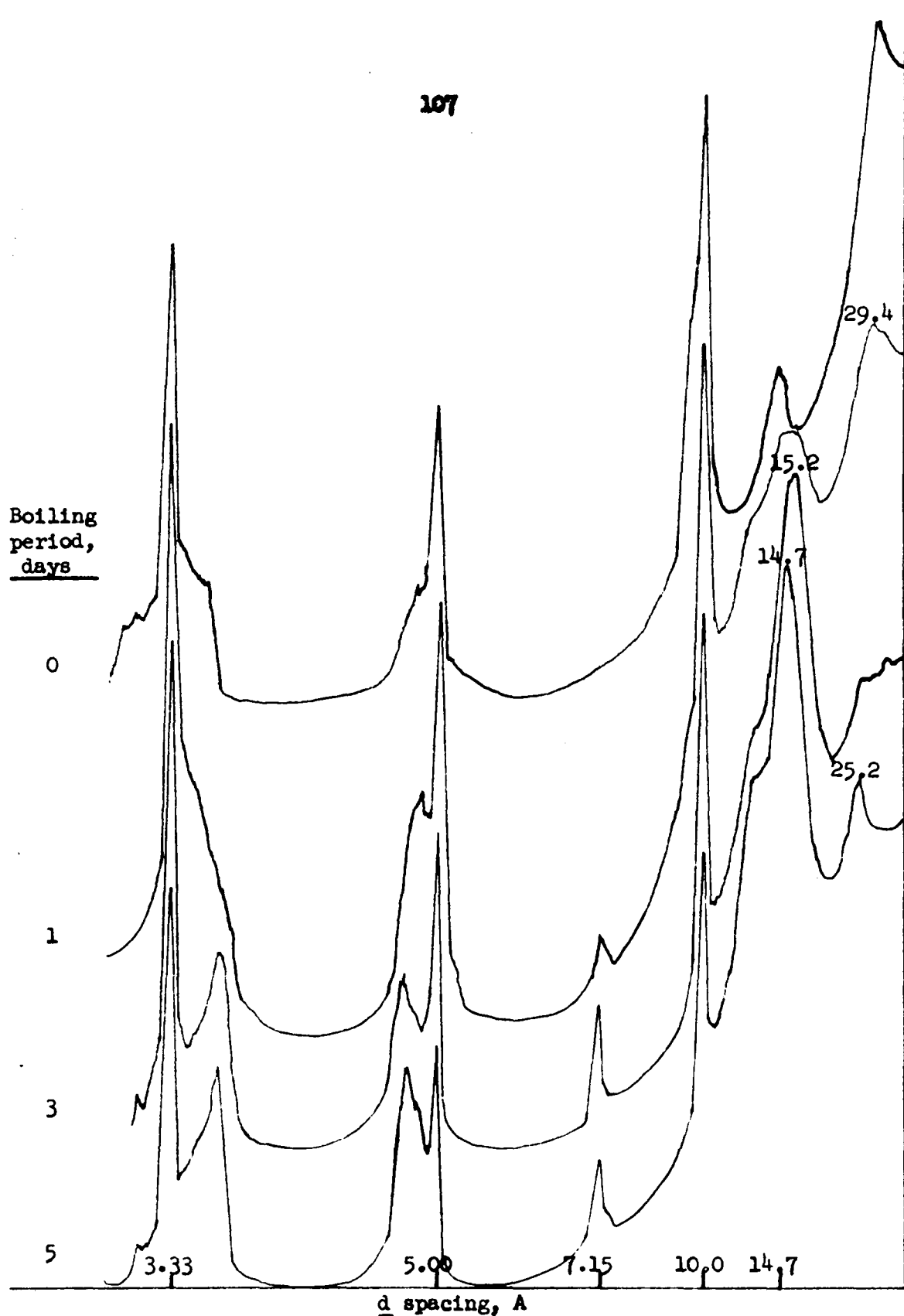


Fig. 35. Effect of boiling N Na-citrate on mica OR(5 - 2/u) previously treated with 10% HCl, as denoted by smoothed x-ray diffraction traces of Mg-saturated and glycerol-solvated samples.

TABLE 14. Effect of boiling \bar{N} Na-citrate on K content and CEC of Mica OR (5-2 μ) following 36-hour treatment with 10% HCl.

Boiling period, days	K	Na	CEC	<u>CEC gain</u> <u>K + Na loss</u>
	- - - - - me./100 g. - - - - -			
0	124	6.4	10.0	--
3	69.5	7.0	65.2	1.02
5	56.0	7.2	78.5	1.02

Mica weathering in soil from Prince William County--Preliminary studies on a micaceous soil material from Prince William County indicated the occurrence of montmorillonite. Since the association of montmorillonite with muscovite has been observed only rarely, it was felt that further study of this material would be worthwhile.

Soil samples were taken from a roadbank at the intersection of roads MCS 1 and MCS 6 on the Quantico Marine Base. Sampling was done at 2 foot intervals to a depth of 12 feet. An overburden, or 'cap', of approximately 2 feet of colluvial material affected the clay mineralogy of the upper 4 feet of soil. Since it would be very difficult to isolate the effects of clay eluviation from the overburden the upper 4-foot portion was disregarded as far as its genesis from mica is concerned. Laboratory weathering experiments were conducted on the material sampled at 12 feet. This sample will be designated Mica PW for the purposes of this investigation.

Results--The exchangeable base content and pH values for the soil are given in table 15. A very low base status is apparent, with Ca and Mg the only bases present in amounts of any consequence.

The weathering of Mica PW as a function of depth and particle size is shown in figures 36, 37, and 38. Mica is prominent in the 5 - 2μ fraction, present at only the 10- and 12-foot depths in the 2- 0.2μ fraction, and practically non-existent in the $<0.2\mu$ fraction. The weathering trend is also reflected in the K analyses of the mica, given in table 16. Figure 36 shows the occurrence of montmorillonite-like material in the 5 - 2μ fraction, which is somewhat unusual,

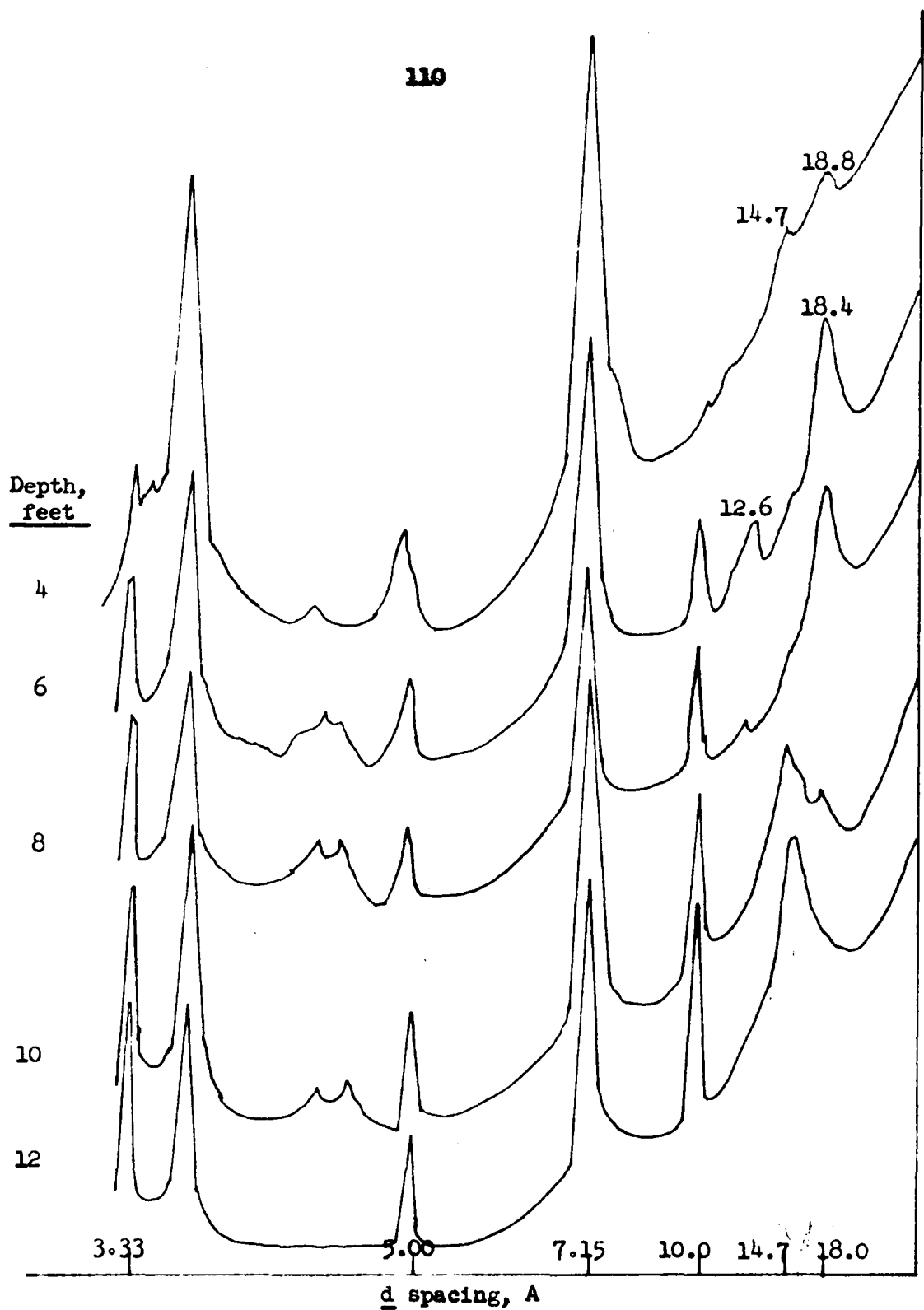


Fig. 36. Variation in weathering of 5 - 2 μ fraction of soil overlying Mica PW, as shown by smoothed x-ray diffraction traces of Mg-saturated and glycerol-solvated samples.

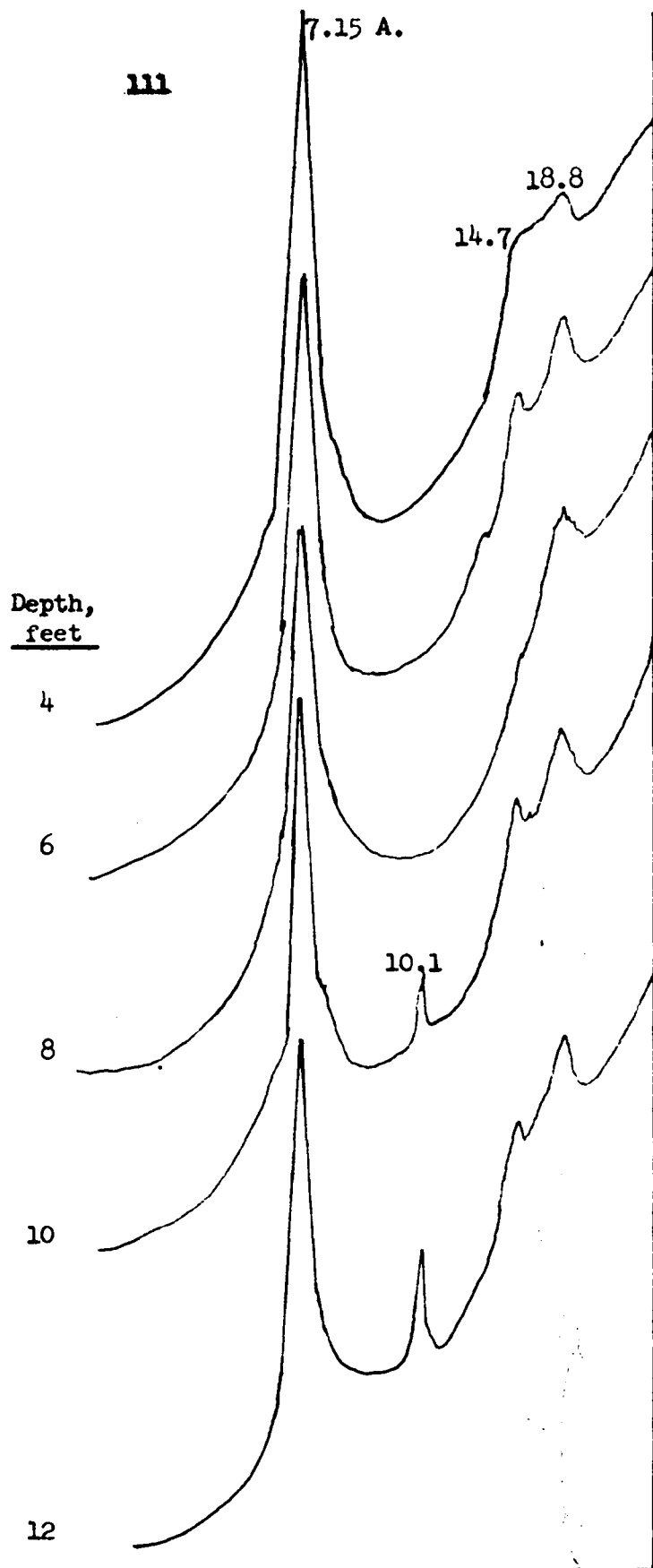


Fig. 37. Weathering sequence in 2 - 0.2 μ fraction of soil overlying Mica PW as a function of depth, as indicated by smoothed x-ray diffraction traces of Mg-saturated and glycerol-solvated samples.

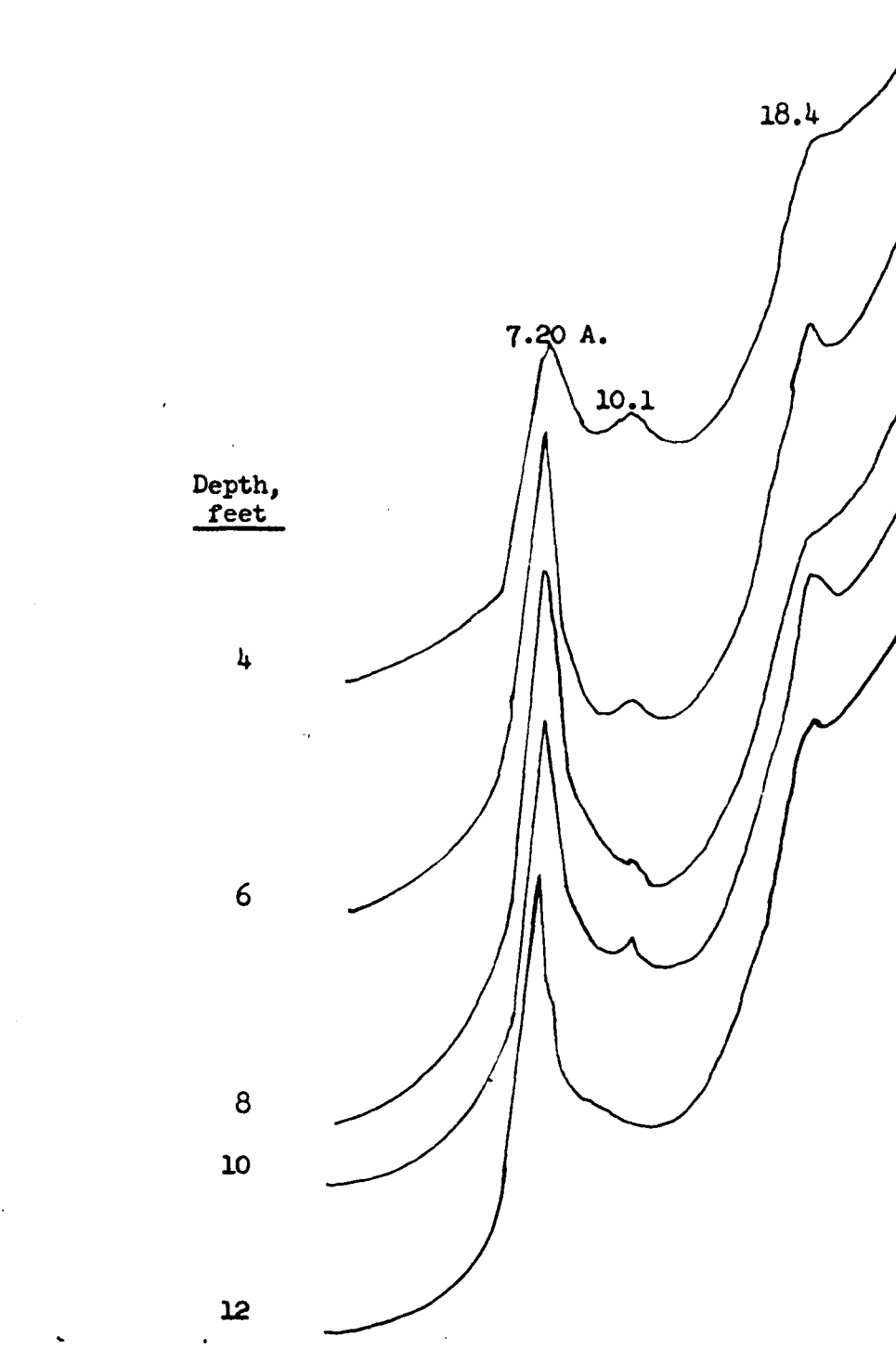


Fig. 38. Characteristics of $<0.2\mu$ fraction of soil overlying Mica PW, as indicated by smoothed x-ray diffraction traces of Mg-saturated and glycerol-solvated samples.

TABLE 15. Exchangeable base content and pH values for whole soil overlying Mica PW, as affected by depth.

Depth, feet	pH	Exchangeable bases (me./100 g.)			
		K	Na	Ca	Mg
4	5.2	0.03	0.07	0.03	0.76
6	5.2	0.02	0.07	0.08	0.97
8	5.1	0.01	0.06	0.13	1.10
10	5.3	0.01	0.08	0.40	1.23
12	5.4	0.01	0.09	0.78	1.80

TABLE 16. Contents of K and Na in Mica PW and overlying soil as a function of depth and particle size.

Depth, feet	Particle Size							
	5-2 μ				2-0.2 μ			
	K		Na		K		Na	
	%	me./100g.	%	me./100g.	%	me./100g.	%	me./100g.
4	0.68	17.4	0.17	7.37	0.33	8.45	0.12	5.20
6	0.65	16.6	0.21	9.10	0.33	8.45	0.08	3.47
8	0.89	22.8	0.28	12.1	0.34	8.70	0.08	3.47
10	0.95	24.3	0.22	9.55	0.44	11.3	0.15	6.50
12	1.52	38.9	0.24	10.4	1.55	39.7	0.13	5.64

because the fine-grained character of montmorillonite usually restricts it to the clay-sized particles ($< 2\mu$). The evidences of montmorillonite are based primarily on x-ray diffraction results and CEC measurements. Montmorillonite is characterized by its expansion to approximately 18 Å. when glycerol-solvated and by a CEC of 100-125 me./100 g. Closer examination of figure 36 indicates strongly that the mica weathers to montmorillonite. At the 12-foot depth, mica and a vermiculitic component (14.7 Å.) predominated. As weathering intensity increased up to the 6-foot depth, the mica peak decreased while the 14.7 Å. peak shifted to 18.4 Å. Very intense weathering occurred at 4 feet, as denoted by the disappearance of the mica peak and enhancement of the kaolinite peak. A similar trend was noted in the 2 - 0.2 μ fraction (figure 37). Easy collapse of the montmorillonite-like material is indicated by the x-ray diffraction traces in figures 39 and 40.

Perhaps a better clue to the magnitude of montmorillonite is given by the CEC results in table 17. The increase in CEC with decreasing particle size is attributed to montmorillonite because the highest values approximate those for montmorillonite. In the $< 2\mu$ fraction, the CEC increases with depth. This suggests that montmorillonite of that fine particle size moves down by eluviation after once being formed.

A boiling experiment using $\frac{1}{2}$ N Na-citrate was carried out on 20 - 5 μ sized material of Mica FW to see if montmorillonite would be formed. The character of Mica FW, before and after pretreatment, is

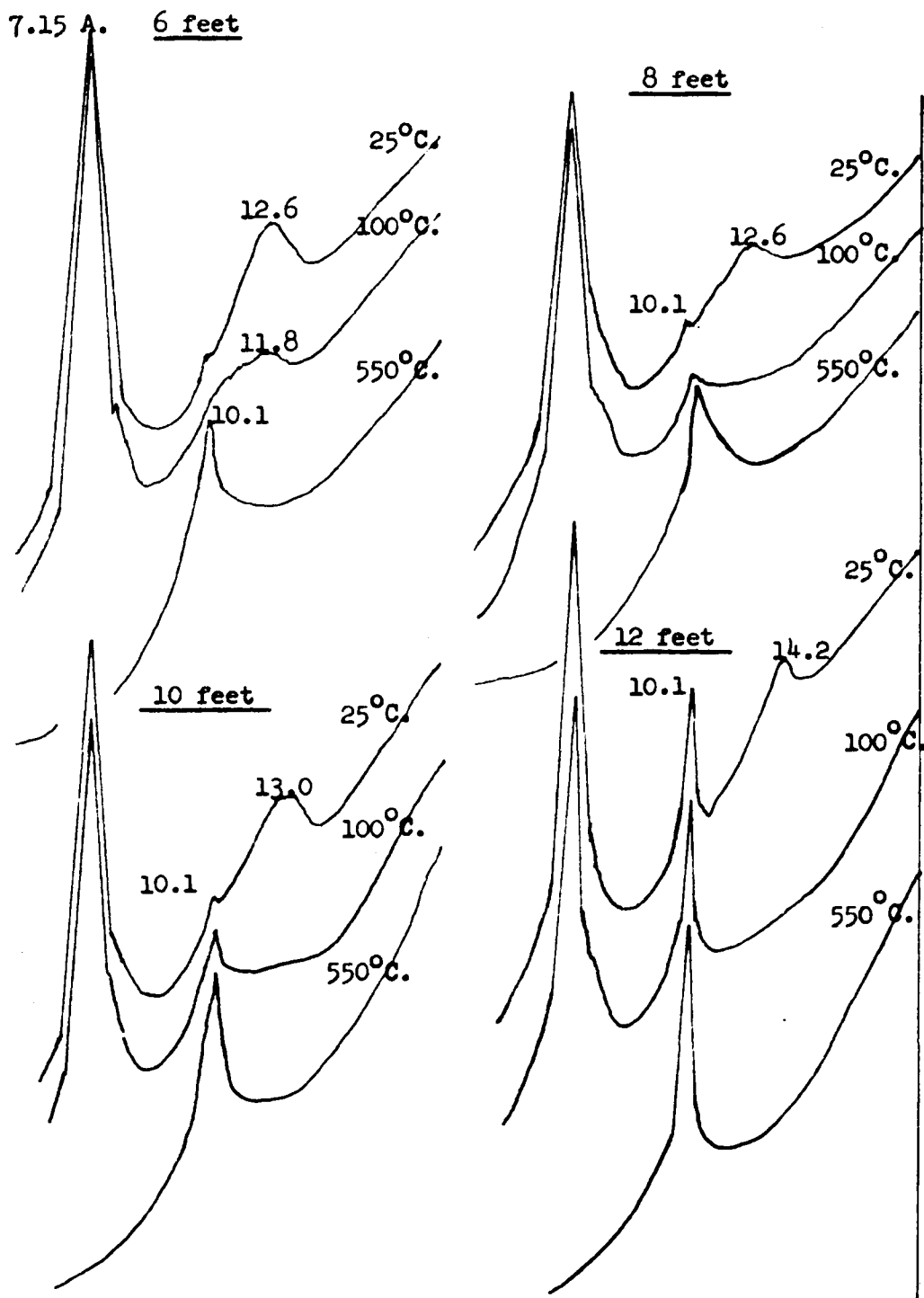


Fig. 39. Effect of K-saturation and heating on 2 - 0.2/μ fraction of soil overlying Mica PW, as denoted by smoothed x-ray diffraction traces.

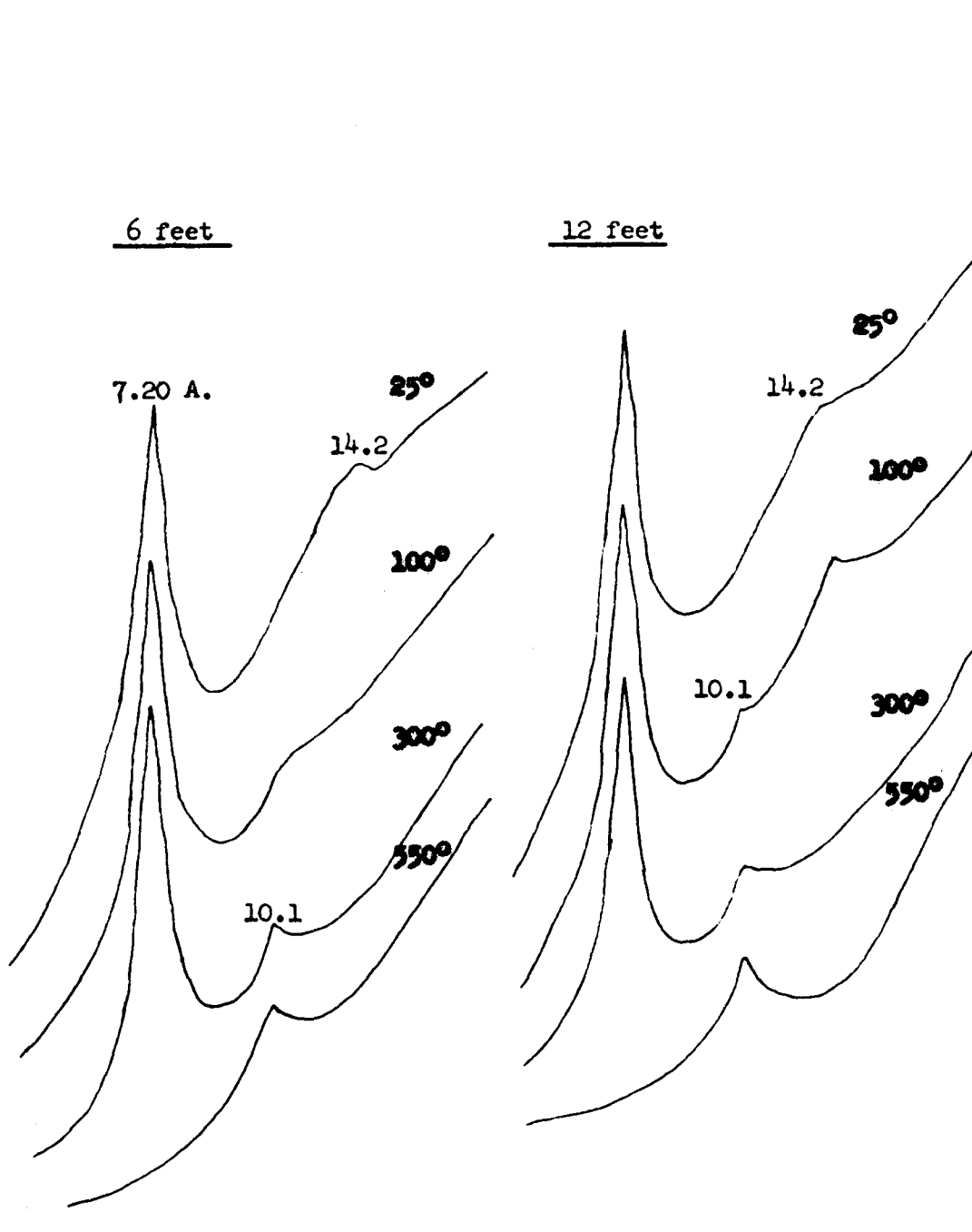


Fig. 40. Effect of K-saturation and heating on $< 0.2\mu$ fraction of soil overlying Mica PW, as revealed by smoothed x-ray diffraction traces.

TABLE 17. Cation-exchange capacities of Mica PW and overlying soil as a function of depth and particle size.

Depth, feet	Particle Size			
	20-5 μ	5-2 μ	2-0.2 μ	<0.2 μ
	- - - - - CEC (me./100 g.) - - - - -			
4	21.2	29.4	21.4	39.1
6	12.5	29.6	48.3	45.2
8	11.2	40.6	40.0	49.4
10	12.7	46.3	36.4	87.0
12	11.2	45.0	40.4	99.0

shown in figure 41. The effect of boiling N Na-citrate on Mica FW was essentially the same as that on Mica OR. A mica-vermiculite interstratification was again produced, as shown in figure 42. There was a slight broadening of the 25.2 Å. peak in the 18 Å. area, but any evidence of montmorillonite was not clear-cut. It is interesting to note the appearance of the 14.2 Å. spacing after 4 days treatment and its disappearance after 8 days treatment. Apparently the vermiculite reverted to mica. The boiling suspension was allowed to cool before removing the sample and this period of time may have been sufficiently long to allow K to re-enter the crystal. The small amount of K removed after 4 days suggests that this may have occurred (table 18). Weaver (1958) noted that there is sufficient K in sea water to reenter montmorillonite and accomplish contraction. He reached this conclusion by placing 1 g. of montmorillonite in 1 gallon of sea water and shaking the suspension mildly for 10 days. Collapse of the expanded components produced upon boiling is shown in figure 43.

The 14.2 Å. component apparently was the main source of CEC, because the CEC increased up through the 4-day treatment, then decreased sharply through 8 days (table 18). A perplexing characteristic of the mica-vermiculite intermediate (12.2 Å.) is its very low CEC. When the 14.2 Å. phase was removed, the CEC decreased sharply, despite the fact that the 12.2 Å. phase was very prominent. The CEC was checked indirectly by saturating one portion of the boiled sample with Ca^{++} and another portion with K^+ , then determining

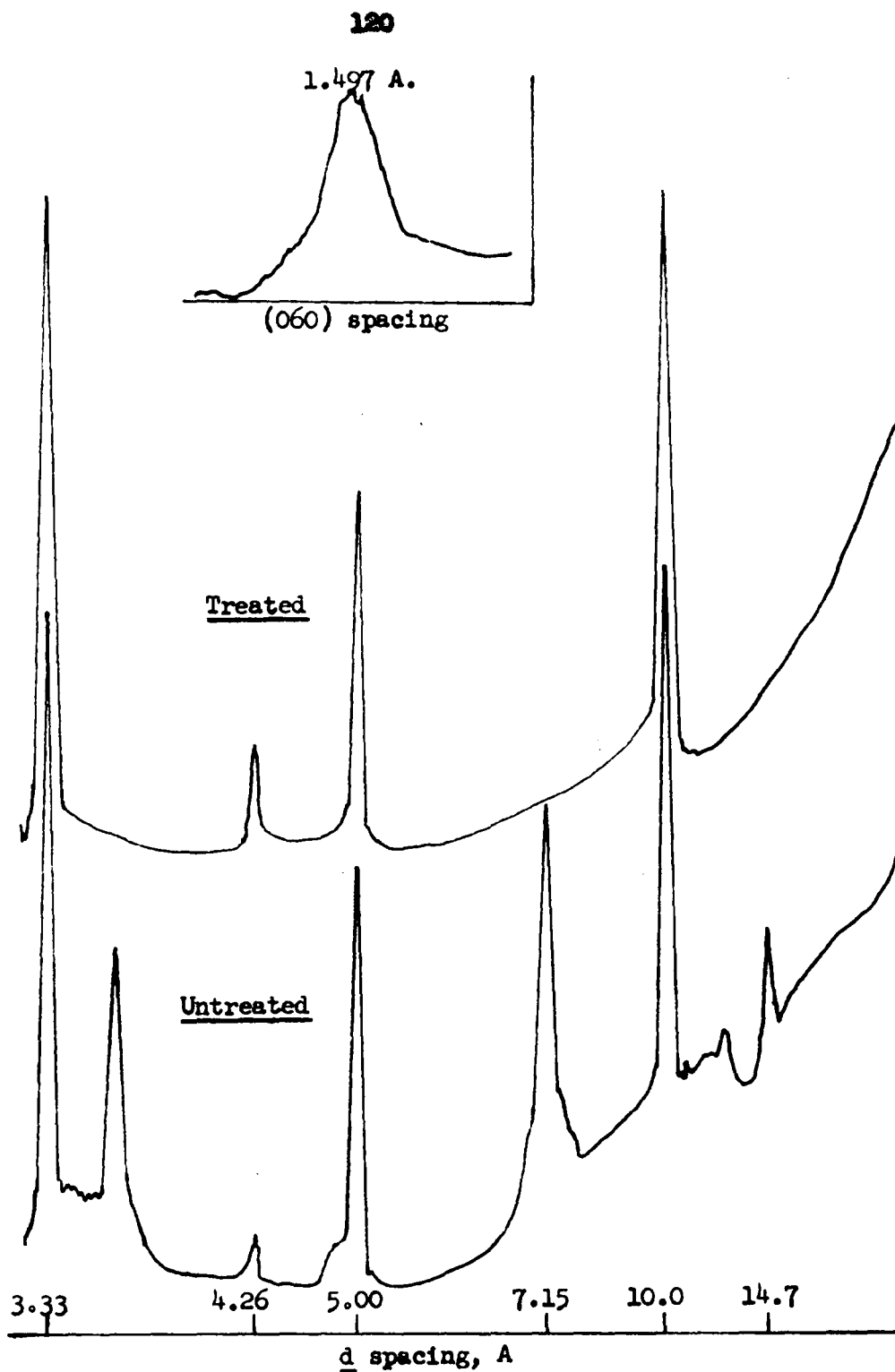


Fig. 41. Smoothed x-ray diffraction traces of Mica PW(20 - 5/u), showing effect of NaOH treatment and free Fe-oxide removal. Inset shows (060) spacing.

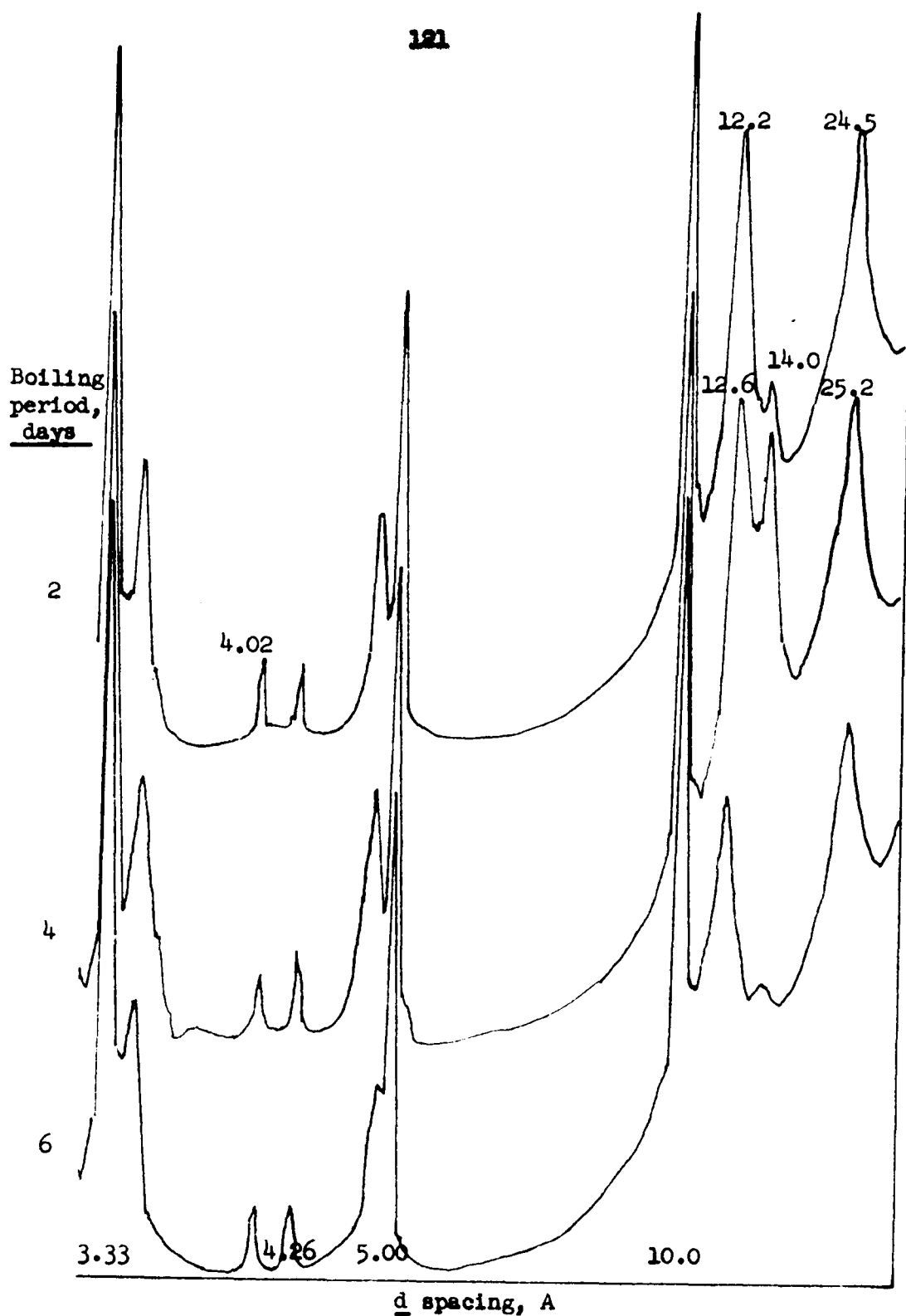


Fig. 42. Expansion of Mica PW(20 - 5/u) as a result of boiling $\underline{\text{N}}$ Na-citrate treatment, as shown by smoothed x-ray diffraction traces of Mg-saturated and glycerol-solvated samples.

TABLE 18. Effect of boiling \overline{N} Na-citrate on K and Na contents and CEC of Mica PW(20- $\overline{5}$ μ).

Boiling period, days	K	Na	K + Na	CEC	CEC gain
					K + Na loss
			-me./100 g.		
0	136	49.8	186	11.2	--
2	112	50.2	162	23.2	0.50
4	101	48.8	150	30.5	0.54
6	101	46.5	148	16.6	0.14
8	96.8	43.4	140	16.5	0.12

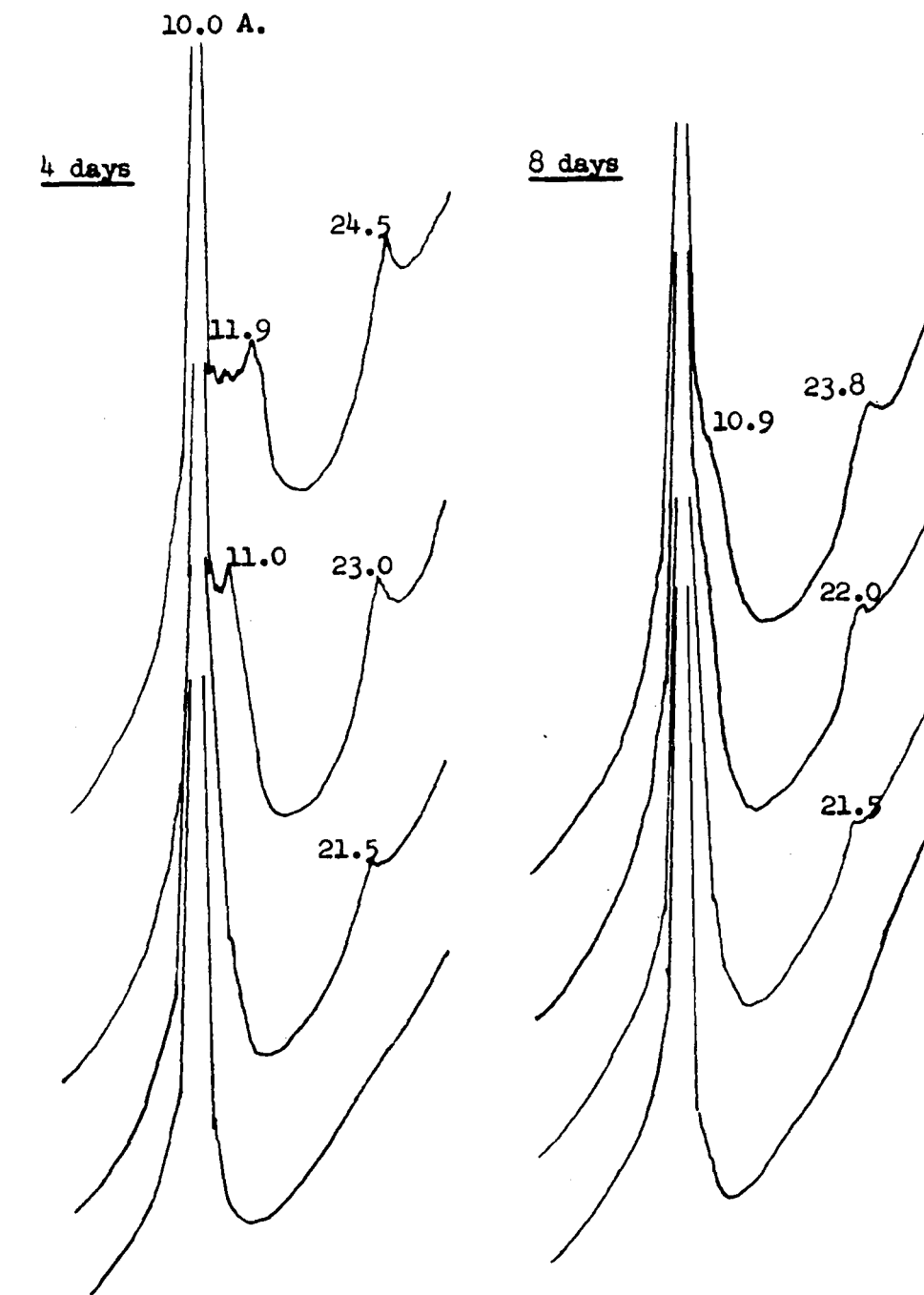


Fig. 43. Effect of K-saturation and heating on Mica PW (20 - 5/u) following N Na-citrate boiling treatment, as indicated by smoothed x-ray diffraction traces. (Tops of 10 Å. peaks omitted due to their high intensity.)

K in each portion. The amounts of K in each sample were 96.8 me./100g. and 113.8 me./100 g., respectively. The difference, or CEC, was 17.0 me./100 g., which agrees closely with the 16.5 me. CEC/100 g. obtained by the usual procedure. Another significant result of this determination was the reduction in charge of the mica as a result of the boiling Na-citrate treatment. Assuming that K was sorbed on all the exchange spots, the total K in the K-saturated sample should approximate the original total charge of the mica. However, only 113.8 me./100g. was measured in the K-saturated sample contrasted with an initial K Na content of 186 me./100 g. This indicates that some mechanism neutralized the charge within the mineral, since the 'blocking' mechanism should be inoperative in boiling Na-citrate. These results also suggest that expansion can occur without an increase in CEC, and that interlayer charge may not be the most important factor in expansion of three-layer silicates. This opinion is held by Jonas and Roberson (1960).

A puzzling observation was the weathering of Mica PW to montmorillonite, whereas the other micas studied seemed to weather to vermiculite. (It should be pointed out that the line of demarcation between montmorillonite and vermiculite may be quite vague. The terms as used here are based on degree of expansion only). One factor influencing this kind of weathering could be the composition of the original mica. It was suggested that Mica PW could be phlogopite, a trioctahedral mica containing Mg and a common source of montmorillonite. However, chemical analysis of the mica showed a Mg content of only 0.04%, and the mica was definitely dioctahedral (figure 41).

These properties would seem to preclude the possibility of phlogopite being present. Despite these facts, the higher amount of Mg relative to the other exchangeable bases in the soil (table 15) would seem to indicate mineral source of Mg. It is possible that the original mica contained both phlogopite and muscovite, with the phlogopite weathering out and leaving the muscovite mica relic. Yoder (1959) observed a mixed layering of phlogopite and muscovite, but pointed out that no continuous solid solution series exists between a dioctahedral and a trioctahedral mica. Another possibility might be that the mica contained some Mg even though it is dioctahedral. Yoder (1959) stated that slightly more than two-thirds of the octahedral sites in muscovite may be filled. In other words, muscovites as a group need not be exactly dioctahedral but may have some trioctahedral character that is difficult to detect (Yoder, 1959). This latter fact may be important since the presence of additional ions in the octahedral layer would reduce the charge on the tetrahedral layers, and thus permit expansion more readily.

Another interesting observation, which probably is associated with the montmorillonite occurrence, was the ease of weathering of Mica PW as compared to the other micas. This was very obvious in the Na-citrate boiling treatment of the 20 - 5 μ fraction. After only 2 days, considerable expansion was observed. Several factors are postulated for the easy weathering. The Mica PW may have a low charge or the seat of charge may be in the octahedral layer rather than the tetrahedral layer. Perhaps part of the mica is more weatherable than another part. This would occur if some of the mica

were phlogopite-like, as was suggested earlier.

Other laboratory treatments--Other methods of artificial weathering were attempted, but experimental difficulties prevented the collection of valid data. Experiments with sodium tetraphenylboron (NaPh_4B) were tried, in which K was precipitated as KPh_4B . Difficulty was encountered when the precipitated Na and K were brought into solution for measurement with the flame photometer. Sodium was present in such great excess that its strong background masked the K emission. Gravimetric determination on the precipitate was not attempted due to the difficulty of distinguishing KPh_4B from NaPh_4B , both of which are highly insoluble.

Leaching experiments with CO_2 -charged water, similar to the experiments of Dekeyser (1956), were attempted. Among the problems encountered were flow-rate control and CO_2 loss from the solution before reaction with the sample. The reaction also proceeds very slowly.

DISCUSSION

Alteration of Dioctahedral Micas

The processes by which micas are broken down during weathering have long been a subject of speculation. Older hypotheses assumed hydrolysis of aluminosilicates with the formation of colloidal silicic acid and aluminum hydroxide, which later reacted to give clay minerals. However, it is now known that some micas may not undergo complete breakdown of the lattice during weathering. They may alter directly to clay minerals by ionic substitution of K^+ , or other cations in the normal position of K^+ . The original sheet structure is maintained. Nevertheless, the mechanisms of ionic substitution and its consequences are not well understood.

Comparison of soil micas with muscovite--The preceding data need more substantiation, but a number of relations are apparent and some interesting speculations can be made. On the basis of both natural and artificial weathering results, it seems apparent that muscovite-type micas found in soils are quite different from the specimen-type muscovites obtainable from mineral supply houses. This difference likely is important in mica weathering studies, which heretofore have been conducted primarily on the specimen-type muscovites. The alteration and expansion characteristics of the soil micas upon boiling treatment differed from those of a well-crystallized Ontario muscovite in that the Ontario muscovite was affected only slightly by boiling treatments (Rich, unpublished date). The $LiNO_3$ treatment seemed especially illustrative of the fact that the micas are dif-

ferent. The Ontario muscovite exhibited the montmorillonite-like property of expansion to ~ 18 Å. when treated with LiNO_3 , whereas the Loudoun phyllite expanded like vermiculite to 14.7 Å. This vermiculite-like product was formed by the NaCl , MgCl_2 , and Na-citrate boiling treatments and resembled the naturally-occurring vermiculite-like product in soils. The fact that the Ontario muscovite expanded to 18 Å. is interesting from the standpoint of determining the alteration product of muscovite-type micas. The occurrence of montmorillonite-like material in Mica PW would seem to indicate that muscovite may alter to montmorillonite. Perhaps it is difficult for muscovite-like micas in soils to expand to 18 Å. due to release of Al from its original sites and subsequent fixation in interlayer positions. This fixed Al inhibits expansion beyond about 14 Å., and thus gives the expanded clay mineral formed a vermiculitic appearance. In trioctahedral micas, which contain Fe and/or Mg, this type of fixation does not occur during acidic weathering. Magnesium remains in ionic form, whereas Fe forms insoluble compounds. Therefore, the presence of Al in dioctahedral micas may be a very important factor in distinguishing the weathering of dioctahedral micas from that of trioctahedral micas.

Several possibilities may account for the differences observed. The micas studied in this investigation originated in meta-sediments, where more ionic substitution has occurred than in igneous rocks. This greater substitution would lead to a less stable mica than one found in an igneous environment. Another factor important in mica

alteration is the amount of negative charge originating in the silicate layers because of substitution and vacancies in the tetrahedral and octahedral positions. If this charge is low, there are fewer K^+ ions than there are positions in the intersilicate layer. This would give rise to a greater mobility of K^+ ions and, hence, greater susceptibility to alteration. Thus, the greater ionic substitution in soil micas may give rise to lower-charged micas than the specimen types. The weaker stability of the soil micas also could be attributed to the presence of ions other than K^+ in the interlayer position. It was found in this study that Na^+ may proxy for K^+ to a large extent, and this substitution may affect appreciably the structural relationships of the micas. A later discussion is concerned with the Na-K substitution and some of its consequences.

Muscovite-vermiculite alteration-- The results obtained from both natural and artificial weathering conditions suggest strongly that an expanded clay mineral of the vermiculite-type can form by alteration of muscovite-type mica. The formation of vermiculite from trioctahedral micas has been shown to occur in areas where trioctahedral micas can exist, e.g., the alkaline soil conditions in certain areas of the western United States. However, the micas studied in this investigation definitely were dioctahedral, as indicated by the (060) reflections.

An interesting observation resulting from the boiling treatments was the regular interstratification of mica and vermiculite. The reason for this may be attributable to the 2M structure of the micas.

In the 2M structure, the unit cell consists of a "packet" of two mica layers. Since the bond strength between the individual layers probably is different from the bond strength between the two-layer repeating units, it is likely that a plane of weakness occurs regularly between alternate layers. As a result of expansion of each alternate layer, the two-layer "packet" exhibits a spacing larger than the original mica unit cell.

Perhaps this is an indication of the manner of alteration of muscovite-type mica to vermiculite. If it is, it should be helpful in understanding how dioctahedral micas weather to vermiculite. A dioctahedral mica to vermiculite transition has been proposed only in recent years (cf., Literature Review). Previous thought on the subject was that trioctahedral micas tend to give a 14 Å mineral but that alteration of dioctahedral micas may not show well-defined steps (MacEwan, 1949).

Muscovite-kaolinite alteration--It was observed that kaolinite was always present with the vermiculite under natural weathering conditions. In fact, kaolinite often appeared before the vermiculite, indicating that it is one of the early weathering products of muscovite. This observation is in keeping with that of Sand (1956), who noted that primary muscovite always altered to kaolinite in mica deposits. He attributed the alteration to "compositional and structural control imposed by the mica", but did not elaborate on the mechanism of transfer of Si and Al from a three-layer structure to a two-layer structure. Perhaps more pertinent to this investiga-

tion is the occurrence of kaolinite rather than vermiculite in the C horizon of a Hayesville soil (Dr. R.J. McCracken, personal communication)¹. These findings suggest that kaolinite is the natural weathering product of well-crystallized muscovite and that vermiculite may be associated with smaller particle size of the mica. Bates (1960) pointed out that development of a mica intermediate is necessary for the formation of kaolinite from feldspar. He observed in Hawaii the conversion of a gibbsite-rich zone to a material rich in halloysite. This conversion took place in the absence of mica. Since K is required for development of the mica intermediate, it seems logical to associate kaolinite with the presence of K in the feldspar to muscovite alteration.

Although the mechanism involved in the muscovite to kaolinite alteration cannot be defined specifically, it seems that some general statements can be made. The necessity of a platy progenitor, muscovite or fine K-mica, suggests that kaolinite needs the basic layer-silicate structure for its formation. The hexagonal network of silica tetrahedra apparently permits a complete replacement of the vacant apical O^{--} positions by OH^- to give a kaolin crystal structure. It might be that the layer silicate network acts as a framework, on which Si-O and Al-OH groups recombine from solution.

¹ Personal communication between Dr. R.J. McCracken, North Carolina State College, and Dr. C.I. Rich, Virginia Polytechnic Institute.

In acid conditions, the tetrahedral layer should be more stable than the octahedral layer due to the high insolubility of silica in acid media. A regrouping of the fragments of the tetrahedral layer could lead to the formation of kaolinite. A similar mode of formation of the kaolinite sheet structure was suggested by DeVore (1959).

An interesting idea on kaolinite formation was proposed by Tamura and Jackson (1953), who visualized allophane, an amorphous mineral, as an intermediate product in the mica to kaolinite transition. This idea is of interest since amorphous material apparently was present in the soil micas studied.

Effect of artificial weathering on charge relationships in mica--

One of the most striking results of the investigation was the stoichiometry observed between K and Na loss and CEC gain of the Mica OR when it was boiled in Na-citrate following HCl treatment. Although more information is needed on this point, the results seem sufficient to require reconsideration of the apparent decrease in charge of dioctahedral micas during weathering. It might well be that the relationship between CEC increase and K (or other substituted ions) loss is a stoichiometric one. Difficulties arise when materials extraneous to the mica enter the system and produce non-stoichiometry by neutralizing the charge in a nonexchangeable manner or changing the weight basis of calculation.

The above example points out one of the main problems in studying mineral weathering in soils. The soil system is such a complex one that it is difficult, if not impossible, to relate what is present in soils now to what the original parent rock was thought to be prior to undergoing weathering. The approach to such a problem is usually made through an interpretation of total chemical analyses, but there are several criticisms to this approach when it is used alone. There is the question of how to allocate elemental percentages to the various mineral components, to allow for elements removed through dissolution, and to account for the effects of new minerals that are formed upon weathering of the original minerals. Through various treatments, such as those used in this study, a monomineralic specimen may be obtained, but it is doubtful that it is an exact replica of the mineral in its original state.

Comparison of artificial weathering methods--Due to the fact that the source material was not the same for all the various treatments used in this investigation, a comparison of the different methods may not be meaningful. However, it is felt that several general statements can be made relative to the greater effectiveness of certain treatments over others. In general, the boiling treatments produced greater alteration the higher the solution to sample ratio. Thus, more drastic changes can be observed by employing small (~ 20 mg.) samples in large volumes of solution.

The boiling NaCl salt solution more effectively replaced K than did Na-citrate. This is believed to be due to the greater degree of

ionization of the salt and, hence, greater ionic strength of Na^+ . Sodium-citrate is advantageous over NaCl , though, in that citrate complexes Al and Fe. This characteristic of Na-citrate makes it a better reactant from the standpoint of CEC studies. This is shown in the results of several boiling experiments (tables 11, 12, and 14). Aluminum is complexed by Na-citrate; therefore, a greater increase in CEC occurred following Na-citrate treatments than with acid treatments. But whereas the acid treatments increased the CEC much less than it decreased the K and Na contents, the Na-citrate treatment increased the CEC above the amounts of K and Na released. This latter discrepancy was accounted for on the basis of amorphous material being removed during the boiling period. It is likely that much of the amorphous material is mixed with the mica and is replaced with difficulty. Apparently the brief ($2\frac{1}{2}$ minutes) NaOH pretreatment does not remove all the amorphous material, but the prolonged boiling in Na-citrate does remove it.

From the standpoint of ionization, one might conclude that HCl should be more effective in weathering than HOAc . However, due to its greater ionization, HCl is a strong unbuffered acid. As a result, the structure of the mineral is attacked rather than substitution of interlayer ions taking place. This was exemplified in the 10% HCl treatment of Mica OR.

A criticism of all the methods employed could be that they are not representative of natural weathering conditions in soils. However, the fact that the products formed by the artificial treatments

are similar to the natural weathering products formed in soils suggests that the mechanism of mica alteration was the same. This points out the fact that the approach to a given problem must not always be a direct approach in order to give useful information.

Mechanisms of mica weathering--Finally, some speculations will be made regarding the mechanism initiating mica alteration in soils. The mechanism responsible for the initial penetration of the mica interlayers is difficult to envisage from the standpoint of relative sizes of the interlayer space and the penetrating ions. The c-spacing of muscovite is 9.94 Å. If the layers are completely closed, as in the case of pyrophyllite, the c-spacing is 9.30 Å. The difference, 0.64 Å., is approximately the distance between layers in muscovite. It is readily seen that this space will not permit entry of any of the common cations or H_2O . The only possible ion that could penetrate into the small interlayer space would be the H^+ ion, but its occurrence is doubtful. The H^+ ion has unique properties. It consists of a charged nucleus, the proton, which has no orbital electrons associated with it and so is exceedingly small. It acts rather like a dimensionless center of positive charge. In an acid solution, the fundamental ion is H_3O^+ , which is similar in size to the H_2O molecule (Pimentel and McClellan, 1960). Perhaps, then, the first step in mica weathering is not that of ion entry between the mica layers, but is some precursory action which sets the stage for ionic substitution. One possibility might be the attack of acids on the aluminosilicate framework. It will be recalled that

the 10% HCl treatment removed only a very small amount of K (10 me. /100 g.), yet there was evidence of alteration of the mica structure. The alteration probably resulted from changes in the octahedral layer, since it is attacked first by acidic solutions. If the edges of the octahedral layer are attacked first, it seems possible that dissolution of the edges of the octahedral layers would remove the 'underpinnings' from the mica structure and allow the tetrahedral layers to bend slightly toward each other. This would permit cations and H_2O molecules to enter and initiate expansion. Once the initial penetration has been made and stress placed on the interlayer surfaces, it would be expected that weathering would proceed more rapidly. After the initial entry, assuming that micas are exposed to acidic aqueous solutions during soil formation, it is possible for the H_3O^+ ion to enter between the layers, replacing K^+ ions. This replacement of K produces a strong acid, comparable in strength to perchloric acid (Pauling, 1960). As K^+ ions are released, the forces holding the layers together are weakened, the internal surface between layers becomes accessible to ions from the soil solution, and the CEC increases. It should be pointed out, however, that a H^+ - or H_3O^+ - saturated clay mineral is unstable and remains H^+ -saturated only for a short time due to the hydrolysis of Al^{+++} in the mineral (Coleman and Harvard, 1953). The hydrolysis reaction produces Al-hydroxy groups, which may be described by the general formula, $Al(OH)_n^{3-n}$. Of great importance is the fact that the Al-hydroxy groups are positively charged and thus can

satisfy the negative charge developed when the K^+ ions are released. However, when polymerized, these groups are non-exchangeable and, as a result, produce an apparent decrease in CEC. The possible role of other ions should not be underestimated. In addition to Al^{+++} and H_3O^+ in an acidic solution, Fe may influence weathering significantly through its oxidation. Potassium and Na^+ ions released from mica also are rate-determining factors, no doubt.

Examination of the nature of the mica structure has revealed certain properties that may influence the initial weathering mechanism. Macroscopically, micas exhibit smooth, even cleavage surfaces and they are assumed generally to have few irregularities along the cleavage plane. However, Tolansky (1945) showed that the surfaces of a mica sheet is violently contorted and crossed by cleavage steps, the heights of which appeared to be multiples of the c -spacing. Smith and Yoder (1956) suggested that in muscovite the sheets of tetrahedra collapse about the vacant octahedral sites and, as a result, the cleavage surfaces appear buckled. It was their view that the inferred distortion gives a direct linkage between the upper and lower surfaces of each mica layer. If their view is correct, then it seems plausible that certain stresses would exist in the dioctahedral mica structure because of the different energies of bond control. Thus, as mechanical breakage occurred, or chemical weathering took place around the edges, the bond control may shift and cause other distortions of the mica surfaces. Once there is a distortion of sur-

ficient magnitude to permit entry of cations and H_2O , weathering by ionic substitution could proceed as previously described.

Coexistent Sodium-Potassium Mica

The occurrence of the Na-mica, paragonite, in intimate association with the K-mica, muscovite, is believed to be an important finding. To the writer's knowledge, paragonite in Virginia has been reported only once previously (Dietrich, 1956). The materials studied by Dietrich were designated as Wissahickon on the Geologic Map of Virginia (Stose, 1928), the same designation given the material denoted as Candler phyllite in this study. Not only is the fact of its occurrence significant, however, but the implications regarding the role of paragonite in soil genesis are significant also.

The relatively constant 1:1 ratio of Na and K in the phyllites and soils indicate that muscovite and paragonite weather at similar rates. The interesting question arises as to the manner of mixing of the two micas that can account for this observation. The x-ray diffraction results suggest a random mixing of paragonite and muscovite. The (002) spacing of 9.80 Å. is intermediate between the muscovite (10.0 Å.) and paragonite (9.60 Å.) spacings, and the higher orders are non-integral with respect to the (002) spacing. It is believed that the 2M stacking sequence is of paramount importance and cannot be overemphasized with respect to the way alteration occurs. If weathering proceeds faster between two-layer "packets" than between individual mica layers, as suggested in the

earlier discussion, then one would expect a "stripping" of alternate layers, which would result, on the average, in equivalent amounts of K and Na being removed.

An indication of the extent of solid solution may be ascertained from the degree of shift in the c_0 spacings of the two minerals when they exist in solid solution (Eugster and Yoder, 1955). Since the shift in c -spacings was negligible, it was concluded that only a very small amount of solid solution existed within each phase. This is in agreement with the findings of Eugster and Yoder (in Abelson, 1955), who observed the smallest extent of solid solution in fine-grained micaceous phyllites than in all other types of rocks examined that contained muscovite-paragonite mixtures. Evidently, then, muscovite and paragonite occurred primarily as a mechanical mixture, but they could be mixed so intimately that separation on the basis of small differences in density is impossible.

The effect of the difference in ionic sizes of Na and K is reflected in the c_0 lattice parameter for muscovite and paragonite. The difference in c -spacing, 0.40 Å., is of the order of magnitude that would be expected from consideration of the ionic radius of Na^+ (0.97 Å.) versus that of K^+ (1.33 Å.). The a_0 and b_0 parameters are unaffected; thus, the only basic structural difference between paragonite and muscovite is the geometric configuration of the inter-layer cation and surrounding anions. As a result, the prime factor governing the rates of weathering in muscovite and paragonite should be the relative ease with which the layers contracted around the Na^+

and K^+ ions can be expanded.

In addition to the similarity in rates of weathering of muscovite and paragonite in the rocks and soils studied, the kind of weathering of the two micas appears to be similar. This conclusion is deduced from the nature of one of the weathering products, vermiculite, which has the same characteristics whether formed from a K-Na mica or a predominantly K-mica. As K^+ and Na^+ are released from their fixed interlayer positions and made exchangeable, one should expect the Na-vermiculite to be more expanded than K-vermiculite due to differences in the hydrated character of the two ions. Hofmann et al. (1956) observed that Na-vermiculite expanded to 14.9 Å. when H_2O was added, whereas K-vermiculite in H_2O had only a 10.4 Å. spacing. Perhaps the intimate mixing of the two micas inhibits the independent action of Na and K, causing the whole system to behave as if it were K-vermiculite. Furthermore, upon weathering, the mica is no longer strictly K-or Na- mica, but an Al^{+++} , $\left[Al(OH)_n\right]^{3-n}$, K, Na mica.

Excellent work on the occurrence and field relations of paragonite and the muscovite-paragonite join has been done at the Geophysical Laboratory of the Carnegie Institution of Washington by Dr. H.S. Yoder and Dr. H.P. Eugster. Reference will be made to their equilibrium diagram, reproduced as figure 44, in discussing the interrelationships between paragonite and muscovite. It is readily seen that two phases of solid solution exist, namely, paragonite in muscovite, and muscovite in paragonite. The maximum amount of solid

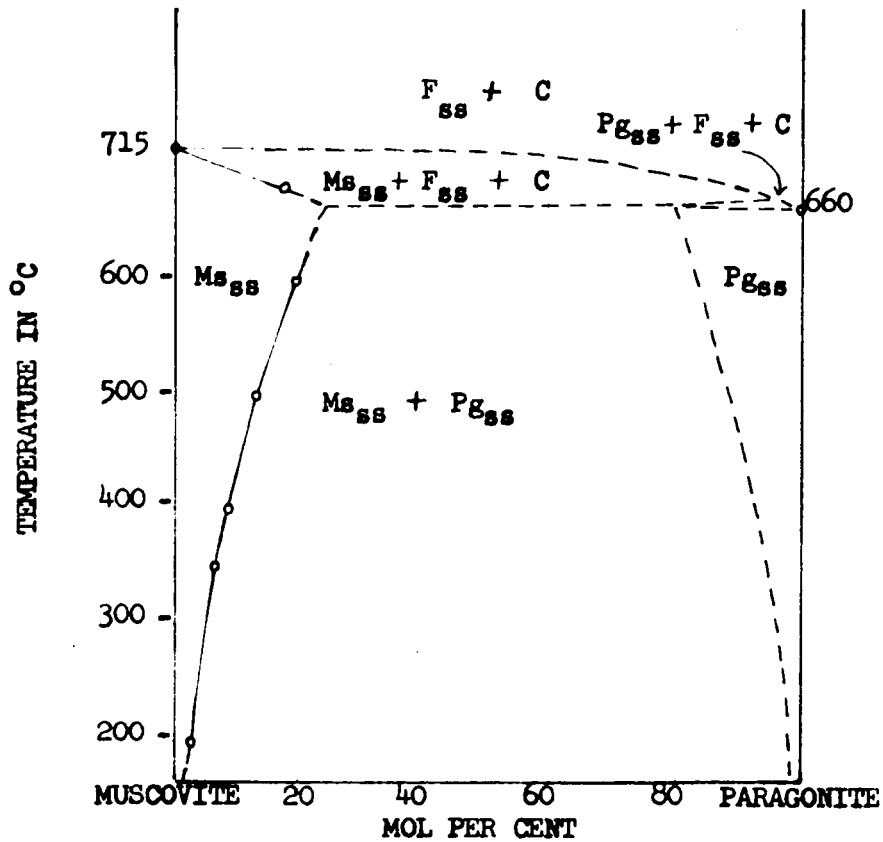


Fig. 14. Preliminary phase diagram for the subsolidus region of the muscovite-paragonite join (after Eugster and Yoder, in Abelson, 1955.)

solution is very limited within each phase, only about 20 mol per cent at the highest temperature. This is further indication that the micas studied are essentially mixtures of the two phases of solid solution, which consist primarily of muscovite and paragonite, respectively.

Referring to figure 44 again, it can be deduced from the position of the determined points that a mixture of paragonite and muscovite breaks down at a slightly lower temperature than a pure muscovite. Although the temperatures of concern in soils are much less than the decomposition temperature, one may assume from the diagram that the addition of Na to muscovite decreases the stability of muscovite. As indicated earlier, the Na^+ ion (0.97 Å.) is considerably smaller than the K^+ ion (1.33 Å.). It is apparent, therefore, that in the solid solution consisting primarily of K, K_{Na} , the Na^+ ions could oscillate more easily than the K^+ ions and, hence, could exchange more readily. Such a mica would be weathered easier than either pure muscovite or paragonite. Moreover, it is likely that the predominantly paragonite phase of solid solution, Na_K , would weather more easily than either pure muscovite or paragonite because such a mica is under a strain to expand to a K^+ -size interlayer and in doing so, the Na^+ would be more easily removed. In both cases K_{Na} and Na_K , as soon as the Na^+ begins to come out, there is more expansion and K^+ also is exchanged.

It is very probable that the mixed composition of the micas accounts for their rapid alteration in the laboratory boiling experi-

ments, whereas specimen-type muscovites were highly resistant to such treatments. Nevertheless, the stability of the Na-K mica apparently is very high. This is indicated by its persistence in the surface horizons of soils despite the fact that weathering forces have been in action for millions of years.

It is a moot point whether the presence of paragonite in mica-ceous soil parent material justifies a reclassification of the soils overlying it. The micas in the Piedmont area have always been considered to be K-micas only. Many studies (e.g., Reitemeier et al., 1951) have indicated varying degrees of availability to plants of K released from mica during weathering. However, Na may not be used by plants in the same way as K. Thus, from an inherent fertility standpoint, soils developed from paragonite or paragonite-muscovite mixtures may be quite different from those developed from muscovite.

SUMMARY

One of the purposes of this investigation was to examine the apparent non-stoichiometric relationship between loss of K and increase in CEC of dioctahedral micas during weathering. The problem was approached from the standpoint of artificially weathering relatively pure soil micas in the laboratory and following the loss of K (and Na in certain cases) and increase in CEC. Micas used in the artificial weathering studies consisted of a phyllite from Orange County and two micaceous samples from soil parent material in Orange County and Prince William County.

The most fruitful results were obtained from boiling the micas in various kinds of solutions. The results of the boiling treatments are summarized as follows:

1. Boiling 0.20 N HOAc released considerable amounts of K and Na, produced slight expansion of the mica, but no increase in CEC resulted. The high acidity apparently released large amounts of Al, which hydrolyzed later to form non-exchangeable, positively charged Al-hydroxy groups that blocked the exchange sites.

2. Boiling 5 N NaCl and 5 N MgCl₂ removed K preferentially to Na, produced considerable expansion, but the CEC increased only about 1/3 the amounts of K and Na removed. The reason for the small increase in CEC was believed to be due also to the blocking mechanism of hydroxy-Al groups. This is supported by the fact that salts tend to enhance Al-hydrolysis.

3. Boiling M Na-citrate removed K effectively, produced significant expansion, and increased the CEC more than could be accounted for by K loss. The high CEC probably resulted from the complexing of Al by citrate.

4. Removal of amorphous material with 10% HCl prior to Na-citrate boiling helped achieve stoichiometry between K loss and CEC gain. Therefore, amorphous material probably is more important in weathering than previously recognized.

5. Boiling treatments caused the formation of vermiculitic material resembling that found naturally in soils. This suggests that the mechanism of mica alteration in the artificial treatments is similar to that occurring in nature.

6. Soil micas weathered more easily than an Ontario muscovite. This indicates that soil micas may be quite different from specimen muscovites. Reasons which could account for this difference are a lower charge in the soil micas and perhaps less structural control than in the specimen-type muscovite micas.

7. Differences in weathering of dioctahedral and trioctahedral micas likely are due to the Al in dioctahedral micas. In addition to its greater ionic bonding than Fe or Mg, Al also hydrolyzes, which encourages the formation of hydroxy-Al polymers.

The second part of the investigation developed as a result of the interesting and significant occurrence of paragonite in association with muscovite in phyllites and soils. The following conclusions

were made from this part of the study:

1. Paragonite and muscovite occurred in a 1:1 molar ratio in the phyllites and soils. This seems to indicate similar weathering of the two micas, and also suggests that paragonite has a rather persistent nature.

2. Paragonite perhaps is of wider occurrence than previous work has indicated. Its influence in soil formation may be significant,

LITERATURE CITED

- Abelson, P.H. 1954. Annual Report of the Director of the Geophysical Laboratory, 1953-54. Carnegie Institution of Washington Yearbook No. 53, pp. 95-145.
- Abelson, P.H. 1955. Annual Report of the Director of the Geophysical Laboratory, 1954-55. Carnegie Institution of Washington Yearbook No. 54, pp. 95-152.
- Aguilera, M.H., and Jackson, M.L. 1953. Iron oxide removal from soils and clays. Soil Sci. Soc. Amer. Proc. 17:359-364.
- Andreatta, C. 1949. A new type of illite-hydromica in a hydrothermal deposit. Clay Minerals Bull. 1:96-99.
- Andrew, R. W., Jackson, M. L., and Wada, K. 1960. Intersalation as a technique for differentiation of kaolinite from chloritic minerals by x-ray diffraction. Soil Sci. Soc. Amer. Proc. 24:422-424.
- Bannister, F. A. 1943. Brammallite (sodium-illite), a new mineral from Llandeby, South-Wales. Mineral. Mag. 26:304-307.
- Barshad, I. 1949. Vermiculite and its relation to biotite as revealed by base-exchange reactions, x-ray analyses, differential thermal curves, and water content. Amer. Mineral. 33:655-678.
- Barshad, I. 1950. The effect of interlayer cations on the expansion of the mica type of crystal lattice. Amer. Mineral. 35:225-238.
- Barshad, I. 1954. Cation exchange in micaceous minerals. II. Replaceability of ammonium and potassium from vermiculite, biotite and montmorillonite. Soil Sci. 78:57-75.
- Barshad, I. 1960. X-ray analysis of soil colloids by a modified salted paste method. 7th National Conference on Clays and Clay Minerals, pp. 350-364. Pergamon Press, New York.
- Bassett, W.A. 1960. Role of hydroxyl orientation in mica alteration. Bull. Geol. Soc. Amer. 71:449-456.
- Bates, T.F. 1960. A mineralogical study of parent rock to clay mineral alteration in the Hawaiian Islands. Mimeographed report to the National Science Foundation, Contract G 5809.
- Berry, L.G., and Mason, B. 1959. Mineralogy. W.H. Freeman and Co., San Francisco.

- Brammell, A., Leech, J.G.C., and Bannister, F.A. 1937. The paragenesis of cookeite and hydromuscovite associated with gold at Ogofau, Carmarthenshire. *Mineral. Mag.* 24:507-520.
- Brown, G. 1953. The dioctahedral analogue of vermiculite. *Clay Minerals Bull.* 2:64-70.
- Brown G., and MacEwan, D.M.C. 1951. X-ray diffraction by structures with random interstratification, in X-ray Identification and Crystal Structures of Clay Minerals, Chap XI. Mineralogical Society of Great Britain Monograph.
- Brown, G., and Norrish, K. 1951. Hydrous Micas. *Mineral. Mag.* 29:929-932.
- Brown, W.R. 1958. Geology and Mineral Resources of the Lynchburg Quadrangle, Virginia. Virginia Div. of Mineral Resources Bull. 74.
- Clarke, F.W. 1924. The Data of Geochemistry. U.S. Geol. Survey Bull. 770, 5th Ed.
- Coleman, M.T., and Harward, M.E. 1953. The heats of neutralization of acid clays and cation-exchange resins. *Jour. Amer. Chem. Soc.* 75:6045-6046.
- Corey, R.B., and Jackson, M.L. 1953. Silicate analysis by a rapid semimicrochemical system. *Analyt. Chem.* 25:624-628.
- Dekeyser, W. 1956. Clay minerals research at Ghent University. Proc. 4th Natl. Conf. on Clays and Clay Minerals, Natl. Acad. Sci.-Natl. Research Council Publ. 456:372-380.
- Dekeyser, W., Van Keymeulen, J., Hoebeke, F., and van Rijssen, A. 1958. L'alteration et l'évolution des minéraux micacés et argileux. *Compt. rend, recherches Inst. encouragement recherches sci, ind. et agr.* 14:91-101.
- Dehnumbrum, L.E. 1959. Exchangeable potassium levels in vermiculite and K-depleted micas, and implications relative to potassium levels in soils. *Soil Sci. Soc. Amer. Proc.* 23:192-194.
- Denison, J.A., Fry, W.H., and Gile, P.L. 1929. Alteration of Muscovite and Biotite in the Soil. USDA Tech. Bull. 128.

- DeVore, G.W. 1959. The surface chemistry of feldspars as an influence on their decomposition products. 6th Natl. Conf. Clays and Clay Minerals, pp. 26-41. Pergamon Press, New York.
- Dietrich, R.V. 1956. Trigonal paragonite from Campbell and Franklin Counties, Virginia. *Amer. Mineral.* 41:940-941.
- Droste, J.B., and Tharin, J.C. 1955. Alteration of clay minerals in Illinoian till by weathering. *Bull. Geol. Soc. Amer.* 69: 61-68.
- Erdélyi, J., Koblenz, V., and Tolnay, V. 1958. Über hydroparagonit, ein neues glimmer-mineral, sowie über seine beziehungen zum hydromuskovit, natronillit und brammalit. *Acta Geologica* 5:168-186.
- Fieldes, M., and Swindale, L.D. 1954. Chemical weathering of silicates in soil formation. *New Zealand Jour. Sci. Tech.* 36B: 140-154.
- Gaines, G. L., Jr. 1957. The ion-exchange properties of muscovite mica. *Jour. Phys. Chem.* 61:1408-1413.
- Gaines, G.L., Jr., and Rutkowski, C. P. 1957. The extraction of aluminum and silicon from muscovite mica by aqueous solutions. *Jour. Phys. Chem.* 61:1439-1440.
- Galpin, S.L. 1912. Studies of flint clays and their associates. *Amer. Ceramic Soc. Trans.* 14:301-346.
- Ganguly, A.K. 1951. Hydration of exchangeable cations in silicate minerals. *Soil Sci.* 71:239-244.
- Gardiner, R.F., and Shorey, E.C. 1917. The actions of solutions of ammonium sulfate on muscovite. *Jour. Ind. Eng. Chem.* 9:589-590.
- Garrels, R.M., and Howard. p. 1959. Reactions of feldspar and mica with water at low temperature and pressure. *Proc. 6th Natl. Conf. Clays and Clay Minerals*, pp. 68-88. Pergamon Press, New York.
- Goldich, S.S. 1938. A study in rock weathering. *Jour. Geol.* 46:17-58.
- Grim, R. E., and Bradley, W.F. 1948. Rehydration and dehydration of the clay minerals. *Amer. Mineral.* 33:50-59.

- Grim, R.E., Bradley, W.F., and Brown, G. 1951. The mica clay minerals, in X-ray Identification and Crystal Structure of Clay Minerals, Chap. V. Mineralogical Society of Great Britain Monograph.
- Grim, R.E., Bray, R.H., and Bradley, W.F. 1937. The micas in argillaceous sediments. *Amer. Mineral.* 22:813-829.
- Gruner, J.W. 1942. Conditions for the formation of paragonite. *Amer. Mineral.* 27:131-134.
- Hashimoto, I., and Jackson, M.L. 1960. Rapid dissolution of allophane and kaolinite-halloysite after dehydration. *Proc. 7th Natl. Conf. Clays and Clay Minerals*, pp. 102-113. Pergamon Press, New York.
- Hathaway, J.C. 1955. Studies of some vermiculite-type clay minerals. *Proc. 3rd Natl. Conf. Clays and Clay Minerals*, Natl. Acad. Sci.-Natl. Research Council Publ. 395:74-86.
- Hendricks, S.B., and Jefferson, M.E. 1939. Polymorphism of the micas. *Amer. Mineral.* 24:729-771.
- Hickling, G. 1908. China-clay and its nature and origin. *Inst. Mining Engr. Trans.* 36:10-32.
- Hofmann, U., Weiss, A., Koch, G., Mehler, A., Scholz, A. 1956. Intracrystalline swelling, cation exchange, and anion exchange of minerals of the montmorillonite group and of kaolinite. *Proc. 4th Natl. Conf. Clays and Clay Minerals*, Natl. Acad. Sci.-Natl. Research Council Publ. 456:273-287.
- Hsu, P. H., and Rich, C. I. 1960. Aluminum fixation in a synthetic cation exchanger. *Soil Sci. Soc. Amer. Proc.* 24:21-25.
- Jackson, M.L. 1956. Soil Chemical Analysis--Advanced Course. Mimeograph. Published by the author. Madison, Wisconsin.
- Jackson, M. L. 1958. Soil Chemical Analysis. Prentice-Hall, Englewood Cliffs, N.J.
- Jackson, M. L. 1959. Frequency distribution of clay minerals in major Great Soil Groups as related to the factors of soil formation. *Proc. 6th Natl. Conf. Clays and Clay Minerals*, pp. 133-143. Pergamon Press, New York.

- Jackson, M. L., Hseung, Y., Corey, R.B., Evans, E.J., and Vanden Neuvel, R.C. 1952. Weathering sequence of clay-size minerals in soils and sediments. II. Chemical weathering of layer silicates. *Soil Sci. Soc. Amer. Proc.* 16:3-6.
- Jackson, M.L., and Truog, E. 1939. Influence of grinding soil minerals to near molecular size on their solubility and base exchange properties. *Soil Sci. Soc. Amer. Proc.* 4:136-143.
- Jackson, W.W., and West, J. 1931. The crystal structure of muscovite-- $KAl_2(AlSi_3)O_{10}(OH)_2$. *Ztschr. Krist.* 76:211-227.
- Jackson, W.W., and West, J. 1933. The crystal structure of muscovite-- $KAl_2(AlSi_3)O_{10}(OH)_2$. *Ztschr. Krist.* 85:160-164.
- Jeffries, C.D., Rolfe, B. N., and Kunze, G.W. 1953. Mica weathering sequence in the Highfield and Chester soil profiles. *Soil Sci. Soc. Amer. Proc.* 17:337-339.
- Johnson, L. J., and Jeffries, C.D. 1957. The effect of drainage on the weathering of the clay minerals in the Allenwood catena of Pennsylvania. *Soil Sci. Soc. Amer. Proc.* 21:539-542.
- Jonas, A. I. 1927. Geologic reconnaissance in the Piedmont of Virginia. *Geol. Soc. Amer. Bull.* 38:837-846.
- Jonas, E.C., and Roberson, H.E. 1960. Particle size as a factor influencing expansion of the three-layer clay minerals. *Amer. Mineral.* 45:828-838.
- Jones, L.H., and Thurman, D.A. 1957. The determination of aluminum in soil, ash, and plant materials using Eriochrome Cyanine R.A. *Plant and Soil* 9:131-142.
- Kelley, W.P., and Jenny, H. 1936. The relation of crystal structure to base exchange and its bearing on base exchange in soils. *Soil Sci.* 41: 367-382.
- Klages, M.G., and White, J.L. 1957. A chlorite-like mineral in Indiana soils. *Soil Sci. Soc. Amer. Proc.* 21:16-20.
- Levinson, A.A. 1953. Studies in the mica group: Relationship between polymorphism and composition in the muscovite-lepidolite series. *Amer. Mineral.* 38:88-107.
- MacEwan, D.M.C. 1949. Some notes on the recording and interpretation of x-ray diagrams of soil clays. *Jour. Soil Sci.* 1:90-103.

- Mackenzie, R.C. 1955. Potassium in clay minerals. Potassium Symposium, 1955, pp. 123-137. International Potash Institute, Bern, Switzerland.
- McCormick, R.B. 1934. Paragonite from Pizzoformo, Picino, Switzerland. *Amer. Mineral.* 19:431-432.
- Merrill, G.P. 1906. Rocks, Rock-weathering, and Soils. The Macmillan Co., New York.
- Morey, G.W., and Chen, W.T. 1955. The action of hot water on some feldspars. *Amer. Mineral.* 40:996-1000.
- Mortland, M.M. 1958. Kinetics of potassium release from biotite. *Soil Soc. Amer. Proc.* 22:503-508.
- Murray, H.H., and Leininger, R.K. 1956. Effect of weathering on clay minerals. *Proc. 4th Natl. Conf. Clays and Clay Minerals, Natl. Acad. Sci.-Natl. Research Council Publ.* 456:340-347.
- Osthaus, B.B. 1956. Kinetic studies on montmorillonites and nontronite by the acid-dissolution technique. *Proc. 4th Natl. Conf. Clays and Clay Minerals, Natl. Acad. Sci.-Natl. Research Council Publ.* 456:301-321.
- Pauling, L. 1960. The Nature of the Chemical Bond, 3rd Ed. Cornell University Press, Ithaca, New York.
- Perkins, A.T. 1949. Reactions of muscovite, bentonite, and their treated residues. *Soil Sci.* 67:41-46.
- Pettijohn, F.J. 1941. Persistence of heavy minerals and geologic age. *Jour. Geol.* 49:610-625.
- Pimentel, G.C., and McClellan, A.L. 1960. The Hydrogen Bond. W.H. Freeman and Co., San Francisco.
- Radoslovich, E.W. 1959. Structural control of polymorphism in micas. *Nature* 183:253.
- Radoslovich, E.W. 1960. The structure of muscovite, $KAl_2(Si_3Al)O_{10}(OH)_2$. *Acta Cryst.* 13:919-932.
- Reiche, P. 1945. A Survey of Weathering Processes and Products. Univ. New Mexico Publ. in Geol., No. 1.

- Reitameier, R.F., Brown, I.C., and Holmes, R.S. 1951. Release of Native and Fixed Nonexchangeable Potassium of Soils Containing Hydrous Micaceous. USDA Tech. Bull. 1049.
- Rich, C. I. 1954. Clay minerals in Tatum silt loam soil. Virginia Jour. Sci. 2:300.
- Rich, C. I. 1957. Determination of (060) reflections of clay minerals by means of counter type x-ray diffraction instruments. Amer. Mineral. 42:569-570.
- Rich, C. I. 1958. Muscovite weathering in a soil developed in the Virginia Piedmont. Proc. 5th Natl. Conf. Clays and Clay Minerals, Natl. Acad. Sci.-Natl. Research Council Publ. 566:203-212.
- Rich, C. I. 1960. Aluminum in interlayers of vermiculite. Soil Sci. Soc. Amer. Proc. 24:26-32.
- Rich, C. I. 1961. Calcium determination in cation-exchange capacity measurements. Soil Sci. 92: (in press).
- Rich, C. I., and Obenshain, S. S. 1955. Chemical and clay mineral properties of a Red-Yellow Podzolic soil derived from muscovite schist. Soil Sci. Soc. Amer. Proc. 19:334-339.
- Rolfe, B.N., and Jeffries, C.D. 1953. Mica weathering in three soils in central New York, U.S.A. Clay Minerals Bull. 2: 85-93.
- Rosenfeld, J.L. 1956. Paragonite in the schist of Glebe Mountain, southern Vermont. Amer. Mineral. 41:144-147.
- Rosenfeld, J.L., Thompson, J.B., and Zen, E. 1958. Data on co-existent muscovite and paragonite. Geol. Soc. Amer. Bull. 69:1637.
- Ross, C.S., and Kerr, P.F. 1931. The kaolin minerals. U.S. Geol. Survey Prof. Paper 165-E, 151-180.
- Roy, R. 1949. Decomposition and resynthesis of the micas. Jour. Amer. Ceramic Soc. 32:204-209.
- Schaller, W.T. 1950. An interpretation of the composition of high-silica sericites. Mineral. Mag. 29:406-415.
- Schaller, W.T., and Stevens, R.E. 1941. The validity of paragonite as a mineral species. Amer. Mineral. 26:541-545.

- Scott, A.D., Humziker, R.R., and Hanway, J.J. 1960. Chemical extraction of potassium from soils and micaceous minerals with solutions containing sodium tetraphenylboron. I. Preliminary experiments. *Soil Sci. Soc. Amer. Proc.* 24:191-194.
- Scott, A.D., and Reed, M.G. 1960. Determination of the precipitated potassium in sodium tetraphenylboron-micaceous mineral systems. *Soil Sci. Soc. Amer. Proc.* 24:326-327.
- Shen, M.J., and Rich, C.I. 1961. Aluminum fixation in montmorillonite. *Soil Sci. Soc. Amer. Proc.* 25: (in press).
- Smith, J.V., and Yoder, H.S. 1956. Theoretical and X-ray study of the mica polymorphs. *Mineral. Mag.* 31:209-235.
- Starik, I.E., and Litvina, L.A. 1958. Use of the method of leaching for evaluation of the suitability of samples for determination of age by the argon method. *Geokhimiya*, pp. 163-165.
- Stelle, V. 1907. Über verwitterung und kaolinbildung hallescher quarzporphyre. *Ztschr. Naturwiss.* 79:321-323.
- Stose, G.W. 1928. Supervisor of preparation, Geologic Map of Virginia. Virginia Geological Survey, map.
- Strunz, H. 1957. Mineralogische Tabellen. 3 Aufl., s. 323.
- Tamura, T. 1958. Identification of clay minerals from acid soils. *Jour. Soil Sci.* 9:141-147.
- Tamura, T., and Jackson, M.L. 1953. Structural and energy relationships in the formation of iron and aluminum oxides, hydroxides, and silicates. *Science* 117:381-383.
- Tanner, C.B., and Jackson, M.L. 1947. Nomographs of sedimentation times for soil particles under gravity or centrifugal acceleration. *Soil Sci. Soc. Amer. Proc.* 12:60-65.
- Thorp, J., Cady, J.G., and Gemble, E.E. 1959. Genesis of Miami silt loam. *Soil Sci. Soc. Amer. Proc.* 23:156-161.
- Thoulet, J. 1913. Notes de lithologie sous-marine. *Ann. Inst. Oceanogr.* V, fasc. 9.
- Tolansky, S. 1945. The topography of crystal faces. II. The topography of cleavage faces of mica and selenite. *Proc. Royal Soc. London, Ser. A*, 184:51-63.

- Van Hise, C.R. 1904. A Treatise on Metamorphism. U.S. Geol. Survey Monograph 47.
- Walker, G.F. 1949. Decomposition of biotite in soil. Mineral. Mag. 28:693-703.
- Walker, G.F. 1950. Trioctahedral minerals in the soil-clays of northeast Scotland. Mineral. Mag. 29:72-84.
- Walker, G.F. 1959. Diffusion of exchangeable cations in vermiculite. Nature 184:1392-1393.
- Warshaw, C.M. 1960. Experimental studies of illite. Proc. 7th Natl. Conf. Clays and Clay Minerals, pp. 303-316. Pergamon Press, New York.
- Weaver, C.E. 1958. The effects and geological significance of potassium "fixation" by expandable clay minerals derived from muscovite, biotite, chlorite, and volcanic material. Amer. Mineral. 43:839-861.
- White, J.L. 1956. Reactions of molten salts with layer-lattice silicates. Proc. 4th Natl. Conf. Clays and Clay Minerals, Natl. Acad. Sci.-Natl. Research Council Publ. 456:133-146.
- White, J.L. 1958. Layer charge and interlamellar expansion in a muscovite. Proc. 5th Natl. Conf. Clays and Clay Minerals, Natl. Acad. Sci.-Natl. Research Council Publ. 566:289-294.
- Winchell, A.N. 1951. Elements of Optical Mineralogy, 5th Ed. John Wiley and Sons, New York.
- Yoder, H.S., and Eugster, H.P. 1955. Synthetic and natural muscovites. Geochim. et Cosmochim. Acta 8:225-280.
- Yoder, H.S., Jr. 1959. Experimental studies on micas: A synthesis. Proc. 6th Natl. Conf. Clays and Clay Minerals, pp. 42-60. Pergamon Press, New York.

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ALTERATION OF DIOCTAHEDRAL MICAS IN SOILS

Abstract

Artificial and natural weathering studies were conducted on four dioctahedral micas found in soil parent material of the Virginia Piedmont. Emphasis was given to the relationship between loss of K (also Na in certain cases), increase in CEC, and expansion characteristics.

Boiling treatments with several different solutions were used to promote artificial weathering. In terms of the three parameters of primary interest, the results were of three general types, depending upon the nature of the boiling medium. Boiling solutions of HCl and HOAc removed K and Na, but produced only slight expansion and a negligible increase in CEC. The acid solutions, being at low pH, liberated from the mineral large amounts of Al, which likely underwent hydrolysis later to form hydroxy-Al polymeric groups. These groups can occupy exchange sites, but they remain nonexchangeable. Boiling salt solutions of NaCl and $MgCl_2$ removed K and Na in large amounts, produced considerable expansion, but only a slight increase in CEC resulted. The explanation for the small increase in CEC was believed to be due also to blocking of exchange sites by nonexchangeable hydroxy-Al groups, because salts tend to accelerate the hydrolysis reaction. A boiling Na-citrate solution removed K effectively, produced marked expansion, and caused a large increase in CEC. Citrate complexes Al, which probably accounted for the high CEC. When a sample was treated with hot HCl prior to Na-citrate boiling, the loss

of K and increase in CEC was stoichiometric. The equivalence was attributed to the removal of amorphous material by HCl and complexing of Al by Na-citrate.

Vermiculite and kaolinite were the natural weathering products of the dioctahedral micas studied. There was a striking similarity between the artificially-produced vermiculite and that occurring under natural conditions. The product formed under both circumstances expanded to approximately 14 Å. when glycerol-solvated and contracted to 10 Å. upon K-saturation and heating. Although the artificial weathering media were not representative of natural weathering conditions, the basic mechanism of mica alteration apparently was similar.

The soil micas altered easily in the laboratory compared to an Ontario muscovite. Thus, it was concluded that soil micas are quite different from the specimen-type micas. They may possess a lower charge or lack the structural control of specimen muscovites.

The difference in ease of weathering between dioctahedral and trioctahedral micas likely is attributable to the difference in chemical composition, especially in the octahedral layer. Dioctahedral micas appear to be more strongly bonded than trioctahedral micas as a result of the higher-charged Al^{+++} ion in the octahedral layer. This stronger bonding would tend to restrict initial alteration. Subsequent alteration also would be hindered because, as weathering proceeds, greater hydrolysis of Al in dioctahedral micas would result in more fixation of positively-charged hydroxy-Al polymers in

the interlayer position. This fixed Al inhibits expansion of dioctahedral micas. In trioctahedral micas, which contain Fe and/or Mg, this type of fixation does not occur during acidic weathering.

A significant finding was the occurrence of paragonite, the Na analogue of muscovite, in intimate association with muscovite. A relatively constant Na/K molar ratio of approximately one was maintained in both the parent rocks and soils. This indicated that equal molar quantities of paragonite and muscovite were present and that weathering of the two micas was similar. Paragonite is believed to be of more widespread occurrence than previous work has indicated. Its influence on soil genesis, morphology, and classification may be significant.