

CHARACTERISTICS OF 14 Å CLAY MINERALS IN THE B HORIZONS OF PODZOLIZED SOILS OF ALBERTA

by

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ABSTRACT

Recent investigations of soils from widely distributed sites reveal the presence of clay minerals with 14 Å *d* spacings in the *B* horizons of podzolized soils in Alberta. The minerals appear to be concentrated in the 2.0–0.2 micron clay fraction, the fraction less than 0.2 micron being comprised primarily of material amorphous to X-ray. Despite the presence of montmorillonite in the eluvial horizon and soil parent material only interstratified minerals of this group appear in association with the 14 Å mineral. Smaller amounts of quartz, kaolinite and illite are also noted in these *B* horizons.

The data available reveal that the 14 Å mineral is derived from montmorillonite and that formation occurs *in situ* in the *B* horizons.

It is apparent from the investigations conducted that weathering of associated feldspars under mildly acid conditions, releases hydrated alumina ions. These ions not only move into the interlayer regions of montmorillonite of fine clay size, where they exist in a discontinuous manner, but are also adsorbed onto the surfaces of these minerals binding adjacent particles into aggregates of coarse clay size. Adsorbed hydrated alumina hydroxy ions in the interlayer region are responsible for the observed 14 Å *d* spacings.

INTRODUCTION

Recent investigations into the nature of Podzol soils in Alberta revealed the presence of clay minerals with 14 Å *d* spacings in the *B* horizons. Absence of these minerals in the upper *A* horizon and the parent material suggests that these minerals are formed *in situ*. Furthermore, the presence of montmorillonite in the parent material and *A* horizon and its decrease in the *B* horizon together with increased development of the 14 Å clay mineral in this horizon suggests that the 14 Å clay mineral is a modification of montmorillonite. The data reported herein are the result of study undertaken to help elucidate the nature of the transformation.

Soil samples from two profiles were collected for this study. One profile was that of a well-developed Podzol in which the 14 Å clay mineral appeared to be in an advanced stage of development. The other was a Bisequa profile in which a micro-Podzol profile is developed in the eluviated horizon of a Grey Wooded soil. Since the stage of development in this soil is less advanced than that of the previous profile, transformation of clay minerals appeared to have

reached an intermediary stage of development. The latter profile was emphasized in this study.

Despite morphological similarities between Alberta Podzols and those described in the literature (Joffe, 1949) their chemical constitutions differ widely. These variations are believed to be partially due to the different soil environmental conditions. The conditions in Alberta are conducive to the observed clay transformations and may further explain the apparent absence of 14 Å clay minerals in Podzol soils described elsewhere.

The soil environmental conditions prevailing in the *B* horizons of the sampled profiles are those of moderate acidity with pH values ranging from 5.6 to 6.2. The clay mineral exchange complex varies from 30 per cent to 50 per cent saturation with exchangeable hydrogen and aluminum ions while calcium and to a lesser extent magnesium make up the majority of the remaining exchangeable cations. Adequate aeration of these soils maintains a fairly constant oxidized state in this horizon.

Quantitative estimates of extractable iron and aluminum oxides in the *B* horizons of these soils (up to 1.5 per cent for the former and 0.5 per cent for the latter) are much lower than reported for typical Podzols and many Grey Wooded soils. The *B* horizon is further characterized by a high quantity of fulvic acids comprised of a wide array of low molecular weight straight chain and aromatic hydrocarbons. Mineralogical investigations have revealed a high degree of feldspar weathering in the sola of these soils (Pawluk, 1960). Although immature podzolic soils also contain large quantities of fulvic acid and extractable iron oxide, the low quantity of extractable aluminum oxide (less than 0.1 per cent) and the near neutral pH values (6.8–7.0) appear to largely inhibit clay transformations. The clay transformations also appear to be absent in profiles containing high quantities of clay despite low pH and base saturation values (Pawluk, 1961).

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EXPERIMENTAL PROCEDURES

In the initial investigations conducted on the Podzol soils, all horizons were sampled for study. Routine laboratory analyses revealed the presence of clay minerals with 14 Å *d* spacings in the 2.0–0.2 micron clay fraction of the *B* horizons while the fraction less than 0.2 micron in size contained material largely amorphous to X-ray. The parent geological material contained primarily montmorillonite in the fine clay fraction and illite, fine grained quartz and kaolinite in the coarse clay fraction.

Bulk samples of *B* horizons were collected for more detailed study. Sedimentation techniques were employed for clay separations. Organic matter was removed by treating the sodium saturated clay with 20 per cent hydrogen peroxide and 0.2 N HCl. Free iron oxide was removed with sodium hydrosulfite (Mackenzie, 1954). A portion of the clay sample was then boiled very gently in a 5 per cent sodium carbonate solution for 2 min in order to remove soluble aluminum as well as any remaining weak alkali-soluble organic matter. X-ray analyses were conducted before and after each treatment in order to evaluate any possible effects of such treatments. Other than reducing background intensities, no differences were observed in the X-ray spectrograms for the peroxide and sodium hydrosulfite treated clays. The sodium carbonate treatment brought about a collapse of the 14 Å peak to 13.4 Å for the clay undergoing transformation. This treatment was therefore avoided in preparing the clay samples for analyses. Numerous tests were conducted on the prepared clay minerals in order to evaluate their characteristics and to determine their similarities to clay minerals with 14 Å *d* spacings reported in the literature (Tamura, 1958).

RESULTS

Chemical Investigations

Elemental composition of the clay minerals, as determined by fusion analyses, shows remarkable similarities between the *B* horizons of the two profiles and the soil parent material of the Podzol (Table 1). Despite the degree of transformation, the silica to sesquioxide ratios are close to 2:1 after accounting for the presence of 10 to 15 per cent fine grained quartz which appears to be present.

TABLE 1.—CHEMICAL ANALYSES FOR CLAYS EXTRACTED FROM PODZOL SOILS

Fusion Analyses	<i>B</i> horizon of Podzol	<i>B</i> horizon of Bisequa	<i>C</i> horizon of Podzol
SiO ₂	55.92	55.63	55.16
Al ₂ O ₃	20.32	19.76	21.11
Total Fe as Fe ₂ O ₃	3.45	3.11	3.92
TiO ₂	0.88	1.11	1.01
CaO	0.60	0.78	0.81
MgO	1.60	2.04	2.08
Na ₂ O	0.51	0.53	0.52
K ₂ O	1.91	1.78	2.43
H ₂ O (110°C)	4.94	5.08	3.78
H ₂ O (110°C–290°C)	—	4.16	—
H ₂ O (280°–500°C)	—	3.29	—
L.O.I. (1000°C)	10.78	10.26	10.34
Silica/Sesquioxide	2.4	2.4	2.2
CEC meq/100 g	42.0	—	41.0

X-ray Diffraction Investigations

The clay minerals under investigation bear a similarity to both chlorite and vermiculite in d spacings but differ considerably in other respects. The ordering of the peaks suggest regular periodic nature with the first order peak having the greatest intensity. Strong third order peaks were also evident.

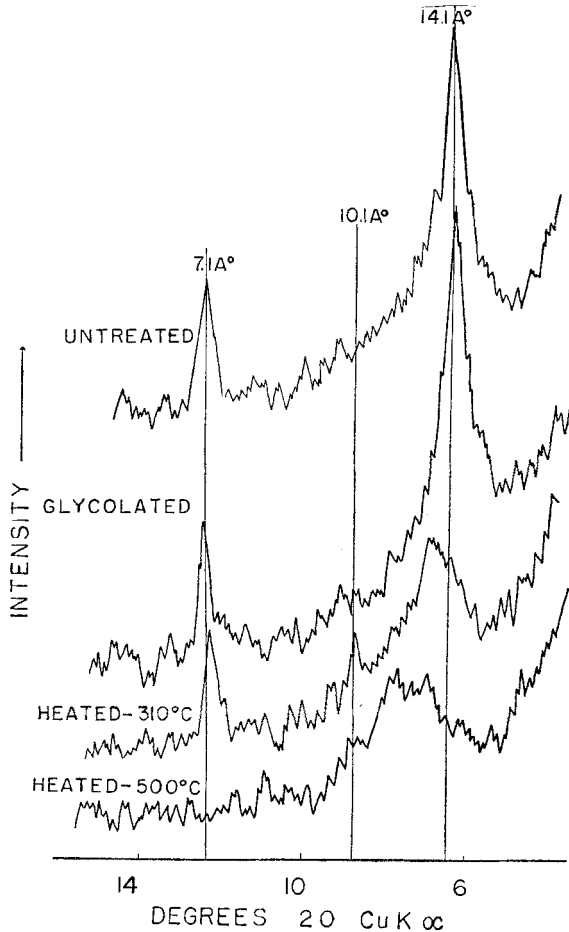


FIGURE 1.—X-ray diffraction patterns for coarse clay extracted from the B_f horizon of a podzol. The exchange positions were saturated with calcium ions.

In order to evaluate the nature of these clays, X-ray diffractions were obtained after their subjection to a wide array of treatments. While glycolation had no effect upon the transformed clay mineral (Fig. 1) those undergoing transformation showed expansion characteristics of interstratified

chlorite and montmorillonite (Fig. 2). Heating of the clay minerals brought about a gradual decrease in peak intensity and an irregular collapse of the lattice structure.

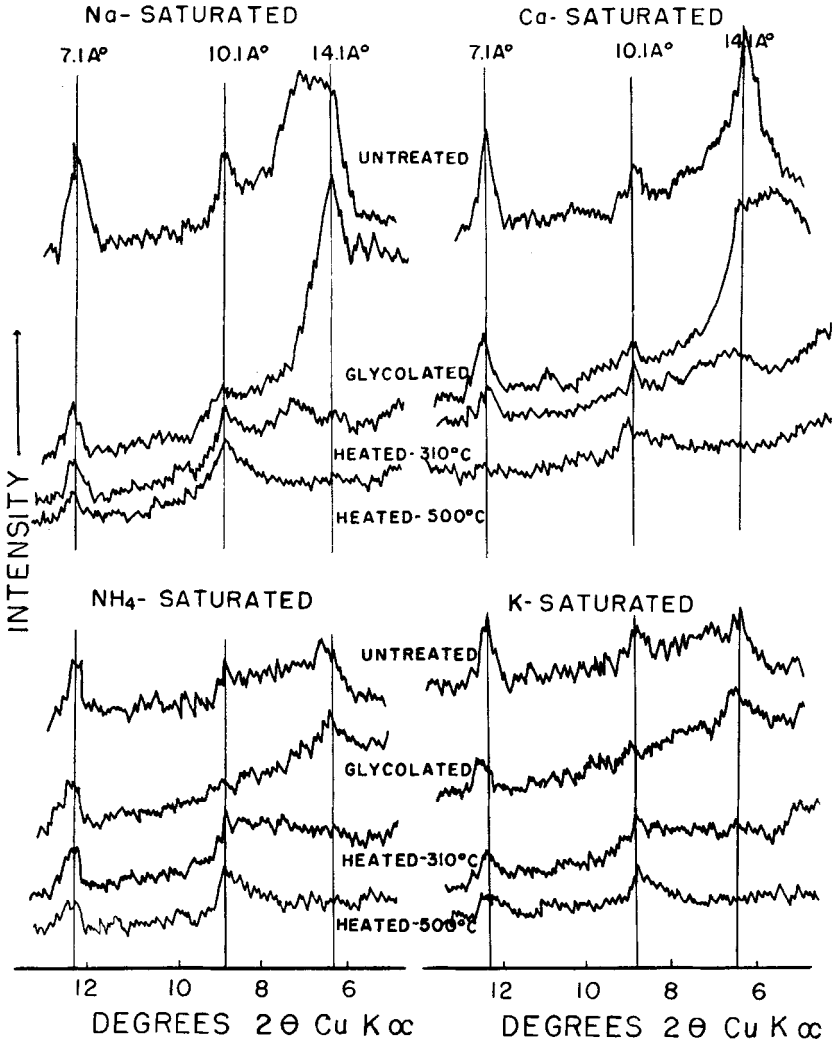


FIGURE 2.—X-ray diffraction patterns for coarse clay extracted from the B_f horizon of a Bisequa Podzol-Grey wooded soil. The exchange positions were saturated with four different cations.

The exchange complexes of the clay minerals examined were also saturated with various cations prior to examination. The type of exchangeable cation had no effect upon peak intensities of spacings for the 14 Å clay mineral found

in the Podzol soil. However, the clay minerals from the Bisequa profile did show variations in X-ray diffraction patterns. It is apparent that the greatest cation influence was upon the least altered and partially transformed montmorillonite. The diffraction patterns for the untreated and glycolated Na- and Ca-saturated clays resemble those reported for interstratified chlorite-montmorillonite minerals. However, X-ray patterns for the heat treated samples discount this possibility. Both K and NH_4 ions appear to collapse

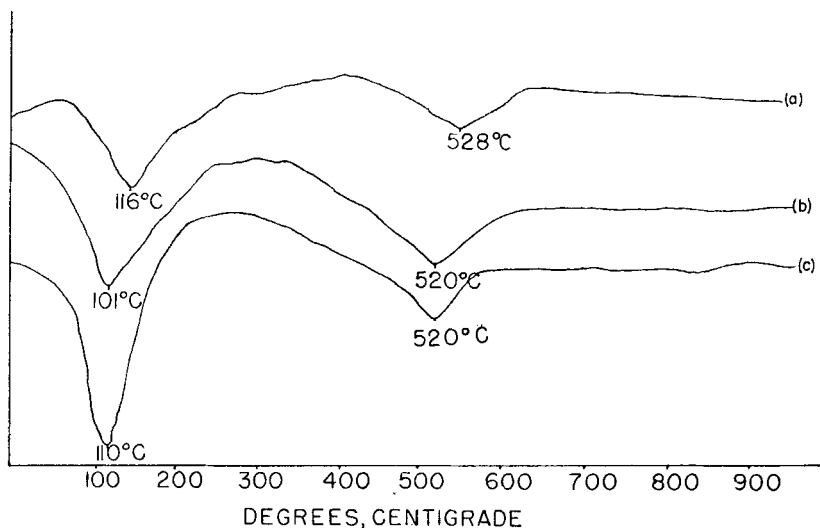


FIGURE 3.—(a) and (b) illustrate DTA curves for the coarse clay fraction from the B_f horizon of a Bisequa Podzol-Grey Wooded soil heated in a nitrogen and oxygen atmosphere respectively. (c) illustrates the DTA curves for the similar fraction obtained from a Podzol soil and heated in an oxygen atmosphere.

the minerals and lower the intensity of the peaks. This probably results from the movement of these ions into the hexagonal spacings of the silica sheet, thus reducing the degree of hydration. Glycolation only slightly expanded the d spacings of the collapsed minerals. Heat treatments as low as 310°C resulted in a diffuse irregular pattern where the clay minerals appear to have collapsed in an irregular manner. After digesting the coarse clay minerals with warm 1 N sodium citrate for 5 hr, alumina was dissolved and removed while the 14 Å clay mineral reverted to a montmorillonite of fine clay size.

Differential Thermal Curves

Differential thermal curves were established for the coarse clays under study (Fig. 3). Variations in peak intensities among the three curves is attributable to the use of three different furnaces and thermal blocks for the analyses.

The curves are characterized by hygroscopic moisture peaks that are large and only one dehydroxylation peak. The dehydroxylation peak occurs at a temperature that is much lower than that expected for a chlorite. A comparison of the curves obtained in a nitrogen and oxygen atmosphere for the clay minerals from the Bisequa profile suggest the presence of a slight exothermic rise between 200°C and 320°C which is likely due to organic matter. A similar rise may be noted for the clay obtained from the Podzol profile.

Infrared Analyses

Coarse clay from the Bisequa profile was further characterized by I.R. analysis (Fig. 4). The absorbance curve for the Ca-saturated clay conforms closely to that of an illite. The similarity results from the low hydration caused by the "fixed" nature of the lattice structure. Partial dehydration of the sample

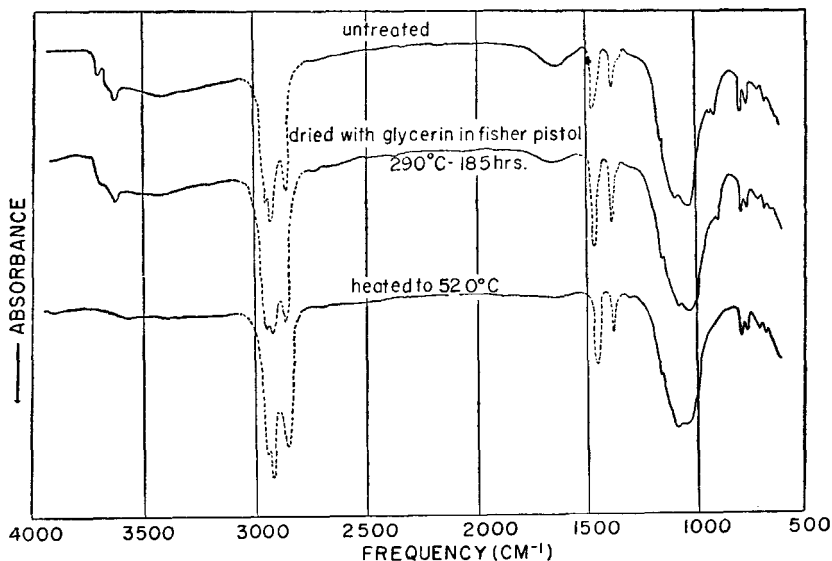


FIGURE 4.—Infrared spectra for the coarse clay fraction obtained from the B horizon of a Bisequa Podzol-Grey wooded soil. The calcium saturated clays were muller with nujol.

appeared to be the only significant alteration which resulted from drying the sample with glycerin in a fisher pistol at 290°C for 185 hr. Flattening of the peaks at approximately 3200 cm^{-1} to 3750 cm^{-1} and 1650 cm^{-1} upon heat treatment at 520°C confirms the complete removal of bound and unbound hydroxyls. The presence of fine grained quartz is confirmed by the stable doublet at approximately 750 cm^{-1} and the shoulder at approximately 1160 cm^{-1} .

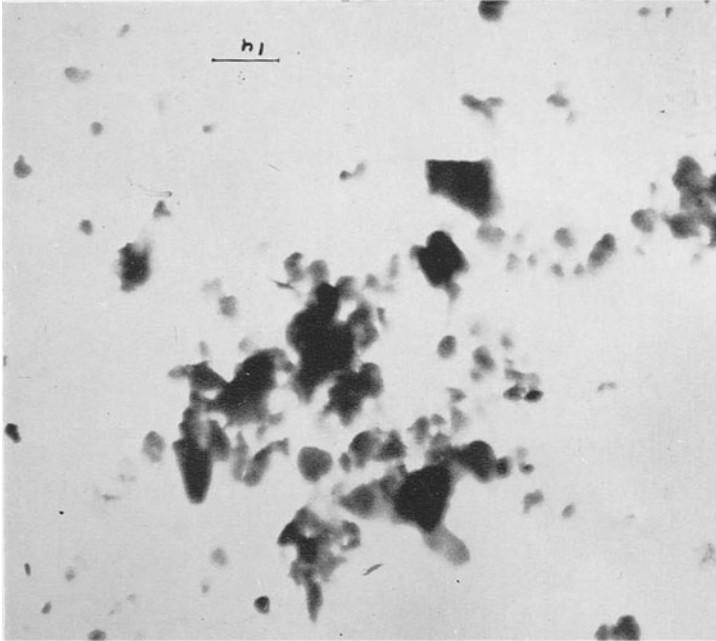


PLATE 1.—Electron micrograph of coarse clay extracted from the *B_f* horizon of a Bisequa Podzol-Grey Wooded soil.

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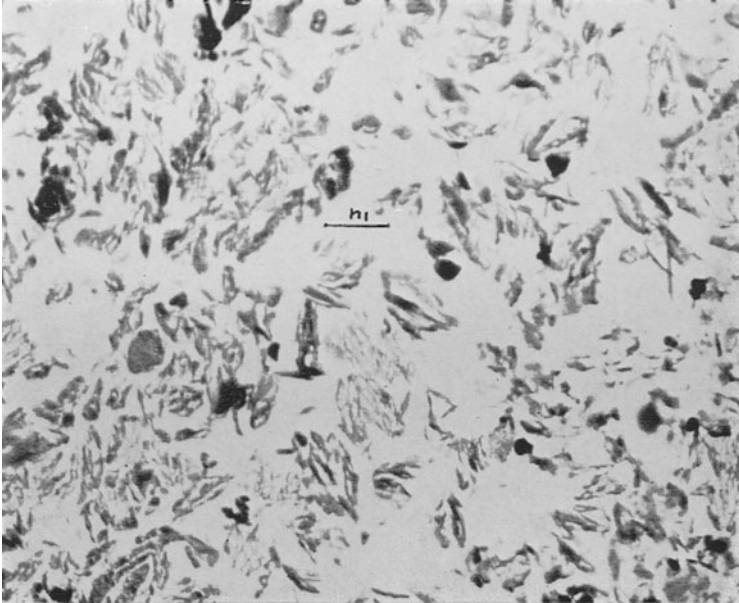


PLATE 2.—Electron micrograph of a thin section in which the clay mineral illustrated in Plate 1 was suspended in a methyl methacrylate plastic polymer.

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Electron Micrographs

Examination of the clay mineral particles with the electron microscope revealed patterns similar to those expected for montmorillonite. Thin sections prepared by impregnating the clay minerals in a plastic polymer provided further evidence for the aggregated nature of this material.

Discussion and Conclusions

The presence of clay minerals with "fixed" 14 Å d spacings in soils has been widely acknowledged in the literature. These minerals have been referred to by such names as "dioctahedral analogues of vermiculite", "chlorite-like", "vermiculite-chlorite mixed layering", etc. (Tamura, 1958). Their formation has been widely accepted as being attributable to hydroxyl and/or hydrated aluminum ions moving into the interlayer positions of both illite and montmorillonite.

The clay minerals observed in the soils under investigation have specific characteristics which distinguish them from most other clay minerals. Examination of these clays revealed a hydrated clay mineral which when well developed has its d spacings unaffected by glycolation or exchangeable cations. The partial collapse of the lattice structure by dehydration at relatively low temperatures and the diffuse nature of the collapsed peaks suggest that hydration in the interlayer regions is partially responsible for the characteristic spacing. The failure of the heat treatment to collapse the clay mineral to a 10 Å d spacing at 510°C confirms the existence of the interlayer alumina ions in hydroxy as well as the hydrated form. The presence of a single endothermic peak at the high temperature range in the DTA thermogram is most likely due to a dual endothermic reaction in the same temperature interval. This is also true of the modifications having characteristics between montmorillonite and the 14 Å clay mineral as was confirmed by both X-ray and infrared analyses. The similarity in chemical composition and the limited variation in the 2:1 silica-sesquioxide ratios for the altered and unaltered clays largely discount the possibility of a gibbsite structure occupying the interlayer positions.

Observable characteristics for the soils under study strongly suggest that the transformations observed do not result from the weathering of the clay minerals but rather from the weathering of associated less stable feldspars, during which montmorillonite of fine clay size in the original soil parent geologic material is transformed into a clay mineral with 14 Å d spacings and of coarse clay size. The transformation occurs as part of the pedogenic development of the Podzol *B* horizon. Under the observed conditions of acidity, fulvic acids released by the transformation of surface organic matter readily contribute hydronium ions which gradually bring about the dissolution of feldspar mineral surfaces, releasing hydrated alumina ions into the soil solution. The co-precipitation of silica and alumina would be limited by the low solubility of silica at the observed pH values, where the hydrated alumina ion exist in hydroxy form. The soluble hydrated alumina hydroxy ions could

then occupy some of the exchange positions both within the interlayer region and on the external surfaces of montmorillonite, the degree of saturation of which would depend upon surface charge density of the montmorillonite and the concentration and charge of associated ions. Hydrated alumina hydroxy ions appear to move first into the outer edges of the interlayer regions of montmorillonite becoming "fixed" in a manner suggested by Jackson (1960). The resulting structures are relatively unstable at this stage as observed for the clay minerals from the *B* horizon of the Bisequa profile. The clay mineral from the Podzol, however, appears to be much more stable. This is probably due to an increase in strength of binding between layers as transformation progresses. Chemical analyses and X-ray data suggest that the hydrated alumina hydroxy ions do not form a continuous sheet but rather are discontinuous in distribution within the interlayer region. The hydrated alumina hydroxy ions adsorbed onto the surfaces of the clay minerals in a similar manner would bind adjacent particles of fine sized montmorillonite to form clay mineral aggregates of coarse clay size exhibiting 14 Å *d* spacings. This process accounts for the absence of montmorillonite in the fine clay fraction of the *B* horizon despite its presence in the parent material.

The clay minerals occurring in this manner are resistant to mechanical dispersion as well as the commonly employed dispersing agents. Warm sodium citrate, however, readily dissolves and removes the associated hydrated alumina hydroxy ions and the clay mineral reverts back to montmorillonite of fine clay size.

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