

INTERSTRATIFICATION OF LAYER SILICATES IN TWO SOIL CLAYS

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ABSTRACT

X-ray and chemical analyses were made of two soil clays from Colorado. X-ray diffraction analysis of glycerol-solvated samples oriented in parallel gave poor diffraction patterns. Randomly oriented powder x-ray diffraction analysis showed an intense 4.45 Å band indicating the predominance of layer silicates. Total potassium analysis confirmed the presence of illite. Cation-exchange capacity and specific-surface measurements showed that high-charge layer silicates were present. The effect of differential cation saturation and differential heat treatment on the x-ray diffraction patterns of parallel oriented samples suggests interstratification of layer silicates in these soil clays.

INTRODUCTION

Broad x-ray diffraction maxima are commonly observed for parallel oriented samples of soil clays whereas deposits of relatively pure layer silicates generally give sharp peaks. There are several reasons for line broadening (Brindley, 1951), but in many soil clays, interstratification of layer silicates is the principal cause of the broad diffraction effects. Other soil clays may show poor x-ray patterns because not much crystalline material is present, because of amorphous material between the crystalline units increasing the irregularities in basal spacings, or because of crystal imperfections. This paper presents examples of soil clays showing x-ray diffraction evidence of interstratification of the layer silicates.

MATERIALS AND METHODS

The colloidal fractions of Billings clay and Monticello loam soils were segregated by standard procedures. Magnesium-saturated samples were solvated with glycerol and oriented in parallel on glass slides for x-ray diffraction analysis at room temperature and after heating to 110° C. Potassium-saturated samples were oriented on glass slides for x-ray diffraction analysis after drying at 25°, 400°, and 500° C. Randomly oriented x-ray diffraction patterns were taken for Ca-saturated clays. The x-ray diffraction patterns were obtained with a General Electric diffractometer or powder camera using Cu radiation filtered with Ni.

The cation-exchange capacity of H-saturated fractions dried from benzene was determined by a rapid semimicro method similar to that described by Swindale and Fieldes (1952). Total potassium was determined following hydrofluoric

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acid dissolution (Corey and Jackson, 1953). Specific surface was determined by the procedure of Vanden Heuvel and Jackson (1953).

The Billings clay is a Sierozen soil developed on alluvium coming from the Mancos shale formation. The sample analyzed was the A_p horizon of a soil near Grand Junction in Mesa County, Colorado. The Monticello soil came from a virgin area near Cortez in southwestern Colorado (Montezuma County). This is a Chestnut soil developed on reddish loess.

The mineral content of each fraction was estimated by using both x-ray diffraction and chemical analyses. Mineral allocations for the Billings and Monticello soils are given in Table 1.

TABLE 1. — MINERAL CONTENT OF CLAY FRACTIONS OF BILLINGS AND MONTICELLO SOILS.

Soil	Particle size fraction (microns)	Percentage mineral in each fraction ¹						
		Fl	Qr	Il	Chl	Vm	Mt	Kl
Billings	2 to 0.2	10	20	30	5	5	15	15
	0.2 to 0.08	—	—	45	—	15	30	10
	<0.08	—	—	35	—	15	50	—
Monticello	2 to 0.2	3	25	30	5	10	12	15
	0.2 to 0.08	—	—	25	—	15	45	15
	<0.08	—	—	20	—	15	60	5

¹ Fl = feldspars; Qr = quartz; Il = illites; Chl = chlorites; Vm = vermiculites; Mt = montmorillonite; Kl = kaolinite and halloysite.

RESULTS WITH BILLINGS SOIL CLAY

X-ray diffraction analysis of medium clay from the Billings soil is shown in Figure 1, left. With Mg-saturation and glycerol solvation, a diffraction maximum at 10 Å establishes the presence of illite. Total potash analysis of the clay establishes a minimum of 45 percent illite (Jackson and others, 1954), but an exchange capacity of 77 meq per 100 g indicates that considerable material of high exchange capacity must also be present. A strong diffraction maximum at 4.45 Å observed for a randomly oriented sample indicates that crystalline layer silicates predominate. Heating the Mg-saturated sample to 110° C gives a 14.7 Å spacing; this treatment causes some of the minerals with higher basal spacings to close to about 14 Å and reduces irregularities in spacings. Potassium saturation followed by heating to 500° C shows the absence of chlorite. The 14 Å spacings produced by heating the Mg-saturated sample to 110° C are, therefore, largely 2:1 expanding layer silicates.

When there is a random interstratification of two layer silicates, the scattering predicted by Hendricks and Teller (1942) shows that there are diffraction peaks, but their positions depend upon the proportions and the basal spacings of the two minerals. Brown and MacEwan (1949) point out that interstratification may cause a marked increase in scattering at small angles and that there may be a broadening of lines as the number of layers in each crystallite decreases. Some types of random interstratification of more than two components may result in broad peaks, high scattering at small angles, or the absence of diffraction maxima.

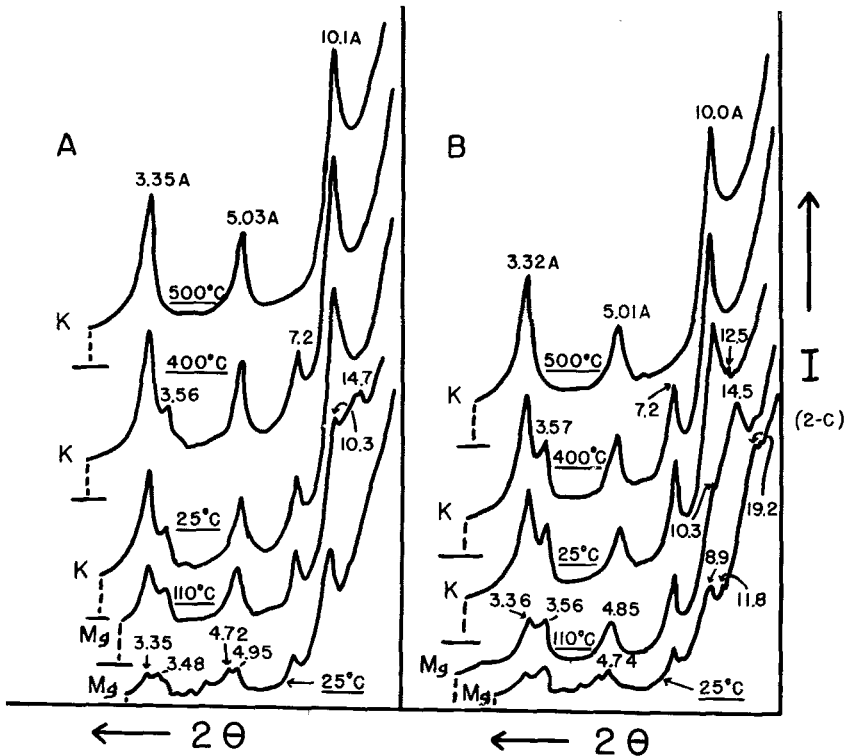


FIGURE 1.—X-ray diffraction patterns of medium clay from Billings and Monticello soils as affected by cation saturation and heating. The Mg-saturated samples were solvated with glycerol. A, Billings soil clay, 0.2 to 0.8 micron, Grand Junction, Colorado. B, Monticello soil clay, 0.2 to 0.8 micron, Ouray, Colorado.

In the Billings clay, there are no small-angle diffraction maxima to indicate montmorillonite or vermiculite although expanding 2:1 layer silicates are known to be present. Some of the diffraction peaks for the Mg-saturated sample at room temperature are higher-order basal spacings of illite or kaolinite. There are other peaks which are not integral and thus are not higher orders of the illite and kaolinite; these peaks indicate random interstratification of layer silicates (Brindley, 1951). The high scattering and lack of diffraction peaks at small angles suggest a complex interstratification of more than two components. X-ray diffraction and chemical analyses confirm illite as a constituent, and specific-surface measurements indicate that both vermiculite and montmorillonite are present, apparently randomly interstratified with illite. Illite also is present in crystallites of sufficient size to give an x-ray pattern for the mineral.

The mineral content of the medium clay estimated from combined data is shown in Table I with the results for fine and coarse clay from the Billings soil. The x-ray diffraction patterns for the fine clays were similar to those for the medium clay except for the absence of kaolinite. Interstratified layer silicates

were noted in the coarse clay but diffraction peaks were shown at 18, 14, and 10 Å. The 14 Å peak was resolved into chlorite and vermiculite.

Random powder x-ray analysis of the medium-clay fraction gives a strong 1.50 Å line which identifies this clay fraction as dioctahedral (MacEwan, 1949). A line of very low intensity at 1.54 Å is probably from a small amount of trioctahedral 2:1 layer silicate or from chlorite. Quartz also has a 1.54 Å spacing, but no other lines characteristic of this mineral are shown.

Montmorillonite and vermiculite in the Billings clay seem to be minerals of variable properties which have formed by weathering of illite. In the glycerol-solvated state these minerals occur in zones too small to be observed by x-ray diffraction. After dehydration of the K-saturated clay at 500° C, the intense diffraction maximum shows high uniformity of the 10 Å spacings of the 2:1 lattices present.

RESULTS WITH MONTICELLO SOIL CLAY

The x-ray diffraction patterns for oriented samples of medium clay from the Monticello soil are presented in Figure 1, right. With Mg-saturation the diffraction maxima are broad, but they suggest montmorillonite, kaolinite, and possibly illite. Several small peaks which are nonintegral higher orders for montmorillonite, kaolinite, or illite indicate an interstratification of minerals, possibly both random and regular sequences. Peak broadening and high background at small angles noted for this soil clay may also be the result of complex interstratification. The broad diffraction maxima at 19.2 Å and higher spacings could result from a series of regularly interstratified sequences associated at random with montmorillonite. Heating the Mg-saturated sample to 110° C produces a diffraction maximum at 14.5 Å. This peak is more intense than the broad diffraction maximum at 19.2 Å for the unheated sample. The loss of glycerol has apparently caused closure of some of the montmorillonite minerals to 14 Å, then coinciding with vermiculite-type minerals and increasing the sharpness and intensity of the peak. Since the spacing is 14.5 Å, not all of the montmorillonite layers have closed to 14 Å (Hendricks and Teller, 1942).

Potassium saturation produces a 10.4 Å peak with higher orders and a 12.5 Å spacing of lower intensity. The 10.4 Å spacing is apparently a combination of illite, vermiculite, and possibly montmorillonite which has closed to a spacing near 10 Å. The 12.5 Å spacing is probably that of a montmorillonite (Barshad, 1950). Heating the K-saturated sample to 500° C shows a 10 Å diffraction maximum characteristic of a relatively uniform, dehydrated 2:1 layer silicate which is free of or low in chlorite.

Total potassium analysis confirms the presence of a minimum of 25 percent illite. The lack of a sharp 10 Å peak for the Mg-saturated sample heated to 100° C indicates that illite is largely mixed with other minerals and does not exist appreciably as large crystallites of illite.

It should be noted that 25 percent of illite in the Monticello medium clay is not readily seen on the x-ray diffraction pattern; on the other hand, 45 percent of illite in the Billings clay shows a strong diffraction maximum. This emphasizes the need for caution when x-ray diffraction analysis is used for quantitative estimations in soil clays containing interstratified minerals. Likewise, it demonstrates the value of total-potassium determinations in the mineralogical analysis of clays containing illite.

X-ray diffraction and potassium analyses of the Monticello clay confirm the presence of illite, kaolinite, and montmorillonite minerals. There must also be considerable vermiculite in the clay to account for the observed exchange capacity of 100 meq per 100 g. An intense diffraction band at 4.45 Å shown by randomly oriented samples precludes the presence of large amounts of amorphous material of high exchange capacity. The 2:1 layer structures in this clay appear to vary continuously in properties from illite (nonexpanding) through intermediate minerals (vermiculite) to montmorillonite. The effects of differential ion saturation and heat treatment on the x-ray diffraction behavior shows that the 2:1 layer silicates are complexly interstratified, possibly as both random and regular sequences mixed with crystallites of nonstratified minerals.

A quantitative estimate of individual minerals in the Monticello clay is given in Table 1. X-ray diffraction analysis shows more extensive interstratification in the medium and fine clay than in the coarse clay. In the coarse clay there were sharp 18, 14, and 10 Å diffraction maxima. Heat treatment showed both vermiculite and chlorite in this fraction.

Brindley (1951) has discussed four factors causing broadening of x-ray diffraction peaks. For soil clay particles oriented in parallel, the causes of broadening may be summarized as (1) decreasing particle size, (2) crystal strain, (3) interstratification, and (4) decreasing degree of parallel orientation. With the samples discussed here, particle size and crystal strain remain constant for each soil fraction, thus the changes in x-ray pattern as the result of the various treatments could be caused only by changes in degree of parallel orientation or by changes in the regularity of the basal spacings, or both. When the intensities of the kaolinite peaks are compared, K saturation appears to give a higher degree of parallel orientation than Mg saturation; however, part of the intensity of the 7 Å spacing for the Mg-saturated sample is lost in background. Also, evidence has been presented which shows that there is an interstratification of layer silicates. It is difficult to separate the two effects, but interstratification along the Z-axis is probably the major cause of peak broadening shown by the Mg-saturated Monticello clay.

WEATHERING RELATIONSHIPS

MacEwan (1949) reported that trioctahedral micas tend to weather stepwise to give a 14 Å mineral but that alteration of some dioctahedral micas may not show well-defined steps. He suggested that the alteration product of these dioctahedral micas may be more like montmorillonite than vermiculite. If the vermiculite forming from mica were weathered rapidly to montmorillonite, it could be x-amorphous in its distribution along the Z-axis. During early stages of weathering only basal spacings of 10 Å would be observed. Montmorillonite and vermiculite would be obscured by complex interstratification with illite. As weathering progressed, spacings for montmorillonite would appear. A 14 Å basal spacing for vermiculite would not be seen at any time but vermiculite would be present as long as mica existed.

Rapid alteration of dioctahedral vermiculite may be the cause of diffraction effects noted for the medium clay in the two soils reported here. In the Billings clay, complex interstratification of illite, vermiculite, and montmorillonite obscures the two expanding minerals. In the Monticello soil clay, alteration has proceeded farther and montmorillonite spacings appear on x-ray diffraction

patterns. Both random and regular interstratification of the 2:1 layer silicates are indicated by the positions and broadness of the diffraction maxima. The estimated mineral content of the medium clay (Table 1) shows more illite in the Billings clay and more montmorillonite in the Monticello clay. A knowledge of the kinetics of the reactions involved would help characterize the origin of the interstratification noted.

Diocahedral micas do not uniformly weather rapidly to montmorillonite. Rich and Obenshain (1955) and Brown (1953) have found considerable amounts of diocahedral vermiculite in some soils. The rate of weathering is undoubtedly determined by the makeup of the vermiculite and by the environment.

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