Clays and Clay Minerals, Vol. 50, No. 3, 364–370, 2002.

CLAY MINERAL CHANGES IN THE MORROW EXPERIMENTAL PLOTS, UNIVERSITY OF ILLINOIS

B. VELDE[1,*] AND T. PECK[2]

[1] Laboratoire de Géologie, UMR 8538 CNRS, Ecole Normale Supérieure, 75231 Paris, France
[2] Department of Natural Resources and Environmental Sciences, University of Illinois, Urbana, IL 61081, USA

Abstract—The clay mineralogy of soil samples from the Morrow Plot Experiment (University of Illinois, Urbana Campus) was investigated. Analysis of soil samples taken at various intervals between 1913 and 1996 indicates that there is a significant influence of cropping method on the clay minerals in the soils. Curve decomposition methods were used to identify and follow the evolution of the different clay minerals: mica, illite and two randomly mixed-layered illite-smectite phases. The most striking difference is seen for continuous corn and corn-oats-hay rotations. Little change in clay mineralogy is seen in the rotation plot while a significant loss of illitic material from different phases was noted for the continuous-corn cultivation plots. Use of NPK fertilizer since 1955 appears to restore the clay mineralogy in continuous-corn cropping compared to that of the 1913 samples. From these data it appears that the I-S minerals play the role of a K buffer, becoming K-poor when the soil cannot furnish enough K from mineral reserves of detrital phases and K-rich when the soil is able to release enough K to enter into the I-S minerals, where it is available during a growing season, for plant growth.

Key Words—Clay Minerals, Corn-cropping, Morrow Plots, Soil, USA.

INTRODUCTION

The Morrow Plot experiments (Urbana Campus, University of Illinois) have been carried out since 1876. Different aspects of a more and more interventionist agriculture meant a greater subdivision of the plots as methods changed and different aspects of plant growth and productivity were investigated. The most important aspect to experimentors was that of productivity, especially of the amount of corn grown in the plots. Until now the effect of different cropping methods and different plants grown on the silicate substrate minerals of the soil had not been measured. We attempt to remedy this through the use of detailed X-ray diffraction (XRD) of the major clay mineral phases in the soils of the Morrow plots as they have been collected systematically over the years. Our study began with samples taken in 1913, well after the initiation of the Morrow Plot project. However, the samples span 87 years, sufficient to be relevant to modern agricultural practices. The observations are made on soils from two types of cropping: one of continuous corn, the other on rotations of corn, oats and hay. The impact of chemical fertilizer (NPK), which was first applied in 1957, has also been studied.

EXPERIMENTAL METHODS

Morrow Plots

The Morrow Plots are developed on a loessic Flanagan silt loam (mesic Aquic Argiudoll). The land had been farmed for ~70 years, on and off, prior to the establishment of the present experiment (Darmody and Peck, 1996).

The samples come from the plots 3 and 5, reserved for continuous-corn and corn-oats-hay rotations without fertilizer. Several gram sub-samples were obtained from the samples collected in 1913, 1923, 1933, 1944, 1955, 1957, 1968 and 1996. Over this period, the soil organic C content of the plots decreased regularly from 2.2 to 1.5% for continuous-corn (CC) whereas the C content stayed at roughly the same level for the corn-oats-hay (COH) rotation. Corn productivity decreases in these plots from ~2800 to <1400 kg/hectare until hybrid species were introduced in 1938 when original productivity levels were reached and subsequently surpassed. In the COH plots, the productivity did not change significantly until hybrid species were introduced with a resultant increase to ~4750 kg/hectare in later stages (Aref and Wonder, 1998).

Clay mineral investigation methods

The soil samples were dispersed in distilled water by ultrasonic treatment and allowed to settle overnight. The supernatant material was drawn off and treated with several drops of 1 M $SrCl_2$. The concentrated, flocculated clay fraction (<2 μm) was deposited on a glass slide and allowed to dry. Some samples were initially treated with H_2O_2 overnight and the fine fraction was then obtained and treated with $SrCl_2$. X-ray diffraction (CuKα radiation) data were obtained with a step-scanning program (0.02°2θ, 10 s/step). Samples were run in air-dried, glycol- and glycerol-saturated states.

The method of treatment to obtain the clay fractions used here is not that of normal soil clay protocol. No

* E-mail address of corresponding author:
papa@geologie.ens.fr

chemical treatments were used to eliminate free or crystalline Fe oxides (Dixon and Weed, 1989, Chapters 7, 8). Furthermore, most data are reported for samples without H_2O_2 treatment. The reason for this lack of treatment in the present study is that we wished to observe the soil clays as they would respond to cations in a natural state, that which plant roots would experience in the soil. Such factors as cation exchange capacity (CEC) and K fixation can only be understood in the context of the natural sample. Treated samples give results on soil silicates which resist the chemical attacks used in the laboratory but they do not necessarily show the response to ambient chemical forces experienced by plants. As the experiment carried out in the Morrow experimental plots is plant oriented, we wish to retain this emphasis.

The XRD patterns of Sr-saturated samples indicate the presence of kaolinite, mica-illite and mixed-layer illite-expanding minerals. The proportion of kaolinite did not seem to change significantly among the samples, being similar in area to the mica peak in the samples investigated. Kaolinite was not considered further in the assessment of mineral change over time.

Clay mineral identification

Identification of the clay minerals present in the clay-sized fraction of the agricultural soils was made using a numerical treatment of the XRD patterns. Decomposition of the complex peak pattern was performed using the program and conditions suggested by Lanson (1997). We compare mainly the 001 peaks between samples in order to follow the major trend of mineral change. In the decomposition process, peak width at half height (WHH) and intensity are obtained and are used to determine peak areas which are compared on a scale of 100% for the total of the peak areas investigated. The peaks near 5 Å were studied in order to substantiate some identifications. The initial hypotheses of the decomposition program, used on a pattern smoothed with a 7-point routine and after background stripping, were a four-peak XRD pattern. In most cases the decomposition program converged on a unique solution. The following attributions were made.

Mixed-layer smectite-illite. (1) A narrow peak (0.4°2θ width at half height, WHH) near 10 Å indicates the presence of mica.

(2) A larger peak (0.8°2θ WHH) near 10.3 Å represents illite or poorly-crystallized mica.

These identifications are similar to the those made for diagenetically-altered sediments (Gharrabi *et al.*, 1998; Lanson *et al.*, 1998).

These peak positions at 10 Å and 10.3 Å did not change position significantly with glycol or glycerol treatment. In the 5 Å region, these peaks form one band near 5.01 Å, as expected using the simulation methods of Reynolds (1985) for micas of different coherent domain sizes (CDS).

(3) A large (1.5°2θ WHH) peak near 13 Å in the air-dried state (Sr saturation). Simulations using the Reynolds NEWMOD® program for a disordered (R = 0) illite-smectite mineral give a large peak (near 2°2θ WHH) at 13.8 Å in the two-water smectite configuration for a 60% illite mixed-layer mineral. It is displaced to 17 Å using glycol and glycerol. This mineral is referred to here as illitic I-S. The simulations show a peak width similar to those observed in the Morrow plot samples.

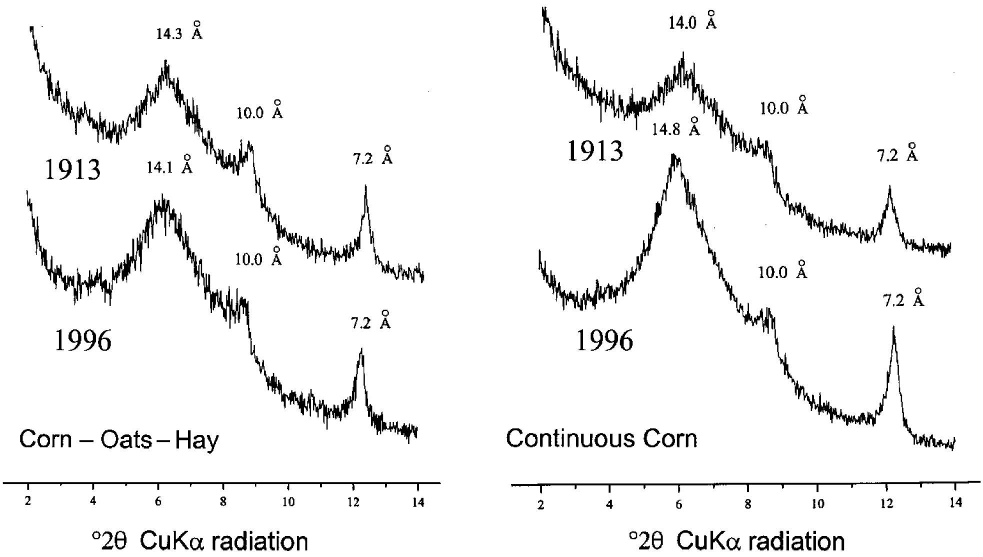

Figure 1. X-ray diffraction patterns of Sr-saturated, air-dried clay fractions of the Morrow plots for samples at the beginning of the observation period (1913) and the end (1996). The XRD patterns from soils of the two cropping systems of corn-oats-hay (COH) and continuous corn (CC) are shown.

https://doi.org/10.1346/000986002760833738 Published online by Cambridge University Press

(4) A peak near 15 Å was identified in the XRD patterns of air-dried samples. Its width was ~2.2°2θ. Glycol and glycerol treatment displace this peak, as well as the 13 Å peak to near 17 Å. Using the Reynolds NEWMOD® simulation program, one can produce a peak at 15 Å in the two-water layer smectite configuration at this position for disordered (R = 0) illite-smectite minerals with >50% smectite. It is referred to here as smectitic I-S.

The XRD patterns in the 5 Å region show relatively sharp peaks at near 5 Å in the glycol-treated state but only large very ill-defined bands to greater spacings can be detected. No decompositon analysis could be made of these bands.

Vermiculite. In the XRD identification protocol of Moore and Reynolds (1997) and Reynolds (1985), vermiculite is considered, in fact, to be a hydroxy-interlayered mineral. Its peak position does not change with glycol treatment. Thus, we consider that this mineral does not expand. However, high-charge smectite or expanding minerals can also be considered to be vermiculite minerals (Meunier *et al.*, 2000) identified in the behavior of diagenetic mixed-layer minerals. Vermiculite of this type will expand upon glycolation but will show layer contraction (non-expanding behavior) upon K saturation at room temperature (Howard, 1981). These two types of vermiculite behavior can be seen in the descriptions of soil and other minerals given in Chapters 5, 13 and 16 in Dixon and Weed (1989).

In the present study, K saturation does not significantly affect the XRD patterns of the samples. Thus we assume that the high-charge smectites (vermiculites) are not present in great abundance in the expanding mixed-layer minerals. There is little evidence of a strong peak at ~14.5 Å which is not affected by glycol treatment. This behavior would indicate that there is little hydroxy-interlayer vermiculite mineral material present. The

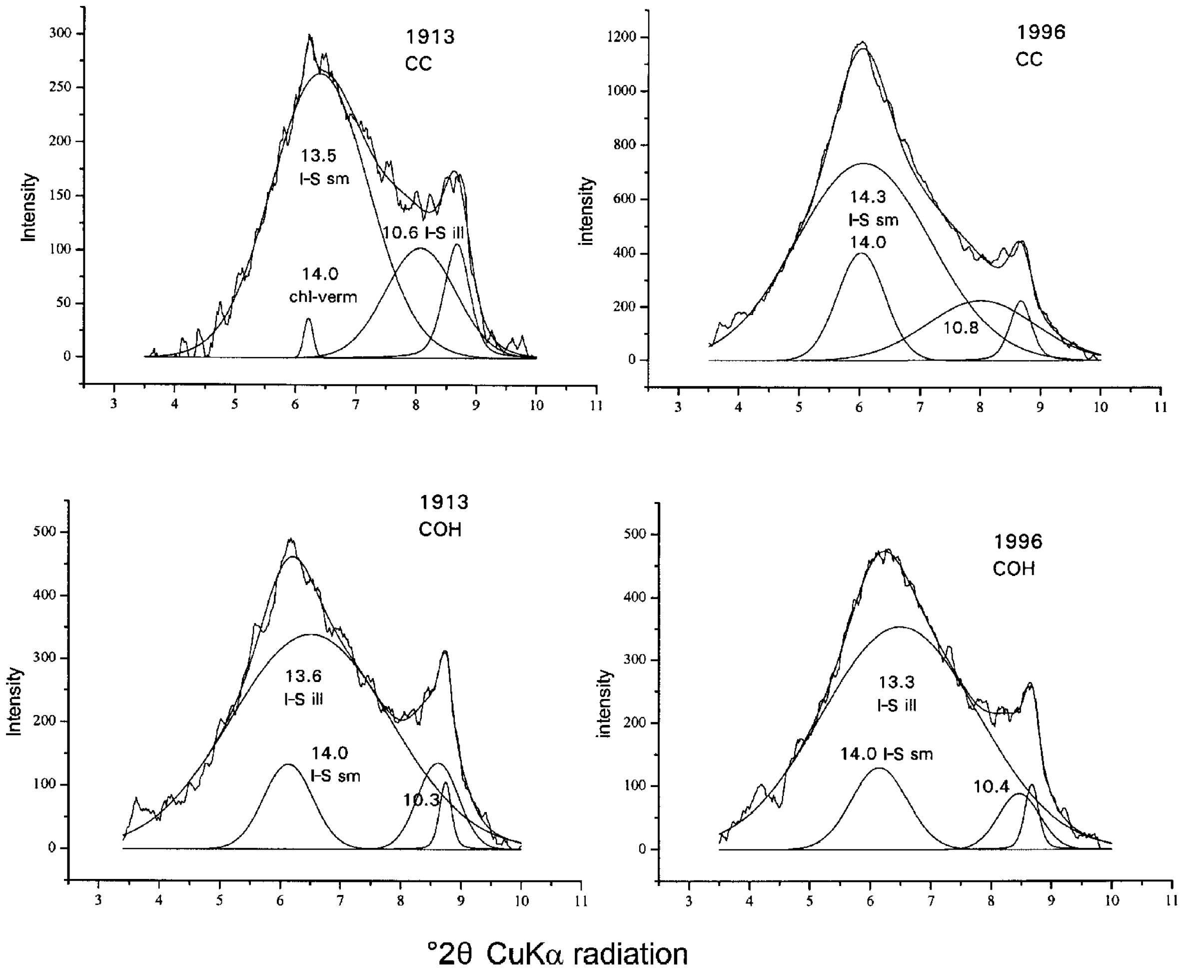

Figure 2. Numerically-treated XRD patterns of the clay fractions. These are smoothed on a seven-point routine and background stripped. The curves shown are fitted using the routine and methods described by Lanson (1997). Two major peaks were postulated, one near 14.3 Å (I-S sm) and another near 13.5 Å (I-S ill) both of which are initially assumed to be >1.5°2θ wide at half above background.

small change between glycerol- and glycol-treated materials again suggests that there is little vermiculite (according to some of the definitions in Dixon and Weed, 1989).

Treatment with H_2O_2 does affect the XRD patterns of the samples, producing at the same time more abundant high-smectite content mixed-layer minerals and a high-illite content expanding mineral of lower expandability (lower *d*-spacing) in the air-dried state.

OBSERVATIONS

The XRD patterns of natural clay fractions of the 1913 and 1996 samples for the two cropping experiments do not show significant changes. In the continuous-corn (CC) cropping plot there is a tendency to show a strong smectitic mineral (Figure 1). However, the decomposed XRD patterns reveal significant changes in the mineralogy of the clays (Figure 2). The major clay phases present in the 3–10°2θ range are mica (10 Å), illite (10.4–10.2 Å) and two mixed-layer illite smectite (I-S) minerals, one with a peak near 13.5 Å and the other near 14.6 Å in the air-dried, Sr-saturated state. Glycol and glycerol produced a unique peak near 15.5–16.8 Å and a mica-illite peak (Figure 3) indicating that all of the I-S material is disordered in nature. The peak positions well below 17 Å indicate the presence of some layers that do not swell to 17 Å, and hence an heterogeneous I-S phase is likely to be present. The H_2O_2-treated samples showed a tendency to increase the relative intensity of the more expandable I-S mineral (near 14.6 Å) seen in Figure 4, while shifting the less expandable I-S peak to lower *d*-values. The peak positions, relative intensities and peak widths at half height (WHH) changed with time in different ways for minerals in the two experimental plots, CC and COH. Changes in peak position of the Sr-saturated, air-dried state XRD patterns as a function of time are shown in Figure 5 for the two crop-rotation experimental plots. It is evident that the COH peak positions and relative intensities change only slightly with time whereas those in the CC samples tend to increase in *d*-spacing with time. All phases, except mica, show a shift to larger spacings. This indicates an increase in the smectite or expandable layer content of

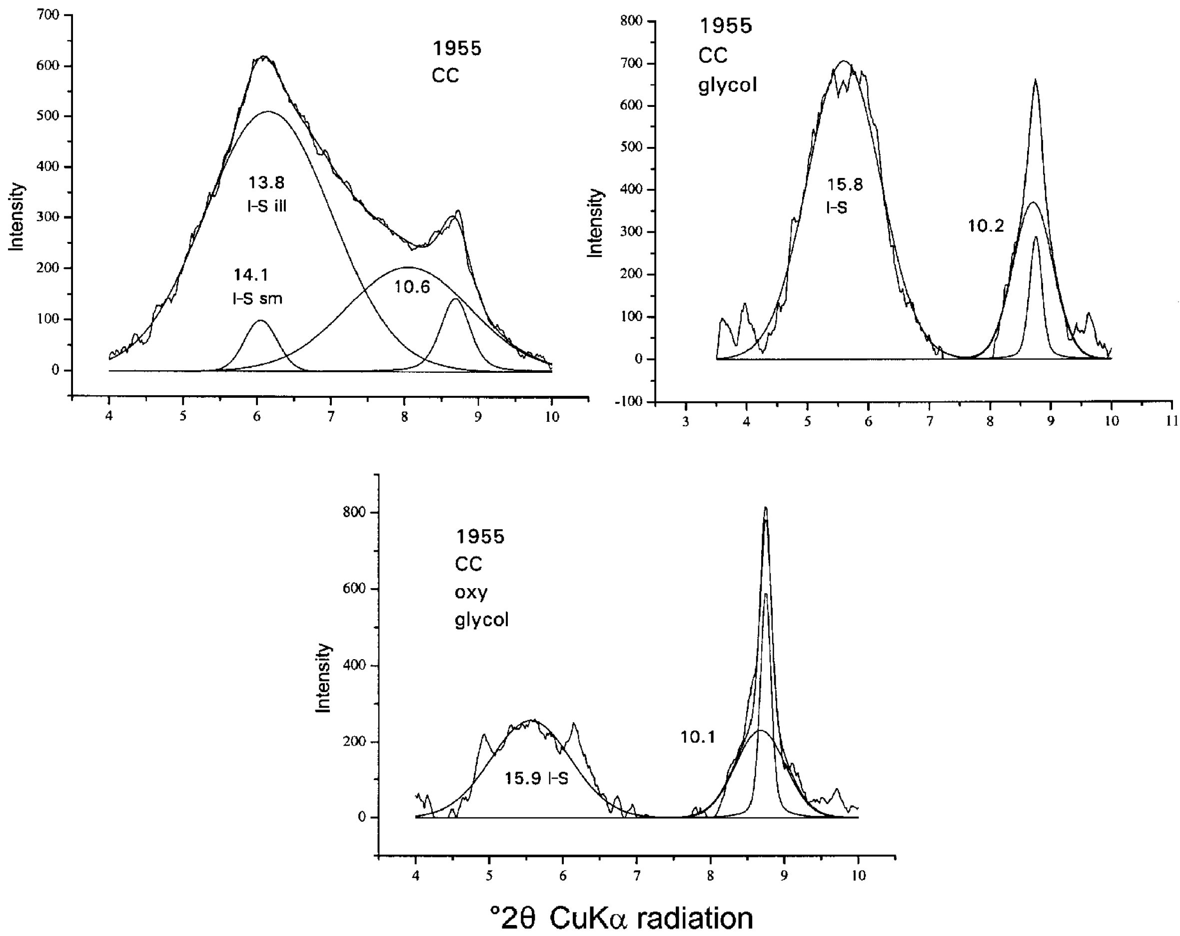

Figure 3. Curve-decomposed XRD patterns of ethylene glycol-saturated samples showing the grouping of the four initial peaks into two or three bands. The I-S minerals form one peak at <17 Å and the illite-mica peaks persist. Oxy = H_2O_2-treated sample.

https://doi.org/10.1346/000986002760833738 Published online by Cambridge University Press

the individual clay mineral components in their natural state (*i.e.* no H_2O_2 treatment nor extraction of oxides) for the clay minerals in the CC plots.

COH plot

In the crop-rotated COH plot, the XRD patterns are much the same for the samples taken over the 87 year period. The illitic illite-smectite mixed-layer mineral (I-S smectite) forms the bulk of the sample of illite and mixed-layer phases. It has a peak position of ~13.5 Å and represents 80% of the total peak areas. Smectitic I-S minerals show a peak near 14.0 Å. The illite peak remains near 10.3 Å with a WHH value of <1°2θ (Figure 2). It appears that there are no major changes in clay mineral compositions or relative mineral abundances in the COH-rotation plot soils.

CC plots

There is a marked similarity between the COH and CC plot clay mineral XRD patterns for the 1913 samples but significant change occurs with time in the CC plot samples. Major changes begin to occur between the 1944 and 1955 sampling where the major I-S peak begins to shift to higher *d*-spacings. In the 1996 sample the position is at 14.3 Å. This can probably be interpreted, for the most part, as a change in the amount of smectite or expandable component in the I-S phase given that peak widths are similar in the series of samples using the Reynolds simulation program. Along with this change, one finds a broadening of the illite peak and a shift to higher *d*-spacings making it an I-S mineral of high illite content. The relative importance of the illite and mica peaks decreases significantly, by about half.

NPK fertilizer

In samples where the cropping was continuous corn but where NPK fertilizer was used since 1955, the clay mineralogy resembles the initial 1913 mineralogy for either the CC or COH plots (Figure 6). This suggests that the change in clay mineralogy during CC cropping is due to a lack of K which is removed by plant cropping. Tributh *et al.* (1987) gave similar XRD results for soil

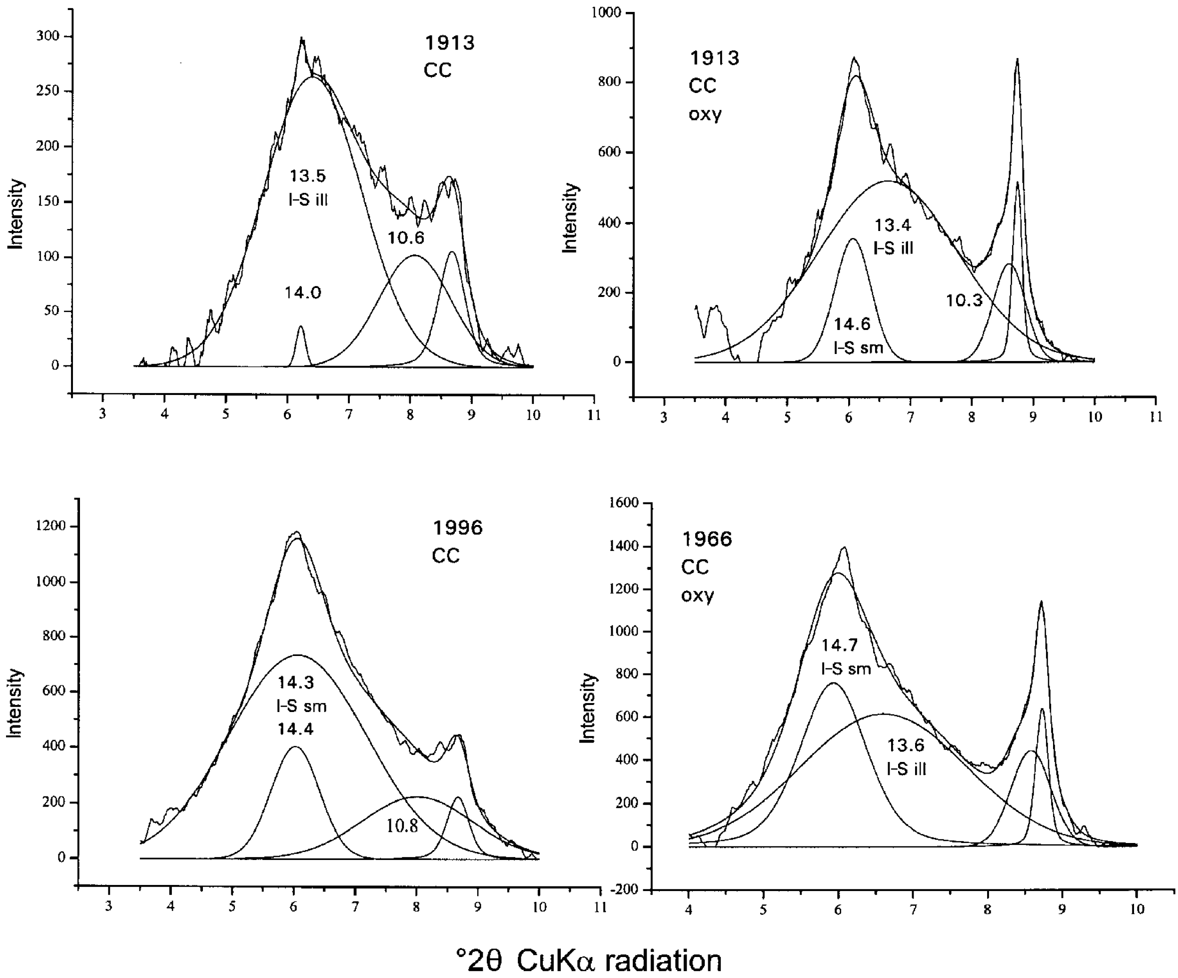

Figure 4. Treated XRD patterns for samples from the plots at the end of the observation in the Sr-saturated, air-dried state for natural clays and those oxidized by H_2O_2 (oxy).

https://doi.org/10.1346/000986002760833738 Published online by Cambridge University Press

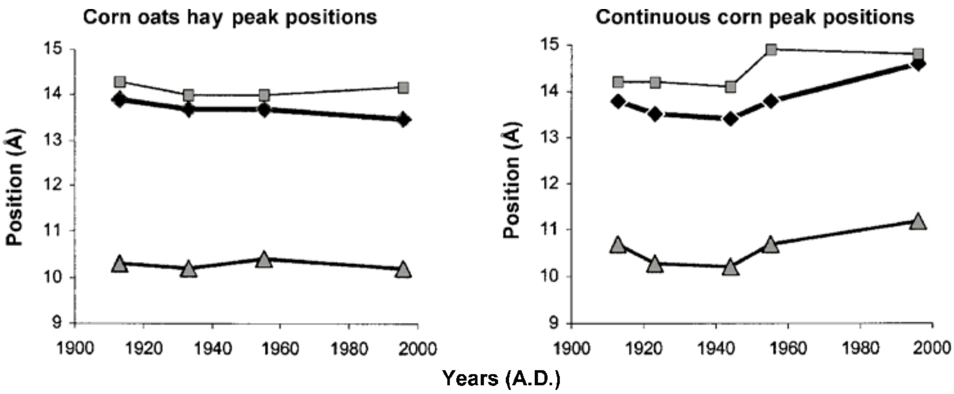

Figure 5. Plots of peak positions for the four phases in the COH and CC plots for XRD patterns of Sr-saturated, air-dried samples. Squares = smectitic I-S; diamonds = illitic I-S; triangles = illite.

materials treated to remove organic matter and free Fe oxides, but the XRD data were less precise and only a general idea of smectite content can be obtained. However, the overall effect is the same.

DISCUSSION

As mentioned in the experimental procedure section, saturation with KCl solution in the laboratory did not seem to change the XRD patterns to any significant extent. This indicates that most of the smectite layers do not have a high charge (Howard, 1981). The partial elimination of organic matter by oxidation with H_2O_2 shows an increase in the abundance of the more expandable I-S mineral which suggests that the organic matter present closes some smectite layers to interaction with hydrated cations (Sr in this case). However, the peak position of the lower expandable I-S mineral shifts to a lower position suggesting that there is a decrease in the amount of expandable material in this phase. In a general study of Central United States agricultural top soils, Velde (2001) found that the expandability of the I-S minerals was increased to a certain extent upon removal of organic matter. In the Morrow Plot samples, the effect of the presence of organic matter seems to close some layers and open others with the overall effect being somewhat insignificant. This judgement, however, is only qualitative. Thus, as far as the clay minerals are concerned, the organic matter does not affect the overall expandability greatly.

From the above summary of the changes in clay mineral XRD patterns for clay minerals in the Morrow plots as a function of time, it seems that the cropping practice of continuous corn changes the clay minerals significantly whereas the corn-oats-hay rotation does not change the clays noticeably.

The major change in the XRD patterns of the clay fraction in untreated clay samples of the Morrow Plots is one of increase in smectite content in the I-S minerals and a change in the illite fraction from a micaceous mineral (*i.e.* non-expanding) to an interstratified mineral. This suggests a loss of K from the clay mineral fraction of these soils under continuous-corn cropping practices.

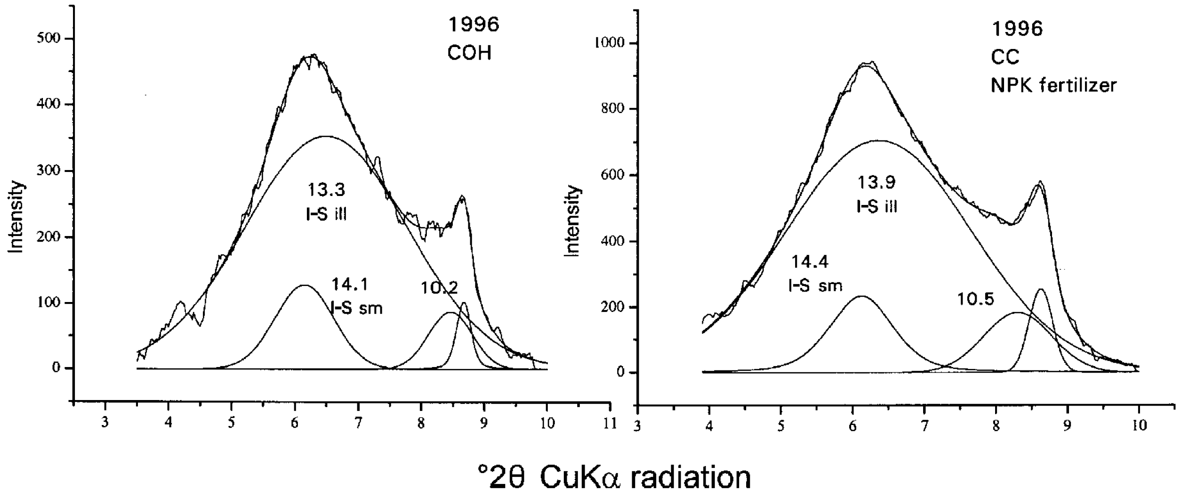

Figure 6. Comparison of the COH-rotated plot clays at the end of the observation period and clays from the CC plots treated from 1955 onwards with NPK fertilizer. The XRD patterns are essentially the same.

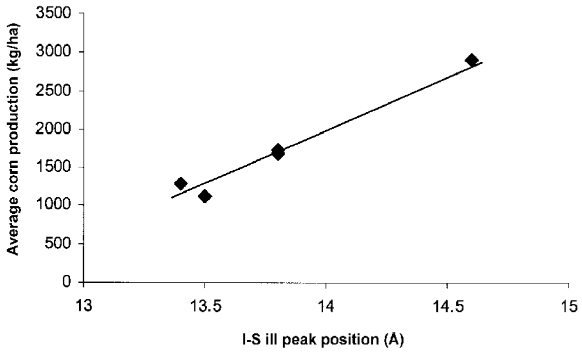

Figure 7. Plot of corn production (5 year average) and I-S peak position (indicating relative smectite content and hence K in illitic mixed-layer clay).

If one plots the average (five year period) corn production against the peak positions of the smectitic I-S minerals in the Sr-saturated, air-dried state for the different samples, it can be seen that there is a reasonable relationship (Figure 7). The introduction of hybrid species in the 1950s increased the corn production for all of the Morrow plots. The effect in the continuous-corn, unfertilized plot was apparently the extraction of K from the clay minerals present with the consequence of increasing the peak position and the smectite content of the I-S mineral.

One can then summarize from the data presented here that the crops grown on a given plot can affect the clay mineralogy over periods of time pertinent to modern agriculture. Even though the potential K reserves in the Illinois soils investigated are great, of the order of 4000 kg/hectare in the cultivated horizon, and extraction of K by corn is small in comparison (56 kg/hectare/year), one sees a significant change in clay mineralogy over only 80 years. This indicates that the K resources are liberated from their initial mineralogy at lower rates than that of extraction by continuous cropping of corn. However, a three year crop rotation allows the clay mineralogy with respect to smectite content to remain unchanged, indicating that K is liberated in sufficient quantities to restore the necessary balance in the soil clay complex in the three year cropping cycle. This suggests that the detrital (non-clay) minerals react sufficiently rapidly to restore initial levels of K in soil solutions to maintain a given mineralogy in periods of 2 to 3 years. This also indicates that the reserves of K are in fact great in the Illinois soils and that farming practices can degrade by reducing available K (producing more smectite layers) in a soil but this soil can be restored reasonably rapidly using appropriate cropping practices.

REFERENCES

Aref, S. and Wander, M. (1998) Long-term trends in corn yield and soil organic matter in different crop sequences and soil fertility treatments on the Morrow plots. *Advances in Agronomy*, **62**, 153–197.

Darmody, R.G. and Peck, T.R. (1996) Soil organic carbon changes through time at the University of Illinois Morrow Plots. Pp. 161–169 in: *Soil Organic Matter In Temperate Agroecosystems* (E.A. Paul, K. Paustion, E.T. Elliott and C.V. Cole, editors). Long Term Experiments in North America, CRC Press, Boca Raton, Florida, USA.

Dixon, J.B. and Weed, S.B. (editors) (1989) *Minerals in Soil Environments* 2nd edition. Soil Science Society of America Book Series, **1**. Soil Science Society of America, Madison, Wisconsin, 1244 pp.

Gharrabi, M., Velde, B. and Sagon, J.-P. (1998) The transformation of illite to muscovite in pelitic rocks: Constraints from X-ray diffraction. *Clays and Clay Minerals*, **46**, 79–88.

Howard, J.J. (1981) Lithium and potassium saturation of illite/smectite clays from interlaminated shales and sandstones. *Clays and Clay Minerals*, **29**, 136–142.

Lanson, B. (1997) Decomposition of experimental X-ray diffraction patterns (profile fitting): A convenient way to study clay minerals. *Clays and Clay Minerals*, **45**, 132–146.

Lanson, B., Velde, B. and Meunier, A. (1998) Late-stage diagenesis of illitic clays minerals as seen by decomposition of X-ray diffraction patterns: Contrasted behaviors of sedimentary basins with different burial histories. *Clays and Clay Minerals*, **46**, 69–78.

Meunier, A., Lanson, B. and Beaufort, D. (2000) Vermiculitization of smectite interfaces and illite layer growth as a possible dual model for illite-smectite illitization in diagenetic environments: a synthesis. *Clay Minerals*, **35**, 573–586.

Moore, D.E. and Reynolds, R.C. (1997) *X-ray Diffraction and the Identification of Clay Minerals*, 2nd edition. Oxford University Press, Oxford, UK, 378 pp.

Reynolds, R.C. Jr. (1985) *NEWMOD a computer program for the calculation of one dimensional diffraction patterns of mixed layer clays.* R.C. Reynolds, 8 Brook Road, Hanover, New Hampshire, USA.

Tributh, H., von Boguslawski, E., von Lieres, A., Steffens, D. and Mengel, K. (1987) Effect of potassium removal by crops on transformation of illitic clay minerals. *Soil Science*, **143**, 404–409.

Velde, B. (2001) Clay minerals in the agricultural horizon of loams and silt loams in the Central United States. *Clay Minerals*, **36**, 277–294.

(*Received 1 February 2001; revised 19 October 2001; Ms. 519*)