

## EVOLUTION OF CLAY MINERALS IN A CHRONOSEQUENCE OF POLDERED SEDIMENTS UNDER THE INFLUENCE OF A NATURAL PASTURE DEVELOPMENT

B. VELDE\*, B. GOFFÉ AND A. HOELLARD

Laboratoire de Géologie, UMR 8538 CNRS Ecole Normale Supérieure, 24 rue Lhomond, 75231 Paris, France

**Abstract**—Clay minerals appear to change significantly under the influence of pasture development on poldered sediments in the Baie d'Authie area (Somme, France). Cores 40–90 cm deep from recent salt marsh sediments and poldered sediments developing grass pastures since 1737, 1575 and 1158 indicate that the natural mineral suite of kaolinite, mica, illite, and two disordered mixed-layered illite-smectite (I-S) phases common to the sedimentary input changes gradually but significantly in the materials. In the oldest, best-developed profile, there is a dominance of a disordered, illitic I-S in the humic upper part of the profile and a more abundant, more smectitic I-S mineral below. It appears that grass-derived humic materials tend to stabilize closed (collapsed) or illitic behavior in I-S clays. The natural evolution of the sediment (lower part of the profile) is towards a smectitic clay assemblage. Destruction of organic matter of the smectitic I-S minerals by oxidation indicates that this material can significantly modify the physical behavior of the clays keeping the structure open to polar molecules.

**Key Words**—Mixed-layer Minerals, Prairie Soils, Salt Marsh Sediments.

### INTRODUCTION

The reaction of clay minerals to changing chemical environments at the Earth's surface has been the subject of only a few recent studies. Most studies of clays in soils are designed to observe clay minerals derived as a function of change in weathering profiles where old, high-temperature minerals are changed by reaction with rainwater to new clay mineral assemblages. Such information combines the kinetics of chemical instability of the high-temperature minerals in the source materials with the changes of the clay minerals themselves which can react to different chemical parameters as they are exposed to conditions nearer the surface of the profile. Hence, most studied soil profiles combine the results of several processes of chemical adjustment; the change from a high-temperature mineral into clay phases and the re-adjustment of these phases as they are moved to the surface of the profile by erosion of surface materials. Therefore the reactivity of clay minerals themselves to changing chemical environment is only partially assessed in such work.

In order to obtain pertinent data concerning the response of clay minerals to chemical change, one should observe a clay mineral assemblage which is affected by new chemical conditions, *i.e.* other than those of its formation. Such a system can be found in salt marsh sediments which have been poldered. These clay-rich sediments, derived for the most part from soils (near 50% clay-sized grains), deposited along a shallow coast, are subjected to new chemical constraints under soil weathering conditions. Such a study was conducted by Righi *et al.* (1995) where the poldered sediments had

been put into culture systematically at various intervals since 1674. The chemical parameters were those of an influx of rainwater and an extraction of some elements through cropping plus the effects of increases in organic matter from growing plants (roots and leaf-stem residue). The results of such a new chemical influence on the clay assemblage were shown to be a reduction of the smectitic material and an increase in the illitic component either in the illite mineral present or in the illite layer component of the mixed-layer minerals. The physical-chemical context of such a system is one of highly unsaturated, slightly acidic rain water reacting to form new phases and certainly some illuviation of new, fine clays to the lower part of the agricultural soil horizons sampled.

Another situation where clays can react to a new chemical environment is one where the poldered sediments are subject to a development of permanent, continuous vegetation which is undisturbed by human activity and where the influence of perennial plants becomes the dominant factor of chemical equilibrium. The Baie d'Authie salt marsh sediment and poldered zones, north of the Baie de Somme along the Channel on the northern coast of France, provide an example of such chemical change. We have undertaken a study of the clay mineralogy of core material in polders and recent sediments dating from 1158 to younger than 1868. This system should indicate the rate and type of clay change in clay-dominated sediments under natural pasture soil development.

### EXPERIMENTAL

#### *Samples*

The sampling sites are shown on the map (Figure 1) where the river Authie is located just north of the

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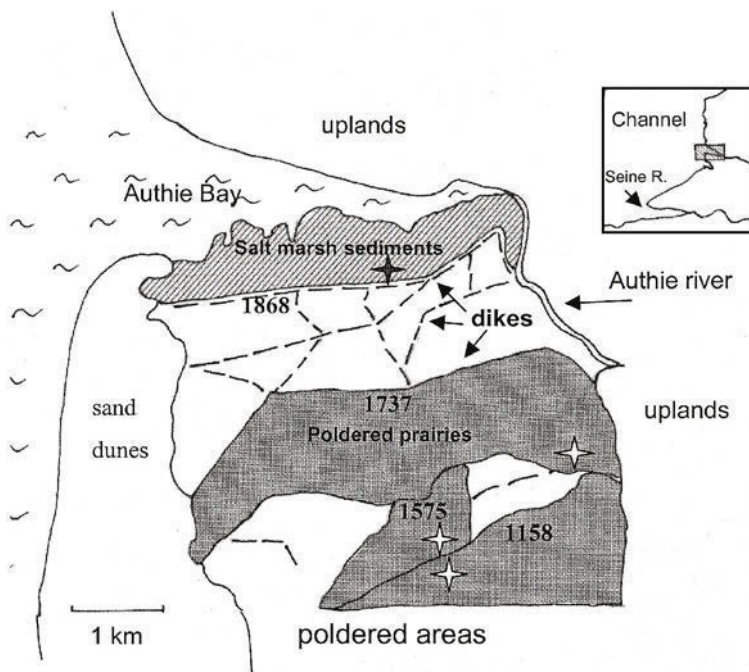


Figure 1. Sketch map of the poldered area to the south of the Authie river bay. To the left is the English Channel and to the right the uplands of the continent. Sampled salt marsh sediments and poldered areas are shaded. Stars indicate the position of sampling in the areas poldered by the dikes (age indicated on the map).

Somme River estuary. The Authie river marsh area has been poldered at different intervals since 1158. The zone of actual sedimentation and the poldered zones of different ages of the diking are shown on Figure 1. The non-poldered core is taken from salt marsh sediments near the last diking in 1868 [see geologic map XX1-6, Rue 1-50,000, (BRGM, 1981) and Hamiot (1999)]. The development of a humic layer due to the growth of grasses, cropped by domestic animals, produces a type of soil profile where the upper portion is defined by plant activity. The color of the material changes from black in the more developed epipedon humic layers (20 cm or so in the most developed profiles) to gray in the layers below the humic horizon and in the deepest samples a cream color. Given that the material is relatively recent (850 years at the oldest) and that the imprint of the initial sediments remains strong (no evidence of clay accumulation below the humic zone) and that the soils are most often in a humic condition (drained), it is possible to propose a soil identification as a Thapto-Histic Hydraquent Entisol (USDA Soil Survey Staff, 1998).

Cores ranging from 40 to 90 cm in depth with a 5 cm diameter, were taken in prairie fields in zones where the burrowing activity of moles seemed to be minimal. We found only one point in the core in the oldest sediments, where a hole of mole size was present. The samples showed a dark, humic layer at the surface followed by a gray layer and at greatest depth a whitish sediment. Clay content ( $<2 \mu\text{m}$ ) was variable, ranging from 5 to 30%. This indicates the variation due to fluctuations of

sedimentation during the accumulation of the sediments in the bay.

In the salt marsh sediment sample near the 1868 dike it was noted that a 5 cm sand layer occurred at 20 cm depth. In cores taken just inside the 1868 dike, a strong sand layer occurs at 5–8 cm depth. We assume that there is a correspondence between the two sand layers, and hence the salt marsh sediment core Au2 contains material younger than and older than 1868. Other cores were taken within the poldered areas whose ages are indicated on Figure 1.

#### XRD methods

Two types of analysis sequences were made; one on untreated clay and one on 30%  $\text{H}_2\text{O}_2$ -treated clay. The fine fraction was extracted by settling from material dispersed ultrasonically in distilled water after settling for 10–12 h. This assures that the material was  $<2 \mu\text{m}$  in its largest diameter. The supernatant liquid was flocculated with  $\text{SrCl}_2$  or  $\text{KCl}$  and the concentrate was sedimented on a glass slide. The XRD patterns were obtained using a Philips diffractometer ( $\text{CuK}\alpha$  radiation) with a stepping motor. Counting times were 6 to 20 s at  $0.01\text{--}0.02^\circ 2\theta$  step intervals, depending upon the intensity of the diffraction peaks. The resulting spectra were treated using the methods outlined in Lanson (1997) with a 7-point smoothing routine and background subtraction. The range investigated was  $3\text{--}10^\circ 2\theta$ . Curve decomposition routines were used to determine the components of the XRD patterns. For the air-dried samples, the initial hypotheses were the presence of four

peaks: one of which was at  $10.0 \text{ \AA}$  (mica) with a width of  $0.4^\circ 2\theta$ . A Gaussian-Lorentzian solution was used for this peak as was the case for studies by Gharrabi and Velde (1995) and Lanson (1997). A second peak was postulated near  $10.3 \text{ \AA}$  (illite) with a width of  $0.8^\circ 2\theta$  of Gaussian form. A third peak was postulated near  $12 \text{ \AA}$  with a width of  $3^\circ 2\theta$  and a fourth near  $15 \text{ \AA}$  with a width of  $\sim 1^\circ$ . It became apparent that the peak at lowest  $d$  spacing was better fitted using a Gaussian-Lorentzian shape than with a strictly Gaussian one. This was especially true at the extremities of the peaks. If only Gaussian forms are used, it is necessary to add peaks to the fitting routine which cannot be justified mineralogically due to their high spacings. In the experience of the authors, when a relatively pure smectite phase is present, the peak shape approaches a Lorentzian form. This is the case when observing standard smectite clay minerals. This effect can possibly be explained by the flexible nature of the large, thin clay smectite particles which when sedimented one upon the other form a pseudo-macrocrystal which produces a more ideal diffraction behavior. Such an effect is less likely to occur with more blocky illitic I-S clays or illite/mica particles themselves.

Intensities, width at half height (WHH) and peak positions of the derived peaks were determined from parameters determined by the decomposition least squares refinement after use of the initial postulates.

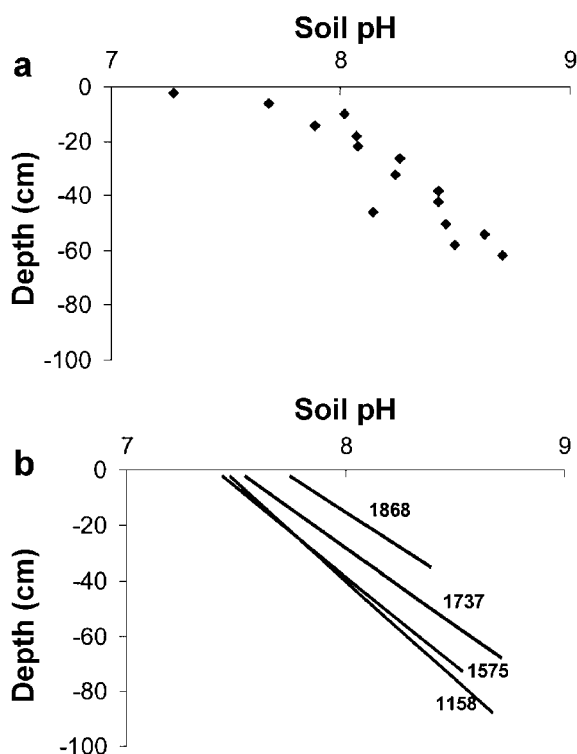


Figure 2. Plot of pH data for the cores. (a) A typical example, 1737 core, and (b) deduced regression lines for the different cores studied.

Use of WHH and intensity allows calculation of peak area. Peak areas can be compared between phases in a relative manner when the phases present are the same in order to indicate changes in relative abundances or the phases in the profiles.

Simulations of XRD patterns of mixed-layered minerals were made using the NEWMOD program (Reynolds, 1985).

### pH

pH measurements were taken on the samples using a 2:1 solid to liquid ratio (solid = dried sample, liquid = distilled water). An example of the results for the 1737 polder core is given as well as regression lines for the determined values of the different cores (Figure 2). The regression fits were good ( $R^2 = 0.98$ ) and no tendency for a non-linear or multi-linear trend was observed by visual inspection.

### Sample color

Visual estimates of sample color classed as black (humic), gray and white give a rough classification of the soil profiles developed in A, B and C horizons, respectively. The Munsell colors are 5Y 4-1, 5Y 6-1 and 5Y 7-1, respectively. The transition of black to gray could be estimated to within  $\sim 1$  cm. These observations are shown in Figure 3.

## EXPERIMENTAL RESULTS

### Untreated clays

Figure 4a shows some of the results for the initial salt marsh sediments compared to the oldest poldered sediment core (1158, Figure 4b). The XRD traces for Sr-saturated, air-dried samples for the salt marsh sediment core show some variability in the general shapes of the curves indicating some mineralogical variation. The peak low-angle, high- $d$  value maxima for air-dried, Sr-saturated samples in the sediments are found at  $<15.2 \text{ \AA}$  while in the 1158 core they are centered near  $15.2 \text{ \AA}$ . The uppermost samples have a

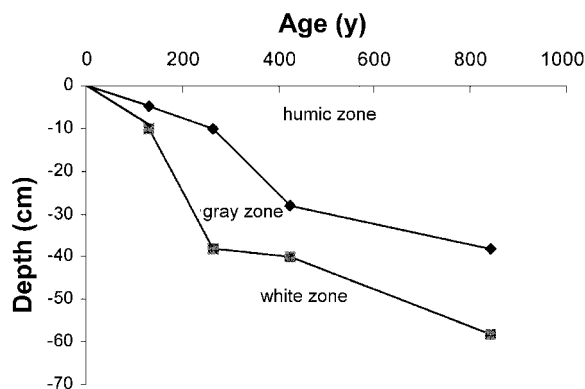


Figure 3. Plot of limits of the color changes observed in the core material. The humic zone is indicated by dark black material.

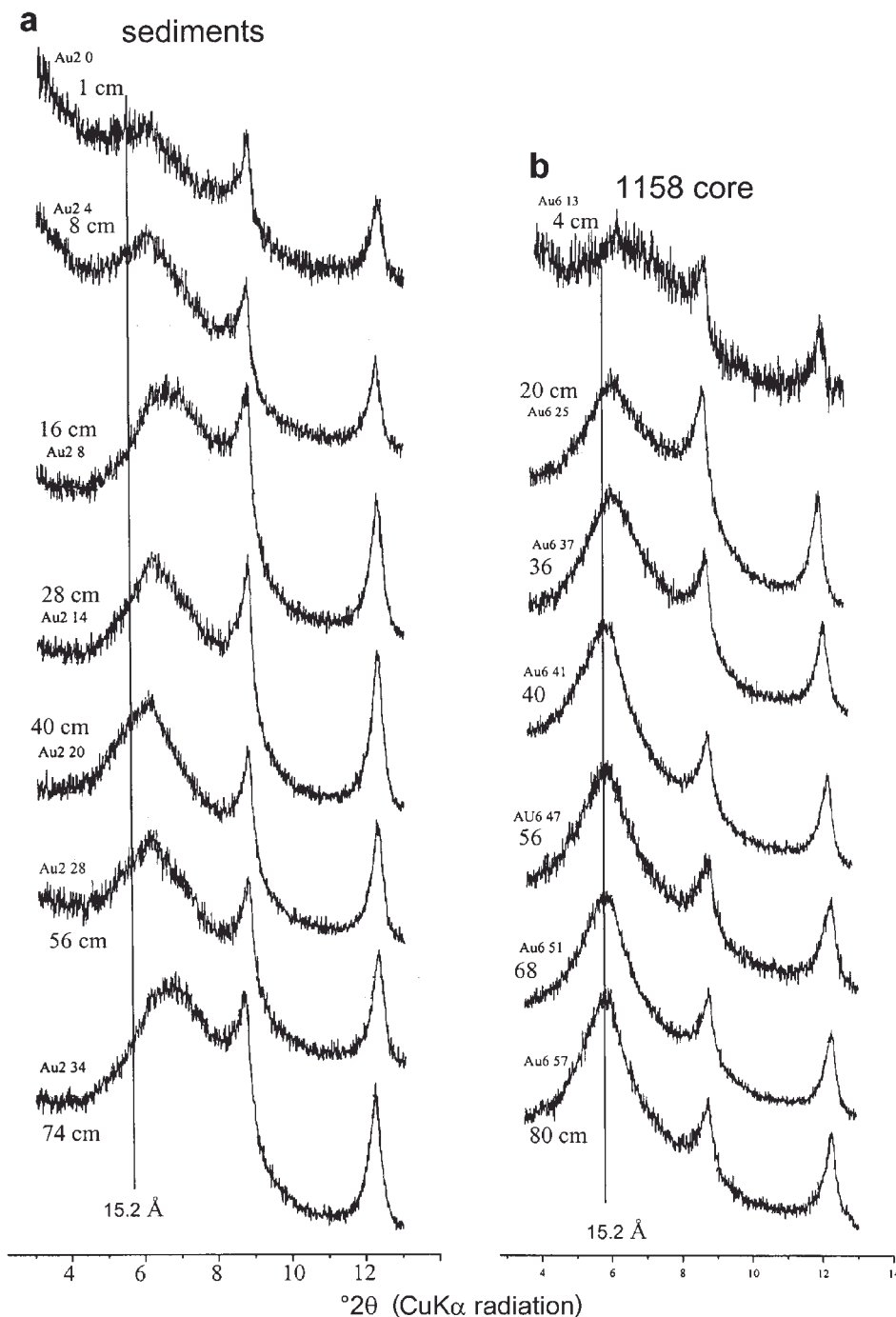


Figure 4. XRD patterns of untreated, Sr-saturated, air-dried clays in the sediment core (a) and in the oldest core, the 1158 polder (b).

high background at low angles upon glycol treatment indicating a large illite content in the I-S minerals which decreases at depth to a value. Such a shift suggests ~70% smectite content assuming two component I-S minerals (Inoue *et al.*, 1989).

The series in the oldest, 1158 polder core, air-dried, Sr-saturated samples (Figure 4b) shows a slightly larger spacing for the I-S maxima below 37 cm with a decided,

but subtle, shift to a spacing  $>15.2 \text{ \AA}$  in the deeper cores. The relatively low background at low angles suggests a relatively large smectite content in the I-S phases; however, these differences appear to be minor. The overall aspect of the XRD patterns indicates a similarity with some scatter indicating some small fluctuations in mineral composition as a function of deposition in the sediments and recent polder core.

### Decomposed spectra

The decomposition of the XRD spectra can give information concerning the peak position, peak intensity and peak width of individual clay mineral components of a multiphase sample. Peak position indicates, for the most part, compositional change, either in mica/illite

composition (see Gharrabi and Velde, 1995) or in the proportion of layers of the illite-smectite components of the mixed-layer phases (see Moore and Reynolds, 1997). Peak width indicates, for the most part, the relative number of layers coherently diffracting in the crystallites. This is probably not true for the high smectite I-S

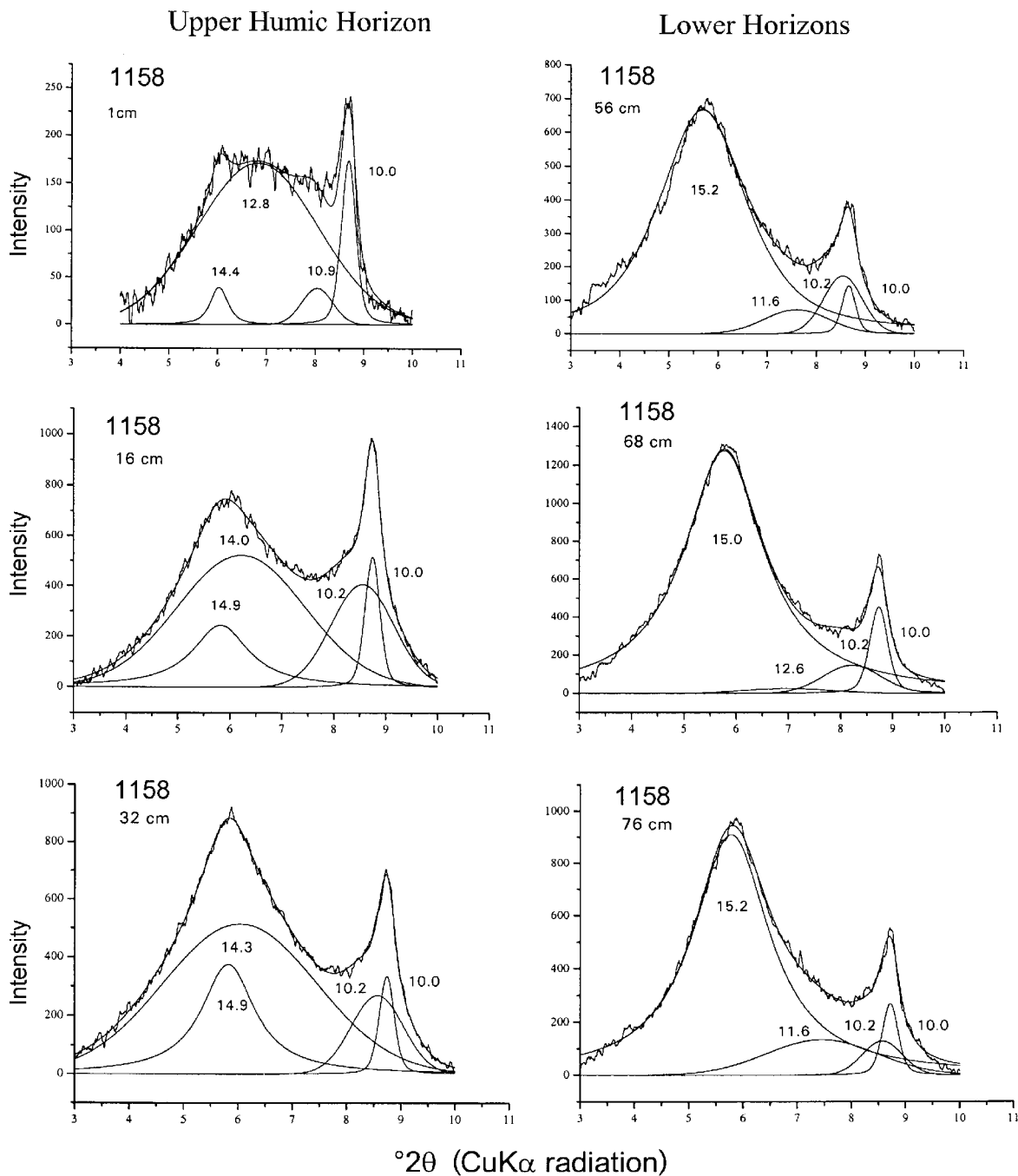


Figure 5. Examples of treated XRD patterns (of untreated, Sr-saturated samples) used to determine the peak positions of the different minerals in the oldest poldered soils showing the variations in the upper, humic horizon and the samples below it. Note that the 15 Å peak in the lower horizons is of a more Lorentzian shape (wider at the base), typical of more smectitic clays.

mineral with a high Lorentzian component which could be the result of artificial stacking to form a pseudo-macro crystal. Peak area can be used to indicate the relative proportions of the different diffracting phases. Since there is no indication that the initial relative proportions of the different phases remained constant over the period of sedimentation (840 years), caution is required when using the relative peak areas to determine mineral abundance. However, the peak areas can be used in a core sequence to identify trends or changes in trends, despite variations in sedimentary input.

#### Phases identified

Mica can be identified by a sharp ( $<0.4^\circ 2\theta$  WHH) peak near  $10 \text{ \AA}$ . Illite is identified here as a broader peak ( $0.5\text{--}1.5^\circ 2\theta$  WHH) found near  $10.3 \text{ \AA}$  (see Gharrabi and Velde, 1995). The mixed-layered phases, assumed to be primarily of two-component layers of smectite and illite, are of two kinds found in each sample, one more illite-rich (near  $12\text{--}13 \text{ \AA}$  in the Sr-saturated, air-dried state) and the other more smectite-rich (peak near  $14\text{--}15 \text{ \AA}$ ). This is a comparative terminology. In the deeper portions of the older cores, both join to form a single peak at slightly less than  $17 \text{ \AA}$  upon glycol treatment indicating that they are both disordered ( $R = 0$ ) structural types (Moore and Reynolds, 1997) which are common in prairie soils (Velde, 2001). They are referred to here as illitic I-S and smectitic I-S. This is a relative term as the smectite/illite content varies for each mineral from sample to sample but since the I-S minerals occur together, one is always more illitic than the other. A  $14 \text{ \AA}$  phase is present at times in the upper portion of the older profiles as well as in the recent sediment. It is of relatively small abundance when present and appears to disappear below  $15 \text{ cm}$  in the older cores ( $1 \text{ cm}$  depth, 1158 core in Figure 5). It does not appear to change position upon glycol treatment. No further identification or characterization is made of this phase due to its erratic occurrence. Kaolinite was present in all XRD traces but given that its composition and XRD characteristics are not especially diagnostic of mineral change, no detailed analysis was made of the kaolinite diffraction peaks. Peak areas for kaolinite indicate an abundance similar to that of mica.

#### Results in different cores

Examples of the different clay assemblage types are shown in Figure 5 as decomposed XRD patterns. These are found most clearly in the oldest poldered prairie (1158).

Figure 6 shows the peak positions of the smectitic and illitic I-S minerals in the different cores as a function of depth for untreated, Sr-saturated, air-dried samples. This state was used in order to indicate the presence of both of the I-S minerals. After glycol treatment, both of the disordered I-S minerals formed a single peak near  $17 \text{ \AA}$  which combines the different

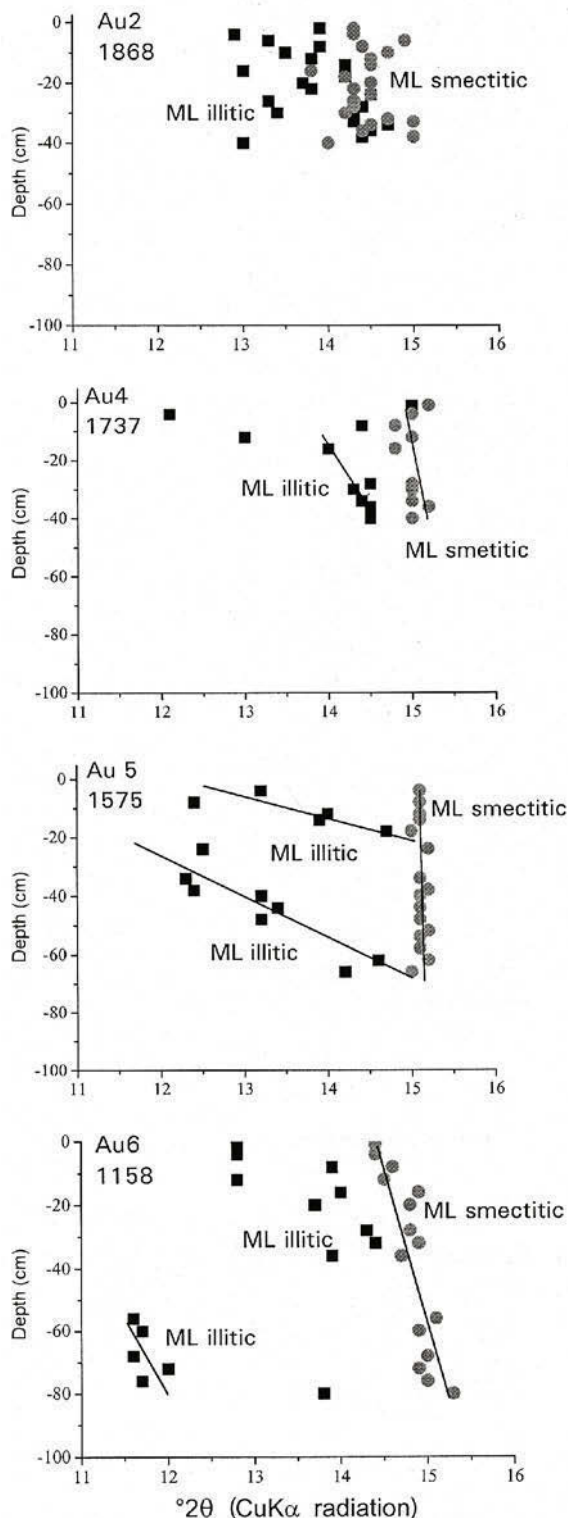


Figure 6. Plot of depth peak positions of the I-S minerals for the cores investigated. Samples in Sr-saturated, air-dried state. The gray zone indicates the humic horizon. Lines suggest individual trends of change for the I-S phases. Squares represent the more illitic I-S minerals of the mineral pairs and circles represent the more smectitic I-S minerals.



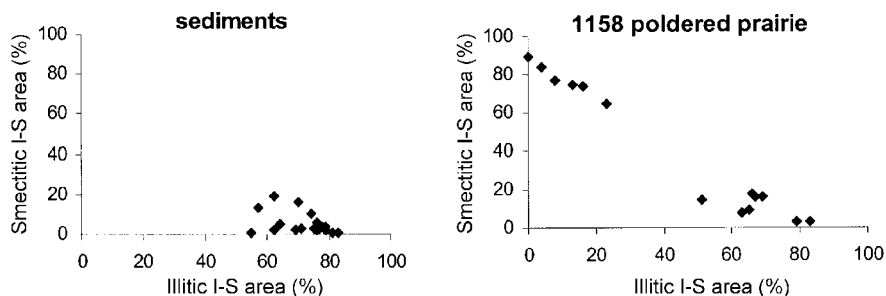


Figure 7. Plots of the relative proportion (peak area) for the two I-S phases in the sediments post- and pre-1868 and the oldest poldered site (1158).

mixed-layer diffraction peaks into one giving a loss of information. It is clear in this figure that a pattern develops with time which is determined by the existence of the humic layer in the poldered materials indicated by the gray zone on the diagram. In all instances, the smectitic I-S mineral shows a peak near  $15 \text{ \AA}$  and the more illitic I-S minerals show strong changes in peak position as a function of depth in the profile.

The relative amounts (normalized peak areas) of the I-S minerals change as a function of depth, where the humic zone has a larger proportion of illitic I-S and the deeper horizon more smectitic I-S minerals. The relative proportions of the I-S minerals are compared for the marsh sediment and the oldest poldered prairie in Figure 7. In the deepest portions of the core, smectitic I-S dominates.

The evolution of peak position and WHH for the I-S minerals for the 1158 poldered prairie is indicated on a graph where position-width values were obtained using the NEWMOD program. The variables affecting the diffraction peaks are percent smectite and size of the coherent diffracting domain in the disordered mixed-layer I-S mineral. These data indicate a reverse relationship for illitic and smectitic I-S with depth (Figure 8). For both minerals the lower the  $d$  spacing (higher illite content) the narrower the peak, suggesting that there are significantly larger diffracting domain sizes as illite (closed layers) increases.

#### Effect of $H_2O_2$ treatment

The samples treated with  $H_2O_2$  in order to oxidize a large portion of the organic matter, showed that the effect of the organic matter was to close some of the smectite layers to the insertion of hydrated exchange cations in the initial sediments. In the upper, humic zone of the most developed profile (1158), however, there is little effect whereas in the deeper part of the profile the smectitic I-S mineral shows a decrease in expandability indicated by a lower peak position (Figure 9). Glycol saturation gave much the same result for oxidized and untreated samples (Figure 10). There is evidence for the formation of a less expandable mineral when treated with  $H_2O_2$  and glycol. Both of the I-S minerals are present in a disordered stacking form.

#### Potassium saturation

In the untreated samples, K saturation closes some of the smectite layers to expandability (smaller  $d$  spacing) in both the illitic and smectitic I-S minerals (Figure 11). There is a pronounced increase in the illite peak (near  $10.3\text{--}10.8 \text{ \AA}$ ) in oxidized and untreated samples. Glycol treatment confirms the above showing that overall, the I-S minerals are less expandable and the mica/illite peaks are more prominent. In the oxidized samples, K saturation closes some of the illitic I-S mineral layers

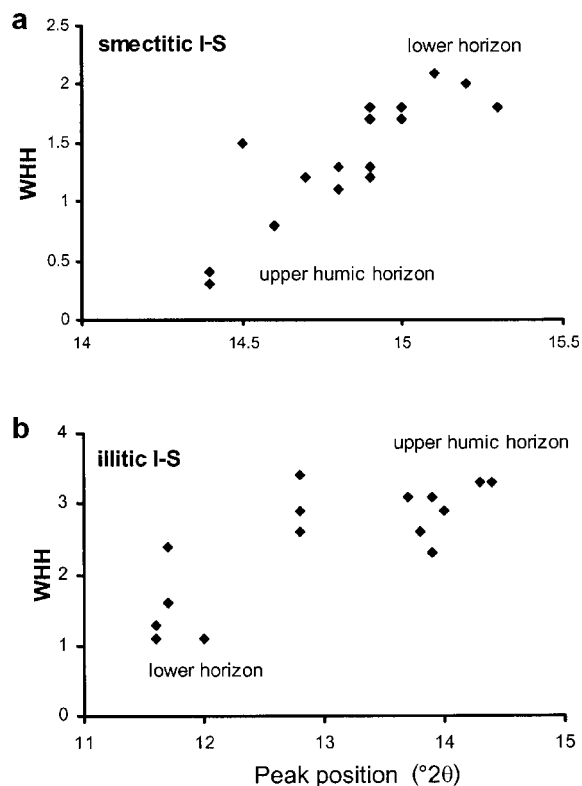


Figure 8. Graph of the peak position and WHH in the air-dried, Sr-saturated state for the (a) smectitic I-S minerals and (b) illitic I-S minerals in the oldest core (1158) based on calculations using NEWMOD. The experimental points showing the evolution with depth in the 1158 poldered core from the top shown by points in the lower left hand portion of the diagrams and lower horizons by points in the upper right hand portion of the figure.

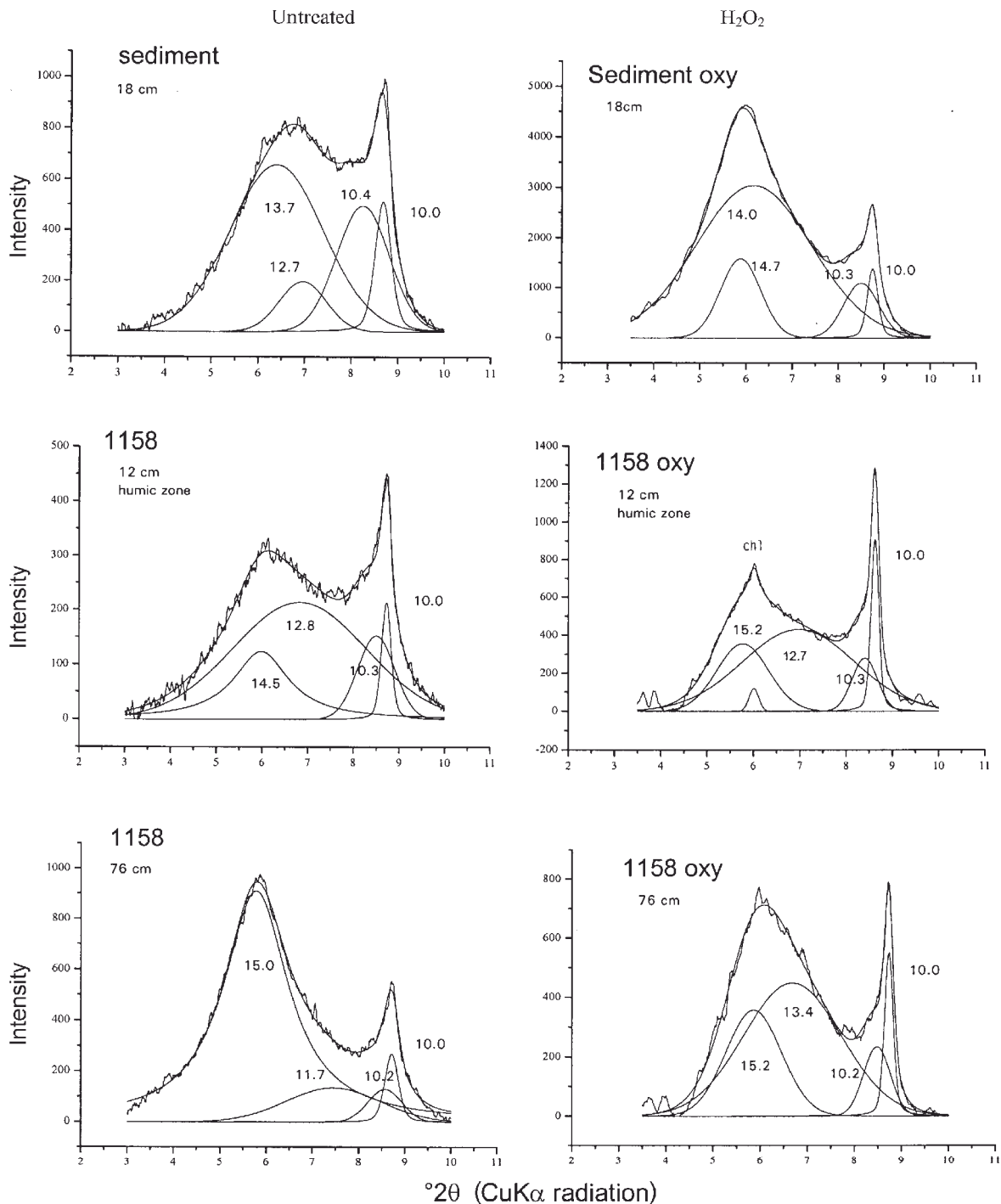


Figure 9. XRD patterns and decomposition values for untreated and oxidized ( $H_2O_2$ ) samples after Sr saturation and run in the air-dried state.

but appears to allow expansion of some of the layers in the smectitic I-S mineral.

The effect of organic matter on the expandability of the two I-S minerals is different in each case, suggesting complex relations perhaps related to the type of charge present, its site or the type of bonding interaction between the organic matter and the clay structure.

## DISCUSSION

Initially we will consider the untreated samples, *i.e.* those not subject to oxidation by  $H_2O_2$ . The XRD characteristics determined for these samples can be considered to approach their response in the natural soil as far as the properties of expandability and hence cation exchange are concerned.



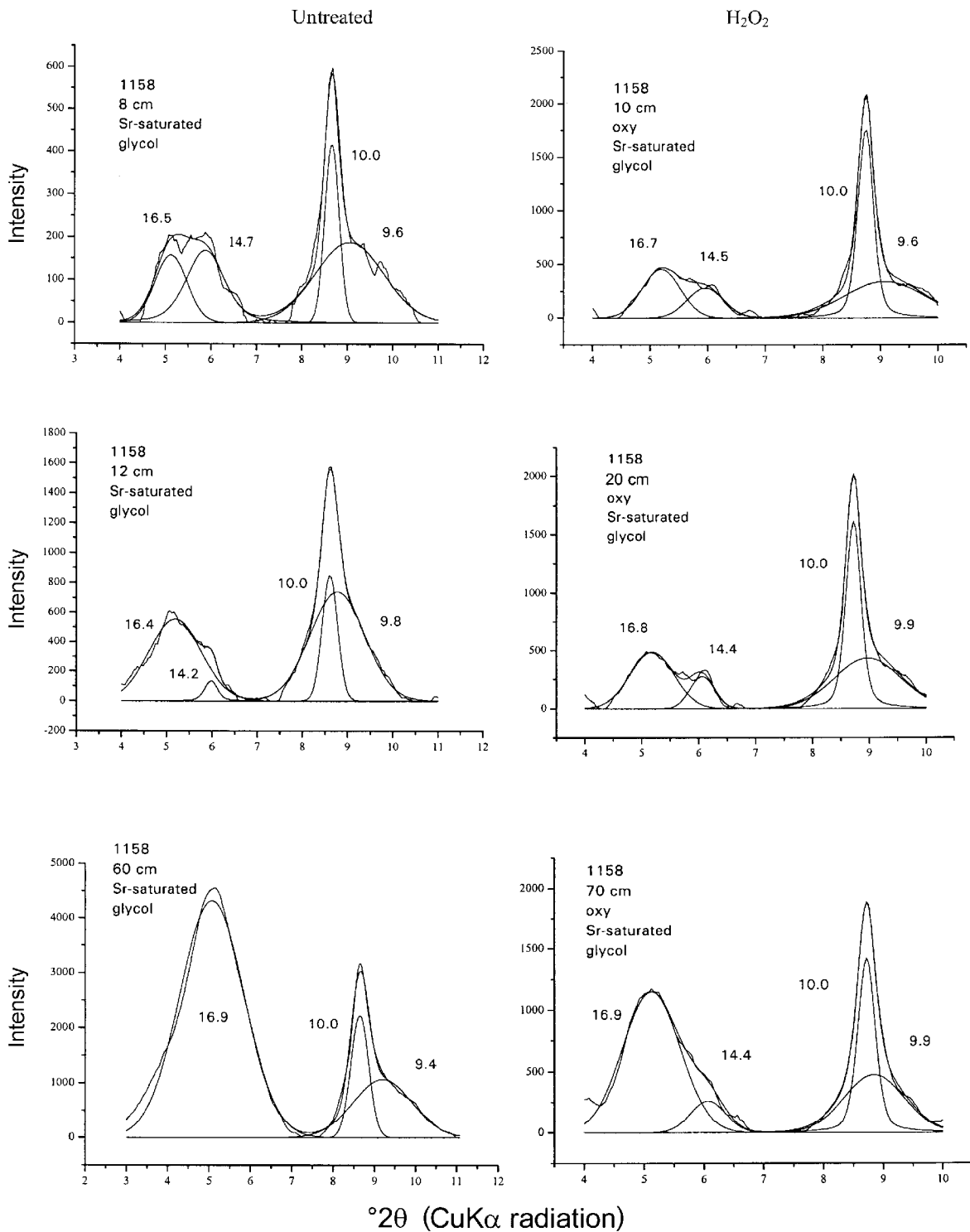


Figure 10. Comparison of glycol-treated, Sr-saturated samples in the untreated and H<sub>2</sub>O<sub>2</sub>-treated samples.

The cores can be considered individually either as depth or time trends where one can observe the effect of time which changes chemical conditions due to the development by the prairie epipedon horizons. In the 1868 salt marsh

sediments and the 1737 poldered area, little systematic change can be seen in the clay assemblages as a function of depth. The grasses have established only a thin layer of humic material in the 1737 poldered area. All of the XRD

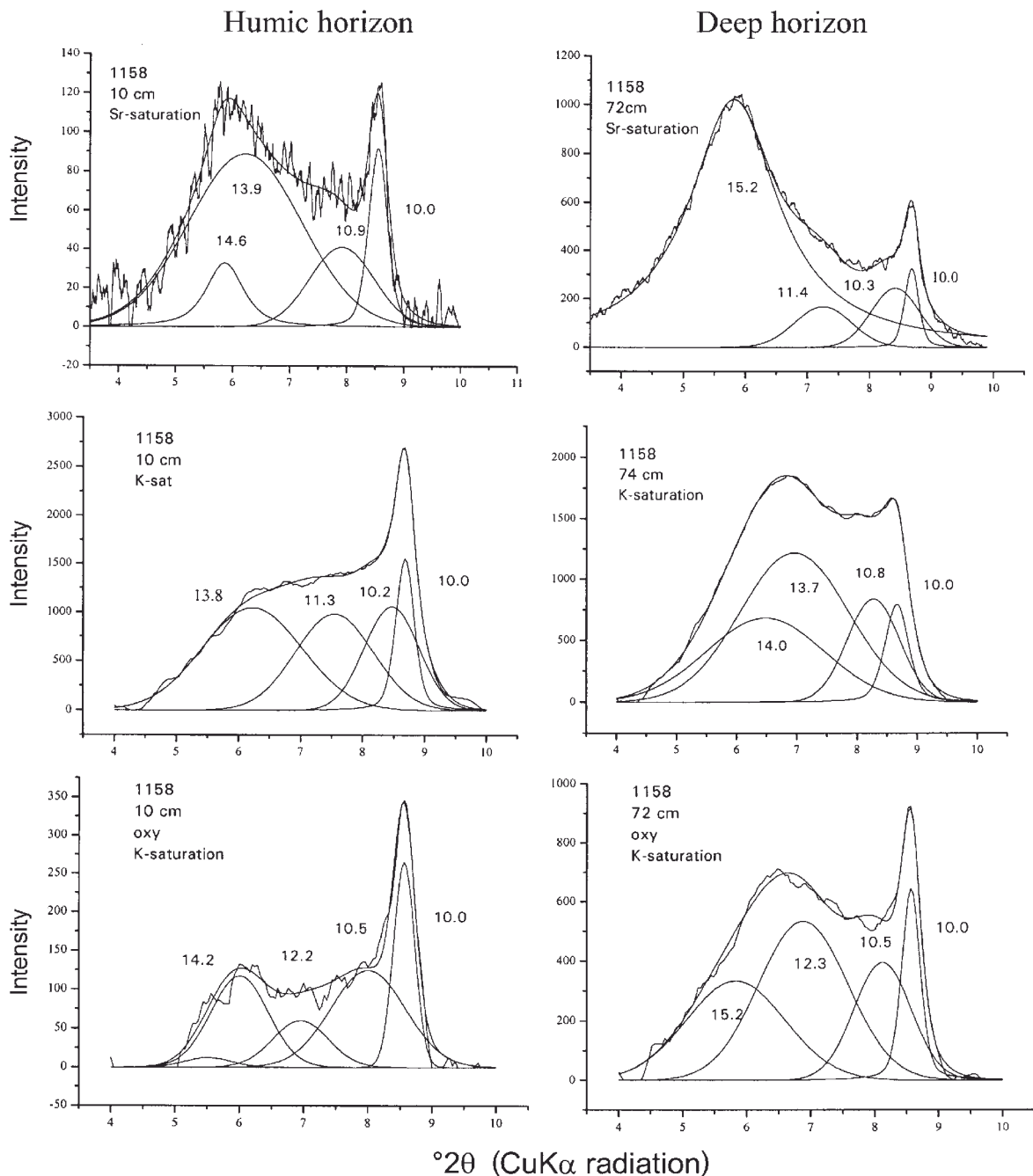


Figure 11. XRD patterns of untreated and H<sub>2</sub>O<sub>2</sub>-treated samples from the 1158 polder core after K saturation.

patterns appear to be rather similar; two I-S minerals are present in varying proportions. However, in the two older cores, 1575 and 1158, strong trends in clay mineralogy occur as a function of depth in the cores (Figure 6).

#### *Characteristics of the I-S clays in the initial sedimentary input*

Little correlation of parameters of the clay mineral XRD peaks can be made as a function of depth in the

salt marsh sediment core material. The positions of the two I-S minerals vary but not in any systematic way. From this we deduce that there is little need of major re-adjustment of the clays to changes in chemical variables of the sedimented material. Little or no change of the clays indicates that they are near a chemical and physical equilibrium in such a clay-saturated system.

*Depth changes for minerals in cores of the older poldered sediments*

Changes of clay characteristics of individual clay minerals with depth in the cores is clearly apparent in only the three oldest cores. It is important to point out the specificity of soils developed in poldered sediments. When poldering takes place, a system of sediment accumulation from the top of the sequence is stopped. Soils develop on a basically homogeneous material from top to bottom. The bedrock or source material is the same essentially in all portions of the soil profile at the beginning of such a system. Some clay transport may take place in the soils as well as some chemical change but since all of the material is composed of weathered materials which are close in composition to soil minerals, one can expect that limited chemical reaction will take place in the traditional sense of weathering and soil formation. The clay minerals of the soil are near the final weathering state found in soils of temperate latitudes and hence near chemical equilibrium with atmospheric conditions.

The changes in clay mineralogy observed can be summarized as below.

*Illite.* The position of illite peaks does not vary systematically in the cores which indicates little change in composition (possible interlayered smectite). However the WHH of the illite peak seems to increase systematically with depth in the 1737 and 1575 cores with a more complicated pattern in the 1158 core (Figure 12). The oldest core shows a double trend broken at the bottom of the humic zone. An increase in WHH at constant peak position suggests a decrease in the average diffracting domain size of the crystallites. This can probably be taken to indicate a destabilization of the initial detrital illite/mica mineral in these cores except in the lower part of the oldest (1158) core. If the illite domains decrease it is probable that this is due to destabilization and the illite can be seen to enter into reaction with its chemical clay environment and the illite enters into the mixed-layered minerals being formed in the soil.

*I-S minerals.* In each sample we have identified two phases which appear to be 'mixed-layered' in character. One is more smectitic than the other. For this reason we have given the term illitic and smectitic I-S to each. This is relative in that some of the illitic I-S minerals have significant smectite content which changes at depth to a less smectitic mineral.

The peak position of the illitic I-S increases with depth in all parts of the cores but in the two oldest cores the change occurs clearly in two steps (Figure 6). The break in the sequences occurs at the point of the change from humic to gray zone in the profiles. This peak position change suggests an overall increase in expandability of the mixed-layer phase with depth in the Sr-

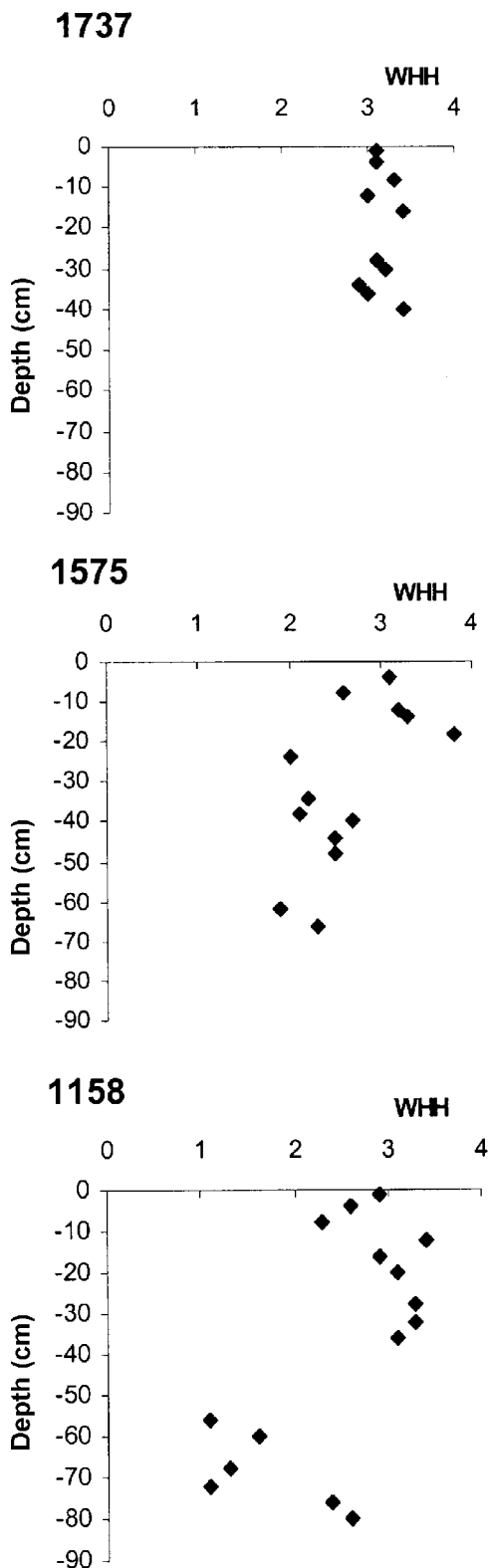


Figure 12. Plot of illite WHH vs. depth in three cores. The lines indicate the general trends of the values with depth.

saturated, air-dried state. The WHH values also follow depth trends increasing in the 1737 core and decreasing with depth in the 1575 and 1158 polder cores. Oxidation of portions of the organic matter ( $H_2O_2$ ) tends to have little effect on the illitic I-S mineral. Potassium saturation closes some of the layers in a portion of the grains forming a less expandable phase. The effect of oxidation appears to be more important in the illitic I-S minerals with higher expandability.

The XRD peak characteristics for the smectitic I-S change less with depth than do those for illitic I-S. In the deepest part of the cores the smectitic I-S attains a 15.2 Å spacing indicating the presence of a >50% smectite I-S mineral using NEWMOD calculations. The smectitic I-S minerals become more dominant in the XRD patterns of the clay fraction (larger relative surface) with depth, below the humic zone in the older cores. Such a change in peak position and width suggest a roughly constant smectite content with small coherent diffracting domains in the deeper parts of the cores. Potassium saturation indicates that the smectitic I-S becomes more illitic in nature (shift of the major peak to lower  $d$  values). Potassium saturation after destruction of much of the organic matter ( $H_2O_2$ ) produces a more abundant, illitic I-S mineral and less of the expandable smectitic I-S mineral. These results indicate that there is a relation between the more easily oxidized organic matter present and the expandability of the smectite layers in the smectitic I-S minerals.

#### Relative mineral abundances

The mixed-layer minerals dominate the clay mineral assemblages, forming ~70% of the clay mineral peak surface area in the XRD patterns. Looking at the relative peak areas, little change is seen in the initial sediment salt marsh cores and in the youngest (1737) polder material. However, in the two oldest cores (1575 and 1158), there is a strong tendency to have a dominant illitic mixed-layer mineral associated with the humic zones of the cores which is replaced by a smectitic mixed-layer mineral below this zone. The illitic I-S and smectitic I-S mineral peak area in the oldest core show reciprocal relations. It is clear from this that the mixed-layer phases react between themselves in these soil and sediment materials. There is also a clear relation between the humic layer and the presence of illitic mixed-layer I-S minerals in the oldest core. Below this layer the stable mineral is a smectitic mixed-layered phase.

## CONCLUSIONS

The above observations show clearly that:

(1) In the samples studied it takes several hundred years to establish a clay mineralogy which is determined by local chemical factors (pasture grasses) that change the clay minerals in response to new conditions in the epipedon portion of the core profiles. This is shown by

the sharp change in clay mineralogy of the I-S phases, smectitic and illitic above and below the humic zone in the oldest profile. Two disordered I-S minerals are present in both the initial sedimentary material and the cored material in profiles of different poldering age.

(2) The most abundant clay mineral developed in the humic zone of the material of the present study is a disordered I-S mixed-layer mineral with >50% illite content. This is also the most abundant mineral in the recent sediment input. However, below the humic zone, a smectitic (>50%) mixed-layer mineral is dominant. The change is abrupt at the interface. Both the mineralogy and mineral abundance show this change.

(3) Both the smectitic and illitic I-S seem to be affected (expandability) by loss of organic matter. The change in expandability in the Sr- and K-saturated state indicates complex interactions of organic material and clay layers in the mixed-layer minerals.

These observations indicate that the mineral most stable in the humic zone of soils tends to behave as an illitic I-S mineral, one which is present in the sediment input in the Baie d'Authie. The illitic (non-expanding) content of this illitic I-S mineral increases with depth in the humic zone. In comparison, a more illitic I-S mineral is favored by agricultural practice in the poldered sediments of the Atlantic Coast (Righi *et al.*, 1995).

The overall tendency of the clays at greatest depth in the investigation (well below the humic zone) indicates the development of a dominant smectitic I-S mineral. Destruction of much of the organic matter in the samples below the prairie humic zone has the effect of producing more closed clay layers in the smectitic I-S, *i.e.* they are not open to expansion under glycol solvation. Potassium saturation of oxidized samples indicates the loss of expandability and hence the 'activation' of high-charge smectite layers.

It is clear in considering these data that the behavior of clay minerals in soils can depend on the biochemical context in which they occur. This effect is enhanced as time carries the reactions further to completion, at least on the scale of 840 years. The formation of a natural pasture humic layer in the epipedon tends to favor the illitic or closed-layer structure behavior in I-S minerals. However, it should be remembered that under the influence of the organic matter, the smectitic layers are in fact expandable, *i.e.* glycol enters into the smectite interlayer spaces. Thus the effect of organic matter in the soils is not to block the smectite layers to interaction with polar ions. Under normal, air-dried conditions with Sr-hydrated interlayer ions the interlayer spacing is normal, *i.e.* 15.2 Å. The organic matter seems to affect the smectite layer swelling properties, keeping them open to polar ion solvation. When portions of the organic matter are destroyed, the swelling properties decrease. It is important to note this interaction, which is not generally assumed to be the interaction of organic and clay layers.

## REFERENCES

- BRGM (1981) *Bureau Recherches Minière et Géologique, Geological map XX-I, Rue 1-50,000*, Orléans, France.
- Gharrabi, M. and Velde, B. (1995) Clay mineral evolution in the Illinois Basin and its causes. *Clay Minerals*, **30**, 353–364.
- Hamiot, S. (1999) *Les Aménagements Littoraux et leurs Impacts en Plaine Maritime Picardie*. SMACOPI, France, 73 pp.
- Inoue, A., Bouchet, A., Velde, B. and Meunier, A. (1989) Convenient technique for estimating smectite layer percentages in randomly interstratified illite-smectite. *Clays and Clay Minerals*, **37**, 227–234.
- 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.
- Moore, D. and Reynolds, R.C. (1997) *X-ray Diffraction and the Analysis of Clay Minerals*, 2<sup>nd</sup> edition. Oxford University Press, Oxford, UK, 378 pp.
- Reynolds, R.C. (1985) *NEWMOD. A computer program for the calculation of one dimensional patterns of mixed layer clays*. Published by the author, R.C. Reynolds, 8 Brook Rd, Hanover, New Hampshire, USA.
- Righi, D., Velde, B. and Meunier, A. (1995) Clay stability in clay-dominated soil systems. *Clay Minerals*, **30**, 45–54.
- USDA Soil Survey Staff (1998) *Keys to Taxonomy*. US Printing Office, 326 pp.
- Velde, B. (2001) Clay minerals in the agricultural surface soils in the Central United States. *Clay Minerals*, **36**, 277–294.

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