THE INFLUENCE OF ALKALINE SOLUTIONS ON THE ALTERATION OF THE CLAY MINERALS

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ABSTRACT

THE influence of an alkaline environment on clay mineral alterations in the laboratory was studied by means of one-dimensional structural analyses. Samples of illite, illite–mixed-layered material, kaolinite, and two montmorillonites (smectites) were treated with NH_4OH solutions of pH 8.5, 9.5, 10.5, 11.5, and 12.5 for 6, 12, 24, 48, 72, and 96 hr at 60°C.

One-dimensional structural analyses of the treated samples are quite demonstrative in determining the effects of laboratory-controlled degradation. These analyses show an oscillatory change in the population of the tetrahedral and octahedral structural sites which is consistent with a core-rind structural concept of the clay minerals. Leaching of clay minerals takes place by the alternate growth of the rind and destruction of this frayed edge by agitation. The extent to which the rind develops is controlled by particle size, variability of chemical composition, and the amount of agitation. The order of increasing development of the frayed edge is; kaolinite, illite, illite–mixed-layered material, and then the montmorillonite.

INTRODUCTION

THE purpose of this investigation was to determine, in the laboratory, the influence of alkaline solutions on samples of kaolinite, illite, illite–mixed-layered material, and two montmorillonites (smectites). It was hoped that this study would provide detailed information on the mechanisms whereby clay minerals respond to changes in the environment of accumulation. One-dimensional analyses were used to detect any alterations produced by artificially degrading the clay minerals.

SELECTION OF SAMPLES

The samples used in this study included Marblehead illite (Gaudette, 1965) and an illite–mixed-layered material marketed commercially as "Grundite". The smectites were represented by a Wyoming-type bentonite from Upton, Wyoming, and a Ca-rich montmorillonite from near Aberdeen, Mississippi. A kaolinite from Dry Branch, Georgia, was also used.

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LABORATORY TREATMENT

The samples were treated with NH_4OH solutions of pH 8.5, 9.5, 10.5, 11.5, and 12.5 for 6, 12, 24, 48, 72, and 96 hr at 60°C.

After treatment, the samples were washed in distilled water and divided into two fractions. One was analyzed by X-ray fluorescent methods for changes in silicon and aluminum content. An oriented aggregate was prepared from the other (Ferrell, 1966).

The oriented aggregates were used to obtain diffraction data for one-dimensional structural analyses. This discussion will be restricted to variations in these produced by increased pH and length of reaction.

SEMI-QUANTITATIVE ASPECTS OF ONE-DIMENSIONAL STRUCTURAL ANALYSES

One-dimensional structural analyses can be used as a semi-quantitative measure of the alteration of the above samples. This is illustrated on a theoretical basis for a kaolinite in Fig. 1. The relative electron density curves shown here were calculated on the basis of 4.0, 3.5, and 3.0 silicon and
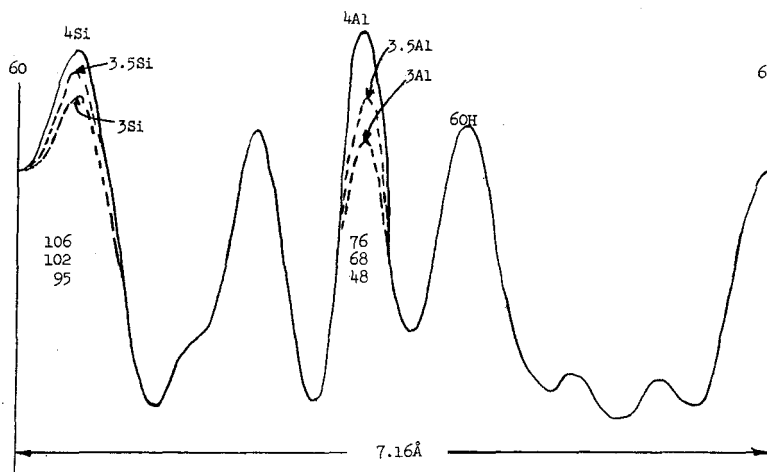

FIG. 1. Changes produced in theoretical structural plots of kaolinite by reducing the silicon and aluminum content.

aluminum atoms in the tetrahedral and octahedral structural sites, respectively. When the number of silicon atoms per unit cell in a theoretical kaolinite is reduced as above, the area under the combined silicon–basal oxygen peak is reduced from 106, to 102, to 95 units. The area under the octahedral aluminum peak behaves in the same manner, changing from 75, to 60, to 48 units with the removal of 0.5 and 1.0 atoms of aluminum per unit cell.

Relative electron density curves were generated for each of the treated samples, and semi-quantitative estimates of the amount of change were obtained by measuring the areas under the tetrahedral and octahedral peaks. These values were then plotted with respect to length of treatment for each pH to demonstrate the behavior of the clay minerals. This type of structural analysis diagram is illustrated in the following figures.

DISCUSSION OF RESULTS

Illite

The changes in the areas of the tetrahedral and octahedral peaks on the one-dimension structural analyses for the illite used in this study are illustrated in Fig. 2. For clarity, the curves have been separated. The upper one contains the analyses for pH 8.5, 9.5, and 10.5. The 10.5 pH curve has also been repeated on the lower diagram to facilitate comparison to the changes produced at pH 11.5 and 12.5.

The tetrahedral layer undergoes the following changes at pH 8.5, the area increases slightly with treatment and then decreases from 6 to 72 hr of reaction. Between 72 and 96 hr, the area again shows an increase, becoming almost as large as it was initially.

At pH 9.5, the area under the tetrahedral peak decreases at first. Then, after only 12 hr of reaction it steadily increases. When the pH is increased to 10.5, the area of the tetrahedral unit is once again at a minimum after 12 hr of reaction, but two maxima are clearly present after 24 hr and 72 hr of treatment. The effect of this pH is to produce an oscillation in the area. At least two of the cycles are present in this diagram.

These cycles are also present in the diagram representing samples treated at pH 11.5 and 12.5. The illite shows little change in the tetrahedral layer with the increase from 10.5 to 11.5, but at pH 12.5, the first minimum is shifted to the shorter reaction time of 6 hr.

The octahedral layer responds to pH and time in much the same manner as the tetrahedral. However, the maximum and minimum peak areas do not always occur at the same times. Two maxima are present at pH 10.5 and above. The first minimum is shifted to 6 hr at pH 11.5 instead of at the higher pH.

Illite–Mixed-layered Material

The structural analysis diagrams for the illite–mixed-layered material (Fig. 3) are very similar to those for the illite. It is possible to observe the same oscillatory pattern in the areal changes of the tetrahedral and octahedral peaks. The number of cycles increases with pH, and the inflection points are also shifted to lower reaction times. A general increase in amplitude is also present with increased time and pH. In addition, the minimum on the 8.5 pH curves occur at lower times giving some indication of the more poorly ordered
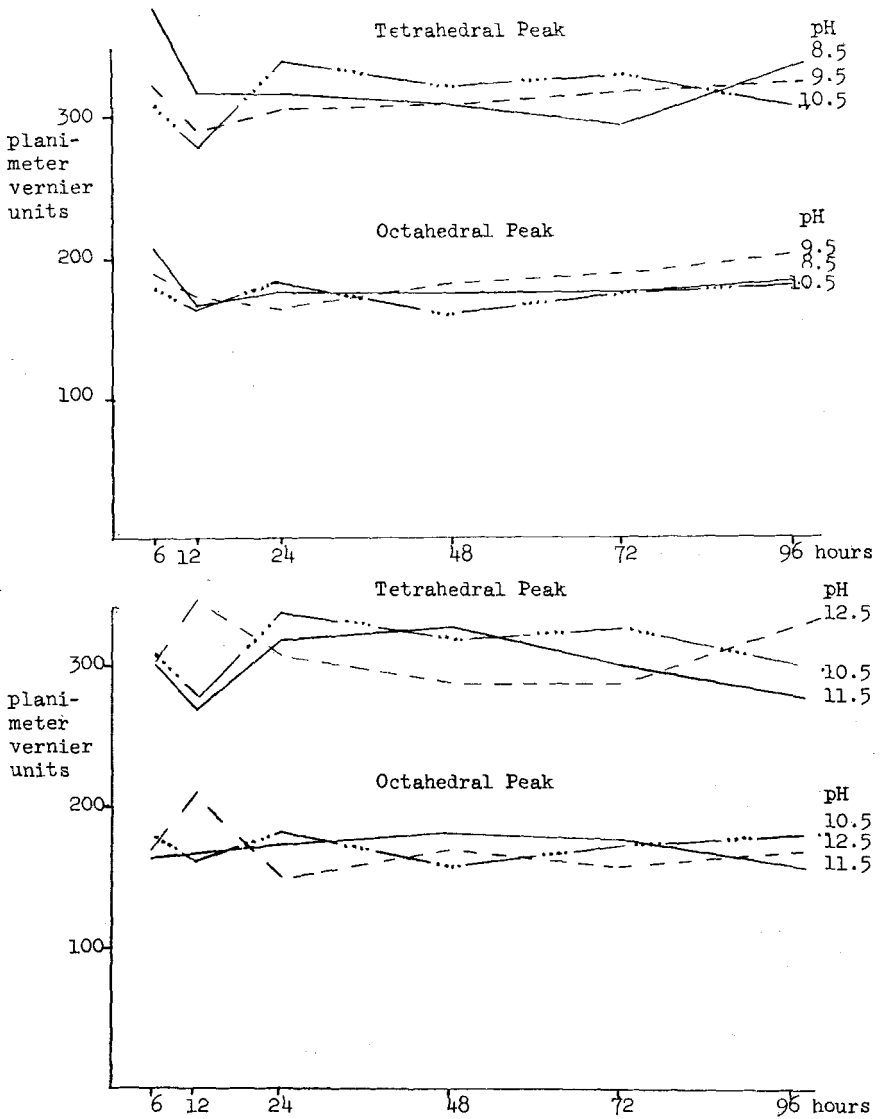
FIG. 2. Structural analysis diagram of illite showing changes in octahedral and tetrahedral peak areas with treatment.
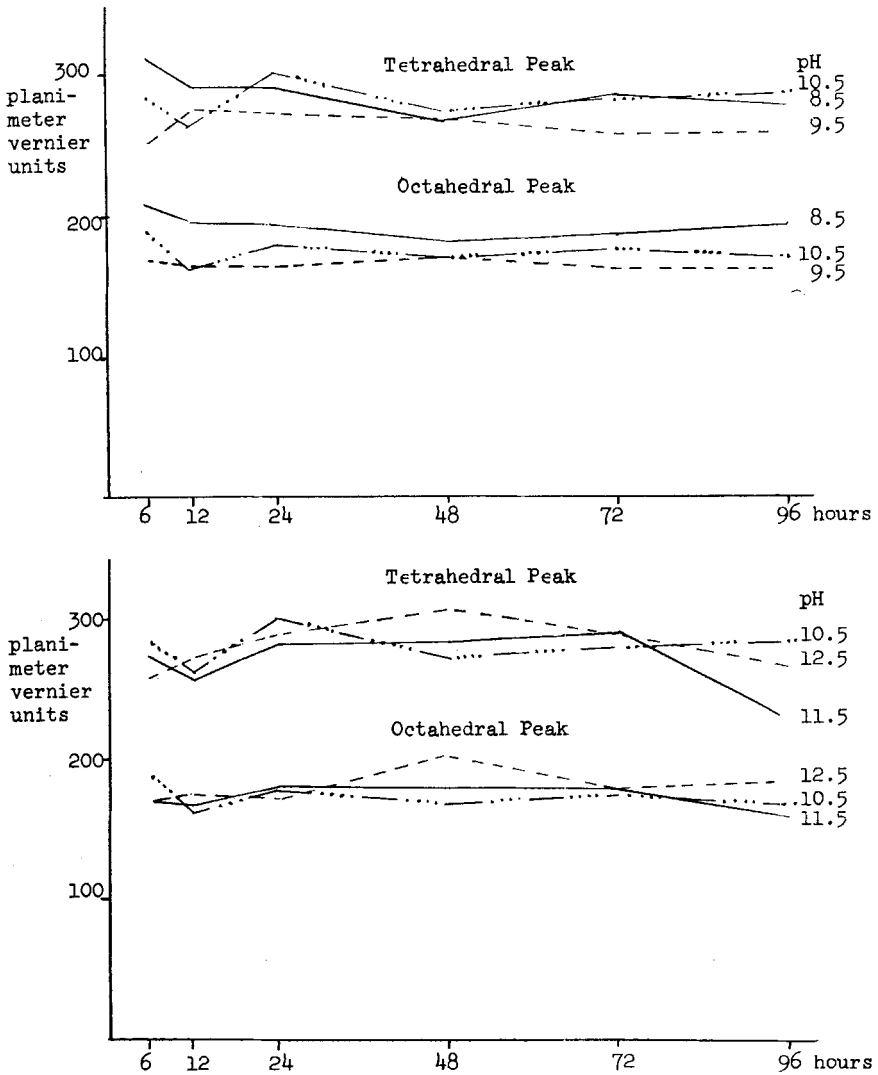
FIG. 3. Structural analysis diagram of illite–mixed-layered material showing changes in octahedral and tetrahedral peak areas with treatment.

nature of this illite. There is also less difference in the reaction time at which minimum areas are produced by the two layers.

Kaolinite

The structural analysis diagrams for kaolinite (Fig. 4) are regular. They do not show as much variation as the illitic material does.

It can be seen that the areas of the tetrahedral peaks reach a minimum between 6 and 12 hr for all pH values. The area then remains relatively constant up to 96 hr of treatment, the only exception being a second minimum point on the pH 8.5 curve at 72 hr.

The behavior of the octahedral peak area is in harmony with that of the tetrahedral one. It decreases from 0 to 12 hr and then stays about the same.

The structure of kaolinite does not respond to treatment with NH_4OH solutions in the same way as the illite and illite–mixed-layered materials do. The oscillations in the peak areas are not present. The tetrahedral and octahedral peaks decrease in area fairly rapidly and are little affected by increased reaction times or changes in pH.

Ca-Montmorillonite

Structural analyses of this Ca-montmorillonite (Fig. 5) reveal a high degree of variability. The general trends are similar to the changes produced in the illite samples.

The tetrahedral and octahedral peak areas oscillate, their magnitudes decreasing with pH and prolonged treatment. The number of cycles increases with pH and the minimum points are displaced to shorter times.

In contrast to the illite, the effects of pH increases are not as pronounced in this montmorillonite. The tetrahedral and octahedral variations are independent of one another at the low pH values, but change synchronously when the pH is 10.5 or above.

Na-Montmorillonite

Changes in the structure of this Na-montmorillonite are very similar to those described for the Ca-montmorillonite and the illitic materials (Fig. 6). The oscillations are present and behave in the same manner. The areas of the tetrahedral and octahedral peaks vary independently.

In some cases, the small particle size of this material appears to exert a control on the magnitude of the cycles. For example, the flatness of the tetrahedral curve at the pH 11.5 after 24 hr of treatment may be due to the effect of particle size on the development of a "frayed-edge". This concept is proposed in the next section.

INTERPRETATION OF RESULTS

General

The variations in the structural analyses of all the minerals presented in the preceding section can be accounted for with the modified structural
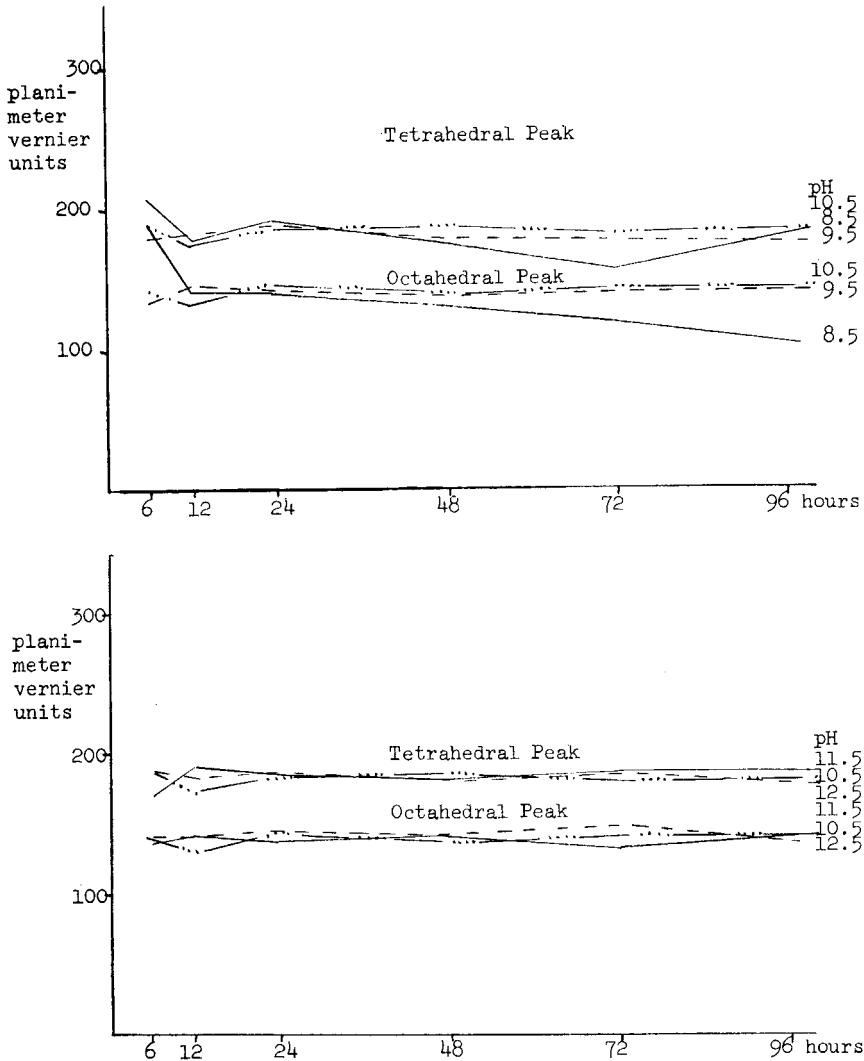
FIG. 4. Structural analysis diagram of kaolinite showing changes in octahedral and tetrahedral peak areas with treatment.

representation of illitic clay minerals proposed by Gaudette, Grim, and Metzger (1965). They assume that illite has a structurally coherent core and an incoherent rind similar to the "frayed edge" of Jackson (1963).

The core is assumed to be well crystallized. Because of the high degree of order present in this area, it is also responsible for the characteristic X-ray
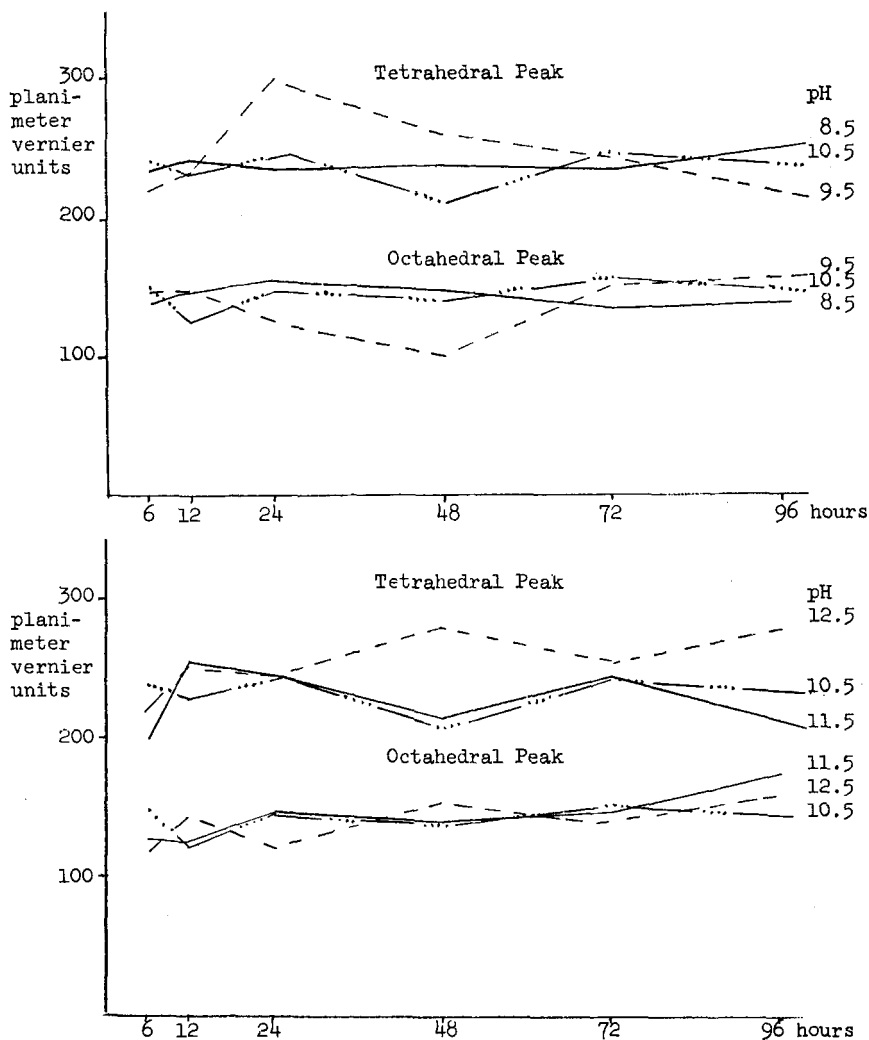
FIG. 5. Structural analysis diagram of Ca-montmorillonite showing changes in octahedral and tetrahedral peak areas with treatment.

diffraction patterns of the illitic minerals. The chemical composition of the core would be that of an ideal illite.

Grading laterally from the core, the rind is less well ordered. It contains less potassium and the amount of silicon and aluminum may also be reduced. The less coherent rind has an irregular "c" dimension, possesses a skeletal
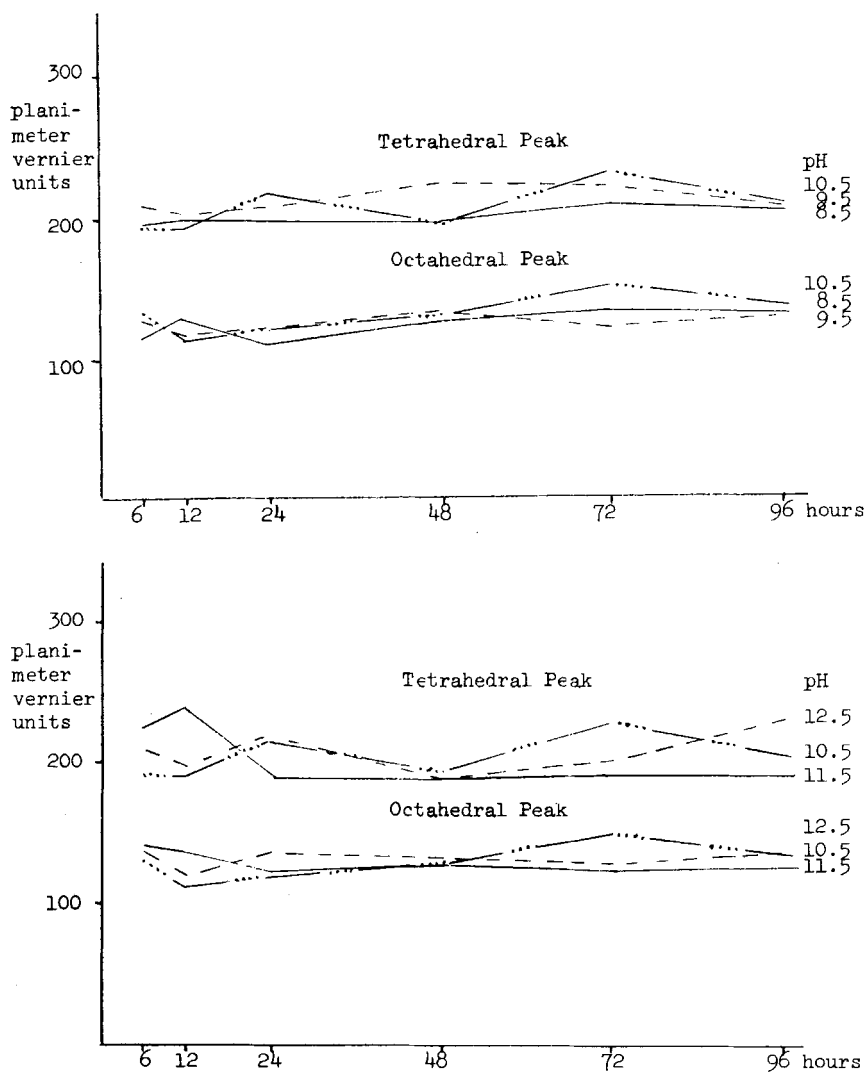
FIG. 6. Structural analysis diagram of Na-montmorillonite showing changes in octahedral and tetrahedral peak areas with treatment.

framework similar to that of the core, and as described by the above authors contributes little to the X-ray diffraction pattern.

In applying the model proposed by Gaudette *et al.* (1965) to this study, a modification must be made. Instead of the coherent core being the principal locus of diffraction, the elements in the core and the rind must produce

diffraction equally as well. The quality of the diffraction is a function of the relative amounts of the elements in the core and the rind and the degree of local order. In the rind, potassium, sodium, calcium, magnesium, iron, silicon, aluminum and others are less abundant. The atomic planes in which they lie are not as regular as in the core. Therefore, as the relative area of the rind increases, the quality of the diffraction pattern should decrease because fewer elements are contributing to the diffraction and with a less orderly arrangement of atomic planes there should be more destructive interference between them.

Illite

The structural analysis diagrams for illite (Fig. 2) support this hypothesis. The changes in the respective peak areas after treatment are produced by the extent to which the frayed edge has developed.

At pH 8.5 there is a decrease in both the tetrahedral and octahedral peak areas with time and then an increase. The decrease is a result of frayed edge development. As the rind grows, the increase in the number of irregular atomic plane produces more destructive interference in the resulting diffraction patterns. The incoherent part of the illite platelets continues to widen until a maximum is reached. This corresponds to the low point on the peak area curves.

Once this point is reached, the frayed edge is such a loosely held framework that with continued treatment it begins to break up. As the rind breaks up, the size of the flake is reduced but the overall order is increased. Thereafter, the area under the peaks on the one-dimensional structural analyses should increase. This might also represent the length of treatment for a given pH at which the concentration of hydroxyl ions is no longer great enough to continue degradation and agitation removes part of the frayed edge.

The positions of the points corresponding to the minimum octahedral and tetrahedral peak areas do not occur at the same time at pH 8.5. The octahedral minimum occurs after 12 hr of reaction, but the tetrahedral one does not occur until the illite has been treated for 72 hr. This may indicate that the aluminum is released at an initially faster rate than silicon, but then slows down.

Illite–Mixed-layered Material

The illite–mixed-layered material behaves in a manner consistent with the above description of illite.

The structure analysis diagrams (Fig. 3) exhibit the same changes present in the illite samples. But, because this material was initially poorly crystalline, or partially degraded, the frayed edge develops more rapidly than on well-crystallized illite. The higher magnitude of the oscillation in the peak areas also indicates that the incoherent rind is more extensively developed.

Kaolinite

The structural analysis diagrams for kaolinite (Fig. 4) indicate a restricted frayed-edge development. The initial reaction is fairly sharp, but then the peak areas level off and remain essentially constant.

Montmorillonite

The structural analyses of calcium- and sodium-montmorillonite after treatment are consistent with the proposed core-rind structural model. The one-dimensional structural analyses (Figs. 5 and 6) undergo greater extremes of oscillation. These larger deviations are probably caused by the variable chemical composition of the original materials and their small particle size. Therefore, the frayed edge is developed to its greatest extent in montmorillonitic clay materials.

CONCLUSIONS

One-dimensional structural analyses of treated samples of illite, illite–mixed-layered material, kaolinite, and two montmorillonites reveal a behavior consistent with a core-rind structural concept. The frayed edge develops by disrupting tetrahedral and octahedral bonds at the edge of the clay mineral platelets and removing silicon and aluminum from their structural positions. The extent to which the leached rind develops is controlled by particle size, variability of chemical composition, pH, and the amount of agitation present. When the rind reaches a certain thickness, the reaction ceases unless the rind can be removed from its role as a reaction barrier. Then, if the pH is high enough, a second phase of rind formation may begin.

Illite is the best illustration of this process. As it responds to the alkaline environment, a frayed edge develops. There is also an indication that under alkaline conditions, aluminum is removed at an initially faster rate from the octahedral layer than silicon is removed from the tetrahedral. Increased pH speeds up the rind formation and produces more than one cycle in the reaction.

Illite–mixed-layer material shows an even stronger tendency toward an oscillatory development of a frayed edge than the illite does. The montmorillonite samples show an even more pronounced variation. Thus, extensive frayed-edge development is favored by a reduction in particle size and greater range in the chemical composition of a clay mineral.

The two-layered clay, kaolinite, does not behave in the same manner as the above minerals. The frayed edge developed the smallest amount on kaolinite. This is probably due in part to its more regular chemical composition and larger particle size.

A clay mineral series can be established, indicating that the order of increased frayed edge development is kaolinite, illite, illite–mixed-layered material, and then calcium and sodium montmorillonite. It can also be

established that clay mineral dissolution within the limits examined is not a congruous solubility reaction, but instead it is accomplished by an oscillatory development of an incoherent rind.

ACKNOWLEDGMENT

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