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## **The Identification of Montana Clays by X-Ray Analysis**

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THE IDENTIFICATION OF MONTANA  
CLAYS BY X-RAY ANALYSIS

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A Thesis  
Presented to  
the Faculty of the Department of Metallurgy  
Montana School of Mines

---

In Partial Fulfillment  
of the Requirement for the Degree  
30513  
Bachelor of Science in Metallurgical Engineering

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by  
James Francis Donovan  
May 1960

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## CHAPTER I

### INTRODUCTION AND PROBLEM

The state of Montana has never been a large producer of clay products, and only recently has there been any published information with regard to these minerals. The presence of good quality clays has come to light in recent years and there is no doubt that these deposits will be used as the need for them arises.

This investigation is concerned primarily with the determination of the various clay minerals comprising certain deposits throughout the state.

In recent years, the use of x-rays has played an important role in the identification of clay minerals. This investigation was accomplished with the use of x-ray diffraction equipment and it can be easily understood why this equipment has been of such benefit to the clay mineralogist.

#### Problem:

The main purpose of this investigation is to identify, by means of x-rays, various clay minerals present in certain deposits throughout the state. The removal of non-clay minerals, by thermal and chemical means, was attempted to make more positive the identification of the important clay minerals. X-rays alone are insufficient as a means of identification; therefore, chemical and thermal treatments must be used in conjunction with x-rays to obtain satisfactory results.

## CHAPTER II

## REVIEW OF LITERATURE

A review of the characteristics of the more common clay minerals, along with a sound definition of clay, will enable the reader to understand more fully the purpose of this report.

Definition:

Clay is used as a rock term and as a particle-size term in the mechanical analysis of sedimentary rocks and soils. As a rock term it is difficult to define precisely, because of the wide variety of materials that have been called clays. In general, the term clay implies a natural, earthy, fine-grained material which develops plasticity when mixed with a limited amount of water. Chemical analysis of clays shows them to be essentially silica, alumina, and water, frequently with appreciable quantities of iron and alkali compounds.

The term clay has no genetic significance; it is used for inorganic materials that are the product of weathering, hydrothermal action, or have been deposited as a sediment.

As a particle size term, the clay fraction is that size fraction composed of the smallest particles. The maximum size of the particles in the clay size grade is defined differently in different disciplines. In geology the tendency has been to follow the Wentworth scale and to define the clay grade as particles finer than 4 microns\*.

\* One micron equals  $10^{-3}$ cm.

Clays contain varying degrees of clay-grade material and therefore, varying relative amounts of non-clay mineral and clay mineral components. Many materials are called clays in which the clay mineral component makes up considerably less than half of the total rock.

In general, fine-grained materials have been called clays so long as they had distinct plasticity and insufficient amounts of coarser material to warrant the name silt or sand. If particle size analyses are made, the clay would then be reserved for material in which the clay-grade dominates. However, names have been and are applied most frequently on the basis of the appearance and bulk properties (e. g. plasticity) of the sample. (4,2)

#### STRUCTURE AND ANALYSIS OF CLAY MINERALS

The following discussion will be concerned with the structure of clays, and the relationship between the structure and the identification of the clay minerals by x-ray diffraction.

##### Chlorites:

A. G. Werner appears to have first used the name chlorite. It has been used for a group of green hydrous silicates which are closely related to the micas and in which ferrous iron is prominent. A very large variety of minerals have been described as chlorites so there has been much confusion regarding the identity of species belonging to the group. (4,36)



Pauling and McMurchy showed the general structural form of the chlorites, and recently Barshad and Brindley have provided information on relating chlorites to other micas and on variations in structure within the group itself. Structurally, the chlorites are regular interstratifications of single biotite-mica and brucite layers. The chlorites provided an early example of interlayering of units into more complex structures, a phenomenon which is known to be common in clay minerals.

Recently, chlorites have been recognized as important constituents of many clay minerals, and it is likely that chlorites are more abundant than is recognized. Very frequently, small amounts of chlorites are very difficult to detect when mixed with other clay minerals. This is particularly true when kaolinite is also a part of the mineral being studied. (4,37)

The structure of chlorite was first suggested by Pauling. McMurchy later studied the mineral in considerable detail and verified the structure suggested by Pauling. Recently, Brindley and Robinson studied the mineral and considerably extended knowledge of the general chlorite structure and the variations existing in the members of the group. (4,69)

The same general structural framework is exhibited by all true chlorites. "The structure consists of alternite mica-like and brucite-like layers. The layers are continuous in the a and b dimensions and are stacked

in the c direction with the basal cleavage between the layers. The mica-like layers are trioctahedral with the general composition  $(OH)_4(SiAl)_8(MgFe)_6O_{20}$ . The brucite-like layers have the general composition  $(Mg \cdot Al)_6(OH)_{12}$ . The mica layer is unbalanced by substitution of  $Al^3$  for  $Si^4$ , and this deficiency of charge is balanced by an excess charge in the brucite layer as a consequence of substitution of  $Al^3$  for  $Mg^2$ . The general chlorite structure is illustrated in Fig. 1." (4,69)

"Two brucite-like layers and mica-like layers form the unit cell. McMurchy gives the following specifications for the chlorite he studied: monoclinic,  $a = 5.3$  A,  $b = 9.3$  A,  $c = 28.52$  A, and  $\beta = 97^\circ 8'$ . Subsequently, Robinson and Brindley have stated 'the displacements are exactly  $a_0/3$  and since  $b_0/a_0 = \sqrt{3}$ , the unit cell may be regarded as rhombohedral with the triagonal axis perpendicular to the cleavage plane, or alternatively as an orthohexagonal cell with a volume three times that of the monoclinic prism and with dimensions in  $kX^*$  units  $a_0 = 5.32$ ,  $b_0 = 9.21$ , and  $c_0 = 3 \times 14.2$ .' " (4,71)

#### Identification of Chlorites by X-Rays:

Chlorite minerals occurring in fine grained materials can be recognized easily as chlorites, provided sufficient care is taken. It is essential to clearly record reflections from spacings up to at least 14 kX. Most

\* One kX unit equals 1.00202 A.

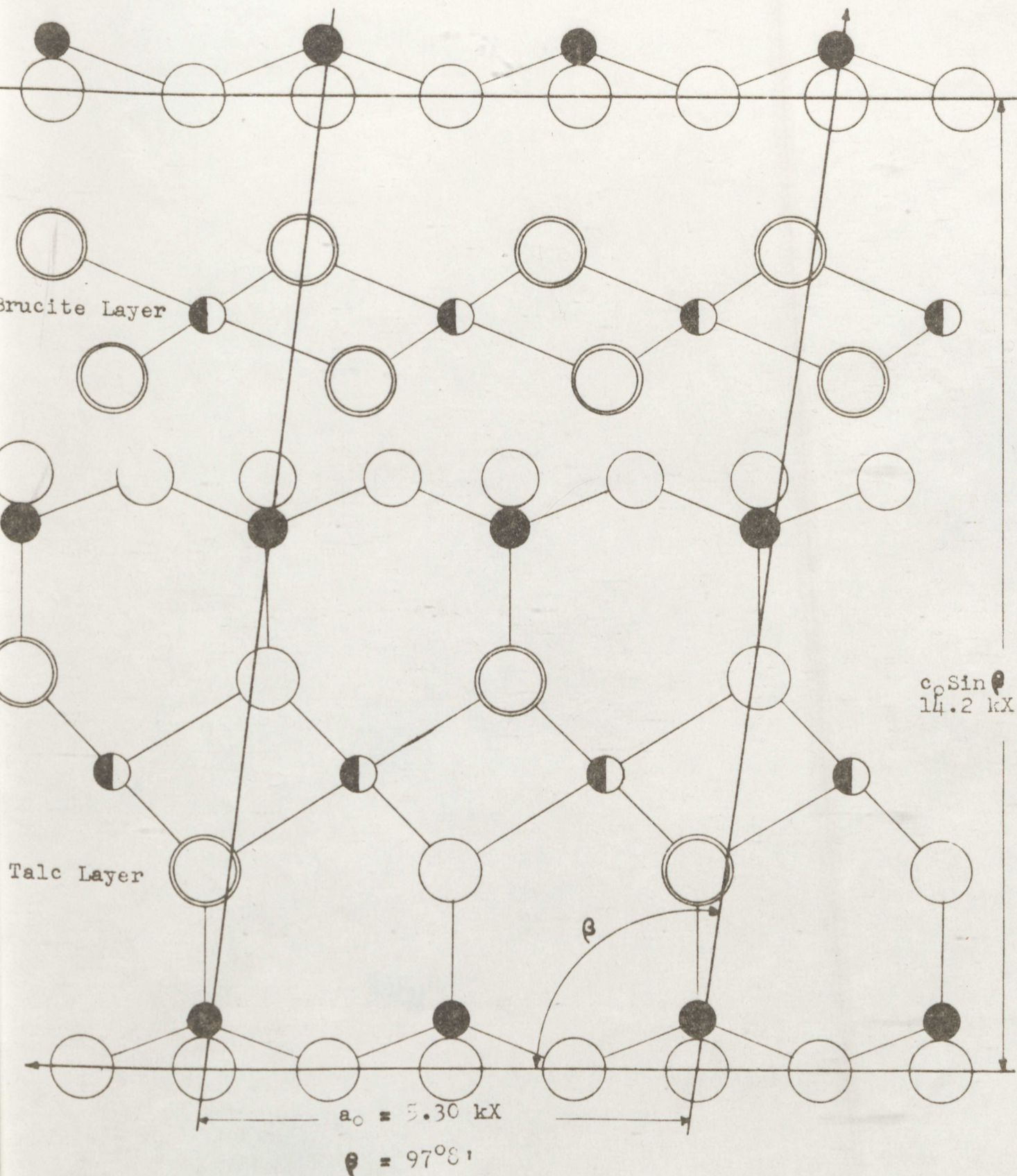
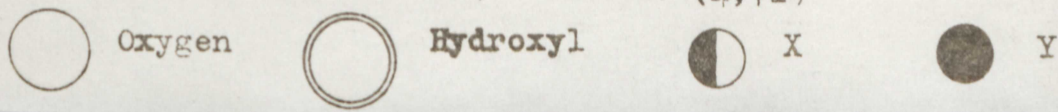


Fig. 1

Projection of the chlorite structure on the  $ac$  plane, after McIhurchy. X and Y represent the electropositive atoms in the octahedral and tetrahedral positions. (4,71)



chlorites, if not rich in iron, give a clear sequence of the first four or five basal reflections from the 14 kX basal spacing. If iron is present, weak first and third orders and strong second and fourth orders occur. Confusion with the montmorillonite type mineral is unlikely because of the much sharper basal reflection of the chlorite minerals, a more positive distinction consists in testing whether the 14 kX spacing is variable with change in humidity or as a result of treatment. Change of spacing suggests a montmorillonite-type mineral, whereas the chlorite mineral will remain unaffected. Stephen and MacEwan discovered a swelling in chlorite, which means that greater care is necessary in arriving at a firm conclusion. If the chlorite is of the type having a weak 14 kX reflection, which may be overlooked if the mineral is present only in small amounts, then observance of the second-order line at about 7 kX might be confused with the occurrence of a kaolin-type mineral. These may be generally be distinguished by combining acid treatment or heat treatment with x-rays. (2,188)

With regard to acid treatment, the chlorite minerals are generally soluble in warm hydrochloric acid, while minerals such as kaolinite are unaffected. However, kaolin-type minerals such as amesite and certain forms of chamosite (i. e. minerals which contain iron) are also readily soluble in hydrochloric acid. Therefore, acid treatment, while very useful, is not an infallible method

for distinguishing between minerals of these kinds. Heat treatment is probably more useful; heating for  $\frac{1}{2}$  hour at 550-600°C is sufficient to decompose minerals such as kaolinite and halloysite, and also kaolin types of chamossite, with most true chlorites resisting this treatment. While thermal method combined with x-ray examination is probably the best way of recognizing chlorites, it must be used with care and its limitations recognized. (2,189)

Kaolinites:

Ross and Kerr discuss in great detail the nomenclature of the kaolin minerals, and their usage has been generally accepted. According to them,..."by kaolin is understood the rock mass which is composed essentially of a clay mineral that is low in iron and is usually white in color. The kaolin forming clays are hydrous aluminum silicates of approximately the composition  $2H_2OAl_2O_3 \cdot 2SiO_2$  and it is believed that other bases if present represent impurities or absorbed materials. Kaolinite is the mineral that characterizes most kaolins". (4,29)

Johnson and Blake, in 1867, appear to have first clearly intended the name kaolinite for the "mineral of kaolin". (4,30) Pauling first suggested, the general outline, the structure of kaolinite. It was worked out in more detail by Gruner and was later revised by Brindley. The structure is composed by a single silica tetrahedral sheet and a single alumina octahedral sheet

combined in a unit so that the tips of the silica tetrahedral and one of the layers of the octahedral sheet form a common layer.

The minerals of the kaolinite group consist of sheet units of the type just described continuous in the a and b directions and stacked one above the other in the c direction. The variations between the members of this group consist in the way in which the unit layers are stacked above each other, and in the arrangement of the alumina atoms in the positions open to them in the octahedral layers. (4,47)

In the case of kaolinite, Brindley has investigated the stacking of the unit layers, and the following statements are taken largely from his works. The mineral is triclinic;  $a = 5.16 \text{ \AA}$ ,  $b = 8.94 \text{ \AA}$ ,  $c = 7.38 \text{ \AA}$ ,  $\alpha = 91.8^\circ$ ,  $\beta = 104.5^\circ$ . (Fig. 2)

#### Identification of Kaolinite by X-Rays:

In this investigation the term kaolinite is used as a general heading for all the minerals in the kaolin and no differentiation between the various minerals in this group was attempted. Therefore, in discussing the identification by x-rays, the minerals in the kaolin group will be discussed as a whole.

The kaolin minerals, as a group, have a number of features which distinguish them fairly well from other materials, both clay minerals and non-clay minerals. If

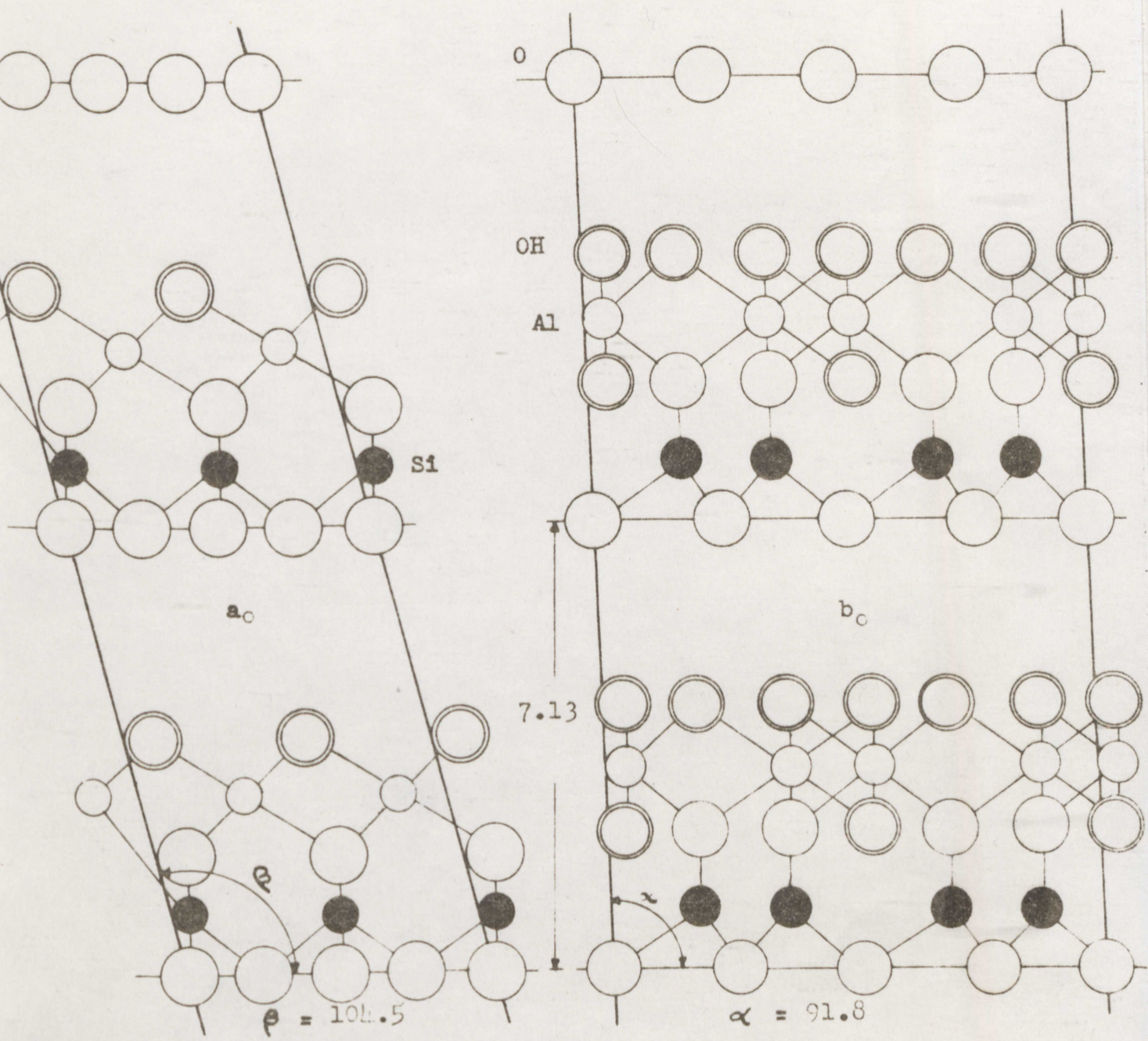


Fig. 2.

The stacking of unit layers of kaolinite along the a and b axis, after Brindley, (4,49)

the mineral under study consists principally of clay minerals, then a preliminary x-ray pattern of the material may be usefully taken. If, as frequently occurs, the clay minerals present are only a small fraction of the total mass, then a preliminary separation of particles coarser than one or two microns may be carried out by sedimentation in distilled water or some clay suspending chemical; the finer material left in suspension can then be obtained by centrifuging. Kaolin minerals sedimented in this manner are usually well orientated and the prominent basal reflections (001) and (002), with spacings of about 7.14 and 3.57 kX, give clear indications of a kaolin mineral. (2,48)

The basal reflections alone afford a very good indication of the presence of kaolinite. Other clays of the illite and montmorillonite types will cause no confusion, since the illite minerals are indicated by reflections at about 10 kX and often 5 kX, while montmorillonite has a characteristic 15 kX spacing. Chlorite minerals, however, may be confused with kaolinite, especially if a weak 14 kX spacing for chlorite is present. The second and fourth orders of this reflection at about 7.0 kX and 3.5 kX reflections are close to the corresponding spacings of the kaolinite minerals but the third order at 4.7 kX is easily seen.

Considerable difficulty arises however, if a chlorite is present with a weak first and third order reflection



which is characteristic of chlorites rich in iron; casual inspection would then suggest a kaolin mineral with a small admixture of chlorite. In such a case, additional tests are essential. Many chlorites are dissolved in warm dilute hydrochloric acid (see section on chlorites), which does not affect the true kaolin minerals, although kaolins containing iron will probably dissolve. Kaolinite fireclays and metahalloysite, heated for  $\frac{1}{2}$  hour at  $600^{\circ}\text{C}$ , decompose to a non-crystalline state, whereas most chlorites will not decompose fully with this treatment; they will probably suffer partial dehydration, which will then increase the intensity of the 14 kX reflection. In difficult cases the use of thermal and/or dehydration methods may be valuable. (2,49)

#### Montmorillonites:

Ross and his colleagues, in a series of classical studies, published from about 1926 to 1945, established and identified montmorillonite as a valid clay-mineral group. In addition, the variations in composition that are found in this group were classified. For example, they showed the possible variation in the ratio of silica to  $\text{R}_2\text{O}_3$  and the possible complete replacement of aluminum by iron and magnesium. (4,29)

In 1933, a structure for montmorillonite showing the expanding-lattice characteristics of the mineral was published by Hofmann, Endell, and Wilm. This attribute is now generally considered to be an essential charac-

teristic of the group. The composition presented by Le Chatelier and accepted by Dana is  $4\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ .

"The montmorillonite minerals occur only in small particles so that single-crystal x-ray diffraction data cannot be obtained. Structural concepts, therefore, must be deduced from powder data and interference from better known structures, with the result that there is considerable uncertainty regarding details of their structure. Currently, the generally accepted structure for the montmorillonite minerals follows the original suggestion made in 1933 by Hofmann, Endell, and Wilm modified later by suggestions of Maegdefrau and Hofmann, Marshall, and Henricks." (4,60)

According to their concept, montmorillonite is composed of units made up of two silica tetrahedral sheets with a central alumina octahedral sheet. All the tips of the tetrahedrons point in the same direction, toward the center of the unit. The tetrahedral and octahedral sheets are combined so that the tips of each silica sheet and one of the hydroxyl layers of the octahedral sheet form a common layer. The atoms common to both the tetrahedral and octahedral layers becomes O instead of OH. The layers are continuous in the a and b direction and are stacked one above the other in the c direction. (4,55)

In the stacking of the silica-alumina-silica units, O layers of each unit are adjacent to O layers of the neighboring units with the result that there is a very

weak bond and an excellent cleavage between them. The outstanding feature of the montmorillonite structure is that water and other polar molecules, such as glycerol, can enter between the unit layers, causing the lattice to expand in the c direction. The c-axis dimension of montmorillonite is not fixed, but varies from about 9.6 A, when no polar molecules are present between the unit layers, to substantially complete separation, in some cases, of the individual layers. (4,56)

"Exchangeable cations occur between the silicate layers; and the c-axis spacing of completely dehydrated montmorillonite depends somewhat on the size of the inter-layer cation, being larger the larger the cation. In the case of adsorption of polar organic molecules between the silica layers, the c-axis dimensions also vary with the size and geometry of the organic molecules. The thickness of the water layers between the silicate layers depends on the nature of the exchangeable cation at a given water-vapor pressure. Under ordinary conditions, a montmorillonite with Na as the exchange ion, has a one molecular water layer and a c-axis of about 12.5 A; with Ca ion there are usually two water layers and a c-axis spacing of about 15.5 A." (4,57)

The expansion properties are reversible, but it may be difficult to get the mineral to reexpand by adding water or other polar molecules after all of the inter-polar molecules have been removed.

The opinion has frequently been expressed that the structure of Hofmann, Marshall, and Hendricks does not sufficiently account for all the properties of montmorillonite, notably its capacity for ion exchange.

Edelman and Favejee have suggested an alternate structure that explains these properties more adequately. This structure differs from the structure of Hofmann in that every other silica tetrahedron in both silica sheets is inverted, so that half of them point in the opposite direction. Those that point away from the silicate sheets would have the top O replaced by OH. In this structure the silicon atoms are not all in a single plane in the silica tetrahedral sheets, and there must be some substitution of the OH for O in the octahedral layers to balance the structure. (Fig. 3) (4,61)

#### Identification of Montmorillonites by X-Rays:

The x-ray diffraction of the montmorillonite minerals can be placed in two categories. One class consists of basal reflections, which vary with the state of hydration of the mineral, i. e., with the thickness and regularity of the water layers between the silica sheets. The c-axis spacing, the diffuseness of the reflections, and the number of orders vary from sample to sample depending on the thickness of the water layers and their regularity. These factors in turn depend on the exchangeable cations present and the conditions under which the sample was prepared. (4,91)

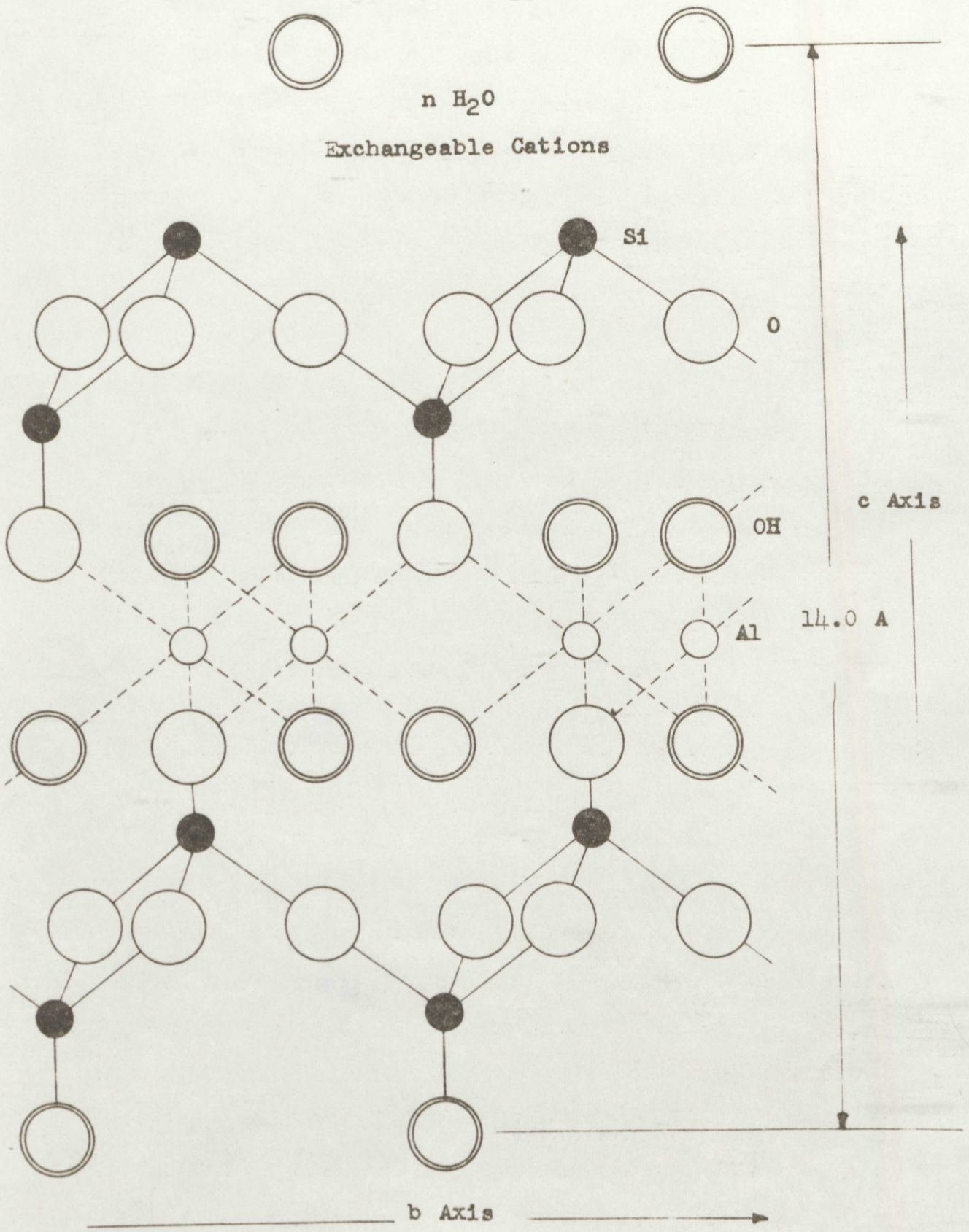


Fig. 3

Schematic presentation of the structure of montmorillonite suggested by Edelman and Favejee. (4,63)

Montmorillonites possess the property of adsorbing certain organic molecules between the individual silicate layers with a consequent shift in the c dimension depending on the size and configuration of the organic molecules. Such resulting montmorillonite-organic complexes, as Bradley showed, have a high degree of regularity, yielding sharp (001) lines of many orders. For example, treatment of a sample of montmorillonite with ethylene glycol provides a sharp (001) reflection at 17.7 kX. Treatment with organic compounds permits the detection of small amounts of the mineral which would be otherwise missed in complex structures. (2,117)

Untreated montmorillonites will usually reflect from the 14 to 15 kX spacing. Treatment with an organic compound will expand the lattice to 17.7 kX which enables one to identify this mineral. Interference from chlorite is explained under chlorites above.

#### Illite Minerals:

The structure of the micas, the variation in their chemical composition, and their polymorphic variations have been worked out in great detail by Pauling, Mauguin, Jackson, West, Winchell, Hendricks, and Jefferson.

"The basic structural unit is a layer composed of two silica tetrahedral sheets with a central octahedral sheet. The tips of the tetrahedrons in each silica sheet point toward the center of the unit and are combined with the

octahedral sheet in a single layer with suitable replacement of OH by O. The unit is the same as that for montmorillonite except that some of the silicons are replaced by aluminums. In many of the well crystallized micas one-fourth of the silicons are replaced by aluminum atoms. The unit layers extend indefinitely in the a and b directions and are stacked in the c direction." (4,65)

The illite minerals differ from the well crystallized micas in several different ways, all of which occur in any given sample; these are as follows: "There is less substitution of the  $Al^3$  for the  $Si^4$ ; in the well crystallized micas one-fourth of the  $Si^4$  are replaced, whereas in illites about one-sixth are replaced. As a consequence of this smaller substitution, the silica-to-alumina molecular ratio of the illites is much higher than that of the well-crystallized micas, and the net-unbalanced-charge deficiency is reduced from two per unit cell to about one point three per unit cell." (4,66) There is some variation in the stacking of the unit layers in the c direction, and the size of the illite particles occurring naturally is very small, of the order of one to two microns.

Because of the previous variations, illite clay minerals show differences in their characteristics from those of the well-crystallized micas. The 10 A diffraction line of the micas is shown by illite usually

as a characteristic diffraction effect. It is however, often modified into a band which tends to tail off slightly toward the low angle region as a consequence of the small particle size, variation in the interlayer cation, and occasional interlayer hydration. The occasional layers may be simply the non-typical features associated with any particle surface. (4,68)

#### Identification of Illites by X-Rays:

The illites can be differentiated from the other groups of the clay minerals by a series of basal reflections. The first order of the basal reflection occurs at 10 kX, and if the aggregate is well oriented it should be possible to see an integral series of orders of this reflection. In certain cases, the second order may be so weak as to be invisible. This series of basal reflections will show no appreciable change in spacing when treated with hydrochloric acid or saturated with glycerol. If the 10 kX line on the original pattern is somewhat broadened, structural irregularities may be postulated. If on heating to 500°C for several hours, the 10 kX line becomes sharper; the irregularities are probably due to a proportion of water between the sheets. Apart from the sharpening of the basal reflections, no appreciable change should take place on heating the mineral to 500°C. As a check on the identification, the diagram should be compared to standard charts found in various texts.



### Mixed Layer Structures:

In the case of separate clay-mineral particles, the diffraction pattern will contain reflections characteristic of each component present. The characteristics will be no different from those resulting from a mixture of clay minerals and non-clay minerals; for example when quartz is a component of the material.

"In the case of a mixture which is a regular interstratification of layer clay minerals, the diffraction effect is equivalent to a larger unit cell which is a multiple of the individual layers. The regularity of the structures is maintained on a larger scale, and an integral series of (001) reflections is obtained from the larger unit cell. The structure of chlorite is an example of this kind of mixing." (4,102)

If the mixture is a random interstratification of layer clay minerals, and only a few layers of the second are present, the reflections will differ very slightly from those of the dominant layer. If, however, the second type layer is present in any great amount new diffraction effects will arise; a nonintegral series of reflections is obtained from the basal planes. Also, the layers can contribute only as individuals.

In mixed layer structure, the basal reflections are composites of adjacent reflections of the same orders of the different layers. The position and intensity of the composite reflections will vary with the relative abundance of the individual layers. For example, in a random

mixed-layer structure of 10 kX and 15 kX reflections, the first observed reflection will be a composite of the (001) of both layers with a spacing somewhere between the 10 and 15 kX reflections, the exact position depending on the relative amounts of the layers present. A strong reflection at 5 kX will appear; this will be a composite of the (002) of the 10 kX layers and (003) of the 15 kX layers. Only if the amount of the 15 kX layer is large will a reflection occur at 7.5 kX. (4,104)

In the case of random mixture of a 17.7 kX layer and a 10 kX layer where both are present in large quantity, the first reflection will be a composite of (001) of both layers, and the second will be a composite of (001) of the 10 kX layer and (002) of the 17.7 kX layer. The position and intensity of the composite peaks will vary with the abundance of the two layers. It should be pointed out that the position of the composite peaks do not necessarily vary in a straight line relationship with the relative abundance of the constituent layers.

#### Impurities in Clay Minerals:

Impurities as used here may be somewhat misleading; perhaps it would be much more adequate to use the term non-clay minerals. The minerals calcite, dolomite, pyrite, feldspar, gibbsite and other such minerals are typical and are very abundant in some clay minerals. One should not omit quartz from this group since it is probably the most common material associated with clay minerals.

It is impossible and unjustifiably time-consuming to get all the data concerning the non-clay minerals in this investigation. For this reason, no mention of the minerals indicated above will be covered in the discussion to follow.

## CHAPTER III

### EQUIPMENT AND ANALYTICAL PROCEDURE

The following discussion will pertain to the equipment and analytical procedures used in the identification of the various clay minerals encountered in this investigation.

#### Equipment:

The diffraction equipment used in this investigation consists of three main parts, the x-ray generator, the goniometer, and the recorder.

The x-ray generator used is a Norelco type, number 12045/B, and has a maximum output of 50 milliamps at 60 kilovolts. The output from this generator was applied to an x-ray tube containing a copper target, with the power regulated at 15 milliamps and 35 kilovolts.

The Norelco goniometer is the wide range type and was operated at a scanning speed of  $2^{\circ}$  -  $2\theta$  per minute. A geiger tube is mounted on the goniometer in such a manner that it is activated by the x-rays diffracted by the sample under observation.

The output from the geiger tube is connected to an automatic balancing potentiometer. As the impulse from the tube is received by the potentiometer it automatically balances. A recording pen is attached to the slide wire of the potentiometer and makes a continuous recording of the varying output from the geiger tube.

(Fig. 4)



FIGURE 4

X-Ray Diffraction Equipment with Goniometer and Power Generator on the Left and Recorder on the Right.

### Analytical Procedure:

The procedure followed in the identification of the various clay minerals is not the same for each sample and depends entirely on the components present in the material under observation. Eighteen samples were analyzed and each one produced a somewhat different diffraction pattern.

The samples were ground to -100 mesh before treatment and approximately one half gram of each was used.

All samples were initially treated in the same manner. The first step was to obtain a primary diffraction pattern of the clay; after this pattern was obtained the clay minerals were suspended in a defloculating agent (sodium metaphosphate) - the purpose of this defloculating agent is to suspend the clay minerals for an indefinite length of time, while the non-clay minerals settle out of solution - and later filtered, either by vacuum or centrifuging. This filtering or centrifuging tends to orientate the clay particles so that the basal planes, namely (001) and (002) are aligned horizontally. This orientation will then produce a diffraction pattern that enables the investigator to estimate with more accuracy the clay minerals present in the material under study.

The analytical procedure is as follows:

1. If montmorillonite is thought to be present the sample was treated with glycerol. If the lattice expands from 15 to 17.7 Å, montmorillonite is present. (Fig. 5)

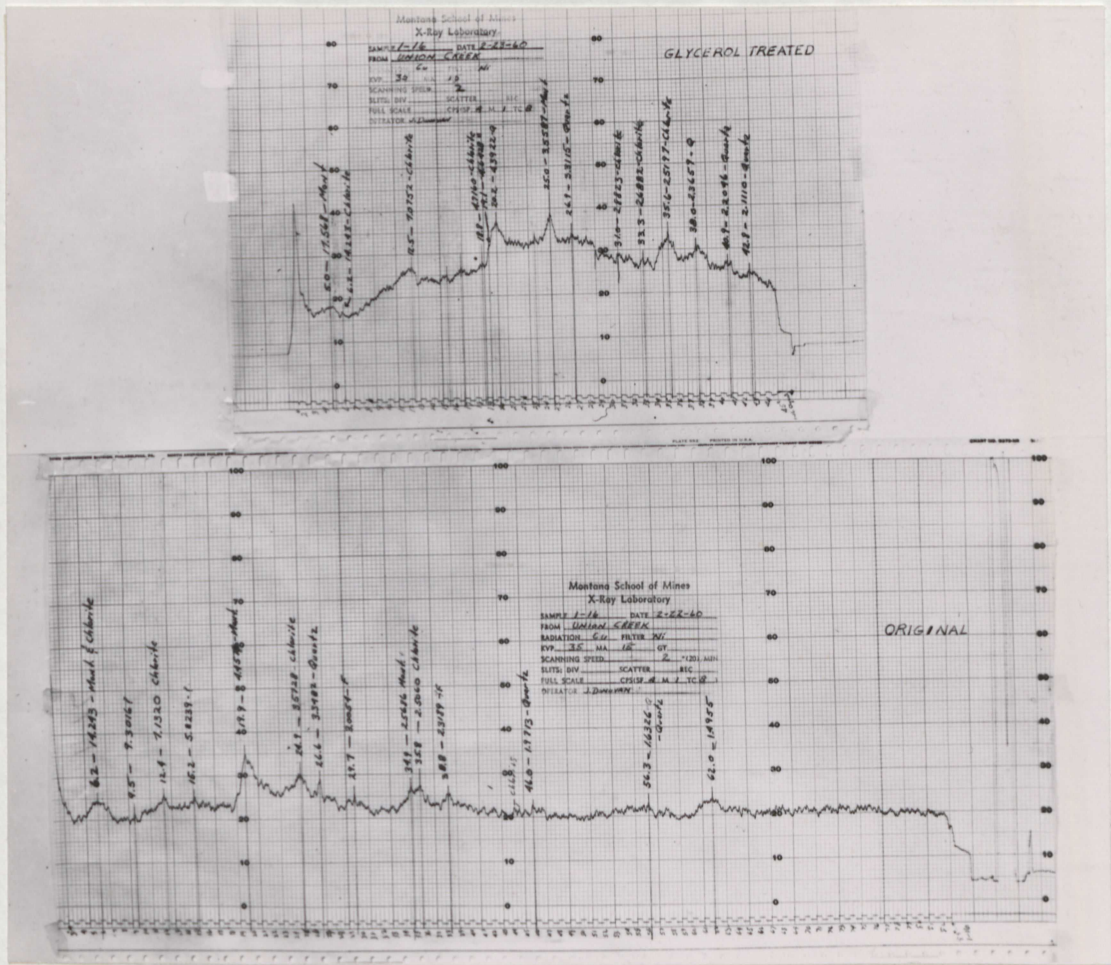


FIGURE 5

Diffraction Pattern of a Montmorillonite Clay  
Before and After Treatment with Glycerol.

2. If chlorite is thought to be present the sample is treated with hydrochloric acid. Characteristic peaks of chlorite will not appear if samples have been treated in this manner. The acid used is about 1 part HCL to 5 parts water. The acid can be filtered through the clay or the clay can be heated in the presence of acid for about 15 minutes. (Fig. 6)
3. Kaolinite will be destroyed by heating to  $550^{\circ}\text{C}$  for about one-half hour. If confusion, as to the presence of either kaolinite or chlorite arose, the effect of hydrochloric acid was relied upon to distinguish between the two minerals. Kaolinite is not affected by warm dilute hydrochloric acid.

Other tests are mentioned in the literature review above.

A special boiling technique was used as a means of removing the non-clay minerals present in the material under observation. The following procedure was followed:

1. Twenty five grams were boiled for three hours in one liter of water. Water, to make up for evaporation loss, was added as needed.
2. Four milliliters of "Diasperse C"\* were added.
3. The solution was allowed to stand for eight hours after one hour of brisk agitation.

\*Commercial defloculating agent.





4. Approximately 500 milliliters of this solution were siphoned off; filter discs were placed in the solution and time allowed for the clay particles to settle on them.
5. These discs can then be placed directly in the specimen holder of the diffractometer.

This procedure removed a major portion of the non-clay minerals and brought about a high degree of orientation in the clay particles. The effects of the procedure used, showed up exceedingly well in patterns obtained after this treatment.

## CHAPTER IV

## RESULTS AND DISCUSSION

The following is a discussion of the results and methods of treatment accorded to each sample encountered in this investigation. All the samples contained, to some degree, non-clay materials. However, no special attention was accorded these minerals. This investigation was only concerned with clay minerals.

Sample 1-1 Iron Mountain:

The patterns of the original and centrifuged samples contained peaks at 13.58 Å, 10.6 Å, and 7.9 Å and were identified as containing chlorite, illite, and iron oxide. The specimen was then treated with warm dilute, 1:5, hydrochloric acid. On examination of the pattern obtained after this treatment, no chlorite lines appeared; the lines due to the iron oxide were considerably diminished with the illite peaks affected only slightly in terms of intensity. The sample was identified as containing mostly chlorite, with smaller amounts of illite and iron oxide. The presence of iron causes a weak 14 Å chlorite peak as was evidenced in this specimen.

Sample 1-4 Camp Creek:

The patterns of the original and centrifuged samples contained peaks at 14.0 Å, 9.92 Å, and 7.07 Å, and identified as containing chlorite, illite, and either chambsite or kaolinite. Heat treatment at 550° had no

affect on the 7.07 A peak; therefore, the assumption that kaolinite was present was incorrect. Hydrochloric acid treatment removed the 14.0 A peak and therefore verified the presence of chlorite. This acid treatment did not have any appreciable affect on the position of the peaks thought to be caused by the chamosite present in the sample; but did, however, decrease the intensity of these peaks.

Heat treatment also decreased the intensity of the chamosite peaks. From the treatments of hydrochloric acid and heat, the sample was identified as chlorite, illite, and a mixed layer type of chamosite with characteristics similiar to both chlorite and kaolinite. Illite was the predominant mineral in this sample.

Sample 1-11:

The pattern of the original and centrifuged samples contained peaks at 13.6 A, 9.9 A, and 7.13 A and was identified as containing chlorite, illite and kaolinite. Treatment with hydrochloric acid removed the peaks due to chlorite so the assumption that chlorite was present is correct. The peaks due to illite and kaolinite remained. Therefore, the sample was identified as chlorite, illite, and kaolinite. The sample contained relatively small amounts of the identified minerals.

Sample 1-16 Union Creek:

The pattern of the original and centrifuged samples contained peaks at 14.2 A and 7.13 A. The breadth of the

14.2 A peak indicated the presence of montmorillonite and chlorite. Treatment with glycerol expanded the 14.2 A peak to 17.5 A and thus verified the presence of montmorillonite. The 14.2 chlorite was also present after this treatment and was eliminated upon treatment with hydrochloric acid. This mineral is thought to contain mostly montmorillonite with a considerable amount of chlorite.

Sample 1-18:

The patterns of the original and centrifuged samples showed peaks at 13.18 A, 10.1 A and 8.83 A. The minerals assumed present were chlorite, illite, and complex silicates. The peaks due to chlorite were removed upon treatment with hydrochloric acid. The sample contained a major amount of chlorite, considerable illite, and complex silicates.

Sample 1-19:

The patterns of the original and centrifuged samples contained peaks at 14.9 A, 13.7 A, and 10.1 A. The sample was assumed to contain montmorillonite, chlorite and illite. The montmorillonite lattice expanded to 17.8 A upon treatment with glycerol; therefore, the presence of montmorillonite was verified. The peaks due to chlorite were removed upon treatment with hydrochloric acid. The sample was then identified as mostly chlorite with a minor amount of illite and montmorillonite.

Sample 1-27:

This sample showed nothing more than illite; the major peak at 9.92 A was combined with some complex silicates along with the common non-clay minerals.

Sample 1-28:

The original sample contained peaks at 13.5 A, 10.0 A, 8.26 A, and 7.13 A. This sample was believed to contain chlorite, illite, complex silicates and kaolinite. Treatment with hydrochloric acid removed all lines pertaining to both chlorite and kaolinite, Therefore, the assumption that kaolinite was present was incorrect while the presence of chlorite was established. The sample was identified as chlorite, illite, and complex silicates. Chlorite was the predominant mineral present.

Sample 6-17:

The patterns of the original and centrifuged samples showed peaks at 9.7 A and 7.13 A. From this it was assumed that the sample contained illite and either chlorite or kaolinite. Treatment with hydrochloric acid had no affect on the peaks in question; therefore, they were attributed to kaolinite. The sample was dominantly kaolinite with a minor amount of illite, along with the common non-clay minerals present.

Sample 6-25:

The patterns of the original and centrifuged samples contained peaks at 13.6 A, 10.0 A, and 7.18 A. The sample

was thought to contain chlorite, illite, and kaolinite. Treatment with hydrochloric acid proved the presence of chlorites. The peaks assumed to be kaolinite were not affected. The sample contained chlorite, illite, and kaolinite in considerable quantity. Kaolinite was the major mineral present with smaller amounts of chlorite and illite.

Sample 6-31:

The patterns of the original and centrifuged samples contained peaks at 15.2 A, 10.5 A, 14 A, and 7.2 A. This sample was initially identified as montmorillonite, illite, chlorite and kaolinite. Confusion as to the presence of either chlorite or kaolinite resulted because of a low intensity peak at about 14 A with a similar peak at about 7.2 A. Treatment with hydrochloric acid reduced the intensity of the peaks associated with chlorite. However, there were still indications of kaolinite after this treatment. Treatment with glycerol expanded the 15 A montmorillonite peak to 17 A, thus confirming the presence of montmorillonite. This sample contained montmorillonite, illite, kaolinite, and chlorite. Illite was the predominant mineral with small amounts of montmorillonite, chlorite, and kaolinite.

Sample 6-49:

The patterns of the original and centrifuged samples contained peaks at 14.7 A, 10.2 A, and 7.3 A. From these patterns it was assumed that the sample contained

montmorillonite, chlorite, illite, and kaolinite. Treatment with glycerol caused the montmorillonite lattice to expand to 17.7 Å, thus confirming the presence of montmorillonite. Treatment with hydrochloric acid removed the peaks caused by chlorite leaving no trace of chlorite or kaolinite. Thus, the confusion between chlorite and kaolinite in connection with the peak at about 7.2 Å was solved. The sample contained montmorillonite, chlorite, and illite. Illite was the major constituent of this sample with montmorillonite and chlorite being present in smaller quantities.

Sample 6-83:

The patterns of the original and centrifuged samples showed peaks at 14.4 Å, 10.6 Å, 7.55 Å, and 7.13 Å. From this pattern it was assumed that montmorillonite, chlorite, illite, gypsum, and kaolinite were present. The presence of montmorillonite in the sample was proved when the lattice was expanded to 19.6 Å with glycerol. It is believed that some expansion was caused by water along with the glycerol, thus causing the overexpansion of the lattice. After the expansion of 14.4 Å peak no presence of chlorite was indicated. Hydrochloric acid had no effect on the remaining peaks; therefore, these peaks were attributed to kaolinite. The sample, therefore, was said to contain montmorillonite, illite, kaolinite, and gypsum.



Montmorillonite was present in major portions, while illite, kaolinite and gypsum were minor in quantity.

Sample 6-87:

The patterns of the original and centrifuged samples showed peaks at 14.47 Å, 10.5 Å, and 7.13 Å. From this pattern it was assumed that the sample contained montmorillonite, chlorite, illite, and kaolinite. Treatment with glycerol failed to expand the 14.47 Å peak so the assumption that montmorillonite was present was incorrect. The chlorite peaks were removed upon treatment with hydrochloric acid, thus showing the presence of chlorite. After this treatment, the kaolinite peaks, at 7.13 Å, remained. The sample contained minor amounts of chlorite, illite, and kaolinite.

Sample 6-89:

The patterns of the original and centrifuged samples showed peaks at 10.04 Å and 8.03 Å. Although no chlorite peaks appeared there was evidence of chamosite at 4.7 Å. This peak disappeared upon treatment with hydrochloric acid. The sample contained mostly illite, with minor amounts of chamosite and complex silicates.

Sample 7-1:

The patterns of the original and centrifuged samples showed peaks at 9.8 Å and 7.0 Å. From these, the sample contained illite and amesite in small amounts.

Sample 7-2:

The patterns of the original and centrifuged samples showed peaks at 13.6 A, 9.77 A, and 7.28 A. From these peaks it was assumed that the clay contained chlorite, illite and kaolinite. Chlorite peaks were removed on treatment with hydrochloric acid; kaolinite peaks were removed on heating to 550°C. Therefore, the sample contained chlorite, illite, and kaolinite in small amounts.

Sample 7-3\*:

The patterns of the original and centrifuged samples showed peaks at 10.2 A and 7.5 A. From this, it was assumed that the sample contained illite and kaolinite. Hydrochloric acid had no effect on the peaks thought to be kaolinite. Chlorite peaks which coincide closely with kaolinites would have disappeared. The sample contained small amounts of illite and kaolinite.

\*For data other than clay minerals present, see references 9 and 10.

## CHAPTER V

## CONCLUSION AND RECOMMENDATION

The use of x-rays had proved very satisfactory in this investigation. The data obtained by this means is considerably accurate as long as precautions have been taken in the alignment and calibration of the equipment used. In the use of x-rays for this type of work, or any other for that matter, extreme care should be taken in the preparation of samples for study. Improper sample preparation can lead to erroneous results.

Recommendations for further study are as follows:

1. Improving on the method for obtaining a more pure clay mineral, i.e., eliminate quartz as much as possible.
2. In this investigation hydrous micas were considered as illite. Further work on the differentiation of minerals in the hydrous mica group, such as illite, mica, vermiculite, hydrobiotite, etc., should be attempted.
3. It is thought that some time may be saved in further investigation if the sample is centrifuged before being exposed to x-rays. This would eliminate the first step in the procedure. This first pattern is not important unless the investigator is interested in the presence of minerals other than the clay groups.

4. Investigation and comparison of different means of orienting the clay particles after they have been suspended in solution. The methods generally used are sometimes slow and inadequate.
5. Make some estimation as to the amounts of each clay mineral present in the sample.



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## APPENDIX

1. List of "d spacings" for various clay minerals.
2. Effect of the various thermal and chemical treatments on the common clay minerals.



2-95	Montmorillonoid (glycerol) (1)-(3)	2-97-3-00	Felspars (3)-(7)	2-94	Maghemite (7)
2-86-2-88	Muscovite (5)	—	—	2-88	Dolomite (10)
2-82-2-87	Chlorites (1)-(6)	2-81-2-89	Felspars (4)-(8)	2-85	Rhodochrosite (10)
2-81-2-84	Vermiculite (1)-(4)	—	—	—	α-Cristobalite (8)
2-80	Muscovite (4)	—	—	2-79	Siderite (10)
2-67-2-70	Chamosite (3)-(9)	2-70	Cronstedtite (7)	2-76-2-83	Apatites (10)
2-65	Biotite (8)	—	Mullite (6)	2-75	Ilmenite (10)
2-61	Palygorskite (8)	—	—	2-74	Magnesite (10)
—	Sepiolite (8)	—	—	2-69	Haematite (10)
—	Hydrobiotite (4)-(8)	2-60	Talc (5)	—	—
2-60-2-63	Vermiculite (1)-(5)	2-58-2-60	Amesite (2)-(5)	—	—
2-57-2-59	Chlorites (1)-(7)	—	—	—	—
2-57	Muscovite (9), Illite (7)	—	—	—	—
2-56	Metahalloysite (7)	—	—	2-55	Corundum (9)
2-55-2-60	Montmorillonoids (2)-(10)	2-54	Mullite (7)	2-54	Ilmenite (8)
2-52-2-55	Chlorites (2)-(6)	2-51-2-55	Felspars (4)-(8)	2-53	Magnetite (10)
—	Palygorskite (3)-(10)	—	Pyrophyllite (2)-(7)	—	—
—	Kaolinite (8)	2-51-2-52	Antigorite (4)	2-51	Maghemite (10)
2-51-2-52	Chamosite (5)-(10)	—	—	—	Haematite (8)
2-50	Dickite (6)	2-47-2-48	Talc (6)	2-48	α-Cristobalite (9)
2-49-2-50	Kaolinite (9)	2-46	Amesite (7)	2-47	Lepidocrocite (8)
2-45	Biotite (8)	—	—	—	Wüstite (7)
—	Sepiolite (7)	2-44-2-45	Chrysotile (3)	2-43	Goethite (7)
2-43-2-46	Chlorites (2)-(6)	2-42-2-40	Pyrophyllite (4)-(7)	—	—
2-42	Nacrite (10)	2-41	Cronstedtite (7)	2-41	Spinel (10)
2-40	Chamosite (0)-(10)	—	—	2-38	Corundum (8)
2-37-2-38	Kaolinite (7)	—	—	—	γ-Al <sub>2</sub> O <sub>3</sub> (8)
2-37	Vermiculite (4)	—	—	2-34	Boehmite (10)
2-32-2-33	Dickite (5)-(8)	—	—	2-31	Diaspore (8)
—	Kaolinite (8)-(10)	—	—	2-28	Calcite (7)
2-28	Kaolinite (9)	—	—	2-22	Bayerite (10)
—	Sepiolite (6)	2-20	Mullite (7)	2-20	Haematite (7)
2-18	Biotite (8)	—	—	2-14	Wüstite (10)
2-14	Chamosite (0)-(5)	2-11	Mullite (5)	2-12	Diaspore (7)
2-13	Muscovite (8)	2-09	Talc (4)	2-09	Magnesite (8)
2-09	Sepiolite (5)	2-07	Pyrophyllite (3)	2-09	Calcite (7)
2-00-2-05	Chlorites (2)-(8)	2-02	Cronstedtite (5)	2-08	Corundum (10)
2-00	Micas (5)-(10)	—	—	2-07	Diaspore (7)
—	Hydrobiotites (5)-(10)	—	—	2-01	Spinel (8)
1-99-2-01	Chlorites (2)-(6)	—	—	1-98	Aragonite (9)
1-98	Kaolinite (7)	1-90-1-92	Amesite (5)-(7)	1-97	γ-Al <sub>2</sub> O <sub>3</sub> (10)
1-79	Dickite (3)	1-87	Talc (5)	1-93	Lepidocrocite (7)
1-78	Kaolinite (5)	—	—	1-92	Calcite (9)
1-68	Metahalloysite (5)	—	—	1-87	Calcite (8)
1-66-1-72	Montmorillonoids (1)-(5)	1-68	Talc (5)	1-85	Boehmite (10)
1-66	Kaolinite (8)	—	—	1-83	Haematite (7)
1-65	Micas, Illites (2)-(7)	1-63	Pyrophyllite (5)	1-81	Quartz (8)
1-62	Kaolinite (6)	1-58	Cronstedtite (8)	1-80	Dolomite (7)
1-56-1-58	Chlorites (3)-(7)	1-56	Antigorite (3)	1-77	Rhodochrosite (8)
1-55-1-56	Chamosite (2)-(8)	—	—	1-74	Corundum (8)
1-54	Kaolinite (5)	1-52-1-53	Amesite (5)-(7)	1-73	Siderite (8)
—	Biotite (8)	—	Mullite (7)	1-72	Bayerite (7)
1-53-1-56	Chlorites (2)-(8)	—	Talc (4)-(8)	—	Ilmenite (7)
1-53	Vermiculites (5)	—	Chrysotile (3)-(4)	1-70	Magnesite (9)
—	Hydrobiotites (5)	1-49	Pyrophyllite (2)-(8)	1-69	Haematite (8)
1-50	Muscovite, Illites (7)	—	—	—	—
1-50	Palygorskite (5)	—	—	1-63	Diaspore (8)
1-49-1-52	Montmorillonoids (2)-(10)	—	—	1-60	Corundum (10)
1-49	Kaolinite (9)	—	—	—	—
—	Nacrite (8)	—	—	1-54	Spinel (8)
—	Metahalloysite (8)	—	—	—	—
—	Dickite (5)	—	—	1-51	Wüstite (9)
1-45	Nacrite (4)	—	—	—	—
1-39-1-41	Chlorites (3)-(8)	—	—	1-48	Magnetite (7)
				—	Haematite (7)
				1-47	Maghemite (7)
				1-45	Haematite (8)
				1-42	Spinel (10)
				1-40	Corundum (7)
				1-39	γ-Al <sub>2</sub> O <sub>3</sub> (10)



	Basal spacing free from foreign matter	How affected by Hydrochloric acid	How basal spacing affected by polar molecule	Heating
Chlorite	14 A	Warm HCl dissolves it completely.	Unaffected	Changes to olivine at 800-850 C
Kaolinite	7.2 A	Unaffected	Unaffected	Becomes amorphous at 500 C
Montmorillonite	12.5 15 (under normal conditions of water)	Dissolves some forms of it.	Swells to a higher value, depending upon type molecule.	Loses water basal spacing drops to 9.6 A
Illite	10 A	Dissolves some forms of it	Unaffected	Loses water from lattice destroyed around 800-850 C

Appendix 2. Chemical and thermal treatments and their effect on the clay minerals. (5,24)