

AN X-RAY DIFFRACTION STUDY OF SOIL MINERALS

by

GALEN FRANCIS GLESSNER

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INTRODUCTION

The following study of several of the soil minerals has been undertaken to follow the structural changes during the adsorption of water and to observe the manner in which the particles of soil minerals settle out from suspensions in water rather than to arrive at a structure for any of the minerals studied. It is hoped that this study of some of the pure minerals found in various soils may be of value in the study of the more complicated soil itself.

To investigate the structure of a substance by means of x-rays, use is made of the fact that a crystalline substance consists of regularly spaced atoms and that these atoms form planes within the crystal. Since the distance between these planes is of approximately the same order as the wave length of x-rays, then the crystal may be used as a satisfactory diffraction grating for x-rays. The Bragg method of x-ray analysis makes use of the following simple law, $n\lambda = 2d \sin\theta$ where d is the distance between the planes of the crystal, λ is the wave length of the incident radiation, and θ is the angle of reflection from the planes of the crystal. n represents the order of the reflection, and is some small whole number. In this method of analysis,

the wave length λ is known accurately and the $\tan 2\theta$ can be obtained from the film measurements. From this the $\sin \theta$ can be calculated and thus the ratio $\frac{d}{n}$ may be evaluated. Since it is usually possible to determine n , d may be found. In practice, the crystal is oscillated about one of the axes through the required angle to obtain the diffraction from the planes. This method of analysis is best used with crystals of sufficient size that they may be easily handled.

In the following investigation, the particle size of the mineral was far too small to permit the use of the method described. Debye and Scherrer in Europe and Hull in America discovered independently that a powder may be used very satisfactorily, to a certain extent, in a determination of the structure. Advantage is taken of the fact that in a powder there are a large number of minute crystals arranged in an entirely chaotic manner, but in this chaotic arrangement there are enough particles situated in the correct position to give diffraction from any one set of planes. Furthermore, because of the large number of particles in the random arrangement, all the planes are represented in the pattern. Thus, a diffraction pattern of this type consists of concentric rings around the primary beam.

Each ring is of uniform intensity and corresponds to one particular set of planes at a distance d from each other. Consequently, this method of obtaining a diffraction pattern lends itself particularly well to a study of the soil minerals and the changes they undergo when they take up water whether the change is the formation of a compound or merely swelling.

In the powder pattern, the particles are situated in an entirely random position giving rise to concentric rings of uniform intensity. If a fibered material is x-rayed instead of a powder and the diffracted rays recorded on a flat film perpendicular to the primary beam, the pattern will consist of rings that are not of uniform intensity. Instead, the diffraction rings are very intense in certain localities indicating there are more particles so situated for that particular reflection and in other localities of the same ring, the intensity is very weak indicating only a few particles oriented for that reflection. Thus, a fiber pattern consists of arcs or spots through which may be drawn a ring that would ordinarily exist in that position if there were no orientation.

Since the individual particles of bentonite, pyrophyllite, talc, and the micas are thought to be plates or

lamellar in shape, then, upon settling out from suspension in water onto a smooth surface, these plates should show a tendency to lie flat on this surface resulting in a layer of particles that has more symmetry than a random arrangement. By carefully removing and drying this film, it may be examined by x-raying small strips or fibers cut from the dried film to test for any orientation of the particles. The kind and size of particles and the time of settling before inserting the flat surface to catch them are the most important factors for obtaining good orientation patterns.

REVIEW OF THE LITERATURE

A study of the moisture content of soils and soil minerals reveals that the water taken up and held by the soil may be classified into different groups. Eaver and Horner (1) consider three groups:

- (1) Combined water, or water that is chemically bound into the structure.
- (2) Adsorbed water, or that water which is adsorbed upon the surface and in the pores of the colloid.
- (3) Capillary and osmotically imbibed water.

The combined water consists of the water that is driven off by ignition but not at 110°C . The adsorbed water

(hygroscopic water) is the amount of water taken up on the exposure of the dry substance to an atmosphere of known relative humidity. The capillary and osmotically imbibed water is that water taken up by the substance when brought into contact with a water surface. The exact nature of the forces which hold the osmotically imbibed water are not known (13).

Kelley, Jenny, and Brown (12) further define the "adsorbed water" as that amount of water given off below 400° C. They also speak of "crystal lattice" water and define it as being that portion of the total water which comes off at the nearly vertical branch in the dehydration curve. The adsorbed water, as they speak of it, may be divided into two groups; the feldspar and the bentonitic types. This division is based upon the two different kinds of dehydration curves as given by the feldspars and the bentonitic types of minerals, the former losing its adsorbed water at a rather uniform rate and the latter losing about 88 per cent at 100° C. An explanation of these differences is offered by calling the feldspar water "broken bond" water and the bentonitic type as being "planar" water.

Jaeger (10) depicts his arrangements of ultramarine

(a mineral very similar to the zeolites and having a very high base exchange capacity) in which an arrangement of the silicon and aluminum tetrahedra allows a cavity to form in the center of the space grouping. It is in this cavity that a large number of the exchangeable cations and loosely held water molecules exist. At the edges of the arrangement, there exist broken bonds that attract the strongly polar water molecules and they are thus tightly held. Since other arrangements of the tetrahedra are possible, an explanation of the bentonitic or planar type of water is offered. Here the "Si-O-Si" and "OH-Al-OH" planes are made up of rings consisting of six linked tetrahedra and theoretically, at least, have an infinitely large area. The important feature of these planes is the absence of broken bonds and free electric fields within the plane itself. The only attraction present in these planes is the weak extraneous electric fields and consequently the water thus held is easily given off, even at low temperatures. This type of water, then, is held between layers within the molecule and thus a large amount of water between the planes would tend to cause these planes to be swelled apart. This phenomenon has been reported by Hofmann, Endell, and Wilm (9), Hofmann and Bilke (8), and Bradley,

Grim, and Clark (2). Most of the swelling takes place between the 001 planes.

Kelley, Jenny, and Brown (12) show (from the dehydration curves) that beidellite and the bentonites contain considerable adsorbed water and are of the planar type, whereas kaolin and halloysite show the presence of considerable crystal lattice water. These curves agree well with those given by Ross and Kerr (14, 15).

It has been suggested by Wherry (13) that bentonite is a one dimensional colloid being microscopic in breadth but of colloidal thickness. Ross and Shannon (16) show that the most important constituent of certain bentonites is the micaceous crystalline mineral, montmorillonite and conclude that the crystals of bentonite are lamellar in form. Kelley, Dore, and Brown (11) agree that this is likely and also report that bentonite saturated with various exchangeable cations gives x-ray patterns essentially the same as the original bentonite.

The work of Bragg (3) has been of great value in determining the actual structure of many of the minerals and naturally occurring silicates. The actual size of the individual ion is one of the determining factors of the shape of the building unit in constructing a crystal, al-

though it cannot be said that any particular ion has a rigid boundary inside which all the electrons are grouped, it may be assumed that such a hypothetical boundary exists because the repulsive forces do not permit the approach of one ion to another closer than the value of the interatomic distance. These ions, then, may be considered as impenetrable spheres of characteristic diameters. A few of the ionic radii in Å. (Ångstrom units) as listed by Bragg (3) are as follows: Na 0.98, Mg 0.78, Al 0.57, Si 0.39, K 1.33, Ca 1.06, Fe 0.83, and Fe 0.67.

Knowing the relative sizes of the various ions that make up the silicates, it is more easily seen why the elements arrange themselves into a tetrahedron or octahedron. According to Bragg (3), Clark (4), and Wyckoff (19), the silicon ion, because of its small diameter, is always found located between four oxygen atoms. The silicon-oxygen distance is given by Bragg (3) as 1.6 Å. and the oxygen-oxygen distance as being 2.6 Å.

The framework of the silicates may be considered as the result of a linking of the silicon tetrahedrons in a manner similar to that of polymerization. The simplest are the orthosilicates or those containing separate SiO_4 groups. Each oxygen is attached to one and only one silicon atom, the other bond being attached to some metallic ion. Two of

these tetrahedra may be linked together by a common oxygen atom to form the group Si_2O_7 . The common oxygen in this case is inert, leaving the three oxygens at each end of the double tetrahedra with one negative charge each. These are called the active points of the complex and have cations attached to them. Three of these groups attached in such a manner to form a ring give the grouping Si_3O_9 . A ring of four tetrahedra is given by Bragg (3) and by Jaeger (10) as the likely structure of certain zeolites although they think that these rings are linked together by aluminum-oxygen tetrahedra. Still another possibility is the six tetrahedron ring having the group Si_6O_{18} . Chains of these six membered rings are formed when the rings are joined to each other in a fashion similar to that of naphthalene and anthracene. Sheets of these rings are formed when the rings are joined to each other in a fashion similar to that of phenanthrene.

According to the accepted ideas of the structure of talc, pyrophyllite, kaolinite, and the micas, as given by Bragg (3), and Wyckoff (19), the atoms are arranged in sheets. Because of these sheets, these minerals possess a flaky structure and cleave easily between these sheets, giving rise to smaller particles of lamellar shape. This

agrees well with Ross and Shannon (16) and Kelley, Dore, and Brown (11) in that they believe that the crystals of bentonite and montmorillonite are lamellar in shape. Hendricks and Fry (7) report that during the evaporation and drying of suspensions of certain minerals in water the particles tend to orient themselves into a regular arrangement as was shown by petrographic study. Clark, Grim, and Bradley (5) have obtained x-ray patterns from flakes of kaolinitic and micaceous clays which show a fibred structure.

Sideri (17) reported there was no difference in x-ray patterns for dry and swollen soils and concluded that the crystalline substance did not take part in the swelling. He showed, however, that the main constituent of the crystalline material studied was quartz.

Figure 1, taken from Hofmann and Bilke (8), depicts their arrangement of the montmorillonite crystal and the variable 001 spacing within which the water may be adsorbed. Figure 2, also from Hofmann and Bilke (8), shows an arrangement of a silicon-oxygen plane and the broken bonds which result from breaking the crystal. Ions or molecules held to these broken bonds are tightly held but are replaceable.

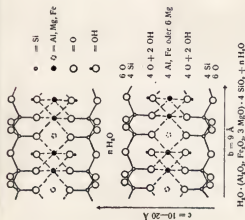


FIG. 1

FIG. 1. CRYSTAL STRUCTURE OF MONTMORILLONITE SHOWING THE VARIABLE (001) SPACING ALONG THE C AXIS

Reproduced from Hofmann and Bilke (8)

FIG. 2. BROKEN BONDS RESULTING FROM THE BREAKING OF A SILICON-OXYGEN PLANE OF A CLAY CRYSTAL

Reproduced from Hofmann and Bilke (8)

Hofmann, Endell, and Wilm (9) reported that bentonite and related clays, upon adsorption of water or other polar compounds, exhibits a reversible, one dimensional, inner crystalline swelling between the 001 planes of the montmorillonite crystal. Hofmann and Bilke (8) found that the maximum swelling in the 001 spacings of sodium montmorillonite was much larger than that of the hydrogen or calcium saturated montmorillonite. This, they say, is evidence that some of the exchangeable cations are held within the variable spacing of the crystal. Furthermore, Hofmann and associates (8, 9) and Bradley, Grim, and Clark (2) showed that the magnitude of the 001 spacings of some soil minerals depended on the amount of water in the sample. Gieseeking (6) reports that bentonite saturated with various large substituted ammonium ions did not show the same swelling of the 001 planes when treated with water as did the calcium, hydrogen, and sodium bentonite when so treated.

EXPERIMENTAL PROCEDURE

Source and Preparation of Materials

The soil minerals used in this study were obtained through the Ward Mineral Company and came from various parts of the United States. The montmorillonite came from Yavapai county, Arizona. The kaolin was taken from Mitchell county, North Carolina and contained no large lumps. The source of the pyrophyllite was near Badin, North Carolina. Both the halloysite and allophane were obtained near Bedford, Indiana. The bentonite was a Wyoming bentonite. All the minerals seemed to be fairly free from impurities except the halloysite which contained a few inclusions suggesting the presence of iron. The montmorillonite, pyrophyllite, halloysite, and allophane, as received, were lumpy.

The calcium and ammonium saturated bentonites were obtained from the Kansas Agricultural Experiment Station. The potassium bentonite was prepared by the author by leaching bentonite with a saturated solution of potassium chloride to remove the exchangeable bases. The bentonite

was centrifuged from suspension after each leaching and was washed once with distilled water and then repeatedly with 80 per cent ethyl alcohol till free from chlorides. To prevent caking, the potassium bentonite was dehydrated by a process of washing, first with absolute alcohol and then with anhydrous ether followed by rapid filtering and drying in a vacuum desiccator. This procedure resulted in a dry, powdered product.

Except for the bentonite, which was already very finely divided, all the minerals were further ground. The montmerillonite, pyrophyllite, halloysite, and allophane were lumpy and had to be first crushed and then ground in a Braun Pulverizer. This product represents the crudely ground mineral. X-ray diffraction patterns of this product (in the case of pyrophyllite and kaolin) indicated that the particles were still relatively large. To obtain a mineral of still smaller particle size, the samples were ground in a ball mill constructed of solid steel, the bowl of which was two and one-half inches in diameter and four and one-half inches deep and turned out in such a manner that there were no corners for the mineral to gather in. The top of the bowl was turned out in a similar fashion. Sixty steel ball bearings, three-eighths inch in diameter, were used inside. To prevent the mineral from clinging to

the sides of the bowl and the balls, the bowl was partially filled with petroleum ether. A lead gasket prevented the escape of the fluid. Grinding in this ball mill from ten to twenty-four hours reduced the mineral to particles of almost colloidal size and gave smooth x-ray diffraction patterns. At the end of the grinding operation, it was only necessary to evaporate off the petroleum ether to obtain the dry powdered material.

X-ray Equipment Used

The x-radiation was from a Philips Metalix Fein Struktur x-ray tube employing a hot filament and copper target and was operated at a potential of 27 kilovolts and a current of 20 to 25 milliamperes. The radiation was filtered with a nickel foil 0.001 inch thick to give nearly monochromatic Cu $K\alpha$ x-rays of wave length 1.54 Å.

The transmission patterns were obtained by mounting the sample over the pinhole system through which emerged a small "pencil" of x-rays. The diffracted x-rays were recorded upon a flat film set perpendicular to the primary beam and at a distance of 5 cm. from the sample. The size of the pinhole varied from 0.025 to 0.04 inch in diameter.

In obtaining the long narrow patterns, a round camera was used in which the powdered sample was shaped into a wedge and mounted at the center of the camera. A small beam of x-rays was allowed to impinge upon this wedge from its side and the diffracted x-rays were recorded upon the long narrow film held in place on the circumference of the camera.

Since the distances between the various planes of sodium chloride are accurately known, this substance was used to calibrate the round camera. The distances (cm.) from the undeviated beam to the lines on the film were plotted against their interplanar spacings in $\text{\AA}$. so that in order to obtain the interplanar spacings it was only necessary to measure the distance on the film and read the spacing from the graph directly in $\text{\AA}$. This calibration eliminates the errors that would be caused by the film's not being located exactly on the circumference of the camera.

Determination of Adsorbed Water

A study of the adsorption of water by certain of these minerals was undertaken and the structural changes

accompanying this adsorption were followed by the change in the mineral's x-ray diffraction pattern. The minerals employed, for this study, were pyrophyllite, montmorillonite, bentonite, and bentonite saturated with calcium and ammonium ions. The method consisted of bringing weighed samples of the minerals to constant weight in atmospheres over 10, 26, 45, and 96 per cent sulfuric acid solutions kept in desiccators. The total amount of water held by the minerals is given in Tables 1 and 2. At first some difficulty was experienced in bringing the samples to constant weight due to the fluctuations of the room temperature. Keeping the temperature constant within 5° C. eliminated most of this trouble. When equilibrium was reached (usually in about four to six weeks) samples were removed from the desiccators and quickly sealed into the moisture tight cell with mica windows and x-rayed. To obtain the maximum swelling possible, the mineral was stirred up with an excess of distilled water in a test tube and allowed to soak for a period of time (usually from three to six days) and then sealed into a moisture tight cell with mica windows and x-rayed. The minimum swelling was determined by igniting samples of the minerals and x-raying them as mentioned above. The x-ray

patterns for the minerals thus treated were measured and the results are given in Tables 3, 4, 5, 6 and 7.

Orientation of Particles Settling from Suspension

The samples to be x-rayed were prepared in the following manner:

Approximately one gram (0.5 gram for all bentonite samples) of the crudely ground mineral was thoroughly shaken up in 100 cc. of water in a volumetric flask and allowed to soak from 24 hours to 3 weeks to insure thorough wetting of the sample. During this soaking period, the suspension was frequently shaken. After thoroughly soaking, the suspension was again shaken, poured into a clean 100 cc. beaker and the particles allowed to settle for a time varying from two minutes to six hours depending upon the mineral and the size of the particles. At the end of this settling period, a clean glass plate (one-half of a microscope slide) was carefully and slowly lowered into the suspension so as to catch the remainder of the settling particles. When the suspension had cleared or when no change was noticed in the amount of material remaining suspended, the glass plate was slowly

and carefully removed and allowed to dry, usually from one to three days. To be x-rayed, the samples were cut from the glass plate in the form of a fiber with a sharp razor blade in such a manner as to get a section of the settled film approximately one-fourth to one-half mm. wide and five or six mm. long and of the thickness of the film. These fibers were mounted onto a small, thin piece of wood in such a manner that the x-ray beam was passed through the fiber parallel to the plates but perpendicular to the direction of settling.

RESULTS

The total amount of water taken up and held by the montmorillonite, pyrophyllite, and the calcium and ammonium bentonites upon the exposure to atmospheres of varying relative humidity is given in Table 1. Table 2 gives similar data for the original bentonite. The percentages given are based upon the muffle dry material. The concentration of the sulfuric acid solutions referred to in Table 1 was determined by titrating portions of weighed samples of the acid with a standard base. The concentration of the sulfuric acid solutions mentioned in Table 2 was determined by their specific gravities.

The x-ray diffraction patterns obtained from the bentonite, montmorillonite, pyrophyllite, calcium bentonite, and ammonium bentonite have been measured and the values of the interplanar spacings are given in Tables 3, 4, 5, 6 and 7. The spacings are expressed in Å. and the letters following the spacings designate their intensities as follows:

vs = very strong
 s = strong
 m = medium
 w = weak
 vw = very weak
 vvw = very, very weak

Spacings followed by vvw are definitely present but the exact position of the line is somewhat uncertain.

The interplanar spacings of air-dried samples of pyrophyllite, montmorillonite, and halloysite are given in Table 9. Table 8 shows the variation of the 001 spacings of the minerals upon adsorption of water in atmospheres of different relative humidities. Figs. 3, 4 and 5 show respectively the x-ray diffraction patterns for the air-dried pyrophyllite, the pyrophyllite suspension film as x-rayed perpendicular to the plates and the same suspension film as x-rayed parallel to the plates. Figs. 6, 7 and 8 give similar patterns for bentonite.

Plate III shows the x-ray diffraction patterns for calcium bentonite with different degrees of hydration. The spots that appear on these diffraction patterns are Laue spots of the mica used as windows for the moisture sight cell and in no way affect the position or measurement of the rings.

Table 1. Moisture content (in per cent) of minerals kept over sulfuric acid solutions.

Mineral	Strength of H_2SO_4 (in per cent)			
	96	45	26	10
Montmorillonite	11.53	32.42	45.27	58.47
Pyrophyllite	7.61	8.19	9.76	15.43
Calcium bentonite	7.51	20.52	27.53	35.14
Ammonium bentonite	7.85	14.07	18.39	29.72

Table 2. Moisture content (in per cent) of bentonite kept over sulfuric acid solutions.

	Strength of H_2SO_4 (in per cent)					
	92	74	55.9	40.3	28.3	10.3
Per cent water	1.31	2.33	3.54	9.79	20.4	30.4

Table 3. Interplanar spacing in A. for bentonite with different degrees of hydration.

Line: Ignited; no. material:	Strength of H_2SO_4 (in per cent)						: Excess : water	
	92	74	53.9	40.3	28.3	10.3		
1	15.77 m	16.10 m	16.80 m	17.70 m	19.30 m	22.70 s	25.70 s	
2	9.27 s	9.97 s	10.36 s	10.30 s	11.90 vs	15.45 vs	16.10 vs	
3 $\frac{1}{2}$	4.70 w	4.94 w	4.77 vvw	4.98 vvw	4.82 vw	5.09 vw		
4	4.37 vs	4.48 vs	4.35 vs	4.44 vs	4.41 vs	4.44 s	4.44 s	4.36 w
5	3.31 m	3.37 m	3.27 m	3.35 m	3.30 m	3.32 m	3.32 m	3.30 w
6	3.11 m	3.22 w	3.10 m	3.21 m	3.10 m	3.07 m	3.10 w	
7	2.80 w	2.55 w	2.60 w	2.64 w	2.63 w	2.56 w	2.64 w	2.56 vvw

Table 4. Interplanar spacing in A. for montmorillonite with different degrees of hydration.

Line: Ignited: no. material:	Strength of H_2SO_4 (in per cent)				: Excess : water
	90	45	25	10	
1	17.95 m	21.60 m	25.70 m	25.70 m	30.85 m
2	9.72 m	12.90 vs	15.45 vs	15.77 vs	17.56 vs
3 $\frac{1}{2}$			4.94 vw		18.83 s
4	4.395 s	4.41 vs	4.41 s	4.395 m	4.33 s
5	3.24 vw				4.395 m
7	2.52 vw	2.525 v	2.545 v	2.525 vw	2.31 vw
					2.54 w

Table 5. Interplanar spacing in A. for pyrophyllite with different degrees of hydration.

Line: no.	Ignited material:	Strength of H_2SO_4 (in per cent)				:Excess :water
		96	45	26	10	
1	19.83 m	32.10 m	33.50 m	33.50 m	36.75 m	
2	9.27 m	8.86 m	9.06 m	9.16 mm	8.96 m	8.96 m
4	4.33 vs	4.53 s	4.37 s	4.395 s	4.53 s	4.53 s
4½	vw	4.05 m	4.09 w	4.09 w	4.07 m	4.11 w
5	3.035 s	2.97 m	3.01 m	3.028 m	2.99 m	3.00 w
7	2.51 w	2.48 m	2.51 m	2.535 m	2.48 m	2.50 w
8	2.38 w	2.36 m	2.38 m	2.395 m	2.34 m	2.38 w

Table 6. Interplanar spacing in A. for calcium bentonite with different degrees of hydration.

Line: Ignited: no. material:	Strength of H_2SO_4 (in per cent)				Excess water
	96	45	26	10	
1	19.35 w	22.05 w	23.95 m	25.70 m	26.01 m
2	9.38 s	10.93 s	14.08 vvs	15.13 vs	18.35 vvs
2½					9.27 w
3					6.12 vvw
3½	4.72 vvw	4.92 vw	5.055 vw	5.15 w	
4	4.398 vs	4.43 s	4.44 s	4.415 s	4.37 s
5	3.31 m	3.32 m	3.31 m	3.31 m	3.275 m
6	3.12 m	3.10 vw	3.09 vw	3.035 vw	3.045 vw
7	2.64 vw	2.54 w	2.50 vw	2.515 vw	2.50 vw

Table 7. Interplanar spacing in A. for ammonium bentonite with different degrees of hydration.

Line Ignited: no. material:	Strength of H_2SO_4 (in per cent)				:Excess :water
	96	45	26	10	
1	17.95 m	20.30 m	20.85 m	20.85 m	24.96 m
2	9.61 m	10.79 s	11.56 vs	11.90 vs	13.10 vs
3			5.96 vw		14.40 m
4	4.395 s	4.395 s	4.395 s	4.53 s	4.596 m
5	3.275 m	3.29 m	3.31 m	3.246 m	3.52 m
6	3.095 m	3.12 vw	3.096 vw	3.04 vw	
7		2.525 w	2.53 w	2.50 w	2.54 w
8			2.41 vw	2.40 w	

Table 8. Variation of 001 spacing with different degrees of hydration.

Mineral	Ignited ; material:	Strength of H_2SO_4 (in per cent)			Excess water
		36	45	58	
Bentonite	9.27 s	9.27 s	11.90 vs	15.45 vs	16.10 vs
Montmorillonite	9.72 m	12.90 vs	15.45 vs	15.77 vs	17.56 vs 18.83 s
Pyrophyllite	9.27 m	8.96 m	9.06 m	9.16 m	8.96 m
Calcium bentonite	9.38 s	10.93 s	14.08 vs	15.19 vs	15.45 vs 18.35 vs
Ammonium bentonite	9.61 m	10.79 s	11.56 vs	11.90 vs	13.10 vs 14.40 m

Table 9. Interplanar spacings in Å. for the air-dried samples of pyrophyllite, montmorillonite, and halloysite.

Line number	:	Interplanar spacing
Pyrophyllite		
1		19.30
2		9.46
3		4.36
4		3.05
5		2.64
6		2.52
Montmorillonite		
1		20.85
2		14.08
2½		4.70
3		4.31
4		2.47
Halloysite		
1		too indefinite
1½		9.97
2		7.25
3		4.35
4		3.53
5		3.27
6		2.51

DISCUSSION OF RESULTS

The moisture content of the minerals as given in Tables 1 and 2 shows wide variations in the amount of water taken up by the various minerals in different atmospheres. The montmorillonite over 10 per cent sulfuric acid took up 58.47 per cent of its weight of water or more than five times as much as it took up over 96 per cent sulfuric acid. Pyrophyllite doubled its water content from an atmosphere over 96 per cent sulfuric acid to one over 10 per cent sulfuric acid. The calcium and ammonium bentonites¹ took up five and four times, respectively, as much water over the 10 per cent sulfuric acid as they did over 96 per cent sulfuric acid. The original bentonite² took up almost 17 times as much water over 10.3 per cent sulfuric acid as it did over 92 per cent sulfuric acid. It should be noted that the bentonite was brought to constant weight over dif-

¹ The calcium and ammonium bentonites were prepared by and obtained from Dr. A. T. Perkins of the Kansas Agricultural Experiment Station.

² The moisture content of the original bentonite was determined by Dr. A. T. Perkins of the Kansas Agricultural Experiment Station.

ferent sulfuric acid solutions than those used for the other materials. At the end of the moisture determination for the calcium and ammonium bentonites, a mold appeared on the surface of the minerals kept over 10 per cent sulfuric acid.

The x-ray diffraction data, as given in Tables 3, 4, 6, 7 and 8, show that considerable change occurs in the longer spacings when water is introduced into the sample. These changes were very large for all the minerals studied, except pyrophyllite, which shows practically no change even for wide variations in treatment such as heating in the muffle or soaking in water.

According to Hofmann, Endell, and Wilm (9), Hofmann and Bilke (8), Bradley, Grim, and Clark (2), and Giesecking (6), the 001 spacing is the innermost ring so prominent in the diffraction patterns. In this study, it was this ring that was most prominent and sharp and showed large variations when the minerals, except pyrophyllite, were treated with water. Table 8 gives the value of these spacings for the different minerals and the treatment given for that particular spacing. It is interesting to note that, except for the pyrophyllite, the spacings were all increased by the introduction of water into the sample indicating that

the adsorbed water had increased the interplanar distance of the 001 planes.

Tables 3, 4, 5, 6 and 7 give, with a few exceptions, values for d greater than that for the 001 spacings. This value is obtained from an inner halo (Plate III) which lies very close to the primary beam. Measurement was made of its edge which was rather poorly defined being, in some cases, very diffuse. Usually, the higher the water content of the sample, the more definite was its edge. Because of the diffuse nature of these halos, the interplanar distance given for them must be taken cautiously. No satisfactory explanation of the cause of this spacing is offered.

When bentonite was treated with an excess of water and allowed to soak and then x-rayed, the ring corresponding to the 001 spacing, as well as the inner halo, disappeared into the central spot indicating a very large swelling of these planes. When potassium bentonite was treated in a similar fashion, the same results were obtained. With the calcium and ammonium bentonites, however, the results are different. The 001 spacing is increased considerably, but not to the extent of disappearing as it did for the bentonite and potassium bentonite. As with the inner halo, the intensity and sharpness of the 001 spacing was enhanced by increasing the amount of water in the mineral.

The measurements for the x-ray diffraction patterns for the air-dried montmorillonite, pyrophyllite, and halloysite are given in Table 9. Attempts to secure orientation patterns from allophane resulted in very poor orientation or none at all. Halloysite exhibited some orientation though it was not pronounced. The pyrophyllite and bentonite gave excellent orientation patterns even to the extent of complete extinction of parts of certain rings and very intensive interference in other parts of the same ring. Even in the best of the orientation patterns, certain rings appear without much change in intensity.

As has been mentioned previously, the orientation patterns were obtained by x-raying the strip with the beam passing through the strip parallel to the plates. When the same strip was x-rayed by passing the beam through the strip perpendicular to the plates, a very smooth pattern, somewhat similar to a powder pattern, was obtained. A few distinct differences, however, were observed.

The powder patterns for air-dry pyrophyllite and bentonite showed the presence of particles too large to give smooth diffraction rings, Figs. 3 and 6. In the patterns taken from the strips, the rings and arcs were all smooth which indicated the absence of the large particles, Figs. 4, 5, 7 and 8.

In the settling process, the larger particles undoubtedly had settled out faster than the smaller ones and were thus eliminated from the sample.

Fig. 5 shows a fiber pattern of pyrophyllite x-rayed parallel to the plates and is typical of some of the better orientation patterns obtained. Fig. 4 shows a fiber pattern of pyrophyllite x-rayed perpendicular to the plates and was cut from the same sample as that for Fig. 5. Differences other than the arcs and rings of these patterns were observed.

It will be noticed in Figs. 4 and 7 that the rings in the position where the arcs form in Figs. 5 and 8 are either absent or weak. A satisfactory explanation of this can be made by assuming the particles to be plate-like in shape and as they settled out they built up on the flat surface in layers. When strips of this dried layer or film are x-rayed with the beam parallel to these plates, the regular arrangement of particles with certain layers parallel to each other act as a diffraction grating and give rise to the arcs mentioned above. Furthermore, if these strips were x-rayed with the beam perpendicular to these plates it should give rise to a pattern somewhat similar to a powder pattern because to the beam of x-rays

Explanation of Plate I

- Fig. 3. X-ray diffraction pattern of air-dried pyrophyllite.
- Fig. 4. X-ray diffraction pattern of pyrophyllite film x-rayed perpendicular to plates.
- Fig. 5. X-ray diffraction pattern of pyrophyllite film x-rayed parallel to plates.

Plate I



Fig. 3



Fig. 4

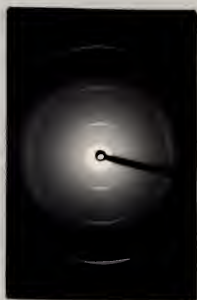


Fig. 6

Explanation of Plate II

- Fig. 6. X-ray diffraction pattern of air-dried bentonite.
- Fig. 7. X-ray diffraction pattern of bentonite film x-rayed perpendicular to plates.
- Fig. 8. X-ray diffraction pattern of bentonite film x-rayed parallel to plates.

Plate II

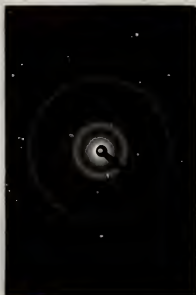


Fig. 6



Fig. 7



Fig. 8

Explanation of Plate III

- Fig. 9. X-ray diffraction pattern for calcium bentonite with excess water.
- Fig. 10. X-ray diffraction pattern for calcium bentonite kept over 10 per cent sulfuric acid.
- Fig. 11. X-ray diffraction pattern for calcium bentonite kept over 26 per cent sulfuric acid.
- Fig. 12. X-ray diffraction pattern for calcium bentonite kept over 45 per cent sulfuric acid.
- Fig. 13. X-ray diffraction pattern for calcium bentonite kept over 95 per cent sulfuric acid.
- Fig. 14. X-ray diffraction pattern of ignited calcium bentonite.

Plate III



Fig. 9

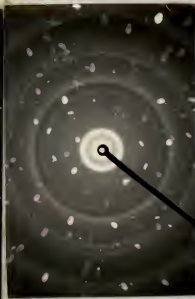


Fig. 10



Fig. 11

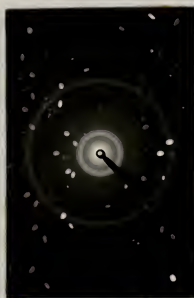


Fig. 12



Fig. 13



Fig. 14

the fiber in this position presents its particles only in a random position. In this case, the "diffraction grating" is seen on its edge by the x-rays and thus no arcs are formed. Since the plates are lined up to give diffraction when seen on their sides, they could not give diffraction when "seen" from above and thus certain of the lines should be absent or very weak.

In the pyrophyllite films (Fig. 5), very definite and intense arcs occur at 9.06, 4.56, and $3.05 \text{ \AA}$. and are undoubtedly the first, second and third order reflections. Ring 3 in the pyrophyllite pattern (Fig. 4) seems to show two separate rings and in the fiber pattern (Fig. 5) two very definite rings appear.

The bentonite film (Fig. 8) shows very definite orientation at 10.79, 4.33, and $3.05 \text{ \AA}$. The arcs at $4.33 \text{ \AA}$. are found perpendicular to the others. It seems characteristic of the orientation patterns of bentonite to have the arcs in ring 4 set perpendicular to the other arcs.

Plate IV offers a visual comparison of the x-ray diffraction patterns of the air-dried samples of bentonite, montmorillonite, pyrophyllite, halloysite, and allophane. These patterns were taken in the round camera which gives greater spread to the broad lines showing, in some cases,

that they are actually made up of more than one line. This fact was indicated by the diffraction patterns obtained by x-raying the pyrophyllite film (Fig. 4) perpendicular to the plates in which the heavy ring 3 was split into two rings. In the case of the air-dried sample (Fig. 3), ring 3 was broad and intense but did not show its composition as being different than a single ring.

Explanation of Plate IV

- Fig. 15. X-ray diffraction pattern of bentonite.
Fig. 16. X-ray diffraction pattern of montmorillonite.
Fig. 17. X-ray diffraction pattern of pyrophyllite.
Fig. 18. X-ray diffraction pattern of halloysite.
Fig. 19. X-ray diffraction pattern of allophane.

Plate IV

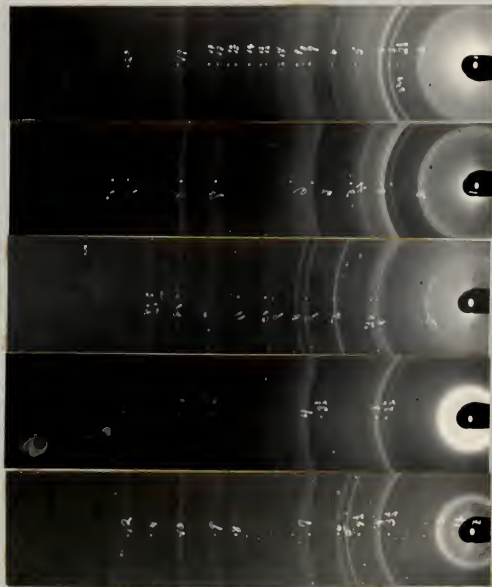


Fig. 15 Fig. 16 Fig. 17 Fig. 18 Fig. 19

SUMMARY

1. The x-ray diffraction patterns of the calcium and ammonium bentonites were essentially the same as that of the original bentonite. The bentonite and the calcium and ammonium bentonites adsorbed nearly equal amounts of water over 10 per cent sulfuric acid. The montmorillonite adsorbed nearly four times as much water over 10 per cent sulfuric acid as did the pyrophyllite.

2. The atomic structure of pyrophyllite remained practically unchanged regardless of the treatment while the longer spacings of montmorillonite, bentonite, and the calcium and ammonium bentonites were increased by the adsorption of water. The intensity and sharpness of the longer spacings, inner rings, were increased by increasing the amount of water, except where an excess was used, in the material.

3. Pyrophyllite and bentonite gave very good orientation patterns for particles settling out from a suspension in water, while for allophane and halloysite, the orientation was poor. Montmorillonite did not show very good orientation under these conditions but was better

than allophane and halloysite.

4. The three most important factors contributing to a good orientation pattern are: (1) the kind of mineral and its crystalline form, (2) the size of particles, and (3) the length of time the suspension is allowed to settle before insertion of the flat plate.

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