


AN ABSTRACT OF THE THESIS OF

Antoine Hanna Sayegh for the Ph.D. in Soils
(Name) (Degree) (Major)

Date thesis is presented April 8, 1964

Title CHANGES IN LATTICE SPACING OF EXPANDING CLAY
MINERALS

Abstract approved 
(Major professor)

The expanding and collapsing properties of montmorillonite, beidellite, nontronite, and vermiculite were studied in relation to humidity, to organic liquids, and to charge density and charge location.

The c-spacing of the K-saturated montmorillonite, beidellite, and nontronite in the normal hydrated state was variable, and this was found to be correlated to the humidity in the atmosphere. When the humidity was controlled, reproducible results were obtained. All of the unheated K-saturated minerals collapsed to about 10.4\AA when X-rayed under a controlled humidity of 7%. It was concluded that humidity control during X-raying is essential. It was also found that the rate of hydration and dehydration of the samples was very rapid and detectable within the time it took to scan a sample by the usual method.

Ca and Mg-montmorillonite expanded to 17.2 and 17.5 \AA

with ethylene glycol and glycerol, respectively. Ca and Mg-vermiculite expanded to 14.3 Å with either liquid. Ca and Mg-beidellite expanded to 17.2 Å with ethylene glycol but only to 14.5 Å with glycerol.

The cation exchange capacity of 17 montmorillonite samples ranged from 61.1 to 201.8 me per 100 g. The vermiculite silt sample had cation exchange capacity of 141.7 me per 100 g. The identification of these minerals based on charge density was not applicable and could lead to misinterpretation of certain minerals. Thus, charge density cannot be used as a criterion for separation of montmorillonite from vermiculite.

A more reliable spectrum was established which leads to more positive identification of the minerals. The following spectrum is based on the expansion and collapse of the minerals which in turn is correlated to the location of the isomorphous substitution.

	<u>Montmorillonite</u>	<u>Beidellite</u>	<u>Vermiculite</u>
<u>Treatments</u>			
Ca + Mg with ethylene glycol	17.2	17.2	14.3
Ca + Mg with glycerol	17.5	14.6	14.3
K-saturated at 55% relative humidity	12.3	11.8	10.3

CHANGES IN LATTICE SPACING OF
EXPANDING CLAY MINERALS

by

ANTOINE HANNA SAYEGH

A THESIS

submitted to

OREGON STATE UNIVERSITY

in partial fulfillment of
the requirements for the
degree of

DOCTOR OF PHILOSOPHY

June 1964

APPROVED:

[REDACTED]

Associate Professor of Soils

In Charge of Major

[REDACTED]

Head of Soils Department

[REDACTED]

Dean of Graduate School

Date thesis is presented April 8, 1964

Typed by Opal Grossnicklaus

ACKNOWLEDGMENTS

The author gratefully acknowledges the advice offered by Dr. Moyle E. Harward in conducting this study. I wish to acknowledge the help of Dr. Ellis G. Knox who made many constructive criticisms during the preparation of the manuscript. Also the author expresses deepest appreciation to Dr. David Moore for reviewing it. Thanks is expressed to Richard Drosman who aided in the preparation of the graphs. Special acknowledgment is made to United States Public Health Service for the financial support of this research project.

Appreciation is extended to my wife Ruth for the patience and cooperation she gave me during the pursuance of this work.

TABLE OF CONTENTS

	Page
INTRODUCTION.....	1
EXPERIMENTAL METHODS AND MATERIALS.....	4
Sources of Clay Minerals	4
Preparation of Montmorillonites, Beidellite, and Non-tronite	6
Sample Pretreatments.....	6
Particle Size Separation.....	8
Sodium Hydroxide Solubility Treatment.....	9
Iron Removal.....	10
Calcium Saturation.....	11
Preparation of African Vermiculite	11
Separation of Silt Fraction.....	11
Calcium Saturation.....	12
Alteration of Mica-Vermiculite Mixture to Vermiculite.....	12
Cation Exchange Capacity.....	13
X-ray Diffraction	14
X-ray Equipment	14
Lithium Test.....	14
Cation Saturation and Solvation.....	15
RESULTS AND DISCUSSION	20
Effects of Organic Liquids	20
Humidity Effect on Clay Minerals	23
Humidity Effect on Ca and Mg-saturated Clays	23
Humidity Effect on K-saturated Clays	25
Rate of Hydration and Dehydration.....	33
Discussion.....	35
Effect of Lattice Charge Density	38

TABLE OF CONTENTS (Continued)

	Page
Effect of Charge Location.....	44
Location of Charge.....	45
Expansion.....	48
Collapse.....	50
Suggested Identification Spectrum.....	50
SUMMARY	53
BIBLIOGRAPHY.....	56

LIST OF FIGURES

Figure	Page
1. Change of X-ray diffraction intensity of a K-saturated clay with time: (a) introduction of air at 7% relative humidity, (b) exposure to room condition.....	34
2. X-ray patterns of a K-saturated clay: (a) under 7% relative humidity, (b) under uncontrolled humidity conditions.....	37

LIST OF TABLES

Table	Page
1. Basal spacings, in Angstrom units, of clay minerals saturated with Ca and Mg and solvated with ethylene glycol and glycerol.....	22
2. Basal spacings, in Angstrom units, of unheated clay minerals saturated with K and subjected to various relative humidities.....	26
3. Basal spacings, in Angstrom units, of clay minerals saturated with K, heated at 65°C and subjected to various relative humidities.....	28
4. Basal spacings, in Angstrom units, of clay minerals saturated with K, heated at 100°C and subjected to various relative humidities.....	30
5. Basal spacings, in Angstrom units, of clay minerals saturated with K, heated at various temperatures and subjected to various relative humidities.....	32
6. Cation exchange capacity of the clay minerals.....	42
7. Cation exchange capacity and basal reflections of the clay minerals.....	44

CHANGES IN LATTICE SPACING OF EXPANDING CLAY MINERALS

INTRODUCTION

It has been recognized that X-ray diffraction is a major tool in characterization of clays. Since its introduction in this capacity in 1930 by Hendricks and Fry (19) and Kelley et al. (23), a great deal of time and effort has been spent in developing techniques which would permit positive identification and characterization of clay materials with X-ray diffraction.

In general there are two factors which affect the expansion and collapse of clay minerals: First, the charge density referred to as layer charge, and second, the site of the isomorphous substitution in the minerals. The currently accepted concept is that the charge density of the silicate layers is the dominating factor in relation to expansion and collapse (1; 2; 3; 29; 41). Gjems (15) indicated that a collapse to 10 \AA is not generally limited to vermiculite since according to Brown and Jackson (10) a montmorillonite with high layer charge can show a similar partial collapse to 10 \AA on K saturation. In the literature there is confusion between charge density and isomorphous substitution. Apparently this confusion is due to the fact that these researchers have related

expansion and contraction phenomena in clays to charge density without giving sufficient consideration to location of the isomorphous substitution. Some investigators (1; 2; 4; 40; 41) used clays that possessed charge densities of around 120 me per 100 g to compare with clays having charge densities of about 170 me per 100 g. In doing this, due consideration was not given to the fact that the low charge density clays had octahedral isomorphous substitution while the substitution in the high density clays was primarily tetrahedral. Therefore, these two factors were not differentiated from each other.

One objective of this work is to reexamine this problem and to determine what influence the location of isomorphous substitution exerts in causing variations in the 001 spacing of the expanding silicate structures. In particular, it is of interest to examine how the tetrahedral substitutions in layer silicates affects the variations in the 001 spacing.

The approach to the above problem is to study a set of expanding lattice mineral samples from montmorillonite to vermiculite with a range in tetrahedral substitution and an independent range in charge density. The montmorillonite samples have different degrees of charge densities with the higher ones overlapping the minerals that have tetrahedral substitution. These clays will be treated with various cations and solvated with different organic

liquids to determine the effect on expansion of the c-axis spacing. The potassium saturated minerals will be used to study the influence of humidity on the ease of collapse of the c-axis spacing.

Another objective of this study is to point out the possibilities of certain ambiguities which may exist in the present methods of identifying expanding lattice minerals based on the criteria of charge density (1; 2; 3; 29; 41). An attempt will be made to establish a more reliable spectrum based on expansion and collapsing properties of these minerals.

Objectives

The objectives of this study may be stated as follows:

1. To investigate the expanding and collapsing properties of expanding lattice minerals
 - a. with respect to charge density and charge location.
 - b. with respect to humidity.
 - c. with respect to different organic liquids.
2. To establish a spectrum for the distinction of the different members of the expanding lattice group of minerals by their expanding and collapsing properties.

EXPERIMENTAL METHODS AND MATERIALS

Sources of Clay Minerals

A fairly large number of sample specimens were obtained. A preliminary analysis was performed on all the samples, and the following were selected to provide a range in structural features and properties. Descriptions of the minerals used in this study and their sources are given below:

1. Bentonite - Vol clay, Aberdeen, Panther Creek, American Colloid Company, 5100 Suffield Court, Skokie, Illinois,
2. Bentonite - Vol clay, SPV, American Colloid Company, 5100 Suffield Court, Skokie, Illinois
5. Montmorillonite 21 - Chisholm Mine, Polkville, Mississippi, Ward's Natural Science Establishment, Inc., Rochester, New York
6. Montmorillonite 24 - Otay, California, Ward's Natural Science Establishment, Inc., Rochester, New York
7. Na - Montmorillonite S 44-4 - Clay sealing investigations report, Colorado State University, Fort Collins, Colorado
8. Montmorillonite S 34 - 6 - Clay sealing investigations report, Colorado State University, Fort Collins, Colorado
9. Montmorillonite S 34 - 1 - Clay sealing investigations

report, Colorado State University, Fort Collins, Colorado

11. Montmorillonite S 49 - 8 - Clay sealing investigations report,
Colorado State University, Fort Collins, Colorado

14. Montmorillonite S 79 - 1 - Clay sealing investigations report,
Colorado State University, Fort Collins, Colorado

16. Na - Bentonite S 00 - 3 (Johannesburg, South Africa) - Colorado clay report, Colorado State University, Fort Collins, Colorado

17. Montmorillonite 30a - Bayard, New Mexico, Ward's Natural
Science Establishment, Inc., Rochester, New York

19. Montmorillonite 23 - Chambers, Arizona, Ward's Natural
Science Establishment, Inc., Rochester, New York

20. Montmorillonite 26 - Clay spur, Wyoming, Ward's Natural
Science Establishment, Inc., Rochester, New York

21. Montmorillonite 20 - Husband Mine, Polkville, Mississippi,
Ward's Natural Science Establishment, Inc., Rochester,
New York

22. Montmorillonite 27 - Belle Fourche, South Dakota, Ward's
Natural Science Establishment, Inc., Rochester, New
York

25. Montmorillonite 32 - Pioche, Nevada, Ward's Natural Science

Establishment, Inc., Rochester, New York

26. Montmorillonite 11 - Santa Rita, New Mexico, Ward's Natural

Science Establishment, Inc., Rochester, New York

30. Nontronite 33A - Garfield, Washington, Ward's Natural Sci-

ence Establishment, Inc., Rochester, New York

32. Beidellite R 4762 - Black Jack Mine, Carson District, Owyhee

Co., Idaho, United States National Museum

61. Vermiculite - Northern Transvaal, Africa, Ward's Natural

Science Establishment, Inc., Rochester, New York

Preparation of Montmorillonites, Beidellite,
and Nontronite

Sample Pretreatments

The minerals were ground in a mortar to pass through a 20 mesh sieve and stored in glass bottles.

Samples were washed two times with dilute HCl to remove carbonates. The acid remained in contact with the sample until no further effervescence was seen or heard.

Each sample was treated with 30% H_2O_2 to destroy organic matter. The H_2O_2 was added slowly while stirring. The sample was left overnight and then heated on a hot plate for about 30 minutes (24).

The samples were then transferred to polyethylene centrifuge cups¹ using distilled water as the flushing and policing liquid. Each sample was washed twice with distilled water. The purpose of the washings was to facilitate subsequent dispersion by removal of the soluble organic matter not completely oxidized by the H_2O_2 treatments and to remove the soluble salts that might be present.

Free iron oxides were removed essentially as described by Jackson (20, p. 57). To approximately 15 g of the washed, organic matter-free minerals in the polyethylene centrifuge cup, 80 ml of 0.3 N sodium citrate were added. This was buffered at pH 7.3 with 10 ml of M NaHCO_3 . The sample was heated in a water bath until the temperature was brought to 78°C . Two g of $\text{Na}_2\text{S}_2\text{O}_4$ was then added immediately and the mixture was stirred constantly for one minute after which the sample was returned to the bath for 15 minutes. The samples were then centrifuged to remove the soluble iron.

Jackson's treatment (20, p. 73) of 2% boiling Na_2CO_3 was used to obtain a more nearly complete dispersion, since the samples were suspected of containing amorphous aluminum and silicon oxides which act as cementing agents.

¹ The polyethylene centrifuge cups were made by cutting off the top of 60 x 125 mm polyethylene 250 ml bottles just below the cap so as to leave a 1 1/4 inch opening. A suitable pouring lip was made with a heated glass rod.

The samples were transferred with 2% Na_2CO_3 used as the flushing and policing solution to 500 ml stainless steel beakers. Then 4 g of anhydrous Na_2CO_3 was added to the suspension, and total volume was brought approximately to 200 ml with distilled water. The sample was agitated for about one minute with a high speed rotary stirrer.² The suspension was brought to a boil as quickly as possible with a gas burner, then boiled for exactly five minutes, poured back into the polyethylene cups and centrifuged again. The sediment was washed twice with Na_2CO_3 solution.

Particle Size Separation

Particle size fractions of 2 to 0.2 and less than 0.2 microns effective spherical diameter were separated as described by Jackson (20, p. 101-164) with one exception. Since a continuous flow centrifuge was unavailable it was not feasible to carry out the clay size separations by progressing to successively smaller particle sizes.

Around 200 ml of dilute Na_2CO_3 (1 g per 9 liters) were added to the samples treated with boiling Na_2CO_3 , stirred with the rotary stirrer and centrifuged at 750 r.p.m. for five minutes using either International centrifuge size 1 or Serval Superspeed GSA centrifuge.

²A malt mixer of the type commonly used for mechanical analysis was adapted by replacing the metal blade with a rubber policeman.

This separates the clay from sand and silt at two microns. Four washings were usually sufficient for the above separation.

The clay suspension saved from the separation above was poured into the centrifuge tubes and centrifuged for seven minutes at 6000 r.p.m. using Serval Superspeed SS-1 centrifuge. The sediment was the coarse clay 2 to 0.2 micron. Dilute Na_2CO_3 was used to extract the less than 0.2 micron fraction from the 2 to 0.2 micron fraction. Five washings were usually sufficient for this separation.

The sediments, 2 to 0.2 micron clay, to be used in this study were transferred to one liter Erlenmeyer flasks using dilute Na_2CO_3 as the flushing and policing solution.

The amount of clay in the suspension was determined by weighing oven dried aliquots.

Sodium Hydroxide Solubility Treatment

Alkaline treatments (NaOH or Na_2CO_3) have been used for a number of years for "cleaning" soil clays. However, it is only recently that the variables have been scrutinized and their effect on the layer silicates evaluated (18). This method was used to determine the amounts of amorphous inorganic material in the soils studied.

To a four liter stainless steel beaker 3000 ml of 0.5 N NaOH were added and brought to gentle boiling. Enough volume of the 2

to 0.2 micron clay suspension to provide 18 g of clay (0.6 g per 100 ml of NaOH) was measured with a graduated cylinder. The measured suspension was poured into 500 ml stainless steel beakers and brought to boiling stage. The boiling suspension was poured into the boiling NaOH solution. The new suspension was brought to a boil as quickly as possible, then boiled for exactly 2.5 minutes and was immediately cooled in a water bath to room temperature in the four liter stainless steel beakers. As a result, the clay was flocculated and settled at the bottom of the beaker. The supernatant liquid was decanted. The remaining suspensions were then transferred to centrifuge cups and were centrifuged in the supercentrifuge, washed twice with 1% NaHCO_3 , stirred with rotary stirrer. The supernatant was decanted after each centrifuging.

Iron Removal

The sediments from the previous NaOH treatment were treated for removal of free iron oxides as described previously except for the additional steps outlined below. The iron removal treatment was repeated to remove the free iron oxides released by the removal of the amorphous inorganic materials.

The additional steps were:

1. The sediments were washed twice with sodium citrate. After

each washing the suspension was stirred with a rotary stirrer.

2. The sediments were washed twice with a 2:1 acetone-water mixture to remove the citrate ions.

Calcium Saturation

The sediments from the iron oxides removal treatment were calcium saturated by four washings with 1 N CaCl_2 (34). Two water and three methanol washings were used to remove excess salts. The last washing was tested for the chloride ion using AgNO_3 to assure complete removal of the excess salts.

The calcium saturated clay, 2 to 0.2 micron, was stored in methanol in polyethylene bottles which then constituted the working stock of clay for the remaining determinations.

Preparation of African Vermiculite

Separation of Silt Fraction

Silt was found to be the most desirable fraction for the study of vermiculite.³ In order to obtain the silt fraction, portions of 20g of natural vermiculite (mica-vermiculite mixture) were ground in an Osterizer blender in the presence of 400 ml of 2% Na_2CO_3 as a

³ Unpublished results, Dumitru Carstea, Department of Soils, Oregon State University.

medium of dispersion. The duration of grinding was about two minutes and care was taken to prevent heating. About 10 g of the above material were boiled for five minutes in 200 ml of 2% Na_2CO_3 .

The material was then transferred from the stainless steel beaker to 250 ml polyethylene centrifuge cups and centrifuged. Dilute Na_2CO_3 (2 g Na_2CO_3 in 18 liters distilled water) was added to the centrifuge cups and centrifuged to 750 r.p.m. for 4.6 minutes. This was repeated until the supernatant was fairly clear.

The silt fraction was separated from the coarser material by wet sieve method using 300 mesh sieve. In order to remove any clay from the silt fraction that might not have been removed by the above centrifugation, the clay removal process was repeated.

Calcium Saturation

Ten g portions of silt were washed with 1 N CaCl_2 . The soluble salts were removed by two washings with distilled water followed by four washings with ethanol until no positive test for chlorides was observed. The material was dried at 65°C and stored until used.

Alteration of Mica-Vermiculite Mixture to Vermiculite

Five g of Ca-saturated silt fraction were treated with 3000 ml of 5N NaCl and digested in a water bath at approximately 80°C for

seven days.⁴ After seven days digestion the potassium interlayer from the mica was replaced by sodium and converted into a vermiculite. The content of potassium in unaltered silt was 3.70% while after alteration the content of potassium was only 0.31%.

Cation Exchange Capacity

A sample from the stock of calcium saturated clay suspension was taken for cation exchange determination. The exchangeable calcium was extracted as described by Rich (34) with one exception. Sodium was used instead of magnesium because of the difficulty of determining calcium in the presence of excess magnesium salts. Also Walker (39) has pointed out that sodium with its larger hydrated radius would have a tendency to insure a more complete removal of calcium. The extraction was also done a second time for ten minutes to insure complete calcium extraction.

The exchangeable calcium was determined by titrating with cyclohexanediamine tetraacetic acid (CyDTA) using calcein as an indicator as described by Carlson and Johnson (13).

⁴ Unpublished results, Dumitru Carstea, Department of Soils, Oregon State University, based on Rich's method (33).

X-ray Diffraction

X-ray Equipment

Diffraction patterns were made with a North American Philips Norelco diffraction spectrometer equipped with a Geiger-Mueller tube and a Brown recorder. Cu K-alpha X-ray radiation was used with tube potential and current of 50 kilovolts and 38 milliamperes, respectively. Divergence and scatter slits of 1/4 degree and a 0.006 inch receiving slit were found to be most advantageous for optimum peak height and resolution. The scanning speed was 1 degree 2 θ per minute for all samples. Patterns were run from 14 degrees 2 θ to 2 degree 2 θ except as specified. The choice of the rate meter settings and the time constant setting depended on the sample. The X-ray diffraction unit was equipped to permit circulation of air of controlled vapour pressure during sample analysis.

Lithium Test

Greene-Kelley (16) has demonstrated that montmorillonite alone of the montmorillonite group shows irreversible collapse perpendicular to the plane of the silicate sheets, when it is saturated with Li ions and the mineral dehydrated by moderate heating.

The calcium clays were saturated with lithium as suggested

by Greene-Kelley (16). The excess salt was removed by washing three times with methanol. A small amount of sediment, sufficient to give a thin layer, was removed from the centrifuge tube with a semi-microspatula and smeared on a petrographic microslide so as to provide a smooth surface (38). The samples were dried at room temperature and then in a muffle furnace at 200°C for 24 hours (16). The samples were removed from the muffle furnace and cooled in a desiccator for half an hour. Each slide was put in an aluminum dish, and with a medicine dropper enough p-chlorotoluene⁵ was added to cover the whole slide completely. The aluminum dish containing the slide was put in a tin can, and the can was closed and left overnight. The next day the slides were removed, air dried and subjected to diffraction analysis.

Cation Saturation and Solvation

Calcium. A small amount of the calcium clay methanol suspension was placed in a 50 ml centrifuge tube. The samples were washed once with distilled water to remove alcohol in order to facilitate preparation of the slides. Duplicate samples were prepared by taking a small amount of sediment, sufficient to give a thin

⁵Personal communication with R. Greene-Kelly, Rothamsted Experiment Station, Harpenden, England.

layer, from the centrifuge tube with a semi-microspatula and smearing it on a petrographic microslide so as to provide a smooth surface (38). The samples were dried at room temperature and then in an oven at 30°C for two hours to insure uniform conditions of dryness. The slides were transferred to a desiccator containing a saturated solution of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with a relative humidity of about 55%, and vacuum was applied. The samples remained in vacuum for four days over the saturated $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. The samples were then X-rayed in a controlled atmosphere of 55% relative humidity. Following analysis by X-ray diffraction, one of the duplicates was solvated with ethylene glycol using the procedures recommended by Kunze (25), and the other duplicate was solvated with glycerol according to Brown and Farrow (12). X-ray diffraction was then run on both slides.

Magnesium. The clay fractions were withdrawn from the calcium clay-methanol suspension and transferred to 50 ml centrifuge tubes. They were washed four times with 1N MgCl_2 and then three times with distilled water. Additional steps were identical with those for calcium clay.

Potassium. Samples of the calcium clay-methanol suspension were K saturated by washing four times with 1N KCl followed by

three washings with water. The paste method (38) was used for the preparation of slides for the X-ray diffraction. The following treatments were done on the K-saturated samples.

1. Samples were air dried at room temperature and X-rayed.
2. Samples were air dried at room temperature and X-rayed under controlled relative humidity of 7%.
3. Samples were heated at 65°C for two hours, cooled in a desiccator containing drierite and X-rayed.
4. Samples were heated at 65°C for two and four hours and X-rayed directly.
5. Samples were heated at 65°C for two and four hours and X-rayed directly in the range of the critical peak only.
6. Samples were heated at 65°C for two hours and X-rayed in the range of the critical peak only under controlled relative humidity of 7%.
7. Samples were heated at 65°C for two hours and stored in a desiccator containing saturated $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, relative humidity of 55%, for four days and X-rayed under controlled relative humidity of 55%.
8. Samples were heated at 100°C for two hours and X-rayed directly under controlled relative humidity of 7%.
9. Samples were heated at 100°C for two hours, cooled in a

desiccator containing drierite and X-rayed.

10. Samples were heated at 100°C for two and four hours and X-rayed immediately.

11. Samples were heated at 100°C for two hours and X-rayed directly in the range of the critical peak only.

12. Samples were heated at 100°C for two hours and X-rayed in the range of the critical peak only under controlled relative humidity of 7%.

13. Samples were heated at 100°C for two hours and stored in a desiccator containing saturated $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, relative humidity of 55%, for four days and X-rayed under controlled relative humidity of 55%.

14. Samples were heated at 200°C for two hours, cooled in a desiccator containing drierite and X-rayed.

15. Samples were heated at 200°C for two and four hours and X-rayed directly.

16. Samples were heated at 200°C for two hours, stored in the $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ desiccator for four days and X-rayed under controlled relative humidity of 55%.

17. Samples were heated at 300°C and 550°C for two hours and X-rayed directly.

18. Samples were heated at 300°C and 550°C for two hours and

X-rayed directly.

19. Samples were heated at 300°C and 550°C for two hours and stored in the $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ desiccator for four days and X-rayed under controlled humidity of 55%.

RESULTS AND DISCUSSION

Effects of Organic Liquids

It is obviously an advantage to use a liquid of low volatility which is readily miscible with water, so that the natural hydrated clay minerals may easily be changed into the complex. Glycerol (27; 28) and ethylene glycol (6) are the liquids normally used. No special precautions are necessary to exclude water, as the spacings are not altered even by the presence of some water (27).

The ability of montmorillonites to imbibe double sheets of interlayer glycerol ($d_{001} = 17.7\text{\AA}$) and ethylene glycol ($d_{001} = 17\text{\AA}$) molecules respectively was reported by MacEwan (27; 28) and Bradley (5).

Bradley (6; 7) noted that certain vermiculites expanded to form double-sheet interlayer complexes with ethylene glycol whereas other specimens failed to do so. Barshad (1) found that certain vermiculite when saturated with H^+ , Li^+ , Na^+ , Mg^{2+} , or Ba^{2+} gave single-sheet glycerol complexes ($d_{001} = 14.3\text{\AA}$), and Walker (42) reported the formation of single-sheet glycerol complexes with Mg-vermiculites. In the past the usual practice has been to consider the mineral a montmorillonite if a double-sheet glycerol complex is formed, and vermiculite if a single-sheet complex is formed.

The position with regard to ethylene glycol is less clear, but some workers seem to have assumed that both organic liquids behave in a similar fashion and hence that a double-sheet ethylene glycol complex excludes the possibility of vermiculite. More recently, in an attempt to evaluate the criteria currently employed for the differentiation between vermiculites and montmorillonites in clays, Walker (40) observed the formation of double-sheet glycerol and glycol complexes with vermiculites when saturated with cations other than Mg.

Weir (45) observed that the d_{001} spacing of Ca-beidellite is 16.8 and 17.6 \AA in ethylene glycol and glycerol respectively.

Table 1 shows that all the 17 Ca and Mg-montmorillonites expanded to about 17.5 \AA with both ethylene glycol and glycerol. This means that double sheets of either interlayer glycerol or ethylene glycol were formed in the montmorillonites. This agrees with the general findings of other workers.

The Ca-nontronite expanded to about 17.0 \AA with ethylene glycol and glycerol. The Mg-nontronite also expanded with ethylene glycol but not with glycerol. The Mg-nontronite with glycerol expanded only to 14.7 \AA .

The Ca and Mg-beidellite expanded to about 17.3 \AA with ethylene glycol while it expanded to about 14.7 \AA with glycerol. The

Table 1. Basal spacings, in Angstrom units, of clay minerals saturated with Ca and Mg and solvated with ethylene glycol and glycerol.

Clays	Ca	Mg	Ca ethylene glycol	Ca glycerol	Mg ethylene glycol	Mg glycerol
2 to 0.2 μ						
1 M	15.5	15.8	17.4	18.3	17.7	17.7
2 M	15.5	15.7	17.2	18.0	17.4	17.7
5 M	15.8	15.7	17.3	17.7	17.3	17.4
6 M	15.5	15.7	17.2	17.7	17.4	16.7
7 M	15.8	16.0	17.3	17.9	17.4	18.4
8 M	15.5	15.7	17.2	17.8	17.3	17.9
9 M	15.4	15.8	17.6	18.0	17.7	18.4
11 M	15.5	15.8	17.2	17.9	17.3	18.0
14 M	15.5	15.7	17.4	17.7	17.3	17.3
16 M	15.5	15.7	17.3	17.7	17.4	17.6
17 M	15.5	15.7	17.2	17.7	17.5	17.5
19 M	15.5	15.8	17.3	17.7	17.3	17.3
20 M	15.5	15.8	17.0	17.7	17.3	17.7
21 M	15.5	15.8	17.0	17.3	17.3	17.7
22 M	15.5	15.8	17.0	17.7	17.6	18.0
25 M	15.2	15.5	17.3	17.0	17.3	17.4
26 M	15.2	15.5	16.8	17.7	17.3	17.7
30 N	15.5	15.2	17.3	17.0	17.2	14.7
32 B	15.5	15.0	17.3	14.7	17.2	14.5
61 V	14.7	14.7	14.5	14.2	14.2	14.2

M stands for montmorillonite

N stands for nontronite

B stands for beidellite

V stands for vermiculite

result of Ca-beidellite with glycerol did not agree with the results of Weir. This is probably attributed to the difference in technique used in solvating the beidellite with glycerol. Weir and the other workers solvated their samples by applying the organic liquid directly on the sample instead of solvating the samples with organic vapour as was done in this study.

The Ca and Mg-vermiculite expanded to about 14.2\AA with both organic liquids. This is the spacing of single-sheet organic complexes.

The different behaviour of the various minerals with the organic liquids will be explained in the section of cation exchange capacity.

Humidity Effect on Clay Minerals

Humidity Effect on Ca and Mg-saturated Clays

Barshad (1) and Norrish (32) showed that different cations may retain different amounts of water of hydration. Therefore, it is necessary that a clay sample prepared for diffraction analysis be homoionic to ensure that expansion as a result of hydration will be uniform within all crystals of a species. As will be shown later, the relative humidity of the homoionic system should be controlled in order to minimize the changes in the interlayer water adsorption due to the fluctuations in relative humidity.

During the course of preliminary investigations it was observed that there was some variation in the 001 lattice spacings of Ca-saturated clay samples. These variations were correlated with relative humidity in the atmosphere. It was apparent that more precise control of environment would be necessary in order to relate expansion and collapse properties to structure. Attempt was therefore made to modify the X-ray diffraction unit in order to permit control of vapour pressure in equilibrium with the sample during analysis.

To control the humidity, a 35x12x23 inch box was built from acrylic plastic plexiglass⁶ sheets. Two holes were drilled in the top of the box as well as in the shield of the sample holder of the X-ray. The box and the shield were connected by rubber tubes through the holes. The opening in the shield was covered with cellophane tape to allow continuous air circulation around the slide. A fan for air circulation and a pump were put inside the box. The humidity inside the box was read from a Durotherm hygrometer. The air was circulated over a pan containing saturated magnesium nitrate solution to give 55% relative humidity. For the 7% relative humidity, the air was passed through a column containing drierite.

Table 1 gives data for 001 reflections of the Ca and Mg

⁶Plexiglass "G" sheets, colorless, masked was obtained from Universal Plastics Company, 43 S. E. Salmon street, Portland 14, Oregon.

saturation clays under controlled 55% relative humidity. As seen in table 1, a diffraction spacing of approximately 15.5\AA was obtained from a Mg and Ca-saturated montmorillonite, nontronite, beidellite, and vermiculite. These values are higher than the 14\AA reported in literature on air-dried basis. As it was pointed earlier that during the course of preliminary investigations a spacing of 12.4 to 14.4\AA in the 001 lattice of Ca-saturated clay samples on air-dried basis was observed. The high value of approximately 15.5\AA is due to the presence of two sheets of water molecules between the interlayer space of the clay minerals.

Humidity Effect on K-saturated Clays

Although positive identification of a clay mineral can rarely be made solely on the basis of its thermal behavior, the changes observed in X-ray diffraction patterns as a result of the heat treatment have been frequently used as a means of identification. Greene-Kelley (17) showed that the amount of water sorbed by K-saturated montmorillonite was not significantly affected by drying at temperature below 400°C . Most of the work done in relation to the effect of heating in clay identification was primarily at temperatures higher than 150°C . No work has been reported to control the humidity of K-saturated clays in relation to clay identification. The prevailing

concept of K-saturated of expanding lattice minerals is that the montmorillonites collapse to about 11.5\AA , beidellite and nontronite to about 10.5\AA and the vermiculites to about 10.3\AA when heated at low temperatures.

One of the objectives of this work is to study the swelling and collapsing properties of expanding lattice minerals with respect to humidity.

Table 2 gives the data on basal reflections of the unheated clay minerals saturated with potassium. A very unexpected result was noticed in that all of the K-saturated expanding lattice minerals collapsed to about 10.3\AA when the humidity was controlled to 7%. From this result we can observe that even the montmorillonites collapsed to about 10.3\AA .

Table 2. Basal spacings, in Angstrom units, of unheated clay minerals saturated with K and subject to various relative humidities

Clays 2 to 0.2 μ	Humidity		Clays 2 to 0.2 μ	Humidity	
	7%	uncontrolled		7%	uncontrolled
1 M	10.4	11.2	19 M	10.5	11.5
2 M	10.4	11.5	20 M	10.4	11.0
5 M	10.4	11.5	21 M	10.4	11.6
7 M	10.4	11.6	22 M	10.5	11.2
9 M	10.6	12.1	25 M	10.5	11.5
11 M	10.5	11.6	26 M	10.5	11.0
14 M	10.5	11.9	30 N	10.5	11.3
16 M	10.5	11.6	61 V	10.3	10.3

M stands for montmorillonite

N. stands of nontronite

V stands for vermiculite

Column two of table 2 shows the 001 spacings of the unheated expanding lattice minerals under uncontrolled humidity. It is shown that the montmorillonites and nontronite collapsed to about 11.5\AA and the vermiculite to 10.3\AA . Beidellite, as shown in table 3, is similar to montmorillonite. The uncontrolled humidity condition was carried as follows: after the K-saturated slides were prepared and air dried, they were X-rayed without humidity control.

Table 3 gives the basal spacings of clay minerals saturated with potassium, heated at 65°C and subjected to various relative humidities. First column shows the basal spacings of the K-saturated samples heated at 65°C , cooled in a desiccator for about one hour and X-rayed in uncontrolled humidity conditions. The values of the 001 spacings were about 12.0\AA . The second column shows the basal spacings of the samples treated similarly to those of column one except each slide was removed from the oven in turn and X-rayed directly. In order to study the effect of length of heating, the samples were heated for two and four hours and were X-rayed directly. It was found that there was no difference in the 001 spacing as a result of the different heating times. The 001 spacings were about 11.5\AA , similar to column two. Column three shows the same effect as column one of table 2, though in table 3 the samples were heated to 65°C .

Table 3. Basal spacings, in Angstrom units, of clay minerals saturated with K, heated at 65°C and subjected to various relative humidities.

Clays 2 to 0.2 μ	Humidity				
	uncontrolled		controlled		
	cooled in desiccator	X-rayed directly	X-rayed directly 7%	peak 7%	55%
1 M	11.3	10.9	10.4	10.4	11.8
2 M	11.8	11.3	10.5	10.5	12.1
5 M	11.8	11.8	10.5	10.4	12.3
6 M	11.8	11.8	10.5	10.4	12.4
7 M	11.9	11.8	10.3	10.3	12.3
8 M	12.3	12.1	10.5	10.3	12.4
9 M	12.3	11.9	10.4	10.4	12.4
11 M	12.1	12.1	10.4	10.4	12.4
14 M	12.1	11.9	10.4	10.4	12.3
16 M	12.1	12.1	10.4	10.3	12.4
17 M	12.1	11.6	10.5	10.4	12.1
19 M	12.1	11.5	10.4	10.3	12.3
20 M	12.1	11.8	10.4	10.4	12.4
21 M	12.1	11.6	10.5	10.5	12.4
22 M	11.9	10.9	10.5	10.4	12.1
25 M	12.2	11.3	10.5	10.4	12.4
26 M	11.9	11.8	10.5	10.5	12.3
30 N	11.8	-	10.4	10.4	12.4
32 B	11.8	11.8	10.4	10.4	11.8
61 V	-	-	-	-	10.3

M stands for montmorillonite

N stands for nontronite

B stands for beidellite

V stands for vermiculite

In order to show the effect of humidity, the samples were heated at 65°C and were removed from the oven in turn and X-rayed directly in the range of the critical peak only without any humidity control. That is, the slide was X-rayed from ten to seven degrees 2θ . The collapse was similar to those slides run under 7% humidity control. This similarity is attributed to the fact that by X-raying the critical peak directly, the time was not sufficient for rehydration of the sample. In contrast, when the sample is X-rayed by the standard method starting at 14 degrees 2θ , the sample has already rehydrated by the time the peak is reached. The critical time for hydration and dehydration will be discussed later at the end of this section. To further confirm the effect of humidity, the K-saturated samples, heated at 65°C , were stored in a desiccator containing saturated $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, relative humidity of 55%, for four days and X-rayed under the same relative humidity. The basal spacing is about 12.0\AA as shown in column five.

Also the heating time was studied in the range of the critical peak. The slides were heated for two and four hours and X-rayed without humidity control. The results were comparable with those that were obtained under 7% humidity control as shown in column four.

Table 4 shows the basal spacings of the clay minerals

Table 4. Basal spacings, in Angstrom units, of clay minerals saturated with K, heated at 100°C and subjected to various relative humidities.

Clays 2 to 0.2 μ	Humidity				
	uncontrolled			controlled	
	cooled in* desiccator	X-rayed* directly	X-rayed* directly	7%	55%
1 M	10.5	10.4	10.4	-	11.9
2 M	11.0	10.7	10.6	-	12.3
5 M	11.8	11.3	11.2	10.4	12.3
6 M	11.8	11.0	10.6	-	12.3
7 M	11.9	10.8	10.4	-	12.1
8 M	11.9	11.3	10.6	10.3	12.3
9 M	11.9	11.6	10.5	-	12.4
11 M	11.8	11.9	10.5	-	12.3
14 M	11.8	11.8	10.5	-	12.3
16 M	11.8	12.1	10.4	-	12.3
17 M	11.9	11.3	11.0	10.4	12.3
19 M	11.9	10.6	10.6	-	12.3
20 M	11.2	10.3	10.4	-	12.4
21 M	11.9	10.7	10.9	-	12.3
22 M	10.7	10.4	10.3	-	12.3
25 M	12.3	10.4	10.6	-	12.3
26 M	11.9	10.6	10.8	-	12.3
30 N	10.6	-	10.4	-	12.3
32 B	11.8	11.8	11.8	10.4	11.8

* run on different days

M stands for montmorillonite

N stands for nontronite

B stands for beidellite

saturated with K, heated at 100°C and subjected to various relative humidities. Column one shows the same results as its equivalent treatment in table 3. Although the samples in columns two and three were treated similarly to each other, they were X-rayed on different days. The variation in the results is no doubt attributable to differences in the atmospheric relative humidities. Even the samples of any one column were run at different days which explains the variations in the basal spacings under the uncontrolled relative humidity. On the other hand column five shows rather consistent basal spacings when the relative humidity was controlled.

The results shown in table 5 are the basal spacings of the K-saturated samples, heated to 200, 300, and 550°C and X-rayed under different relative humidities. At 200°C when the samples were cooled in the desiccator, (column one) the basal spacings were affected by relative humidity, whereas, when the samples were X-rayed directly, (column two) the collapse generally was observed. At 300°C the collapse occurred on all samples cooled in the desiccator except number 11 M but when the samples were X-rayed directly all of them collapsed. At 550°C the collapse generally was slightly more and was not affected by relative humidity when X-rayed under uncontrolled conditions. Samples heated to 200 and 300°C and subjected to 55% humidity behaved similarly to those heated to 100°C .

Table 5. Basal spacings, in Angstrom units, of clay minerals saturated with K, heated at various temperatures and subjected to various relative humidities.

Clays 2 to 0.2 μ	200°C			300°C			550°C		
	Cooled in desiccator	X-rayed directly	55% humidity	Cooled in desiccator	X-rayed directly	55% humidity	Cooled in desiccator	X-rayed directly	55% humidity
1 M	10.4	10.3	11.8	10.3	10.0	11.5	9.9	9.9	9.8
2 M	10.2	10.3	12.0	10.1	10.0	12.0	9.9	9.9	12.1
5 M	11.6	10.7	12.3	10.6	10.2	11.9	10.0	10.0	9.9
6 M	11.3	10.5	12.1	10.3	10.3	12.1	10.3	10.1	10.1
7 M	10.8	10.3	12.1	10.6	10.4	11.9	10.4	10.0	10.0
8 M	11.5	10.5	12.4	10.3	10.5	12.3	10.3	10.1	10.2
9 M	11.5	10.5	12.3	10.4	10.5	12.4	10.0	9.8	10.1
11 M	11.3	10.5	12.3	11.8	10.4	12.3	10.0	10.1	12.3
14 M	11.3	10.8	11.9	10.0	10.1	12.1	10.1	9.9	10.3
16 M	10.7	10.4	12.3	10.3	10.5	12.3	10.0	9.9	10.3
17 M	11.6	11.2	12.3	10.1	10.1	12.3	10.0	-	-
19 M	11.3	10.5	12.3	10.4	10.4	12.1	10.3	10.3	10.1
20 M	10.1	10.1	12.3	10.0	10.0	12.3	9.9	10.0	12.3
21 M	10.5	10.5	12.4	10.5	10.5	12.4	10.0	10.0	10.0
22 M	10.1	10.2	12.1	10.1	10.1	11.9	9.9	10.1	10.0
25 M	10.5	10.3	12.3	10.1	10.3	12.3	9.9	10.1	10.3
26 M	11.6	10.6	12.4	10.2	10.4	12.2	10.0	10.2	10.6
30 N	10.1	-	12.3	10.2	-	11.9	10.3	-	-
32 B	11.8	-	-	-	10.0	-	10.3	-	-

M stands for montmorillonite

N stands for nontronite

B stands for beidellite

Those heated at 550°C and subjected to 55% humidity, except for three samples, showed irreversible dehydration as evidenced by the collapse to about 10.2\AA .

Rate of Hydration and Dehydration

The following technique was used to study the rate of hydration and dehydration of the expanding lattice minerals. The peak of the hydrated sample was first determined in the usual way. For example, for sample 26M the peak was found to be at $7.3^{\circ} 2\theta$. This angle was then locked on the goniometer and the intensity of this peak was recorded for about one minute. At this point, 7% dry air from the humidity box was introduced over the sample. The intensity began dropping almost instantaneously and reached equilibrium at the lower intensity within one minute (figure 1). After ascertaining that equilibrium had been reached, the dry air flow was discontinued and rehydration in room air was allowed to proceed. The intensity of the peak began to increase within one minute and continued to rise over a period of eight to ten minutes. These observations are easily accounted for by the shift in the peak as dehydration and rehydration of the sample occurred. It is apparent from the data above that the rate of hydration is so rapid that the dehydrated state will not be detected by the usual method of scanning the

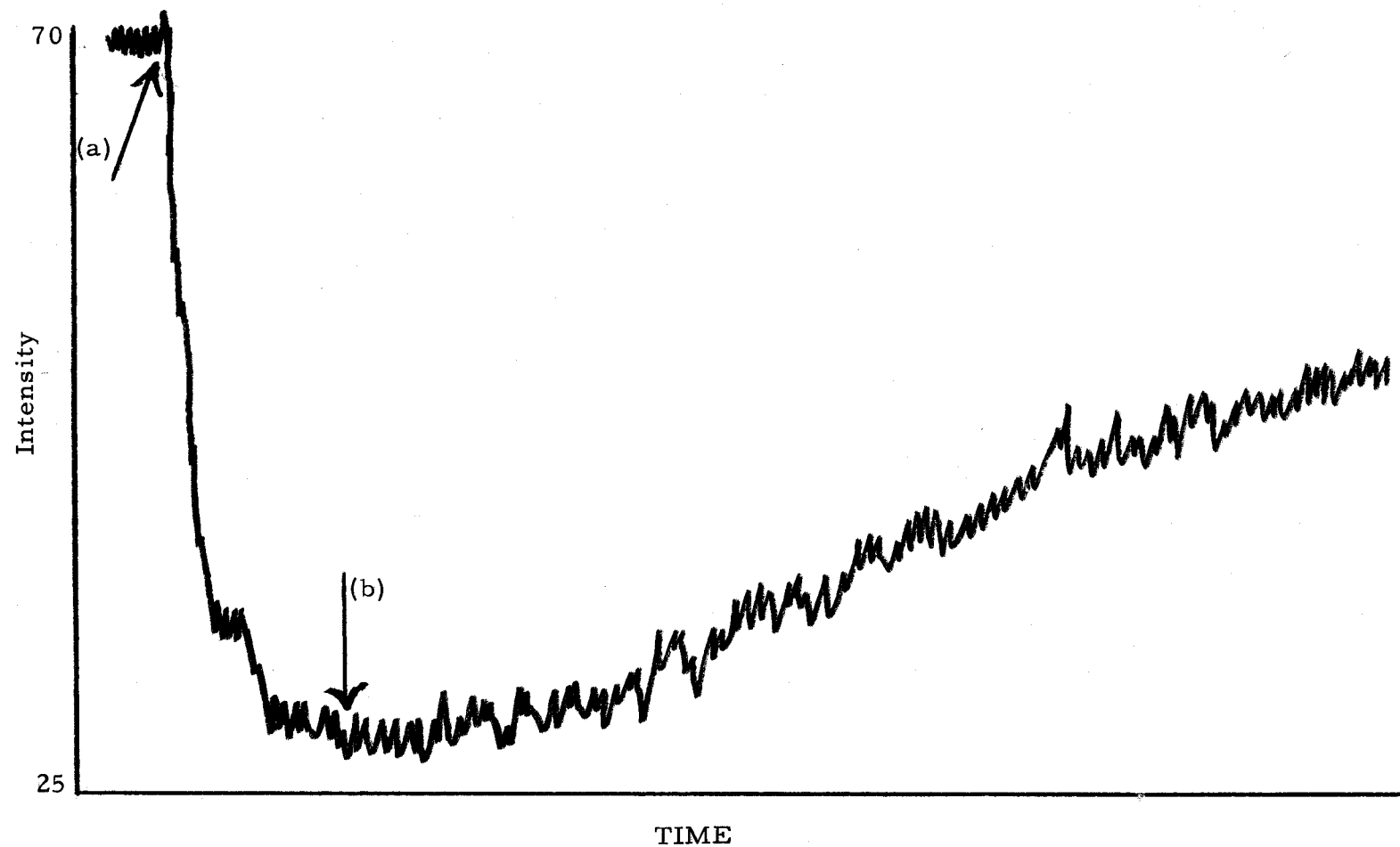


Figure 1. Change of X-ray diffraction intensity of a K-saturated clay with time: (a) introduction of air at 7% relative humidity, (b) exposure to room condition.

sample. This may account for the fact that this phenomena was not detected by other researchers. The importance of recognizing this phenomena in the interpretation of data and identification of clay minerals was pointed out earlier in this section.

Discussion

It has been well known for many years that the different types of clay minerals exhibit characteristic behaviour on heating. The changes that occur on heating are accompanied by changes in the X-ray diffraction patterns which are characteristic for the different mineral families, and which are used as a means of identification of some of the clay minerals. However, in addition to temperature, the factor of relative humidity must be considered if one is to use heating for identification.

As a result of these experiments, it has been possible to summarize the changes which occur in the various members of the expanding layer silicate minerals with respect to temperature of heating and humidity control.

The vermiculite sample collapsed to 10.3\AA without heating and was not affected by humidity even when stored at 55% relative humidity for four days under vacuum in a desiccator containing $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution. The montmorillonites, beidellite, and nontronite

were affected by temperature and humidity. Generally it was found that humidity control was important up to 200°C . When these K-saturated samples were heated and cooled in a desiccator, it was found that as the temperature was increased up to 100°C , samples 1M, 22M, and 30N collapsed to about 10.5\AA under the uncontrolled condition while the rest of the samples remained in the vicinity of about 11.5\AA . Increasing the temperature to 200°C another seven samples collapsed to about 10.5\AA under the uncontrolled condition. When heated to 300°C only sample, 11M, did not collapse but at 550°C all the samples collapsed.

When the samples were taken in turn from the oven and X-rayed directly, they all collapsed to about 10.5\AA at 200°C without humidity control except sample 17M.

It was also observed that the samples of the same treatment gave significant variation in the basal spacings when run on different days. Therefore, if reproducible results are to be obtained, humidity must be controlled.

It was found that when humidity was controlled the K-saturated sample reflected a very sharp peak compared to a broad peak obtained when humidity was not controlled (figure 2).

The humidity control is important not only from the standpoint of mineral identification but also from the standpoint of data

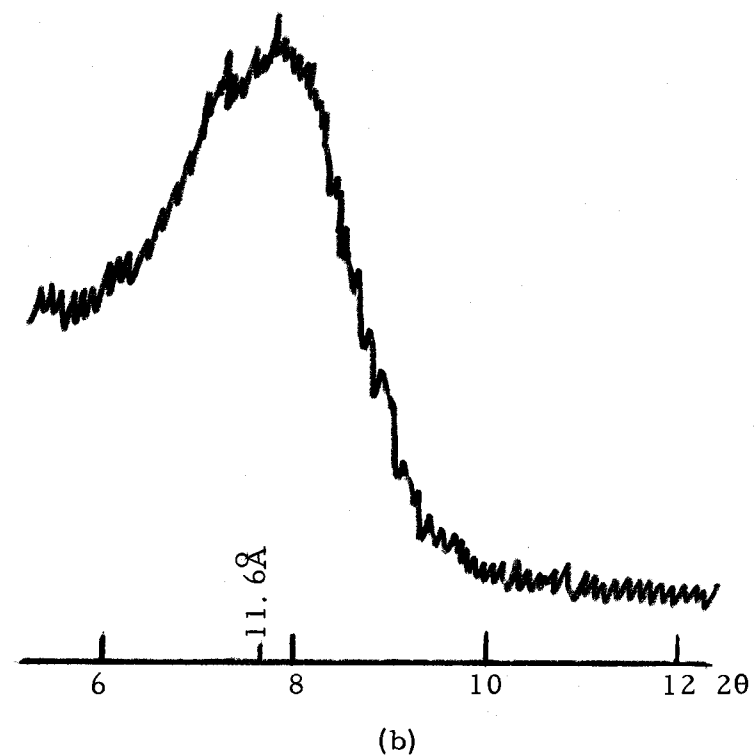
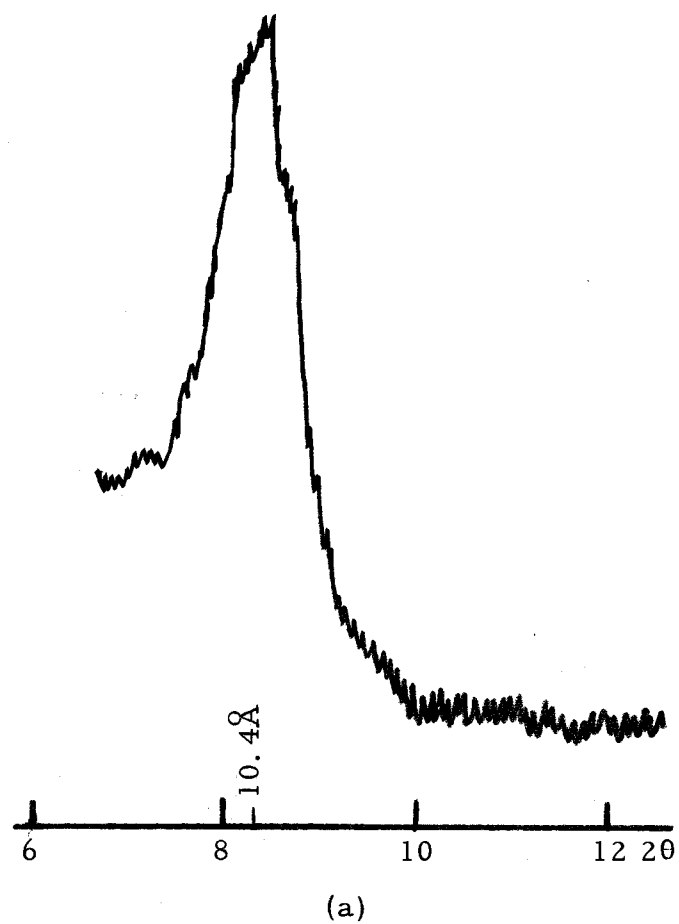


Figure 2. X-ray patterns of a K-saturated clay: (a) under 7% relative humidity, (b) under uncontrolled humidity conditions.

interpretation. For example, Wear and White (43) observed that K fixation occurred with the contraction of an expanded lattice. Kunze and Jeffries (26) indicated that those minerals which showed no collapse of the interlayer spaces when K-saturated should be relatively low fixers; whereas, those that showed a collapse should be relatively high fixers. Rich (33) found that some samples failed to produce a contracted lattice. He attributed the failure of collapse upon K saturation to variable amounts of non-exchangeable Al in the interlayer space. Rich and Obenshain (35) described the difficulty of collapse of some minerals due to a high internal surface, high base exchange capacity and low divalent cation content. Milne and Shott (31) even suggested that montmorillonite of certain sediments was poorly crystallized because it gave a basal spacing of 12\AA .

If the factor of humidity control had been considered in the above interpretations by the various researchers it is possible that different conclusions might have been reached.

Effect of Lattice Charge Density

The rate and degree of expansion have been related to the layer charge of the minerals (1; 2; 3; 29; 41) and have been used as a basis for the differentiation between vermiculites and montmorillonites. Walker (41) indicated that a clay vermiculite pretreated with Mg^{2+}

should not expand beyond about 14.5\AA with glycerol. Mg-montmorillonites, on the other hand, according to Barshad (1), Walker (40) and others, expand to about 17.7\AA on glycerol solvation. Walker (41) suggested that the rate and degree of expansion are related to the layer charge density of the vermiculites. Barshad (2) showed that the effect of the total charge on expansion with glycerol and water was greater the smaller the charge. He (3) observed that differences in interlayer expansion with a given cation between vermiculites and montmorillonites were due mainly to the higher interlayer charge of vermiculite. He also showed that with K-saturated samples, the (d_{001}) spacing of those with a charge of 150 or more me per 100 g became 10.4\AA , while the samples with 110 or less me per 100 g had a (d_{001}) spacing of about 12\AA .

Brindley and MacEwan (9) attempted to classify the expansion properties of different minerals in relation to the layer charge density. Norrish (32) indicated that the expansion of minerals decreased as charge density increased. Barshad (4) found that K saturation of vermiculite derived from biotite caused the collapse of the 14.3\AA basal spacing to about 10\AA . However, the 14.7\AA mineral from other samples showed a progressive resistance to collapse on K saturation. He (1) believed that it was the magnitude of the interlayer charge rather than the origin which determines "fixation". Weaver

(44) agreed that the interlayer charge greater than 150 me per 100 g was responsible for K fixation but also he indicated that with minerals having an interlayer charge of less than 150 me per 100 g the origin of the charge was quite significant in regard to the ability to "fix" K or to contract to 10\AA . Barshad (1) showed that minerals with 100 me per 100 g behaved like montmorillonite when saturated with potassium and contracted to only 12.4\AA . He also, on the basis of contractibility, divided the minerals into two groups: those which contracted to about 10.3\AA when tested with K and those which contracted to 11 to 12.7\AA when treated with potassium. Weaver (44) suggested the division of montmorillonite and vermiculite on the basis of the degree of contractibility when the minerals were K-saturated.

Previously, the X-ray diffraction diagrams in identifying clay vermiculites was most likely to be confused with those of the montmorillonites since both groups consist of expanding 2:1 lattices. This confusion was attributed to the lack of considering the interlayer cations present when the identification was made. Then some workers, as discussed in the above literature review, proposed that the classification of the expanding 2:1 lattice minerals be based on the expansion of the Ca and Mg minerals with glycerol and ethylene glycol and on the collapse of the lattice K minerals upon heating at

different temperatures. The rate and degree of expansion and collapse was then attributed to the charge density of the minerals. Attention was drawn to the presence of the interlayer cations and to the difference of usage of ethylene glycol and glycerol.

In an attempt to evaluate the criteria currently employed for the differentiation between vermiculites and smectites⁷, Walker (40) observed the formation of double-sheet glycerol and glycol complexes with vermiculites when saturated with cations other than Mg. Walker (41) also found that Mg-vermiculites with charge density less than 175 me per 100 g expanded to about 15.5 \AA or more and Ca-vermiculites regardless of charge density expanded to about 15.6 \AA with ethylene glycol. Mg-vermiculites regardless of charge density expanded to 14.3 \AA , and Ca-vermiculite with 185 me per 100 g or less expanded to about 17.6 \AA with glycerol. Ca-vermiculite with charge density of 212 me per 100 g expanded to 14.3 \AA with glycerol.

Table 6 shows the cation exchange capacity of the clay minerals. The cation exchange capacity of the montmorillonites which is related to charge density varied from 61.1 to 201.8 me per 100 g. The high charge density of some of the montmorillonites, 26M and 22M, fell in the range of the charge density of the vermiculite.

⁷ The word smectite has been proposed (30) as group name of montmorillonites.

Table 6. Cation exchange capacity of the clay minerals.

Clays 2 to 0.2 μ	me/100g	Clays	me/100g
1M	117.8	17M	128.2
2M	107.1	19M	126.6
5M	122.5	20M	98.9
6M	128.1	21M	121.8
7M	61.1	22M	174.3
8M	120.3	25M	98.3
9M	139.3	26M	201.8
11M	131.9	30N	121.3
14M	104.7	32B	130.0*
16M	113.7	61V	141.7**

*Due to sample shortage this value was taken from Weir (45,p. 142).

**This value is of the silt fraction.

M stands for montmorillonite, N stands for nontronite,

B stands for beidellite, V stands for vermiculite.

Likewise the charge density of the vermiculite⁸, 61V, is in the range of the charge density of the montmorillonites. Since all the Ca and Mg-montmorillonites with varying charge density expanded to about 17.5Å and the Ca and Mg-vermiculite with charge density in the range of the montmorillonites expanded to 14.5Å with both ethylene glycol and glycerol, this proves that charge density is not a factor to influence the expansion and thus distinguishing different members

⁸ Walker's (41) work indicates that the charge density of macroscopic size vermiculite approximates that of the less than one micron fraction.

of the expanded lattice minerals. Similarly since all the members of the expanding lattice minerals, montmorillonites, beidellite, nontronite, and vermiculite, collapsed under 7% controlled relative humidity to about 10.5\AA when unheated, this disproves that the ability of a mineral to fix K can be determined by contractibility. As pointed out in the section on the effect of humidity of K-saturated minerals, the failure of some of the minerals to collapse to 10.5\AA was due to the humidity.

From table 7 it is shown that the Ca-vermiculite, with cation exchange capacity of 141.7 me per 100 g, expanded to 14.3\AA with both organic liquids. This finding does not agree with that of Walker (41), and this might be attributed to the technique used in solvating the sample. Therefore this study, with a range of montmorillonite minerals with different cation exchange capacity, showed that both Ca and Mg-montmorillonites expanded with both ethylene glycol and glycerol. This proves that charge density is not enough to characterize montmorillonite from vermiculite. It is suggested that isomorphous substitution plays an important part as it will be pointed out in the next section.

Table 7. Cation exchange capacity and basal reflections of the clay minerals.

Clay minerals	Saturation cation	55% Å	Ethylene glycol Å	Glycerol Å	Cation exchange capacity me/100 g
Montmorillonite	Ca		17.2	17.5	61.1-201.8
Montmorillonite	Mg		17.3	17.5	
Montmorillonite	K	12.3			
Nontronite	Ca		17.3	17.0	121.3
Nontronite	Mg		17.2	14.7	
Nontronite	K	12.4			
Beidellite	Ca		17.3	14.7	130.0
Beidellite	Mg		17.2	14.5	
Beidellite	K	11.8			
Vermiculite	Ca		14.5	14.2	141.7
Vermiculite	Mg		14.2	14.2	
Vermiculite	K	10.3			

Effect of Charge Location

The kind and extent of isomorphous substitution in a variety of silicate minerals is reasonably well established (11; 22; 36; 37).

Jackson and West (21) showed that in mica clay minerals the distance from the center of the K ion to the site of charge in the tetrahedral position is 2.19Å and to the site of the charge in the octahedral position is 4.99Å . Since K ions are twice as far from the octahedral sites as from the tetrahedral sites, they should be held by tetrahedral charge with a force almost four times as strong as by octahedral

charge. In general the charge density and the site of the isomorphous substitution are the factors considered which affect the expansion and collapse of clay minerals. As it was previously pointed out, earlier workers considered the charge density as the dominating factor in relation to expansion and collapse. The reason for this assumption was due to the fact that they were working with montmorillonite clays that possessed low charge density as compared with vermiculite clays having higher charge density, and no consideration was given to the fact that the low charge density montmorillonite clays had octahedral isomorphous substitution while the substitution in the high charge density vermiculite clays was mainly tetrahedral.

As it was indicated earlier in this study that the charge density is not responsible for the expansion and collapse of the clay minerals, it is then suggested that the expansion and collapse is attributed to the seat of the isomorphous substitution. This suggestion is substantiated by the results obtained in this study.

Location of Charge

The location of the charge in the materials used in this study was established as indicated below.

Greene-Kelley (16) devised a simple test which distinguishes

montmorillonite from beidellite, nontronite, and vermiculite. This depends on the observation that Li-saturated montmorillonite heated to 200°C does not expand when treated with p-chlorotoluene whereas the others similarly treated do expand. A 001 spacing of about 9.5Å indicates montmorillonite. A 12.5Å spacing indicates beidellite, nontronite or vermiculite. This method seems to depend upon both location of isomorphic substitution and numbers of cations in the octahedral layer.

This test is interpreted on the basis of penetration of the Li ion into vacant octahedral positions. Dioctahedral minerals react irreversibly when heated only if there are vacant octahedral positions and the layer charge resides dominantly or entirely in the octahedral positions. Thus, montmorillonite loses its capacity to expand but nontronite, beidellite, and vermiculite do not. Expansion of the vermiculite may be due both to absence of vacant octahedral positions and to presence of tetrahedral charge.

This test was applied to the minerals used in this study and the following results were obtained: First, the montmorillonite minerals show irreversible collapse, confirming that the source of the isomorphous substitution is in the octahedral layer. Second, the beidellite, nontronite, and vermiculite show a 001 spacing of about 12.5Å. This is consistent with the previous identification of

these minerals.

It has also been considered (30, p. 157) that if the Si:Al ratio in clay minerals is about 2.5, then there is sufficient silica to occupy all tetrahedral positions and the minerals are considered to be only octahedrally substituted as in the case of montmorillonites. In as much as the montmorillonite samples used in this study have a Si:Al ratio of about 2.5⁹, it is concluded that they are octahedrally substituted.

The Black Jack Mine beidellite used in this study is the same as that used by Weir (45) who made a complete study of the mineral and established that tetrahedral substitution occurs. But the magnitude of tetrahedral substitution in the beidellite is not as great as that of the vermiculites.

The tetrahedral substitution of nontronites was established by Ross and Hendricks (36) and MacEwan (30, p. 158). Ross and Hendricks also indicated that nontronites are not as rich in the Al in the tetrahedral layer as beidellites.

Vermiculites generally are tetrahedrally substituted. The substitution in their tetrahedral layer is the highest among the expanding lattice group. The degree of tetrahedral substitution is

⁹ Unpublished results, Antoine Sayegh, Department of Soils, Oregon State University.

discussed by Walker (42).

Expansion

The Ca and Mg-montmorillonite samples expanded with both organic liquids regardless of the charge density. This is attributed to the fact that montmorillonite is octahedrally substituted, that is, the location of the charge is deep seated, and the force exerted on the surface of montmorillonite is low as shown by Jackson and West (21). On the other hand, the Ca and Mg-vermiculites expanded only to 14.3\AA with both organic liquids. This is related to the tetrahedral substitution in which the seat of charge is near the surface. The beidellite represents a transition between the montmorillonites and vermiculites regarding the sites of the isomorphous substitution in the sense that it is found in both layers. The Ca and Mg-beidellite expanded only to 14.7\AA with glycerol while with ethylene glycol it expanded to about 17.2\AA . The reason for the expansion with ethylene glycol and not with glycerol is due to the higher dipole moment of the former. This is attributed to the fact that since the amount of tetrahedral substitution in the beidellite is not as great as that of the vermiculite it appears that the force of ethylene glycol to penetrate the interlayer is sufficient to overcome the attraction exerted by the tetrahedral substitution on the plates of the mineral.

The use of glycerol with its lower dipole moment and the technique of solvating the sample with its vapour give a good correlation between expansion and the location of the isomorphous substitution. In the case of beidellite with tetrahedral and octahedral isomorphous substitution, both organic liquids are necessary to establish its identity.

The behaviour of Mg-nontronite with glycerol was similar to that of beidellite while the Ca-nontronite with glycerol was similar to that of montmorillonite. This behaviour is considered to result from the following: First, the nontronite sample might be less tetrahedrally substituted than the beidellite sample as pointed out by Ross and Hendricks (36). Thus, the Mg cation with glycerol correlates better with tetrahedral substitution than the Ca cation, as shown in table 7. Second, in as much as iron rich minerals are known to be rather unstable compared to the other minerals it is possible that the above behaviour resulted from the effect of the various pre-treatments, although the identity of the nontronite was established by the lithium test. Third, it is also possible that the above behaviour could be attributed to certain properties of the nontronites since their octahedral layer is composed mostly of the ferric iron and not a mixture of aluminum, iron, and magnesium as in the beidellite.

Collapse

The K-saturated montmorillonite collapsed to about 12.3\AA while the K-vermiculite collapsed to 10.3\AA with 55% relative humidity. In the case of the montmorillonites, with the charge originating in the octahedral layer, the surface hydration energy overcomes the force that holds the plates together. While in the case of vermiculite, the charge originating in the tetrahedral unit is presumed to result in forces strong enough to hold the plates together and prevent the entrance of water and expansion. Although the charge in beidellite and nontronite originates in the tetrahedral layer, the forces originating from the lower degree of substitution are insufficient to hold the plates together.

Suggested Identification Spectrum

The second objective is to establish a spectrum for the distinction of the different members of the expanding lattice minerals by their expanding and collapsing properties.

At present, the differentiation of minerals belonging to the expanding lattice group is generally based on the expanding behaviour of the minerals saturated with either Ca or Mg and solvated with an organic liquid and on the collapsing behaviour of the

K-saturated minerals. Other workers have considered charge density as a basis for the differentiation. Weiss et al. (46) and Hofmann et al. (14) suggested the idea of a continuous gradation between montmorillonites and vermiculites. They also propose that the groups should be defined by reference to a layer charge value of 0.55 equivalents per $0_{10}(\text{OH})_2$ unit of structure. This value, which is equivalent to a cation exchange capacity of about 115 me per 100 g air dry Mg-vermiculite, was selected by them because expanding lattice minerals with a capacity less than this value showed hk reflections while the hkl reflections were observed on those minerals having values in excess of 115 me per 100 g. In order to include two of Hofmann's specimens, the Groschlattengrün saponite and the Unterrupsroth beidellite, with the montmorillonite group Walker (41) suggested that the above threshold value should be set slightly higher. Because of the overlapping of cation exchange capacity of the minerals within the expanding lattice group, it seems inadvisable to set an arbitrary threshold value in relation to cation exchange capacity as the dividing line between the minerals. In addition, a direct comparison of the cation exchange capacity determinations of different investigators is very difficult to make because the results vary with the methods of determination. Also the nature of the interlayer cation and the amount of interlayer water influence the

value obtained.

It is evident that considerable difficulties may be encountered in the positive identification of the minerals of the expanding lattice group in relation to cation exchange capacity.

The classification proposed here is based on (1) the expansion characteristics of the minerals saturated with Ca and Mg and solvated with glycerol and ethylene glycol and (2) on the collapsing properties of the minerals saturated with potassium. The following spectrum is suggested for the characterization of the minerals of the expanding lattice group.

Treatments	Montmorillonite	Beidellite	Vermiculite
Ca + Mg with ethylene glycol	17.2	17.2	14.3
Ca + Mg with glycerol	17.5	14.6	14.3
K-saturated at 55% relative humidity	12.3	11.8	10.3

This proposed spectrum seems to provide a more logical basis for identification and improves the possibility of positive identification. This classification supports the idea of continuous gradation as was suggested.

Fundamentally, the 2:1 lattice layer structure of the expanding lattice minerals seems to be the same. However, the characteristic differences in relation to expansion and collapse are related to the variation in degree and location of the isomorphous substitution.

SUMMARY

Montmorillonite, beidellite, and nontronite samples were treated for the removal of flocculating and cementing agents and the 2 to 0.2 micron fraction was separated. A vermiculite sample was treated by the Rich method to transform interlayered mica to vermiculite. The silt fraction was separated and used.

The results of the lithium test after the various chemical treatments above showed a clear difference between montmorillonites and the other clay minerals.

The clay minerals were saturated with Ca and Mg, solvated with ethylene glycol and glycerol and were X-rayed with a North American Philips Norelco diffraction spectrometer. The study showed that the c-spacings of the montmorillonite clays saturated with Ca and Mg and solvated with ethylene glycol are about 17.2\AA while with glycerol they are about 17.5\AA . This increase in basal spacing resulting from the adsorption of two layers of ethylene glycol or glycerol made it relatively easy to distinguish montmorillonite from vermiculite which expanded only to about 14.3\AA with the same treatments. Ca and Mg-beidellite expanded to about 17.2\AA with ethylene glycol and to about 14.7\AA with glycerol. Nontronite saturated with Ca and Mg expanded to 17.2\AA with ethylene glycol;

Ca-nontronite with glycerol also expanded to 17.0\AA while Mg-nontronite with glycerol expanded only to 14.7\AA .

The c-dimension of the K-saturated montmorillonites, beidelite, and nontronite in the normal hydrated state were variable and this was correlated to the humidity in the atmosphere. When the humidity was controlled during X-ray runs, reproducible results were obtained. With a relative humidity of 55% the c-spacing is 12.3\AA while with a 7% relative humidity the c-spacing of the unheated mineral is about 10.4\AA . The effect of heating at 65°C , 100°C , 200°C , 300°C and 550°C was studied in relation to the c-spacing. It was found that the clays subjected to temperatures up to 200°C and X-rayed under uncontrolled humidity had spacings of about 11.5\AA , indicating a rehydration. Clays heated to temperatures 300°C and above collapsed to 10.4\AA when X-rayed immediately under uncontrolled humidity. Clays heated up to 300°C and stored in a humidity chamber of 55% relative humidity and X-rayed under the same humidity conditions showed a c-spacing of 12.2\AA . The unheated K-saturated vermiculite collapsed to 10.3\AA was not affected by the 55% relative humidity.

It was also found that the rate of hydration and dehydration was very rapid. The time needed to scan the slide by the usual method from $14^{\circ} 2\theta$ to $2^{\circ} 2\theta$ was sufficient for the

sample to rehydrate.

The cation exchange capacity of the minerals was determined. It ranged from 61.1 to 201.8 me per 100 g for the montmorillonites and was 141.7 me per 100 g for the vermiculite. The expanding and collapsing properties of these minerals did not correlate with the cation exchange capacity as proposed by many investigators. Therefore the distinction between montmorillonite and vermiculite based on lattice charge density was found to be not applicable. A more reliable spectrum is established for the characterization of the minerals of the expanding lattice group based on the expanding and collapsing properties which in turn are correlated with the location of the isomorphous substitution. This proposed spectrum seems to provide a more logical basis for characterization and improves the possibility of positive identification.

BIBLIOGRAPHY

1. Barshad, Isaac. Effect of the interlayer cations on the expansion of mica type of crystal lattice. *American Mineralogist* 35:225-238. 1950.
2. _____. Factors affecting the interlayer expansion of vermiculite and montmorillonite with organic substances. *Proceedings of the Soil Science Society of America* 16:176-182. 1952.
3. _____. Cation exchange in micaceous minerals. 11. Replaceability of NH_4^+ and K^+ from vermiculite, biotite and montmorillonite. *Soil Science* 78:57-76. 1954.
4. _____. Vermiculite and its relation to biotite as revealed by base exchange reaction, X-ray analysis, differential thermal curves, and water content. *American Mineralogist* 33:655-678. 1956.
5. Bradley, W. F. Molecular associations between montmorillonite and some polyfunctional organic liquids. *Journal of the American Chemical Society* 67:5-12. 1945a.
6. _____. Diagnostic criteria for clay minerals. *American Mineralogist* 30:704-713. 1945b.
7. _____. Interstratified growths in clays and clay-like minerals. *Transactions of the 4th International Congress of Soil Science* 1:101-105. 1950.
8. _____. X-ray diffraction criteria for the characterization of chlorite material in sediments. *Clays and Clay Minerals* 4:324-335. 1956.
9. Brindley, G. M. and Douglas M. C. MacEwan. Structural aspects of mineralogy of clays and related silicates. *Ceramics Symposium, British Ceramic Society*, 1953, p. 15-59.
10. Brown, B. E. and M. L. Jackson. Clay mineral distribution in the Hiawatha sandy soils of northern Wisconsin. *Clays and Clay Minerals* 5:213-226. 1958.

11. Brown, G. Report of the clay minerals group sub-committee on nomenclature of clay minerals. Clay Minerals Bulletin 2:294-302. 1955.
12. Brown, G. and R. Farrow. Introduction of glycerol into flake aggregates by vapour pressure. Clay Minerals Bulletin 3:44-45. 1956.
13. Carlson, R. M. and C. M. Johnson. Chelometric titration of calcium and magnesium in plant tissue. Journal of Agricultural and Food Chemistry 9:460-463. 1961.
14. Hofmann, Ulrich et al Intracrystalline swelling, cation exchange, and anion exchange of minerals of the montmorillonite group and of kaolinite. Clays and Clay Minerals 4: 273-287. 1956.
15. Gjems, G. A swelling dioctahedral clay mineral of a vermiculite-smectite type in the weathering horizons of podzols. Clay Minerals Bulletin 5:183-193. 1963.
16. Greene-Kelley, R. The identification of montmorillonoids in clays. Journal of Soil Science 4:233-237. 1953.
17. _____. Dehydration of the montmorillonite minerals. Mineralogical Magazine 30:604-615. 1955.
18. Hashimoto, Isao and M. L. Jackson. Rapid dissolution of allophane and kaolinite-halloysite after dehydration. Clays and Clay Minerals 7:102-113. 1960.
19. Hendricks, Sterling B. and William H. Fry. The results of X-ray and microscopical examinations of soil colloids. Soil Science 29:457-479. 1930.
20. Jackson, M. L. Soil chemical analysis- advanced course. Madison, University of Wisconsin, Published by the author, 1956. 991p.
21. Jackson, W. W. and J. West. The crystal structure of muscovite. Zeitschrift fur Kristallographie 76:211-227. 1930.

22. Johns, William D. and Edward C. Jonas. Some observations on the relation between isomorphism and properties of clays. *Journal of Geology* 62:163-171. 1954.
23. Kelley, W. P., W. H. Dore and S. M. Brown. The nature of base exchange material of bentonite, soils and zeolites as revealed by chemical investigation and X-ray. *Soil Science* 31:25-55. 1931.
24. Kilmer, V. J. and L. T. Alexander. Methods of making mechanical analyses of soils. *Soil Science* 68:15-24. 1949.
25. Kunze, G. W. Anomalies in the ethylene glycol solvation technique used in X-ray diffraction. *Clays and Clay Minerals* 3:88-93. 1955.
26. Kunge, G. W. and C. D. Jeffries. X-ray characteristics of clay minerals as related to potassium fixation. *Proceedings of the Soil Society of America* 17:242-244. 1953.
27. MacEwan, Douglas M. C. Identification of the montmorillonite group of minerals by X-rays. *Nature* 154:577-578. 1944.
28. _____. The identification and estimation of the montmorillonite group of minerals with special reference to soil clays. *Journal of the Society of Chemical Industry* 65:298-305. 1946.
29. _____. Complexes of clays with organic compounds. 1. Complex formation between montmorillonite and halloysite and certain organic liquids. *Transactions of the Faraday Society* 44:349-367. 1948.
30. _____. Montmorillonite minerals. In: G. Brown's *The X-ray identification and crystal structures of clay minerals*. London, The Mineralogical Society, 1961. P. 143-207.
31. Milne, I. H. and W. L. Shott. Clay mineralogy of recent sediments from the Mississippi sound area. *Clays and Clay Minerals* 5:253-265, 1958.
32. Norrish, K. The swelling montmorillonite. *Discussions of the Faraday Society* 18:120-134. 1954.

33. Rich, C. I. Aluminum in interlayers of vermiculite. *Proceedings of the Soil Science Society of America* 24:26-32. 1960.
34. _____. Calcium determination for cation exchange capacity measurements. *Soil Science* 92:226-231. 1961.
35. Rich, C. I. and S. S. Obenshain. Chemical and clay mineral properties of a red yellow podzolic soil derived from muscovite schist. *Proceedings of the Soil Science Society of America* 19:334-339. 1955.
36. Ross, Clarence S. and Sterling B. Hendricks. Minerals of the montmorillonite group. *United States Geological Survey Professional Paper* 205B:23-77. 1945.
37. Stubican, V. and Rustum, Roy. Isomorphous substitution and infrared spectra of the layer lattice silicates. *American Mineralogist* 46:32-51. 1961.
38. Theisen, A. A. and M. E. Harward. A paste method for preparation of slides for clay mineral identification by X-ray diffraction. *Proceedings of the Soil Science Society of America* 26:90-91. 1962.
39. Walker, G. F. Diffusion of interlayer water in vermiculite. *Nature* 177:239-240. 1956.
40. _____. On the differentiation of vermiculites and smectites in clays. *Clay Minerals Bulletin* 3:54-63. 1957.
41. _____. Reactions of expanding-lattice clay minerals with glycerol and ethylene glycol. *Clay Minerals Bulletin* 3:302-313. 1958.
42. _____. X-ray identification and structures of clay minerals. In: G. Brown's *The X-ray identification and crystal structures of clay minerals*. London, The Mineralogical Society, 1961. p. 297-324.
43. Wear, John I. and J. L. White. Potassium fixation in clay minerals as related to crystal structure. *Soil Science* 71:1-14. 1951.

44. Weaver, Charles Edward. The effects and geologic significance of potassium "fixation" by expandable clay minerals derived from muscovite, biotite, chlorite and volcanic material. *American Mineralogist* 43:839-861. 1958.
45. Weir, A. H. and R. Greene-Kelley. Beidellite. *The American Mineralogist* 47:137-146. 1962.
46. Weiss, Armin, G. Koch and Ulrich Hofmann. Saponite. *Bericht der Deutschen Kermischen Gesselschaft* 32:12-17. 1955.