

A CLASSIFICATION OF THE 2:1 CLAY MINERALS

CHARLES EDWARD WEAVER,* *The Pennsylvania State College,
State College, Pennsylvania.*

ABSTRACT

A classification of the 2:1 clay minerals is presented in which the per cent of the total replacement which occurs in the octahedral and tetrahedral sheets is considered to be of primary importance. The secondary division is based upon the degree of expansion and the nature of the external cations.

INTRODUCTION

During a study of the potassium bentonites from the Ordovician limestones of Pennsylvania (Weaver and Bates, 1951) additional evidence was found indicating that the differences between illite and montmorillonite are not as great as is commonly supposed. Bradley (1944) found that many of the illite-like clays such as glimmerton, bravaisite, Grundy illite, metabentonite, and some glauconites contain expanded layers. Nagelschmidt (1944) found that when illite is treated with CaCl_2 , portions of the non-expanded layers expand. White (1950) has shown that by treating illite with MgCl_2 and precipitating the exchanged potassium the illite expands and gives a montmorillonite x-ray pattern. It is thought that many of the montmorillonite minerals, particularly beidellite, contain some non-expanded layers which are indicated by the presence of potassium in the chemical analyses. Caillère and Hénin (1949) have shown that by boiling montmorillonite in KOH the 001 spacing shifts to the 10 Å value characteristic of illite. Barshad (1948) has shown that biotite will exchange K for Mg and form an expanded lattice with a value greater than 10 Å. Many soils scientists have shown that K can be "fixed" by montmorillonite and recently Mortland and Giesekeing (1951) caused both montmorillonite and hectorite to collapse to 10 Å by placing them in a solution of K_2SiO_3 and drying at 110° C. Kunze (1952) was able to collapse several 14 Å soil vermiculites to 10 Å by drying them from a solution of $\text{K}_2\text{C}_2\text{H}_3\text{O}_2$.

These findings suggest that the same fundamental 2:1 layers can form either an expanded or a non-expanded clay and that it is relatively easy to change the state of expansion. It is proposed that the existence of an expanded or a non-expanded lattice is dependent upon the cations in interlayer positions rather than upon the composition of the 2:1 layers in the lattice and that the type of cation present is independent of the composition of the layers.

The ideas formulated above are illustrated by the illite-montmorillonite groups of minerals and are further supported by studies of K-bentonites.

* Shell Development Company, Exploration and Production Research Laboratory, Houston 25, Texas.

ILLITE VERSUS MONTMORILLONITE

General

Three criteria provide the fundamental means of differentiating between the illite and montmorillonite clay groups. Naturally all three were developed from a study of many clays. However, it is significant that the great majority of montmorillonites investigated are those formed from volcanic ash, usually of Cretaceous or Tertiary age. The majority of the illites described in the literature have been found in the Carboniferous sediments. Clays of either type from other sources often do not possess the properties which are diagnostic of the "type" materials. The criteria referred to are as follows:

1. Illite, as usually defined, has a non-expanded lattice, with a c -spacing of 10 Å. Montmorillonite has an expanded lattice, 12 to 30 Å in the direction of the c axis.
2. Illite commonly gives a hydroxyl-endothermal reaction in differential thermal analysis curves at 500–600, whereas the montmorillonite reaction usually occurs at 600–750° C.
3. Except for the external cations K, Na, Mg, and Ca, the structural formulas of illites and montmorillonites are similar, and in many cases identical. The predominance of K as an external cation is characteristic of illite.

X-ray Data

Probably the most widely used and most reliable means of identifying the minerals of these two clay groups is by x -ray diffraction. When a 10 Å value for the first 001 spacing is obtained the clay is considered to be non-expanded and is called illite. If the x -ray line has a value of 12 Å or greater, the clay is considered to have an expanded lattice and is called montmorillonite (assuming it is not vermiculite or chlorite).

However, recent laboratory work has shown that the degree of expansion and hence the basal spacings of illite, montmorillonite and many other 2:1 minerals can easily be changed by varying the type of external cation. Table 1 lists some of the 2:1 minerals which have been altered, the original 001 spacing, the physical or chemical treatment and the resulting 001 spacing. It is apparent that by proper treatment the external cations in the expanded 2:1 minerals can be replaced by K and the resulting clay will be of the non-expanded variety. In addition a wide variety of non-expanded 2:1 minerals can be made to expand by replacing the external K by more highly hydrated cations. In the case of the Na based mica, paragonite, it is necessary only to grind the material to clay size in order for it to expand.

TABLE 1. VARIATIONS PRODUCED IN 001 SPACINGS

Author	Original Material	Original 001 Spacing in Å	Treatment	Time	Final 001 Spacing in Å
Nagelschmidt (1944)	Illite	9.7-11.4	Soaking in CaCl ₂	5 weeks	9.7-12.5
Barshad (1948)	Biotite	10.29	<1 μ material leached with MgCl ₂	3 months	14.47
Barshad (1950)	Paragonite	9.7	After grinding to <0.5 μ		14.3
White (1950)	Illite	10.0	Soaking in MgCl ₂		14.0
Caillère and Hénin (1949)	Montmorillonite Nontronite	? ?	Boiling in KOH Boiling in KOH	32 hours	10.2 10.0
Barshad (1948)	Vermiculite	14.33	Leaching with KC ₂ H ₃ O ₂	10 days	10.42
Nortland and Gieseck (1951)	Montmorillonite Hectorite	13.15 14.72	Drying from K ₂ SiO ₃ solution		9.90 10.09
Kunze (1952)	Vermiculite	14.0	Boiling in KC ₂ H ₃ O ₂ solution	10 minutes	10.0
Weaver and Bates (1951)	Mixed layer	10.9	Wetting and drying from KOH solution	15 times	10.1

This evidence would indicate that the 001 spacing of the 2:1 layer lattice silicates and therefore their state of expansion is independent of the composition of the 2:1 lattice and depends only upon the type of external cation present.

Differential Thermal Analysis Data

An examination of the differential thermal data shows that the characteristic hydroxyl-endothermal reaction of illite occurs between 500 and 650° C.; however, this figure is determined largely from samples obtained from the Carboniferous rocks. When illites from totally dif-

ferent sources are examined it can be expected that this range will be extended; this is indicated by the Ballater illite described by MacKenzie, Walker, and Hart (1949). The hydroxyl-endothermal reaction of this material occurs at 713° C.

The majority of the montmorillonites derived from the Cretaceous and Tertiary ash beds have a hydroxyl-endothermal reaction which is restricted to a 650–700° C. range. However, Mg and Fe montmorillonites from varied sources extend this range down to 500 and up to 800° C.

It is generally believed that the temperature of the hydroxyl-endothermal reaction is controlled largely, if not entirely, by the various cations in the octahedral layers. As the range in temperature of this reaction for the two clays is almost identical, it would appear that the composition of the octahedral layers varies within the same limits.

Chemical Composition

As is suggested by the temperatures of the hydroxyl-endothermal reaction, the chemical analyses indicate that the octahedral layers for illites and montmorillonites are quite similar and in many cases the same in composition.

The composition of the tetrahedral layers in the clays of the two groups can be indicated only by chemical analysis. Although the ranges of the percentage of aluminum replacing silicon overlap to a considerable extent, the available analyses (largely of bentonites) indicate that many of the montmorillonites have a very small amount of aluminum in the tetrahedral layer, as compared to the known illites. However, this does not mean that a 2:1 lattice with little aluminum in the tetrahedral layers cannot attract potassium and form a 10 Å lattice. It is simply more probable that the potassium was never available. Neither is the converse true. For, even if there is 15 to 20 per cent replacement in the tetrahedral layer but no potassium is available, the lattice will be expanded. This can easily be appreciated by a study of the data presented by Ross and Hendricks (1945). In 25 of the 82 dioctahedral montmorillonites analyzed, nearly 15 percent or more of the silicon ions in the tetrahedral layer are replaced by aluminum. Using a classification based on the chemical composition of the impure pyrophyllite lattice these 25 clays would be referred to as illites whereas on the basis of their degree of expansion they would be called montmorillonites. The fact that expansion is unrelated to the amount of replacement in the tetrahedral layers is further indicated by the work of Barshad (1950) which showed that when the Na mica, paragonite, which has approximately 25 per cent replacement in the tetrahedral layer, is ground to less than 0.5 microns in size it will expand.

Case of the K-bentonites

An excellent example of the similarity of expanded and non-expanded dioctahedral 2:1 clay lattices is shown by the K-bentonites (Weaver and Bates, 1951).

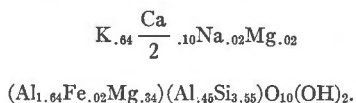
An *x*-ray study of several samples of K-bentonite revealed that the material is composed of randomly interstratified layers of expanded and non-expanded dioctahedral 2:1 clay minerals (montmorillonite and illite) in the ratio of 1:4.

This ratio was determined by varying the extent of expansion of the expanded layers by treating the clay with a variety of cations. When the expanded layers were reduced to approximately 12 Å by substituting K, Na, and NH₄ as the external cations the resulting 001/001 value was 10.3 Å. When the expanded layers were increased to 14–15 Å by treating the clay with H and Ca the 001/001 value was increased to 10.9 Å. When expanded to 17 Å with ethylene glycol the 001/002 value occurred at 9.5 Å. Using the curves computed by Brown and MacEwan (1950) the ratio of 1:4 was determined.

When the mixed layer clay was alternately wetted and dried in a KOH solution the expanded layers were reduced to nearly 10 Å and the resulting 001/001 value for the clay was 10.1 Å indicating that most of the clay was in a non-expanded state.

The differential thermal curves of these mixed layer K-bentonites contain only a single hydroxyl-endothermal peak at approximately 700° C. (A 600° C. peak due to chlorite is sometimes present.) The presence of this single peak indicates that the composition of the octahedral sheets of the expanded and non-expanded layers are similar if not identical.

The structural formula of a K-bentonite sample is:



The K is probably present in the non-expanded layers, whereas the Ca, Na and Mg are held on the expanded layers. This relationship is indicated by the fact that K forms 80% of the total external cations and the *x*-ray data reveals that 80% of total clay layers are non-expanded.

This data on the mixed layer K-bentonites indicate that the compositions of the expanded and non-expanded lattices are similar, that the amount of non-expanded layers is directly related to the amount of K present, and that by supplying more K in the proper manner the clay can be transposed into the non-expanded (illite) type.

NEED FOR NEW APPROACH

The above discussion suggests that in any given impure pyrophyllite-talc structure, an expanded or a non-expanded lattice is obtained depending upon the external cations attached to it. The hydroxyl-endothermal reaction occurs at a variety of temperatures, depending upon the composition of the octahedral layers, and does not show any correlation with the c dimension.

Although throughout the complete range of impure pyrophyllite-talc compositions, either an expanded or a non-expanded lattice can be formed under a variety of conditions, there appear to be compositional poles where one type is predominant. These poles may be the result of three factors: (1) selected sampling in age, location, and variety of source rock, (2) the tendency of certain cations to occur together in nature and, (3) the limited stability of certain combinations of exchangeable cations with cationic substitutions in the lattice.

It is believed that the present poles are primarily due to the first factor. As more clays are described and these poles become less sharply, rather than more sharply, defined, the question arises as to whether these clays should be divided into separate mineral groups when the distinction apparently rests entirely upon the type of external cation present, and particularly when minerals of these groups frequently occur interstratified. It is believed that such a division is not a self-perpetuating concept because it is based upon criteria resulting from modifying processes acting upon the clay, rather than upon the more fundamental composition of the impure pyrophyllite-talc structure which reflects more accurately the original composition of the clay and of the source material.

PROPOSED CLASSIFICATION

The result of over-emphasizing the importance of the expandability of 2:1 clays had led only to confusion which increases geometrically as more information is acquired. The author believes that the idea of expandability must be made of secondary importance and all 2:1 dioctahedral and trioctahedral clays treated as one group, with a breakdown into varieties based on chemical composition of the impure pyrophyllite-talc lattice. The terms expanded and non-expanded (or K, Ca, Mg, etc.) can be prefixed to the variety names to indicate the external cations present. At this stage in the development of clay mineralogy it is considered best to use a classification based on hypothetical end members that will include all 2:1 clay minerals.

Table 1 shows how all dioctahedral and trioctahedral 2:1 minerals with varying degrees of expansion can be organized into a compact classification.

Degree of Expansion	Ex. Cations	Per Cent of Total Replacement in 2:1 Lattice								
		>75% in Tetrahedral			>25 and <75% in Both			>75% in Octahedral		
		Tetrite			Tetoctrite			Octrite		
		Diocahedral		Tri.	Diocahedral		Tri.	Diocahedral		Tri.
		Al	Fe	Mg	Al	Fe	Mg	Al	Fe	Mg
Expanded	Ca Na Mg									
Expanded & non-expanded	Ca Na Mg K									
Non-expanded	K									

TABLE 1. CLASSIFICATION OF THE 2:1 CLAY MINERALS

Primary Division

The main breakdown of the 2:1 clay minerals is based upon the location of the replacement in the impure pyrophyllite-talc lattice. Clays having greater than 75% of the total replacement (of cations of a greater charge by cations of a lesser charge) occurring in the tetrahedral sheets are referred to as tetrites. Clays having greater than 75% of the total replacement occurring in the octahedral sheet are called octrites. Clays having greater than 25% of the total replacement occurring in both types of sheets are called tetoctrites.

Each of these sub groups is further divided on the basis of whether the clay is dioctahedral or trioctahedral. The dioctahedral clays are divided into Al and Fe depending upon which is the predominant element in the octahedral sheets. The trioctahedral clays contain Mg (Zn and others are rare) as the predominant element in the octahedral sheets.

Secondary Division

The secondary division is based upon the nature of the external cations and therefore the degree of expansion. The expanded clays have Ca, Na and Mg, etc., as the external cations. The non-expanded clays have K. Clays having both kinds of external cations are of the mixed layer type containing both expanded and non-expanded layers.

TERMINOLOGY

Eventually names might be given to all possible combinations of the two divisions; however, for the present it is believed that the use of descriptive terms will help to avoid confusion. The illite-like minerals are referred to as non-expanded Al 2:1 clays. Where the composition is known they can be further defined and called non-expanded Al tetrates or KAl tetrates, and non-expanded Al tetoctrates; glauconites are non-expanded Fe tetoctrates; trioctahedral illites are non-expanded Mg tetoctrates. Many of the montmorillonites are expanded Al octrites or Ca, Na, Mg., etc., Al octrites; most nontronites are expanded Fe tetrates. Beidellites and other mixed layer minerals are classed as expanded and non-expanded Al tetrates or tetoctrates, or, for example, as CaKAl tetrates or tetoctrates.

CONCLUSION

It is thought that this arbitrary breakdown on the basis of the location of the predominant replacement in the lattice, will avoid the confusion caused by trying to classify newly described minerals by comparing them with established species. From the name the general composition of the impure pyrophyllite-talc lattice and the state of expansion can be inferred. And by making the state of expansion secondary and independent of composition of the impure pyrophyllite-talc lattice a more realistic approach to the origin and genesis of these clays can be used. The composition of the 2:1 lattice reflects the original source of the clay mineral. The composition of the external cations, and degree of expansion, reflects environment and environmental changes occurring during and after formation of the clay. Using this classification it is possible to apply a descriptive name which is based upon the amount of information available rather than a general name which implies much more than is actually known about the clay mineral.

It is realized that this classification may be incorrect and that eventually it may be found that the total amount of excess charge occurring in the 2:1 lattice, or some other factor, is the controlling force in expansion. However, it is believed that this classification is consistent with present data and that it is a pragmatic tool that can be used as a clarifying agent.

REFERENCES

- BARSHAD, I. (1948), Vermiculite and its relation to biotite as revealed by base exchange reactions. X-ray analysis, differential thermal curves and water content: *Am. Mineral.*, **33**, 655-678.
- BARSHAD, I. (1950), The effect of the interlayer cations on the expansion of the mica type crystal lattice: *Am. Mineral.*, **35**, 225-238.
- BRADLEY, W. F. (1944), Diagnostic criteria for clay minerals: *Am. Mineral.*, **30**, 704-713.

- BROWN, G., AND MAC EWAN, D. N. C. (1950), The interpretation of x-ray diagrams of soil clays. Part II, *Jour. Soil Sci.*, **1**, 606-12, 1949.
- CAILLÈRE, W., AND HÉNIN, S. (1949), Transformation of minerals of the montmorillonite family into 10Å micas: *Mineral. Mag.*, **38**, 606-612.
- KUNZE, G. W. (1952), Weathering of micas and their role in potash fixation. Ph.D. Thesis, Pennsylvania State College.
- MACKENZIE, R. C., WALKER, C. F., HART, R. (1949), Illite occurring in decomposed granite at Ballater, Aberdeenshire: *Mineral. Mag.*, **28**, 707-714.
- MORTLAND, N. M., AND GIESEKING, J. B. (1951), Influence of the silicate ion on potassium fixation: *Soil Science*, **71**, 381-385.
- NAGELSCHMIDT, G. (1944), X-ray diffraction experiments on illite and bravaisite: *Mineral. Mag.*, **27**, 59-61.
- ROSS, C. S., AND HENDRICKS, S. B. (1945), Minerals of the montmorillonite group: *U. S. Geological Survey, Prof. Paper*, **205-B**, 27-79.
- WHITE, J. L. (1950), Transformation of illite into montmorillonite: *Soil Science Soc. of Am. Proc.*, **15**, 129-133.
- WEAVER, C. E., AND BATES, T. F. (1951), Mineralogy and petrology of the Ordovician K-bentonites and related limestones: *Geol. Soc. Am., Bull.* **62**, 1438 (Abs.).

Manuscript received Oct. 13, 1952.