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**MINERALS OF THE
MONTMORILLONITE GROUP
THEIR ORIGIN AND RELATION
TO SOILS AND CLAYS**

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**MINERALS OF THE
MONTMORILLONITE GROUP**
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BY
CLARENCE S. ROSS AND STERLING B. HENDRICKS

Shorter contributions to general geology, 1943-44
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MINERALS OF THE MONTMORILLONITE GROUP

THEIR ORIGIN AND RELATION TO SOILS AND CLAYS

By CLARENCE S. ROSS, Geological Survey, United States Department of the Interior, and STERLING B. HENDRICKS, Bureau of Plant Industry, Soils, and Agricultural Engineering, United States Department of Agriculture.

ABSTRACT

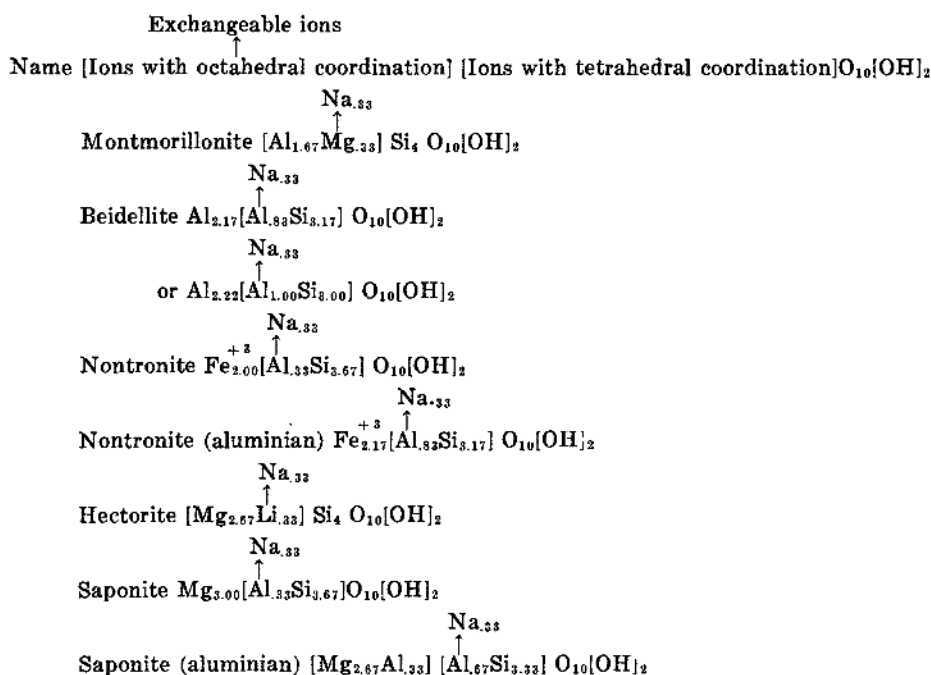
A detailed study has been made of the montmorillonite group of clay minerals, one of the most widely occurring of all mineral materials. Minerals of this group are exceedingly fine grained crystalline aggregates, and they present an unusually wide range in composition. Essential information on the group was obtained only after study, by all available mineralogical methods, of more than 100 carefully selected specimens. This information has made possible the determination of the limits of variation in composition and the function of various ions in the crystal lattice. The underlying causes for the important property of base exchange have been established. This property plays a prominent part in determining the physical properties of minerals of the montmorillonite group, and in particular their behavior towards water.

Interpretations of chemical analyses are based on knowledge of the crystal lattice of montmorillonite and related minerals. This lattice is of a layer type in which silicon and aluminum ions have tetrahedral coordination with respect to oxygen. Aluminum, ferric and ferrous iron, magnesium, lithium, chromium, manganese and manganous manganese, and some other ions occupy positions having octahedral coordination with respect to oxygen. Exchangeable cations are on the surfaces of the silicate layers, and their amounts are determined by the excess negative charge within the layer. These cations usually are sodium and calcium

but potassium, magnesium, hydrogen, and aluminum may be exchangeable.

The composition and mineral relations of the clay minerals are intimately related to the conditions under which they form. In general, alkalic feldspars and the micas tend to alter to kaolin minerals, whereas ferromagnesian minerals, calcic feldspar and volcanic glasses commonly alter to members of the montmorillonite group. Presence of magnesium ions in the altering system is favorable for the formation of montmorillonite-type minerals, in many of which it is characteristically present. The formation of montmorillonite-type minerals is favored by alkaline conditions, and that of kaolinite by acid conditions. These relations are modified by climatic factors, such as the length of time during which weathering continues. Montmorillonite-type minerals form as weathering products in soils and are formed at moderately high temperatures up to at least 200°C., in association with many types of mineral deposits.

Formulas of a special type are used to express the composition of the members of the montmorillonite group. In these formulas the name and the ions forming the crystal lattice are given on one line, and the exchangeable ions on the line above. Arrows are placed over the groups having a deficiency of charge, which require the presence of additional base external to a silicate layer.



INTRODUCTION

This paper on the clay minerals of the montmorillonite group presents the results of a detailed systematic study of an important group of minerals, whose wide occurrence and varied uses give them unusual interest. The clay minerals are the dominant materials of shales and surficial rocks and so are among the most important structural materials of the earth's surface. They are the end products of weathering of a wide variety of rocks. Clays are the characteristic materials of soils and play a fundamental part in the physical and chemical properties of soils and soil fertility; thus, the very existence of life, both plant and animal, is related to clay mineralogy. The physical and chemical properties of

clays, which constitute the most abundant raw material of the ceramic industry, are related to their mineral identity. Clay mineralogy in its relation to the physical properties of soils, shales, and other poorly consolidated rocks is an essential factor in a wide variety of engineering problems. Progress in the science of clay mineralogy has aided not only in an understanding of the clay minerals, but also in an understanding of the large group of minerals characterized by platy structure—the group that includes the clay minerals. No mineral group, therefore, has a more fundamental bearing on so wide a variety of human interests.

METHODS OF STUDY

Mineralogic studies of the clay minerals present unusual difficulties and their systematic investigation has therefore been long delayed. All the members of the montmorillonite group are exceedingly fine-grained; they vary in chemical composition within very wide limits; and they are commonly admixed with other fine-grained mineral materials. Progress in methods of mineral research has tended to overcome some of these difficulties and to encourage a study of the clay minerals. The information furnished by chemical analyses, including base-exchange experiments, and by X-ray, petrologic, and thermal methods of mineralogic research has been brought to bear on the minerals of the montmorillonite group and has provided a means of determining the limits of variation. It also permits the presentation of chemical formulas that express relations within the group.

The development of a technique for studying small mineral grains in immersion oils improved the means for direct study of finely crystalline materials like the clays and facilitated the recognition of impurities. The perfection of X-ray methods for determining crystal structure and for studying crystalline materials in minute grains, however, provided the most fundamental mode of attack on clay problems. About the time that these methods were being newly applied a renewed demand for more definite information developed. Many ceramic engineers were not content with scanty knowledge of their most essential raw material, and students of soils came to see the inadequacy of purely chemical methods unrelated to mineral identity. The complex composition of most soils introduced so many variables that the preliminary study of pure minerals of the types present in soils seemed necessary. The marked base-exchange properties of bentonite and the evidence that its characteristic mineral, montmorillonite, was a widespread component of soils suggested its usefulness in the study of the fundamental property of base exchange. The properties and possible uses of bentonite attracted widespread interest in this material, whose mode of origin (alteration of glassy volcanic ash) gave a clay mineral that was commonly very pure or contained only fairly large volcanic-rock phenocrysts, thus providing ample supplies of an essentially pure clay mineral for experimental purposes. All these factors seemed to make a renewed study of the clay minerals opportune, and about 1924 an intensive study was started in the laboratories of the Geological Survey, United States Department of the Interior, initiating the modern attack on the problem of clay mineralogy. The fundamental bearing of clay mineralogy on many soil problems led to the study of clay minerals in the Bureau of Plant Industry, Soils, and Agricultural Engineering, United States Department of Agriculture. The two lines of research developed an interdependence that led to the present cooperative study.

The montmorillonite group contains minerals of widely varying chemical composition, but the aluminous members are most widespread in occurrence. Less abundant members of the group are characterized by ferric iron, magnesium, chromium, or nickel. These elements as well as ferrous iron, manganese, lithium, and perhaps other elements may occur as minor components proxying aluminum. Calcium, sodium, and potassium also are present in varying proportions, and a determination of their role has presented a distinct problem.

Water is present in several forms, and its function also has been a problem.

Modern X-ray technique has given a means of determining the role of the various ions in the crystal structure. Aluminum may play two roles, one as the characteristic ion having octahedral coordination with respect to oxygen, as in montmorillonite, the type mineral of the group, and the other as partly proxying silicon in tetrahedral positions, as in beidellite. A large group of ions may occupy octahedral coordination positions, and other ions, exchangeable bases, occupy positions between the lattice sheets. The proportion of these exchangeable bases varies within certain limits and thereby introduces another variable, in that the unsatisfied valencies within the crystal lattice are not constant.

PREVIOUS WORK

The present paper on the minerals of the montmorillonite group is the result of studies that have been under way since about 1924. Minerals of bentonite and related clays were first investigated, but they presented so many complex problems that attention was turned to the kaolin minerals, which afforded simpler relationships, because they showed little isomorphism between distinct end members and because some of them occurred as well-crystallized material. However, work on members of the montmorillonite group has continued from the initiation of the program, and many workers have been making essential contributions.

The investigation of the montmorillonite group of clay minerals began with a study of bentonites. These exhibit certain interesting properties and uses, but their detailed study has resulted largely from the ease with which pure clay material of this type can be secured from bentonites. Another source of pure clay minerals is the clay developed in certain pegmatites. Only rarely do approximately pure sedimentary clays occur naturally; they commonly contain detrital rock grains, of which quartz is in general the most abundant. These admixed materials are so fine-grained that it is always difficult and commonly impossible to separate impurities completely from the clay. Soils also are of limited usefulness for this investigation because they are commonly made up of exceedingly fine-grained mixtures of several clay minerals. Gouge and vein clays, including some nontronites and saponite, occasionally occur in pure condition.

About a hundred years ago there was a marked interest in clays but the work was largely chemical, and on this basis numbers of names were proposed. Some of this work was good, but for much of it there has been no way of determining its character or the purity of the material analyzed. Later, the limitations of purely chemical studies came to be realized, and the likelihood of mixtures of minerals, the exceeding fineness of grain, and the difficulty of microscopic study led to a lessened interest in clays. On the basis of accumulated information, Edward S. Dana (1892), in "The System of Mineralogy," 6th edition, assigned species rank to some of the large number of names that had been proposed and listed others as probably synonyms. Considering the difficulties presented, his judgment has been shown to have been remarkably good and his conclusions valid.

Minerals of the montmorillonite-beidellite group have been qualitatively identified as components of the clay fractions of soils by many workers. A number of attempts have been made to carry out approximately

quantitative estimates of the amounts of these minerals in selected soil samples. This has been accomplished chiefly by a coordination of chemical analyses, differential thermal analyses, and X-ray diffraction methods. The identity, character, and methods of identification of the minerals of soils have more than usual significance, and some of the authors who have contributed papers illustrating these studies are listed below. (For titles, see Bibliography, pp. 72-77.)

- 1930
Hendricks and Fry.
- 1931
Kelley, Dore, and Brown.
- 1935
Bray, Grim, and Kerr.
Jacob, Hofmann, and Loofman.
- 1936
Antipov-Karataev and Brunowsky.
Correns and Schlünz.
Kawamura and Funabiki.
- 1937
Clark, Riecken, and Reynolds.
Kelley and Dore.
Engelhardt.
- 1939
Alexander, Hendricks, and Nelson.
Edelman, van Baren, and Favejee.
Favejee.
Hardon and Favejee.
Kelley, Dore, Woodford, and Brown.
Kelley, Woodford, Dore, and Brown.
Sedletsky.
- 1940
Hendricks and Alexander.
Maegdefrau and Hofmann.
Russel and Haddock.

The first of a series of papers on the clay minerals were written by Ross and Shannon (1925, 1926) in a cooperative study made by the Geological Survey and the United States National Museum. Further work, done by Ross and Kerr (1931a, 1931b, 1934) in cooperation with Columbia University, included studies of the kaolin minerals as well as a preliminary paper on the minerals of the montmorillonite group. Kerr also has published papers independently, which will be referred to on later pages of this report. He rendered great help in determining relationships within the group, showing the identity of the different numbers by means of their X-ray diffraction patterns.

Later stages of the work were carried on by Ross in cooperation with Sterling B. Hendricks, of the Bureau of Plant Industry, Soils, and Agricultural Engineering, United States Department of Agriculture, who has been interested in the bearing of clay mineralogy on soil problems. Progress of this work has been recorded in a number of papers by Hendricks (1936, 1938, 1939, 1941, 1942), Hendricks and Alexander (1939, 1940a, 1940b), Hendricks and Fry (1930), Hendricks and Jefferson (1938, 1939), Hendricks, Nelson, and Alexander (1940), Hendricks and Ross (1938), and Ross (1943).

ACKNOWLEDGMENTS

Aid in the study of the clay minerals has come from many sources. D. F. Hewett (1917), of the Geological Survey, had recognized the character and mode of origin of bentonite before the present study began and thus had laid the foundation for further work. In particular we wish to acknowledge the help of Waldemar T. Schaller, of the Geological Survey, who has aided by his advice throughout the study and also has critically read the manuscript. W. F. Foshag, of the National Museum, has generously placed the collections of the Museum at

our disposal, and his advice has been helpful. Edgar T. Wherry, of the University of Pennsylvania, has long been interested in problems of clay mineralogy and has been ever ready with advice. W. P. Kelley, of the California Citrus Fruit Experiment Station and the University of California, who has a deep interest in the more fundamental soil problems, has been generous with his helpful advice. C. E. Marshall, first with the University of Leeds, England, but now at the University of Missouri, has made fundamental contributions to the clay studies and has added valuable advice. Those who have aided by the contribution of materials or in other essential ways are too numerous to list individually.

The study of the clay minerals was for some time under the auspices of the National Research Council; and David White, Waldemar Lindgren, and W. H. Twenhofel, as chairmen of the Section of Geology and Physiography, were deeply interested in the progress of the work. Many of the chemical analyses used in the work were made by Forrest A. Gonyer under a fund granted by the National Research Council. Later the chemical work was carried forward by members of the Section of Chemistry of the Geological Survey. P. G. Nutting, of the Geological Survey, has been engaged in a study of the oil clarification properties of clays and has made a large number of dehydration tests, which have been most helpful to the mineralogical studies.

In the course of the studies on which this paper is based the selection of material and the optical examinations were made by C. S. Ross, most of the dehydration tests by P. G. Nutting, and the earlier X-ray studies by P. F. Kerr. The base-exchange experiments, the study of the relation between exchangeable bases and interlayer water, many of the X-ray experiments, and the calculations of mineral composition were made by S. B. Hendricks in the laboratories of the Bureau of Plant Industry, Soils, and Agricultural Engineering. Many other independent contributions will be referred to in the body of this paper. Wide cooperation has been one of the most pleasant factors in the work, and this has greatly contributed to its successful culmination.

NOMENCLATURE

The clay minerals present unusually difficult problems in nomenclature. Some of the names were proposed long ago, before an accurate knowledge of chemical composition was available; for some the identity of the original material is in doubt; and for others the purity of the sample and, therefore, the accuracy of the chemical analysis, is questionable. Many of the old names have fallen into disuse and are met with only in the early literature.

Parts of the discussions of nomenclature in previous papers by Ross and Kerr (1931b, 1934) and by Kerr (1932) apply to the minerals included in the present paper and need not be repeated in detail, but others require consideration.

MONTMORILLONITE

The name montmorillonite was proposed by Damour and Salvetat (1847) for a clay material for which they gave the following chemical analysis:

Analysis of montmorillonite from Montmorillon, France

SiO ₂	49.40	CaO.....	1.50
Al ₂ O ₃	19.70	Na ₂ O }.....	1.50
Fe ₂ O ₃80	K ₂ O }.....	
MgO.....	.27	H ₂ O.....	25.67
			98.84

Although the sample is unusually low in MgO and anomalous in other ways, it is essentially montmorillonite.

Breithaupt (1832, p. 99) described galapectite from Angleur, France. An analysis of material from Angleur by Le Chatelier (1887, p. 210) was that of a typical halloysite, although optical properties of another sample from the same locality, studied by Ross and Kerr (1934), proved to be those of montmorillonite. Thus, some galapectite is definitely montmorillonite, but in general it is probably to be correlated with halloysite rather than montmorillonite.

Other names of minerals that were considered by Dana (1892) to be at least in part montmorillonite but proposed since 1847, the date for montmorillonite, are confolensite, described by Dufrenoy (1856, p. 583), from Confolens, at St. Jean-de-Cole near Thiviers, France, and delanonite, described by Kenngott (1853, p. 633), from Millac near Nontron, France.

Le Chatelier (1887, p. 210) presented the formula $4\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O} + n\text{Aq}$ for montmorillonite. Dana (1892, p. 690) quotes Le Chatelier and gives the composition of montmorillonite as probably $\text{H}_2\text{Al}_2\text{Si}_4\text{O}_{12} + n\text{Aq}$, or $\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O} + n\text{Aq}$. Ross and Shannon (1926) proposed the formula $(\text{Mg}, \text{Ca}) \cdot \text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2 \cdot n\text{H}_2\text{O}$ to explain the MgO and CaO which were found to characterize all of the many new analyses presented. Later X-ray studies showed the different role of Mg and Ca and the inadequacy of this formula.

Wherry, Ross, and Kerr (1930) stated: "Chemically the original mineral so-called [montmorillonite] was a hydrous aluminum silicate with the ratio $\text{SiO}_2:\text{Al}_2\text{O}_3 = 4:1$, and perhaps the majority of other occurrences have this ratio. Many vary from it, however, some being higher in silica, up to at least 5:1, while others are lower, reaching 3:1 or even 2:1, without change in structure, although with a slight alteration of the unit-cell dimensions as shown by X-rays. In addition, MgO is frequently present, apparently as an essential constituent."

Ross and Kerr (1931) published a preliminary paper in which the several members of the montmorillonite group of clay minerals were listed. These were montmorillonite; beidellite, with an assumed $\text{Al}_2\text{O}_3:\text{SiO}_2$ ratio of 1:3; an unnamed member with a ratio of 1:2; nontronite with a $\text{Fe}_2\text{O}_3:\text{SiO}_2$ ratio of 1:3; and saponite, a magnesian member containing a little Al_2O_3 .

The only name that antedates montmorillonite and appears to have included at least in part clay materials of the montmorillonite type is smectite. This name was at one time widely used in the mineralogical texts of the 18th century and appears to have been, in general, synonymous with "fuller's earth." Cronstedt, in an original paper (1788, p. 98) and in a later translation by Magellan, mentions "smectis," but lists it among magnesian earths, which seems to correlate it with saponite rather than montmorillonite. Kirwan (1794, p. 184) used the terms "walkerda" and "smectis" in addition to fuller's earth. Haüy (1801, p. 444) used the terms smectite clay and fuller's earth. The general impression seemed to have prevailed, as indicated by Breithaupt (1841, p. 544), that smectite was a hydrous aluminum silicate containing magnesium, calcium, and other constituents.

Kerr (1932) has shown that certain clays that have been described as smectite from Cilly, Lower Styria, and Woburn Sands of England are typical bentonites—derived from glassy volcanic ash—and are composed of

the mineral that has commonly been known as montmorillonite.

Since the time of its proposal, the name montmorillonite has been commonly used and has been accepted by Dana (1892, p. 690), while smectite has fallen into disuse, and where used at all, apparently has implied a fuller's earth rather than a definite mineral. Kerr (1932, p. 198) concludes:

Since the X-ray diffraction patterns, chemical analyses, and refractive indices show such close relationship, it seems hardly worth while to retain the two names smectite and montmorillonite for what appears to be the same mineral. In view of the large amount of modern literature on montmorillonite it seems in the best interests of science to continue the use of montmorillonite and to drop that of smectite.

BEIDELLITE

Larsen and Wherry (1917) described the clay mineral that occurred as a gouge clay in a mine at Beidell, Colo., under the name leverrierite. Leverrierite had been first described by Termier (1890), after a study of material from Beaubrun, Rive-de-Gier, near St. Etienne, France. The identity of the original leverrierite with kaolinite was recognized by Dana (1892, p. 687) and later by Cayeux (1916). Optical and X-ray studies by Ross and Kerr (1931b) of type material from France, kindly supplied by the Museum of Natural History, Paris, confirmed Dana's conclusion that the original material was kaolinite. The Colorado material was a distinct mineral, therefore, Larsen and Wherry (1925) proposed the name beidellite for the material previously described by them as leverrierite, and Ross and Shannon (1925) described the properties of beidellite.

Even since the withdrawal of the name leverrierite by Larsen and Wherry, however, that name has been applied to a mineral of low index of refraction and comparatively high birefringence, which is distinct from the type material. De Lapparent (1934) has restudied type material and reports that it is composed of alternating plates of kaolinite and muscovite. The identity of the type leverrierite with kaolinite, or a mixture of kaolinite and muscovite, seems, therefore to be generally accepted, and the name leverrierite should be discarded.

SAPONITE

An early reference to claylike materials that seem to have included saponite was made by Cronstedt (1758, pp. 98, 236, 237) under such names as "smectis"; "walkerda," that is, fuller's earth; "kessikel," used as a substitute for soap; and "terra lemnia," which the translator remarks is used as a fuller's earth in England. Saponite appears to have been included under "steatite" by Kirwan (1794, p. 152). Svanberg (1840, p. 153) described saponite, and his paper, which was republished later (1842), contained the following chemical analysis:

Analysis of saponite from Svärdsjö, Sweden

SiO_2	50.8	CaO7
Al_2O_3	9.4	H_2O	10.5
Fe_2O_3	2.0		
MgO	26.5		99.9

In the meantime the same material was described under the name "piotin," by Svanberg (1841). Nickles (1859) described a mineral under the name saponite, but, as the combined K_2O , MgO , and FeO amounted to only 0.63 percent, the material was clearly not saponite.

Hilgard (1916) described under the name "lucianite" a claylike material from Hacienda Santa Lucia near Mexico City. The analysis given below shows that it is essentially similar to saponite and differs only in being a little higher in calcium oxide and lower in magnesia than most saponites. The high calcium content strongly suggests impurities.

SiO ₂	43.00	Insoluble.....	1.83
Al ₂ O ₃	3.48	Loss on ignition.....	19.60
Fe ₂ O ₃	1.76	Soluble salts.....	2.60
MgO.....	17.11		
CaO.....	9.06		98.44

Thalite was described by Owen (1852), who concluded that it contained a new rare earth, which he proposed to call thalium. Bolingite was described by Hannay (1877), but his analysis contained approximately 5 percent of calcium carbonate and obviously was impure.

Analyses quoted by Dana (1892, p. 682) all contained alumina, and he made no attempt to assign a formula to the mineral. Ross and Kerr (1931) published a preliminary paper on the clay minerals in which they identified saponite as a member of the montmorillonite group.

HECTORITE

Foshag and Woodford (1936) described an unusually interesting clay mineral from Hector, Calif. This unique mineral has provided a key in understanding some of the relationships in the montmorillonite group. It is essentially the magnesian end member of the group (see p. 47), and the almost total absence of Al₂O₃, the presence of essential Li₂O, and the dominance of F over OH seem to establish the Hector clay as a distinct mineral species. For this species the name hectorite has been proposed by Strese and Hofmann (1941).

The name hectorite was applied by Cox (1882) to a "hydrated pyroxene mineral" from the serpentine rocks of the Dun Mountains of New Zealand, and it is listed by Dana (1892, p. 364) under the pyroxenes, as one of the "more or less well defined alteration products of various kinds of pyroxenes," although the analysis suggests that it is an amphibole related to cummingtonite. Its identity, however, was never established, the name as proposed by Cox never gained acceptance, and in this meaning it has fallen into complete disuse. As Cox's proposal was made more than 50 years ago, the reassignment of the name will not conflict with the rules of nomenclature as given by Dana (1892, p. xliii).

Marshall (1937b, p. 938) states: "An end member of the series is probably Foshag and Woodford's magnesian bentonite, in which practically all the aluminum has been replaced by magnesium." Hofmann, Endell, and Bilke (1935, p. 469) have examined a synthetic magnesium silicate, which they conclude is this same end member.

The paper by Foshag and Woodford (1936) presented two chemical analyses, one by Dr. Foshag and the other by R. E. Stevens, of the Geological Survey. These are as follows:

SiO ₂	53.68	51.26	K ₂ O.....	.07	.10
Al ₂ O ₃60	.36	Li ₂ O.....	1.12	.60
Fe ₂ O ₃09	.09	H ₂ O +.....	8.24	5.14
FeO.....	.06	.06	H ₂ O -.....	7.28	11.56
MgO.....	25.34	23.25	Cl.....	.31
CaO.....	.52	2.60	CO ₂	1.35
SrO.....	Tr.	F.....	None
Na ₂ O.....	3.00	3.47		100.16	99.84

For some unknown reason the standard qualitative test for determining fluorine gives a negative reaction when applied to hectorite; consequently, these analyses failed to show fluorine, although Stevens specifically looked for it. Thus the presence of fluorine in hectorite escaped detection until reported by Harold R. Eyrich, who has been engaged in the commercial production of the Hector clay. Mr. Eyrich submitted the following analysis made by the Sharp, Schurtz Co., of Lancaster, Ohio:

SiO ₂	59.77	Na ₂ O.....	2.73
Fe ₂ O ₃026	F.....	5.35
Al ₂ O ₃49	Loss on ignition.....	4.00
CaO.....	.45		
MgO.....	27.46		100.276

The hectorite was reanalyzed by Stevens and the results are given in table 4 (p. 35). Some samples of Hector clay contain varying amounts of calcium carbonate, but the material supplied by Mr. Eyrich is seemingly free from this and other impurities.

The low atomic weight of lithium makes the 1 percent of that element an important constituent of hectorite. The studies given on pages 37 to 39 show that this element provides the correct substitution of a monovalent base for the bivalent magnesium required to give a member of the montmorillonite group its distinctive physical and base-exchange properties. A distinctive name for the Hector clay, therefore, seems fully justified.

NONTRONITE

The name nontronite was proposed by Berthier (1827), who stated that the mineral was discovered by Lanoue and was associated with the manganese ore of Perigueux in the Arrondissement of Nontron, near the village of Saint Pardoux. It forms onion-shaped masses commonly smaller than a man's fist. Associated impurities are quartz sand, manganese oxides, and clay, but pure material is easily obtained for analysis. The color is canary yellow, slightly greenish. The following chemical analysis was given:

SiO ₂	44.0	H ₂ O.....	18.7
Al ₂ O ₃	3.6	Clay.....	1.2
Fe ₂ O ₃	29.0		
MgO.....	2.1		98.6

Breithaupt (1829) described pinguite from Volkerstein Erzegebirge. No chemical analysis was given, but the mineral was described as being siskin to oil green in color.

Krantz (1857) reported a mineral from the vicinity of Menzenberg in the Siebengebirge for which he proposed the name gramenite. No chemical analysis was given and no reason for differentiating it from pinguite or nontronite, which it was described as resembling. About the same time Bergmann (1857) published an analysis of gramenite not essentially different from nontronite.

Nontronite, together with faratsihite, a material described by Laroix (1914), has been assigned to the kaolin group by Mügge (Rosenbusch, 1914), following the conclusion of Weinschenk (1897). An optical examination of faratsihite shows that much of the material has too high a birefringence to be purely a member of the kaolin group. Recently a study of faratsihite by Hendricks (1939) has shown that it is a mixture of kaolinite and nontronite. He concludes that it is very improbable that the kaolinite lattice will accommodate appreciable

amounts of iron in solid solution and that nontronite and kaolinite, therefore, belong to distinct groups of minerals.

The first to recognize the relationship between nontronite and montmorillonite appears to have been Collins (1877) who stated that chloropal, nontronite, gramenite, and montmorillonite must be regarded as belonging to the same series. Larsen and Steiger (1928) published a study of nontronite and compiled the chemical, dehydration, and optical properties of this and related minerals. They pointed out that nontronite and beidellite form an isomorphous series.

Chloropal was described from Unghwar, Hungary, by Bernhardt and Brandes (1822). One sample was listed as being an opaline mineral, but an earthy form also was described, and chemical analyses of both were given. That of the earthy variety is given below. The color is siskin, or light yellowish, green.

Analysis of earthy chloropal from Unghwar, Hungary

SiO ₂	45.00	MnO }	traces
Al ₂ O ₃75	K ₂ O }	
Fe ₂ O ₃	32.00	H ₂ O }	20.00
MgO.....	2.00		99.75

Glocker (1839) described material from the same locality under the name unghwarit.

The name chloropal has a slight priority over nontronite. However, the material has been shown to be definitely crystalline by both optical and X-ray methods, and the name chloropal, suggesting a deeply colored opaline mineral, is unsuitable. Dana (1892, p. xliii) has laid down the rule that a name having priority may properly be set aside when its signification is glaringly false. Mineralogists for sometime have used the name nontronite as the most suitable for this mineral.

VOLCHONSKOITE

Kammerer (1831) described a claylike mineral containing chromium which was obtained from Okhansk, Russia, and a description and analysis were published by Kersten (1839). Since then, several other analyses of similar material have been presented, and these are quoted in table 6, page 35. Dana (1892, p. 696) made no attempt to determine its relationships and listed it under the heading, "appendix to clays."

Angel (1913) described "wolkonskoit" in some detail and presented new analyses, but likewise refrained from suggesting relationships. Larsen and Berman (1934, p. 164) list volkonskoite as a chromium kaolinite.

Serdiuchenko (1933, table 3) described a number of chrome-bearing beidellites and concluded that volchonskoite was a member of the group including beidellite and nontronite. From Serdiuchenko's discussion, however, it is not clear that he had an opportunity to study the original material directly.

Through the courtesy of W. F. Foshag, material from the type locality of Okhansk was made available for study from the collections of the United States National Museum. Studies of volchonskoite under the microscope indicate that the material has optical properties similar to those of nontronite except for the color, which is "dark green" by Ridgway's color standard. An examination of the material by X-ray methods showed a typical nontronite pattern.

KAOLIN MINERALS

The mineral relationships discussed in this paper, particularly the mineral paragenesis, involve references to several clay minerals that do not belong to the montmorillonite group. These should be briefly mentioned.

The kaolinite group includes five minerals; of these, kaolinite, dickite, halloysite, and nacrite (Poss and Kerr, 1930) have the same chemical composition, Al₂Si₂O₅[OH]₄, and endellite has the composition Al₂Si₂O₅[OH]₃.

Kaolinite is the most important member of the group, being a widespread component of soils, where it is the result of weathering processes. Rarely it is the result of low-temperature hydrothermal processes. Dickite is a widely occurring mineral in certain types of mineral veins, where it is normally the result of hydrothermal processes, as is also the very rare mineral nacrite. Halloysite may occur in some soils but the X-ray diffraction patterns of halloysite and kaolinite are so similar that they are difficult to recognize where associated with other clay minerals, as in soils. The relations between halloysite and endellite have been described by Alexander, Faust, Hendricks, Insley, and McMurdie (1943), who have shown that halloysite is an alteration product of endellite. Endellite, which loses two molecules of water and inverts to halloysite at 50° C., is very unstable. The wide occurrence of halloysite, however, indicates that endellite is an important, although evanescent, material.

The name halloysite was proposed by Berthier (1826) and this usage established by him has been followed for more than a century by mineralogists throughout the world. Notwithstanding this, a shift of names was proposed by Hofmann, Endell, and Wilm (1934), calling halloysite metahalloysite, and applying halloysite to the new mineral characterized by 8(OH). Such a shift of names is precluded by the long-established rules of scientific nomenclature and cannot be accepted. For this reason Alexander, Faust, Hendricks, Insley, and McMurdie (1943) have applied the name endellite to the form with the higher content of OH and have used the name halloysite as originally proposed by Berthier.

HYDROUS MICAS (ILLITE)

Minerals related to the micas, but containing less potassium, are commonly in association with other clay minerals and therefore will be briefly mentioned. These minerals, in general, have not been distinguished from the true micas, but have commonly been grouped together under such descriptive terms as hydro-micas (Galpin, 1912), hydrous micas (Bayley, 1920), glimmer-ton (Endell, Hofmann, and Maegdefrau, 1935), and illite (Grim, Bray, and Bradley 1937). The use of these descriptive terms has been due to the realization that specific names should await a better understanding of the group. The only specific mineral name that has been proposed for minerals of this group is bravaisite (Mallard, 1878), used for a mineral of the muscovite type. Grim's analyses of illite (1942) are similar to that of bravaisite, and Nagelschmidt (1943) has published a number of analyses of similar material.

The relationships of the potassium-bearing soil materials are only partly known, and a final decision about grouping is not yet possible; however, a large number of chemical analyses are available, which show the presence of about 6 percent of potassium, and the variation from this value generally is small. Bravaisite has precedence

as the name for this micalike mineral with about half the potassium of muscovite. Other clays contain much less potassium—quite a number show about 1 percent of that element, others 2 or 3 percent. (See tables 1-3, analyses 7, 30, 46, 47, 54, 62, 69, and 70.) The studies of mixed-layer minerals (see below and Grim and Rowland, 1942, p. 803) show that these materials are made up of mixed layers of muscovite or bravaisite and beidellite or, less commonly, mixed layers with montmorillonite; that is, minerals of the montmorillonite group are commonly dominant in these materials. The evidence, therefore, seems to indicate that these mixtures are not specific minerals and do not merit a specific mineral name, at least not until more adequately understood.

Bravaisite and those materials of problematic relationship to it are important soil-forming materials, which characterize many mineral deposits. They will be discussed briefly; detailed study is desirable but aside from the scope of this paper.

The presence in soils of minerals related to the micas was first recognized by Hendricks and Fry (1930). Ross and Shannon (1926) gave an analysis of potash-bearing bentonites of Ordovician age and of a similar clay from China. In a subsequent paper Ross and Kerr (1931) state that the potash clays resembled sericite. Maegdefrau and Hofmann (1937) published a detailed study of micalike minerals in clay fractions of soils. The most thorough study of this group of clay minerals belonging to the mica group has been made by Grim, Bray, and Bradley (1937), who show the wide distribution of a low-potash mica mineral among the clay minerals. Another paper in which the micalike minerals in soils are discussed is that by Hendricks and Alexander (1939), from which the following is quoted:

"The amount of K_2O is very variable, the total range being from the order of 1 percent to that required for muscovite (11.8 percent K_2O). Many of the analyzed samples, however, contain approximately 5 percent K_2O , which can be taken as the average value. * * * Perhaps * * * the gradation in composition is so continuous as hardly to justify the naming of intermediate minerals. For this reason the entire series will simply be referred to as "hydrous micas." * * * This type of mixed minerals is difficult to recognize, but is probably a common constituent of soils. In particular, montmorillonites and hydrous micas probably occur together."

There is widespread geologic evidence of a strong tendency for the fixation of K_2O at the expense of Na_2O in the rocks of the earth's surface. Spencer and Murata, in an unpublished paper, have shown that, although there is a preferential adsorption of K_2O by the normal clay minerals, adsorption does not afford an adequate explanation of this fixation. Seemingly, the only other explanation is that micas or micalike minerals tend to form and thus fix K_2O .

Students of soils have long recognized that potassium added to soils tends to become fixed and becomes unavailable or difficultly available as plant food. Truog and Jones (1938) have shown that the tendency of potash to become fixed in an unavailable form is increased by wetting and drying, and that clays of the bentonite type have this property more strongly than other minerals that were tried.

Thus several lines of evidence indicate the wide occurrence of mixed layers of micas and minerals of the montmorillonite group. This makes the petrologic estimation of these minerals very difficult in the clay fractions of soils. It also results in some question about selection of mineralogic specimens of montmorillonite from soils for analysis and study.

When the amount of K_2O present in a specimen is one percent or more, then the presence of mica-type minerals or of micalike layers in the montmorillonite is probable. About ten of the samples examined in this work contained such amounts of K_2O . These are retained since it was not considered entirely justifiable to eliminate them on the basis of analyses alone.

MIXED-LAYER MINERALS

The importance of mixed-layer minerals among those with a platy structure is gaining recognition, and the effect of such intermixtures with minerals of the montmorillonite group must be considered. Gruner (1934, p. 561) in describing vermiculite, a mineral closely related to montmorillonite, states that potassium-bearing minerals of this group are made up of interstratified layers of mica and vermiculite.

Hendricks and Jefferson (1938), who also have studied vermiculite, state, "It is not surprising to find that vermiculites form mixed structures with the chlorites and micas. In fact, any mixture of mica, vermiculite, pyrophyllite * * * and talc layers would not be unreasonable." In the same way, the clays of the montmorillonite group may contain mixed layers of mica, chlorite, talc, or brucite, and possibly other minerals of similar character.

CRYSTAL STRUCTURE

Studies of the micas made by Maugin (1927, 1929, 1930), followed by that of Pauling (1930) on micas and related minerals, laid the foundation for an understanding of minerals with platy structure. Pauling proposed structures for gibbsite, $Al_2(OH)_6$; brucite, $Mg_3(OH)_6$; talc, $3MgO \cdot 4SiO_2 \cdot H_2O$; pyrophyllite, $Al_2O_3 \cdot 4SiO_2 \cdot H_2O$; the micas; and the chlorites. He considered these minerals to be made up of layer lattices, the silicates being formed by combination of gibbsite or brucite layers with silicate layers.

This work and that of W. L. Bragg and his associates (1932, 1937, 1938) showed that Al^{+3} , Mg^{+2} , Fe^{+2} , Fe^{+3} , Mn^{+2} , Mn^{+3} , Ti^{+4} , Ni^{+2} , and Li^{+1} could play similar roles in the crystal structures. These ions can all be in the lattice positions surrounded at the corners of an approximately regular octahedron by oxygen and hydroxyl or fluorine ions; that is, they have octahedral coordination. Silicon, Si^{+4} , can undergo substitution, in part, only by Al^{+3} , since it has tetrahedral coordination with respect to oxygen.

Pauling's work was significant also in its recognition of the similarity in structure of pyrophyllite and talc. These minerals, as shown below, have the sequence of atomic planes along the pseudohexagonal axes, which are normal to the micaceous cleavage. N in the table is a large factor giving the number of units of structure in a layer.

PYROPHYLLITE		TALC	
Atomic planes		Atomic planes	
N X		N X	
Silicate layer (tetrahedral)	$\left\{ \begin{array}{l} 6 O^{-2} \\ 4 Si^{+4} \end{array} \right.$	Silicate layer (tetrahedral)	$\left\{ \begin{array}{l} 6 O^{-2} \\ 4 Si^{+4} \end{array} \right.$
Gibbsite layer (octahedral)	$\left\{ \begin{array}{l} 4 O^{-2} \cdot 2(OH)^{-1} \\ 4 Al^{+3} \\ 4 O^{-2} \cdot 2(OH)^{-1} \end{array} \right.$	Brucite layer (octahedral)	$\left\{ \begin{array}{l} 4 O^{-2} \cdot 2(OH)^{-1} \\ 6 Mg^{+2} \\ 4 O^{-2} \cdot 2(OH)^{-1} \end{array} \right.$
Silicate layer (tetrahedral)	$\left\{ \begin{array}{l} 4 Si^{+4} \\ 6 O^{-2} \end{array} \right.$	Silicate layer (tetrahedral)	$\left\{ \begin{array}{l} 4 Si^{+4} \\ 6 O^{-2} \end{array} \right.$

This succession of atomic planes forms a neutral structure, which can be considered as one layer. Crystals

are formed by superposition of these extended layers and, as each layer is neutral, there is only a small attractive force between them, resulting in excellent cleavage.

In the micas, as shown by the work of Pauling (1930) and of Jackson and West (1931, 1933), the succession of atomic planes within a layer is approximately as follows:

MUSCOVITE		PHLOGOPITE	
	N ×		N ×
Tetrahedral layer	$\left\{ \begin{array}{l} 6 \text{ O}^{-2} \\ 3 \text{ Si}^{+4}.1\text{Al}^{+3} \end{array} \right.$	Tetrahedral layer	$\left\{ \begin{array}{l} 6 \text{ O}^{-2} \\ 3 \text{ Si}^{+4}.1\text{Al}^{+1} \end{array} \right.$
Octahedral layer	$\left\{ \begin{array}{l} 4 \text{ O}^{-2}.2[\text{OH},\text{F}]^{-1} \\ 4 \text{ Al}^{+3} \\ 4 \text{ O}^{-2}.2[\text{OH},\text{F}]^{-1} \end{array} \right.$	Octahedral layer	$\left\{ \begin{array}{l} 4 \text{ O}^{-2}.2[\text{OH},\text{F}]^{-1} \\ 6 \text{ Mg}^{+2} \\ 4 \text{ O}^{-2}.2[\text{OH},\text{F}]^{-1} \end{array} \right.$
Tetrahedral layer	$\left\{ \begin{array}{l} 3 \text{ Si}^{+4}.1\text{Al}^{+3} \\ 6 \text{ O}^{-2} \end{array} \right.$	Tetrahedral layer	$\left\{ \begin{array}{l} 3 \text{ Si}^{+4}.1\text{Al}^{+3} \\ 6 \text{ O}^{-2} \end{array} \right.$
Interlayer	K^{+1}	Interlayer	K^{+1}

Here the layer as a whole has an excess negative charge resulting from the substitution of Al^{+3} for Si^{+4} . This is compensated for by K^{+1} situated between successive layers on the surface along which the excellent cleavage occurs. Each of the K^{+1} ions has 12 neighboring oxygen ions, 6 being at the corners of a hexagon in the top of one layer and 6 similarly placed in the bottom of another layer. Potassium, K^{+1} , in the micas can be replaced by Cs^{+1} , Rb^{+1} , Ca^{+2} , and Na^{+1} . The appreciably smaller radius of Li^{+} apparently prevents its substitution for K^{+} , as has been substantiated by recent work on lithium micas by Miser and Stevens (1938) and by Stevens (1938).

Hofmann, Endell, and Wilm (1933, 1934) proposed a structure for montmorillonite similar to that of the silicates with layer lattices. The lattice was the same as that of pyrophyllite, the composition being taken as $\text{Al}_2\text{O}_3.4\text{SiO}_2.H_2\text{O}$. In the structure proposed, the water absorbed bore a definite relation to the spacing of the plane parallel to the layer surface. (See p. 54.)

In 1935, several papers were published that added to the knowledge of the relationships of the various elements occurring in minerals of the montmorillonite group. The conclusion of Collins (1877) about the relationship of nontronite and montmorillonite, and those of Larsen and Steiger (1928) and Ross and Shannon (1925) about the relationships between beidellite and nontronite were confirmed by Gruner (1935), who concluded:

An X-ray examination of nontronite, morencite, pinguite, faratsihite, chloropal, and stilpnochloran shows that these so-called species are structurally identical. * * * The structure is practically identical with that of montmorillonite (bentonite). Therefore, montmorillonite, beidellite, and nontronite form an isomorphous series.

Importance of isomorphous replacements in the montmorillonite lattice similar to that in the micas was first emphasized by Marshall (1935b, 1935c, 1936b) and Holzner (1935). Marshall particularly called attention to the fact that the silicate layers in montmorillonite carry a negative charge, in the same manner as do the micas, which has to be balanced by ions external to the layers. These ions are the ones that take part in the base exchange shown by montmorillonites. One of Marshall's conclusions was:

Montmorillonite, beidellite, and some of the nontronites are members of a single series. In montmorillonites the chief lattice replacement is that of magnesium for aluminum; in the beidellites that of aluminum for silicon predominates; in many nontronites each of these is overshadowed by the substitution of iron for aluminum.

In recent years Gruner (1934b) and Hendricks and Jefferson (1938) have studied the manner in which the silicate layers of minerals, with layer lattices are superimposed. However, absence of any pronounced regularity in montmorillonite makes a detailed discussion unnecessary.

Typical X-ray powder-diffraction data from montmorillonite are to be found in several review articles that have appeared and in various original publications by Englehardt (1937), Nagelschmidt (1938), Edelmann, van Baren, and Favejee (1939), and Mehmel (1939).

LOCATION AND DESCRIPTION OF ANALYZED CLAYS

The following section gives the location and mode of occurrence, so far as known, of the clays whose analyses and mineral composition are considered in this paper. The color was determined wherever samples could be directly compared with the Ridgeway color standards, and those color descriptions are indicated by (R) after the name of the color. The physical properties will be described in a later section. (See pp. 48-57.) Where analyses are copied from earlier studies, the author's name and the date of publication are given. (See bibliography, pp. 72-77.) Some of the analyses made in the course of this study were published previously in a report by Ross and Shannon (1926, p. 90) and in a compilation of chemical analyses made in the laboratories of the Geological Survey (Wells, 1937).

MONTMORILLONITE-BEIDELLITE SERIES

1. Santa Cruz, N. Mex., sec. 6, T. 20 N., R. 9 E. Bentonite Very pure cream-buff clay. Wells (1937, p. 108). J. G. Fairchild, analyst.
2. Cilly, Styria. "Smectite" (montmorillonite). Described by Kerr (1932). A. M. Smoot of Ledoux & Co., analyst. The United States National Museum collection of minerals contains a sample of type material from Cilly (U. S. Nat. Mus. No. 13098).
3. Amargosa Valley, Calif. Bentonite. An unusually friable, light-gray clay. Wells (1937, p. 107). J. G. Fairchild, analyst.
4. Tehachapi, Calif. Bentonitic clay forming a bed about 8 feet thick, light-grayish white to greenish white; described by Kerr and Cameron (1936). A. M. Smoot of Ledoux & Co., analyst.
5. Dixon, N. Mex. Bentonite. A compact pinkish cream-colored clay. Wells (1937, p. 107). J. J. Fahey, analyst.
6. Tatatila, Veracruz, Mexico. A very pure bentonite varying in color from almost white to La France pink (R). Transmitted to the United States National Museum by Manuel Santillan, Director, Instituto Geologica, Mexico. U. S. Nat. Mus. No. 101,836. Unpublished analysis, K. J. Murata, analyst.
7. Maricopa, Kern County, Calif. Bentonite. Ross and Shannon (1926, p. 89). Earl V. Shannon, analyst.
8. Conejos quadrangle, Colo. Bentonite, buff pink (R). From between lava flows. Washed to free clay from included igneous rock phenocrysts. Collected by Ross. Ross and Shannon (1926, p. 89). Earl V. Shannon, analyst.
9. San Diego County, Calif. Bentonite. Wells (1937, p. 107). J. G. Fairchild, analyst.
10. Near Landshut, Mainburg, Nieder-Bayern, Germany. Pinkish-buff (R) bentonite, so-called "Tonsil" clay. Unpublished analysis, J. G. Fairchild, analyst.
11. Near Rideout, Utah (exact locality unknown). So-called saponite. Unpublished analysis, F. A. Gonyer, analyst.
12. Ardmore, S. Dak. Bentonite, gray, used in making "refinite" (water softener). Wells (1937, p. 69). W. T. Schaller, analyst.
13. Irish Creek, Rockbridge County, Va. Gouge clay formed in shear zone in granodiorite, Irish Creek tin mines. Friable, cream-colored. Collected by Ross. Unpublished analysis, J. G. Fairchild, analyst.
14. Hector, San Bernardino County, Calif. (3 miles south of Hector). Pale-gray bentonite associated with hectrite, sample 76. Collected by Bernard Moore. Unpublished analysis, R. E. Stevens, analyst.

15. Otay, San Diego County, Calif. Bentonite, selected white material associated with pink material (sample 38). J. E. Whitfield, analyst.

16. Polkville, Smith County, Miss. Glaze farm. Bentonite, deep olive buff (R). Wells (1937, p. 107). R. C. Wells, analyst.

17. Anglar, France. So-called galapectite, U. S. Nat. Mus. No. 4777. Pinkish buff (R). Wells (1937, p. 107). J. G. Fairchild, analyst.

18. Montmorillon, France. Montmorillonite from the type locality was described by Damour and Salvétat (1847), who describe the occurrence as follows: "The mineral occurs in nests penetrating a brownish shale in the vicinity of Montmorillon (Vienne)." Lacroix (1910, p. 749) states that the rose-colored montmorillonite of Vienne "was encountered 25 meters below the surface in the course of digging a well at Bordes in La Trimoille. It forms a bed a meter in thickness in the recent gravels."

The present study is based on type material obtained from Professor Lacroix of the National Museum of Natural History, Paris. The color is La France pink (R) and greatly resembles that of some of the pegmatite clays. Examination under the microscope reveals no clear evidence as to its mode of origin. It is apparent that the material is not quite homogeneous. No non-clay materials are present, but the material appears to contain two slightly different types of clay. This is confirmed by a dehydration curve that shows slight irregularities. The X-ray diffraction pattern, however, indicates that the material is essentially montmorillonite of the same type as that in bentonites and pegmatite clays. Unpublished analysis, Roger C. Wells, analyst.

19. Upton, Wyo. Bentonite, ivory color. Wells (1937, p. 71). J. G. Fairchild, analyst.

20. Lemon, Smith County, Miss. (Husband farm). Bentonite, olive buff (R). Nos. 20 and 23 are parts of the same sample. No. 20 forms irregular, paler, more opaque patches associated with the denser, more translucent material of No. 23. As this bentonite contains marine fossils, principally echinoids, the ash from which it formed was evidently deposited in the ocean, but alteration may have occurred later. Wells (1937, p. 107). R. E. Stevens, analyst. (See electron micrograph pl. 7, D.)

21. Spokane, Wash. Salmon buff (R). Fillings of vesicular cavities in basalt. Collected by Edward Sampson. Unpublished analysis, J. G. Fairchild, analyst.

22. Atzacapozalco, Mexico, on the southern slope of Cerro de Malinche. Very pure clay associated with basalt fragments below a basalt flow. Buff pink, mottled carrot red (R). Collected by W. F. Foshag. U. S. Nat. Mus. No. R-7591. Wells (1937, p. 107). E. T. Erickson, analyst.

23. Lemon, Smith County, Miss. Bentonite. (See sample 20.) R. E. Stevens, analyst.

24. Mexico, exact locality unknown. Pure white and shows the lowest iron content of the bentonites examined. Wells (1937, p. 107). J. G. Fairchild, analyst.

25. Rosedale, Alberta, Canada. (See pl. 5, A.) Pale olive-gray (R) bentonite, received from H. S. Spence, Mines Branch, Department of Mines, Canada. It is described as follows by Spence (1924, p. 14): "At Rosedale, the bentonite seen in the workings of the Rosedale Coal Co. measures 6 to 10 inches in thickness, and the material compares favorably in point of colloidal with the type Wyoming Clay." This is a sodium bentonite that forms unusually perfect gel-like masses, which swell to nearly eight times the original volume without breaking down or losing shape. A. Sadler, Mines Branch, analyst.

26. Santa Monica Mountains (north slope), Los Angeles County, Calif. Bentonite. Collected by M. N. Bramlette. Wells (1937, p. 66). Charles Milton, analyst.

27. Near San Antonio, Tex. (16 miles west of San Antonio on the Castroville road). Ivory-yellow (R) bentonite. Ross and Shannon (1926, p. 89). Earl V. Shannon, analyst.

28. Greenwood, Maine. Pale Hermosa pink (R) pegmatite clay, reported to be an alteration product of pollucite. Wells (1937, p. 107). J. G. Fairchild, analyst.

29. Fort Steel, Wyo. Bentonite, pale yellow. Purified by washing to free from igneous-rock phenocrysts. Ross and Shannon (1926, p. 89). Earl V. Shannon, analyst.

30. Osage, Wyo. Bentonite from the lower part of the Belle Fourche shale member. A sodium bentonite with tendency to disperse and remain in permanent suspension. Collected by W. W. Rubey. Wells (1937, p. 71). J. G. Fairchild, analyst.

31. Lemon, Smith County, Miss. Husband farm. Buff pink (R) bentonite. Wells (1937, p. 107). J. J. Fahey, analyst.

32. Otay, Calif. Bentonite associated with sample 14. Light grayish vinaceous (R). Ross and Shannon (1926, p. 88). Earl V. Shannon, analyst.

33. Branchville, Conn. Pegmatite clay described by Brush and Dana (1880, p. 283), rose red in color. Possibly contains a phosphate-bearing impurity. G. J. Brush, analyst.

34. Near Leakey, Real County, Tex. (6 miles west of Leakey), in the Edwards Plateau. Nearly white bentonitic clay received by Dr. R. F. Ryan, Vacuum Oil Co., Houston, Tex. Wells (1937, p. 108). J. J. Fahey, analyst.

35. Twin Falls, Idaho. Clay encountered in tunnels of Twin Falls irrigation project. Tawny olive with a little buff-pink (R) material. Forms masses 2 to 14 inches, rarely several feet, in thickness. Commonly cut by minute fractures in which a darker-colored but equally pure clay has been deposited. (See pl. 3, B.) Submitted by Lynn Crandall, district engineer. Wells (1937, p. 98). J. J. Fahey, analyst.

36. Pala, Calif. Pegmatite clay, rose pink to deep rose pink (R). Associated with pink tourmaline and lepidolite in gem-bearing pegmatites. Collected by W. T. Schaller. (See pl. 7, B.) Wells (1937, p. 107). J. G. Fairchild, analyst.

37. Montmorillon, France. (See also sample 18.) Ross and Shannon (1926, p. 90). Earl V. Shannon, analyst.

38. Booneville, Miss. (2 miles east). Bentonite from Eutaw formation. Upper Cretaceous. Buff pink (R). Collected by Ross and Nutting. Unpublished analysis, J. G. Fairchild, analyst.

39. Maniquipi, Chihuahua, Mexico. Princessa mine. Nearly white. Occurs in fault zone in quartz latite. Collected by W. F. Foshag. Wells (1937, p. 98). E. T. Erickson, analyst.

40. Clairmont (2 miles north), Los Angeles County, Calif. Pegmatite clay, white to pale buff. Forms mass from 1 to 2 inches thick in a pegmatite. Described by Loudermilk and Woodford (1934, p. 263). J. D. Loudermilk, analyst.

41. Glen Riddle, Pa. Clay filling horizontal joint seams in gabbro described by Tomlinson and Meier (1937). Nearly white in color. Adolph E. Meier, analyst.

42. Pala, Calif. Pegmatite clay, similar to No. 26. Collected by W. T. Schaller. Unpublished analysis, F. A. Gonyer, analyst.

43. Clay from Master Products Corp., Los Angeles, Calif. Ross and Shannon (1926, p. 89). Earl V. Shannon, analyst.

44. Beidell, Colo. Gouge clay from the Esperanza mine at the gold and silver mining camp of Beidell, Saguache County, Colo. (U. S. Nat. Mus. No. 93239), described by Larsen and Wherry (1917, 1925) and by Ross and Shannon (1925). It forms masses of gouge clay as much as several feet across and occurs as platy masses as much as several inches across. The color is pecan brown (R) with a slightly reddish tint, and the material is very plastic. Collected by Larsen. Edgar T. Wherry, analyst.

45. Embudo, N. Mex. Pegmatite clay, collected by Frank Hess. Purified by washing. Ross and Shannon (1926, p. 91). Earl V. Shannon, analyst.

46. Fairview, Utah. Submitted by R. O. Baker, Fairview, Utah. Shows very fine laminations. Color, ferruginous (P). Wells (1937, p. 90). J. G. Fairchild, analyst.

47. Wagon Wheel Gap, Colo. "Gouge clay." Mouse gray (R), forms platy masses as much as a foot across in a fluorite mine. Collected by Ross. Unpublished analysis. Charles Milton, analyst.

48. South Bosque, McLennan County, Tex. Bentonitic clay collected by L. W. Stephenson. Unpublished analysis, J. J. Fahey, analyst.

49. Carson District, Idaho. Blackjack vein, collected by Shannon. Ross and Shannon (1926, p. 94). Earl V. Shannon, analyst.

50. Pontotoc, Miss. (railroad cut $\frac{1}{2}$ mile southwest of Pontotoc). Color, warm buff (R). Clay material, which has replaced calcareous shells. Collected by L. W. Stephenson and described by Ross and Stephenson (1939). (See pl. 7, A.) J. G. Fairchild, analyst.

51. Nashville, Ark. Color, mineral gray (R). Bentonitic clay associated with volcanic rock minerals (phenocrysts of orthoclase), purified by washing. Collected by Ross. Ross and Shannon (1926, p. 94). Earl V. Shannon, analyst.

52. Nashville, Ark. Same locality as sample 51. Earl V. Shannon, analyst.

53. Ancon, Canal Zone. Blackish-brown (R) laminated clay; contains organic matter. Ross and Shannon (1926, p. 9^a). J. G. Fairchild, analyst.

54. Roseland, Va. Mine, American Rutile Co. Clay filling joint cracks in anorthosite. Pinkish cinnamon (R). Collected by Ross. Unpublished analysis, R. C. Wells, analyst.

NONTRONITES

55. Sary-Krym, near Mariupol, southern Russia. Nontronite. Described by Serdiuchenko (1929) as occurring in the graphite mines of Sary-Krym, about 12 kilometers north of Mariupol in a region of the Priasov crystalline slates. It forms platy crusts, which are dark olive or locally yellow in color. Serdiuchenko, analyst.

56. Woody, Calif. Nontronite from veinlets as much as 1 inch across in a garnet-pyroxene rock that represents roof pendants of a metamorphosed limestone included in granodiorite. Larsen and Steiger (1928). Earl V. Shannon, analyst.

57. Petrovsk, Krivoi-Rog region, southern Russia. Nontronite described by Serdiuchenko (1929) as occurring with graphite in layers, in veins 1 to 5 mm. by 1 to 2 cm., and as single phenocrysts in crystalline rocks. It is dark green to yellow green and is plastic where fresh. Serdiuchenko, analyst.

58. Spokane, Wash. Nontronite-beidellite. Intermediate between nontronite and beidellite, thus showing the isomorphism of the iron and alumina end members. Yellowish citrine (R) claylike material lying between two basalt flows. Collected by Edward Sampson. Ross and Shannon (1926, p. 94). Shannon, analyst.

59. Near Spokane, Wash. (about 17 miles southeast of Spokane in SW $\frac{1}{4}$, sec. 5, T. 23 N., R. 45 E.). Relations unknown. Color clear dull yellowish green (R). Unpublished analysis, J. G. Fairchild, analyst.

60. Santa Rita, N. Mex. Yellowish-green claylike material. Wells (1937, p. 109). R. C. Wells, analyst.

61. Chevy Chase, Md. Claylike zone in schist, associated with a little mica, which was removed by washing. Collected by P. G. Nutting. Wells (1937, p. 109). R. C. Wells, analyst.

62. Szekes-Fejervar, Hungary. "Pinguite"-like decomposition product with grass-green color from Rac quarry. Described by Erdelyi (1927). Excess $Fe_2O_3 = 0.80$. Erdelyi, analyst.

63. Sary-Krym, near Mariupol, southern Russia. Same locality as sample 55. Serdiuchenko (1929), analyst.

64. Paulusbrunn, near Tachau, Germany. Same locality as sample 67. Rosenbusch (1927, p. 594). Gulmann, analyst.

65. Sandy Ridge, N. C. Forms veinlets 5 to 10 mm. wide in schist. Collected by J. B. E. Shaffer, Sandy Ridge. Color, clear dull green (R). (See electron micrograph, pl. 7, B.) Wells (1937, p. 109). R. C. Wells, analyst.

66. Spruce Pine, N. C. Nontronite. Yellowish-green clay. Alteration zone in gneiss; collected by P. G. Nutting. Wells (1937, p. 109). L. T. Richardson, analyst.

67. Paulusbrunn, near Tachau, Germany. Described by Noll (1930) as light-green compact clay, which is an alteration product of hornblende-rich gneiss. Noll, analyst.

SAMPLES FROM SOILS AND CHROMIUM-BEARING SAMPLES

68. Maniquipi, Chihuahua, Mexico. Princessa mine. Liver brown (R). Associated with sample 39. Collected by W. F. Foshag. Wells (1937, p. 98). E. T. Erickson, analyst. An X-ray examination shows that this clay from the Princessa mine contains about 20 to 25 percent of kaolin, together with a small proportion of ferric iron. Notwithstanding this admixture, it gives very definite optical properties characteristic of a member of the montmorillonite group and is included to illustrate the intimacy of the admixture of clays that may occur in some samples.

69. Rothamstead, England. A soil clay of the montmorillonite type described by Marshall (1935b). Marshall, analyst.

70. Missouri. Putnam clay. A very pure montmorillonite type of soil clay separated and analyzed by Marshall (1935b). The Putnam clay characterizes soils in southern Ohio, Indiana, and Illinois and in northeastern Missouri.

71. Emerald mines, Urals. Beidellite (chromian). Analysis listed by Serdiuchenko (1933).

72. Cheghet-Lakhran Valley, Urals. Beidellite (chromian). Serdiuchenko (1933) reports that it overlies the metamorphosed serpentine and underlies the ore. Occurs as a discontinuous lenticular bed of olive-green clay matter, 40 cm. thick. L. N. Venerovsky, analyst.

73. Same as sample 72, but material washed. L. N. Venerovsky, analyst.

74. Bolshia-Laba River. Beidellite (chromian). Reported by Serdiuchenko (1933) to form emerald-green pebbles and spots in the Carboniferous red conglomerate along the upper course of the river. N. Nikolski and E. Marklennikova, analysts.

75. Gedmayshkh Valley, in the territory of the Malka iron-chrome-nickel deposits, Kabardino-Balkaria. Beidellite (chromian). Reported by Serdiuchenko (1933) to serve as a cementing material in a thin bed of sandstone lying on a green serpentine rock. S. T. Derkacheva, analyst.

SAPONITE-HECTORITE SERIES

76. Hector, San Bernardino County, Calif. Hectorite. Material received from Harold R. Eyrich. New analysis, R. E. Stevens, analyst. Occurs about 3 miles south of Hector. Described by Foshag and Woodford (1936) as a bentonitic magnesian clay mineral. It is overlain by a basaltic lava flow and developed at the top and in the cracks of a tuff bed. It seems evident that highly magnesian solutions have caused the formation of a magnesian bentonite rather than the normal aluminum mineral. The material has a marked translucency when moist and resembles very pure tallow, but it is pure white and opaque when dry.

77. Montreal, Canada. Saponite collected by Dr. J. A. Bancroft and described by Graham (1918), who reports as follows: "The saponite * * * was * * * collected near the western end of the Canadian Northern Railway tunnel * * * which passes from east to west under Mont Royal * * * and traverses the intrusive contact between the nepheline syenite and Trenton limestone. When first collected, this substance is somewhat translucent, soft, and quite plastic, with very much the consistency and appearance of candle grease. * * * The dry material is soft, has a somewhat soapy feel when rubbed between the fingers, and does not adhere to the tongue. Moistened with water, it forms a claylike paste."

78. Svärdsjö, Sweden. Original analysis of saponite by L. F. Svanberg (1842).

79. Ahmeek mine, Mich. Saponite.

80. Kearsarge mine, Mich. Saponite.

The materials from the Ahmeek and Kearsarge mines of Michigan have been described by Palache and Vassar (1925) as follows: "Saponite was found in quantity in the South Kearsarge mine and in less abundance but better crystallized in the Ahmeek mine. In the former it is one of the latest hydrothermal minerals to form, occurring in cavities left by excessive solution during replacement of the amygdaloid. It thus lines the walls, a last generation of adularia alone being later. In the Ahmeek mine it was found chiefly as solid filling of replacement vugs in which it surrounded crystals of copper and quartz; it was also found with copper and epidote crystals in open cavities, as minute stalactites as much as half an inch in length but less than a tenth of an inch in diameter. These were composed of spherulitic groups of fibers and plates, radiate to axial lines. It is white to light-buff colored, 1 or less in hardness, with an unctuous feel, somewhat plastic, but not adherent to the tongue." Helen E. Vassar, analyst.

81. San Bernardino County, Calif. (12 miles south of Needles). From a shaft about 20 feet deep. Obtained through Frank Sanborn, California State Mining Bureau. Walter L. Gibson, analyst.

82. Glasgow, Scotland. U. S. Nat. Mus. No. 4727. Wells (1937, p. 110). L. T. Richardson, analyst.

SAMPLES CONTAINING SILICA OR AN IRON-BEARING IMPURITY

83. Quilchina, British Columbia. Soda bentonite. Collected by Hugh Spence (1924, p. 14). Described by Ross and Shannon (1926, p. 84). Earl V. Shannon, analyst.

84. Santa Rita, N. Mex. Bentonite (montmorillonite). Nearly pure white; free from visible impurities but contains a little cristoballite. Collected by Ross. Unpublished analysis, R. E. Stevens, analyst.

85. Tierra Amarilla grant (three miles east of), N. Mex. Bentonite. Pink sample freed from crystal grains by washing. Collected by Ross (1926, p. 89). Earl V. Shannon, analyst.

86. Westcliffe, Colo. Unpublished analysis, R. E. Stevens, analyst.

87. Baschenowski, Russia. Nontronite from an asbestos mine. Described by Kurnakov and Cernykh (1929). V. V. Cernykh, analyst.

88. From Magnitnaja Mountains, Urals. Nontronite. Described by Kurnakov and Cernykh (1929). Excess $Fe_2O_3 = 14.68$. A. N. Zavaritsch, analyst.

89. Okhansk, Siberia. Volchonskoite; material originally described by Kammerer (1831), redescribed by Kersten (1839). Correlated with nontronite by Serdiuchenko (1933). Ilimow, analyst.

90. Woody, Calif. Nontronite with a somewhat different origin from sample 56, also described by Larsen and Steiger (1928). Found at the Woody locality and at many contact metamorphic garnet-hedenbergite zones. It is a platy to fibrous, citron-green to light yellowish green aggregate, derived from the alteration (probably hydrothermal) of hedenbergite. George Steiger, analyst.

91. Unghwar, Hungary. The "chloropal" described by Bernhardt and Brandes (1822). Described as occurring mixed with opal. Brandes, analyst. The United States National Museum collection contains chloropal from Unghwar, specimen 3882.

92. "Stilpnochloran" from Gobitschau, Moravia. Described by Holzner (1934) as being light-brown fibrous material. Gruner (1935) studied the material by X-ray and reported that it is structurally identical with nontronite. He also reports that Holzner stated in a private communication that he suspected that the material was identical with nontronite.

93. Morenci, Ariz. "Morencite." (U. S. Nat. Mus. No. 86033.) Described by Lindgren and Hillebrand (1904) as follows: "In a lime shale on the intermediate level of the Arizona Central mine, Morenci, 200 feet below the surface, brownish or greenish spreading masses are found, containing brownish-yellow silky seams. The enclosing material consists largely of the same material as the seams, but impure and mixed with a little chlorite and pyrite. * * * The minute fibers are brownish yellow and slightly pleochroic." Hillebrand, analyst.

94. St. Andreasberg, Harz. Nontronite. Collected 1920. Rose Geilmann, analyst.

95. St. Andreasberg, Harz. Nontronite. Described by Iskud (1935) as occurring as fine fibers.

96. Okhansk, Siberia. Described by Kokscharow (1858). V. Iwanow, analyst.

97. Baltatarak, Kazakstan. Nontronite described by Serdiuchenko and Iskull (1933) as follows: "The nontronite is associated with graphite deposits, which are confined to metamorphic schists, traversed by granitic rocks. The nontronite is the result of reactions in the zone of weathering." Serdiuchenko, analyst.

98. Island of Magee, County Antrim. Nontronite. Described by Tomkief (1934). Occurs, together with calcite, in cavities in a basalt agglomerate. Excess $Fe_2O_3 = 1.60$.

99. Nontron, France. Nontronite, described by Berthier (1829), forms onionlike masses associated with manganese ore of Perigueux near the village of Saint Pardoux. Specimens containing a chlorite or vermiculite impurity, probably as mixed layers, or an iron-bearing impurity.

100. Cathkin Hills, Blackburn, Scotland. Saponite (bowlingite). Described by Caillere (1935).

101. Webster, N. C. Nickel saponite. The dunite of the Webster area is cut by hydrothermal veins in which talc and anthophyllite form the borders in contact with dunite and vermiculite commonly forms the middle portion. A few of the larger veins contain discontinuous lenses of oligoclase in their middle parts. During weathering the small proportion of nickel in the olivine (commonly about 0.25 percent NiO) is released and tends to become fixed in the vermiculite. Further weathering converts part of the vermiculite to a very plastic apple-green clay. The material was washed, and the portion that stayed in almost permanent suspension was analyzed. Unpublished analysis, R. C. Wells, analyst.

102. Cathkin Hills, Scotland. Saponite (bowlingite). Described by Caillere (1935).

CHEMICAL ANALYSES

The following tables give chemical analyses of clays belonging to the montmorillonite group. Although the greater part of these analyses have been made in the course of the present work, some were published in earlier papers. A few have been copied from recent papers on the clay minerals, especially some of the analyses of nontronites and chromium-bearing beidellites.

TABLE 1.—Analyses of montmorillonite-beidellite series

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
SiO ₂	52.30	52.43	54.58	53.88	51.37	52.09	50.33	54.46	53.96	54.28	50.41	51.64	50.50	53.02	50.30	50.20	50.86	51.14
Al ₂ O ₃	14.43	15.95	16.44	11.66	15.41	18.98	16.42	16.84	15.44	17.92	13.25	18.25	17.23	18.50	15.96	16.19	18.76	19.76
Fe ₂ O ₃	2.00	1.42	2.59	4.60	0.6	2.42	3.36	1.12	3.88	2.51	1.24	2.36	2.33	4.13	2.07
FeO.....	Tr.	1.40	None
MnO.....	0.5	1.8	0.6
MgO.....	6.15	5.02	4.90	8.61	6.22	3.80	4.10	4.84	6.99	3.76	8.27	3.41	3.71	4.04	6.53	4.12	3.48	3.22
CaO.....	2.12	2.97	1.56	Tr.	3.28	1.39	3.20	1.80	2.18	2.40	8.0	1.24	2.18	1.76	1.62
K ₂ O.....
Na ₂ O.....
Li ₂ O.....
CO ₂
TiO ₂
Cl.....
P ₂ O ₅
SO ₃
Carbon.....
H ₂ O.....	15.78	13.96	11.10	8.21	15.76	14.75
H ₂ O+.....	6.55	7.60	5.49	9.98	8.20	7.46	23.95	16.10	6.34	7.32	10.24	6.33	7.41	5.44	28.61	15.58	32.84	14.81
Total.....	100.62	100.13	99.94	99.82	99.65	100.48	99.73	99.60	100.76	100.35	99.78	99.88	100.66	100.04	100.14	100.50	99.64	99.75

	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
SiO ₂	55.44	50.37	49.48	50.44	50.39	51.50	54.88	50.03	52.08	54.28	49.20	53.50	49.48	49.56	51.20	51.74	49.55	50.06
Al ₂ O ₃	20.14	17.11	16.30	16.26	17.37	19.44	19.92	16.75	18.20	22.94	17.60	21.57	17.75	15.08	22.14	22.81	17.78	21.32
Fe ₂ O ₃	3.67	2.68	3.12	5.38	2.84	4.10	5.83	2.88	1.60	3.28	3.33	3.44	3.9	6.61
FeO.....
MnO.....
MgO.....	2.49	4.59	4.69	3.92	4.56	5.07	2.83	2.75	4.48	2.92	5.08	1.89	4.42	7.84	3.53	3.32	3.24	4.42
CaO.....
K ₂ O.....
Na ₂ O.....	2.75
Li ₂ O.....
CO ₂
TiO ₂
Cl.....
P ₂ O ₅
SO ₃
Carbon.....
H ₂ O.....
H ₂ O+.....	14.70	12.29	14.41	16.00	13.31	14.50	8.10	13.53	20.80	7.82	25.52	15.20	18.26	22.96	17.08	11.84	15.45	14.05
Total.....	100.69	100.05	100.65	99.44	100.37	99.33	99.50	100.03	100.72	100.24	100.52	99.78	99.82	100.37	99.83	99.83	100.09	99.54

	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
SiO ₂	48.60	50.53	49.34	49.70	48.79	50.72	50.28	47.28	48.24	46.04	48.05	51.37	45.32	46.95	45.12	45.52	44.02	44.23
Al ₂ O ₃	20.03	19.31	22.88	22.10	20.73	22.14	20.00	20.27	22.32	22.60	23.01	26.80	27.84	27.26	28.24	27.52	28.90	31.30
Fe ₂ O ₃	1.25	7.25	2.36	2.12
FeO.....
MnO.....
MgO.....	5.24	2.60	1.67	2.85	5.40	4.28	4.60	7.70	6.64	1.85	2.14	4.42	1.39	2.32	3.00	
CaO.....	1.72
K ₂ O.....
Na ₂ O.....
Li ₂ O.....
CO ₂
TiO ₂
Cl.....
P ₂ O ₅
SO ₃
Carbon.....
H ₂ O.....
H ₂ O+.....	21.52	10.66	14.77	21.14	23.74	11.56	19.60	19.72	20.84	10.00	6.14	22.64	11.10	18.72	19.60	18.64	3.97
Total.....	98.52	100.64	100.25	100.44	99.84	100.10	99.56	100.37	100.44	99.99	99.24	100.68	99.74	100.43	99.40	98.96	99.42	100.10

1—Cl=0.07. 2CuO=0.01; ZnO=0.10; CoO=0.12; NiO=None. 3BaO=0.16; 4Soluble SiO₂=0.45. 5SO₃=0.11.

- Santa Cruz, N. Mex.
- Cilly, Styria.
- Amargosa Valley, Calif.
- Tehachpi, Calif.
- Dixon, N. Mex.
- Tatatila, Mexico.
- Maricopa, Calif.
- Conejos quadrangle, Colo.
- San Diego County, Calif.
- Nieder-Bayern, Germany
- Near Rideout, Utah.
- Ardmore, S. Dak.
- Irish Creek, Va.
- Hector, Calif.
- Otay, Calif.
- Polkville, Miss.
- Angtar, France.
- Montmorillon, France.

- Upton, Wyo.
- Lemon, Miss.
- Spokane, Wash.
- Atzacozalco, Mexico.
- Lemon, Miss.
- Mexico.
- Rosedale, Alberta, Canada.
- Santa Monica, Calif.
- West of San Antonio, Tex.
- Greenwood, Maine.
- Fort Steel, Wyo.
- Osage, Wyo.
- Lemon, Miss.
- Otay, Calif.
- Branchville, Conn.
- Leakey, Tex.
- Twin Falls, Idaho.
- Pala, Calif.

- Montmorillon, France.
- Booneville, Miss.
- Maniquipi, Mexico.
- Clairmont, Calif.
- Glen Riddle, Pa.
- Pala, Calif.
- Los Angeles, Calif.
- Beidell, Colo.
- Embudo, N. Mex.
- Fairview, Utah.
- Wagon Wheel Gap, Colo.
- South Bosque, Tex.
- Carson District, Nev.
- Pontotoc, Miss.
- Nashville, Ark.
- Nashville, Ark.
- Aneon, Canal Zone.
- Roseland, Va.

TABLE 2.—Analyses of nontronite

	55	56	57	58	59	60	61
SiO ₂	49.75	43.51	49.50	46.06	40.72	40.48	46.65
Al ₂ O ₃	10.06	2.94	16.18	12.22	4.96	6.00	17.65
Fe ₂ O ₃	22.06	28.62	13.08	13.54	29.57	29.33	13.39
FeO		.99		.28	.71	.26	Tr.?
MgO	.25	.05	.61	1.62	.74	.31	Tr.?
CaO	2.68	2.22	2.57	1.66	1.98	2.90	1.21
K ₂ O							
Na ₂ O							.55
TiO ₂				.84	.02		
CO ₂						None	
H ₂ O—	9.43	14.05	7.76	17.26	15.46	15.39	5.55
H ₂ O+	6.44	6.62	9.35		6.66	5.65	10.81
Total	100.67	100.02	99.05	98.48	100.82	100.32	100.81

	62	63	64	65	66	67
SiO ₂	39.54	42.74	40.42	41.38	41.88	40.02
Al ₂ O ₃	5.04	9.76	10.42	9.84	11.90	10.55
Fe ₂ O ₃	30.32	26.71	25.31	27.47	26.20	26.16
FeO	Var.		.45	Tr.?	Tr.?	1.37
MgO	Tr.	1.06	.13	Tr.?	.10	
CaO	.04	1.94	.38	Tr.?	.67	
K ₂ O	.32			Tr.?	.52	
Na ₂ O	.24					
TiO ₂						
CO ₂						
H ₂ O—		10.42		12.10	7.67	
H ₂ O+	22.27	6.74	21.80	9.25	10.78	21.83
Total	98.86	99.37	98.91	100.04	99.72	99.93

¹CuO=1.02.

²SrO=0.09; BaO=Tr.

- 55. Stary-Krym, Russia.
- 56. Woody, Calif.
- 57. Petrovsk, Krivoi-Rog region, Russia.
- 58. Spokane, Wash.
- 59. Spokane, Wash.
- 60. Santa Rita, N. Mex.
- 61. Chevy Chase, Md.

- 62. Szekes-Fejevar, Hungary.
- 63. Stary-Krym, Russia.
- 64. Tachau, Germany.
- 65. Sandy Ridge, N. C.
- 66. Spruce Pine, N. C.
- 67. Tachau, Germany.

TABLE 3.—Analyses of samples from soils and chromium-bearing specimens from Russia

	68	69	70	71	72	73	74	75
SiO ₂	43.76	45.04	49.50	45.83	43.14	44.47	46.09	36.69
Al ₂ O ₃	27.88	24.51	21.74	18.55	16.07	19.63	24.04	16.77
Fe ₂ O ₃	6.42	11.90	8.81	9.29	4.70	10.85	3.96	8.70
Cr ₂ O ₃				.74	5.02	1.02	1.12	3.76
FeO	Tr.		.42	.71	.61	.47	.33	7.83
MnO		.03	.02	Tr.	.21	Tr.	.49	
NiO				.09	.30	.10	Tr.	
MgO	1.23	1.91	1.99	2.12	3.45	1.86	6.99	1.60
CaO	.90		.28	1.69	1.46	1.50	1.86	2.57
K ₂ O	1.18	1.65	.94	.31		.15		
Na ₂ O	.30	.20	.44	.32		.14		
TiO ₂	.30	.53	.70	.22	.96	.20	1.04	
P ₂ O ₅		.58	2.16					
H ₂ O—	10.59				16.66		5.67	8.42
H ₂ O+	7.67	13.20	13.05	20.20	7.32	20.00	7.26	12.90
Total	100.23	99.55	100.05	100.07	100.06	100.39	98.85	99.24

¹P=0.01; S=0.15.

- 68. Maniquipi, Mexico.
- 69. Rothamstead, England.
- 70. Putnam clay, Missouri, U. S. A.
- 71. Emerald mines, Urals.
- 72. Cheghet-Lakhran Valley, Urals.
- 73. Cheghet-Lakhran Valley, Urals.
- 74. Bolshia-Laba River.
- 75. Gedmayshkh Valley.

TABLE 4.—Analyses of hectorite and saponite

	76	77	78	79	80	81	82
SiO ₂	55.86	46.45	50.8	42.99	42.78	44.00	40.16
Al ₂ O ₃	.13	3.32	9.4	6.26	6.44	10.60	8.03
Fe ₂ O ₃	.03	.42	2.0	1.83		Tr.	8.50
FeO		.72		2.57		1.27	3.83
MnO	None		.11	.12			
MgO	25.03	25.91	26.5	22.96	24.78	24.30	19.40
CaO	Tr.		.7	2.03	2.35	2.00	1.91
K ₂ O	.10			Tr.	Tr.		Tr.
Na ₂ O	2.68			1.04	.75		
Li ₂ O	1.05						
TiO ₂	None						
CO ₂							
F	5.96						
H ₂ O—	9.90	14.48		18.65	13.96	12.60	11.15
H ₂ O+	2.24	8.13	10.5	6.85	7.90	6.20	7.60
Total	102.98	99.43	99.9	100.29	100.35	99.70	100.58

¹O=F, 102.98-2.51=100.47.

- 76. Hector, Calif.
- 77. Montreal, Canada.
- 78. Svgrdsjö, Sweden.
- 79. Ahmeek mine, Mich.
- 80. Kearsarge mine, Mich.
- 81. San Bernardino County, Calif.
- 82. Glasgow, Scotland.

TABLE 5.—Analyses of samples containing excess silica

	83	84	85	86
SiO ₂	56.20	54.15	51.56	54.77
Al ₂ O ₃	13.20	15.99	13.42	15.88
Fe ₂ O ₃	5.08	.59	3.22	.58
FeO		.06		.62
MgO	2.92	4.48	4.94	4.99
CaO	1.60	1.90	2.04	2.08
K ₂ O		.19	.38	.25
Na ₂ O		.42	.24	1.06
TiO ₂		.11	.78	.17
CO ₂				
H ₂ O—	20.32	13.29	23.46	9.26
H ₂ O+		8.99		10.25
Total	99.32	100.17	100.04	99.91

- 83. Quilchina, British Columbia.
- 84. Santa Rita, N. Mex.

- 85. Tierra Amarilla, N. Mex.
- 86. Westcliffe, Colo.

TABLE 6.—Analyses of nontronites containing an iron-bearing impurity

	87	88	89	90	91	92	93
SiO ₂	33.98	31.09	36.84	47.51	45.00	36.45	45.74
Al ₂ O ₃	2.77	5.96	3.50	3.37	.75	6.03	1.98
Fe ₂ O ₃	33.19	40.77	17.85	35.17	32.00	34.24	29.68
Cr ₂ O ₃			18.85				
FeO	Tr.	Tr.				None	.83
MnO						.04	Tr.
MgO	3.98	.82		1.40	2.00	.97	3.99
CaO	.98	2.32	1.89	2.50		1.91	1.61
K ₂ O				.06		.35	.20
Na ₂ O				.09		None	.10
TiO ₂				Tr.		.02	Tr.
CO ₂						.31	.18
H ₂ O—	19.93	19.18	22.46	7.16	20.00	11.01	13.92
H ₂ O+				5.90		9.20	
Total	99.83	100.14	100.89	100.16	99.75	100.53	98.89

	94	95	96	97	98	99
SiO ₂	39.88	42.02	37.01	50.41	42.08	48.82
Al ₂ O ₃	.54	6.18	6.47	2.07	3.93	4.30
Fe ₂ O ₃	36.73	28.65	10.43	31.11	31.69	35.83
Cr ₂ O ₃			17.98			
MnO	.41	.44		1.74	.09	
FeO	Tr.		1.66	.27		.63
MgO	.33	.40	1.91	2.14	.53	.35
CaO	2.23	2.18		.79	1.99	
K ₂ O	.02	.03			.09	
Na ₂ O	.01	.01			.12	
TiO ₂						
P ₂ O ₅	.06	.05				
H ₂ O—	14.06			2.22	8.50	
H ₂ O+	6.08	20.45	21.84	9.66	11.30	9.66
Total	100.35	100.41	98.26	100.41	100.27	99.64

¹FeS=0.66.

²PbO=1.01.

- 87. Baschenowski, Russia.
- 88. Magnitnaja Mountains, Urals.
- 89. Okhansk, Siberia.
- 90. Woody, Calif.
- 91. Ungvár, Hungary.
- 92. Gobitschau, Moravia.
- 93. Morenci, Ariz.

- 94. St. Andreasberg, Harz.
- 95. St. Andreasberg, Harz.
- 96. Okhansk, Siberia.
- 97. Baltatarak, Kazakistan.
- 98. Island of Magee, County Antrim
- 99. Nontron, France.

TABLE 7.—Analyses of samples containing chlorite, vermiculite, or other iron-bearing impurity

	100	101	102
SiO ₂	40.04	39.14	39.37
Al ₂ O ₃	6.76	7.00	8.11
Fe ₂ O ₃	9.29	1.81	5.94
FeO	2.38		7.36
NiO		11.30	
MnO		.02	
MgO	19.13	22.15	21.47
CaO	2.27	.02	.69
K ₂ O		.08	
Na ₂ O		.07	.07
TiO ₂	.41	.07	
H ₂ O—	11.91	6.59	7.69
H ₂ O+	7.84	11.45	9.23
Total	100.03	99.70	99.93

- 100. Cathkin Hills, Scotland.
- 101. Webster, N. C.
- 102. Cathkin Hills, Scotland.

IMPURITIES IN CLAYS

All the analyses made in the course of this study and used in mineral interpretations have been on material whose purity and suitability for analysis have been studied under the petrographic microscope and much of it checked by X-ray. Other analyses whose descriptions indicated careful selection of material have been compiled from the literature. Nevertheless, in a material that is as fine-grained as the clays, minor impurities will escape detection in some of the materials. The most probable impurities are silica, which may be present in an amorphous condition or as cristobalite, and materials that are recorded as excess Al_2O_3 and Fe_2O_3 in the analysis and may be present as chlorite or more rarely as iron and aluminum oxides or hydrous oxides. Ferric oxide and hydroxide have so strong a pigmenting effect that any appreciable proportion of these impurities would be revealed by the color in most clays, but disseminated magnetite might not be so recorded. Aluminum hydroxide would not be so revealed and may be present to the extent of several percent in some specimens. Similar amounts of sulfides and sulfates were observed in several specimens. Other samples from soils and from some veins contain kaolin or excessive amounts of mica-like minerals, and are unsuitable as a basis for conclusions, but they have been included in the tables of analyses for purposes of illustration. The same is true of a group of analyses high in silica or in ferric iron.

Some of the specimens undoubtedly contained excess alkali salts adsorbed as such. Thus, a number of bentonites from arid regions have a marked saline taste. A few of the darker-colored ones contained small amounts of organic matter, and carbonates were undoubtedly present in a few samples. These impurities, however, are not expected to exceed a few tenths of a percent in most of the specimens.

Titanium may be present as part of the crystal lattice (see p. 37), but it probably is more commonly present as an impurity—rutile, anatase, or so-called leucoxene. Rutile is a common detrital mineral in sedimentary materials, and ilmenite commonly alters to one of the materials known as leucoxene. Leucoxene has been studied by Tyler and Marsden (1938), who found that it was a microcrystalline form of rutile, anatase, or perhaps brookite. Tests in the laboratories of the Geological Survey showed that leucoxene from Roseland, Va., was sphene, whereas samples from Magnet Cove, Ark., were anatase. Leucoxene occurs in clays as irregular areas that are almost opaque to transmitted light but are white or rusty brown by reflected light. Areas of leucoxene in clay materials from Magnet Cove are shown in plates 1 and 2, and similar material is commonly present in residual clays, especially those from ferromagnesian rocks. In bentonites the titanium may have been present as part of the original glass or as minute microlites, but this titanium would not normally exceed a fraction of one percent.

Some specimens no doubt contain mica-like minerals as mixed-layer minerals with montmorillonite (see p. 29), and finely disseminated detrital mica commonly is present in sedimentary clay materials. These are to be suspected when the amount of K_2O is as much as one percent. (See analyses 46, 47, 54, 68, 69.) Kaolinite and other clay minerals of the kaolin type are associated with montmorillonite in many soils but probably are not even present as minor impurities in the nonsoil clays used in this study. None was detected in samples

examined by differential thermal methods, but a kaolin-bearing clay from Maniquipi, Mexico, is represented by analysis 68.

A consideration of the relation between the various components indicates that the total amount of impurities, other than admixtures of mixed-layer minerals in the montmorillonites used in mineral interpretation, might be as great as 5 percent in a few of the specimens. However, in all but a few of the analyses impurities probably do not exceed one percent. The presence of even greater amounts of impurities does not seriously impair the calculations to be made and does not interfere at all with the drawing of logical conclusions about chemical relationships, since these depend upon results from many samples.

Several chemical analyses show an excess of silica over that required for the montmorillonite formula when only Si^{+4} is assumed to be present in tetrahedral coordination. Though some of these undoubtedly contain cristobalite, as has been noted by Gruner (1940a, 1490b), some probably contain no crystalline nonclay mineral. Reference to pages 43, 44 and tables 5 and 14 shows that the excess of SiO_2 commonly is small and in the materials here considered does not approach the large amount observed by Gruner.

Some of the specimens, the analyses of which can be interpreted in terms of a montmorillonite formula, nevertheless, probably contain small amounts of silica as an impurity. The significance of this will be discussed later.

Of the high-silica clays, the material from Quilchina, British Columbia, contained an unusually large excess of SiO_2 , although careful examination under the microscope revealed no recognizable impurity that would give such an excess. This material and a check sample from Otay, Calif., were tested for soluble silica. A one-gram sample of each clay was added to 100 cc. of water, together with 5 grams of sodium carbonate, and boiled for 5 minutes. The filtrate was tested for SiO_2 and Al_2O_3 . The Quilchina sample gave 17.50 percent of soluble SiO_2 and 0.81 percent of Al_2O_3 . The Otay sample gave 0.16 percent of soluble SiO_2 and 0.07 percent of Al_2O_3 . Crystalline forms of SiO_2 are not appreciably soluble under such treatments. This test indicated that a normal bentonite like that from Otay was not appreciably broken down by the sodium-carbonate treatment. On the other hand, the Quilchina sample contained 17.5 percent of soluble SiO_2 , but with only a small proportion of Al_2O_3 . This indicates that the silica was not released by breaking down the clay mineral itself and suggests very strongly that the excess silica of the Quilchina sample was an opaline form of SiO_2 , perhaps adsorbed between the crystal sheets. Sodium clays, a type that includes the Quilchina clay, appear to be commonly characterized by an excess of SiO_2 .

Another moderately high-silica material is that from Santa Rita, N. Mex., which contains an excess of 4 percent SiO_2 after all the Al_2O_3 and MgO have been combined with SiO_2 in the ratio of 2 to 4. This clay showed no visible crystalline impurities under the microscope, either in its original form or after a delicate test devised by Nutting. This test involves a 24-hour treatment on the steam bath with dilute HCl , which breaks montmorillonite down completely into an amorphous hydrated form of SiO_2 with a very low index of refraction. Any anisotropic crystalline impurities, even though unusually minute, tend to stand out as birefracting material with an index of refraction much higher than that

of the silica residue; even isotropic materials are revealed by their higher index of refraction. The Santa Rita sample seemed unusually pure even under this test. This material was examined by X-ray diffraction and found to contain appreciable amounts of cristobalite.

This study has made use of a large number of analyses of montmorillonite derived from bentonites, and this is due largely to the geologic relations under which bentonite forms. These relations go far toward assuring materials of much more than ordinary chemical purity. The volcanic glass from which bentonites are derived was uniform in chemical composition throughout any one deposit. The alteration of this glass to clay material occurred under conditions that favored the attainment of equilibrium. These two factors taken together tend to produce a single uniform mineral product. Where the exchangeable base is calcium, the excess silica and bases seem to have been effectively removed from the system. On the other hand, sodium clays commonly retain excess silica. The light color, the limpid character, and the low indices of refraction in small grains or in thin section greatly facilitate the detection of minute impurities. Most of the possible impurities have a much higher index of refraction and tend to stand out in relief or appear as opaque areas because of dispersal of light. Only amorphous silica, or the most finely disseminated cristobalite, will in general be beyond microscopic detection.

MINOR CONSTITUENTS

Several minor constituents that commonly occur in clays also may be considered. Marshall (1935) observes, "Phosphorous, in virtue of its small size and great tendency to assume a coordination number of 4, would appear well fitted to enter the Si layer, but this would require a positive charge of one unit per atom of phosphorous." This proxying of Si by P tends to be confirmed by the work of McConnell (1937) on the apatite group, where he shows that 17.31 percent of SiO_2 proxies P_2O_5 in ellestadite. The mineral wilkeite, which was described by Eakle and Rogers (1914) and belongs to the same group, contains 9.62 percent of SiO_2 .

Phosphorus was not determined in many of the analyses. Of the twelve specimens in which P_2O_5 is reported, the quantity exceeds 0.30 percent in only three—Putnam clay, Mo. (2.16 percent P_2O_5), Rothamstead, England (0.53 percent P_2O_5), and Branchville, Conn. (1.42 percent P_2O_5). The first two were materials that C. E. Marshall separated from soils and analyzed. They were not intended to be mineralogical specimens and the phosphorus probably was not a constituent of the montmorillonite or the mixed-layer minerals associated with those materials. The unusually high P_2O_5 in the Branchville clay strongly suggests the presence of a phosphorus mineral.

The form in which titanium may be present in clay materials is related to the mode of occurrence in related minerals and to the materials from which the clays are derived. Titanium is commonly present in the silicates having layer lattices. Since the work of W. H. Bragg, Ti^{+4} is generally considered to proxy for Al^{+3} or Mg^{+2} , having octahedral coordination with respect to oxygen, rather than for Si^{+4} , as had previously been the accepted interpretation. Thus TiO_2 may possibly be present as part of the crystal lattice of the clay minerals, but this does not necessarily follow, especially for clay minerals formed under cool, strongly hydrating conditions.

Some micas contain titanium that is clearly a part of

the crystal lattice, as in an unpublished analysis of biotite showing 5.26 percent of TiO_2 . On the other hand, micas commonly contain rutile needles, which tend to be arranged parallel to the basal cleavage of the mica and are the cause of the commonly observed asterism. Thus titanium may or may not be present as part of the crystal lattice of micas, which also is probably true of clay materials, especially as the discussion on page 36 indicates the common presence of leucoxene.

Constituents such as Mn^{+2} , Mn^{+3} , Ni^{+2} , Fe^{+2} , Li^{+1} , which can proxy for Al^{+3} , Fe^{+3} , Cr^{+3} , or Mg^{+2} in octahedral coordination, and Ba^{+2} or Sr^{+2} , which probably are situated outside the silicate layer, are to be considered as unusual rather than minor constituents. Under favorable geological environments there is no obvious reason why they should not become appreciable in amount.

Sulfides, sulfates, carbonates, and organic matter reported in some of the analyses are more likely present in impurities. Their quantities are invariably small.

BASE EXCHANGE

PHYSICAL CHEMISTRY OF BASE EXCHANGE

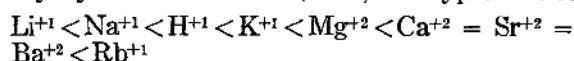
When a clay is treated with a solution of a salt a stoichiometric exchange of cations takes place. This process of cationic exchange, or base exchange as it generally is called, is a very important factor influencing the properties of clays and soils. The modern study of the subject was initiated by J. T. Way (1850, 1852, 1855) and H. S. Thompson (1850). They were concerned with the possible loss of soluble fertilizers from soil by leaching. Way demonstrated the equivalence of the exchange and further showed that it was due to organic matter and to hydrous aluminum silicates that lost the property upon ignition. His work came very close to being a discovery of the law of mass action and was so thorough that for half a century it was followed by none other of comparable value.

Natural zeolites and artificial permutites have pronounced base exchange. The name permutite is derived from *permutare*, to change. As these materials were formerly considered to be better-defined than the clays, they have in the past, unfortunately, been studied as prototypes; in fact, the literature prior to about 1930 is confused by a rather free usage of the term zeolite to include zeolites and permutites as well as clay materials that show base exchange. It failed to recognize that clays are neither. (See the reviews by Wiegner, 1831.)

The study of bentonites and related clays by Ross and Shannon (1926) had indicated that montmorillonite was present in soils, and by 1930 it had become generally recognized that montmorillonite was a common constituent of many soils. Kelley, Dore, and Brown (1931) and Kelley and Jenny (1936) shortly afterward set about determination of base-exchange reactions of bentonites. Their work was followed by a significant contribution of Marshall and Gupta (1933), who studied the dissociation of the montmorillonite salts in detail. This period in the development of concepts about the base exchange of montmorillonite has been reviewed by Kelley (1939).

Numerous studies have shown that various cations differ greatly in ease of replacement in montmorillonite. Thus if the mineral is treated with an equimolar mixture of a potassium and sodium salt much more K^{+1} than

Na⁺¹ will be taken up. These "orders of replacement" are discussed by Marshall and Gupta (1933) and more recently by Schachtschabel (1940). A typical series is:



Bivalent cations such as Ca⁺² are preferentially held with respect to univalent ions. Partly for this reason, the naturally occurring montmorillonites generally have Ca⁺² as the dominant exchangeable base, although some are sodium salts, others are magnesium salts, some are free acids, and some possibly are basic aluminum salts.

Although lithium and magnesium salts of montmorillonite can be prepared, these ions are essentially not exchangeable as found in the mineral. This is also true to a lesser extent for K⁺¹. In general Na⁺¹ is exchangeable, but it is not always completely so. The exchangeable ions are usually Ca⁺², Na⁺¹, Mg⁺², and some K⁺¹. A few of the specimens examined were found to be acid clays; that is, the exchangeable ion is in part H⁺¹.

Base-exchange capacities as determined for 22 of the analyzed specimens are listed in table 9. The clay used in these determinations was first dispersed by grinding in a slightly ammoniacal solution for a few minutes and then was placed on a shaking machine for 30 minutes. The dispersed clay was separated by centrifuging and then was treated with three successive lots of dilute (1 to 50) hydrochloric acid solutions in tenfold excess. After centrifuging, the acid clay was washed three times by resuspending in water and then twice in alcohol. It was dried in air at room temperature and then in vacuum over phosphorus pentoxide.

The acid equivalent of the treated clay was determined by titration of a weighed amount with sodium-hydroxide solution to pH 8.3, phenolphthalein being used as an indicator. In four samples H⁺¹ was displaced by shaking with several lots of neutral barium-chloride solution in large excess and titrated after removal of clay by centrifuging. The two methods gave close to the same result.

The numbers of milliequivalents per gram of Ca⁺², Na⁺¹, and K⁺¹ present in the various specimens also are listed in the table. The summation of these amounts agrees with the observed base exchange for seven of the clays—approximately one-third. It is too low for nine of them and too high for five. Three of the five that are high, contain large amounts of Na⁺¹ and are alkaline to phenolphthalein. This excess sodium in part is probably absorbed as a salt, such as the carbonate or chloride. It also is probable that in some of the samples the summation is too high because of the presence of nonexchangeable Na⁺¹ or K⁺¹ or the presence of calcareous impurities.

Alkalis were not determined on four of the samples for which the summations of the number of milliequivalents per gram of Na⁺¹, Ca⁺², and K⁺¹ were lower than the observed base exchanges. The amount of H⁺¹ in the nontronite sample from Sandy Ridge, N. C., was determined by direct titration and may be slightly low in comparison with the observed base exchange because of difficulty in thoroughly dispersing the clay. However, the possibility exists, in this and other clays with low summations, that other exchangeable ions, such as aluminum, iron, and magnesium, are present after the manner described by Paver and Marshall (1934). Samples 3, 22, and 24 were tested qualitatively for replaceable aluminum by shaking them with a large excess of 0.5N KCl solution having a pH equal to 4.5. Each

gave as much as 3 milligrams of Al₂O₃ per gram of clay in the first extraction and markedly less on successive extractions. It is thus apparent that appreciable aluminum, in terms of exchangeable base, can be present external to the lattice.

The nature of the replaceable ions in two clays containing a large amount of sodium was determined by K. J. Murata of the Geological Survey. One, the magnesium clay, hectorite, was from Hector, Calif., and the other was from Amargosa Valley, Calif. The clays were analyzed after washing with water to remove adsorbed salts and after treatment with ammonium-acetate solution in large excess. The results are given in table 8.

TABLE 8.—Analyses of hectorite and a clay from Amargosa Valley before and after treatment with ammonium acetate

	76	76a	76a (recalculated)	3	3a	3a (recalculated)
SiO ₂	57.54	56.31	57.54	55.43	58.13	56.43
R ₂ O ₃74	.77	.79	20.53	20.85	20.25
MgO.....	25.90	25.70	26.27	5.13	5.31	5.16
CaO.....	1.07	.50	.57	.10	None	None
Na ₂ O.....	2.21	.52	.53	2.87	.23	.27
K ₂ O.....	.16	.14	.14	.31	.10	.10
Li ₂ O.....	.80	.82	.84	.07	.05	.05
H ₂ O.....	4.28	9.25
Ignition loss H ₂ O.....	6.69	5.27
CO ₂	Present ²	None	None	None	None	None
MnO.....	.01	.01	.01	.02	.02	.02
Total.....	99.40	99.98

¹Water at 160° C.

²About 1 percent calcite visible under the microscope.

76. Hectorite, Hector, Calif., clay, untreated.

76a. Hectorite, Hector, Calif., clay, after treatment with ammonium acetate.

3. Amargosa Valley clay, untreated.

3a. Amargosa Valley clay, treated with ammonium acetate.

Possible exchange of lithium for magnesium was also studied by treating a sample of hectorite on a steam bath with normal lithium-acetate solution. After several weeks, the preparation was approximately freed of the solution and then was treated with fresh lithium-acetate, the treatment being continued for a total time of about 4 months. The preparation then was treated with two successive lots of normal ammonium-acetate solution and thoroughly washed to remove any Li⁺¹ held by ordinary base exchange. Before treatment the sample contained 0.80 percent of Li₂O and after treatment, 1.05 percent of Li₂O. This means that replacement of Mg⁺² by Li⁺¹ at most was very slight, and it confirms the view that these ions are within the crystal lattice and hence nonreplaceable.

Summation of the number of milliequivalents of replaced base per gram in the sample from Amargosa is 0.93 which is only slightly less than the value found by titration of the acid clay—1.00 milliequivalents per gram. The summation for the magnesium clay is 0.75 milliequivalents per gram if calcium is included. It further is to be noted that neither magnesium or lithium is replaced.

DETERMINATIONS OF EXCHANGEABLE BASES

Correlation between observed base-exchange capacities and analytical results might appear poor and confusing. The significant observation, however, is the directly observed value. It is surprisingly constant for the 22 clays examined, the range being between 0.66 and 1.00 milliequivalent per gram and the mean value being 0.84. This apparently is one of the most significant characteristics of montmorillonite and affords a key to the interpretation of the analytical results.

TABLE 9.—Base-exchange capacities of some montmorillonite clays

Sample No.	Locality	Silicon in tetrahedral coordination.	Milliequivalents of exchangeable base per gram.	Total milliequivalents of Ca ²⁺ , Na ⁺ , K ⁺ , H ⁺ per gram (from analyses).	Milliequivalents per gram of			
					Ca ²⁺	Na ⁺	K ⁺	H ⁺
8	Amargosa Valley, Calif.	3.90	1.00	1.04	0.04	0.93	0.07	
6	Tatahila, Mexico	3.94	.81	1.17	1.17			
10	Nieder-Bayern, Germany	3.92	.70	1.72	.64	.03	.05	
11	Ridgout, Utah	3.92	.85	1.58	.34	.20	.04	
12	Ardmore, S. Dak.	3.91	.66	1.47	.78	.67	.02	
13	Irish Creek, Va.	3.91	.97	1.91	.86		.05	
14	Hector, Calif.	3.90	.84	1.54	.28	1.22	.04	
15	Otay, Calif.	3.90	.85	1.92	.44	.38	.10	
19	Uptown, Wyo.	3.88	.85	1.20	.18	.89	.13	
20	Lemmon, Miss.	3.87	.88	1.62	.46	.16	.01	
22	Atzacapozalco, Mexico	3.87	.70	.25	.25			
24	Mexico	3.85	.70	.23	.17	.06		
27	W. of San Antonio, Tex.	3.84	.89	.81	.81			
28	Greenwood, Maine	3.83	.83	1.16	1.13	.03		
29	Fort Steel, Wyo.	3.83	1.00	.93	.93	.54		0.39
32	Otay, Calif.	3.80	.87	.39	.39			
36	Pala, Calif.	3.75	.80	.60	.45	.11	.04	
50	Pontotoc, Miss.	3.46	.67	.40		.07	.09	.24
52	Nashville, Ark.	3.29	.78	.19	.19			
58	Spokane, Wash.	3.63	.88	.60	.60			
65	Sandy Ridge, N. C.	3.42	.90	.74	0	0	Tr.	.74
84	Santa Rita, N. Mex.		.86	.84	.67	.13	.04	
..	Belle Fourche, S. Dak.		.77					

The base exchange of montmorillonite is generally held to be due to an excess negative charge of the silicate layers, but the possible location of the exchangeable ions with respect to the lattice has been a subject for much speculation. Hofmann, Endell, and Wilm (1934) suggested that these ions were around the edges of the cleavage plates and were held by lack of neutrality at those places arising from termination of the lattice. Marshall (1935) considered the exchangeable cations chiefly to be between the silicate layers and, to a lesser extent, within the layers. He indicated that K⁺, Na⁺, and Ca²⁺, particularly when nonexchangeable, might be in positions within the lattice layers. Van der Meulen (1935) raised the question whether films of mixed Al(OH)₃ and SiO₂·XH₂O gellies originating from surface hydrolysis of mineral particles could be a site of base exchange.

The work of Gieseck (1938) and of Hendricks (1941) on the salts of montmorillonite with organic cations shows that such ions give characteristic values to the cleavage spacing $d_{(001)}$, depending upon the size of the organic cations. The cleavage spacing of these salts, moreover, does not vary with water content, and the total sorption of water at a particular relative humidity is small compared with that found when the exchangeable ions are inorganic. Both of these properties indicate that the exchangeable ions are located between the silicate layers of the minerals.

Observations on the hydration of montmorillonites having various replaceable inorganic ions lead to a similar conclusion by Hendricks, Nelson, and Alexander (1940). Typical results are those obtained when the replaceable cation is Ca²⁺. The first step in the sorption of interlayer water is the hydration of each cation with six water molecules, which takes place at a relative humidity of about 5 percent. This is followed at higher relative humidities by further water sorption without increase in the cleavage spacing. The total amount of water taken up in these two steps corresponds to that required for the formation of a single layer of water molecules on the surfaces of the silicate layers.

The only reasonable positions for the exchangeable ions on the surfaces of the silicate layers are those oc-

cupied by K⁺ in the micas and Ca²⁺ in the brittle micas. Ions such as Na⁺, Ca²⁺, Mg²⁺, K⁺, probably occupy these positions. Absence of hydration for the proton, H⁺ in acid clays and its small size suggest that it is deeply buried within the silicate layer. These replaceable ions, however, do not tie the layers together as they do in micas unless the montmorillonite is heated to about 400° C.

MINERALOGY OF THE MONTMORILLONITE GROUP

GENERAL RELATIONS

The minerals of the montmorillonite group have been recognized as an allied series, but the chemical formulas either have not been established or, where given, are inadequate to express chemical composition or show relations within the group. The commonly accepted formula for montmorillonite neglects essential MgO; those for beidellite and nontronite fail to show the correct relations between Al₂O₃ and SiO₂; and no generally accepted formula for saponite is available.

A study of crystal structure by X-ray method has now made available a knowledge of the ionic substitutions occurring in silicates of the clay mineral type; without this knowledge no adequate development of mineral formulas is possible. X-ray diffraction studies have indicated the minerals that should be assigned to the montmorillonite group, and an adequate number of chemical analyses is now available to show the probable limits of variation.

Typical montmorillonite has been assumed to be composed only of Al₂O₃, SiO₂, and H₂O, and the chemical composition has been given by Dana (1892, p. 69) as Al₂O₃·4SiO₂·H₂O, a formula widely accepted as representing the aluminous end member. However, preliminary studies by Ross and Shannon have indicated the almost invariable presence of essential amounts of MgO and CaO, or more rarely of Na₂O. The large number of additional analyses presented in this paper confirm the essential character of MgO and of replaceable bases. The above formula is that of pyrophyllite, a mineral without interlayer water or replaceable bases, and it seems evident that the differences in physical properties of montmorillonite and pyrophyllite are a result of the bases other than Al₂O₃ that characterize members of the montmorillonite group but are absent in pyrophyllite. (See pp. 70-71.) The crystal lattices of the two minerals are similar (see pp. 29-30); therefore, the bases, essentially MgO, constitute the only apparent foundation for their marked differences.

The bases Al³⁺, Fe³⁺, Cr³⁺, Fe²⁺, Mn³⁺, Mn²⁺, Mg²⁺, Ni²⁺, and Li⁺, as naturally present in clays of the montmorillonite group, are essentially nonreplaceable and clearly form part of the crystal lattice; Ca and Na, on the other hand, and perhaps minor amounts of other bases are, in general, replaceable. The research discussed on pages 37-39 shows that these replaceable bases occupy a position between the silicate layers where they are associated with the interlayer water.

X-ray studies, discussed in detail on pages 29-30 show that like the micas the minerals of the montmorillonite group are made up of silicate layers formed from double sheets of linked silicon-oxygen tetrahedral groups joined by aluminum-oxygen-hydroxyl octahedral groups. The essential feature of such a lattice, in addition to its layer characteristic, is the constancy of the

oxygen-hydroxyl frame work. In this structure, for every twelve (oxygen plus hydroxyl) ions, that is, $10 O^{-2} + 2 (OH^{-1})$, there are four tetrahedral positions. These positions must be completely filled, predominantly by silicon ions, which in part can be replaced by aluminum ions. Correspondingly, there are three positions having octahedral coordination, of which two to three may be occupied by Al^{+3} , Fe^{+3} , Fe^{+2} , Mg^{+2} , Ni^{+2} , and Li^{+2} . If, in a neutral framework, an ion of lower valence takes the place of one of higher valence [$Si^{+4} \rightarrow Al^{+3}$, $Al^{+3} \rightarrow Mg^{+2}$, or $Mg^{+2} \rightarrow Li^{+2}$] a negative charge will be developed. This charge can be neutralized either (1) by further addition of positive ions into vacant octahedral position, (2) by presence of positive ions external to the silicate layer, or (3) by substitution of O^{-2} by $[OH]^{-1}$. The last, if present, would be expected only for those oxygen ions that are present in tetrahedral coordination about aluminum and are not shared with other tetrahedral groups. As it apparently is not operative it will not be discussed further until the section on thermal studies (p. 48).

The experiments described on pages 38-39 show that base-exchange value is surprisingly constant and is about one-third of the K^{+1} in the equivalent muscovite formula. In table 10 samples that approximate the value of one-third of the K^{+1} of a normal muscovite are designated by a dagger (†). This constancy means that the amount of the negative charge is neutralized by ions between the layers; however, the substitutions of Al^{+3} for Si^{+4} , and Mg^{+2} for Al^{+3} are commonly so great that the resulting number of external ions (exchangeable bases) would be much larger unless the first factor, the additional ions with octahedral coordination, was also important. Seemingly, there is a balance between the two tendencies, and this balance is responsible for the approximately constant base exchange; that is, a stable structure demands that the lack of balance within the lattice shall not exceed a certain limit.

As pointed out on pages 40-41 there are three possible octahedral positions within the crystal lattice of the layer type of minerals. It has been commonly assumed that exactly two of these positions are occupied, as for the heptophyllite micas, represented by muscovite, or exactly three, as for the octophyllite micas represented by phlogopite. With three positions available, however, there is no reason to assume that there is no variation from the value 2 or 3, although there is evidently a tendency to vary only moderately from those values.

Nagelschmidt (1938) in discussing montmorillonite states, "It seems also that in the micas there is a strong tendency for the number of cations in the middle layer to be either two or three, or very nearly two or three, but not any intermediate number."

Where only Mg^{+2} proxies Al^{+3} , Li^{+1} proxies Mg^{+2} , or Al^{+3} proxies Si^{+4} , conventional mineral formulas can be devised, although the small proportion of replaceable bases (Na^{+1} or Ca^{+2}) makes the resulting numbers rather large. On the other hand, where two such substitutions occur in the same mineral the numbers showing ratios become so large that they are cumbersome and fail to give a readily comprehensible picture of relations. The alternative is to keep the number representing ions in the tetrahedral positions definitely fixed—that of a unit or half-unit cell—and to use fractional numbers to represent proportions of the various ions. Thus, the proportions of ions in different positions will be directly shown in the formulas and will be strictly comparable

in all members. Another arbitrary convention will be to represent the replaceable ion directly above the ion within the crystal lattice that it balances. In the formulas the exchangeable base has been represented as Na, although more commonly it is Ca in natural clays, and less commonly other ions. Strictly, the exchangeable bases should be represented as $(Na,Ca)_{\frac{2}{2}}$,

tion is so obvious that the added complexity introduced into the equations is not justified. This method also has the advantage that assumed end members and all intermediate members may be represented by similar formulas, and the proportions of the various ions may be shown as directly for intermediate members as for end members.

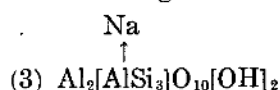
The same method of expressing the composition of minerals has been used by the authors, Hendricks and Ross (1941), in a paper on glauconite and celadonite—minerals belonging to the mica group. In a study of nontronite, attapulgite, and saponite, Caldwell and Marshall (1942) have used a method of representation that is not essentially different.

Discussion of relationships in the montmorillonite series may start with the pyrophyllite and talc formulas, which follow, the various formulas used being numbered successively:

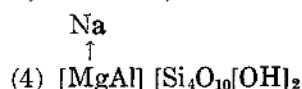
- (1) Pyrophyllite $Al_2Si_4O_{10}[OH]_2$
- (2) Talc $Mg_3Si_4O_{10}[OH]_2$

Because the charge is completely balanced within the lattice, no replaceable ions are to be expected; and experiment shows that essentially none are present.

If a sodium mineral analogous to muscovite is assumed to have all its Na replaceable, it would be shown as follows according to this method of representation:

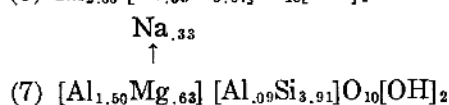
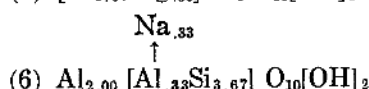
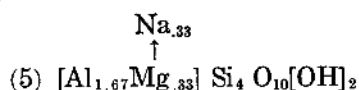


A hypothetical mineral in which Mg proxied one-half of the Al, ion for ion, could be represented as follows:



Experiment, however, shows that in montmorillonite only about one-third as much Na or Ca is replaceable as represented in formulas (3) and (4), and that substitution of either Mg^{+2} for Al^{+3} , or of Al^{+3} for Si^{+4} may be the factor that induces base exchange.

The observed base exchange means merely that the charge on the lattice is unbalanced only to a limited extent. This can be represented by the following formulas, in which fractional numbers are introduced:

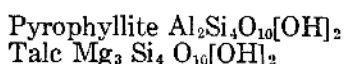


The lack of balance in the charge of the lattice arises from the substitution in formula 5 of Al^{+3} by Mg^{+2} and in formula 6 of Si^{+4} by Al^{+3} . The more general case is

illustrated by formula 7, where both substitutions operate and where the lack of balance in the charge of the lattice is partly compensated by the increase above 2.00 of the number of ions with octahedral coordination. The negative charge is shown as balanced by Na⁺¹ placed above the line, the arrow showing the connection with the effective negative group. If desirable the Na⁺¹ may be transferred to follow the [OH]₂.

METHODS OF CALCULATION OF MINERAL FORMULAS

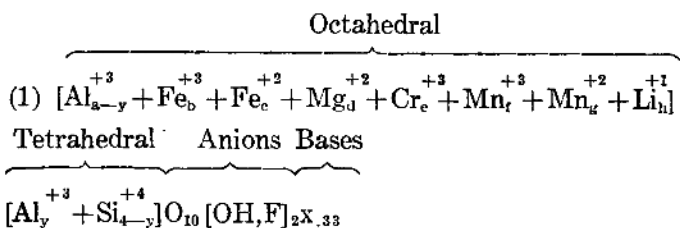
Previous discussions of crystal structure, chemical relationships, and base-exchange experiments provide the basis for the calculation of mineral formulas of members of the montmorillonite group. These relationships as they apply to the development of mineral formulas will be briefly restated. The minerals of the montmorillonite group are members of a larger group, all of which are characterized by micaceous habit and have the same fundamental structure. Of these, two of the simplest are as follows:



In general the micaceous minerals differ from the foregoing minerals in that members of the montmorillonite group contain an additional group of ions, the exchangeable bases Ca, Na, etc.; the micas contain K, which is not exchangeable; and the brittle micas contain Ca, which also is nonexchangeable. As these formulas indicate, the minerals of this type are characterized by a variable number of ions in octahedral positions—Al₂ or Mg₃ in the foregoing formulas. This means that there are 3 possible octahedral positions, of which 2 to about 2.2 are occupied in the montmorillonite-beidellite-nontronite series, and about 3, but not more than 3 are occupied in the hectorite-saponite series. In tetrahedral coordination there are 4 positions, all of which must be occupied. In most members of the group, Al⁺³ partly proxies Si⁺⁴ in tetrahedral positions. There are always 10 oxygen ions and 2 hydroxyl groups.

Titanium is present in the analyses of many of the clays, as well as other silicate minerals. In general, titanium is an essential part of the crystal structure of silicate minerals where it proxies aluminum. However, in the clays it is believed to be present as one of the titanium oxides and hence is to be considered as an impurity. Phosphorous is also believed to be most commonly an impurity. For these reasons TiO₂ and P₂O₅ are neglected in calculating mineral formulas.

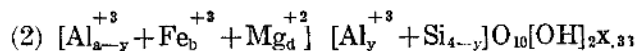
The 10 oxygen ions and 2 hydroxyl groups complete the unit used as the basis of calculation, and these ions have a negative valency of 22. The most general formula for members of the montmorillonite group is



where x represents the exchangeable bases, which on the average appear to be near 0.33 and are so assumed irrespective of the observed amounts, since these commonly are not determined completely and are of questionable accuracy. A formula can, of course, readily be

calculated in which the observed quantities of exchangeable bases, rather than assumed values, are used.

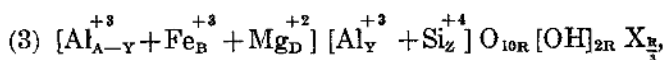
The subscripts a-y, b, c, d, e, f, g, h, y, and Si_{4-y} represent the proportions of cations in the formula. A shortened formula containing only the more typical ions of the group will be adequate to illustrate mineral calculations, as other ions will be handled by the same methods. This is



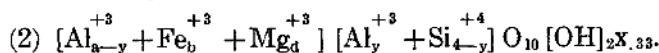
The total number of ions in octahedral positions is represented by Σ; that is

$$a-y+b+d \dots = \Sigma$$

Let atomic proportions of Al = A, Fe⁺³ = B, Mg = D, Si = Z, Al in tetrahedral positions = Y, and O (oxygen) = R; then the atomic proportions as derived from the chemical analysis, and with Al properly allocated between octahedral and tetrahedral positions, must bear such a relation to the mineral formula² (2) that



when multiplied by a constant, K, will become



It is to be remembered that the subscript to x is assumed to be 0.33 in keeping with the general results of all analyses, and does not correspond to the particular analysis.

The negative valency of O₁₀[OH]₂ = 22. Also the number of ions in tetrahedral positions, that is, Al_y⁺³ + Si_z⁺⁴, must always equal 4.

The first step in the calculation is the reduction of the analytical values to atomic proportions. The calculations are based on the distribution of single ions, and SiO₂, MgO, and the like, containing single cations are divided by the molecular weights, as usual; but Al₂O₃, Fe₂O₃, K₂O, and Na₂O are divided by one-half the molecular weight. The proportion of exchangeable bases depends on the number of ions required to neutralize the charge of the remainder of the formula. Thus, one-half as much Ca⁺² is required as Na⁺, and for this reason the number of equivalents of CaO are to be used, obtained by dividing the percentage of CaO by one-half the molecular weight.

To obtain a formula from analytical data it is necessary to determine the number of ions having octahedral coordination (Σ); the factor (K), by which the atomic proportions are to be multiplied to give the required formula; and the number (Y × K) of aluminum ions in tetrahedral coordination. There are thus three unknowns Σ, K, and Y, which are defined by the three equations. From equations (2) and (3) it follows that

$$(4) K[A \times 3 + B \times 3 + D \times 2 + Z \times 4] + .33 = 22$$

$$\text{or } K = \frac{22 - .33}{A \times 3 + B \times 3 + D \times 2 + Z \times 4}$$

If the determined value of X, the exchangeable base, is to be used in the calculation, this equation becomes

$$K[A \times 3 + B \times 3 + D \times 2 + Z \times 4 + X] = 22$$

$$\text{or } [A \times 3 + B \times 3 + D \times 2 + Z \times 4 + X] = \frac{22}{K}$$

This equation represents a balance of valence and expresses the condition that the sum of the valences of the positive ions with the exchangeable base, assumed to be 0.33, is 22.00. The factors 3, 3, 2, and 4 are the respective valences of Al, Fe, Mg, and Si. This equation thus uniquely defines K.

Equations (2) and (3) also indicate that

$$[Z + Y]K = 4 \quad \text{or} \quad \frac{4}{K} - Z = Y$$

This equation expresses the condition that the atoms Si + Al, having tetrahedral coordination, equal 4. Since Z, the atomic proportion of Si, namely, the percent of SiO₂ divided by the molecular weight of SiO₂, is known and K is fixed by the first equation, Y × K can immediately be calculated.

Also, it follows that

$$K[A+B+D-Y] = \Sigma$$

This equation is an expression for the total number of ions (Σ) having octahedral coordination. Since A, B, and D are given by the analysis and Y and K by the preceding equations, Σ can immediately be calculated.

The method may be illustrated by a calculation of the formula of analysis 40, table 1, as follows:

Constituent	Percent	Factor	Atomic proportions and symbols	Equivalents and symbol
SiO ₂	49.70	60.06	0.828 = Z
Al ₂ O ₃	22.10	51.00	.433 = A
Fe ₂ O ₃	2.12	79.92	.027 = B
MgO.....	2.85	40.32	.071 = D
CaO.....	1.08	28.00	0.38
Na ₂ O.....	1.17	31.1039} .077 = X
TiO ₂28
H ₂ O.....	21.14
Total.....	100.44

Substituting numerical values for Z, A, B, D, and X in equation (4) and using the assumed value for X (.33) rather than the value of x = (.077) × K

$$K = \frac{22.00 - .33}{.433 \times 3 + .027 \times 3 + .828 \times 4 + .71 \times 2} = \frac{21.67}{4.832} = 4.481$$

$$K[Z + Y] = 4.00 \quad \text{or} \quad 4.481 [.828 + Y] = 4.00$$

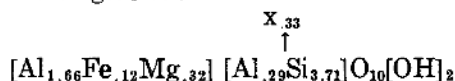
which gives $Y = \frac{4.00}{4.481} - .828 = .064$

$$K[A + B + D - Y] = 4.481 [.433 + .027 + .071 - .064] = 4.481 \times .467 = 2.10 = \Sigma$$

The final formula, therefore, is obtained by multiplying each of the above number of ions by their corresponding valences and adding X = 0.33, as follows:

$$\begin{aligned} a-y &= [A-Y]K = [.433 - .064]4.481 = 1.66 \\ b &= BK = .027 \times 4.481 = .12 \\ d &= DK = .071 \times 4.481 = .32 \\ y &= YK = .064 \times 4.481 = .29 \\ 4-y &= 4.0 - .29 = 3.71 \end{aligned}$$

These values give the formula



The calculated subscript of x is really 0.077 × 4.481 = 0.345, which is in better agreement with the assumed value 0.33 than usually is found.

The same method is applicable to other related mineral groups, such as the micas. It was used by Hendricks and Ross (1941) in their study of the composition of glauconite and celadonite. Here the analytical value of the bases (essentially K for minerals of the mica group) is used in calculations.

In some analyses the amount of SiO₂ was so great as to exceed that required for tetrahedral coordination. In those specimens SiO₂ was probably present as an impurity, and it was possibly present also in a minor amount in some samples for which formulas could be calculated. Similarly, some specimens, particularly nontronites, contained more Fe₂O₃ than could be accounted for by the formula. In those samples and possibly in some others, iron-bearing impurities such as free oxides, hydrous oxides, or more probably mixed-layer minerals of the chlorite type are present.

Thus there are three possible variations from the ideal conditions that have been assumed as a basis for calculations. The presence of free oxides or hydroxides, or of mixed layers of chloritic minerals may make the ions that are assumed to occupy octahedral positions too large; the presence of SiO₂ as quartz, cristobalite, or amorphous silica may make the assumed SiO₂ too large; and the base-exchange value may not be exactly 0.33. These possible variations, as previously pointed out, probably are so small that they introduce no major errors into the calculations. They would involve only a minor shift of slightly more or less Al (ions) into octahedral positions where it proxies Si and would have little effect on the assumed relations.

The results of the calculations as outlined in the preceding sections are given in table 10. The generalized formula for minerals of the montmorillonite-beidellite, nontronite-saponite group is

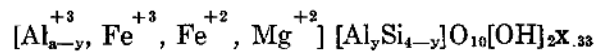


TABLE 10.—Relation of ions to crystal structure

[The analyses that approximate the base-exchange value of one-third of the K⁺ of a normal muscovite are designated by a dagger (†). Total equivalence of 0.21 or less may be considered low.]

Sample No.	Locality	Tetrahedral coordination		Octahedral coordination				Total equivalence of external ions and pre-dominion	
		Si	Al	Al ⁺	Fe ⁺	Fe ²⁺	Mg ²⁺		Σ
1	Santa Cruz, N. Mex.....	4.00	1.30	0.11	0.72	2.13	0.49 Ca
2	Cilly, Styria.....	3.99	0.01	1.43	.0857	2.08	.48 Ca
3	Amargosa Valley, Calif.....	3.98	.02	1.40	.14	0.01	.53	2.08	.61 Na
4	Tehachpi, Calif.....	3.98	.02	1.00	.2695	2.22	† .31 Ca
5	Dixon, N. Mex.....	3.96	.04	1.37	.05	.01	.72	2.15	.15
6	Tatutla, Mexico.....	3.94	.06	1.6342	2.05	.53 Ca
7	Maricopa, Calif.....	3.94	.06	1.46	.1447	2.07	† .34 Ca
8	Conejos Quadrangle, Colo.....	3.94	.06	1.38	.1852	2.08	.50 Ca
9	San Diego County, Calif.....	3.93	.07	1.32	.0679	2.17	† .31 Na
10	Nieder-Bayern, Germany.....	3.92	.08	1.44	.2140	2.05	† .31 Ca
11	Near Rideout, Utah.....	3.92	.08	1.14	.1496	2.24	† .27 Ca
12	Ardmore, S. Dak.....	3.91	.09	1.54	.07	.09	.38	2.08	.70 Na
13	Irish Creek, Va.....	3.91	.09	1.50	.1442	2.06	† .42 Ca
14	Hector, Calif.....	3.90	.10	1.49	.13	.01	.44	2.07	.66 Na
15	Otay, Calif.....	3.90	.10	1.3605	.75	2.16	† .43 Ca, Na
16	Polkville, Miss.....	3.89	.11	1.36	.2449	2.09	† .40 Ca
17	Angleur, France.....	3.88	.12	1.56	.1139	2.06	† .34 Ca
18	Montmorillon, France.....	3.88	.12	1.64	.0536	2.05	† .38 Ca
19	Upton, Wyo.....	3.88	.12	1.55	.19	.02	.26	2.02	.50 Na
20	Lemon, Miss.....	3.87	.13	1.43	.1652	2.11	† .28 Ca
21	Spokane, Wash.....	3.87	.13	1.38	.1856	2.12	† .40 Ca
22	Atzacapozalco, Mexico.....	3.87	.13	1.34	.3044	2.08	.12
23	Lemon, Miss.....	3.86	.14	1.44	.1651	2.11	† .28 Ca

TABLE 10.—Relation of ions to crystal structure—Continued
Formulas for montmorillonite-beidellite series—continued

Sample No.	Locality	Tetrahedral coordination		Octahedral coordination					Total equivalence of external ions and predominant ion	
		Si	Al	Al ³⁺	Fe ³⁺	Fe ²⁺	Mg ²⁺	Σ		
24	Mexico	3.85	.15	1.56				.57	2.13	.11
25	Rosedale, Alberta	3.85	.15	1.50	.21	{Fe .01 Li .10}		.29	2.11	.58 Na
26	Santa Monica, Calif.	3.85	.15	1.38	.33			.32	2.06	† .30 Ca
27	West of San Antonio, Tex.	3.84	.16	1.44	.16			.51	2.11	† .38 Ca
28	Greenwood, Maine	3.83	.17	1.74	.01			.30	2.05	.48 Ca
29	Fort Steel, Wyo.	3.83	.17	1.46	.09			.60	2.15	† .35 acid
30	Osage, Wyo.	3.82	.18	1.64	.18			.20	2.02	.46 Na
31	Lemon, Miss.	3.81	.19	1.41	.19	.01		.52	2.13	.07
32	Otay, Calif.	3.80	.20	1.17	.19			.89	2.25	.18
33	Branchville, Conn.	3.78	.22	1.69		Mn .01		.38	2.08	† .65 Ca
34	Leakey, Tex.	3.76	.24	1.72	.02			.35	2.09	.05
35	Twin Falls, Idaho	3.76	.24	1.36	.37			.36	2.09	No bases reported † .25 Ca
36	Pala, Calif.	3.75	.25	1.62	.01	Mn .01		.50	2.14	
37	Montmorillon, France	3.72	.28	1.51	.07	Mn ⁺⁺ .01		.60	2.19	† .29 Ca
38	Booneville, Miss.	3.72	.28	1.40	.40			.28	2.08	.21
39	Maniquipi, Mexico	3.71	.29	1.74	.13			.18	2.05	† .42 Ca
40	Clairmont, Calif.	3.71	.29	1.66	.12			.32	2.10	† .34 Na, Ca
41	Glen Riddle, Pa.	3.71	.29	1.58				.61	2.19	.06
42	Pala, Calif.	3.69	.31	1.61	.04	Mn(.01)	.04	.46	2.16	† .25 Ca
43	Los Angeles, Calif.	3.69	.31	1.43	.22			.51	2.16	.19
44	Beidell, Colo.	3.64	.36	1.46	.50			.08	2.04	.40
45	Embudo, N. Mex.	3.57	.43	1.53	.02			.72	2.27	† .32 Ca
46	Fairview, Utah	3.54	.46	1.59	.31	.01		.21	2.12	† .42 K, Ca
47	Wagon Wheel Gap, Colo.	3.53	.47	1.52	.37			.23	2.12	† .34 Ca
48	South Bosque, Tex.	3.53	.47	1.67	.07			.46	2.20	† .29 Ca
49	Carson District, Nev.	3.48	.52	2.00	.05			.02	2.07	.47 Ca
50	Pontotoc, Miss.	3.46	.54	1.84	.12	.02		.15	2.13	.08 Acid
51	Nashville, Ark.	3.35	.65	1.74	.15			.33	2.22	.13
52	Nashville, Ark.	3.29	.71	1.73	.23			.26	2.22	.09
53	Ancon, Canal Zone	3.26	.74	1.80	.29	.02		.05	2.16	.18
54	Roseland, Va.	3.18	.82	1.84	.31			.02	2.17	.19

Formulas for nontronites

55	Stary-Krym, Russia	3.77	0.23	0.69	1.26			0.03	1.98	† .34 Ca
56	Woody, Calif.	3.76	.24	.06	1.86	.07		.01	2.00	† .40 Ca
57	Petrovsk, Kriivolrog, Russia	3.74	.26	1.1	8.75			.07	2.00	† .36 Ca
58	Spokane, Wash.	3.63	.37	.77	1.10	.02		.19	2.08	† .28 Ca
59	Spokane, Wash.	3.51	.49	.00	1.92	.05		.10	2.07	† .36 Ca
60	Santa Rita, N. Mex.	3.50	.50	.11	1.91	.02		.04	2.08	.53 Ca
61	Chevy Chase, Md.	3.47	.53	1.02	1.04			.2	2.06	† .26 Ca
62	Szekes-Pejewar, Hungary	3.45	.55	.07	2.00				2.07	.07
63	Stary-Krym, Russia	3.45	.55	.37	1.62			.12	2.11	† .33 Ca
64	Tachau, Germany	3.42	.58	.45	1.61	.03		.01	2.10	.07
65	Sandy Ridge, N. C.	3.42	.58	.39	1.70				2.09	† .26 acid
66	Spruce Pine, N. C.	3.37	.63	.51	1.58			.01	2.10	.18
67	Tachau, Germany	3.36	.64	.40	1.65	.09			2.14	

Formulas for samples from soils and chromium-bearing samples

Sample No.	Locality	Tetrahedral coordination		Octahedral coordination					Total equivalence of external ions and predominant ion		
		Si	Al	Al ³⁺	Fe ³⁺	Cr ³⁺	Fe ²⁺	Mn ²⁺		Mg ²⁺	Σ
68	Maniquipi, Mexico	3.24	0.76	1.69	0.36				0.05	2.16	0.30 K, Ca
69	Rothamstead, England	3.25	.75	1.35	.65				.21	2.21	.18
70	Putnam clay, Missouri, U.S.A.	3.55	.45	1.40	.48		0.08		.21	2.12	.19
71	Emeralds mines, Urals	3.56	.44	1.25	.54	.05	.05		.24	2.13	† .36 Ca
72	Cheghet-Lakhran Valley, Urals	3.54	.46	1.10	.29	.32	.04	(Ni.02)	.43	2.21	† .26 Ca
73	Cheghet-Lakhran Valley, Urals	3.44	.56	1.23	.62	.06	.03		.21	2.15	† .28 Ca
74	Bolshia-laba River	3.29	.71	1.33	.21	.06	.02	.03	.74	2.39	† .29 Ca
75	Gedmayshkh Valley, Russia	3.15	.85	.85	.56	.25	.56		.21	2.43	.47 Ca

TABLE 10.—Relation of ions to crystal structure—Continued
Formulas for saponite and hectorite

Sample No.	Locality	Tetrahedral coordination		Octahedral coordination					Total equivalence of external ions		
		Si	Al	Al ³⁺	Fe ³⁺	Fe ²⁺	Li ⁺	Mg ²⁺	Σ	Calculation	Analysis
76	Hector, Calif.	4.00		0.01			0.30	2.67	2.98		Na 0.44
77	Montreal	3.68	.32		0.02	0.05		2.93	3.00	.30	Mg .28
78	Svärdsjö, Sweden	3.46	.54	.21	.10			2.69	3.00	.23	Ca .10
79	Ahmeek mine, Mich.	3.42	.58		.11	.18		2.72	3.01	.47	Na .16
80	Kearsarge mine, Mich.	3.40	.60		.08	.03		2.92	3.03		Ca .12
81	San Bernardino county, Calif.	3.33	.67	.27				2.73	3.00	.40	Ca † .28
82	Glasgow, Scotland	3.24	.76		.52	.26		2.33	3.01	.24	Ca † .23

†When corrected for P₂O₅ content as Ca₃(PO₄)₂, sample shows total equivalence of 0.40†.

TABLE 11.—Calculations of impurities in representative clays
Samples containing excess silica

Sample No.	Locality	Minimum excess SiO ₂	Minimum value of Σ
83	Quilchina, British Columbia	4.4	2.07
84	Santa Rita, N. Mex.	4.0	2.06
85	Tierra Amarilla, Rio Arriba Co., N. Mex.	3.0	2.09
86	Westcliffe, Colo.	1.1	2.10

Samples of nontronites containing an iron-bearing impurity

Sample No.	Locality	Minimum excess calculated as Fe ₂ O ₃	Maximum value of Σ
87	Baschenowski	18.7	2.21
88	Magnitnaja Mountains, Urals	16.1	2.07
89	Okhansk, Siberia	10.1	2.02
90	Woody, Calif.	6.7	1.96
91	Unghwar, Hungary	5.2	2.01
92	Gobitschau, Moravia	5.0	2.15
93	Morenci, Ariz.	4.7	2.14
94	St. Andreasberg, Harz	9.9	2.16
95	St. Andreasberg, Harz	3.6	2.18
96	Okhansk, Siberia	1.9	2.20
97	Baltarak, Kazakstan	1.2	2.07
98	Island of Magee, County Antrim	1.0	2.05
99	Nontron, France	.7	2.04

Samples containing a chlorite or vermiculite impurity (probably as mixed layers) or an iron-bearing impurity

Sample No. and locality	Ratio
100. Cathkin Hills, Scotland	4:3.15
101. Webster, N. C.	4:3.47
102. Blackburn, Scotland	4:3.48

The ratios given above are calculated with the assumption of the maximum possible number of ions in tetrahedral coordination, that is 4, and the minimum possible number of ions in octahedral coordination. As previously stated, tetrahedral ions must be 4 and octahedral ions cannot exceed 3. Therefore, the excess above the ratio 4:3 illustrates the minimum excess of impurity.

DERIVATION OF FORMULAS

The foregoing discussion of X-ray structure, the base-exchange experiments, and the large number of chemical analyses of clays of extremely varied range in composition provide the basis for the selection of chemical formulas that will present the relationships within the montmorillonite group of minerals. It is believed that the coordination of all these factors, including the large number of analyses and the extreme range in composition that they represent, presents an unusually adequate method for the study of complex mineral groups.

MONTMORILLONITE-BEIDELLITE SERIES

Fifty-four of the 103 analyses listed in tables 1 to 7 correspond to the montmorillonite-beidellite series. Silicon in tetrahedral coordination varies continuously between 4.00, the montmorillonite end, and 3.18, the beidellite end, but it does not go as low as 3.00 in any materials so far examined. Apparently, then, montmorillonite and beidellite form a complete series of solid solutions. Silicon in tetrahedral coordination exceeds 3.8 in six-tenths of the samples, and this excess indicates the somewhat greater predominance of montmorillonite, owing to the large proportion of bentonites included. This preponderance probably would not have been apparent if an equal number of analyses of soil, vein, and shale clays had been available.

The maximum number of ions in octahedral coordination (Σ) is 2.27; however, Σ exceeds 2.20 only in 6 samples and 2.16 only in 12. If oxides or hydrous oxides of iron or aluminum are present, or if part of the aluminum is external to the lattice, the value of Σ will be erroneously high. If excess silica is present Σ will be erroneously low. In deriving the formula the presence of small amounts of impurities will have slight effect, as correction will be made for the impurity by changing the amount of silicon in tetrahedral coordination. While high and low values of Σ thus are of questionable accuracy, a very large proportion of the values probably are accurate to $\pm .02$.

Thus it appears that in the montmorillonite-beidellite series the maximum number of ions in octahedral coordination (Σ) is about 2.20 and the minimum near 2.05. In the 36 samples in which Si in tetrahedral coordination exceeds 3.72 the average value of Σ is 2.10, and in the 19 samples in which tetrahedral Si is less than 3.72, it is 2.15, which is significantly higher. Thus, apparently, the number of ions having octahedral coordination is slightly greater for the beidellite end of the series than for the montmorillonite end. This difference is evidence for a tendency toward internal compensation of charge as the amount of aluminum in tetrahedral coordination is increased. The limited upper value of Σ is evidence that these minerals do not form complete solid solutions with minerals having three ions in octahedral coordination, and the same condition apparently is true for pyrophyllite and talc.

There is, further, an inverse relationship between the amount of aluminum in tetrahedral coordination and the $Mg^{+2} + Fe^{+2}$ in octahedral coordination. The average value for $Mg^{+2} + Fe^{+2}$ in the first 36 samples is 0.53 ions in octahedral coordination, and in 18 of these samples it is above 0.50. In the next 18 samples the average value of $Mg^{+2} + Fe^{+2}$ in octahedral coordination is 0.30, and in only 15 percent of them do these ions amount to more than 0.50. In other words, the excess aluminum in tetrahedral coordination over that re-

quired for the base exchange of beidellites is more commonly neutralized by additional Al^{+3} and Fe^{+3} in octahedral coordination than by Mg^{+2} . This is a tendency either to prefer the ion of smaller radius or the smaller total number of ions having octahedral coordination.

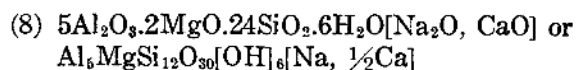
Twenty-six of the 54 samples, or slightly less than half, have a total equivalence of $Na + \frac{Ca}{2} + K$ approximately equal to 0.33, as required by the average base-exchange capacity. In 13 it is too high, and in 15 it is too low. For those with the higher equivalence the average value of Σ is 2.07, whereas for those with the lower equivalence it is 2.14. These proportions strongly indicate that the apparent deficiency in external bases is partly due to the presence of aluminum or iron external to the lattice. In some samples, however, it may be due to inaccuracy of analysis. The samples in which the amount of external base, as obtained analytically, is too high probably fall into several classes. The base exchange may really be high, or nonexchangeable bases may be present. Not infrequently, however, calcium carbonate or some sodium salt, such as the carbonate or chloride, probably is present. Sodium chloride is known to be present in some of the clays from arid regions. In any case, it is with just such minor constituents that experimental uncertainty and questionable purity of materials has the greatest effect. The extent of agreement is perhaps even more striking evidence of the general purity of the specimens examined.

The above discussion depends upon the average tendency of a large group of samples rather than upon the peculiarities of a particular one. This procedure, though seldom followed in mineralogical research, has much to recommend it. Results obtained from an impure sample will be sufficiently distinct to cause suspicion and will be analogous to a curve based on numerous well-spaced points. A few points that do not fall correctly do not invalidate the curve. If a sufficient number of specimens are analyzed, limits can be placed upon the kind and extent of isomorphous replacements.

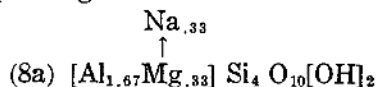
The foregoing chemical analyses and the discussion of the chemical and structural relations delimiting their interpretation provide the basis for the derivation of chemical formulas that will represent relations within the montmorillonite group. The analytical data are believed to be entirely consistent with the type of formulas presented.

A specific chemical formula is necessary to represent a named mineral species; it is useful to represent isomorphous mixtures, by means of end members, even though these are hypothetical; and it is used in calculations of mineral relationships. For these reasons formulas for the deduced end members will be presented, although as pointed out on page 47 they cannot uniquely represent chemical compositions. For these reasons the end-member formulas presented will probably not be as fully representative as those for the plagioclase group, for instance; and one should not lose sight of the limitations imposed on the end-member method of representing mineral compositions where an unusually large number of variables is involved. For these reasons the other type of formulas, 8a, 9a, 10a, etc. (see below), are believed to illustrate relationships better. Where formulas representing end members are presented, some mineral name is demanded. New names are to be avoided wherever possible, and none is proposed in this paper, although this avoidance has necessitated the use of chemical modifiers for three members.

Selection of the most suitable formula for montmorillonite is questionable, within certain rather narrow limits. A possible one is

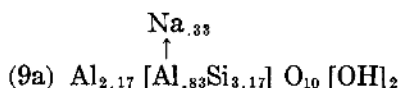
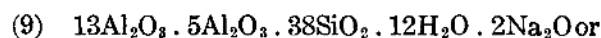


corresponding to

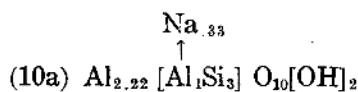
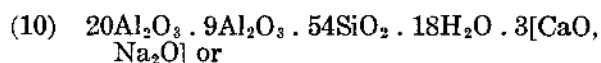


The only serious flaw in it is that the total number of ions in octahedral coordination is 2.00, whereas in all actual specimens this number is exceeded.

The mineral name beidellite will be used for the member having a large amount of Al^{+3} in tetrahedral coordination. A suitable formula is



It is possible that the available analyses do not quite represent the maximum possible replacement of Si by Al and such a greater replacement may be represented by the following formula:



However, the discussion of the value of Σ on page 44 indicates that 2.22 is near the maximum value and that apparently not more than one-fourth of the tetrahedral positions are occupied by aluminum. $\text{Na}_{.33}$ is placed above $\text{Al}_{.83}$ in the foregoing formula (9a) rather than above $\text{Al}_{.33}$, which would be required to balance $\text{Na}_{.33}$ directly. This is due to the fact that the positive charge resulting from Al in excess of 2 in octahedral position is three times as large as the negative charge caused by Al in tetrahedral position; hence,

$$\text{Al}_{.83} - (\text{Al}_{.17} \times 3) = \text{Al}_{.22} \rightarrow \text{Na}_{.33}$$

The same relation applies to formulas 7 and 10, pages 40, 48. Notwithstanding the undesirably high numbers necessary for the oxide ratios, the beidellite formula is an oversimplification, for the usual presence of Fe_2O_3 and small amounts of MgO have been neglected. It is more satisfactory than the montmorillonite formula in that it gives about the correct number of ions with octahedral coordination. Sample 54, from Roseland, Va., closely approximates this formula except that some Fe^{+3} is present, replacing Al^{+3} with octahedral coordination. The material from Beidell, Colo., is intermediate between beidellite, as written above, and the montmorillonite end of the series. It also contains appreciable Fe^{+3} and Mg^{+2} in octahedral coordination.

NONTRONITE

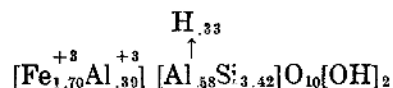
Formulas obtained for nontronites in a manner analogous to that used for the montmorillonite-beidellite series are summarized in table 11. Thirteen of the samples examined appeared to be satisfactory nontronites—that is, montmorillonite-type clays containing

large amounts of ferric iron and relatively free of adventitious materials. The amount of aluminum in tetrahedral coordination in these samples ranges from 0.23 to 0.63, and a fairly uniform series is represented. This range in composition does not justify a distinct name for the members richest in Al, and it will be indicated as nontronite (aluminian) (Schaller, 1951). Wider variation probably is limited only by the restricted number of samples. Thus there is evidence for a nontronite series in which there is a variation from a limited to a marked substitution of Al for Si, similar to that in the montmorillonite-beidellite series.

The maximum number of ions having octahedral coordination is 2.11. The average value is 2.06, and three of the samples have a lower value of Σ than was found for any member of the montmorillonite-beidellite series, of which four times as many specimens were studied. Those nontronites having the greatest amount of aluminum in tetrahedral coordination also have the higher value of Σ . Thus the average value of this summation for seven samples with less than 3.50 Si in tetrahedral coordination is 2.09, whereas six samples with Si greater than 3.50 have an average of 2.03. These averages are strictly in accordance with the behavior of beidellite.

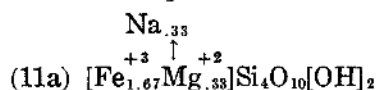
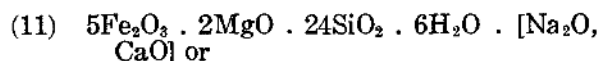
It is striking that the nontronites contain relatively small amounts of magnesium. This relationship is particularly true for the specimens having chiefly Fe^{+3} in octahedral coordination; in fact, of the four samples containing less than 0.12 Al^{+3} in octahedral coordination the highest was 0.04 Mg^{+2} . If anything, the trend in content of Mg^{+2} is opposite to that of the montmorillonite-beidellite series, but even at the most it is not great.

The amount of external Na^{+1} , K^{+1} , H^{+1} , and $\frac{\text{Ca}^{+2}}{2}$ analytically determined again agrees with the expected value, 0.33, in about half the samples. It is too low in four samples and too high in only one. Several of the samples with low amounts of external base may be acid clays. The sample from Sandy Ridge, N. C., is such an acid clay; its analysis shows the presence only of Al_2O_3 , Fe_2O_3 , SiO_2 , and H_2O . Its composition thus is very simple and correlates base exchange with the lack of balance in the charge of the lattice. The formula is



Substitution of Si^{+4} by Al^{+3} in tetrahedral coordination is partly compensated by the external hydrogen ion and partly by additional ions in octahedral coordination above two, Σ being 2.09.

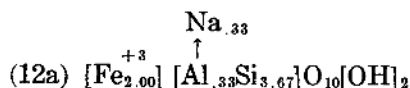
Assignment of adequate formulas of the usual type for nontronites is even more difficult than for montmorillonite. A compromise is to use an analogous formula in which aluminum in octahedral coordination is replaced by ferric iron, namely:



This is unsatisfactory in that it shows essential Mg^{+2} and suggests that base exchange is principally due to

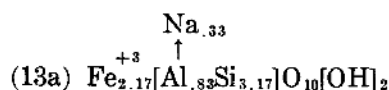
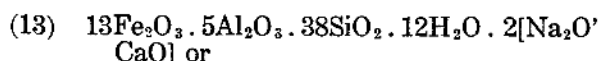
substitution in octahedral positions. For these reasons it cannot be used to express the composition of some samples.

A somewhat better formula is



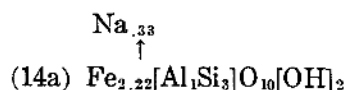
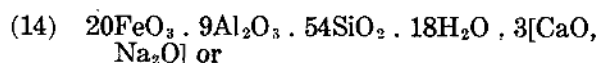
It correctly shows the base exchange as arising from substitutions of Al^{+3} for Si^{+4} in tetrahedral coordination.

Nontronite of the aluminian type, is considered to be similar to beidellite and its suggested formula is



This formula is more satisfactory than that of beidellite in that Mg^{+2} is not present as an essential constituent. It possibly shows too much Fe^{+3} in octahedral coordination, by about 0.04.

As for beidellite, a formula somewhat higher in Al may be possible. It would be similar to No. 10 and could be expressed as follows:



Fourteen of the nontronite samples contained an iron-bearing impurity, as judged from attempts to obtain formulas for them. Many of these samples gave no evidence of essential impurities, suggesting the presence of mixed-layer material of chlorite type. These are listed in table 11. If the iron content is reduced by an amount just adequate to give a possible formula, this formula will have a maximum value of Σ for the specimen. These maximum values are listed in the table, together with the minimum excess of Fe_2O_3 . In only 4 samples does Σ exceed 2.10, so for the remaining 10 samples it would appear that the maximum value of Σ thus calculated is near the true value.

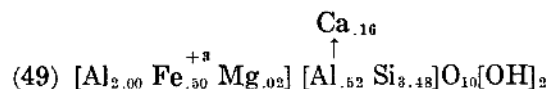
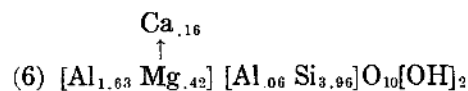
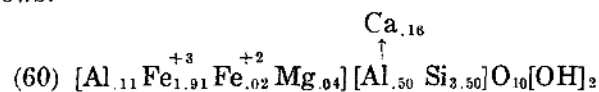
MONTMORILLONITE-BEIDELLITE-NONTRONITE SERIES

These three minerals are members of an apparently continuous series of solid solutions; in other words, Fe^{+3} and Al^{+3} can proxy for one another in octahedral coordination in all proportions, and Al^{+3} can proxy for Si^{+4} apparently not to exceed 1 ion in 4. Analyses of the 54 specimens listed in table 10 and the 13 nontronites in table 10 can be represented in terms of end formulas for montmorillonite, beidellite, nontronite, nontronite (aluminian), and talc. Thus, the nontronite from Santa Rita, N. Mex. (No. 60), the montmorillonite from Tatatila, Mexico (No. 6), and the beidellite from Carson District, Nev. (No. 49), can be approximately represented as shown in table 12. It will be noted with reference to the sample from the Carson District, Nev., that the calculated compositions vary slightly from those observed; that is, the composition is not fully represented by end members.

TABLE 12.—Proportions of end members in selected samples

End-member component	Per-cent	Tetrahedral coordination		Octahedral coordination		
		Si^{+4}	Al^{+3}	Al^{+3}	Fe^{+3}	$\text{Mg}^{+2}, \text{Fe}^{+2}$
Santa Rita, N. Mex., sample 60						
Nontronite (aluminian).....	38	1.20	0.32	0.82
Nontronite.....	55	2.02	.18	1.10
Montmorillonite.....	6	.24	0.10	0.02
Talc.....	1	.0403
Total ions.....	3.50	0.50	0.11	1.9'	0.06
Tatatila, Mexico, sample 6						
Beidellite.....	7	0.22	0.06	0.15
Nontronite.....	1	.03	0.01
Talc.....	4	.16	0.12
Montmorillonite.....	88	3.53	1.4829
Total ions.....	3.94	0.06	1.63	0.01	0.42
Carson District, Nev., sample 49						
Beidellite.....	62	1.96	0.52	1.35
Nontronite.....	2	.08	.01	0.04
Montmorillonite.....	36	1.4459	0.09
Total ions.....	3.48	0.52	2.00	0.04	0.02

Perhaps the most artificial part of such a procedure is the use of talc (p. 48) as one end member. This use is required by the presence in some of the specimens of larger amounts of MgO than correspond to the montmorillonite formula. Though the amount required is small, it further emphasizes the difficulty of assigning formulas of the usual type. In order to give a completely satisfactory representation of the various analyses by means of end members, about 10 formulas for end members would have to be used. These end members, moreover, would have unusually large coefficients for their oxide formulas. Notwithstanding the somewhat oversimplification, the formulas presented probably give a fairly adequate representation of the relations and are preferable to the cumbersome presentation that might be devised by the use of numerous formulas. However, as previously stated, the end-member method of representing minerals of very complex composition is not fully satisfactory. For this reason it is believed that the formulas of these minerals making use of decimal fractions, present a simpler and more readily understandable picture of the compositions and relations of these minerals. These would be as follows:

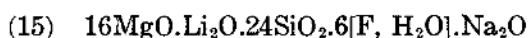


SAPONITE-HECTORITE SERIES

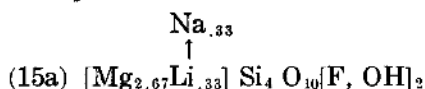
There is another group of clays in which the number of ions having octahedral coordination is 3.00, within limits of experimental error. No intermediate members between these clays and the beidellites of the mont-

morillonite-beidellite-nontronite-iron series were found. Formulas for this group, given in table 10, indicate that the amount of aluminum in tetrahedral coordination ranges from zero to 0.76 in the seven samples examined, and apparently the beidellite type of substitution is operative.

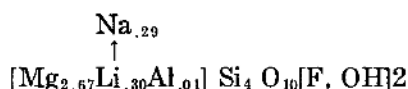
The most interesting of these clays is the hectorite from Hector, Calif., sample 76. Reference to the analyses, table 4, shows that it contains very little Al_2O_3 or Fe_2O_3 . About 1 percent Li_2O is present in a nonexchangeable form—a very substantial proportion, due to its low atomic weight. The substitution of Li^{+1} for Mg^{+2} is the only possible factor accounting for a lack of charge in the lattice, and therefore the presence of an exchangeable base. A suitable formula for this end member is



which corresponds to



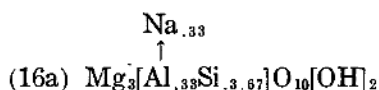
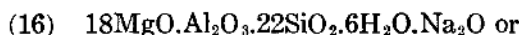
In the calculation of a formula representing analysis 76, only Si is assumed to occupy tetrahedral positions, giving the following formula:



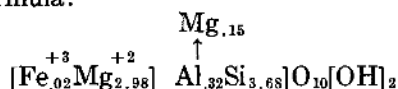
This formula indicates that the analysis conforms remarkably well to the assumed end member. The analysis shows a small excess of Na_2O over that represented by the formula, but this is in part due to absorbed salts.

In the actual formula Σ is 2.98, slightly less than 3.00 and less than the experimental error.

The rest of the samples listed in table 10 do not show Li and owe their base-exchange capacity to the proxying of Si^{+4} by Al^{+3} in tetrahedral coordination. The saponite from Montreal, Canada, sample 77, is one of the simplest of these. Its formula can be written as



The actual composition is represented by the following formula, which is a close approximation of the preceding formula:

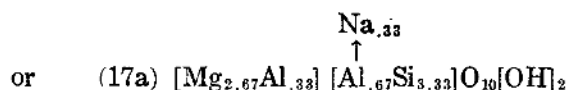
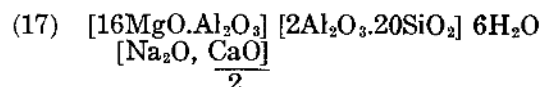


In the formula of the actual mineral, the exchangeable ion is Mg^{+2} instead of Na^{+1} as in (16a). The exchangeable base is represented by Na in the general formulas, but the actual exchangeable base may be indicated in any particular sample. (See pp. 39, 40.)

Substitution of Al^{+3} for Si^{+4} in amounts greater than about 0.40 is balanced by the proxying of Al^{+3} or Fe^{+3} for Mg^{+2} ; thus, in the specimen from Svärdsjö, Sweden, 0.31 ($\text{Fe}^{+3} \text{Al}^{+3}$) is present in octahedral coordination; in the specimen from San Bernardino, Calif., 0.27 Al^{+3} ;

and in the material from Glasgow, Scotland, 0.52 Fe^{+3} . In the last two samples the amount of exchangeable base as determined analytically is in approximate agreement with that required by the formula. This is a very exact condition that is not a matter of assumption and thus adds further confirmatory evidence to the entire scheme. Lack of agreement in several of the other samples, the analytical values of which are too low, does not detract from this evidence. It should really be pointed out that agreement as close as 0.47, calculated for the base exchange, and 0.16 external base, determined analytically, is really not bad considering all the factors involved. All errors are thrown into this one place.

Specimen 81 from San Bernardino, Calif., has approximately the formula



For convenience it might be considered to be an aluminian saponite analogous to beidellite. Other substitutions are so varied that a different formula would be required for each sample; therefore, an attempt to write further end formulas does not seem justifiable. In any formula, oxide representations would be quite complex.

SUGGESTED FORMULAS

So far as it has been possible to deduce formulas according to oxide representation, they are as follows:

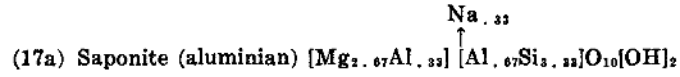
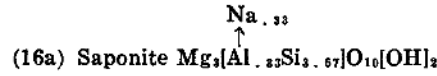
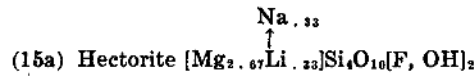
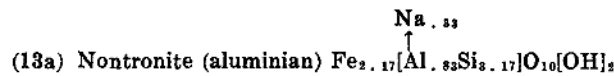
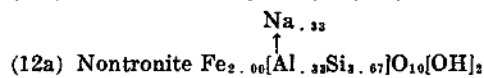
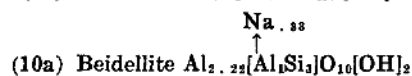
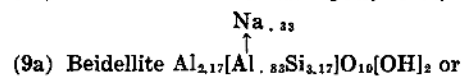
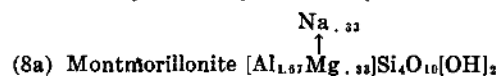
Formulas of minerals of the montmorillonite group

- (8) Montmorillonite
 $5\text{Al}_2\text{O}_3 \cdot 2\text{MgO} \cdot 24\text{SiO}_2 \cdot 6\text{H}_2\text{O}[\text{Na}_2\text{O}, \text{CaO}]$
- (9) Beidellite
 $13\text{Al}_2\text{O}_3 \cdot 5\text{Al}_2\text{O}_3 \cdot 38\text{SiO}_2 \cdot 12\text{H}_2\text{O}[\text{CaO}, \text{Na}_2\text{O}]$, or
- (10) Beidellite
 $20\text{Al}_2\text{O}_3 \cdot 9\text{Al}_2\text{O}_3 \cdot 54\text{SiO}_2 \cdot 18\text{H}_2\text{O} \cdot 3[\text{Na}_2\text{O}, \text{CaO}]$
- (12) Nontronite
 $6\text{Fe}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3 \cdot 22\text{SiO}_2 \cdot 6\text{H}_2\text{O}[\text{Na}_2\text{O}, \text{CaO}]$
- (13) Nontronite (aluminian)
 $13\text{Fe}_2\text{O}_3 \cdot 5\text{Al}_2\text{O}_3 \cdot 38\text{SiO}_2 \cdot 12\text{H}_2\text{O}[\text{Na}_2\text{O}, \text{CaO}]$
- (14) Nontronite (aluminian)
 $20\text{Al}_2\text{O}_3 \cdot 9\text{Al}_2\text{O}_3 \cdot 54\text{SiO}_2 \cdot 18\text{H}_2\text{O}[\text{Na}_2\text{O}, \text{CaO}]$
- (15) Hectorite
 $16\text{MgO} \cdot \text{Li}_2\text{O} \cdot 24\text{SiO}_2 \cdot 6[\text{F}, \text{H}_2\text{O}] [\text{Na}_2\text{O}]$
- (16) Saponite
 $18\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 22\text{SiO}_2 \cdot 6\text{H}_2\text{O}[\text{Na}_2\text{O}, \text{CaO}]$
- (17) Saponite (aluminian)
 $16\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{Al}_2\text{O}_3 \cdot 20\text{SiO}_2 \cdot 6\text{H}_2\text{O}[\text{Na}_2\text{O}, \text{CaO}]$

The composition of volchonskoite would demand formulas similar to that of nontronite, samples 13 and 14. Other elements such as Fe^{+2} , Mn^{+2} , Ni^{+2} , would play a role identical with Mg, and separate formulas need not be written to represent them as they normally occur in very minor proportions.

Expressed so as to keep the ions occupying tetrahedral positions always at 4, these formulas would become:

Structural formulas of minerals of the montmorillonite group



In addition to the above formulas, all of which represent clays with base-exchange capacity, other formulas must be assumed in order to complete the entire group in terms of end members, although these are invariably very minor components. Such formulas are as follows:

Formulas of accessory minerals

Muscovite.....	$\text{KAl}_3\text{AlSi}_3\text{O}_{10}[\text{OH}, \text{F}]_2$
Talc.....	$\text{Mg}_3\text{Si}_4\text{O}_{10}[\text{OH}]_2$
Brucite.....	$\text{Mg}_3[\text{OH}]_6$

As has been pointed out, members of the montmorillonite group, especially beidellite, commonly contain potassium, which is interpreted as being due to mixed layers of a mica mineral. At present it is not known whether this is to be considered as bravaisite, as some other hydrous mica, or as true muscovite. Pending a complete understanding of bravaisite-hydrous mica (illite) minerals, it will be best to represent this interlayered mica mineral as muscovite.

THERMAL STUDIES

Two distinct problems are involved in an investigation of the relations of the water (more precisely of water and OH) in clays of the montmorillonite group. One is the adsorbed water, particularly the interlayer water between the lattice sheets, which is closely related to exchangeable bases; the other is the so-called high-temperature water, or the OH^{-1} , which is an essential part of the crystal lattice. The two problems involved different methods of study, as the adsorbed or interlayer water can be best investigated by means of differential thermal analysis, first proposed by Le Chatelier (1887) and modified by Norton (1939); whereas the OH^{-1} , essential water, is best indicated by plotting retention of water against change in temperature—that is, by dehydration curves. The differential thermal method also has been used in a study of clay minerals by Hendricks, Nelson, and Alexander (1940) and by Grim and Rowland (1942, 1944).

ESSENTIAL HYDROXYL

The dehydration curves of 15 representative clays, plotted as retention of water against change in temperature, are given in figures 5, 6, 7. These are based on the work of P. G. Nutting, of the Geological Survey (Nutting, 1943). The sample is suspended directly from the pan of a balance by a fine wire that passes into a small electric furnace with intervening insulation to protect the balance. This permits weighing of the sample without removal from the furnace, and involves only a slight correction for temperature. The temperature is determined by a thermocouple and read on a calibrated millivoltmeter. The sample is weighed repeatedly at constant temperature until it comes to constant weight. This weighing is repeated at successively higher temperatures until the mineral ceases to lose weight. The retention of water is plotted as one coordinate and temperature as the other.

There is some question about determination of the water present as OH^{-} from dehydration curves. The curves obtained always have an S shape with an inflection point near 300°C ., in a region over which the slope is changing slowly. This is the expected result when two processes having different response to increase in temperature are involved. The inflection marks the point where the rate of water loss with increase in temperature, that is, the second derivative, $\frac{d^2w}{dt^2}$, is zero; in

other words, the decrease in water due to one process is just balanced by the increase due to the other process. If the correct coordinates are chosen and the functions are of the same type, the amount of water lost above the inflection point will truly be equal to that involved in the second process—that is, hydroxyl water. Since the inflection point is difficult to fix in some determinations, it has been thought best merely to select 300°C . as the zero point. Hydroxyl water is lost below 300°C . but, if the analysis is correct, it is compensated for by the layer water lost above 300° . If the general practice were followed of using 100°C . or 110°C . as the point of reference, the curves would be so spread out by the variable loss of water at low temperatures as to make comparison difficult.

According to the formulas in the section on mineralogy the minerals in the group have the following amount of hydroxyl water:

	<i>Percent</i>
Pyrophyllite.....	5.00
Montmorillonite.....	4.93
Nontronite.....	4.46

These percentages now will be compared with those obtained from the dehydration curves.

The dehydration curves of 15 clays are given in figures 5, 6, and 7, with that of the Tatatila clay (6) reproduced in each one for purposes of comparison. Curves for nearly normal montmorillonites, given in figure 5, represent clays from Belle Fourche, S. Dak. (30); Irish Creek, Va. (13); Otay, Calif. (15); Tatatila, Mexico (6); and Polkville, Miss. (16), and another from an unknown locality in Mexico (24). Figure 6 gives curves of clays from Mainburg, Saxony (10), and Montmorillon, France (37), and a pegmatite clay from Pala, San Diego County, Calif. (36). These are clays with calcium as the exchangeable base, except that from Belle Fourche, which is a sodium clay.

In five of the six montmorillonite dehydration curves shown in figure 5, the amount of water lost above 300°C . agrees with the expected value within 0.30 percent.

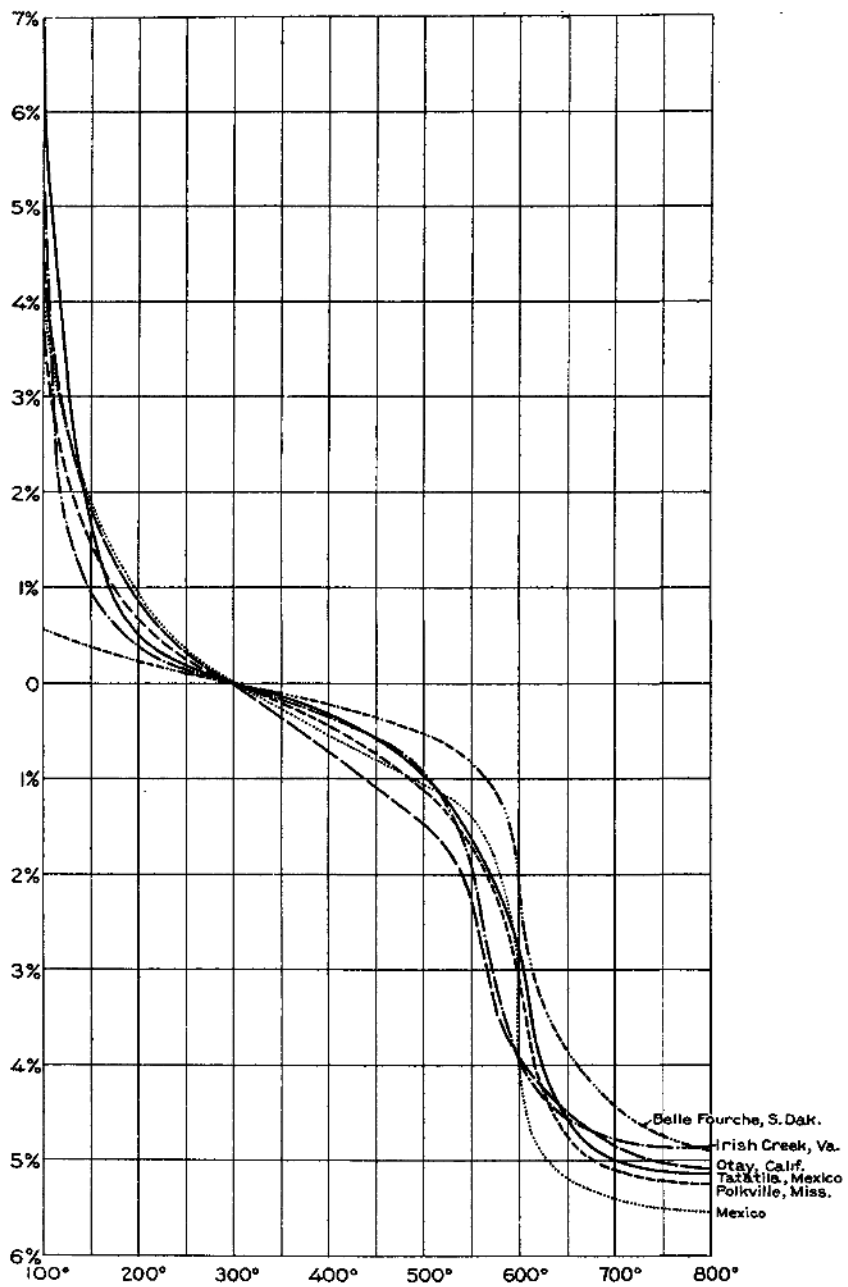


FIGURE 5.—Dehydration curves of montmorillonite clays.

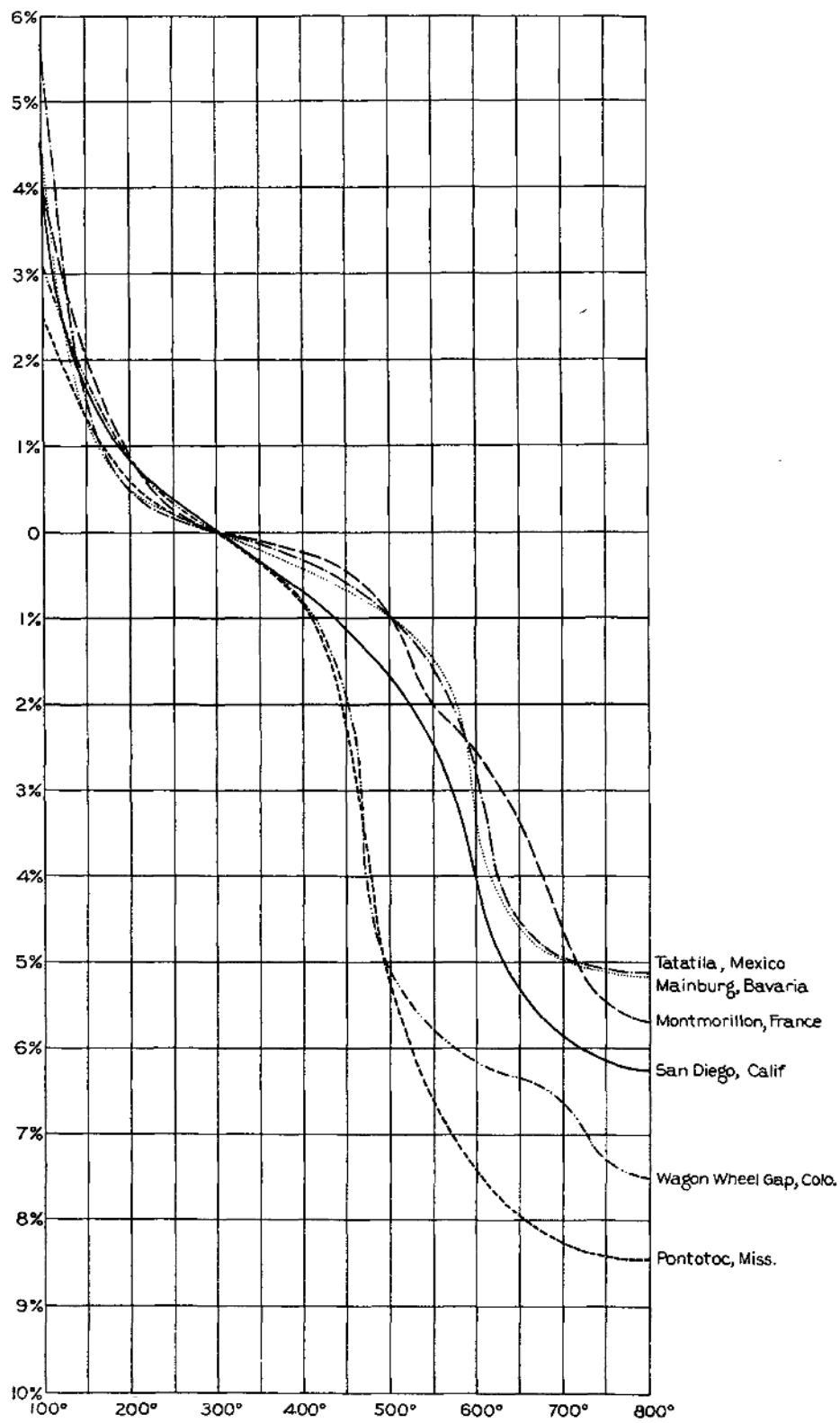


FIGURE 6.—Dehydration curves of montmorillonite clays.

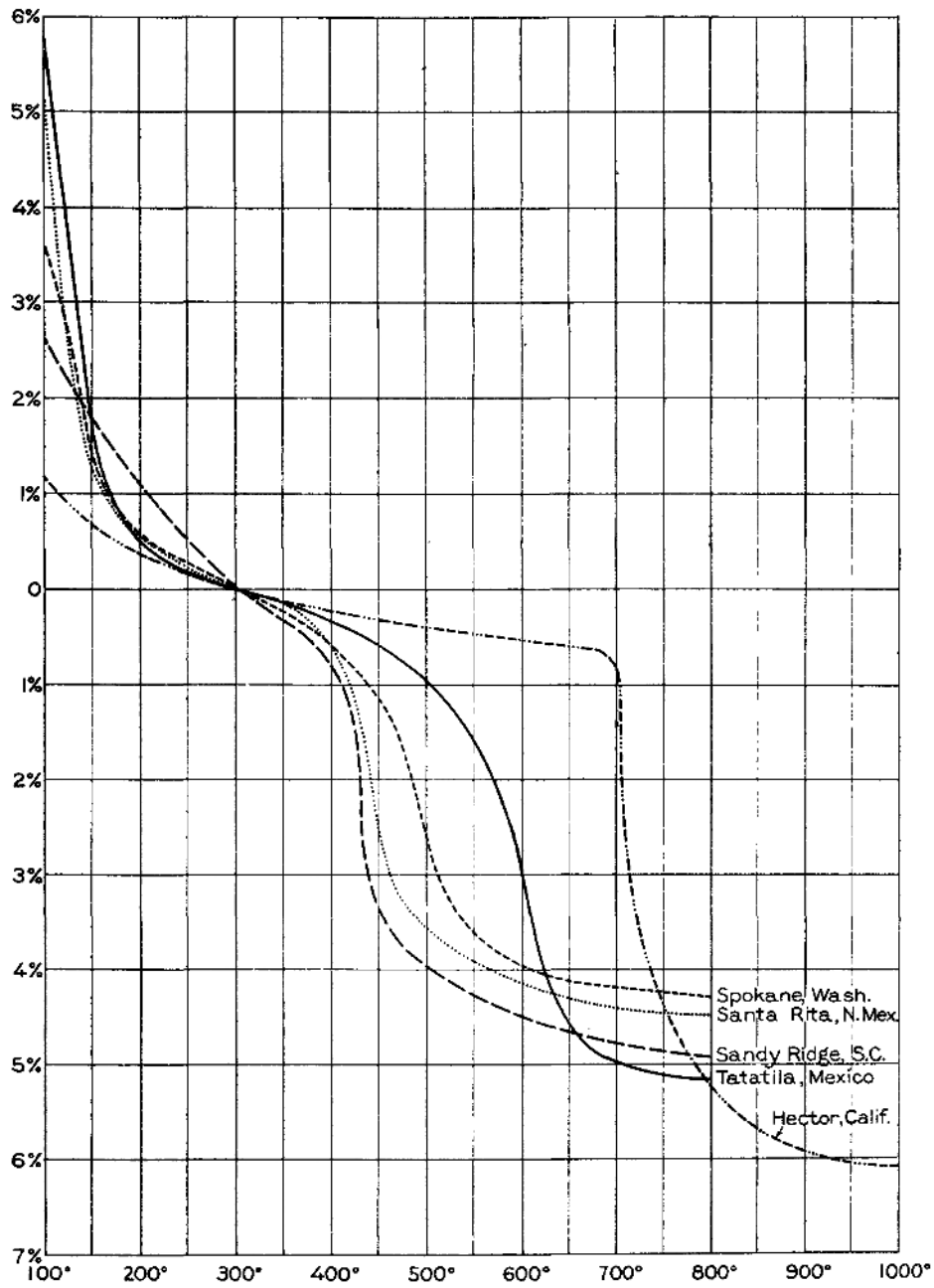


FIGURE 7.—Dehydration curves of montmorillonite clays.

The sample from Mexico shows a slightly greater loss, 5.5 percent, which probably is due to the fact that the inflection point is nearer 400° C. Two of the nontronite samples, those from Spokane, Wash. (58), and Santa Rita, N. Mex. (60), give the expected loss in weight to within 0.1 percent. A higher loss, 4.90 percent, was obtained from the specimen from Sandy Ridge, N. C. (65). It must be recalled, however, that this is an acid clay and thus should contain about 5.0 percent hydroxyl water, which is in close agreement with the observed amount. These results clearly show that for 10 oxygen ions increase in hydroxyl content above 2.00 probably does not take place.

Dehydration curves for several specimens in which the amount of water lost above 300° C. exceeds 6.0 percent are shown in figure 6. Although the sample from Pontotoc, Miss. (50), is partly an acid clay, the additional hydroxyl content is insufficient to account for the observed loss of 8.5 percent. The inflection point for specimens from Pontotoc, Miss. (50), and Wagon Wheel Gap, Colo. (47), are near 300° C., but their dehydration curves have an unusually high slope in the region between 400° C. and 500° C. It is possible that some other constituent, such as a hydrous oxide of aluminum, is present. It also is possible in these clays of the beidellite type that additional hydroxyl groups are present. This, however, would result in an increase of only about 1.2 percent in water content, whereas the observed values are more than twice that amount. The most probable explanation is that the presence of some chlorite-type layers modifies the calculated formula. Failure to consider this factor or the presence of an aluminous impurity gives too high an amount of aluminum in tetrahedral coordination by about 0.10 at the most.

The dehydration curves also show the stability range of the clays of the montmorillonite group. The clays that are approximately normal montmorillonites—that is, those from Tatatila (6), Polkville (16), Irish Creek (13), Otay (15), Mexico (24), and Belle Fourche (30)—begin to break down rapidly at about 500° C. and have lost practically all their water at 800° C.

The nontronites (see fig. 7) appear to have a lower stability range than montmorillonite, as the clays from Sandy Ridge (66) and Santa Rita (61) begin to break down at about 400° C. The clay from Spokane (59), which contains only about 55 percent of the nontronite molecule, begins to break down at a somewhat higher temperature; thus its stability is intermediate between that of nontronite and montmorillonite, as its chemical composition would imply.

The hectorite (76) is unusual in that hydroxyl (OH) is largely proxied by fluorine. The curve given in figure 7 shows that the curve for hectorite has a sharp break at 700° C., about 200° C. higher than is normal for the minerals of the group. This difference, no doubt, is due to the F, which is evidently more tightly held within the lattice structure than OH. The curve in the range 300° C. to 650° C. is nearly flat, whereas there is a steep slope in other curves of the group—that is, in the part just preceding the flexure that indicates mineral breakdown. This difference, no doubt, is due in large part to the higher temperature at which hectorite breaks down and, consequently, to a much more complete escape of interlayer water. It results in a sharper flexure, for there is a minimum of overlap in the escape of interlayer water and OH + F (so-called high-temperature water).

The curve shows that the material was still losing weight at 930° C. The total loss indicated is about 6 percent, though theory demands about 7.32 percent of OH + F. Thus the curve does not give a complete quantitative picture of the loss of OH + F. The sharpness of the flexure, the rapid loss of more than 3 percent in weight, and the lack of a second flexure in this range indicate that OH and F begin escaping together. It is probable that the part still retained at 930° C. is essentially fluorine. The stability of hectorite at higher temperatures, as compared with montmorillonite, is in contrast to its lower stability under another set of conditions. Montmorillonite does not break down rapidly when subjected to electro-dialysis for removal of bases, whereas hectorite under the same conditions readily breaks down into gelatinous silica.

INTERLAYER WATER

One of the most striking characteristics of montmorillonite is the reversible swelling produced by water.

Hofmann, Endell, and Bilke (1935) and Hofmann, Endell, and Wilm (1938), on the basis of X-ray diffraction data have shown that, on swelling, the absorption of water takes place between the silicate layers of the mineral and causes the spacing of the plane parallel to the layers surface to increase, while the other lattice dimensions remain unchanged. Variation in cleavage spacing with water content for calcium montmorillonite is shown by the results of Hofmann and Bilke (1936), as follows:

Relation between water content and cleavage spacing in montmorillonite

GRAMS H ₂ O PER 100 GRAMS OF WATER-FREE SUBSTANCE	SPACING OF CLEAVAGE PLANE (IN ANGSTROM UNITS)
10.0	11.25
13.9	12.1
19.5	13.4
24.2	14.6
29.5	15.1
36.3	15.6
41.8	15.7
59.0	17.8

Hofmann, Endell, and Wilm, moreover, noted that only (*hk0*) and (*00l*) reflections appeared on X-ray powder-diffraction photographs. Absence of (*hkl*) reflections was discussed by Maegdefrau and Hofmann (1937) as evidence for absence of regularity in the orientation of the parallel layers.

The conclusion that swelling is due to absorption of water between silicate layers confirmed the conclusions of Ross and Shannon (1926, p. 85), who stated:

The swelling is primarily due to the micaceous habit and the very slight cohesion between crystal plates, so that films of water penetrate between them. Thus, on wetting and slaking, the crystalline aggregate that makes up the bentonite subdivides into micaceous plates that have large lateral extent, but many of them probably have a thickness that is best expressed in molecular dimensions.

The physical effect of the increase in the thickness of the water layer between the lattice sheets is especially well illustrated by some of the soda bentonites, which may swell to 8 to 10 times their original volume, permitting a great change in volume without destruction of the characteristic structure. A sample of bentonite from Rosedale, Alberta, was placed in water until it expanded to a gel-like mass. Water was removed by repeated treatment with alcohol; then bakelite varnish was added and allowed to permeate the material and finally was hardened by heat. A thin section shows that the

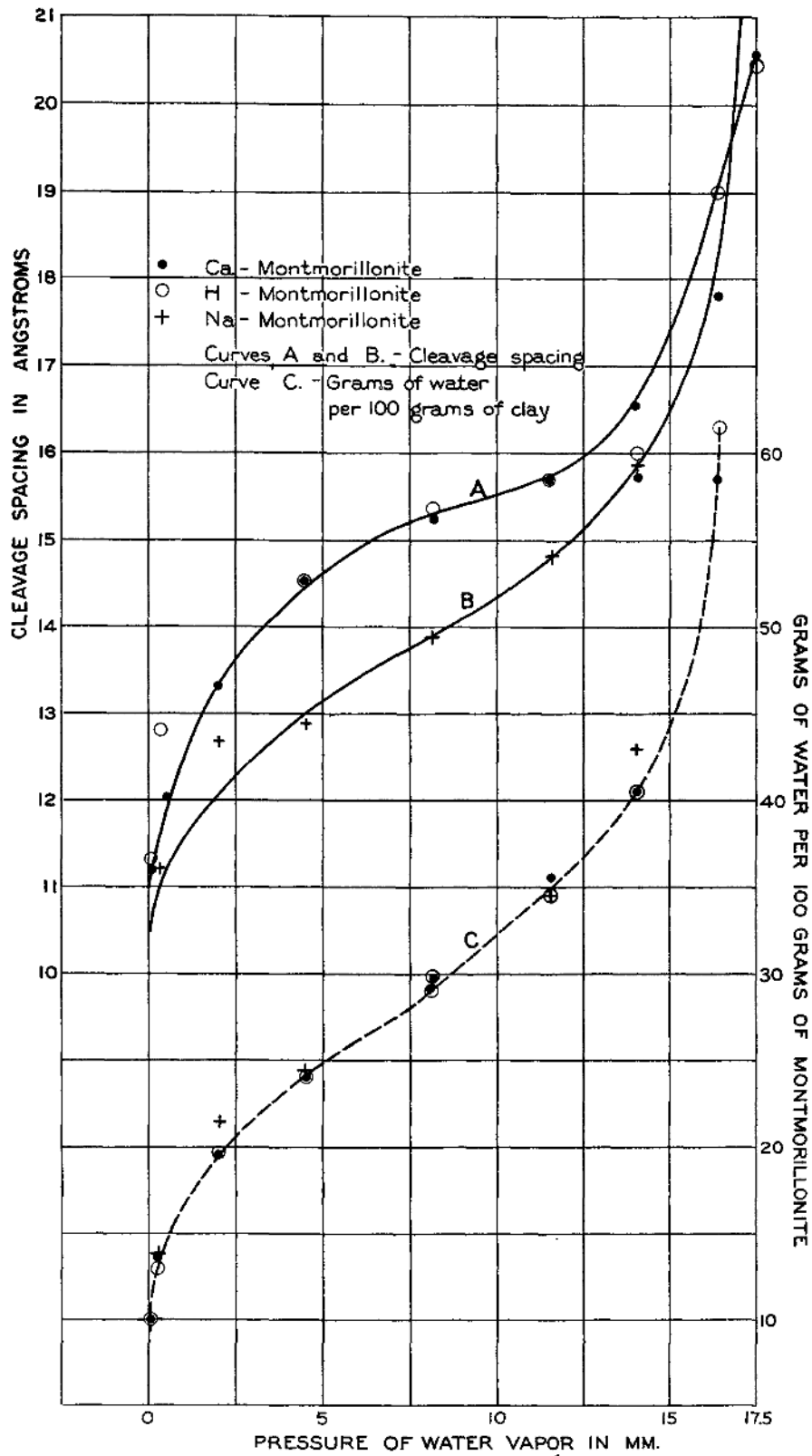


FIGURE 8.—Curves showing relation of vapor pressure to cleavage in montmorillonite. Experiment conducted at 21° C.

characteristic volcanic-ash structure was retained without distortions.

Curves showing the amount of water taken up at particular relative humidities for montmorillonites, with Na^+ , H^+ , and Ca^{+2} , respectively, as the exchangeable ion, and the corresponding cleavage spacings have been published by Hofmann and Bilke (1936) and by Nage'schmidt (1936). Two of the curves published by Hofmann and Bilke (1936, p. 246, curves 1 and 3) are reproduced as figure 8. These authors found that the total amount of water taken up at a given relative humidity did not depend particularly upon the type of the replaceable ion. The cleavage spacing, however, varied greatly, depending upon the replaceable ion.

Hofmann and Bilke found an essentially monotonous change of cleavage spacing with amount of adsorbed water, and they suggested that this water is present in close packing between the silicate layers. Different results were obtained by Bradley, Grim, and Clark (1937). They found that the cleavage spacing did not increase monotonously but rather by stages indicating definite hydrates containing one, two, and three layers of water molecules.

A different approach was used by Hendricks, Nelson, and Alexander (1940). They determined by Le Chatelier's differential method the thermal effects accompanying the loss of water as samples with various replaceable ions are heated at a constant rate. This method allows a somewhat finer distinction of various ways in which interlayer water might be held than do static methods.

The essential result of this study is that the first stage in the sorption of water by montmorillonite is the hydration of the replaceable ion, if it is magnesium, lithium, or calcium. Six molecules of water are required for each ion except Li^+ , which takes three or less. Other ions such as Na^+ , K^+ , and H^+ , apparently do not hydrate. The water molecules are in a single layer parallel to the silicate layer, and at room temperatures they are taken up at a relative humidity of less than 10 percent. At higher relative humidities an amount of water is absorbed adequate to complete the first layer, and this is held somewhat less strongly than is the first kind. At still higher relative humidities, of 40 percent or more, additional layers of water molecules are absorbed. Similar results were obtained by Buswell and Dudenbostel (1941).

In most of the samples examined by Hendricks, Nelson, and Alexander the sorption of water in one manner was not completed before sorption in another set in, as the humidity was increased. In one sample, however, X-ray diffraction results similar to those of Bradley, Grim, and Clark were obtained. Total water sorption follows closely the type of curves found by Hofmann and Bilke (see fig. 9).

OPTICAL PROPERTIES

Optical properties are less definitely determinable for the minerals of the montmorillonite group than perhaps for any other mineral group. These minerals are all definitely crystalline, but no euhedral crystals have been observed, and perhaps the nature of the stacking of the individual sheets prevents any such development in dimensions observable under the ordinary microscope. Areas that show optical unity are in general very small but are observable in thin sections of many materials even at moderate magnifications. Such areas occur in many bentonites, where the replacement of the original glass fragments has proceeded inward from the

outer surface, producing parallel groups of micaceous plates that meet in a suture line, as shown in plate 3A. Even these areas do not permit determination of most of the optical properties, and in general only the mean index of refraction can be determined and the birefringence approximated. The areas are too small for measurement of the optical angle. Indices of refraction could be determined on these areas were it possible to secure them as units for study in immersion oils, but their marked flexibility and distortion on crushing destroys their optical unity.

METHODS OF DETERMINATION

There are, however, several methods by which optical properties may be approximately determined on these clay materials. A few occurrences show a very systematic arrangement of the clay material, and this has built up a kind of pseudo crystal on which optical properties are determinable. As described later films also may be used. (See p. 55.)

Under the microscope these pseudo crystals resemble optically perfect or nearly perfect grains. A study by Hendricks and Ross (1938) shows, however, that these grains are made up of aluminosilicate layers, which have a rather regular arrangement with respect to one another so long as a few orders of reflection (100) can be observed; but on a somewhat larger scale there is only an approximate crystallographic organization of the clay material. The grains give very clear-cut optical properties, which suggest that the departures from crystal uniformity tend to be compensating. Thus the optical properties determined on these materials probably are similar to those determined on films, and closely approximate the true ones.

It is well known that dried films of finely dispersed clays have fairly definite optical properties. Ross and Shannon (1926) gave optical properties that in some specimens had been determined on films, but the method seems to have been first described by Grim (1934).

Some clays form granular aggregates that approximate crystal units on drying; for example, the clay concentrated from the altered feldspar from Magnet Cove, Ark. (p. 68), consisted of remarkably perfect spherulites made up of clay plates with radial arrangement. In general, however, these aggregates are less satisfactory for the determination of optical properties than films of clay.

Some clays—the natural sodium-bearing clays—disperse rather readily in water, but in general dispersion is effected by the following treatment: The clay is added to several times its volume of water after which a large excess of sodium acetate or sodium chloride is added. This mixture is allowed to stand on a steam bath for some hours and, if necessary, is stirred for an hour or more with a mechanical stirrer; then the clay is thoroughly washed, either by repeatedly allowing it to settle and decanting the water or by washing on filter paper. This process commonly requires several days for completion. By the time the clay is free from excess salts it tends to stay in permanent suspension.

Some of this suspension may be allowed to dry on a cover glass, using enough material to give a thin film, but better results have been obtained by placing the clay suspension on a steam bath, where evaporation tends to form a coherent film at the surface. This film may be removed by lifting off on a glass slide and then be allowed to dry slowly at room temperature. The best results were obtained with a dry film about 0.03 mm.

thick. The great vertical shrinkage of the gel-like film tends to bring the individual plates into closely parallel orientation, and at the same time there appears to be a tendency for the plates to assume an orientation within this plane and so build up pseudo crystals, since they give a biaxial figure of nearly constant angle. The film may be broken up and the fragments examined, but better results have been attained by slicing it into narrow ribbons with a razor blade. By working under a binocular microscope, 15 to 20 such ribbons to the millimeter may be cut.

A few of the ribbons of clay material will stand on edge, aided by the curvature developed on slicing. Two indices of refraction may be determined on these and one, the maximum, on those that lie flat.

Assuming that the individual crystal plates that make up the film have assumed complete parallelism to the surface of the film and random orientation perpendicular to that plane, the observed birefringence would be as follows, since the optical character is negative:

$$\frac{\gamma + \beta}{2} - \alpha$$

The departure of this value from the true birefringence will depend on the axial angle, being greatest for an angle of 90°. To illustrate: Assume, $\alpha = 1.5000$; $\gamma = 1.5300$, the birefringence being 0.0300 and axial angle 40°, making $\beta = 1.5265$ by calculation. Then $\frac{1.5300 + 1.5265}{2} = 1.5282$, and $1.5282 - 1.5000 =$

0.0282. That is, the error in determining the birefringence from such a clay film, under ideal conditions, would be negligible for small and medium axial angles.

An axial angle of 90° under the same assumptions would give a birefringence of 0.0225, where the correct value would be 0.0300. These observed values may be designated as γ' and α' . A lack of true parallelism of the crystal plates would tend also to make the observed values converge, and γ' would tend to be low and α' high. However, sharp extinction in plates standing on edge and complete blackness in those lying flat have been observed in some materials, indicating close approximation to true values in the best of such films.

The indices of refraction in tables 13 and 14 were determined on films under nearly uniform conditions.

Studies by Kelley, Dore, Woodford, and Brown (1939) indicate that, although the change from one base to another has little direct effect on the optical properties, a change in the amount of water would probably have a material effect. On the other hand, Marshall (1930) from studies of anisotropic materials in an electric field found that the birefringence varied for different bases.

The conversion of the material to a sodium clay not only permits effective dispersion but also makes all clays uniform in character. Immersion oils with rather high viscosity penetrate the clay slowly; therefore the occluded air is expelled by soaking the clay in acetone for some hours before placing in the immersion oils and then allowing it to stand for 6 to 8 hours for the acetone to diffuse out and evaporate. Usually 6 to 8 preparations of a single sample are made at one time, each treated with a different index oil, to cover the probable range of indices of refraction. The index oil is then removed with absorbent filter paper and fresh oil of the same index of refraction is added. The treatment with acetone seems to expel only a little of the interlayer water and increases the index of refraction but little; however, it

tends to make the amount of this water more nearly uniform in all samples so treated, and to give approximately uniform conditions. In the writers' experiments the use of basic organic immersion oils was avoided, and all determinations were made in mixtures of a very stable petroleum oil and monochlor naphthalene.

DETERMINATIONS OF INDICES OF REFRACTION

Serdiuchenko (Serdintschenko) (1929) gives the optical properties of the nontronite from Stary-Krym (sample 55 of this paper) as follows: Biaxially negative, dispersion $r > v$; 2V about 30°; pleochroism a, bright yellow, b, brownish yellow, c, yellow green.

Kurnakov and Cernych (1929) give the indices of refraction of nontronite from Baschenowski, Russia (see No. 87, table 6), as $\alpha = 1.585$, $\beta = 1.593$, $\gamma = 1.608$. The same authors give the indices of refraction of nontronite from St. Andreasberg, Harz (No. 95, table 6), as $\alpha = 1.584$, $\beta = 1.600$, $\gamma = 1.610$. Iskyul (1935) gives $\alpha = 1.585$, $\gamma = 1.605$ for material from the same locality (No. 95, table 6).

Serdiuchenko and Isükl (1933) give the optical properties of nontronite from Baltatarak (No. 97, table 6) as $\alpha = 1.606 \pm .005$, $\gamma = 1.625 \pm .005$, 2V medium.

Larsen and Steiger give the optical properties of nontronite from Woody, Calif. (No. 62), as $\alpha = 1.560 \pm .01$, $\beta = 1.585 \pm .01$, $\gamma = 1.585 \pm .01$, optically negative, axial angle small; and for another specimen (No. 59) they give $\alpha = 1.57$, $\beta = 1.59$, $\gamma = 1.60$; 2V = 65°.

Optical properties of the saponite described by Palache and Vassar (1925) were determined by Larsen as follows: Kearsarge mine (No. 80), optically negative, 2V small, $\alpha = 1.479$, $\beta = 1.510$, $\gamma = 1.511$; Al meek mine (No. 79), optically negative; 2V moderate, $\alpha = 1.490$, $\beta = 1.525$, $\gamma = 1.527$.

The material collected by W. F. Foshag from the Princessa mine, Maniquipi, Mexico (sample 68), is admixed with 20 to 25 percent of kaolin and a little ferric iron but shows very definite optical properties. These may be noted for comparison with those of purer clays listed in table 13. The following optical properties have been described by Ross and Hendricks (1938): $\alpha = 1.532$, $\beta = 1.544$, $\gamma = 1.557$; birefringence = 0.025; optically negative; 2V = 60° - 80°. These were determined on material that seems not to have been thoroughly impregnated with the immersion oil. Determinations on material from which the air and perhaps some of the interlayer water were completely expelled, are as follows: $\alpha = 1.567$, $\gamma = 1.593$; birefringence .0026. The plates are noticeably pleochroic with the greatest absorption parallel to the plates.

TABLE 13.—Indices of refraction and birefringence as affected by the presence of ferric iron in the montmorillonite-nontronite series

Sample No.	Locality	α'	γ'	$\gamma - \alpha'$	Ferric iron (percentage)
6	Tatatila, Mexico	1.523	1.548	0.025	0.06
50	Pontotoc, Miss.	1.530	1.556	.026	2.26
22	Atzacabazaleo, Mexico	1.538	1.565	.027	5.38
35	Twin Falls, Idaho	1.544	1.570	.026	6.61
44	Beidell, Colo.	1.548	1.575	.027	8.68
58	Spokane, Wash.	1.568	1.606	.038	18.54
65	Sandy Ridge, N. C.	1.590	1.630	.040	27.47

From the data given in table 13 have been plotted the curves reproduced in figure 9, which give variation of indices of refraction with variation in ferric iron. These show a very consistent relation; however, a number of indices of low-iron members given in table 14 fail to fit

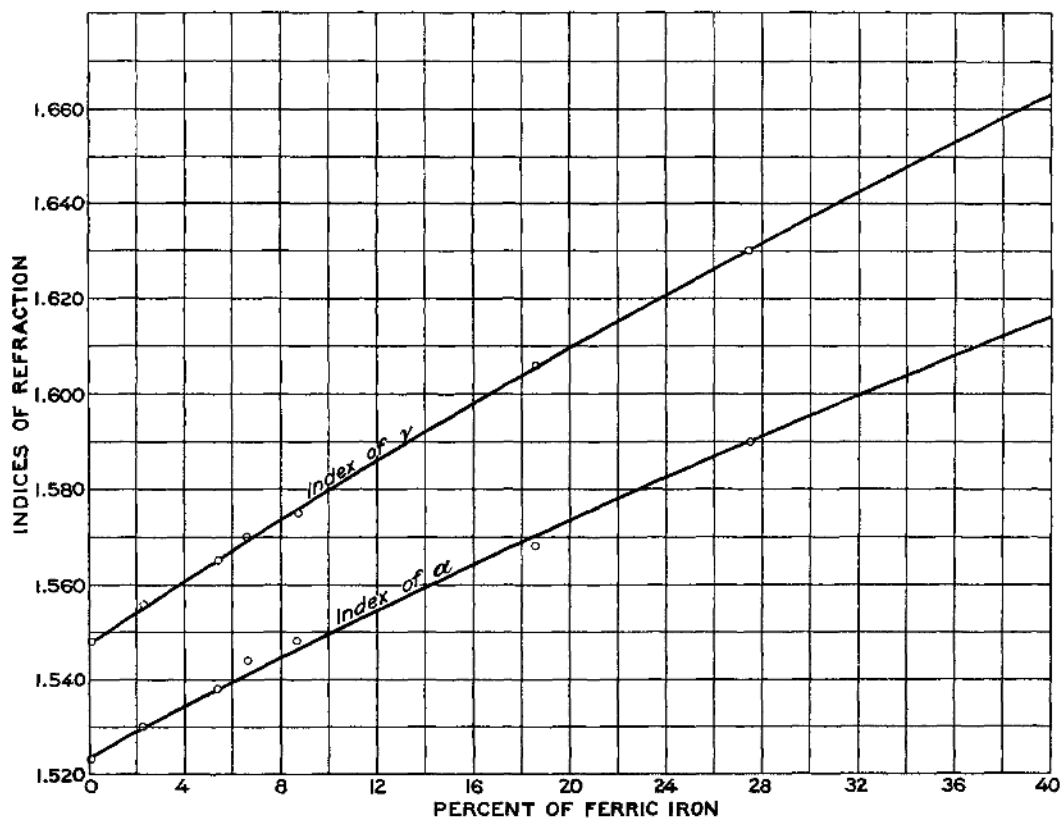


FIGURE 9.—Curves showing relation of indices of refraction to ferric iron in minerals of the montmorillonite-nontronite series.

this curve. This failure probably is due in part to different conditions of determination, but in general it is no doubt the result of other factors. In the high and moderately high iron members the iron is the dominant factor in controlling the indices of refraction. In the low-iron members other factors become much more important; thus, there are variations in the alumina-silica ratio, in the bases, in the water contents, and in the effect of these factors on interlayer spacing and water content, all of which would effect the indices of refraction.

TABLE 14.—Indices of refraction of clays determined on films

Montmorillonite-beidellite series				
Sample No.	Locality	Indices of refraction		Birefringence $\gamma' - \alpha'$
		α'	γ'	
23	Lemon, Miss.	1.528	1.555	0.031
36	Pala, Calif.	1.513	1.538	.025
15	Otay, Calif.	1.512	1.534	.022
24	Mexico	1.508	1.536	.033
45	Embudo, N. Mex.	1.508	1.527	.024
84	Santa Rita, N. Mex.	1.494	1.526	.032
38	Booneville, Miss.	1.498	1.526	.033
Hectorite				
76	Hector, Calif.	1.485	1.516	0.031

The indices of refraction in the table 15, determined on clay grains described on page 54, were made at room temperature and humidity in an air-conditioned laboratory. These grains absorbed oils rather readily; therefore the treatment used for clay films was not necessary.

TABLE 15.—Indices of refraction determined on clay grains

Sample No.	Locality	Indices of refraction		Birefringence $\gamma - \alpha$
		α	γ	
..	Providence mine, Zacatecas, Mexico	1.544	1.565	0.021
45	Fairview, Utah	1.544	1.565	.022
22	Atzacozalco, Mexico	1.533	1.552	.019
47	Wagon Wheel Gap, Colo.	1.526	1.551	.034
44	Beidell, Colo.	1.502	1.533	.031

TABLE 16.—Indices of refraction of minerals related to the montmorillonite group

	Indices of refraction			$\gamma - \alpha$	2V
	α	β	γ		
Talc, Maryland	1.540	1.588	1.588	0.048	Small, variable
Pyrophyllite, Staley, N. C.	1.552	1.564	1.601	.049	61°
Vermiculite, Brinton quarry, Pa.	1.562	1.562	1.597	.035	Nearly uniaxial
Vermiculite (nickeliferous), Webster, N. C.	1.542	1.573	1.573	.031	Small

Indices of refraction were also determined on representative clays after interlayer water had been expelled. The dehydration curves show that there is a flexure at about 200° C., with a marked flattening above that temperature. For that reason the indices of refraction were determined on material that had been maintained at about 210° C. for approximately 36 hours. This treatment did not affect the crystallinity of the material. The interlayer water of montmorillonite and hectorite introduces the only observable difference between the space lattices of these minerals and those of pyrophyllite and talc, minerals without interlayer water. Thus, if the interlayer water were expelled from montmorillonite and hectorite, their optical properties should approximate those of pyrophyllite and talc. Reference

to table 17 below indicates that low-iron montmorillonite and hectorite after dehydration do have indices of refraction comparable to those of pyrophyllite and talc, but the birefringences are lower. The lower birefringence observed in water-free hectorite and montmorillonite may have been due to inability to observe maximum values and was at least in part due to lack of complete parallelism of the component crystal plates.

TABLE 17.—Indices of refraction of clays dehydrated at 210° C.

Sample No.	Locality	α	γ	β	$\gamma - \alpha$
44	Beidell, Colo.	1.559	1.598	0.039
23	Lemon, Miss.	1.555	1.584029
22	Atzacozalco, Mexico	1.555	1.585030
76	Hector, Calif. (hectorite)	1.555	1.584029
47	Wagon Wheel Gap, Colo.	1.543	1.579036
..	Pyrophyllite ¹	1.552	1.600	1.588	.048
..	Talc ¹	1.539	1.589	1.589	.050

¹See Larsen and Berman (1934, p. 164).

PLEOCHROISM

In general, the minerals of the montmorillonite group are light-colored and show no pleochroism, but ar y that have color show distinct pleochroism; thus, films of nontronite from Sandy Ridge, N. C., and Spokane, Wash., are bright green parallel to the elongation and yellow perpendicular to that direction. The nontronite described by Serdiuchenko (1929) is as follows: a, bright yellow; b, brownish yellow; and c, yellow green. The vein clays from Beidell, Colo. (44), Princessa mine, Mexico (68), and Fairview, Utah (46), show slight pleochroism in the red-brown shades.

All the clays of the group are optically negative.

ELECTRON-MICROSCOPE PHOTOGRAPHS

Development of the electron microscope during recent years has made possible examination of clay materials, including members of the montmorillonite group of minerals, under far greater magnification and resolving power than afforded by optical microscopes. In an electron microscope the optical path is similar to that of the usual biological or petrographic microscope, but there are no polarizing devices. Electrons have not been polarized, and there are reasons for doubting that they can be polarized. Electrons accelerated under definite potential drops, usually greater than 25,000 volts, are the radiation used, and lenses are of electrostatic or magnetic types. The wave lengths of the electron radiations, in general, are less than 0.1 A., and the numerical aperture of the objective lens is about 0.01. The very short wave length makes it possible to obtain high resolving power, and the very small numerical aperture gives great depth of focus. Resolving power is really limited by aberration of the lenses and the construction of the microscope. The resolving power is claimed to be adequate in several types of electron microscopes, which have been constructed to permit resolution of features greater than about 20 A. apart.

Electrons of the velocities used have high coefficients of absorption in matter, and so it is necessary to evacuate the microscope and to prepare extremely thin mounts of the material to be examined—less than about 0.1 microns in thickness. For this reason such materials are commonly deposited on very thin films of collodion or similar substance, mounted on wire nets, which can be inserted in the object position in the microscope.

Samples of clay minerals thus must necessarily be dispersed in some liquid, and water is generally selected for this purpose. A drop of an extremely dilute dispersed mineral suspension is evaporated on the film and then examined approximately normal to the film.

Eitel and Radczewski (1940), Ardenne, Endell, and Hofmann (1940), Middel, Ruchmann, and Kausche (1940), Humbert and Shaw (1941), Endell (1941), Shaw and Humbert (1941), Marshall, Humbert, Shaw, and Caldwell (1942), Shaw (1942), and Humbert (1942) have obtained electron-microscope pictures of montmorillonite samples prepared in the manner described above. All samples were found to consist of thin plates very much smaller in dimensions than could be observed by ordinary microscope methods. A photograph (reproduced as plate 7, *D*) of sample 20, montmorillonite from Lemon County, Miss., taken by Mr. H. F. McMurdie of the National Bureau of Standards is typical. Marshall, Humbert, Shaw, and Caldwell (1942) estimated that the mean cross-sectional dimensions of the less than 20 $m\mu$ fraction, separated by sedimentation, of a clay from Putnam soil was $75 \pm 7 m\mu$ and that the thickness did not exceed 5 $m\mu$.

A very thorough study by Shaw (1942) of a bentonite from Rock River, Wyo., showed montmorillonite plates with a more definite euhedral form than those usually observed. Shaw's photograph of the less than 50 $m\mu$ fraction, separated by sedimentation, is reproduced as plate 7, *C*. This fraction contains particles estimated to have an average thickness of 1.9 $m\mu$, which is approximately the structural thickness of two montmorillonite unit sheets. These results and those of other observers indicate that montmorillonite crystals, after dispersing and drying, can contain particles formed of a single structural layer. Particles formed by superposition of a number of layers in such a way as to maintain some euhedral character, such as a definite edge, also are present.

Insley and McMurdie (Alexander, L. T., and others, 1943) and Shaw and his coworkers (Shaw and Humbert, 1941; Humbert and Shaw, 1941) have shown that hectorite contains lathlike particles and is thus different in particle habit from montmorillonite. A typical photograph of the 500 $m\mu$ -200 $m\mu$ fraction of hectorite is reproduced as plate 8, *C* by permission of Dr. Shaw. The average length of the particles is 625 $m\mu$ and the width 63 $m\mu$. The difference in particle habit of hectorite and montmorillonite has raised the question of possible difference in structure. However, dissimilarity of habit does not necessarily imply structural dissimilarity and such an implication is in conflict with the X-ray diffraction data. The difference in crystal habit is not unlike that of the supposedly isostructural minerals, chrysotile and kaolinite, and pyrophyllite and talc. Difference in crystal habit between hectorite and montmorillonite can give rise to pronounced differences in some properties, such as orientation upon drying, swelling in water, and formation of thixotropic gels.

Nontronite from Sandy Ridge, N. C., also was shown by Shaw and his coworkers to be lathlike or ribbonlike in habit. (See pl. 8, *B*.) The range in size from the 200 $m\mu$ down to the 50 $m\mu$ (equivalent spherical diameter) fraction contained particles with an average length of $567 m\mu \pm 57 m\mu$ and width of $108 m\mu \pm 14 m\mu$. The third dimension was estimated to be about $14 m\mu \pm 3 m\mu$. Primary particles in nontronite are thus approximately the same length as those found in hectorite but twice as wide.

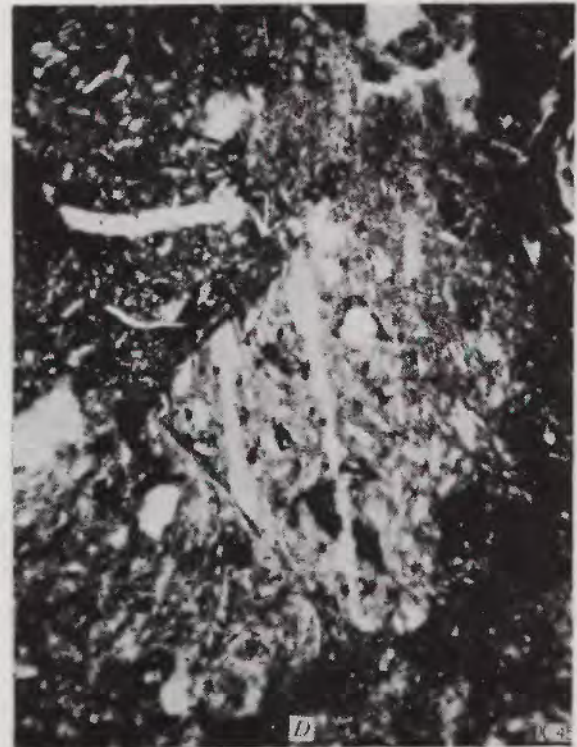
The differences in physical form of montmorillonite, beidellite, nontronite, and hectorite, which are shown in the electron-microscope photographs, might be assumed to indicate a different crystal identity. However, this should be considered in connection with the chemical evidence of isomorphism between the aluminous and ferric-iron members and the close relationship, although limited isomorphism, between aluminous and magnesian members—relationships that are confirmed by X-ray diffraction studies. What then is the significance of the difference in crystal habit?

Detailed studies under the microscope of thin sections indicate that montmorillonite and nontronite show equally perfect micaceous cleavage, and selected areas show perfect optical continuity throughout the thickness of a thin section. This is shown by photomicrographs of nontronite from Sandy Ridge, N. C., and from Dale County, Ala. (pl. 6, *C*, *D*), and may be compared with one of montmorillonite. (See pl. 3, *A*.) Microscope studies show that hectorite also has a micaceous habit (see pl. 6, *B*), though it is somewhat less well developed than that of montmorillonite and nontronite. The micaceous habit of nontronite also is indicated by the parallel grouping of crystal plates, the "pseudo crystals," that were used in determinations of the index of refraction. (See pp. 54, 55.) A thin section of micaceous plates standing on edge would have a thickness nearly a hundred times as great as the width of the nontronite ribbons shown in plate 8, *B*. The perfect optical continuity extending throughout this thickness of a thin section is not compatible with an assumption that these areas are made up of superimposed layers of a hundred or more of the ribbons shown in plate 8, *B*. Thorough dispersion, however, does produce ribbons, which appear to have been absent in undisturbed material. This difference in habit between nontronite and hectorite, as compared with montmorillonite, seems to be analogous to that between chrysotile asbestos and kaolinite, which has been investigated by Warren and Hering (1941) and discussed by Hendricks (1942). These studies indicate that the greater size of the Mg ion results in a strain within the crystal lattice, which restricts the width of the layer to a few units of structure. Growth along the length of the plate, however, is still permitted; in other words, the strain is taken up in one direction. The fibrous character is due to the extreme extension of the plates in one direction. In the same way, the ribbonlike habit of nontronite and hectorite seem to be due to the greater ionic radii and the strain produced by ferric iron and magnesium, resulting in a structure giving potential cleavability perpendicular to the micaceous plates. Such a cleavage would perhaps be analogous to that described by Dana (1892, p. 615), who says that, in addition to the eminent basal cleavage, muscovite shows also planes of secondary cleavage parallel to *b*, and often yields narrow strips or thin fibers parallel to *b*.

Asbestoslike brucite has been observed from Hoboken, N. J., and from Alaska. Also, slender filaments of graphite, another mineral that has a sheet structure and that normally has a mica-like habit, has been described (Gibson, Riley, and Taylor, 1944).

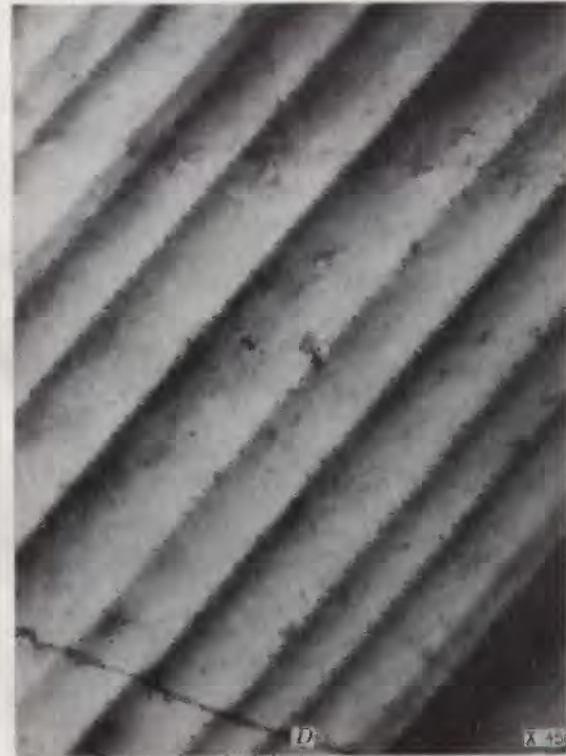
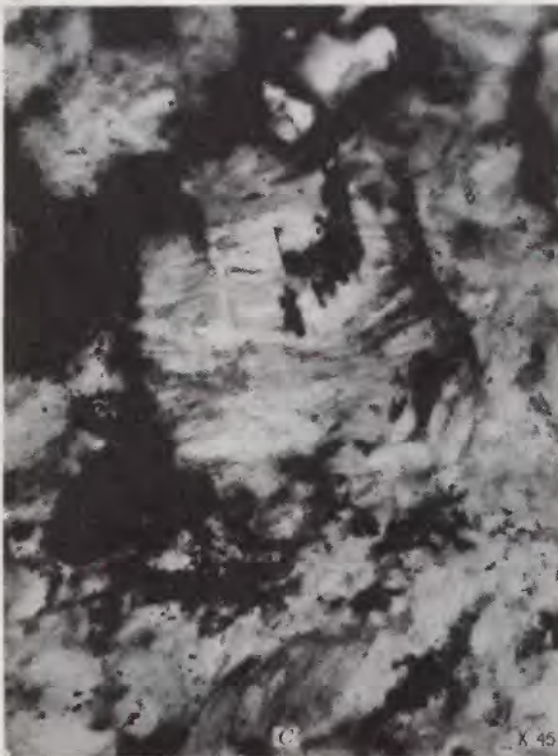
SYNTHESIS

Information on the composition of the montmorillonite group of minerals obtained by chemical analysis affords a basis for the interpretation of their synthesis in the laboratory. Ewell and Insley (1935), Noll



ALTERATION OF VOLCANIC MATERIALS TO MONTMORILLONITE AND KAOLINITE, MAGNET COVE, ARK.

- A.* Tuff fragment showing pumice structure (nearly vertical, wavy-banded structure). Dark gray is montmorillonite; light-gray material at top, with warped structure, is kaolinite embedded in montmorillonite from which it is derived. Light-gray material below is in part finer-grained kaolinite intergrown with montmorillonite.
- B.* Pumice structure shows on right (dark-gray material is montmorillonite; light-gray material is a mixture of fine-grained kaolinite and montmorillonite). An area of warped kaolinite crystals is on left, embedded in montmorillonite.
- C.* Warped and twisted kaolinite crystals embedded in fine-grained montmorillonite. Kaolinite has formed from montmorillonite, as in *A* and *B*. The curved and twisted habit of the kaolinite crystals is characteristic of many occurrences of kaolinite.
- D.* Angular volcanic-rock fragment embedded in similar but finer-grained material, the whole completely altered to montmorillonite. The white areas were originally feldspar phenocrysts.



A, B, AND C, ALTERATION OF VOLCANIC MATERIALS TO MONTMORILLONITE AND KAOLINITE, MAGNET COVE, ARK.

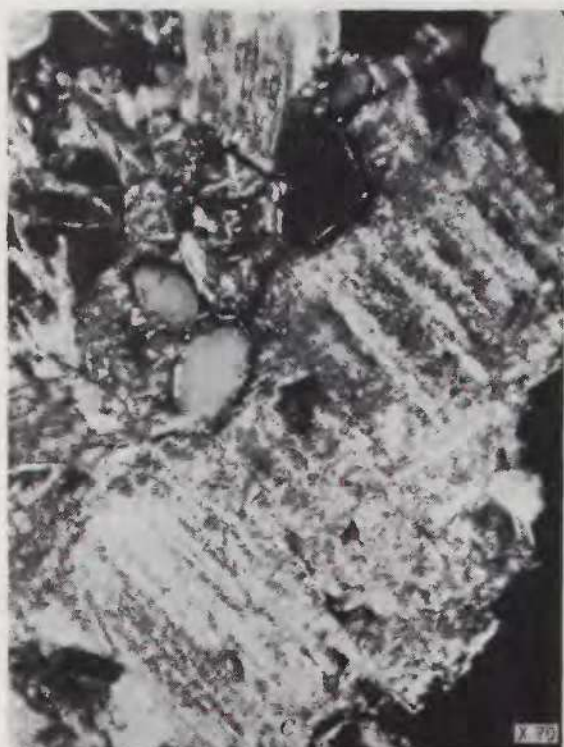
A. Montmorillonite (gray granular material) enclosing residual portions of a single albite crystal. All the montmorillonite is an alteration product of albite. Black areas are leucoxene (anatase).

B. Alteration of albite rock to montmorillonite, with several residual areas of albite embedded in montmorillonite. In neither *A* nor *B* has any kaolinite formed from albite.

C. Central area is a phlogopite crystal partly altered, to hydrous mica and then to kaolinite. Dark-gray portion is phlogopite; light-gray portion is largely kaolinite with hydrous mica on the border. The black areas are leucoxene (anatase).

D. VARVED SEDIMENTARY CLAY FROM FAIRVIEW, UTAH.

The dark zones are due to a concentration of iron oxides. The uniformity of illumination at 45° under crossed nicols, and almost total extinction at 90° , shows the strong tendency for parallel orientation of the individual crystal plates that form the clay. These plates are too small for resolution under the microscope.



A. BENTONITE, WAYNE COUNTY, MISS., SHOWING VOLCANIC-ASH STRUCTURE.

Central area shows the symmetrical arrangement of crystalline clay material derived through the alteration of a single glass fragment. Photographed under crossed and turned 45° from extinction. White areas show the perfect parallelism of the vertical crystal plates. Central area is dark because a large number of the plates is in a horizontal plane.

B. VEIN CLAY, TWIN FALLS, UTAH.

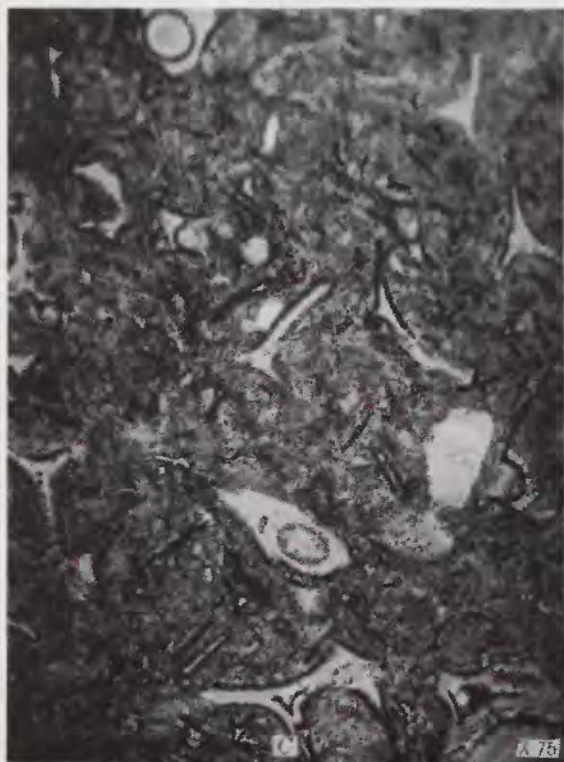
The fine-grained clay aggregate is cut by a series of joint cracks, which were later filled by clay material of the same type. The clay material in these veinlets is uniformly oriented and hence shows its crystalline character under crossed nicols.

C. GRANITE GNEISS, WASHINGTON, D. C.

Lower right shows a single oligoclase grain completely altered to beidellite. Allbite-twinning structure is preserved in the different optical orientation of the clay material. Gray central areas are quartz. Crossed nicols.

D. PLAGIOCLASE PHENOCRYST IN RHYOLITE PARTLY ALTERED TO MONTMORILLONITE, SANTA RITA, N. MEX.

White areas represent fresh plagioclase; gray areas are montmorillonite.



A, B. BENTONITE, OTAY, SAN DIEGO COUNTY, CALIF., SHOWING VOLCANIC-ASH STRUCTURE

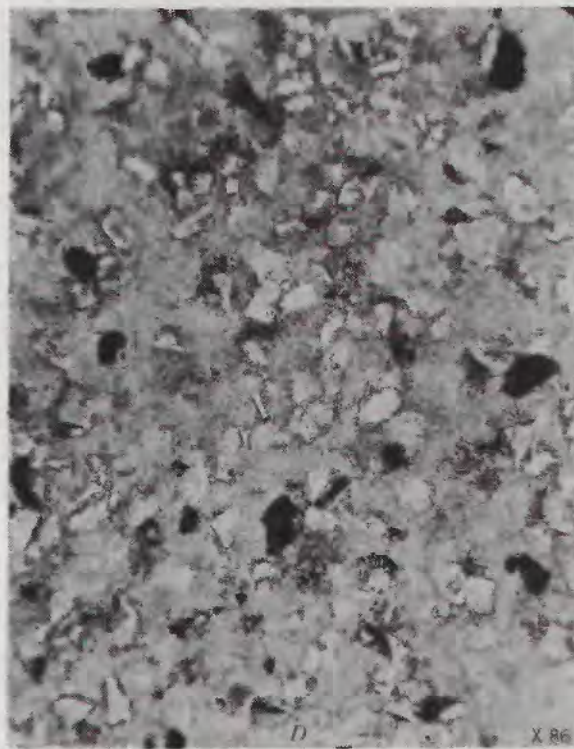
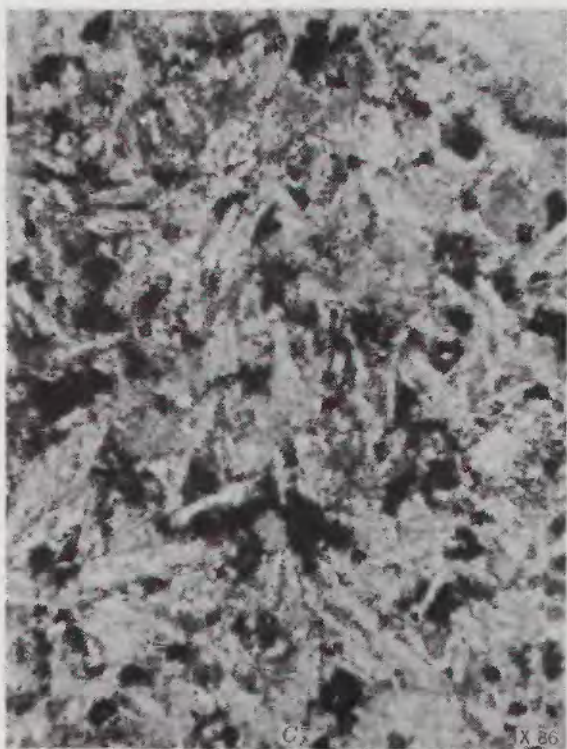
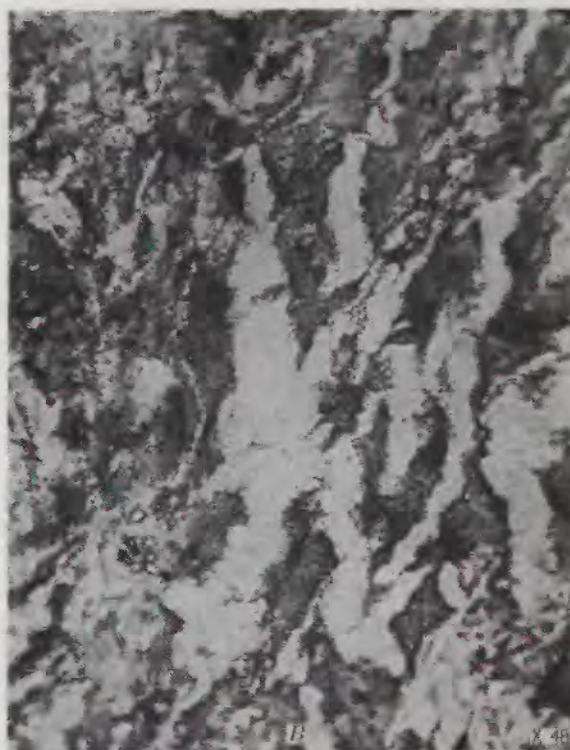
A. Shows several ringlike areas that represent unbroken glass bubbles, some of them—near the top—with the walls between adjacent bubbles still attached. Also near the top is a platelike shard that shows perfect orientation of the crystalline clay material. At left center is a shard showing pumice structure. Just below it is a Y-shaped shard, the lower arm of which shows a double row of crystal plates with a dark dividing line. Crossed nicols.

B. Shows the platelike structure of one type of bentonite. In several places the double row of plates with a central dividing line is discernible. Crossed nicols.

C, D. BENTONITE, NEAR BETTY, NEV.

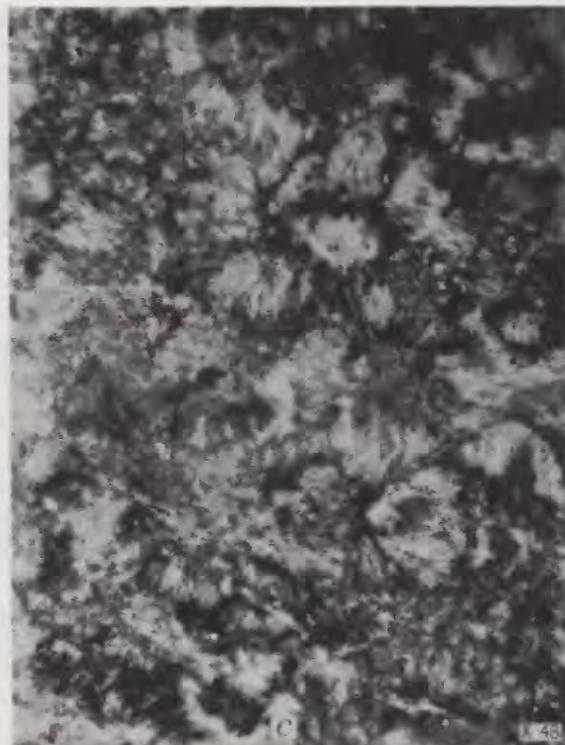
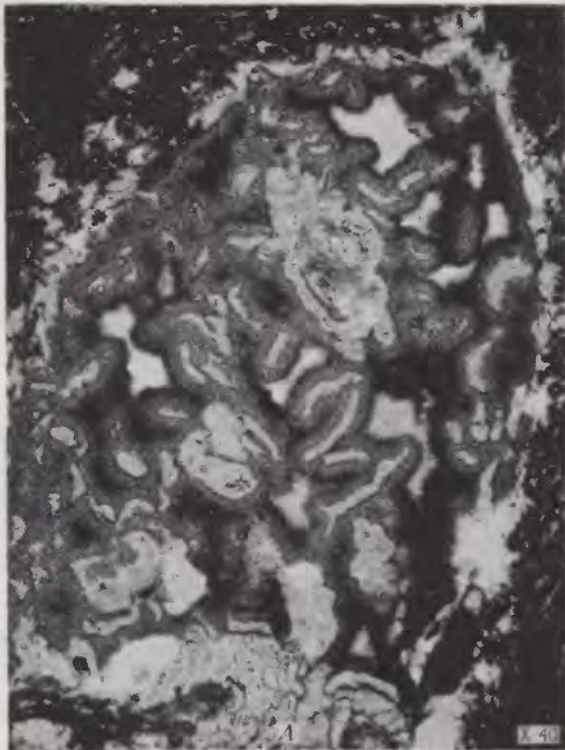
C. Shows the lune-shaped glass fragments that characterize one type of bentonite. Gray areas are montmorillonite; white areas are zeolite. Crossed nicols.

D. Large pumice fragments embedded in finer-grained montmorillonite.



ALTERATION OF ROCKS OF VARIOUS TYPES TO MONTMORILLONITE AND ASSOCIATED MINERALS

- A.* Replacement of perthitic feldspar by montmorillonite, Santa Rita, N. Mex.
- B.* Bentonite, Santa Rita copper mines, Santa Rita, N. Mex. White areas are kaolinite; gray areas are montmorillonite. The kaolinite appears to be the result of partial alteration of montmorillonite, under the influence of sulfate waters derived from oxidizing sulfides.
- C.* Beidellite, Austin, Nev., resulting from the alteration of plagioclase—shown as light elongated areas—in basalt.
- D.* Bentonite of Permian age from a depth of about 2,300 feet in oil test well, 20 miles northeast of Carlsbad, N. Mex. Gray areas are montmorillonite, alteration product of volcanic glass; white areas were originally fragments of feldspar phenocrysts, now altered to kaolinite; black areas are pyrite.



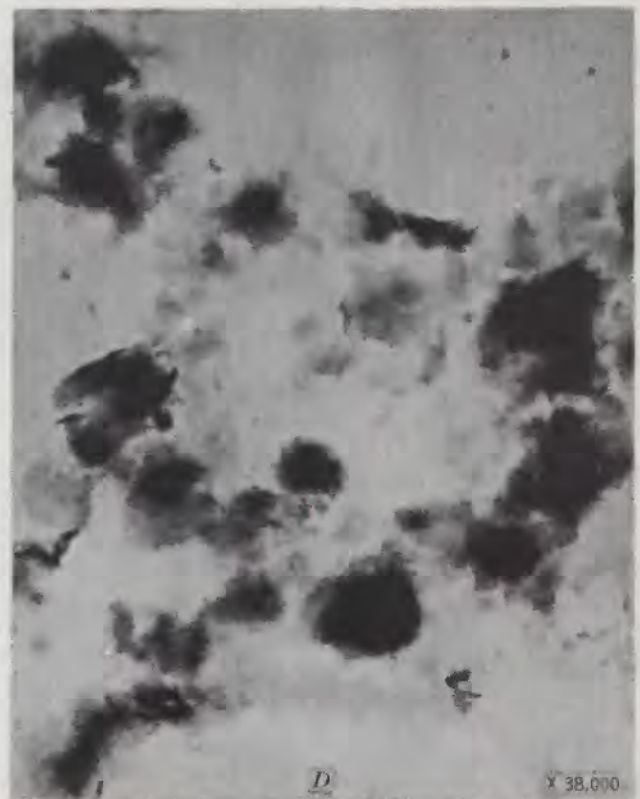
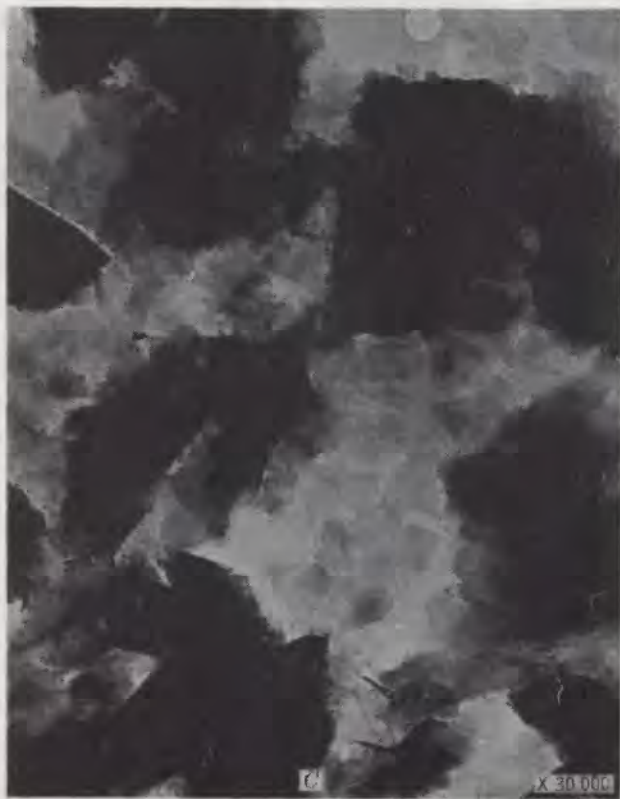
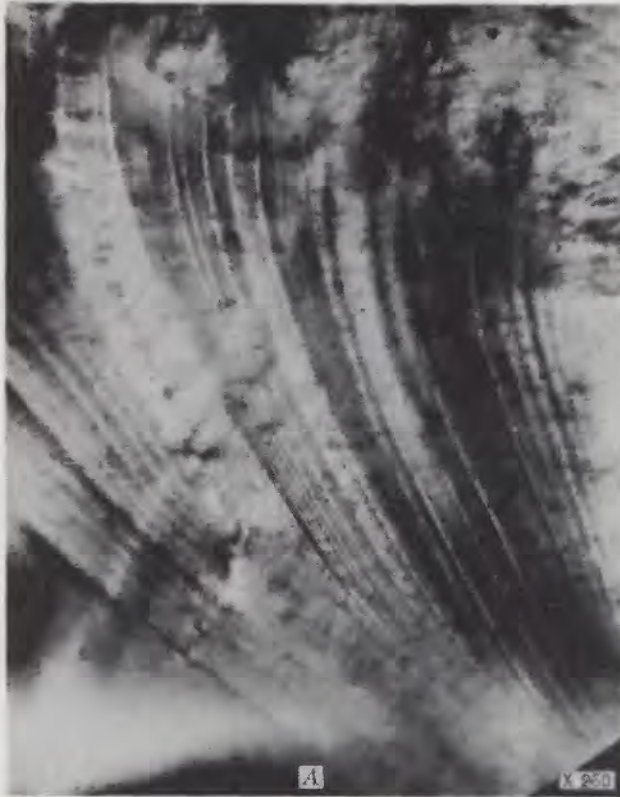
MAGNESIUM AND IRON-RICH CLAYS

A. White areas are saponite enclosed in celadonite (gray). The saponite and celadonite have formed in a vesicular cavity in basalt, saponite being the last to form. Reno Nev.

B. Hectorite, Hector, Calif., in platelike groups, enclosed in very fine-grained aggregates of the same mineral.

C. Nontronite, Sandy Ridge, S. C., forming sheaflike aggregates of plates.

D. Nontronite, Dale County, Ala. Areas of perfect plates surround quartz grains.



A. BEIDELLITE THAT HAS REPLACED A BIVALVE MOLLUSCAN SHELL, FROM PONTOTOC, MISS.

Original structure of shell is well shown under crossed nicols and is due to the different optical orientation of the clay material of the minute shell lamella. Crossed nicols.

B. MONTMORILLONITE FROM PEGMATITE NEAR PALA, SAN DIEGO COUNTY, CALIF. Crossed nicols

C. ELECTRON MICROGRAPH OF MONTMORILLONITE BENTONITE FROM ROCK RIVER, WYO.

Montmorillonite bentonite, less than 50 μ fraction, showing well-formed particles, which perhaps have crystal edges. The thinnest particles are of the order of 2m μ in thickness, which is about that required by a single structural layer. Other particles are more than 20m μ in thickness indicating an orderly superposition of many structural layers. Courtesy of B. T. Shaw and associates, Ohio State University.

D. ELECTRON MICROGRAPH OF MONTMORILLONITE, FROM LEMON, MISS.

Shows featherlike particles without straight boundaries. Many of the particles probably are not more than 5m μ in thickness. Courtesy of Herbert Jusley and E. B. McMurdie, National Bureau of Standards.



ELECTRON MICROGRAPHS OF HECTORITE AND NONTRONITE

- A. Hectorite, from Hector, Calif., showing typical lath-shaped crystals. Most of the laths probably have a thickness greater than $10m\mu$.
- B. Nontronite, from Sandy Ridge, N. C., $200-50m\mu$ fraction. Note the straight edges of many particles. Courtesy of B. T. Shaw and associates, Ohio State University.
- C. Hectorite, from Hector, Calif., $500-200m\mu$ fraction, showing clumps of unseparated needles with radiating acicular particles. Courtesy of B. T. Shaw and associates, Ohio State University.
- D. Hectorite, from Hector, Calif., less than $50m\mu$ fraction, showing very fine acicular character of individual particles. The particle width is about 0.01μ . Courtesy of B. T. Shaw and associates, Ohio State University.

(1936b), Norton (1939), and Hauser and Reynolds (1939) have in recent years succeeded in carrying out syntheses of montmorillonite-beidellite, and Strese and Hofmann (1941) have synthesized hectorite. Their experiments do not duplicate the conditions under which these minerals have commonly been produced in nature, but they nevertheless indicate the importance of some factors in paragenesis.

Ewell and Insley (1935), using slightly alkaline co-precipitated gels of Al_2O_3 and SiO_2 in which the mol ratios were $1Al_2O_3:2SiO_2$, succeeded in forming "beidellite" at $350^\circ C.$ and $390^\circ C.$ in the presence of 167 and 260 atmospheres of water vapor, respectively. Their material was probably truly a beidellite with the composition near $Al_{2.17}[Al_{.33}Si_{3.17}O_{10}(OH)_2X_{.33}]$, which would approximate the $1:2:Al_2O_3:SiO_2$ ratio, and in which the exchangeable base X was probably sodium or $Al(OH)_2^+$,

but part of the sodium may have been present as an impurity. Ewell and Insley similarly prepared nontronite using Fe_2O_3 and SiO_2 gels and, as alumina was absent, the final composition must have approximated $[Fe_{1.89}Si_{4.10}(OH)_2X_{.39}]$; but the replaceable base might have been less than indicated in the foregoing formula. The mixture contained a large excess of Fe_2O_3 for this type of compound, and it appeared in the final material partly as the oxide and partly as an unidentified compound.

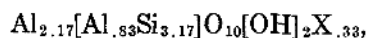
The most elaborate work on synthesis is that of Noll (1936b). He used mixtures of hydrated alumina and silicic acid gels in which the mol ratios were $Al_2O_3:SiO_2::1:4$. All experiments were carried out at $300^\circ C.$ with a water-vapor pressure of 87 atmospheres and in the presence of various bases. Results of his experiments are summarized in table 18.

TABLE 18.—Conditions of synthesis for hydrous aluminum silicates

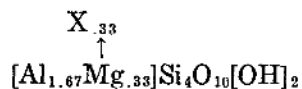
[Investigation by W. Noll of the system $Al_2O_3:SiO_2:H_2O:R'OH$ or $R''(OH)_2$. Aluminum hydrate + silica gel + accessory solute; $Al_2O_3:SiO_2=1:4$. Degree of filling, 0.35. Temperature, $300^\circ C.$]

Accessory solute	Time in hours	Mg. Al_2O_3	Mg. SiO_2	Mg. $R'OH$ or $R''(OH)_2$	Molecular ratio $R'O(R''O):Al_2O_3:SiO_2$	X-ray diagram of the solid phase
N/100 HCl	18	50	117.8			Kaolinite.
H ₂ O	15	50	117.8			Kaolinite.
H ₂ O	15	25	58.9			Kaolinite.
NaOH	16	50	117.8	0.062	0.002:1:4	Kaolinite.
NaOH	16	50	117.8	.62	.02:1:4	Kaolinite (+montmorillonite?).
NaOH	20	100	235.6	6.2	1:1:4	Kaolinite + montmorillonite.
NaOH	24	50	117.8	4.65	15:1:4	Montmorillonite + kaolinite.
NaOH	20	50	117.8	6.2	2:1:4	Montmorillonite + kaolinite.
NaOH	20	50	117.8	31.0	1:1:4	Analeite.
KOH	20	50	117.8	1.1	.02:1:4	Kaolinite.
KOH	20	50	117.8	11.0	2:1:4	Montmorillonite + kaolinite.
KOH	20	50	117.8	55	1:1:4	"Amorph."
CsOH	24	50	117.8	29.39	2:1:4	Montmorillonite(?).
Ca(OH) ₂	20	50	117.8	73	.02:1:4	Kaolin.
Ca(OH) ₂	20	50	117.8	7.3	2:1:4	Montmorillonite.
Ca(OH) ₂	20	50	117.8	36.5	1:1:4	(?)
Mg(OH) ₂	20	50	117.8	57	.02:1:4	Kaolinite.
Mg(OH) ₂	20	50	117.8	5.72	2:1:4	Montmorillonite.
Mg(OH) ₂	20	50	117.8	17.96	.63:1:4	Montmorillonite.
Mg(OH) ₂	20	60	117.8	28.5	1:1:4	Montmorillonite.
Mg(OH) ₂	20	50	117.8	57.15	2:1:4	Montmorillonite.
Be(OH) ₂	24	50	117.8	4.22	2:1:4	Montmorillonite + kaolinite.
Be(OH) ₂	24	50	117.8	42.2	2:1:4	Montmorillonite + kaolinite.

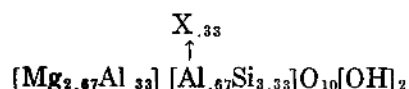
When alumina and silica were used in absence of bases only kaolinite and pyrophyllite were obtained, which would be in harmony with their lack of essential base exchange. Noll found that an essentially higher concentration of base was required for the appearance of montmorillonite than for kaolinite, and his limiting base concentration is near the base-exchange capacity of montmorillonite. In the experiments in which he used NaOH, KOH, CsOH, or $Ca(OH)_2$ beidellite,



probably was formed. A montmorillonite type of mineral was formed over a much wider range of concentrations when $Mg(OH)_2$ was used. The composition probably varied from a montmorillonite-beidellite member to montmorillonite of the composition



at the higher $Mg(OH)_2$ concentrations. The exchangeable base probably was Mg^{++} or $Mg(OH)^+$. At very high $Mg(OH)_2$ concentrations it is possible that some saponite (aluminian) formed as



Formation of montmorillonite-type minerals over a very broad range of concentrations of $Mg(OH)_2$ is full in harmony with their compositions and with the genetic relationships within the group.

The experiments of Noll on synthesis—overemphasize the importance of alkaline conditions in the formation of minerals of the montmorillonite group; the presence of bases is of more importance than alkalinity, as such.

Noll (1940) emphasizes this in a later paper and states that alkalic rocks will alter to kaolin as a result of either acid solution or intensive water leaching. Basaltic or gabbroic rocks, on the other hand, will alter to montmorillonite in consequence of the favorable conditions resulting from the presence of magnesium.

Strese and Hofmann (1941, abstract 1942) carried out synthetic work on magnesian members of the group by boiling $MgCl_2$ solutions with silica gels in the presence of various bases. Formation of hectorite, showing the essential base exchange and other properties, was favored by use of NaOH as the base, but also was observed with medium concentrations of KOH. Higher concentrations of KOH favored formation of mica-like minerals, as might be expected. Antigorite was also synthesized by action of $MgCl_2$ solutions on silica gels.

Norton (1939) studied the hydrothermal alteration of albite, nephelite, orthoclase, leucite, petalite, spodumene, lepidolite, anorthite, beryl, pollucite, and kao-

linite in the presence of high pressures of CO_2 and H_2O at elevated temperatures. A montmorillonite type of mineral was formed only from albite, $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$, whereas anorthite ($\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) gave pyrophyllite. Albite probably gave beidellite in these experiments, but the conditions are very different from those under which it usually forms.

Hauser and Reynolds (1939) studied the devitrification of obsidian and of a glass approximating Wyoming bentonite in composition in the presence of acids and bases at 300°C . Both glasses gave montmorillonite-type minerals, but the obsidian was much the more stable of the two and altered only in acid solution. Basic conditions were not necessary and, in agreement with Noll, a wider range of concentrations was effective when $\text{Mg}[\text{OH}]_2$ was used.

Lovering (1941) has reported a sequence and marked zonal relations between sericite, hydrous micas, kaolinite, and minerals of the montmorillonite group. He concludes that the sequence of mineralization and the control exerted by acid or alkaline solutions corresponds with the results of the synthetic experiments of Noll.

ORIGIN AND MODE OF OCCURRENCE

GENERAL FEATURES

Members of the montmorillonite-beidellite-nontronite-saponite group of clay minerals vary greatly in their modes of formation. They are stable over a rather wide range of temperature; they have formed at temperatures up to at least 200°C . (see pp. 68-69); and they have been formed by purely weathering processes, as well as by low-temperature hydrothermal processes. The important modes of occurrence are (1) in soils, either as essential minerals of the clay fraction or in association with other clay minerals; (2) as bentonites; (3) in pegmatite veins as an alteration product of other minerals; (4) in mineral veins, both as vein minerals and as gouge clays; and (5) as one of the dominant minerals in waterlaid shales.

Some of the factors favoring the formation of the montmorillonite type of clay minerals are indicated by their chemical composition and by the work on their synthesis; others can be deduced from their occurrence in various environments. Experiments on synthesis indicate that the formation of montmorillonite is favored by alkaline conditions or by the presence of salts of alkalis and alkaline earths, in particular by magnesium, which is commonly an essential constituent of these minerals. The formation of hectorite necessarily involves the presence of Li, which in this mineral plays the role of Mg, and evidently takes place in an alkaline or neutral medium, since hectorite is associated with finely divided calcite. In some soils the formation of the montmorillonite type of minerals apparently depends upon the presence of iron compounds, apparently both ferrous and ferric, giving a member of the group containing ferric iron.

As montmorillonite is evidently the typical clay or soil mineral with a crystal lattice into which essential amounts of iron can enter, a clay-forming system containing iron would favor its formation. Organic material in association with certain bacteria results in reducing conditions in the clay-forming system. This would favor montmorillonite formation, either by supplying Fe^{++} directly, where it would play the same role

as Mg^{++} in the crystal structure, or by means of its higher solubility, which would increase the availability of iron to the clay-forming system.

Some bentonites are known to contain more Mg^{++} than the glass from which they were derived, and this may have been supplied either by marine waters, if alterations occurred in the ocean, or by ground waters, if alteration took place after burial. Marine waters are slightly alkaline, and ground waters are alkaline or neutral.

The presence of potassium in sea water, however, favors formation of bravaisite and other mica-like minerals as the end products of marine deposition, and it accounts for the predominance of bravaisite in Ordovician bentonite and marine shales. It seems probable that, in general, the formation of the montmorillonite type of clay minerals occurs only in the absence of appreciable potassium in the clay-forming system. This suggests that in general alteration of glass to montmorillonite was effected in fresh-water bodies or by ground water rather than by marine waters. Orthoclase and muscovite micas are deficient in the bases Mg, Fe^{+2} , and Ca essential for the formation of minerals of the montmorillonite group and so are not favorable sources of montmorillonite, except in the presence of hydrothermal solutions that add these bases and at the same time remove potassium.

A neutral or slightly alkaline medium aids in the removal of silica from weathering feldspars, but it would be less effective than acid solutions in removing bases. Apparently, there also is a tendency for calcic feldspars to give montmorillonite minerals instead of kaolinite clay minerals upon weathering.

From the several examples discussed it seems evident that weathering under conditions which give an adequate supply of magnesium or ferric and ferrous iron and an alkaline environment, together with necessary silica and alumina are the most important factors for development of the montmorillonite type of minerals in soils. Oxidizing conditions or a parent rock whose iron is in the ferric state seem to give kaolinite rather than montmorillonite. Climate and biotic ecology seem to be of secondary importance. However, extremely wet and warm climates, by insuring rapid weathering and oxidizing conditions, probably favor formation of kaolinitic and lateritic types of soils from parent materials that, under other conditions, might have given montmorillonite-type clays. Dry-soil regimes brought about either by lack of rainfall or by prolonged frozen periods result in far less drastic weathering and favor formation of micaceous minerals of the bravaisite-illite type in soils that are dominantly silty.

Minerals of the montmorillonite group have persisted for long periods, but they probably are not the normal end products of weathering. Under continued leaching by acid waters or by long-continued leaching in neutral waters under oxidizing conditions, kaolin minerals tend to form. The tendency for kaolinite to form may be inhibited by the physical relationships; thus, montmorillonite beds and veins may persist indefinitely as a result of their imperviousness to water by which they protect themselves against further weathering. It seems evident that kaolinite seldom if ever reverts to montmorillonite under weathering conditions.

Discussion of these factors will be elaborated in consideration of various types of occurrences of clay minerals belonging to the montmorillonite group.

SOILS AND ROCK WEATHERING

DISCUSSION

The clay minerals are the essential constituent of all soils and shales, and recent mineralogical studies have shown that these fall into three distinct groups—that is, as kaolinite and halloysite of the kaolin group; members of the montmorillonite group; and members of the group of hydrous micas, including bravaisite. Kaolinite was long believed to be the typically clay-forming mineral, but this is not true for large parts of the earth's surface. In areas of deep and long-continued weathering, especially in the tropics and subtropics, and more especially where the parent rock is characterized by alkalic feldspars, kaolinite with its high alumina does form and is commonly accompanied by a high concentration of sesquioxides of alumina and iron. In temperate regions, and in many arid regions, montmorillonite-beidellite or hydrous micas are commonly the dominant clay materials.

So far as known, G. P. Merrill (1902, p. 318) was the earliest investigator to discredit the assumption that kaolinite was the typical clay mineral, but it was rather generally held until the X-ray method gave conclusive evidence of the real mineral nature of clays. However, long before this, microscope studies had shown that kaolin minerals were minor constituents of the soils of large areas of the earth's surface. The differences in indices of refraction, and the still more striking differences in birefringence of the kaolin minerals and of montmorillonites or hydrous micas presented evidence of the absence of kaolinite in a large proportion of clay materials. On the other hand, optical methods do not sharply distinguish the montmorillonite group of minerals from bravaisite and some of the micalike minerals. However, where the mineral occurs as distinct grains, and the iron content is small, montmorillonite has a distinctly lower index of refraction than hydrous bravaisite and the micas. A high iron content of montmorillonite or beidellite raises the indices so that they cannot be distinguished from bravaisite by optical methods alone.

The most widespread occurrence of minerals of the montmorillonite group undoubtedly is in the clay fraction of soils and in shales formed generally in fresh water.

Fine detrital materials such as quartz, micas, feldspar, and other igneous or metamorphic rock minerals generally are present but can be approximately removed by sedimentation. The clay fractions, however, with the exception of the clays in some marine shales, which are predominately bravaisite or altered micas, are in general mixtures of the three principle types of clay minerals. Such mixtures of clays have not yet been separated into their component minerals and there is no great promise of such separations being made. For this reason the analyses listed in tables 1 to 5 do not contain a representative number of analyses of clay minerals from soils and shales. This results in the placing of undue emphasis on montmorillonite-type clay minerals from other sources, especially from bentonites.

Beidellite with a high content of ferric iron is probably the predominant soil clay mineral of the montmorillonite group. Marshall (1935) has published detailed studies, which included chemical analyses of two such clays; one, the Putnam clay, our sample 70, a soil type occurring in parts of Illinois, Indiana, and Missouri, and the other, the Rothamsted clay of England, our sample 69, table 3. The Putnam clay fractions were examined

by Hofmann, Endell, and Wilm, who found no included quartz in the finer fractions. Various fractions gave only the diffraction pattern of a member of the montmorillonite group. This agreed with Marshall's optical studies, which indicated that the Putnam clay is homogeneous beidellite. Formulas for these two clays are given in table 12.

Both the Putnam and Rothamsted clays contain appreciable amounts of nonexchangeable K_2O . Since the Putnam clay probably is homogeneous, this indicates that it possibly is a mixed-layer mineral with layers of the bravaisite or hydrous-mica (illite) type of clay material. The analyses, moreover, differ in many minor ways, such as in P_2O_5 content, from most of the montmorillonite specimens examined. Marshall assumed that in beidellite the TiO_2 proxied for Al_2O_3 and the P_2O_5 for SiO_2 . In this work, however, they were not considered since it seemed more probable that both were present as impurities. The Rothamsted clay probably contains more than 25 percent of kaolinitic clay minerals.

Marshall's work fully illustrates the difficulty of obtaining homogeneous clay minerals of the montmorillonite type from soils. A few clays have formed in very quiet waters in such a way that nearly all detrital rock grains have settled out before the clay was deposited. One of these is the clay from Ancon, Canal Zone (analysis 53, table 1) which contains only 0.50 percent K_2O , and which approaches the limiting formula for beidellite in composition. Moreover it is characteristically low in MgO . Another clay possibly deposited under sedimentary conditions is the one from Fairview, Utah (analysis 46, table 1), which is pictured in plate 2, *D*. It shows closely spaced bedding planes that seem to be varves registering annual variations in conditions of deposition. The very high K_2O content (2.25 percent) of the Fairview clay, however, indicates that it may really be bravaisite or rather than a mixed-layer material made up of both montmorillonite and a mica mineral.

As the beidellite end of the montmorillonite-beidellite series is approached there is a decided tendency toward the formation of mixed-layer type minerals containing potassium. In more fundamental terms the number of nonexchangeable interlayer ions, essentially of K^+ , increases with the increase in replacement of silicon by aluminum in tetrahedral coordination. This indicates that there may be a complete gradation between the beidellite-type clay minerals and moderately high potassium micalike minerals. A detailed investigation of the bravaisite-hydrous mica (illite) type of clay minerals is desirable, and it is unfortunate that circumstances preclude the inclusion of such a study in this paper. Until the mineralogy of these micalike minerals can be cleared up, the question of the extent of solid solution remains open.

Sufficient observations have been made on the distribution of montmorillonite-type clay minerals in soils to permit discussion of factors favoring their formation in the environment of a soil. The nature of the parent material and the chemical environment during alteration are obviously the fundamental factors. Chemical environments are determined by physical and biotic conditions as well as by parent materials. The physical conditions may be continuously arid or humid, or alternately dry and wet; the water table may fluctuate; and materials may differ in porosity. Climatic conditions in general, as they reflect some of the physical factors

and determine the plant cover, will affect the weathering course of the parent materials. However, these are but contributory factors, which combine to form the physical chemical system that controls soil formation.

Formation of minerals of the montmorillonite type in soils developed under five widely different conditions will be discussed to illustrate some of the factors involved. The regions in which the soils formed are Australia, Java, eastern and western United States, and Russia.

AUSTRALIAN SOILS

Hosking (1940a) has studied the mineral composition of Australian soils developed from granitic and basaltic rocks under a wide variety of climatic conditions. After a study of eight granitic soils Hoskins concludes,

It is apparent that granitic types of parent material will weather to kaolinite or halloysite under a wide range of climatic (desert to heavy rainfall) conditions. Whereas the clay type may remain constant, the variation in mineralogical composition of the granite is reflected to a certain extent in the minor constituents of the clay.

From his examination of seven soils developed from basaltic rocks Hoskins reached the following conclusions:

In the case of the basaltic soils, the internal moisture conditions and developmental trends appear to play an important part in determining the mineral clay type formed. Under excessive moisture and dominant leaching conditions, where free drainage is a feature and there is no approach to drought conditions for any period of the year, basaltic parent materials give rise to colloids of the kaolinitic type. Hydrargillite, goethite, and haematite are a further expression of high sesquioxide content and conditions allowing complete oxidation. With a lowering of the moisture status, the practical cessation of active leaching, and the occurrence of protracted drought periods, montmorillonite types become the characteristic mineral type. Where free drainage still prevails kaolinite may still be found, but in its absence montmorillonite alone occurs. * * * In none of the soil samples examined was there any evidence of a mineral of the hydrous-mica type.

It seems evident that the dominant factors for montmorillonite formation in the Australian soils studied by Hoskins are weathering of a suitable parent material under alkaline conditions. Granitic and other highly silicic igneous rocks are not suitable source material. The basic (basaltic) igneous rocks with calcic feldspars and appreciable amounts of ferromagnesian minerals weathering under alkaline and possibly reducing conditions will give soils containing clays of the montmorillonite type. These general observations are in agreement with studies on soil formation from igneous rocks in other regions.

PIEDMONT SOILS

A number of soils characterized by the presence of montmorillonite-type clay minerals have formed from ferromagnesian igneous rocks in the Piedmont region of the eastern United States. In this region residual soils have developed from a great variety of crystalline rocks, and each rock type gives a distinct soil. Small areas of soils derived from ferromagnesian intrusives can readily be recognized in large provinces of granitic and schistose rocks. The boundaries between these different soil types are commonly very sharp and it is apparent that the determining variable in soil formation is the parent material. Plant cover and topography for the various soils often differ widely, but they rather reflect than determine the course of the soil formation.

Piedmont soils, containing essential minerals of the montmorillonite group in their clay fractions, princi-

pally belong to the Iredell, Wilkes, and Orange soil series. Owing in part to the physical characteristics imparted by the montmorillonite type of clays these soils seldom are fertile and generally are used as forest or pasture land. The soils are very shallow compared with many others in the same region where red and yellow soils are most prominent. Their surfaces are not uncommonly covered with unweathered parent rock and the Iredell soil is known as "nigger-head" land on account of the numerous diabase boulders.

A study, detailed in some areas, has been made of these soils, but the factors favoring the formation of montmorillonite are not yet fully evaluated. It is obvious, however, that the nature of the parent rock is a dominantly controlling factor. The diabase intrusives in the Triassic basins weather to give soils containing clays that are predominantly of the montmorillonite type from southern North Carolina to Pennsylvania (Iredell soils). The parent rocks are dominantly calcic plagioclase, with lesser amounts of the ferromagnesian minerals, augite and olivine carrying essential amounts of ferrous iron. Upon weathering, almost all of the iron originally present in the rock becomes a part of the crystal structure of the resulting clay mineral, this being an iron-rich member of the montmorillonite group.

Rocks with a composition only slightly different from those weathering to Iredell soils, which are characterized by montmorillonite, have been observed to give intensely red and deeply weathered lateritic type of soils of the Davidson and Mecklenberg series in Virginia and North Carolina. A thinner soil mantle and lighter red color characterizes the Mount Alto type of soils, which are derived from rather similar rocks in the Piedmont region of Maryland and southern Pennsylvania. The parent rocks from which these soils are derived initially contain no greater amounts of ferromagnesian minerals than do those giving rise to the Iredell type of soils, but their weathering results in the formation of kaolinitic clays and in the liberation of the iron as free oxides and hydrous oxides (Alexander, Hendricks, and Faust, 1941). This difference in weathering pattern, however, must be due to differences in the parent rocks rather than to climatic factors, such as rainfall.

The Orange soil is derived from the Schistose greenstone of the Virgilina district of Virginia and North Carolina and from more coarsely crystalline rocks in other districts. Its clay fraction contains a member of the montmorillonite group, with an appreciable iron content, and relatively large amounts of kaolinite. The greenstone schist at Virgilina is a very fine grained rock and commonly is a recrystallized volcanic tuff. It contains appreciable amounts of ferromagnesian minerals—dominantly hornblende and epidote—and fine-grained feldspar, and its weathering pattern appears to be similar to that of rocks giving the Iredell type of soils.

Epidote greenstone schists of Albemarle and Orange counties, Va., weather deeply to give the intensely red Davidson soils, as do the epidote greenstone schists in central North Carolina. These greenstone schists closely resemble the greenstone schist at Virgilina in chemical composition but contain much less epidote.

The rocks that give the Davidson soil are essentially different in mineralogical character from those giving the Orange and Iredell soils. The Davidson soil is derived from a rock composed largely of epidote, whereas Virgilina greenstone contains abundant hornblende, also epidote, and the Triassic diabase contains augite and olivine. The iron in the epidote greenstone is in the

mineral epidote and hence is essentially all in the ferric state. On the other hand, the Virgilina greenstone and diabase contain a large proportion of ferrous iron.

The presence of iron in the more soluble ferrous state would make it readily available to the clay-forming system and so would promote the formation of montmorillonite-beidellite, even though most of it is eventually fixed in the ferric state. The breakdown of epidote seems to tend to release iron as oxides and under these conditions kaolinite forms rather than montmorillonite-beidellite. Thus, the state of oxidation of the iron in the parent rock seems to be one of the factors that influences the character of the clay mineral formed. Here then is an excellent example where the course of weathering is determined by the mineral composition of the rock rather than by the over-all chemical composition.

In the weathering of diabasic rocks, the minerals decompose almost simultaneously, the augite releasing ferrous and ferric iron, magnesium, and silicon to combine with the calcium, aluminum, and silicon of the feldspar to form montmorillonite. The same general relation seems to hold for certain types of greenstone schists characterized by ferromagnesian minerals containing ferrous iron. In these the clay-forming system seems to be basic and neutral or reducing, but clearly not oxidizing. A different relationship seems to be the controlling factor in clay formation in some types of rocks. In these the ferromagnesian minerals may weather rapidly and their decomposition be far advanced before essential changes take place in the feldspars, which are perhaps less calcic in those rocks. The magnesium has been removed by carbonated waters, and the iron fixed as ferric oxides before the feldspars are decomposed. Under these conditions kaolinite tends to form rather than montmorillonite.

Wilkes soils in many localities are derived from amphibolites or other dominantly ferromagnesian rocks interbedded with highly silicic layers. These soils occur extensively in the region of metamorphic rocks around Young's Mountain in Person County, N. C. Amphibolites in neighboring regions are observed to undergo lateritic weathering with formation of the red, Davidson type of soils. The mineralogic composition of the parent rocks and their petrographic characteristics have not yet been studied in detail adequate to indicate factors controlling the course of weathering.

Soils of the White Store series are derived from shales in the easternmost Triassic basin of North Carolina. These soils are impervious, and the clay fraction is predominantly montmorillonite. This clay fraction, however, is inherited from the parent material, a montmorillonite shale, which was apparently deposited in a fresh-water lake or a sea of low salinity. Montmorillonite has persisted in the soil, even though it has been subject to leaching for a long time in a temperate climate. This shale member is not present in the Triassic regions of Virginia, Maryland, and Pennsylvania. Its probable source and condition of formation has not been studied.

JAVA SOILS

Hardon and Favejee (1939a, 1939b) have examined the clay fractions of a number of soils from Java, which were derived from five principal types of rocks: lateritic soils from ferromagnesian tuffs, "Mergelgronden" soils from young marls and calcareous tuffs, limestone soils, yellow mountain soils from andesitic tuffs, and white and gray earths derived from dacite tuffs. The clay fractions of

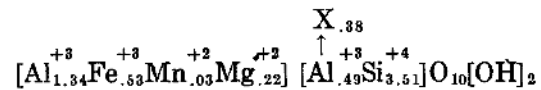
the "mergelgronden" soils consist essentially of the montmorillonite type of clay minerals. These soils are formed by the weathering of a soft marl. Some of the clays still contain calcium carbonate, and it is probable that they were formed under alkaline conditions. These clays probably were formed by the weathering of volcanic materials intermixed with the marl.

Some of the clays separated from the marl soils are quite pure montmorillonite. One of Hardon's analyses (No. 12853) is as follows:

Analysis of montmorillonite from Java

SiO ₂	42.80	K ₂ O.....	0.08
Al ₂ O ₃	19.03	Na ₂ O.....	0.75
Fe ₂ O ₃	8.68	Fe ₂ O ₅	0.06
TiO ₂	0.02	CO ₂	0.00
MnO.....	0.05	(H ₂ O -).....	15.51
CaO.....	1.73	(H ₂ O +).....	8.66
MgO.....	1.81	Organic.....	0.92
			100.10

The clay has a base-exchange capacity of 0.86 milliequivalent per gram. The corresponding formula is as follows:



Calcium is the predominant exchangeable ion. Since these soils are commonly gray or black, it is improbable that an appreciable fraction of the ferric iron is present as oxides or hydrous oxides. The ferric iron content of the montmorillonite is thus probably higher than found for the specimens examined in this work.

Some factors essential for development of the montmorillonite type of clay minerals under the tropical conditions of Java appear to be found in the weathering of a ferromagnesian volcanic effusive in an alkaline medium. These factors are similar to those necessary for formation of the montmorillonite type of clay minerals under the temperate climates of southern Australia and the eastern United States.

GLACIAL SOILS

The grasslands of western United States and Canada and the Steppes of central Russia contain large areas of soils in which montmorillonite is a prominent constituent of the clay fractions. The ecology of the regions is determined to a large extent by the limited rainfall and the continental climate. Soils in general are of Marbut's "northern prairie" and "northern chernozem" types near the boundary between his "pedocals" (soils with a zone of calcium-carbonate accumulations) and "pedalfers."

The parent materials of these soils in the United States are chiefly calcareous glacial accumulations and calcareous loess. Similar types of parent materials and similar conditions for soil formation are present in central Russia. Clays in the soil are partly inherited from the parent material. In the heavy B horizons and in clay pans, increased clay concentration is brought about by weathering of feldspars in place and there is little migration of clay. Feldspar is the source of the aluminum and silica for the montmorillonite type of clay mineral that forms under these conditions. Essential magnesium is supplied by the alkaline earth carbonate of the parent material which also insures an alkaline reaction of the weathering medium.

In the western part of the Great Plains region of the United States the surface material is outwash from the Rocky Mountains and the rainfall is scanty. Farther east, the glacial accumulation contains much ground crystalline rock and reworked shale, which initially contained micaceous minerals of the bravaisite-hydrous mica type. Clay fractions of these soils characteristically contain minerals of that type rather than members of the montmorillonite group.

Lamar, Grim, and Grogan (1938) have studied gumbotil, a weathering product of glacial material and make the following statement:

Gumbotil is derived from glacial till by weathering. * * * Gumbotil does not occur on glacial drift as young as the Wisconsin drift but is common on the older drifts—the Illinois, Kansas, and Nebraskan. It formed under conditions of poor drainage, usually just below the soil layer, over broad, flat upland tracts. * * * The conversion of till to gumbotil in nature involves oxidation, leaching of carbonates and chemical decomposition of the silicate materials. Only the most resistant rock and mineral fragments remain, and some of these are reduced in size. The base of the gumbotil is commonly denoted by a zone containing bands of yellow or brown iron oxide. The original till contained large amounts of clay minerals of the illite group, and in general the processes of weathering have tended to remove alkalis, particularly potassium, and to alter the illite minerals to those of the montmorillonite group. These changes took place in varying degrees on the same drift sheet because of variations in weathering conditions and parent material.

So-called "black-alkali" soils and "slick" spots are widely distributed in the western United States. These are usually due to the presence of sodium-saturated minerals of the montmorillonite type in the clay fractions of the soils. The sodium clay is easier to disperse than is the calcium clay, and its gels shrink greatly upon drying. In the sodium-montmorillonite type "black-alkali" soils the black color results from surface organic matter which drops into shrinkage cracks. The tendency of the soils to disperse when calcium in montmorillonite-type clays is replaced by sodium must be watched carefully in western irrigation projects, and dispersed clays usually must be flocculated before land can be brought into successful tillage.

SUMMARY OF SOILS AND ROCK WEATHERING

In general, it may be stated that soils formed by surface weathering from granitic, highly micaceous, or other silicic rocks do not appear normally to contain montmorillonite as an appreciable part of the clay fraction. Igneous rocks containing essential quantities of amphiboles, pyroxenes, or other ferromagnesian minerals tend to give soils characterized by montmorillonite clays, but in some physical and chemical environments they may undergo lateritic type of weathering. Soils derived from sedimentary formations inherit their clays in part from the parent formation. Calcareous formations apparently will give various types of clay minerals in soils, depending upon the nature of their noncalcareous constituents and the rate of weathering, which determines the pH of the weathering system. Climate and plant ecology are not the all-prevailing factors for soil formation, as now assumed by most pedologists.

The foregoing examples of soil forming processes present a very generalized outline, and many apparent exceptions may be cited. The course of soil formation may be closely followed in some types, but others are inadequately understood. Very little work has been carried through to a rigorous evaluation of all the factors involved in soil formation. It is the difficulty in correlating the various contributory factors that makes many soil problems complex. This necessitates many detailed

studies before generalizations on clay paragenesis are reliable. Beginnings must be made on areas or occurrences where the relations are not too complex and where the maximum number of factors may be evaluated. In some ways soils represent systems more suited for study of clay formation than do hydrothermal deposits, as conditions during soil formation are sometimes constant over long periods and may be determined with some accuracy. On the other hand, the coarser texture, the only partial replacement of the parent mineral, and the associated minerals of veins commonly give a superior record of the sequence of genetic events.

BENTONITES

Bentonites were first recognized from the western United States and for a long time were known only from that region; however, since interest has been aroused in their commercial value and scientific significance, they have been found in nearly all regions of the world. So many occurrences have been described that an attempt to list localities would be almost hopeless. They are present even in England (Kerr, 1932), where they were once believed to be nonexistent.

Bentonites are in general composed essentially of montmorillonite and are among the purest of all clay materials. They thus constitute one of the best-known sources of essentially pure clay material, and numerous clays of this type are represented among the analyses in table 1.

Bentonite had long been recognized as a rather unusual type of clay material, but D. F. Hewett (1917), of the Geological Survey, was the first to recognize its mode of origin. He stated that bentonites commonly contain minerals characteristic of volcanic rocks and that the usual detrital minerals are absent. These facts led him to conclude that bentonite was composed of a clay mineral that was an alteration product of volcanic glass. Later it was found possible to make thin sections of clay materials, and Hewett's conclusions as to the origin of bentonite were confirmed.

STRUCTURE OF PARENT GLASS

Thin sections show that bentonites commonly retain the structure of volcanic ash with surprising perfection. There are three main types of ash structure, although there are complete gradations from one type to another. Perhaps the most abundant is the structure of a very fine grained pumice, rather large fragments of which are represented in plate 4, *D*. The violent explosive eruptions of the parent volcanic vents have drawn out the molten glass with its minute included bubbles of volcanic gases so that the cooled glass fragments have a seemingly fibrous structure. Another type evidently was formed under somewhat similar conditions, but the gas bubbles were larger and had the shape of flattened lenses. The almost complete fragmentation of the glass by explosive action produced glass shards, in large part the platelike remnants of the cell walls that surrounded these flat lenticular bubbles. Such platelike shards are represented in plate 4, *B*. The third type probably was formed by somewhat less violent explosions. This resulted in more or less spherical bubbles; and the shards are therefore curved plates, lune-shaped fragments, or cusps with curved walls, as shown in plate 4, *C*. A single bubble when broken produced shards that form arcs of circles. Where two round bubbles were adjoined, remnants of

the glass wall between them contain the arcs of two circles, and those from three adjoining bubbles form triangular segments bounded by curves rather than by straight lines. Rarely, unbroken bubbles marked by complete circles may be observed in thin sections. (See plate 4, A.) These unbroken bubbles are always filled with clay material of the same character as the replaced bubble walls, showing that some local transportation of clay material has occurred.

The size of the glass shards varies within wide limits. Some of the finest materials are only a few microns in diameter and are perhaps the result of very thorough sorting in water. Wind sorting commonly gives larger and less well sorted glass fragments with sizes in general varying from 0.05 to 0.3 millimeters in greatest dimension. The size is no doubt roughly related to the distance to which the glass fragments were carried from the explosive center. Remnants of a very remarkable ash shower are scattered from the Panhandle region of Texas to east-central Oklahoma, and the more eastern occurrences are marked by a much smaller grain size. In general, bentonite beds have a limited lateral extent, and variation in grain size cannot be readily traced; but there are marked variations in size of grain in the widespread Ordovician bentonites, those in the Alabama-Tennessee region being in general coarser grained than is ash of the same age in regions to the northeast. In some places fragments from 1 to 4 millimeters in diameter have been observed, which had altered to montmorillonite. These probably fell rather close to the volcanic center. Although bentonites are normally derived from pyroclastic materials, one occurrence is known where a small rhyolitic intrusive had altered to montmorillonite.

PHYSICAL PROPERTIES

Bentonites vary greatly in color, although they commonly present some light tint. Cream, light tan, and various shades of gray are most commonly observed, but pink, lavender, pale blue, pale green, and even pure white are not rare. A bentonite from Mississippi is sage green. The texture is most often compact but may be open or porous. Most bentonites resemble paraffin or soap in appearance, especially before thorough drying, and in general they show a distinct translucence in thin fragments. Only rarely are they highly opaque as are nearly all other clay materials.

A few types with sodium as the exchangeable base, as illustrated by hectorite and Wyoming bentonites, form a gel-like mass on absorption of water; but in general, bentonites are characterized by calcium as the replaceable base, and these varieties tend to swell slightly and crumble into a granular mass. The gel-forming types tend to stay in suspension indefinitely, but the more widespread calcium type commonly yields only a small percentage of material that remains in permanent suspension. The calcium bentonites may be converted to sodium bentonites by the substitution of one exchangeable base for another, and dispersion by mechanical means may greatly increase the proportion of material that stays in suspension.

DEFINITION

The definition of bentonite by Ross and Shannon (1926) which has been generally accepted is, "Bentonite is a rock composed essentially of a crystalline claylike mineral formed by the devitrification and the accompanying chemical alteration of a glassy igneous material,

usually a tuff or volcanic ash." In describing it they state:

It [bentonite] often contains variable proportions of accessory crystal grains that were originally phenocrysts in the volcanic glass. These are feldspar (commonly orthoclase and oligoclase), biotite, quartz, pyroxenes, zircon, and various other minerals typical of volcanic rocks. The characteristic clay mineral has a micaceous habit and facile cleavage, high birefringence and a texture inherited from volcanic tuff or ash, and it is usually the mineral montmorillonite but less often beidellite.

MODE OF OCCURRENCE

A few bentonites are derived from materials that fell on land and were redeposited. These materials contain detrital grains, among which quartz is most abundant. Where quartz, feldspar, and other detrital minerals become dominant, the material may be called a bentonitic arkose. Where bentonitic material is reworked after the glass had altered to clay material, or where the shard structure is destroyed before alteration, it is commonly impossible to recognize the resulting clay as definitely of bentonitic origin. It is probable, therefore, that much bentonite has become incorporated in sedimentary materials with no way for definitely recognizing its presence.

The small amount of quartz in most bentonites, as noted by Hewett, has been confirmed by further examination of many hundreds of thin sections. Only a few have been noted where the quartz represented original igneous phenocrysts, although Bramlette (paper in preparation) reports quartz phenocrysts in the San Luis Obispo tuff, which is in part altered to a bentonite.

Magmas high in silica tend to produce rocks characterized by quartz phenocrysts, so the absence of quartz in most bentonites presents evidence that the glass from which it was derived was not excessively rich in silica; in other words, the glass that most readily alters to bentonite tends to have the composition of latite, a rock the crystalline part of which is composed largely of feldspar. Highly silicic glasses evidently have a higher stability and so alter less readily. It is not uncommon to find geologic sections of volcanic rocks where the tuffs of feldspathic composition have altered to bentonite, whereas the rhyolitic rocks in the same section are almost unaltered. Seemingly, there is no composition that definitely limits alteration to bentonite, and it is evident that conditions of formation—chemical environment, depth of burial, and time—also are important factors in controlling its formation.

In the region near Petaca, N. Mex., the base of the section of volcanic rocks is marked by a light-colored, friable, highly permeable rhyolite tuff that has resisted alteration, while higher and less silicic beds in the same geologic section have altered to bentonite.

The comparative sparsity of ferromagnesian minerals other than biotite in bentonites is evidence that the rocks from which they were derived were in general not basaltic and probably in general not andesitic in character. This restriction is no doubt due, at least in part, to the fact that the types of volcanic rock characterized by calcic plagioclase and large proportion of ferromagnesian minerals do not form glassy volcanic ash as readily as do the alkalic types. Where basaltic glass does occur, however, as in Hawaii, volcanic glasses are present and alter very readily to an amorphous material, called palagonite, which is high in iron and very high in water and quite unlike the crystalline clay material that characterizes bentonite. It is possible, however, that given suitable time and conditions, such

material would undergo further change and crystallize into a clay mineral. An exception is the beidellite-nontronite, sample 59, table 2, occurring between two basalt flows in Spokane, Wash., where it is evidently an alteration product of basaltic material.

Ross, Miser, and Stevenson (1929) have described the bentonite represented by analysis 51, table 1, from near Nashville, Ark., where it is associated with fresh fragments of igneous rock. Because the rock fragments are dense and finely crystalline, they have escaped the alteration that changed the unstable glass to clay. The crystalline fragments and the glass shards, which subsequently altered to clay, are so intimately associated that they are believed to be two phases of the same parent magma. The chemical analysis and the norm of these unaltered crystalline fragments are given below.

Chemical composition and norm of volcanic rock from Mine Creek near Nashville, Ark.

CHEMICAL COMPOSITION		NORM	
SiO ₂	62.97	Quartz.....	3.60
Al ₂ O ₃	19.00	Corundum.....	1.80
Fe ₂ O ₃	1.13	Orthoclase.....	63.94
FeO.....		Albite.....	24.10
MgO.....	.26	Anorthite.....	1.95
CaO.....	.54		
Na ₂ O.....	2.86	Salic.....	95.39
K ₂ O.....	10.80		
H ₂ O -.....	.72	Hypersthene.....	1.13
H ₂ O +.....	1.26	Ilmenite.....	.46
TiO ₂26	Apatite.....	.34
P ₂ O ₅10		
	99.90	Femic.....	1.93
		Water.....	1.98
			99.30

The figures given above show that about 92 percent of the Arkansas rock was normative feldspar. The glasses from which bentonites have most commonly formed probably do not have such an extreme composition as that given above, but they seem in general to be highly feldspathic.

An analysis of the clay derived from the volcanic glass is given below.

Analysis of Mine Creek bentonite

SiO ₂	45.12	MgO.....	2.32
Al ₂ O ₃	28.24	CaO.....	.88
Fe ₂ O ₃	4.12	H ₂ O.....	18.72
			99.40

Aluminum is the element least likely to be removed during alteration of glass to bentonite, and for purposes of calculation it may be assumed that Al₂O₃ was neither added or abstracted. This assumption implies that nearly all of the alkalis and an appreciable proportion of silica were removed and that approximately one and one-half parts of trachyte glass were required to produce one part of bentonite. If part of the Al₂O₃ also were removed, the proportion of removed material would be greater.

The clay mineral derived from this rock contained 2.32 percent of MgO, whereas the parent rock contained only 0.26 percent. The additional MgO must have been derived from sea water or from ground water in the presence of which the alteration from glass to clay mineral occurred. This evidence coincides with that presented by Noll (1936) that the optimum conditions for the formation of montmorillonite are in the presence of salts of magnesium.

M. N. Bramlette has had analyzed a vitric volcanic ash that is undergoing alteration to montmorillonite on the north side of Santa Monica Mountains, Los Angeles County, Calif. Analyses are as follows:

TABLE 19.—Analyses of bentonite and related rocks, Santa Monica Mountains, Calif.

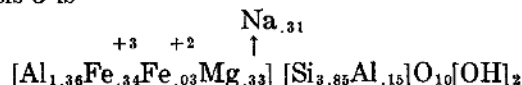
	1	2	3
SiO ₂	70.30	65.66	50.03
Al ₂ O ₃	12.81	12.71	16.75
Fe ₂ O ₃42	1.94	5.83
FeO.....	1.83	1.60	.47
MgO.....	.27	.71	2.78
CaO.....	1.18	1.44	1.20
Na ₂ O.....	2.10	1.10	.26
K ₂ O.....	2.48	1.73	.60
H ₂ O -.....	.68	4.34	13.53
H ₂ O +.....	7.12	8.03	7.52
TiO ₂32	.40	.65
P ₂ O ₅06	.24
MnO.....	.07	.00	.01
BaO.....	.17	.17	.16
Total.....	99.72	99.89	100.08

1. Washed concentrate of larger and least-altered shards of vitric volcanic ash. R. E. Stevens, analyst.

2. Untreated vitric ash, including finer ash and thin films of bentonitic alteration. Charles Milton, analyst.

3. Bentonite from a detailed section 1.18 miles from locality of samples 1 and 2 above. Charles Milton, analyst.

The formula of the montmorillonite represented by analysis 3 is



If the Al₂O₃ is assumed to be constant, about one and one-half parts of glass are required to produce one part of bentonite. As before, there must have been a many-fold increase in magnesium and iron while the alkali content was decreasing. Perhaps the most interesting feature of the analyses is that the amount of water required by the hydroxyl content of montmorillonite was picked up by the glass before devitrification set in. The analysis of the Santa Monica tuff (sample 1) shows that it is a rhyolite and indicates that under suitable conditions glassy ash of rhyolitic character may form bentonites. Bramlette finds a relation between depth of burial, including the time during which leaching continued, and the degree of alteration to bentonite. This implies that alteration was brought about by ground water.

The conditions under which alteration to bentonite takes place are not fully known and probably differ for different deposits. Some bentonites contain marine fossils, notably those in southwestern Arkansas and those in Mississippi that contain beautifully preserved echinoids, and were obviously deposited in a marine embayment. Alteration, however, may have followed rather than accompanied deposition. Some of the bentonites in the southwestern states appear to have been deposited in local saline lakes. In other regions there is no evidence as to whether the ash fell in water or on land, or of the character of the water into which it fell. There is no basis for postulating saline waters as a necessary factor in the formation of bentonites; some bentonites probably have formed in fresh-water lakes or by the percolation of nearly fresh ground water through the porous ash beds. Bentonites have formed in northernmost Alaska and in the tropics; therefore, climate is probably not a completely determinative factor in their formation and persistence.

Very commonly beds of bentonite are marked by a concentration of chertlike material at their bases where

they are in contact with less pervious beds. This concentration shows that alteration occurred under conditions that allowed the waters to move downward and redeposit leached silica. In such bentonites alteration did not take place in the standing water of lake or sea. In other occurrences there is no evidence as to where the silica was deposited, but its removal points to the circulation of water during alteration. Some of the bentonites of the Black Hills and Wyoming regions contain a large proportion of silica in finely granular or colloidal form, and there the silica seems not to have been removed during alteration.

Bentonite thus seems to form most readily from rock types normally rich in potassium and sodium, but with only moderate amounts of calcium and magnesium. Most bentonites, however, are low in potassium and sodium whereas at least some of them contain more essential calcium and magnesium than did the parent glass. The essential character of magnesium in high-silica montmorillonite—the type characterizing bentonites—has been pointed out in a preceding section. (See pp. 39, 40.) There is reason, therefore, to believe that such montmorillonite forms only where Mg is available in the rock or where it can be abstracted from ocean, lake, or ground waters. The fixation of calcium in preference to sodium in most bentonites is obviously due to the relation discussed under base exchange (see pp. 37, 38); that is, bivalent calcium is much higher than univalent sodium in the replacement series. The reason for the very thorough removal of potassium, in view of the possible formation of minerals of the bravaisite type of micaceous clays, is not so clear. The formation of montmorillonite necessitates the removal of very essential amounts of silica, and the presence of alkalis markedly increases its solubility. Thus there may be a marked tendency for escaping colloidal silica to flush alkalis out of the system, possibly before crystallization to montmorillonite. We know little, however, about the relative stability of montmorillonite and the bravaisite type of mica, and can only conclude that montmorillonite is, in general, the more stable mineral of the two under the conditions of formation of bentonite. The Ordovician bentonites mentioned on page 65 are composed of bravaisite, but they seem to represent an unusual type of alteration, and it is not clear whether their mica minerals formed directly or resulted from the recrystallization of montmorillonite in the presence of solutions that supplied K_2O .

ORDOVICIAN BENTONITE

The Ordovician bentonites are made up of a clay material belonging to the bravaisite type which contain 5 to 7 percent of K_2O . These are composed of a mineral that does not belong to the montmorillonite group, but may be briefly mentioned. The term metabentonite has been applied to the potash-bearing Ordovician bentonites as a group (Kay, 1931). This term was suggested by Ross (1928) but only for those occurrences that gave definite evidence of metamorphism. As the Ordovician bentonites, with a few exceptions, are entirely unmetamorphosed, a term implying severe metamorphism is unsuitable.

The Ordovician bentonites have a very wide distribution and have been described by Nelson (1922) from Alabama, Tennessee, Kentucky, and Virginia; they have been reported also from Pennsylvania, New York, the Georgian Bay region of Ontario, and Minnesota;

and Ross (1928) has discussed the Virginia material and its relations. Over very wide areas these bentonites are characterized by abundant euhedral to subhedral crystals of biotite, which represent the only crystalline part of the ash fall, the igneous-rock phenocrysts. More rarely, they contain biotite, together with phenocrysts of orthoclase, and in a few places, as in some of the bentonite beds at Chickamauga Dam near Chattanooga, Tenn., orthoclase and albite are the only phenocrysts. Quartz phenocrysts are totally absent, and soda feldspars may or may not be present. Thus, the mineral composition indicates that the parent rock of the Ordovician bentonites was a potash-rich latite.

VOLCANIC MATERIALS AT MAGNET COVE, ARK.

An unusually complete record of the paragenesis of a group of clay minerals is presented in the Magnet Cove area in Arkansas. About $1\frac{1}{2}$ miles north west of Magnet post office, altered pyroclastic rocks have been exposed in the course of rutile-mining operations.

Magnet Cove has long been a noted locality for interesting minerals and intrusive igneous rocks, and recently Ross (1941) has described volcanic materials from that locality. Volcanic activity, widespread in Cretaceous time throughout the Gulf Coastal region, has been discussed by Ross, Miser, and Stephenson (1929).

Steam-shovel mining has exposed an agglomerate containing highly altered rock fragments of various types, the largest of which are 10 feet or more in diameter. Between these fragments is a fine-grained, nearly white bentonite. The included blocks represent volcanic materials, together with intrusive and sedimentary rocks derived from underlying rock masses. The rock types represented, their variable composition and texture, the fragmental character, and the interstitial, altered volcanic ash, are evidence of violent explosive activity and indicate that the area was the throat of a volcanic vent.

The fine-grained interstitial materials were originally glass, but the larger rock fragments were all crystalline. The freshest of the igneous material is composed wholly of feldspar, but nepheline rocks characterize the region and probably were also present, as was some type of mica-bearing rock.

The feldspar rock is composed entirely of plagioclase whose composition is near the albite end of the series. As nearly pure albite does not crystallize directly from a magma, the rock evidently has undergone albitization. The mica-bearing rock is so altered that its original character is not evident. The glassy material are of two types, one originally a very fine grained ash, the other made up of pumice fragments, some of which were as much as 5 millimeters in diameter. (See pl. 1, A, B.)

These materials have all been very thoroughly altered, seemingly by moderately hot solutions or by volcanic vapors, which rose through the porous mass. Alteration products extend far below the zone of oxidation, as fresh pyrite is abundantly present; alteration, therefore, was not a weathering process. Permeation of the vent-filling materials by altering solutions, which was facilitated by their porous character, promoted very thorough alteration. The secondary minerals formed were montmorillonite, kaolinite, hydrous micas, unusually abundant leucoxene (anatase), apatite, pyrite,

and rutile. The fresh mica remaining is phlogopite, part of which, at least, is evidently the result of early hydrothermal reactions. The fine-grained ash and the pumice fragments were first altered to montmorillonite and later underwent partial further alteration to kaolinite.

The different alteration of feldspar rock and glassy materials is probably due to the greater permeability of the glassy fragmental materials. The nearly pure feldspar rock was partly to completely replaced by montmorillonite, but it did not undergo further alteration to kaolinite. A representative specimen is illustrated in plate 1, *A, B*. The only other alteration of feldspar rock was the local development of micas and hydrous micas, which no doubt preceded the development of montmorillonite. The abundant leucoxene, which seems to have formed at the same time as the clay minerals, shows as black areas. (See pl. 2, *A, B, C*.) An X-ray examination of this material indicated that it was anatase. Most of the kaolinite is the result of further alteration of montmorillonite, as illustrated in plate 1, *A, B, C*, but a little has been derived from phlogopite, which was first altered to hydrous micas, as shown in plate 2, *C*. In none of the numerous specimens examined was there any direct alteration of feldspars to kaolinite.

The alteration of glass and feldspar rocks to montmorillonite was evidently brought about by primary solutions, or more probably by juvenile vapors as they escaped through the porous mass, and was similar to the alteration process at Yellowstone Park, which is described on pages 68-69.

The presence of abundant pyrite associated with rutile in the interstitial clay material shows that the clay was formed under reducing conditions, and the similarity of these relations to those described by Fenner at Yellowstone indicates that these solutions were neutral or alkaline. (See pp. 68-69.) Under these conditions montmorillonite was formed through the alteration of both glass and alkalic feldspars by juvenile vapors. Those vapors that came into contact with air would become acid through oxidation of H_2S to H_2SO_4 . As volcanic activity waned the vapors would tend to condense and penetrate back into the porous aggregate of pyroclastic materials. In zones where acid conditions prevailed there would be further reactions that would change the earlier clay materials to kaolinite. The acid character would be confined to the upper part of the volcanic neck, and in depth only montmorillonite would be expected.

The chemical analysis given below represents montmorillonite that was an alteration product of albite. A specimen was selected with only a small proportion of residual albite—one similar to but containing somewhat less albite than is shown in plate 2, *B*. This was dispersed in water with a mechanical stirrer, and sodium acetate was added to convert it to a sodium clay. After repeated washings, the clay portion remained in permanent suspension, and repeated overnight settling eliminated even the finest of the residual feldspar. After the separation the suspended material was treated with calcium acetate, to change it back to a calcium clay, and washed as before. Examination under the microscope showed that the resulting material was an unusually pure clay of the montmorillonite type. Washing, however, had evidently not removed all the calcium acetate, and probably other organic materials formed from the acetic acid by catalytic action of the

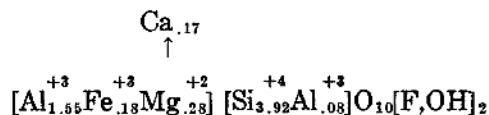
clay, and as a result 4.07 percent of organic material and an excess of CaO remained in the clay. Aside from this, however, the material was a typical bentonite.

Analysis of montmorillonite from Magnet Cove, Ark.

[K. J. Murata, analyst]

SiO ₂	49.33	H ₂ O +.....	7.74
Al ₂ O ₃	17.40	F.....	.31
Fe ₂ O ₃	3.05	Organic impurity.....	4.07
MgO.....	2.37		
CaO.....	4.91		100.26
TiO ₂04	Less O = F ₂18
H ₂ O -.....	11.04		100.18

The following formula represents the chemical composition, assuming a normal amount of exchangeable Ca:



This formula would require about 1.98 percent of exchangeable CaO, indicating an excess of about 2.93 percent of CaO, which was combined, no doubt, with the portion reported as organic material. The foregoing chemical analysis of material from Magnet Cove is that of an almost typical montmorillonite and provides a clear example of a montmorillonite derived from feldspar.

The derivation of the clay minerals at Magnet Cove and their relation to one another is shown in plates 1 and 2. Plate 2, *A*, represents a single feldspar crystal (white) partly replaced by montmorillonite (gray). The black areas are aggregates of leucoxene.

Plates 2, *A* and *B* represent a rock that was originally pure feldspar, but which has been so completely replaced by montmorillonite that only a few residual areas of feldspar remain.

Plate 1, *B* shows excellent preservation of the fibrous structure of the pumice. The medium-gray areas are montmorillonite, and the lighter areas that accentuate the fibrous structure are kaolinite. On the left is an area where typical curved crystals of kaolinite have formed within the groundmass of montmorillonite (gray). The black is leucoxene.

Plate 1, *A* shows a sharper separation between areas of montmorillonite (dark gray), and those of mixed montmorillonite and kaolinite (light gray). An area of curved kaolinite crystals occurs at the top of the figure. As in plate 1, *B*, the fibrous structure shows best in the areas partly altered from montmorillonite to kaolinite, but also is discernible in the areas of pure montmorillonite.

Plate 1, *C* shows typical curved and twisted crystals of kaolinite lying in a groundmass of montmorillonite.

Plate 2, *C* shows a mass that was originally phlogopite partly altered to kaolinite. White areas are kaolinite and gray ones residual areas of phlogopite. Black areas are leucoxene.

CLAYS OF THE GEYSER REGION IN YELLOWSTONE PARK

The formation of clays at Magnet Cove, Ark., deep in a volcanic neck and in the presence of escaping magmatic emanations, bears a close resemblance to that in the geyser region of Yellowstone Park.

The geyser and hot-spring region was intensively studied between 1925 and 1935 by Allen and Day (1935) of the Carnegie Geophysical Laboratory. As a part of this study two areas were explored by drilling and the materials were studied by Fenner (1936). One of these, in the Norris Basin, was selected as representing an area of acid-sulfate waters. In the well, pressures up to 297½ pounds per square inch and temperatures up to 205° C. were recorded.

Allen's work had led him to believe that the acidity in such areas was a superficial condition, caused by the oxidation of H₂S and that it gave way to the alkaline condition at a moderate depth. Fenner (1936), after detailed studies of the drill cores came to the following conclusions:

There is considerable evidence in descriptions given in the literature that kaolinite is formed in acid solutions. The beidellite-montmorillonite-nontronite group seems to be indicative of alkaline conditions, but the evidence is less positive. * * *

Four samples of material from the Norris hole were examined for the writer by Posnjak. In thoroughly leached surface rock * * * Posnjak found kaolinite, together with much cristobalite, quartz, and tridymite. * * * From depth of 95 feet, white clay replacing phenocrysts of feldspar * * * was found by X-rays to be mostly kaolinite, with a little residual feldspar, but it may contain some beidellite also. * * * From 243 feet, cream-colored clay, from feldspar casts, was the beidellite type of clay. * * * These results, considered in connection with the character and occurrence of the materials examined, show that in the surface rock feldspars have been wholly kaolinized. In the core from 95 feet only a few feldspar phenocrysts and * * * a little of the groundmass have been altered, and the clay is probably a mixture of kaolinite and beidellite. At greater depth the alteration has produced beidellite only. * * * The effect of acidity is thus apparent in the formation of kaolinite as far down as 95 feet, and probably extends somewhat beyond that, but only a small amount of feldspar has been altered at this depth, and therefore the action is not vigorous. This does not imply, of course, that meteoric waters do not descend below the shallow zone of acid leaching. They doubtless descend much deeper, but at such a slow rate that the acidity that they tend to impart is overcome by the alkalinity of the bicarbonates. * * * In these rocks the beidellite clays in the casts are usually white, but some are light brown or light green. From appearance and optical measurements they probably vary from nearly pure hydrated aluminum silicate to those members in which considerable ferric oxide and magnesia are present. * * * Destruction of feldspars and formation of the beidellite type of clay is apparently now the active process in the deeper levels at Norris. It is going on slowly and has not yet brought about sufficient changes to obscure previous processes, but the clay penetrates almost everywhere. * * * An interesting feature is the close association of beidellite with pyrite. In innumerable instances the casts of feldspars replaced by clay contain bright little cubes of pyrite, and portions of groundmass that contain an unusual amount of clay are likely to have much pyrite. This does not always hold, but the association is so common that one feels that the same alkaline solutions that formed the clay introduced the pyrite. * * * In the Norris cores it appears that the alteration of feldspars to beidellite is now in operation. It has followed rather than preceded base exchange in the feldspars.

Thus, Fenner presents evidence that kaolinite was formed at higher levels where alteration took place under influence of acid waters, and that at deeper levels where the waters were alkaline, beidellite-montmorillonite formed.

The relations between montmorillonite and kaolinite at Magnet Cove and Yellowstone Park illustrates the essential factor controlling their formation. Kaolinite is most commonly the clay mineral derived from alkaline feldspars, but this is the result of formation in the absence of bases or under conditions that favor their removal. Genetic processes taking place under hydrothermal or vapor-phase conditions are commonly characterized by the introduction of bases including magnesium and iron. Where these bases are introduced,

minerals of the montmorillonite group tend to form; where they are removed, kaolinite forms.

The relationships at Magnet Cove and in the Yellowstone hot-spring area show that feldspar alters to a clay mineral of the montmorillonite type under the influence of vapors or solutions, which add bases to the system and which are alkaline or alkalic in character. On the other hand, the discussion of soil formation indicated that feldspathic rocks tend to alter to kaolinitic material where leaching is the dominant process. It is evident that the controlling factor in the formation of clays of the montmorillonite type is the availability of bases, of which magnesium is the most essential. Granitic rocks are low in ferromagnesian minerals, and ever where these are present in the parent rock, the iron and magnesium tend to be removed under leaching conditions. In the absence of these bases, kaolinite forms. In the presence of mineralizing solutions these bases are commonly contributed to the system, and feldspar that was originally without essential amounts of associated minerals, containing either iron or magnesium, alters to montmorillonite.

VEIN AND GOUGE CLAYS

Montmorillonite-beidellite is the mineral that forms gouge clays in some mineral veins. In many of these it is evidently a hydrothermal mineral formed during the deposition of the vein, but in others it seems to be an alteration product of aluminous minerals which were reduced to extreme fineness during fault movements and thus rendered easily alterable. Other vein clays seem to have been deposited from colloidal solution during a very late stage of mineralization, or even from cold waters. In some veins the gouge clay is later than mineralization and seems to have been deposited in open spaces by percolating waters, which entered through such minute capillary spaces that all but the finest fractions representing colloidal clay material were filtered out. The beidellite (Nos. 44, 47, tables 1 and 10) from the type locality, Beidell, and from Wagon Wheel Gap, Colo., and the varved clay from Fairview, Utah (No. 46; see pl. 2, D), seem to be clays of this type. They form large platy masses whose optical properties closely simulate those of single crystals. This simulation is due to the uniform optical orientation of the minute crystal plates that make up the larger platy masses. The most thorough mixing with a spatula does not destroy the anisotropic character of the moist clay. It merely drags the submicroscopic plates out into oriented smears, which continue to show the characteristic high birefringence of the original aggregates. Many samples of clays of this group show the same property in lesser degree.

Other vein-forming clays are No. 35, Twin Falls, Idaho (see pl. 3, B); No. 49, Carson District, Idaho; Nos. 39 and 68, Maniquipi, Mexico; No. 54, Roseland, Va.; No. 13, Irish Creek, Va.; and No. 41, Glen Riddle, Pa. The clay from Irish Creek, Va., is the result of very thorough alteration along a shear zone several feet wide within granodiorite. This zone lies only a few feet from cassiterite-bearing veins, but the absence of any other products of mineralization associated with the montmorillonite shows that its deposition was later than that of the cassiterite and may have been an unrelated episode.

The color of the vein clays when free from color-imparting impurities, is commonly bluish gray or slightly greenish. The most important impurities are hydrous

ferric iron (limonite), which gives yellowish colors, and ferric iron (hematite), which gives red colors. It is commonly believed that greenish colors are due to ferrous iron, but ferric iron in combination, as in some silicates, may give tints that appear to be greenish rather than red. In discussing colors, however, it must be remembered that very dark yellows appear to the eye to have greenish shades, when in fact no green is present; thus, olive green (23 yellow M of the Ridgway Color Standard) contains no green whatever. Nontronite, however, is chalcedony yellow (25' YG-Y, b of the same color standard) and does contain a green component. The Ordovician bentonites are commonly blue-green, a color no doubt due to the combined effect of iron and potassium.

The pegmatite clays represented by samples 36 and 42 from Pala, Calif. (see pl. 7, B), are of slightly different origin. The Pala clay occurs in the gem-bearing pegmatites of San Diego County, Calif., where it is at least in part an alteration product of feldspars, spodumene, and tourmaline. W. T. Schaller (personal communication) believes that this alteration was probably a late hydrothermal process, though large masses of the clay give no clear evidence of its mode of origin. Similar clays have been described by Brush and Dana (1880), who evidently believed that they were formed by mineralizing solutions. An analysis of this clay is given in table 1, No. 33, and one of a similar clay from Greenwood, Maine, in No. 28.

Nontronite appears to be widely but sparsely distributed. Much of it is associated with mineral veins, and a number of samples have come from small veins of unknown origin in the schists of the southern Piedmont region of this country. The beidellite-nontronite from Spokane, Wash., is an alteration product of basaltic volcanic glass. It would be interesting to know if it first altered to the palagonite mentioned on page 65 and later assumed the crystalline form.

The clay called faratshite from Madagascar (Lacroix, 1914) has been shown by Hendricks (1939) to be a mixture of kaolinite and nontronite.

Saponite also seems to be most commonly associated with mineral veins, but the related hectorite from Hector, Calif., described by Foshag and Woodford (1936), is an exception, being derived from bentonitic material. Saponite is reported also by Heddle (1879) from amygdaloidal cavities in basalt, especially from Scotland where it occurs associated with celadonite. The same association has been noted in basalt from Reno, Nev., where it appears to have developed at a late stage in the cooling of the extrusive rock, and thus seems to be a deuteric mineral.

PYROPHYLLITE AND TALC

Pyrophyllite and talc are not commonly grouped with clay minerals, but the relationship of pyrophyllite to montmorillonite, and of talc to hectorite, makes a comparison advisable. Pyrophyllite occurs as foliated, often radiating groups or as the fine-grained massive material that was named by Hermann (1829). Talc has long been known, having been referred to as "magnetis" by Theophrastus about 315 B. C. in his work, "On stones." The name talc also is old, being derived from the Arabic. Talc occurs in talc schists, as massive material, and in beautiful foliated masses usually of a pale apple-green color and commonly associated with hydrothermally altered serpentines and dunites.

Analyses of several pyrophyllite and talc specimens

are listed in table 20. Only a few recent analyses of talc and pyrophyllite are available, but the older ones given by Dana (1892) no doubt are good, and all agree so consistently that those quoted in this paper (table 28) are believed to be representative. They have been selected from the published analyses because of their low alkali and alkaline-earth content. All specimens represented by these analyses consist of well-crystallized material; they include the radiated pyrophyllite from the Hemp mine, Moore County, N. C., and the large talc folia from Harford County, Md.

Formulas derived from the analyses are given below. In these particular talcs, Al^{+3} is substituted to a slight extent for Si^{+4} in tetrahedral coordination. The valency is balanced by substitution of Fe^{+3} or Al^{+3} for Mg^{+2} in octahedral coordination. The number of ions having octahedral coordination does not differ significantly from 3.00. The slightly higher value, 3.01, for the Harford County, Md., specimen is within the analytical error but is probably due to the presence of a slight amount of ferric iron, which was included as ferrous in the analysis. A summation greater than 3.00, of course, is not possible according to the present concept of the talc structure.

In the pyrophyllite samples, also, Al^{+3} proxies to a slight extent for Si^{+4} in tetrahedral coordination. The resulting decrease in the positive charge is balanced by an increase above 2.00 in the ions having octahedral coordination. Though this increase is slight and within experimental error it probably is real.

TABLE 20.—Analyses of pyrophyllite and talc

	Pyrophyllite			Talc		
	1	2	3	4	5	6
SiO ₂	66.04	64.53	66.25	58.68	61.37	62.63
Al ₂ O ₃	28.25	29.40	27.91	3.75	1.96	.55
FeO.....	.64	.00	1.08			1.07
Fe ₂ O ₃67		5.52	1.47	
MgO.....	.12			26.30	30.23	31.36
Na ₂ O.....	.06	.28				
H ₂ O.....	5.02	5.45	5.25	5.33	5.37	4.84
Total.....	100.13	100.33	100.49	100.08	100.40	100.45

1. Moore County, N. C. Ellen Rist, analyst (unpublished analysis, made in the laboratory of the Bureau of Plant Industry).
2. Moore County, N. C. Charles Baskerville, analyst (Pratt, 1900, p. 26).
3. Carbondon, Moore County, N. C. Oscar D. Allen, analyst (Brush, 1862, p. 219).
4. Harford County, Md. J. G. Fairchild, analyst (Wells, 1937, p. 112).
5. Fichtelgebirge, Bavaria. J. G. Fairchild, analyst (Wells, 1937, p. 112).
6. Deep River, N. C. H. C. McNeil, analyst (Clarke, 1910, p. 295).

Chemical formulas

PYROPHYLLITE

1. Moore Co., N. C.
 $[Al_{1.97}Mg_{.01}Fe_{.03}] [Si_{3.97}Al_{.03}] O_{10}[OH]_2$ 2.01
2. Moore Co., N. C.
 $[Al_{2.00}Fe_{.03}] [Si_{3.90}Al_{.10}] O_{10}[OH]_2Na_{.04}$ 2.03
3. Deep River, Moore Co., N. C.
 $[Al_{1.96}Fe_{.03}] [Si_{3.98}Al_{.02}] O_{10}[OH]_2$ 2.01

TALC

4. Harford Co., Md.
 $[Al_{1.11}Fe_{.30}Mg_{2.60}] [Si_{3.82}Al_{.18}] O_{10}[OH]_2$ 3.01
5. Fichtelgebirge, Bavaria
 $[Al_{1.06}Fe_{.08}Mg_{2.86}] [Si_{3.91}Al_{.09}] O_{10}[OH]_2$ 3.00
6. Deep River, N. C.
 $[Fe_{.08}Mg_{2.95}] [Si_{3.95}Al_{.05}] O_{10}[OH]_2$ 3.00

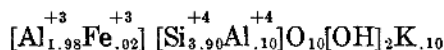
Ions having octahedral coordination

One of the pyrophyllite specimens from Moore County, N. C., contains a small amount of sodium. This is included in the formula as it would be in a paragonite mica. Although the amount of sodium in this sample is small, both alkali and alkaline-earth ions are present to an appreciable extent in many pyrophyllite and talc analyses. A specimen of beautifully bladed pyrophyllite from the Hemp mine, Moore County, N. C., analyzed by R. C. Wells, is typical. The sample was clean platy pyrophyllite containing no observable mica, and it seems probable that the potassium in its analysis, as given below, is present in mixed layers and not as sericite.

Analysis of pyrophyllite from Moore County, N. C.

[R. C. Wells, analyst]			
SiO ₂	64.32	K ₂ O.....	1.20
Al ₂ O ₃	29.05	Na ₂ O.....	None
Fe ₂ O ₃20	TiO ₂30
MgO.....	.05	H ₂ O.....	5.27
CaO.....	None		
			100.39

The chemical formula calculated from this analysis is as follows:



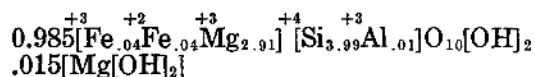
In this sample about 10 percent of the layers would be micalike. It is probable that these micalike layers would only statistically affect the X-ray diffraction pattern, which would not be expected to be appreciably different from that of pure pyrophyllite. Thus C₀ would be expected to change from 8.90 Å., as characteristic of pyrophyllite, to 9.00 Å., while a₀, b₀, and β would not necessarily be changed.

The finer-grained talc and pyrophyllite samples often might contain adventitious materials. Massive talc, especially, contains fine-grained chlorites as impurities, but these impurities are not likely to be found in the foliated varieties. An analysis of a foliated talc from Huntersville, Fairfax County, Va., is given below (Clarke, 1915).

Analysis of talc from Huntersville, Va.

[E. A. Schneider, analyst (Clarke, 1910, p. 295)]			
SiO ₂	62.27	MgO.....	30.95
Al ₂ O ₃15	MnO.....	Tr.
Fe ₂ O ₃95	H ₂ O -.....	.07
FeO.....	.85	H ₂ O +.....	4.84
			100.08

The formula percentages calculated from the foregoing analysis are as follows:



The calculation giving an excess of magnesium merely shows that a small fraction of chlorite layers is present in the specimen.

Pyrophyllite differs in composition from the analogous montmorillonite in several important ways. Very little water is lost at low temperatures; in other words, interlayer water is absent. It contains no Ca⁺, and little or no Na⁺ or other replaceable bases, those present being essentially nonreplaceable; furthermore, it shows no appreciable admixture with a hypothetical ferric end member. The Mg⁺ content also is very small. Montmorillonite, on the other hand, invariably contains appreciable amounts of magnesium and iron and offers evidence of complete solid solutions between the Fe⁺ and Al⁺ end members.

Talc similarly differs from the analogous saponite. In talc, as in pyrophyllite, replaceable bases and interlayer water are absent. Although small but appreciable amounts of Al⁺ and Fe⁺ or Fe⁺ are present in some specimens, there is no indication of a continuous series of solid solutions with an aluminum end member like pyrophyllite, or with an analogous beidellite-like material. Thus, it seems obvious that the essential difference between montmorillonite and saponite and between pyrophyllite and talc is in the substitution of ions that characterize members of the montmorillonite group. The most essential of these substitutions are Al for Si in tetrahedral positions and of Mg for Al in octahedral positions. Both induce valence deficiencies, which are balanced by the exchangeable ions between the sheets. Associated with these bases is interlayer water. The X-ray diffraction patterns of montmorillonite and pyrophyllite and of saponite and talc are similar except for the (00l) reflections, and the substitutions described involve no great chemical differences; but they have fundamentally altered the physical properties of the two groups of minerals.

A logical explanation for these differences between pyrophyllite and montmorillonite on the one hand and talc, hectorite and saponite on the other, is probably afforded by the lattice limitation of montmorillonite, which, in turn, is due to the presence of the exchangeable ions. Thus there need not be exact matching in dimensions between successive layers in montmorillonite. The well-crystallized talcs and pyrophyllites, on the other hand, require lattice continuity to macroscopic dimensions. For this reason, too, they probably are far more limited in the extent and kind of mixed-layer lattices that they might form. Pyrophyllite would be expected to form mixed layers with muscovite-type micas but not with chlorite or brucite, whereas talc would form mixed layers with phlogopite-type micas, chlorite, and brucite but not with pyrophyllite or muscovite mica.

Talc and pyrophyllite are the results of metamorphic or hydrothermal processes. Talc is commonly associated with graphite, serpentine, or chlorite; and pyrophyllite is commonly associated with sericite. Both probably are formed at moderately high temperature or, commonly, as a result of dynamic metamorphism. These conditions would tend to inhibit the interlayer water characteristic of montmorillonite and saponite. Talc and pyrophyllite have yet to be found as constituents of soils that characteristically are formed by low-temperature weathering. Montmorillonite, on the other hand, is predominantly a product of weathering formed in the presence of liquid water. Where there is evidence that minerals of the montmorillonite group were formed by thermal processes, there is every reason to believe that they were deposited late in the paragenetic sequence, when the temperature was low—that is, as much as 200° C. (pp. 68-69) but in general below that temperature. Under these conditions interlayer water and exchangeable cations are present. The mode of origin of montmorillonite and saponite, therefore, is dependent on conditions that permit the formation of materials characterized by interlayer water, solid solution between an unusually large group of end members, and the exchange of bases; in contrast, the origin of pyrophyllite and talc is dependent on conditions of high temperature and high pressure, which inhibited interlayer water, permitted very limited isomorphism, and so precluded the presence of exchangeable bases.

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