THE EFFECTS AND GEOLOGIC SIGNIFICANCE OF POTASSIUM "FIXATION" BY EXPANDABLE CLAY MINERALS DERIVED FROM MUSCOVITE, BIOTITE, CHLORITE, AND VOLCANIC MATERIAL*

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ABSTRACT

When muscovite→vermiculite and muscovite→montmorillonite are subject to mild treatment with KOH they will contract to 10 Å, indicating that they have inherited much of the high interlayer charge of the muscovite. A review of the data on potassium "fixation" indicates that the relation between the amount of "fixed" potassium and the number of contracted 10-Å layers is as yet not clear. Samples of montmorillonite were subjected to various treatments with KOH and it is shown that there is a direct relation between the per cent of contracted 10-Å layers and the per cent of tetrahedral charge.

Potassium treatments with vermiculite indicates that there are highly charged biotite and muscovite→vermiculites which readily contract to 10.0 to 10.2 Å and low-charged nonmica→vermiculites which resist contraction. An attempt is made to organize the easily measured parameters of expanded 2:1 clays and to show how these parameters relate one to the other and ultimately to the source material.

A sample of muscovite→montmorillonite exposed to sea water readily contracted to a 10-Å lattice, indicating the unstable character of such montmorillonites. An examination of clays from marine sediments indicates that muscovite and biotite→vermiculite and montmorillonite are relatively rare and that most of the expanded clays are derived from low-charged nonmicaceous minerals such as volcanic material, chlorite, and hornblende. The sequence illite→montmorillonite→illite is considered to indicate rejuvenation and not diagenesis. Further, it is speculated that mixed-layer illite→montmorillonites have an equilibrium ratio which is determined by the interlayer charge and the composition of the water in the environment of deposition.

A limited study of Recent sediments indicates that most of the expanded clays in the Gulf of Mexico are volcanic→montmorillonites and that those from the Atlantic Coast may be muscovite→montmorillonites.

INTRODUCTION

Agronomists, and to a lesser extent mineralogists, have accumulated a great amount of data on potassium "fixation" by soils and clay minerals. Relatively little effort has been made by geologists and petrographers to evaluate the geologic significance of this phenomenon. The experiments conducted during this investigation were designed to supplement the data in the literature and an attempt was made to obtain some preliminary ideas on the geological significance of the phenomenon of potassium "fixation" by expanded clay minerals.

A number of investigators have reported the alteration of trioctahedral biotite to vermiculite. The vermiculite has a 14.0- to 14.5-Å spacing; it

will not expand when treated with ethylene glycol but will collapse to near 10 Å when treated with K or when heated. (Walker, 1949, 1950; Walker and Milne, 1950; Barshad, 1948, 1954; Van der Marel, 1954.)

Walker (1950) and MacEwan (1954) reported an example of biotite altering to montmorillonite. The montmorillonite was differentiated from vermiculite on the basis that it expanded to 17.7 Å when treated with glycerol and the vermiculite did not.

Recently, Brown (1953), Hathaway (1954), and Rich and Obershain (1955) reported the presence of a dioctahedral vermiculite-like mineral believed to have been formed by the alteration of muscovite. This vermiculite has a 14.0- to 14.7-Å (001) spacing, will not expand when treated with glycerol, but will collapse to near 10 Å when treated with potassium. Aluminum and iron can occur in the interlayer positions where they retard collapse by potassium treatment and by heat treatment.

For a long time it has been noted that many soils "fix" potassium. More recently, numerous instances have been reported where expanded 14 Å clay minerals in soils will collapse to near 10 Å when saturated with potassium and dried at room temperature (Jackson and Hellman, 1941; Rolfe and Jeffries, 1953; Kunze and Jeffries, 1953; Van der Marel, 1954). These clays do not expand appreciably with glycol and are considered by the writers of the latter two papers to be a vermiculite-like mineral derived from the weathering of muscovite and illite.

Muscovite→Montmorillonite and Muscovite→Vermiculite

The Ordovician Womble shale and the Cambrian Collier schist in the Ouachita Mountains of southeastern Oklahoma are composed largely of well-crystallized illite (fine-grained 2 *M* muscovite) and a small amount of chlorite which, when weathered, alter to an expanded 2:1 clay and kaolinite. The expanded clay mineral has a 14.0- to 15.0-Å (001) spacing in its natural state. When treated with ethylene glycol, the Womble clay (BEC 70 meq per 100 gm.) expands to about 17 Å, whereas the Collier clay (BEC 50 meq per 100 gm.) shows no expansion (Fig. 1, Table 1). However, when these clays are allowed to stand in a 1 N KOH solution for 15 hours and dried at room temperature, both collapse to 10 Å. Before KOH treatment the Womble sample had 1.6% K_2O and after treatment 3.8%. Neither of the K-saturated samples will expand when treated with ethylene glycol. The K-saturated Womble sample, dried at room temperature and placed in a 1 N $CaCl_2$ solution for 15 hours, reexpands to 15.0 Å, and then when glycolated absorbs two layers of glycol and expands to 16.6 Å. When the K-saturated Womble sample was dried at 110° C. for one week and then placed in a 1 N $CaCl_2$ solution the expansion was less than for the sample dried at room temperature.
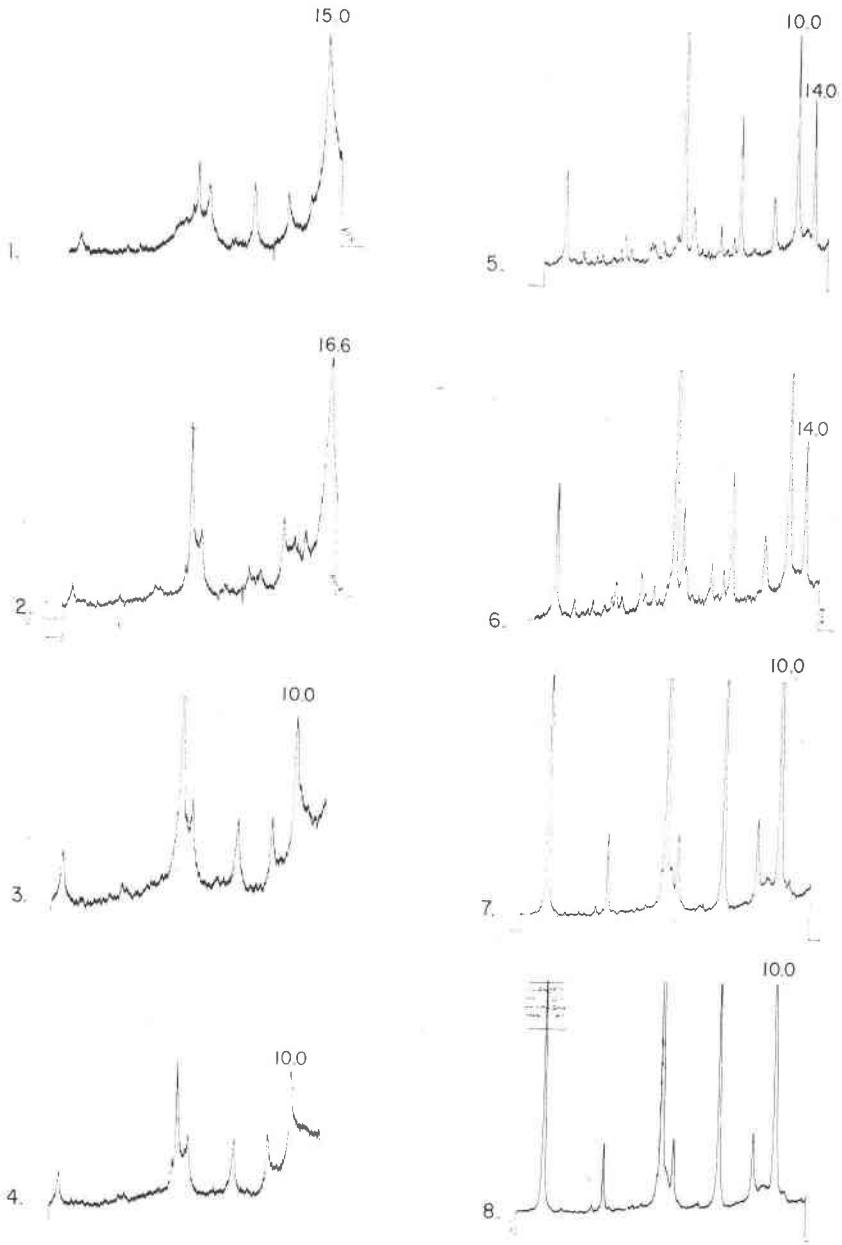
FIG. 1. (1) to (4)—Womble shale: (1) natural state; (2) with ethylene glycol; (3) with KOH; (4) with KOH and ethylene glycol. (5) to (8)—Collier schist; (5) natural state; (6) with ethylene glycol; (7) with KOH; (8) with KOH and ethylene glycol.

TABLE 1. X-RAY DATA ON MUSCOVITE→MONTMORILLONITE AND
MUSCOVITE→VERMICULITE

	Untreated	Ethylene Glycol	KOH	KOH E. G.	KOH CaCl₂	600° C.
Womble Shale	15 A	16.6 A	10 A	10 A	15 A	10 A
Collier Schist	14 A	14 A	10 A	10 A	14 A	—

Further, when the Ca-saturated Womble sample is heated to 600° C. for 15 hours, it will collapse to only 10.0 Å and not the 9.3-Å spacing characteristic of a Ca montmorillonite. An x-ray pattern of a sample of wet, K-saturated Womble clay indicated that it was completely collapsed to 10 Å. X-ray diffraction patterns of both K-saturated samples show a (060) value of 1.495 Å, indicating that the clay is dioctahedral. The series of reflections between 4.4 and 2.6 Å indicate that the clay has the 2 M muscovite structure (Table 2).

These expanded micas appear to have a strong preference for potassium. When placed in a solution containing one part KCl to ten parts $MgCl_2$ the Womble clay adsorbed the potassium and contracted to 10 Å. When given a choice, montmorillonite (volcanic) adsorbs magnesium more readily than potassium (Grim, 1953). This suggests that the preferential adsorption of potassium by the Womble clay may be a function of charge and/or structural order.

The preceding data indicate that these expanded clays were derived from muscovite. The Womble clay has some of the properties of montmorillonite, in that glycolation expands it to near 17 Å. However, it differs from the "typical" montmorillonite because it collapses to 10 Å

TABLE 2. X-RAY SPACINGS AND INTENSITIES; WOMBLE
(K-SATURATED)

d Å	I	Indices	d Å	I	Indices	d Å	I	Indices
10.0	SM	002	2.86	W	115	1.83	W	04$\bar{6}$
5.0	M	004	2.78	W	11$\bar{6}$	1.67	W	13$\bar{1}$0
4.48	S	110	2.67	WW	026	1.64	WM	312
3.90	W	112, 11$\bar{3}$	2.56	S	20$\bar{2}$	1.62	W	313
3.72	W	023	2.46	W	13$\bar{3}$	1.49	WM	060
3.32	S	006	2.38	MW	133	1.34	WM	335
3.22	W	114	2.13	W	043	1.29	W	400
2.98	WM	025	1.98	SM	0010	1.24	W	0016

W—Weak.
M—Medium.
S—Strong.

when saturated with K and dried at room temperature. The ease with which the Womble clay collapses to 10 Å when saturated with K suggests that the interlayer charge is relatively large and that the predominant lattice charge is probably tetrahedral and was inherited from the original muscovite. The ability to contract is less in the finer grain sizes, suggesting that when weathering is sufficiently severe, the high lattice charge can be destroyed. The fact that the Ca-saturated Womble clay will collapse only to 10 Å when heated to 600° C. suggests that a sufficient number of the large K^+ ions remain between the layers to prevent complete collapse but apparently are not enough to prevent expansion. The differential thermal curve of the Womble clay shows the second endothermal reaction occurring at 550° C. The temperature of this reaction is characteristic of illite and approximately 100° lower than for volcanic montmorillonite.

The Collier muscovite→vermiculite is similar to those previously described by Brown (1953), Hathaway (1954), and Rich and Obershain (1955).

A question immediately arises as to how much of this muscovite→montmorillonite and biotite→montmorillonite is present in sediments and soils and has been overlooked or considered as typical montmorillonite (volcanic→montmorillonite). It seems likely that it would be fairly common in soils. In the latter part of this paper some preliminary data will be given concerning its presence in sediments.

The discovery of this material indicates how strongly clay minerals can inherit much of the character of their source material. Whereas the character of muscovite→montmorillonite is largely due to the structure and charge which the muscovite→montmorillonite inherits from the original muscovite, the "typical" montmorillonite is aggraded largely from a glass or gel and inherits no established structure or charge, but only chemical characteristics, and is a separate entity. To be able to differentiate between these various types of montmorillonite can be of considerable geological and agricultural significance.

POTASSIUM "FIXATION"

In the past twenty years many papers have described potassium "fixation" by montmorillonite (Volk, 1934; Truog and Jones, 1938; Page and Baver, 1940; Mortland and Geiseking, 1951; Wear and White, 1951; Dyal and Hendricks, 1952; Barshad, 1954). Reitemeier (1951) has defined "fixed" potassium as "applied potassium which is not immediately replaceable by the usual cation exchange reagents as NH_4 acetate." Barshad (1951) has suggested that "the term 'fixed' cations be applied to those present in a mineral with a contracted-type layered lattice resisting replacement by cations that are unable to expand the lattice,

notwithstanding the application of the most efficient method of replacement." Accordingly, "the 'NH_4^+-fixation' capacity of a soil or a mineral would be defined as the absorbed NH_4^+ not replaceable by K^+, and 'K^+-fixation' capacity as the absorbed K^+ not replaceable by NH_4^+."

Barshad (1948, 1954) has shown that the amount of "fixation" of K^+ and NH_4^+ is a function of the type of cation used as a leaching agent. Thus " . . . cations present in a contracted crystal lattice (K^+ and NH_4^+) may be replaced by those which bring about an expansion of the crystal lattice (Na^+, Mg^{2+}, Ca^{2+}, Ba^{2+}) but not by those which cannot do so (K^+, NH_4^+)." The larger the size of the clay flake, the more difficult it becomes for the contracting-type cations to migrate into the interior of the flake and, as a result, "fixation" tends to increase as flake size increases (Barshad, 1954). Though no "fixation" measurements were made, the x-ray data indicated that Ca^{2+} was much more effective than NH_4^+ in replacing K^+ from the Womble muscovite→montmorillonite.

Barshad (1954) interprets his data to indicate that "fixation" is a function of the amount of total interlayer charge. He has shown that an expanded lattice with an interlayer charge of 150 or more meq per 100 gm. of material heated to 1000° C. will contract to 10.4 Å when saturated with K^+, whereas lattices with a charge of 110 or less meq per 100 gm. have an expansion equivalent to one molecular layer of water (12.4 Å). It appears that for lattices with charges greater than 150 meq per 100 gm., the amount of K^+ "fixed" increases from 51 per cent of the total exchange capacity for a sample with 159 meq per 100 gm. to 99.3 per cent for a sample with a charge of 215 meq per 100 gm. The maximum interlayer charge of the more common layer minerals would presumably be muscovite, which Barshad (1954) reports as having a charge of 262 meq per 100 gm. The muscovite→vermiculite and muscovite→montmorillonite, like Barshad's biotite→vermiculite, also appear to retain much of the high interlayer charge of the original muscovite as shown by their ready collapse to near 10 Å when saturated with K^+.

Truog and Jones (1938) indicated that K^+ could be "fixed" to the extent of 40 per cent of the cation exchange capacity by alternately wetting and drying montmorillonite at 80° C. Mortland and Gieseking (1951) indicated nearly 100 per cent "fixation" by drying the clays from a solution of K_2SiO_3 at 100° C.; however, it was necessary to dry Wyoming bentonite at 400° C. to obtain a contraction to 10 Å. Wear and White (1951) used a milder treatment which consisted of saturating the clay with K^+, washing, drying at 105° C., and wetting and washing with NH_4 acetate. Maximum "fixation" occurred with the Wyoming bentonite where "fixed" K^+ reduced the BEC by 22 to 28 per cent. Using even milder treatment, Barshad (1954) was able to "fix" less than 4 per cent NH_4^+ and less than 8 per cent K^+ in montmorillonite.

Wear and White (1951) reported a slightly greater than 25-per cent reduction in the (001) x-ray diffraction maximum of glycolated K^+ "fixed" Wyoming bentonite and believe that this implied that 25 to 30 per cent of the layers were contracted to 10 Å. If 25 per cent of the layers had collapsed to 10 Å they should be detectable in one of two ways: (*a*) by a discrete reflection at 10 Å, in which case it could be assumed that fairly sizeable packets of layers had collapsed to 10 Å and the resulting clay was essentially a discrete mixture of 10-Å and 17.7-Å layers, or (*b*) by a shifting of the 17.7-Å (001) reflection towards 10 Å, indicating a random interstratification of 10- and 17.7-Å layers. The x-ray patterns presented do not show either of these effects. Further, Jackson and Hellman (1941) state "It has been found in this laboratory that 0.7 to 0.9 per cent K_2O may be fixed in nonexchangeable form in montmorillonite from bentonite and soil clays without affecting the (001) x-ray diffraction line . . . ." As can be seen, the relation between the amount of "fixed" potassium and the number of contracted 10-Å layers is as yet not clear.

MONTMORILLONITE AND NONTRONITE

Both montmorillonites and nontronites have a BEC ranging from approximately 90 to 115 meq per 100 gm. air-dried material (or approximately 110 to 150 meq per 100 gm. of ignited material); however, analysis of the chemical data (Ross and Hendricks, 1945; and Osthaus, 1954, 1955) indicates that montmorillonites generally have from two-thirds to all the total lattice charge originating in the octahedral layer, whereas in the Garfield nontronite approximately 95 per cent of the charge originates in the tetrahedral layer. Three montmorillonites which have similar total interlayer charges but have widely varying ratios of tetrahedral and octahedral substitution were subjected to various potassium treatments (Table 3). In all cases the (00*l*) reflection of the K-treated samples and the glycolated K samples were irrational, indicating that a mixed-layer clay was formed. When the K-treated samples were washed with NH_4Ac a regular (00*l*) series with a fundamental periodicity of 12.4 Å was obtained,

The (00*l*) values for the K-treated samples obviously represent mixed-layered 10- and 12-Å layers; however, in many instances it is difficult to determine the exact ratio of the two types of layers. In several instances it appears that the layers are mixed in two different ratios. Regardless of the exact ratio of the mixed layers, the (001) values of the K-treated samples and the glycolated K samples indicate a shift towards a smaller spacing, therefore an increase in the number of 10-Å layers as the relative amount of tetrahedral charge increases. This is shown by both the room temperature and 90° to 100° C. samples. Of the room temperature sam-

TABLE 3. EFFECTS OF KOH ON VARIOUS MONTMORILLONITES

Samples	Charge meq[1]	Origin of Charge[2]	KOH Solution Room Temperature[3]	KOH Solution 90–100° C.[4]
Polkville	118	100% Octahedral	1:1 Mixed-layer 10/12.4 plus packets 12.4 (001) = 12.3 (001) = 15.5 e.g.	(001 = 12.1 (001) = 14.0–16.0 e.g.
Wyoming	94	45% Tetrahedral	1:4 Mixed-layer 10/12.4 (001) = 12.1 (001) = 13.5 e.g.	1:1 Mixed-layer 10/12.4 (001) = 11.6 (001) = 15.2 e.g.
Nontronite	115	95% Tetrahedral	1:4 and 3:2 Mixed-Layer 10/12.4 (001) = 12.0 and 11.2 (001) = 13.2 and 11.43 e.g.	2:3 and 7:3 Mixed-layers 10/12.4 plus packets 10.0 (001) = 11.5 and 10.0 (001) = 16, 12 and 10.0 e.g.

[1] Per 100 gm. air-dried material.

[2] Based on analyses by Wear and White (1951) and Osthaus (1954).

[3] Allowed to stand in 1 N KOH solution 15 hours, washed with distilled water, dried at room temperature.

[4] 90–100° C., 2 hours in 1 N KOH solution, washed with distilled water, dried at room temperature.

ples, only the K-Polkville sample will absorb two layers of glycol; the K-Wyoming and K-nontronite samples, which have considerable tetrahedral charge, will absorb only one layer of glycol.

The room temperature K-Wyoming samples were subjected to a confining pressure of 40,000 psi for two weeks but no further contraction was obtained. When the untreated Wyoming montmorillonite was boiled for 16 hours in a 1 N KOH solution, the (001) spacing shifted to 11 Å, indicating that 60 per cent of the layers were contracted to 10 Å. Boiling the nontronite for 16 hours caused a shift to 10 Å, indicating approximately 100-per cent contraction. Caillére and Hénin (1949) were able to contract a montmorillonite to 10 Å by boiling it in a 1 N KOH solution for 32 hours. It is certain that boiling these clays for 2 and 16 hours has caused considerable modification of the basic 2:1 lattice; however, the relative difference between the samples is retained. Barshad (1954) believes that it is the magnitude of the interlayer charge rather than the origin which determines "fixation." This may be true for expanded minerals which have an interlayer charge greater than 150 meq per 100 gm. of ignited material; however, as the above data indicate, for ex-

panded 2:1 minerals with an interlayer charge less than 150 meq per 100 gm. of ignited material, the origin of the charge is quite significant in regard to the minerals' ability to "fix" potassium or to contract to 10 Å. These data also suggest why the montmorillonite in marine sediments is seldom pure, but usually contains from 10 to 90 per cent of intergrown 10-Å layers. It seems likely that if nontronite were exposed to sea water for any length of time, it would form a mixed-layer clay. The fact that these K montmorillonites form mixed-layer clays indicates that the distribution of charge among the layers is inhomogeneous and that some layers contain considerably more charge than others.

VERMICULITE

Barshad (1954) has shown that vermiculites with a relatively low interlayer charge of around 160 meq per 100 gm. of ignited material on a percentage basis "fix" only about half as much K^+ as those with a charge of 200. Vermiculites with a charge similar to montmorillonite, 106 meq per 100 gm. of ignited material, behave like montmorillonite when saturated with K^+ and contracts to only 12.4 Å.

Barshad's (1954) data indicate that all of his vermiculites with a relatively low interlayer charge (less than 160 meq per 100 gm of ignited material) contained some chlorite, and all of his vermiculites with a relatively high charge (greater than 190 meq per 100 gm of ignited material) were pure or contained biotite. The possibility that the vermiculites containing chlorite were formed from chlorite and that those containing biotite were formed from biotite immediately suggests that there may be some relation between the total charge and the origin of vermiculites.

Biotites in general have an interlayer charge of between 200 and 250 meq per 100 gm. of ignited material. The interlayer charge on a 2:1 chlorite lattice cannot be so readily calculated, since it is difficult to determine the relative amounts of Al_3^+ substituting in the tetrahedral and the two octahedral layers or to unequivocally account for the oxidation state of any iron.

Mica structural formulas are normally cited as 3 Si:Al in tetrahedral coordinations with a net deficiency of 1 charge per four. Chlorite analyses range from about 2.5 Si:1.5 Al to about 3 Si:1 Al, but internal compensation is assumed to reduce the net deficiency to 1 charge or less. No criterion other than hardness seems to be available generally to support the assumption. Gruner's (1934) average vermiculite analysis as cast by Hendricks and Jefferson (1938) for their vermiculite structure indicates 2.75 Si:1.25 Al, comparable with a chlorite mean, but it has

since been established that vermiculite has a high capacity to exchange Mg.

A rationalization of the magnitude of vermiculite-layer charges was arrived at by W. F. Bradley as follows.

The mean of Gruner's (1934) analyses, cited by Hendricks and Jefferson (1938) in connection with their vermiculite structure was

$$(OH)_3(Mg_{2.75}Fe^{3+}_{0.25})(Al_{1.25}Si_{2.75})O_9 \cdot 3.5\ H_2O.$$
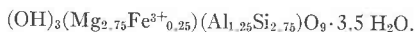
Subsequent observations by Barshad (1948) indicate that of the order of 100 to 200 meq of Mg are exchangeable. If, instead of casting Gruner's average on the basis of seven cations, it be cast on the basis of $7+\frac{1}{2}$ the exchange-capacity cations for a 12 oxygen mica unit, a formula would emerge like

$$Mg_{0.33}(OH)_{2.0}(Mg_{2.55}Fe^{3+}_{0.26}Al_{0.19})(Al_{1.12}Si_{2.88})O_{10}4\ H_2O.$$
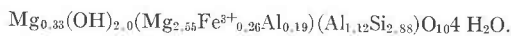
It is seen that allowance for exchangeability of Mg reduces the apparent tetrahedral contribution to the net layer charge deficiency and increases the apparent internal compensation by octahedral contribution.
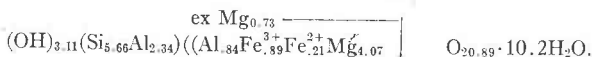
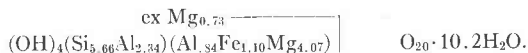Bradley has provided the following analysis of Grudemo's Sample C.

GRUDEMO SAMPLE C*

		Cations per 100 gm. air dry	Oxygen atoms per 100 gm. air dry
SiO_2	33.92	5.66 ⎱ tet=8.00 2.34 ⎰	11.32
Al_2O_3	16.20	.84 ⎱	4.77
Fe_2O_3	7.12	.89 ⎱ oct=6.01	1.34
FeO	1.50	.21 ⎰	0.21
MgO	19.12	4.07 ⎱	4.80
		.73 ex	
exch. capacity meq/100 gm. air dry		1.46	
H_2O (total)	21.12	23.50	11.75

3.11 Hydrogen in OH

34.19 total

20.39 ⟵ ⟶ −.45 correction for Fe^{3+}

water ⟶ −1.55 correction for (OH) by ignition

32.19

22   oxygen in ignited model

10.19

* Grudemo, Å. (1954), An X-ray Examination of the Structure of Vermiculites. *Swedish Cement and Concrete Research Institute, Proceedings*, No. 22.
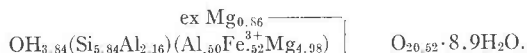
This says that this vermiculite is expressed by the formula:

ex $Mg_{0.73}$

$$(OH)_{3.11}(Si_{5.66}Al_{2.34})((Al_{.84}Fe^{3+}_{.89}Fe^{2+}_{.21}Mg'_{4.07}\ |\ \ \ O_{20.89} \cdot 10.2H_2O.$$

Had it not been oxidized it would have been:

$$\text{ex } Mg_{0.73} \overline{}\Big| $$
$$(OH)_4(Si_{5.66}Al_{2.34})(Al_{.84}Fe_{1.10}Mg_{4.07})\Big| \quad O_{20}\cdot10.2H_2O.$$

Layer charge is 1.50 as compared to 2.0 for micas and 1.00 for montmorillonites. Broken down the same way the Gruner average used by Hendricks makes:

$$\text{ex } Mg_{0.86} \overline{}\Big| $$
$$OH_{3.84}(Si_{5.84}Al_{2.16})(Al_{.50}Fe^{3+}_{.52}Mg_{4.98})\Big| \quad O_{20.52}\cdot8.9H_2O.$$

Layer charge is 1.66, indicating an average exchange capacity around 166 meq/100 gm.

Quality of agreements illustrated

Exch cap'y	By charge	By Mg.
Grudemo	150	146
Gruner	166	172

It therefore seems fair to assume that an upper limit near one charge [per $O_{10}(OH)_2$ unit] exists for vermiculite, and that this limit is most nearly approached by muscovite→vermiculite, closely approached by biotite→vermiculite, and possibly only half reached by chlorite→vermiculite. Vermiculite derived from minerals such as hornblende, serpentine, and talc may have a charge as low as chlorite→vermiculite, possibly ranging as low as a charge of 0.3–0.5 or the charge of a typical volcanic →montmorillonites.

Nine vermiculite samples were studied; two contained considerable amounts of biotite and were believed to have formed from biotite; one sample was obtained by leaching biotite with $MgCl_2$; the other six samples contain such minerals as chlorite, talc, antigorite, and hornblende, and in most cases were formed by alteration of these minerals. It is thought that these last six vermiculites should have a lower interlayer charge than the muscovite→vermiculites and biotite→vermiculites.

Table 4 contains the results obtained when these samples were allowed to stand in a 1 N KOH solution for 15 hours, washed with distilled water, and dried at room temperature, and then placed in 90°–100° C. 1 N KOH solution for 6 hours, washed with distilled water and dried at room temperature. These results indicate that, when treated with potassium, the biotite→vermiculites readily contract to the 10.2 to 10.3-Å spacing characteristic of biotite. The nonbiotite→vermiculites contract to only 11 to 12.7 Å, indicating the retention of one molecular

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TABLE 4. EFFECTS OF KOH ON VARIOUS TRIOCTAHEDRAL VERMICULITES

Sample	Composition	KOH Solution Room Temperature[1]	KOH Solution 90–100° C.[2]	Size
Biotite	Vermiculite (Formed by leaching Biotite with $MgCl_2$)	$V = 10.2$		$<2\mu$
Broderick Mt., Bolton, Mass.	Biotite S Vermiculite W	No effect	$V = 10.2$	100 Mesh
Libby, Montana	Biotite M M.L. Biotite-vermiculite M	$V = 10.2–11$	$V = 10.4$	100 Mesh
Granitized hornblendite, Austin, Tex.	M.L. Biotite-vermiculite M Vermiculite M[3] Hornblende	M.L. $= 10.2–11$ $V = 12.6$	M.L. $= 10.3$ $V = 11.4$	$<2\mu$
Leninite, Lenni, Pa.	Chlorite S Vermiculite W	$V = 12.4$ regular, 00 l	$V = 12$	100 mesh
Jefferisite, W. Chester, Pa.	Antigorite S Vermiculite W	$V = 12.4$	$V = 11.5$ (M.L. 10.3/14, 7:3)	$<2\mu$
Halite, Pa.	M.L. Chlorite-Vermiculite		No effect	100 Mesh
Roan Mt., North Carolina	Vermiculite S Talc, serpentine, Chlorite	$V = 12.5$ and 14.0	$V = 11–14.5$ (some M.L. Chlorite-Vermiculite present)	$<2\mu$
Corrensite, Franklin Mts., Texas	Regular M.L. Chlorite-Vermiculite[3]		$V = 12.7$	$<2\mu$
Cornwall, England	Vermiculite (fibrous; derived from serpentine)[3]	$V = 13.0–14.4$	$V = 13.0$	100 Mesh

[1] Allowed to stand in 1 N KOH solution 15 hours, washed with distilled water, dried at room temperature.
[2] 90–100° C., 6 hours in 1 N KOH solution, washed with distilled water, dried at room temperature.
[3] Samples which expand to 17 Å when treated with ethylene glycol.

layer of water between the vermiculite layers. Where good samples were available, as in leninite, it could be seen that the (00l) series was regular. A mixed-layer 10.3/14 Å, 7:3 clay was obtained in the case of Jefferisite. In many of these samples a portion of the vermiculite remained expanded to 14 Å after K treatment. However, when some of these samples were boiled in 1 N NH_4F for five minutes to remove interlayer Fe and Al, they would contract to 12 Å when subsequently treated with K.

The granitized hornblende contained a mixed-layer biotite-vermiculite and vermiculite. When treated with K, the mixed-layer vermiculite contracted to 10.3 and the unmixed vermiculite to only 11.4 Å. Further, the former would absorb only one layer of glycol but the latter absorbed two layers. This indicates that within one sample two types of vermiculite

were formed. In this same sample the relatively large vermiculite flakes would absorb only one layer of glycol, whereas the vermiculite in the less-than-two-micron fraction absorbed two layers of glycol.

Vermiculites apparently inherit much of their charge from the original source mineral, as do the montmorillonites, and on the basis of contractability they can be divided into at least two inheritance groups: Those which contract to 10 to 10.3 Å when treated with K (biotite→vermiculites and muscovite→vermiculites) and those which contract to 11 to 12.7 Å when treated with K (nonmica→vermiculites).

Summary and Speculations

The above data need more substantiation, but a number of relations are apparent and some interesting speculations can be made. It is apparent that expanded 2:1 clay minerals of either the vermiculite- or montmorillonite-type can form by the alteration of muscovite, biotite, chlorite, serpentine, talc, and material which does not contain a layer-type lattice (volcanic material, hornblende, feldspar). These expanded minerals appear to have inherited enough of the character of their source material that by proper treatments it should be possible to make a reasonable assumption regarding the source.

Expanded clays (both vermiculite and montmorillonite) derived from muscovite (with a probable interlayer charge greater than 260 meq per 100 gm. of ignited material) will contract to near 10.0 Å when subjected to relatively mild treatment (placed in 1 N KOH suspension for 15 hours and dried at room temperature). This same treatment does not usually contract expanded clays derived from biotite, but by warming or boiling the K^+ solution for from 15 minutes to 6 hours these minerals can be made to contract to approximately 10.2 Å. When subjected to these treatments the expanded clays derived from nonmicaceous minerals will in general remain all or partially expanded and afford (001) spacings of 11 to 12.4 Å.

The mild potassium treatment used to contract all the layers of muscovite-derived clays will when used on expanded minerals derived from nonmicaceous minerals apparently contract approximately 40 per cent of the layers to near 10.0 Å if the interlayer charge is primarily tetrahedral in origin. Those clays in which a large portion of the charge originates in the octahedral layer have only 10 to 20 per cent of their layers contracted by this treatment. In order to attain any significant percentage of contracted layers by using potassium with this latter group of clays, it is necessary to apply relatively drastic techniques such as drying at temperatures of 300° to 400° C., alternately wetting and drying at 80° to 110° C., and boiling 20 to 30 hours. With these more drastic tech-

niques it is more than likely that the basic 2:1 lattice is being modified and that it is not the potassium alone which is causing the contraction.

Table 5 summarizes the types of treatment necessary to contract expanded lattices of various interlayer charge. Considerably more data will be required to make a rigid classification of this type, but the present data suggest that a grouping of this sort exists in nature and further that this natural grouping is determined by the original source material.

TABLE 5. POTASSIUM TREATMENT NECESSARY TO CONTRACT EXPANDING
LATTICES OF VARIOUS INTERLAYER CHARGE

| Source Material	Interlayer Treatment Charge, meq*		(001) Spacing
Muscovite, other micas	260	Soak 15 hr. 1 N KOH Sol. Dry at room temperature	10.0 A
Biotite	260–150	Boil 15 min.–6 hr. 1 N KOH Sol. Dry at room temperature	10.2–10.4 A
Nonmicaceous Material	<150	Dry at 110°–400° C. from 1 N KOH Sol.; wet and dry from 1 N KOH Sol.; boil 16 hrs. in 1 N KOH Sol.	10.0–12.4 A

* Per 100 gm. of ignited material.

Figure 2 indicates how the contractibility of expanded minerals can provide a clue to the source material from which the expanded minerals are derived. The first division is based on the number of layers which will contract to 10.0 to 10.4 Å when the clay is placed in a 90° to 100° C. 1 N KOH solution for 2 to 6 hours, washed and dried at room temperature. More elaborate potassium contraction techniques as discussed above can also be used to provide additional information. Then after it is determined whether the mineral is dioctahedral or trioctahedral a reasonable prediction of the source material can be made. The assignment of source materials, as shown in Fig. 2, is not rigid since there will be some overlap; however, it is believed that the assignment is modal in character and will apply in most instances.

The generally accepted definition of vermiculite (absorb one layer of glycol) and montmorillonite (absorb two layers of glycol) is not a genetic one as both types of expanded lattice can be formed from any of the common source materials. Further, Bradley's (1945) investigations and the present study have shown the occurrence of expanded minerals with vermiculite crystallization which will absorb two layers of glycol. An-

other definition is based on the origin of the interlayer charge: mostly tetrahedral—vermiculite, mostly octahedral—montmorillonite. On the basis of this definition most saponites, nontronites, and beidellites, all of which absorb two layers of glycol, would be classed as vermiculites. It is obvious that these two definitions are incompatible.

Barshad (1954) has suggested that the difference between these two types of layers is largely one of total interlayer charge; however, this will
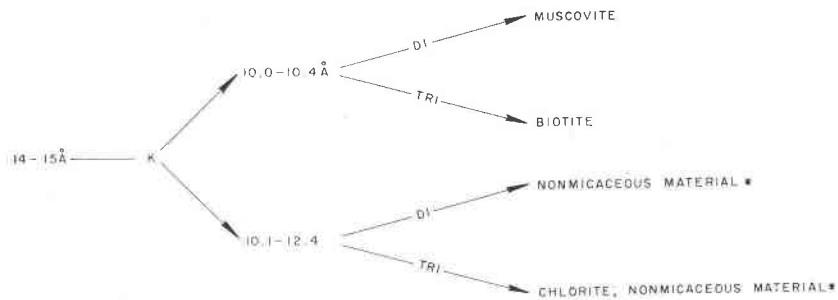
* GENERALLY VOLCANIC AND MAFIC ROCKS AND MINERALS

Fig. 2. Method of obtaining information pertaining to the origin of expanded minerals.

not be known for certain until the interlayer charge on muscovite→montmorillonite and biotite→montmorillonite is determined. The sharpness of the (00l) reflections and the fairly standard sequence of (00l) intensities suggest that relatively large grain size and a specific type of crystal orientation are also attributes of the highly charged vermiculite type of layers. There is apparently a complete spectrum of expanded minerals, as clays can be found that contain nearly all possible combinations of these criteria. For example, an expanded clay derived from a chlorite may give the x-ray pattern of a typical vermiculite, indicating large grain size and good vermiculite crystallization, but because of low interlayer charge may absorb two layers of glycol and not contract to 10 Å when it is potassium-saturated. Similarly, an expanded clay derived from muscovite may have a high interlayer charge but be fine-grained and have a montmorillonite crystallization.*

The type of expanded mineral formed is probably a combined function of the type of source material and the type and degree of weathering,

* It is quite possible that a fundamental difference between these two types of expanded minerals is the relative homogeneity of the silicate sheets. At one extreme are the fine-grained "montmorillonite" minerals which appear to have considerable differences in composition and charge between their silicate sheets; whereas the silicate sheets of the relatively coarse-grained "vermiculite" minerals are probably quite homogeneous.

with the latter probably being the more important. The present division (absorb one or two layers of glycol) between these two types of expanded minerals is more frequently a reflection of weathering differences than of source differences. The present data suggest that the degree of contractibility affected by potassium is of more genetic significance than the degree of glycol expandability. For example, muscovite alters to expanded clays, some of which will absorb one layer of glycol and others which will absorb two layers; however, both types of expanded clays readily contract to 10 Å when treated with potassium.
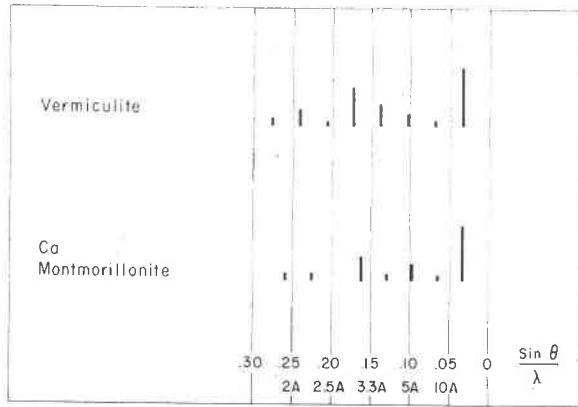

Fig. 3. Characteristic x-ray spacings and intensities of vermiculite and montmorillonite, after Bradley (1953).

It would seem best for the present to divide the vermiculites from the montmorillonites on the basis of the relative sharpness and intensities of their (00l) reflections (Bradley, 1953) (Fig. 3). This division would be based largely on type of crystallization. A further division could then be based on the degree of contractibility when potassium-saturated (Fig. 2). The contractibility would be a reflection of the interlayer charge and, to some extent, the type of source material. Whether the clay absorbed one or two layers of glycol could be the basis of an additional subdivision. Figure 4 is an attempt to organize these easily measured parameters of expanded 2:1 clays and show how these parameters relate one to the other and ultimately to the source material. A useful terminology based on this scheme might be: muscovite-derived vermiculite or muscovite→ vermiculite, chlorite→montmorillonite, volcanic→montmorillonite, hornblende→vermiculite. This is only a preliminary scheme and experiments are being continued to determine whether more quantitative potassium and glycol techniques can be used to provide more specific information.

It might be worth while here to consider the agronomist definition of "fixation" as applied to potassium. Agronomists are primarily concerned with the cation and its ease of extractibility (fixation), whereas the mineralogist and geologist are more concerned with the effects of the cation on the clay lattice (contraction) and the implications regarding the lattice composition, which can be inferred from the contraction data. It is apparent from the available data that fixation does not necessarily imply contraction, and conversely contraction does not necessarily imply fixation. Contraction data may provide more useful geologic information than does fixation.

* GENERALLY VOLCANIC OR MAFIC ROCKS AND MINERALS
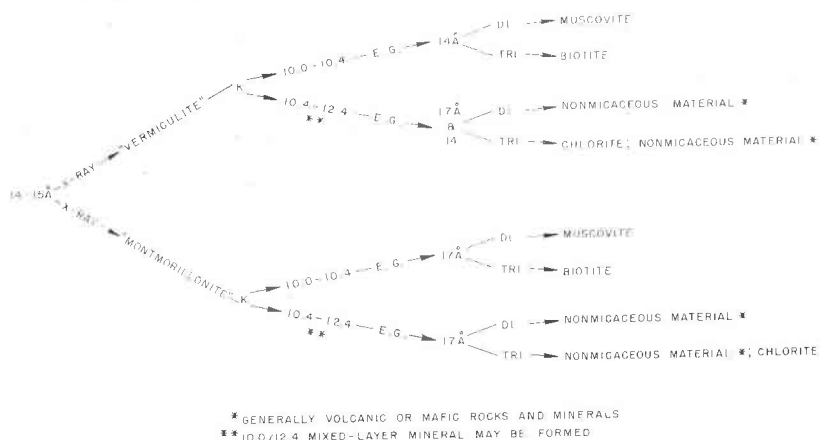** 10.0/12.4 MIXED-LAYER MINERAL MAY BE FORMED

FIG. 4. Organizational scheme to subdivide the expanding clay minerals into groups, and the relation of these groups to source materials.

The degree of contraction appears to afford some measure of the total charge and the amount of tetrahedral charge in a 2:1 layer lattice. In most cases the amount of contraction will be a function of the expanded mineral's origin; i.e., complete collapse will occur only in those expanded minerals which have a relatively high tetrahedral charge, which would be those derived from mica-type minerals. No collapse would indicate relatively low total charge or a high percentage of octahedral charge, and in most cases, an expanded mineral which formed from nonmicaceous material or chlorite. Expanded minerals, in which only part of the layers contract, would imply intermediate amounts of tetrahedral charge and a probable origin from nonmicaceous material or chlorite. This intermediate group may have inheritance implications which are not yet known. It is possible that the amount of contraction in minerals that do not completely contract is a function of the chemical composition of the source material.

Geological Significance

As the preceding section has indicated, if muscovite→montmorillonite will readily contract to 10 Å when mildly treated with KOH, possibly there is sufficient potassium in sea water to accomplish this contraction. One gram of muscovite→montmorillonite was placed in a gallon of sea water and shaken mildly for 10 days. As can be seen from the x-ray pattern (Fig. 5), a sizable amount of the expanded clay has contracted to 10 Å. The glycolated patterns indicate that the expanded clay formed three discrete phases: completely contracted packets, mixed-layer packets (7:3), and completely expanded packets.

At the end of 30 and 60 days, the first two phases increased in amount and the last phase decreased. When the 30-day sample was dried at 105° C., nearly all the clay contracted to 10 Å. When the muscovite →montmorillonite was evaporated to dryness (60° to 80° C.) three times from sea water, most of it contracted to 10 Å (Fig. 5).

These experiments indicate that expanded clays derived from muscovite and probably biotite are unstable and are not likely to be found in marine sediments. Over 100 marine samples containing expanded 2:1 clays and representing 40 formations were treated with potassium to determine the amount of contraction. In only one highly weathered sample was there any suggestion of appreciable 10-Å contraction. Most of these samples expanded to 12.0 to 12.4 Å after being saturated with potassium. In several of the samples, the x-ray reflection remained at 14 Å. This may be due to the presence of H^+ (and associated Al^{3+}) as the exchangeable cation, which as Barshad (1954) has shown tends to inhibit exchange.

It might be thought that many mixed-layer illite-montmorillonite minerals found in sediments are formed by the weathering of micas. However, samples of 35 mixed-layer illite-montmorillonite clay from 20 marine formations were potassium-treated and none contracted to 10 Å. It seems likely that mixed-layer illite-montmorillonites which were formed by the weathering of micas and deposited under marine conditions have already been contracted to 10 Å by adsorbing the potassium from the sea water.

Four expanded 2:1 clay samples from ancient continental shales were found that contracted to 10 Å when saturated with potassium.

These data suggest that most of the expanded 2:1 clays and intergrowths of expanded and nonexpanded 2:1 clays found in marine sediments were derived from nonmicaceous material and that the expanded clays which were derived from micas have largely reverted to mica. Thus, "stripped" micas or expanded clays derived from micas have only a transient existence, remaining expanded during weathering, transportation, and continental deposition, but reverting to near their original state when deposited, as most of them are, in a marine environment.

This type of transformation is merely a rejuvenation and is frequently cited as an example of the diagenesis of montmorillonite to illite. The actual case is more analogous to going from a Mg or Ca montmoril-
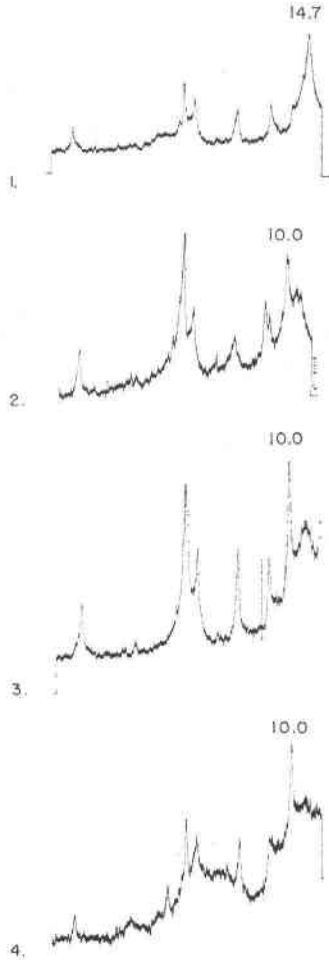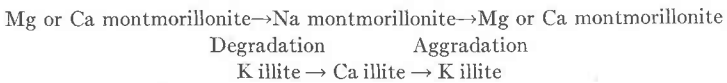

FIG. 5. Womble shale: (1) natural state; (2) in sea water 10 days; (3) in sea water 30 days; (4) evaporated to dryness from sea water 3 times.

lonite to a Na montmorillonite and back to a Mg or Ca montmorillonite.

Mg or Ca montmorillonite→Na montmorillonite→Mg or Ca montmorillonite
Degradation   Aggradation
K illite → Ca illite → K illite

It has been noted also that although mixed-layer chlorite-vermiculite

is quite common in unweathered marine sediments, mixed-layer biotite-vermiculite is rare. This further suggests that the highly charged vermiculite layers derived from biotite when exposed to sea water will contract to near 10 Å, whereas the relatively low-charged chlorite→vermiculite layers will not tend to contract. The low charge in the chlorite →vermiculite is suggested by the fact that the layers usually absorb two layers of glycol and do not contract to 10 Å when treated with KOH.

The montmorillonite in most marine sediments is not a pure montmorillonite but frequently contains 10 to 30 per cent of intergrown contracted 10 Å ("illite") layers and sometimes chlorite layers. If, in areas of relatively slow deposition, it is assumed that the variously charged 2:1 lattices attain some sort of equilibrium with the surrounding sea water, then most volcanic→montmorillonites apparently contain sufficient interlayer charge to afford 10 to 30 per cent of the layers to contract to 10 Å by absorbing potassium from sea water. Expanded clays with a higher interlayer charge, such as bravaisite and the Ordovician K-bentonites, will have 50 to 80 per cent of their layers contracted under similar conditions. The present data on mixed-layer illite-montmorillonite suggest a definite relation between interlayer charge and per cent of contracted 10-Å layers; however, the chemical and x-ray data are not sufficiently accurate to make a positive correlation, nor is it definite that the mixed-layer ratio represents actual equilibrium with sea water; i.e., the original montmorillonite was not in contact with sea water long enough to contract all the layers potentially contractible.

In summary, it might be speculated that for any given expanded mineral there is an equilibrium ratio of expanded to nonexpanded layers which is determined by the location and amount of interlayer charge and the composition of the water in the environment of deposition. Sea water might be considered the standard environment.

It is of interest to note that most of the partially contracted clays that have formed from an expanded lattice by the fixation of potassium have more K_2O than illite clays formed by moderate weathering and mechanical breakdown of muscovite. If all the K_2O in K-bentonite, bravaisite, and most glauconites is assigned to the contracted 10 Å layers, it is found that these layers generally contain 10 to 12 per cent K_2O as contrasted to the 5 to 7 per cent of K_2O normally found in detrital→illites. As both of these types of layers have a relatively high interlayer charge, it is probable that it is slow growth of the aggraded material that allows individual layers to reach an equilibrium condition and absorb the maximum possible amount of potassium. Thus, as might be expected, a high K_2O content between contracted layers might be a reflection of an aggradation and low K_2O of a degradation origin. Further speculation

based on scattered data suggests that the K_2O content of illitic material, or the relative amount of aggraded illite, tends to increase with increasing geologic age.

Recent Muds

Seventeen mud samples from the Brazos River of central Texas and marine and brackish water samples from the western Gulf of Mexico were saturated with potassium to determine the extent of contractibility. All samples contained an appreciable amount of montmorillonite and/or mixed-layer illite-montmorillonite (1:9 to 3:7). The upstream Brazos River muds obtain most of their clay from soils developed on Pennsylvanian illite, chlorite, and kaolinite shales. A sizable portion of the expanded clay in these river samples contracted to 10 Å, which suggests that it was formed by the weathering of illite. Further downstream, the outcropping sediments are of Cretaceous and Tertiary age and contain an abundance of montmorillonite which is thought to have had a volcanic origin. The expanded clays from the mud in the lower sections of the river showed no detectable contraction to 10 Å when saturated with potassium. The clays all contracted from 14 to 15 Å to 12 to 13 Å. None of the clays from the western Gulf of Mexico showed any detectable 10-Å contraction. As these clays are generally derived from the Cretaceous and Tertiary, this is to be expected. Thus, it appears that "stripped" mica or illite→montmorillonite supply only a minor portion of the clays being deposited in the western Gulf of Mexico and that volcanic→montmorillonite is the major expanded mineral present. As illite is the predominant clay mineral in the sedimentary and metamorphic rocks along much of the Atlantic Coast, it might be expected that much of the expanded clay being supplied to the Atlantic Ocean would have been derived from muscovite and illite. Samples were not available for study, but Powers (1953) has reported that expanded clays from the Patuxent River in Maryland, when treated with potassium acetate, contract to 10 Å; further, he shows that the expanded material progressively disappears as the environment becomes more saline.

In considering the diagenesis of montmorillonite to illite in a marine environment, it would be wise to be more specific as to the source material from which the "montmorillonite" was formed. It seems unlikely that low-charged volcanic→montmorillonites would ever alter to 10-Å illite in a marine environment.

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