GLAUCONITES: CATION EXCHANGE CAPACITIES AND INFRARED SPECTRA

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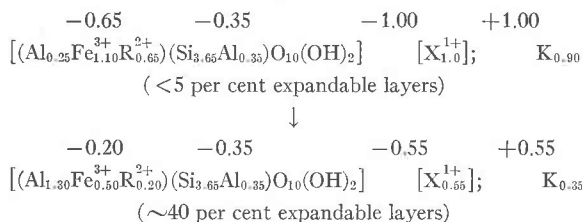*Department of Geology, Montana State University, Missoula, Montana.*

PART I. THE CATION EXCHANGE CAPACITY OF GLAUCONITE

Abstract

The cation exchange capacity and potassium content were determined for 48 glauconites ranging in geologic age from Cambrian to Recent. Variations in both these parameters are related to the per cent expandable (montmorillonite) layers in the glauconite mixed-layer mica/montmorillonite structure. The cation exchange capacity increases (5 to 39 meq/100 gm) and the potassium content decreases (8.3 to 3.4%) with increasing amounts of expandable layers.

Introduction

The mineral glauconite is a dioctahedral 2:1 layer silicate, invariably consisting of mixed 10 Å (illite, mica) and expandable (montmorillonite) layers (Warshaw, 1957; Burst, 1958; Hower, 1961). The 10 Å layers predominate in most samples of gluconite and the amount of expandable layers ranging from <5 to approximately 55 per cent. Variations in the chemical composition and the amount of mixed-layering in glauconite are related. The main variations in composition of glauconite are a variation of iron and aluminum in the octahedral positions and of interlayer potassium. The potassium content is related to the excess negative charge on the basic 2:1 structure. A generalization of the relationship between compositional and structural variations is as follows (Hower, 1962):

$$\overset{-0.65}{}\qquad \overset{-0.35}{}\qquad \overset{-1.00}{}\qquad \overset{+1.00}{}$$
$$[(Al_{0.25}Fe^{3+}_{1.10}R^{2+}_{0.65})(Si_{3.65}Al_{0.35})O_{10}(OH)_2] \qquad [X^{1+}_{1.0}]; \qquad K_{0.90}$$
$$(\text{<5 per cent expandable layers})$$
$$\downarrow$$
$$\overset{-0.20}{}\qquad \overset{-0.35}{}\qquad \overset{-0.55}{}\qquad \overset{+0.55}{}$$
$$[(Al_{1.30}Fe^{3+}_{0.50}R^{2+}_{0.20})(Si_{3.65}Al_{0.35})O_{10}(OH)_2] \qquad [X^{1+}_{0.55}]; \qquad K_{0.35}$$
$$(\sim 40 \text{ per cent expandable layers})$$

where R^{2+} is the sum of magnesium and ferrous iron and X^{1+} is the number of moles of univalent interlayer cation; the potassium contents are noted after the formulas. Relatively few measurements of cation exchange capacity (CEC) have been reported for glauconite. Carroll (1959) gave a range of 10 to 20+ milliequivalents per hundred grams (meq/100

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gm) of glauconite. This paper deals with the correlation between variations in cation exchange capacity and the amount of interlayering in glauconite.

EXPERIMENTAL METHODS

The kinds of data obtained were: (1) the percentage of expandable layers by (a) an x-ray diffraction method in which the position of the combined $(001)_{10Å} /(001)_{exp}$. peak under several kinds of sample treatments allow the determination and kind and amount of interlayering, (b) a measurement of internal surface area of selected samples by glycerol retention as an independent check of the x-ray technique; (2) the cation exchange capacity; (3) the potassium content.

X-RAY DIFFRACTION DETERMINATION OF PERCENTAGE OF EXPANDABLE LAYERS

Glauconite pellets were obtained from both sedimentary rocks and unconsolidated sediments. Rock samples were crushed in a large mortar and pestle. All samples were screened and a specific size fraction was chosen for glauconite separation—usually the 60 to 150 mesh fraction. Separation of the pellets was made with a Frantz Isodynamic Separator. Samples were recycled until the non-pellet constituents were less than five per cent. Fine-grained and micaceous grains were further removed by elutriation. The water-soaked glauconitic sample was scrubbed on a paper towel, thereby letting the micaceous particles adhere to it. Following drying of the concentrate, impurities such as quartz, biotite, argillaceous and calcareous materials, were removed by handpicking under microscope. Minute coatings of siliceous and calcareous material on the glauconite pellets, and other remaining impurities formed less than 2 per cent of the total sample. The New Zealand glauconites (Lipson, 1958) were kindly furnished by Professor G. H. Curtis in cleaned state.

Oriented specimens of glauconite were prepared by the method of Kinter and Diamond (1956). This method consists of disaggregating the sample, preparing a stable suspension, and centrifuging the suspension through a porous porcelain plate. The clay film left behind on the surface of the plate is oriented well enough to eliminate the general x-ray reflections and to greatly enhance the basal reflections.

Brown and MacEwan (1951) and Weaver (1956) have calculated the positions of the basal reflections in mixed-layer clay structures using Hendricks and Teller's (1942) equations. The positions of the various combined basal reflections allow an identification of the kind of interlayering and a determination of the amount of each type of layer (Weaver, 1956). Various treatments such as glycol solvation, heating, and saturat-

ing with several types of exchange ions eliminate any ambiguities. By use of these techniques Hower (1961) found that the mixed-layering in glauconites is almost wholly between 10 Å and expandable layers. We found that treatment with 1N KCl was the most useful procedure. With potassium as the exchange ion expandable (montmorillonite) layers retain one layer of water under a wide range of relative humidities and a spacing of 12.4 Å. The position of the combined first order 10 Å/12.4 Å reflection varies almost linearly as a function of amount of interlayering. Solvation with ethylene glycol was frequently used as a check of the K-saturation determination.

The measurements of per cent expandable layers interstratified with 10 Å layers in the glauconite samples used in this study are reported in Table 1. Diffraction patterns of glauconites showing a range of inter-layering and under different treatments are shown in Fig. 1. The precision of the determination is about $\pm 2.5\%$ at $<20\%$ and $\pm 5\%$ at $>20\%$ expandable layers.

GRAVIMETRIC DETERMINATION OF PER CENT EXPANDABLE LAYERS

The mixed-layering data on the glauconites obtained by x-ray diffraction procedures depends on the validity of the calculated positions of combined basal reflections. As an independent check of this determination we determined the internal surface area of selected glauconites by a gravimetric glycerol retention method. Diamond and Kinter (1958) showed that under the proper conditions montmorillonite retains a monomolecular interlayer sheet of glycerol. They also showed an excellent relationship between the amount of internally retained glycerol in a clay mineral sample and the amount of montmorillonite present. We have used Diamond and Kinter's method as modified by them (Kinter and Diamond, 1959) to determine the per cent expandable layers in glauconites. The glauconite samples were disaggregated by use of a Bendix ultrasonic cleaner. Material of less than 0.2 micron in diameter was separated by centrifugation and saturated with Na^+, using one normal solution of sodium metaphosphate. Values for internal glycerol retained, per cent of expandable layers calculated from the glycerol retained, and the x-ray determination of per cent expandable layers are reported in Table 2. The precision (standard deviation) of the gravimetric glycerol retention method is $\pm 5\%$ as calculated from triplicate determinations on five of the samples.

Figure 2 shows the relationship between per cent expandable layers as determined by the x-ray and glycerol retention methods. The data agree within the precisions of the two methods and lend confidence to the x-ray diffraction determinations.

TABLE 1. PER CENT EXPANDABLE LAYERS, POTASSIUM CONTENT, AND CATION
EXCHANGE CAPACITY OF GLAUCONITE

Sample No.	Formation	Per cent Expandable Layers	K_2O (Wt. %)	C.E.C.[1] (meq/100 gm glauc.)
1	Tonto	5[2]	8.1[2]	5
2	Birkmose Mem., Franconia	5[2]	8.3[2]	12
3	Hatchetigbee	5[1]	7.5[1]	12
4	Green sandstone (England)	5[1]	7.8[1]	11
5	Bonneterre	5[2]	8.3[2]	9
6	Reno Mem., Franconia	10[1]	8.4[1]	13
7	Mt. Whyte	10[1]	—	7
8	Bashi	10[2]	7.0[2]	9
9	Reno Mem., Franconia	10[2]	7.7[2]	12
10	San Saba Mem., Wilberns	10[2]	7.4[2]	16
11	Marshalltown	10[1]	8.4[1]	17
12	Recent glauconite (St. Monica Bay, Calif.)	10[1]	7.9[1]	18
13	Gros Ventre	15[2]	7.5[2]	15
14	Park	15[1]	7.4[1]	19
15	Folkstone	15[2]	7.5[1]	17
16	Riley	15[2]	6.8[2]	20
17	Eutaw	15[1]	6.4[1]	18
18	Nacatosh	15[1]	6.6[1]	17
19	New Zealand[3] #44	15[1]	6.6[1]	17
20	New Zealand #38	15[1]	7.7[1]	16
21	New Zealand #45	15[1]	7.2[1]	17
22	New Zealand #51	15[1]	7.2[1]	16
23	New Zealand #39	15[1]	7.3[1]	18
24	Lion Mt. Mem., Riley	15[1]	6.3[1]	18
25	Winona	15[1]	6.9[1]	20
26	Hatchetigbee #2	15[1]	7.1[1]	13
27	Hazlet, N. J.	20[2]	5.3[2]	18
28	Lomita Marl	20[1]	5.8[1]	20
29	L. Cret. (French Alps)	20[1]	—	22
30	New Zealand #52	20[1]	6.8[1]	18
31	New Zealand #56	20[1]	6.4[1]	20
32	Cane River #1	20[1]	7.5[1]	19
33	Recent (Pratt #5858)	20[1]	6.9[1]	20
34	Colorado	25[2]	5.1[2]	26
35	Marble Falls	25[1]	5.1[1]	21
36	New Zealand #47	25[1]	4.7[1]	24
37	Recent (Point Arguello)	25[1]	5.8[1]	21

(continued on next page)

[1] Present investigation.

[2] Data from Hower (1961).

[3] The numbers of the New Zealand glauconites are those given in Lipson's paper (1958).

TABLE 1—(*continued*)

Sample No.	Formation	Per cent Expandable Layers	K_2O (wt. %)	C.E.C.[1] (meq/100 gm glauc.)
38	Cane River #2	30[1]	6.2[1]	33
39	Sundance	30[2]	4.7[2]	26
40	Moody's Branch	30[2]	4.3[2]	29
41	Byram	40[2]	3.7[2]	35
42	Recent (Monterey Bay, Calif.)	40[1]	3.8[1]	20
43	Brown Bear (U.S. 120, Recent)	45[1]	4.3[1]	37
44	Brown Bear (#108 S 45) (U.S. 60, Recent)	45[1]	4.7[1]	29
45	Recent (Arguello Shelf)	45[1]	—	39
46	Recent (Calif.)	50[1]	3.4[1]	—
47	Recent (Monterey Bay, Calif.) Pratt #6489	50[1]	4.6[1]	28
48	Brown Bear NE Pacific	55[1]	4.1[1]	32

CATION EXCHANGE CAPACITY MEASUREMENT

Cation exchange capacities were determined using the method described by Jackson (1958) with a few modifications. A one gram sam-

TABLE 2. DETERMINATION OF PERCENT EXPANDABLE LAYERS IN GLAUCONITES BY GLYCEROL RETENTION AND COMPARISON WITH *X*-RAY METHOD

Sample No.	Total Retention %	External Retention %	Internal Retention %	% Expandable Glycerol Retention	Layers[2] X-ray
Montmorillonite[1]	20.10	1.60	18.50	100	
9	3.96	2.13	1.83	9.9	10
19	3.19	1.69	1.50	8.1	15
13	4.01	1.89	2.12	11.4	15
14	3.78	2.80	1.98	10.7	15
20	4.51	1.90	2.61	14.0	15
15	4.78	1.55	3.23	17.4	15
33	6.75	2.19	4.56	24.5	20
36	6.17	1.87	4.30	23.1	20
40	7.51	2.29	5.22	28.0	30
41	10.21	2.74	7.47	40.0	40
48	14.16	2.24	11.92	64.0	55

[1] Average of three dioctahedral montmorillonites from Diamond and Kinter (1958) for which both internal and external surfaces were measured.

[2] Based on the mean internal glycerol retention of 18.5% = 100% expandable layers.
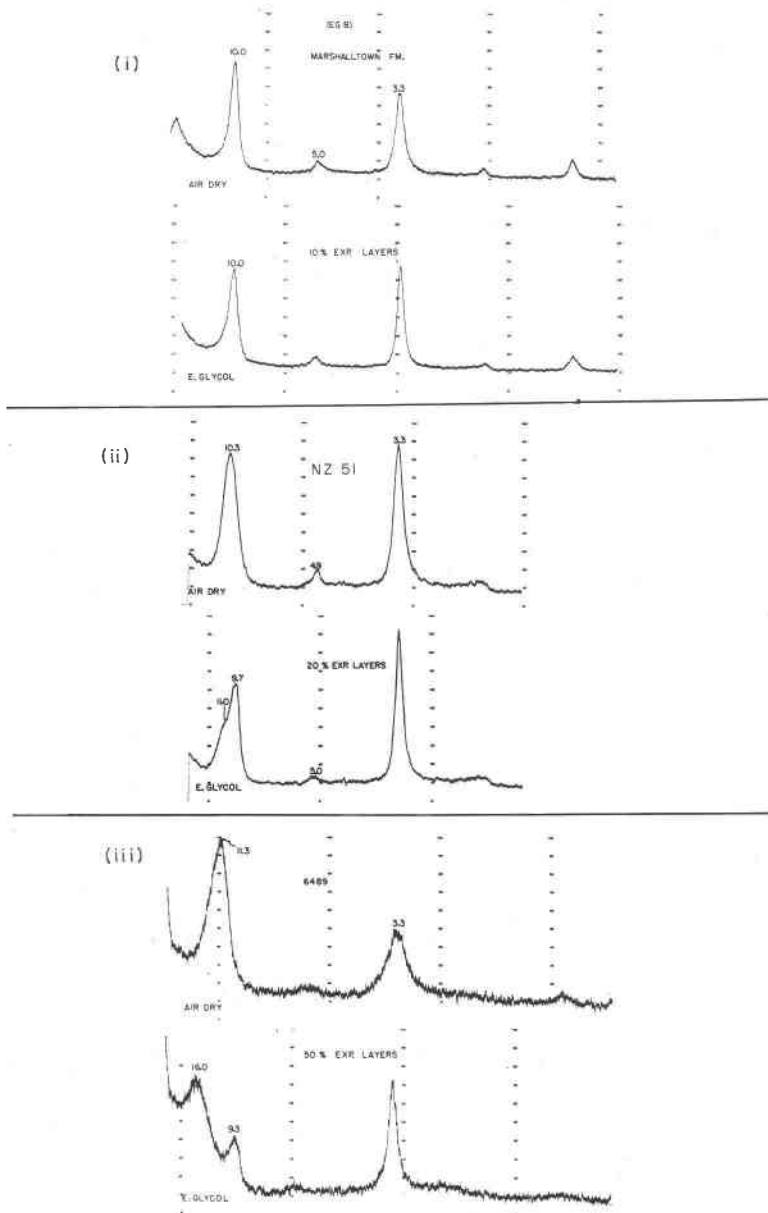
FIG. 1 (a). X-ray diffraction patterns of oriented specimens. Air-dried (upper) and glycolated (lower).

    (i) 10% expandable layers (Sample No. 11).
    (ii) 20% expandable layers (Sample No. 25).
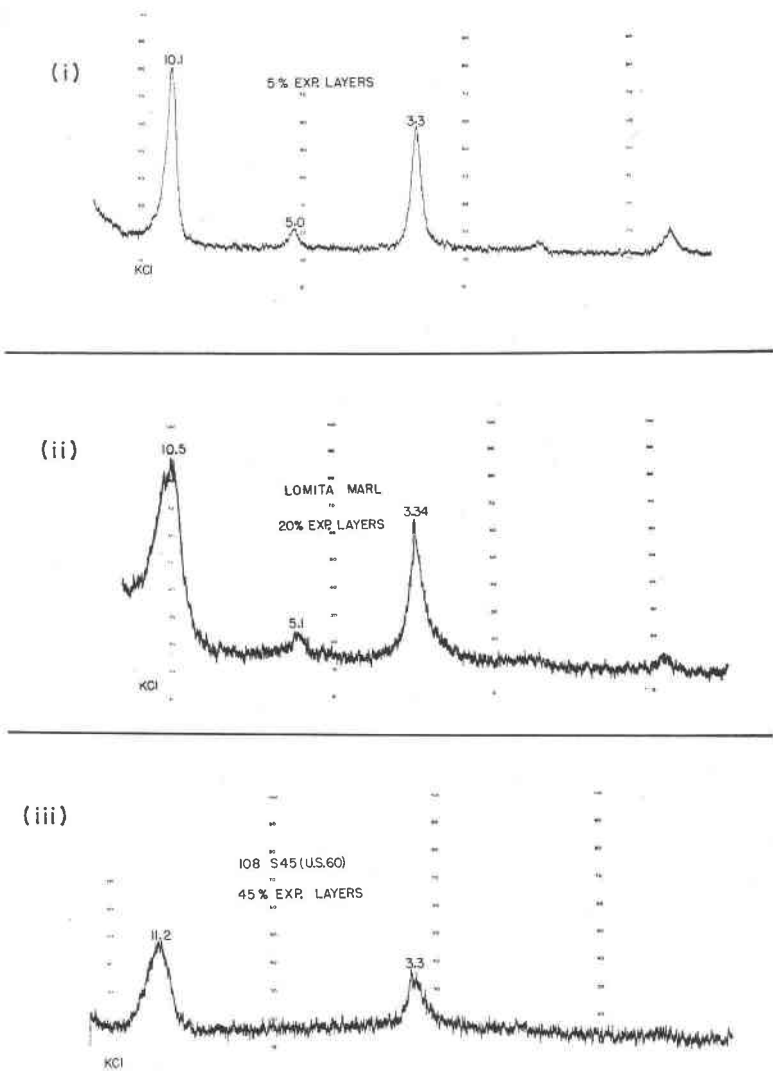   (iii) 50% expandable layers (Sample No. 47).

FIG. 1 (b). X-ray diffraction patterns of oriented specimens of glauconites. The specimens are potassium-treated (in 1N KCl).

(i) 5% expandable layers (Sample No. 4).
(ii) 20% expandable layers (Sample No. 28).
(iii) 45% expandable layers (Sample No. 48).

ple of disaggregated glauconite was acidified with 25 ml of a 1N sodium acetate (pH 5) solution. After washing the sample free of excess salt it was treated with 50 ml of a 1N $CaCl_2$ solution. The $CaCl_2$ was agitated with a wrist-action shaker. Excess $CaCl_2$ was removed by centrifugation and washing. The calcium exchanged on the glauconite was removed by suspending the sample in a known volume of 1N ammonium acetate. An aliquot of the clay-free solution was analyzed for Ca with a Beckman model DU spectrophotometer. The precision of determination is $\pm 7\%$. The accuracy is indicated by CEC measurements made on two API reference clay minerals shown in Table 3 below.

The cation exchange capacities of the glauconites used in this study are reported in Table 1.

TABLE 3. CATION EXCHANGE CAPACITIES DETERMINED FOR API REFERENCE
CLAY MINERALS

Sample	Cation Exchange API	Capacity (meq/100 gm.) This Study
Kaolinite H-4	12.2	11.8
Montmorillonite H-24	103.5	99.0

RELATION BETWEEN CATION EXCHANGE CAPACITY AND PER CENT EXPANDABLE LAYERS IN GLAUCONITE

The relationship between cation exchange capacity and per cent expandable layers in glauconite is shown in Fig. 3. The equation of the best linear fit to the relationship is CEC (meq/100 gm) = 8.2+0.54 (% Exp. Layers). The increasing CEC with increasing expandable layers is readily explained by the increasing amount of exchangeable interlayer cations available from the expandable layers.

The solutions of the equation of CEC as a function of per cent expandable layers at zero and one hundred per cent expandable layers are of some interest. The zero value gives a CEC of 8.2 meq/100 gm. This is within the range expected for a clay mineral in which the exchangeable cations are present only at broken oxygen bonds at the edges of crystals (Carroll, 1959). It is, however, considerably lower than the CEC's of "illites," which are supposedly non-interlayered structures (Grim, Bray, and Bradley, 1937). The 100% expandable layer solution to the equation is 62 meq/100 gm, lower than the range reported by Carroll (1959) for montmorillonite group minerals. This low value is controlled by the low cation exchange capacities of glauconites with more than 30% expandable layers; the 100% expandable layer solution of the equation excluding

these samples is 90 meq/100 gm. Most of the highly expandable glauconites are of geologically recent age. It may be that a portion of the exchange positions are blocked by organic material or that the expandable layers contain a significant amount of fixed cations.

THE STATUS OF POTASSIUM IN GLAUCONITES

The potassium content of glauconites is inversely proportional to the per cent of expandable layers (Burst, 1958; Hower, 1961). The precise nature of the relationship between potassium content and structure is of
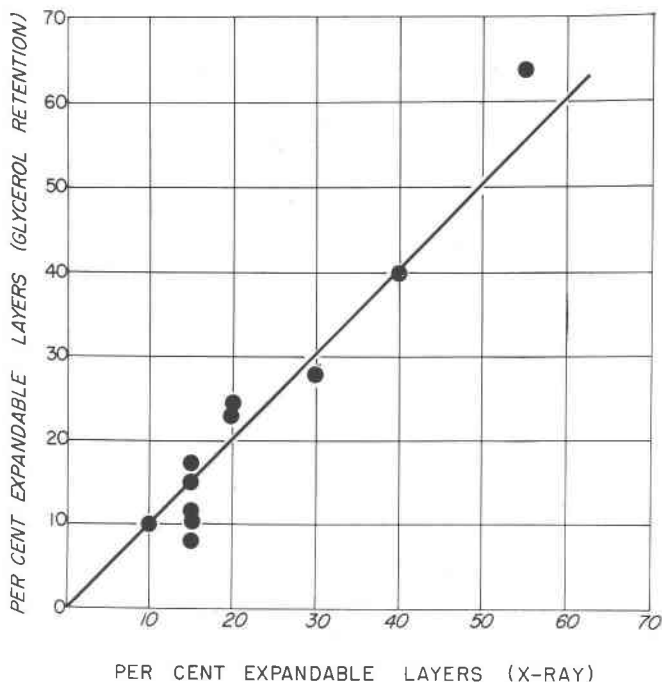
FIG. 2. The relationship between per cent expandable layers as determined by the x-ray and glycerol retention methods.

considerable interest because this relationship is determined by whatever compositional variations cause mixed-layering. A precise determination of the relationship would allow the testing of any model proposed to explain interlayered mica/montmorillonites. It is not the intent of this paper to propose models to explain such mixed-layering, but rather to present a "first-approximation" relationship between potassium content and amount of expandable layers and to point out its difference from the model proposed for mixed-layer mica/vermiculites (Mehra and Jackson, 1959).

Figure 4 shows the relationship between K_2O content and per cent expandable layers in the glauconites used in this study (circles, solid line). Virtually all of the potassium is fixed; the amount of exchangeable potassium determined from 11 glauconite samples ranged from 0.7 to 2.5 meq/100 gm. and averaged close to 1 meq/100 gm. At a maximum only one per cent of the total potassium glauconites is exchangeable.

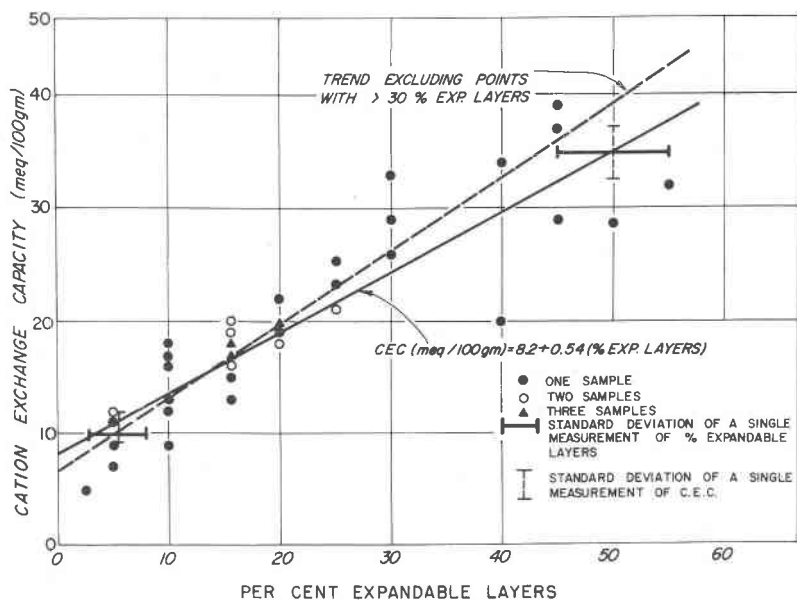Mehra and Jackson (1959) determined the relationship between per

FIG. 3. The relationship between cation exchange capacity and per cent expandable layers in glauconites.

cent expandable layers and K_2O content for mixed-layer "illite/vermicu-lites." They used a heterogeneous assortment of materials ranging from trioctahedral vermiculites through illites and including one glauconite. Many of these samples were soil clays. Mehra and Jackson removed organic material with H_2O_2, free iron oxide by Jackson's (1956) dithio-nate-citrate bicarbonate method, and determined per cent expandable layers by measuring internal surface area by a glycerol retention method very similar to the one described in this paper. Their samples contained impurities (quartz, chlorite, and kaolinite) ranging in amount from 0–30% and average about 15%, which they corrected for by quantitative x-ray diffraction methods. A plot of Mehra and Jackson's data for per cent expandable layers against K_2O after correcting for impurities is also included in Fig. 4. The relationship is remarkably good, particularly
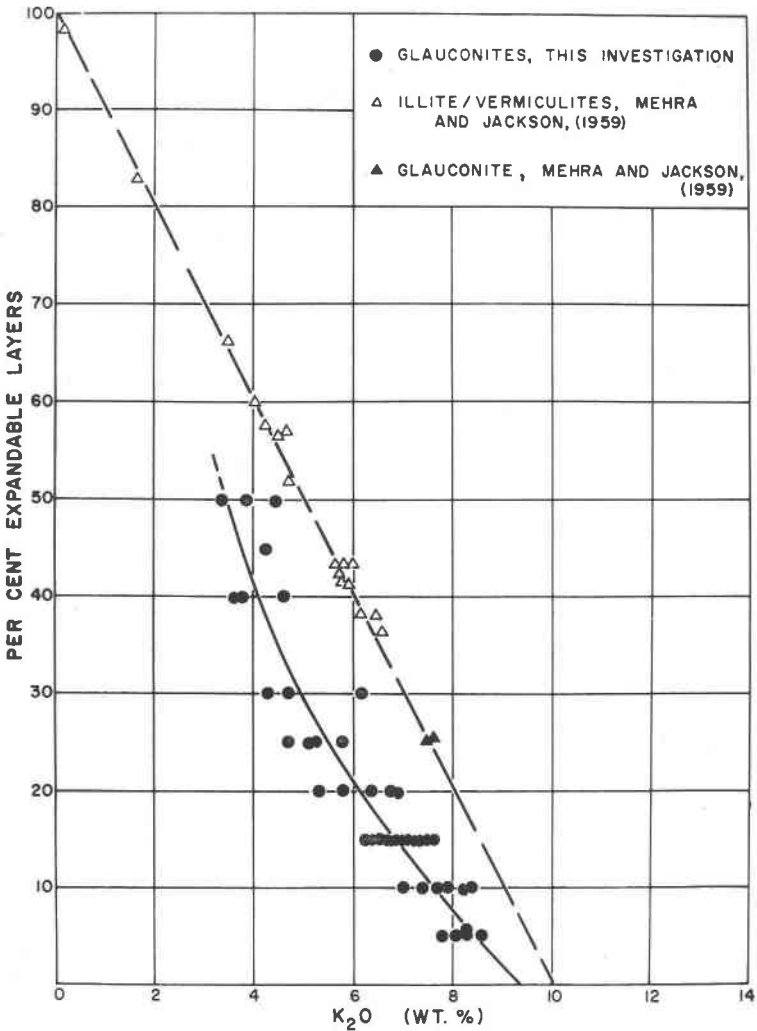
FIG. 4. The relationship between potassium content and per cent expandable layers in glauconites.

when considering that the mixed-layer material included materials with variable formula weights and that it is difficult to perform accurate quantitative analyses by x-ray diffraction. Their data indicate a very constant ($\pm 2\%$ standard deviation) K_2O content of 10.0% for the non-expandable layers in clay size materials that are mica/vermiculites.

Our data for glauconites in Fig. 4 scatter considerably more than Mehra and Jackson's. In addition, the glauconites do not fit their relationship on two counts: (1) The glauconites contain a significantly lower

weight per cent K_2O at all percentages of expandable layers; and (2) The relationship does not appear to be a simple linear function, but one of higher degree. One interesting difference between the two sets of samples is in the nature of the expandable layers. Cation exchange capacities reported by Mehra and Jackson for their samples show a charge approaching that of micas for the expandable layers, indicating that they are vermiculite. The expandable layers of the glauconites used in this study have a low charge, as indicated by their low cation exchange capacity and the fact that the expandable layers do not collapse under any of Weaver's (1958) KOH treatments.

If the layer charge in micas is constant, mixed-layer mica/vermiculites are inherently simpler structures than mica/montmorillonites. Mica/vermiculites in their simplest state would simply consist of a complete replacement of potassium by magnesium and other hydrated ions without an alteration of charge in a certain portion of the interlayer spaces. Assuming a constant formula weight, the relationship between per cent expandable layers and weight per cent K_2O would be simple: (wt.% K_2O) sample = (wt.% K_2O) mica × (100 − % expandable layers)/100. This is precisely the relationship found by Mehra and Jackson for a heterogeneous assemblage of mica/vermiculites. Mica/montmorillonites, on the other hand, demand at least two different layer charges to account for their existence, and it is possible that a distribution of layer charges exists. This charge distribution could account for the more complicated and less precise relationship we find between potassium content and amount of expandable layers in glauconites.

CONCLUSIONS

1. The cation exchange capacity of glauconite is directly proportional to the percent expandable (montmorillonite) layers in the glauconite mixed-layer mica/montmorillonite structure. Glauconites with a range of expandable layers from <5 to 55% range in cation exchange capacity from 5 to 39 meq/100 gm.

2. The x-ray diffraction and glycerol retention (surface area determination) methods for determining amount of expandable layers give comparable results.

3. The potassium content of glauconites is inversely proportional to the percent expandable layers. The relationship between potassium and percent expandable layers is not a simple linear function.

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