DISTRIBUTION OF CLAY MINERALS AND ION-EXCHANGE CAPACITY IN SOME SEDIMENTARY MATERIALS[1]

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ABSTRACT

The cation-exchange capacity of the clay fraction was determined in 67 samples of various types of sedimentary materials, and the clay minerals were identified from x-ray diffractometer patterns of oriented aggregates. The probable quantitative clay mineral composition was established for each sample assuming a comparable degree of crystallinity for the clay minerals in the sample. Agreement was poor between the ion-exchange capacities determined and those predicted from the clay mineral composition. The results suggest that the figure obtained for the ion-exchange capacity of a sample of sedimentary material may be misleading as a guide to the types of clay minerals present.

The residual soils among the sedimentary materials examined had clay fractions with greater variation in ion-exchange capacity than did unconsolidated sediments generally of alluvial origin.

INTRODUCTION

The determination of cation-exchange capacity and the identification of the clay minerals in sedimentary materials ranging from shale to residual soil were undertaken to provide a picture of relationships which may be found in similar types of material from localities within the United States and possibly in other countries.

Types of sedimentary material included in this study can be grouped as follows:

Description	*Number of samples*
Shale	8
Residual soils, parent material unknown	8
Residual soils above limestone and dolomite	12
Unconsolidated sediments	24
Lake deposits (clays)	2
Glacial deposits	7
Clay beds from sedimentary formations	2
Miscellaneous	4
	67

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264

METHODS OF EXAMINATION

Ion-Exchange Capacity

The samples were received in an air-dry condition with the exception of a few that were very wet and had to be dried slowly at a temperature of 60° to 70° C. The raw samples were quartered to provide representative small samples for ion-exchange determination, but fragments larger than 2 mm in diameter were removed by sieving. The preparation of the clay fraction is described in the following section.

The total ion-exchange capacity of the whole material and of the clay fraction ($<$ 2 microns) was determined by Bower and Truog's (1940) colorimetric manganese method using N $MnCl_2$ and N ammonium acetate at pH 7. The intensity of the color developed was measured with a Coleman Model 14 spectrophotometer and the milliequivalents of total exchange capacity per 100 g were read from a prepared graph.

X-Ray Examination

The samples were disaggregated by gentle crushing wherever possible, but a few of the more highly consolidated materials required grinding. Each sample was then sieved through a U.S. Standard Series sieve no. 230 to remove particles greater than 62 microns in median diameter. The material passing the sieve was dispersed in distilled water with sodium metaphosphate added as a dispersing agent. After thorough shaking, the suspensions were placed in 250-ml centrifuge bottles and the clay fractions (less than 2 microns equivalent settling diameter) were removed by repeated centrifuging and decanting until the supernatant water was reasonably clear. Portions of the clay suspensions were set aside for later preparation of oriented aggregates. Most of the water in the suspensions was removed by porcelain filter candles under vacuum. Any remaining water was allowed to evaporate at room temperature. The dry clay was crushed in a porcelain mortar, passed through a U. S. Standard Series sieve no. 400, and packed in aluminum diffractometer sample holders.

X-ray diffraction patterns were made with a North. American Philips wide-range goniometer diffractometer using Ni-filtered Cu radiation at 40 kvp and 20 ma. A 1-degree slit system, a rate-meter scale factor of 2, and a time constant of 8 seconds were employed. The Geiger-Müller tube was operated at 200 v over threshold.

For about half of the samples the scanning speed of the goniometer was set at 1° 2θ per minute, with an accompanying chart speed set so that 2° 2θ per inch were recorded. The scanning speed was changed to 2° 2θ per minute, with a chart scale of 4° 2θ per inch for the remaining samples.

In addition to the patterns produced by the samples mounted in standard holders, patterns were made using oriented aggregates of the clay samples prepared by allowing a portion of the suspension to dry at

room temperature on glass slides (1 by 1¾ in.). Allowing the clay film to cover the entire surface of the slide permits the surface of the clay to lie on the focusing circle of the goniometer as does the surface of the sample in a standard holder. Compression of the clay film by the sample-holder clamp is assumed to be negligible.

A second pattern was made of each oriented aggregate after glycerol treatment. The glycerol was sprayed onto the slide in small amounts until the clay film was damp but not wet.

If a spacing at about 14 A persisted after glycerol treatment, the slide was placed in a muffle furnace and heated to approximately 550°C for about 45 minutes.

The peaks appearing on the diffractometer patterns produced by the glycerol-treated aggregates were identified and the area under the lowest order 00l peak present for each clay mineral was measured. The background on each side of a peak was joined by a line and the enclosed area measured with a polar planimeter. This measured area is referred to hereinafter as a basal peak area.

RESULTS

Clay Minerals

Identification. — Montmorillonite was identified where the x-ray pattern showed a spacing that expanded to about 18 A upon glycerol treatment (MacEwan, 1946) of the oriented aggregate. A spacing of about 14 A, which did not expand with glycerol treatment and persisted after heat treatment, was identified as the 002 spacing of chlorite (Brindley and Robinson, 1951). Collapse of this spacing upon heat treatment was interpreted as indicative of vermiculite (Walker, 1951). Hydrous mica (illite) was identified by the presence of a spacing of about 10 A (Brown, 1951), and kaolinite by a spacing of about 7 A, which disappeared upon heat treatment (Brindley, 1951).

Vermiculite in important amounts was noted in only one sample. Chlorite appears in the patterns for nine samples. The remainder of the samples contain montmorillonite, hydrous mica, and kaolinite in varying amounts. The ratio, expressed in percent of total basal peak area, of the areas under the basal peaks of montmorillonite, hydrous mica, and kaolinite was computed for each sample; and the ratios thus obtained were plotted in a ternary diagram (Fig. 1). The area under a vermiculite peak was allotted to montmorillonite, and under a chlorite peak to hydrous mica.

Problem of quantitative mineral composition. — For comparison of data from mixtures of clay minerals with data from the pure minerals themselves, it is important that the quantitative mineral composition of the mixture be determinable to some degree. It is recognized that the distribution shown in Figure 1 does not necessarily correspond to the true composition of the samples. Talvenheimo and White (1952) have demonstrated
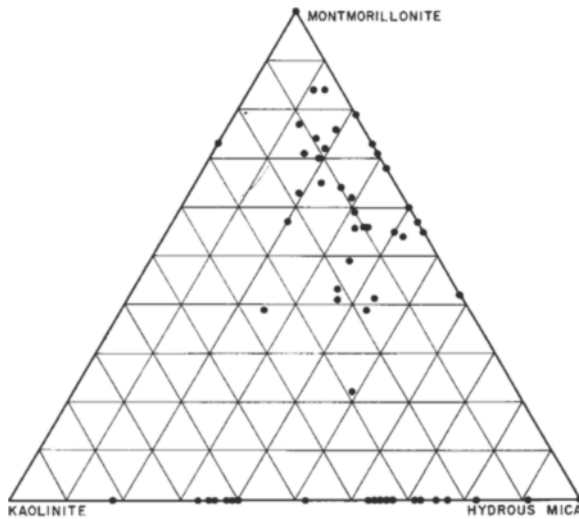
FIGURE 1. — Ternary diagram showing distribution of the samples according to the relationships of the areas under the basal peaks of their component clay minerals.

that the area under a basal peak produced by a glycerol-treated oriented aggregate of a clay mineral is a linear function of the weight concentration of the mineral producing the peak. Figure 2, which is adapted from data presented by these authors, shows the relative increase in peak area with increasing concentration for montmorillonite, kaolinite, and hydrous mica.
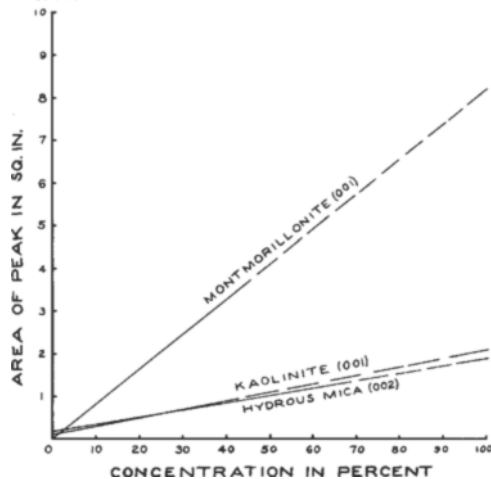

FIGURE 2. — Graph showing variation of the basal peak areas of montmorillonite, kaolinite, and hydrous mica with increase in weight concentration (adapted from data by Talvenheimo and White, 1952, Anal. Chem. 24 : 1784-1789).
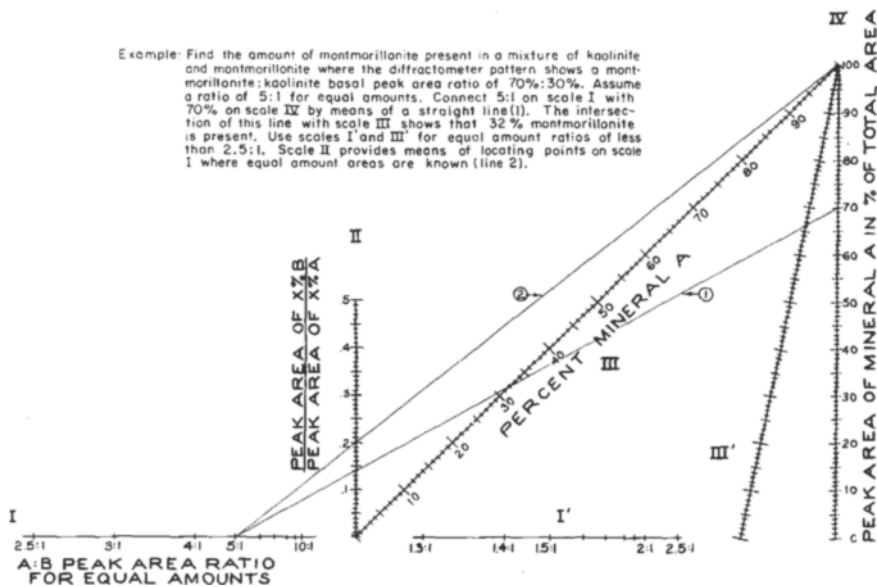
Figure 3. — Nomograph for obtaining composition of sample in percent by weight from the basal peak area values measured on the diffractometer pattern for the sample.

The ratio of areas for a mixture of equal parts of montmorillonite, kaolinite, and hydrous mica is about 5:1:1. Using this ratio, a nomograph (Fig. 3) may be constructed for conversion of peak area percentage to weight percentage. Figure 4 shows the composition relationship of the samples used in the present study obtained from this nomograph. The assumption is made that the crystallinity of clay minerals in the samples is such that the same 5:1:1 ratio of peak areas would be produced by a mixture of equal parts by weight of the clay minerals. It is not necessary that all of the minerals in a sample have the same degree of crystal perfection as the corresponding standard minerals but only that relative crystallinity between the component minerals be the same as the relative crystallinity between the standards.

X-ray patterns of samples from the same localities as those chosen as standards by Talvenheimo and White were compared with patterns of samples from other localities reported by Kerr et al. (1950). This comparison suggests that each of the standards chosen shows as high a degree of crystal perfection as is generally found in its mineral type.

If an arbitrary scale of degree of crystal perfection were to be established, these standards might be assigned a crystallinity value of "100" or "high" crystallinity. Another sample of the mineral, other conditions being constant, might produce a peak with an area one-half that of the
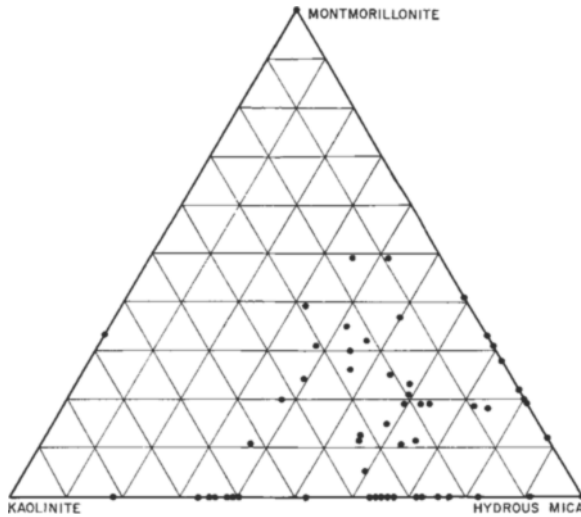
FIGURE 4. — Ternary diagram showing the clay mineral composition by weight of the samples assuming a "5:1:1" montmorillonite : kaolinite : hydrous mica peak area ratio.

standard. This sample could be assigned a crystallinity of "50". If the montmorillonite, kaolinite, and hydrous mica in a mixture all had the same degree of crystallinity (e.g., 20:20:20), then the peak areas would be still controlled by the 5:1:1 ratio found in the standard mineral mixtures. There is, of course, no requirement that all the minerals in a sedimentary material have the same crystallinity, but it is conceivable that over many samples the average crystallinities would approach values that produce the afore-mentioned 5:1:1 ratio. If a portion of each of the component minerals in a sample could be separated in a pure state, the true ratio of peak areas could be determined. As no such separation could be made in this study, the 5:1:1 ratio was accepted as the most probable distribution of areas, with the realization that this could be in error for individual samples.

The presence of impurities such as quartz and calcite, although reducing the absolute areas of the peaks of the clay minerals, should not affect the ratio of those peaks. The ratio should remain the same also where other variations exist such as thickness of the clay film on the slide when less than quasi-infinite.

Ion-Exchange Capacities

The ion-exchange capacities determined on the whole sample and on the clay fraction are given in Table 1 together with the ratios of basal peak areas of the clay fraction. The ion-exchange figures for the whole sample

Table 1. — Ion-Exchange Capacities and Ratio of Basal Peak Areas of Montmorillonite, Hydrous Mica, and Kaolinite of the Sedimentary Materials Examined.

Description and number of samples	Ion-exchange capacities (meq/100 g)		Ratio of basal peak areas		
	A Whole sample (<2 mm)	B Clay fraction (<2 microns)	Montmorillonite 001 spacing	Hydrous mica 002 spacing	Kaolinite 001 spacing
Shale (8)	8.6	19.2		66	34
	11.7	27.2		75	25
	5.4	23.2		91	9
	6.4	19.2		100	
	8.0	23.6		100	
	6.4	35.2		65	35
	11.8	28.0		100	
	8.0	24.0		71	29
Residual soil, parentage unknown (8)	11.8	19.2	41	37	22
	5.8	51.0	60	40	
	4.3	23.6	68	32	
	7.0	66.4		61	39
	10.2	69.6	42	58	
	3.9	84.0		100	
	not det.	25.1		39	61
	not det.	80.8	41	43	15
Residual soil above limestone and dolomite (12)	6.0	72.0	22	44	30
	10.9	47.6	58	42	
	3.2	16.0		18	82
	3.5	26.0		72	28
	9.3	25.6		65	35
	12.6	112.0	76	19	6
	1.9	11.0		36	64
	4.7	15.0		35	65
	13.8	16.0		38	62
	12.5	18.6		33	67
	12.1	20.2		52	48
	7.6	14.4		36	64
Unconsolidated sediments (silty sand and clay) (24)	11.7	37.2	84	18	5
	13.2	38.2	54	42	4
	8.5	45.6	57	20	23
	17.8	36.0	62	29	9
	8.0	25.2	55	40	4
	15.3	18.0	84	13	2
	11.7	24.4	70	19	11
	13.7	42.0	56	34	10
	8.8	33.2	74	16	9
	7.5	24.4	100		
	11.7	16.0	29	71	
	9.8	32.4	63	19	18
	10.0	30.8	77	12	11
	9.5	33.2	71	16	13
	13.0	23.2	56	33	12
	8.7	26.4	65	22	13

Description and number of samples	Ion-exchange capacities (meq/100 g)		Ratio of basal peak areas		
	A Whole sample (<2 mm)	B Clay fraction (<2 microns)	Montmorillonite 001 spacing	Hydrous mica 002 spacing	Kaolinite 001 spacing
	11.3	28.8	72	19	9
	14.3	31.8	49	35	16
	10.5	20.0	55	45	
	9.7	19.2	43	34	
	9.8	34.8	100		
	8.7	18.8		75	25
	10.7	16.8		63	37
	8.9	18.8	79	21	
Lake deposits, clays (2)	7.1	14.4	73	27	
	13.5	34.0	79	21	
Glacial deposits (7)	3.7	13.2		63	36
	1.5	11.8		82	18
	3.5	not det.		55	45
	1.2	8.6		64	36
	1.4	13.2		not det.	not det.
	3.4	58.0	39	43	18
	1.0	16.3		81	19
Clay from formations (2)	9.6	60.8	64	26	10
	19.4	77.2	59	31	10
Miscellaneous (4)	10.0	53.6	56	34	10
	3.8	55.2	76	19	6
	2.8	36.0		77	23
	not det.	64.0	39	25	36

are all rather low because sand and silt are included, and these serve as diluents of the clay concerned in ion-exchange activity. No mechanical analyses are available for most of these samples, so that the quantity of clay present is unknown; but comparison of the figures in columns A and B in Table 1 indicate the dilution of the clay.

Relations Between Ion-Exchange Capacity and Clay Mineral Composition

Figure 5 shows in graphical form the data presented in Table 1. The ion-exchange capacity of each sample is compared with the sample's position on the ternary diagram shown in Figure 1. The height of the lines connecting the points with the base represents the ion-exchange capacity, and the inclined planes delineate expected ranges derived from reported values for standard samples of the end-member minerals. The dashed lines and circles represent those hidden by these planes. It will be noted that the trend toward higher ion-exchange values, which might be expected toward the montmorillonite end of the diagram, fails to appear. Instead the values for many of the samples with predominant montmorillonite basal peak areas fall well below the expected range. It should be remembered that
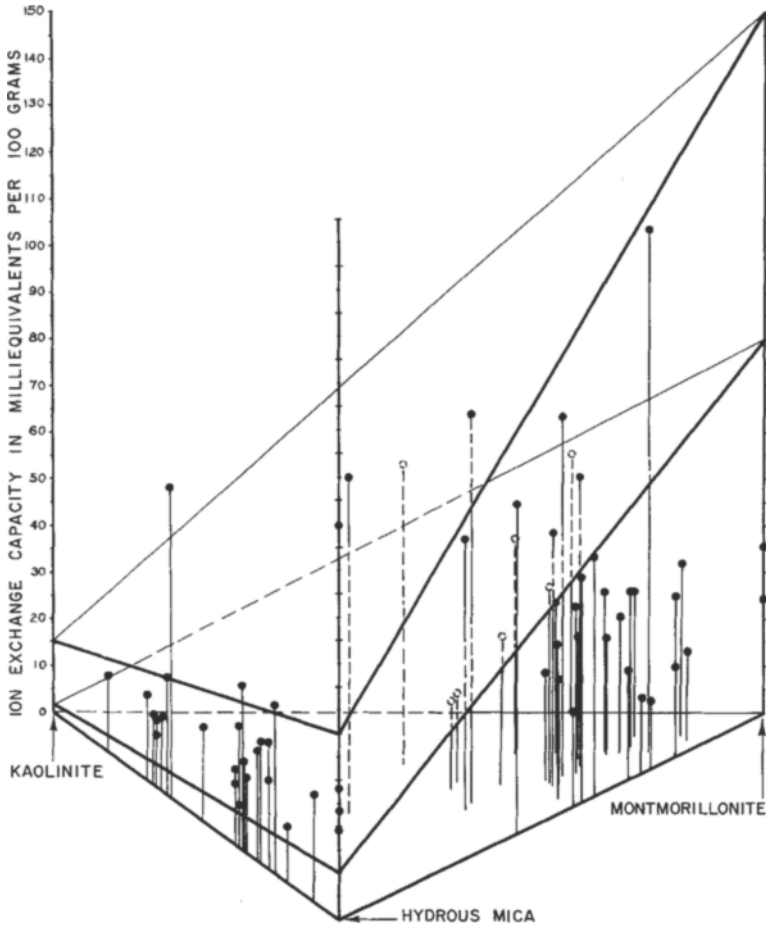
FIGURE 5. — Block diagram showing ion-exchange capacity versus the ratio of the basal peak area. The inclined planes limit the range expected from the reported values for the end-member minerals. Dashed lines and circles represent those obscured by the planes.

the distribution of samples shown is not necessarily indicative of their true composition. As has been stated above, the true distribution probably would fall nearer the kaolinite-hydrous mica end members. In Figure 5 such a shift would cause most of the points lying below the expected range to enter the range.

An additional factor affecting the position of the points is the amount of nonclay-mineral material in the sample. The ion-exchange capacity of a sample containing quartz in abundant quantities, for example, would be appreciably lower than a similar sample containing the same clay

minerals but no quartz as a diluent. For this reason many of the ion-exchange values shown are lower than they would be if the minerals not contributing to the ion-exchange capacity were removed.

As many of the x-ray patterns showed the presence of minerals such as quartz and calcite, the amounts of these diluents were estimated and a revised ion-exchange value computed for each sample. Figure 6 shows these revised values plotted against probable composition as presented in Figure 4. For simplicity the diagram is shown in two dimensions in a plane perpendicular to the line joining the kaolinite and hydrous mica end members. The points are coded to show the type of sedimentary material. It will be noted that for about a quarter of the samples the ion-exchange values lie outside the expected ranges, which include the maximum and minimum values reported by Grim (1942), Ross and Hendricks (1945, p. 39), Kelley (1948, p. 125), Kerr et al. (1950), Grim (1953), and Earley, Osthaus, and Milne (1953).
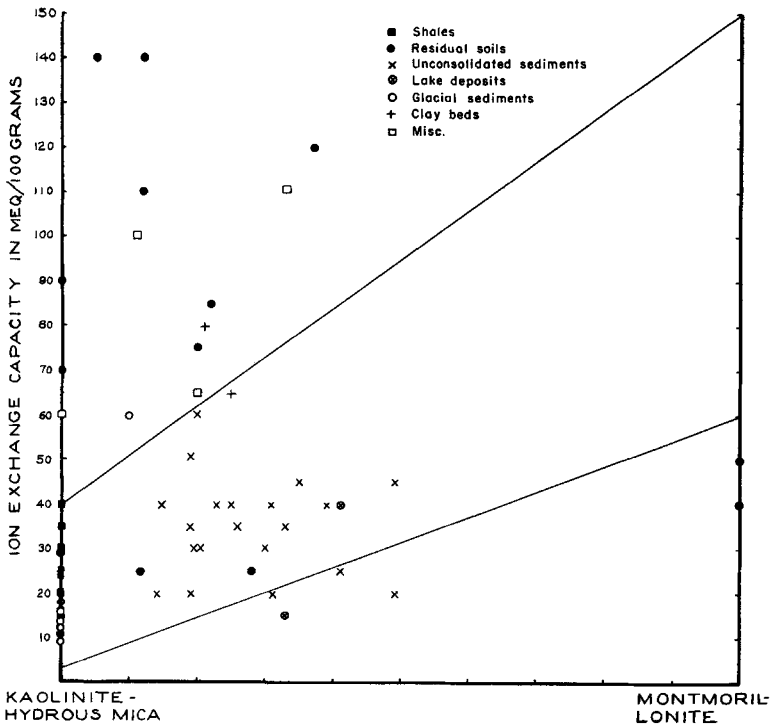
Figure 6. — Diagram showing ion-exchange values corrected for dilution of the sample by "impurities" versus mineral composition based on the "5:1:1" ratio. The plane of the diagram is perpendicular to a line connecting the kaolinite and hydrous mica corners of a diagram similar to Figure 5. The samples show as projections on this plane and are coded as to type of sedimentary material.

DISCUSSION

The lack of agreement between the ion-exchange figures determined in this study and those expected from the apparent clay mineral compositions of the samples as revealed by x-ray examination suggests three possible explanations: (1) the ion-exchange figures determined are either incorrect or are not comparable with those reported from different methods of determination from which the published ranges are derived; (2) the minerals occurring in mixtures in sedimentary materials have larger ranges of ion-exchange capacity than those of corresponding standard minerals as reported in the literature; (3) the composition of the samples as suggested by the x-ray data is incorrect.

In regard to the first possibility, the method used has been demonstrated to give results that are highly reproducible and comparable with those of other methods (Bower and Truog, 1940). The largest source of error (about 10 percent) is probably in the estimation of the amount of dilution of the sample by impurities.

Possibly the second suggestion gives the best explanation for the lack of agreement, but quantitative mineral composition of a more reliable nature is needed to confirm this explanation.

The third possibility could be the major source of error; yet the lack of even a trend toward higher ion-exchange figures with greater montmorillonite peak area and the existence of samples containing only one clay mineral yet with an ion-exchange capacity well above or below the reported range for the mineral (e.g., a hydrous mica with a capacity of 84 meq per 100 g) suggests that the discrepancy does not occur entirely as a result of this error.

The amount of organic matter in the samples is insufficient to explain the high values for ion-exchange capacity obtained for those samples whose values were outside the expected range.

For most of the types of sedimentary materials the number of samples in this study is too small to warrant generalizations on the distribution of clay minerals and ion-exchange capacities within each group (see Table 1). For the residual soils and the unconsolidated sediments, mostly alluvial material, however, certain characteristics may be pointed out. The clay minerals of the residual soils appear to have the greatest variation in ion-exchange capacity, ranging from 11 to 140 meq per 100 g (revised values), whereas the unconsolidated alluvial materials have a fairly narrow range, 16 to 45 meq per 100 g, and, for the most part, fall within the expected ranges for the clay minerals concerned. No consideration has been given here to the influence of weathering and soil-forming processes, climate, or parent material of soils.

SUMMARY AND CONCLUSIONS

The ion-exchange capacity of the clay fraction (less than 2 microns) was determined in 67 samples of various types of sedimentary material, and the clay minerals were identified from diffractometer patterns of oriented aggregates. The areas under the basal peaks of the clay minerals were measured in the diffractometer patterns for each sample, and the ratio of these areas was calculated. Assuming a comparable degree of crystallinity of the minerals, the ratio of the areas is an indication of the amounts of the various clay minerals present. Agreement was poor between the ion-exchange capacities determined and those predicted from the clay-mineral composition. Moreover, some of the ion-exchange figures fell outside the reported ranges for kaolinite, montmorillonite, and hydrous mica. The results suggest that the figure obtained for the ion-exchange capacity of a sample of sedimentary material may be misleading as a guide to the types of clay minerals present.

The residual soils examined had clay minerals with greater variation in ion-exchange capacity than did unconsolidated sediments generally of alluvial origin.

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DISCUSSION

M. L. Jackson. — Is it not possible that the unexpectedly high exchange capacities that you found could result from interstratified montmorin (montmorillonite isomorphous series) and vermiculite spacings interstratified in zones too small to be represented by the x-ray patterns which otherwise show illite (mica) spacings?

John C. Hathaway. — This is quite possible. In several of the samples unusually high backgrounds were observed in the low angle region of the x-ray patterns. As Dr. Jackson has pointed out in his paper, this condition may indicate the presence of the type of interstratification described.

L. D. Swindale. — In soils derived from volcanic parent materials in New Zealand high exchange capacities were found in $<2\mu$ clay where the x-ray crystalline clay minerals were not sufficient to account for the capacity, just as in the present paper. Minerals amorphous to x-rays have been isolated with cation-exchange capacity of about 100 meq per 100 grams (see work of Fieldes, Swindale et al.). Malquori and Wiklander have also synthesised amorphous alumino silicates with cation-exchange capacities of around 200 meq per 100 grams. Such minerals may be present in the present samples and are causing in whole or in part the high cation-exchange capacity figures reported.

John C. Hathaway. — An additional factor may be the high tetrahedral charge in the hydrous micas compared with the relatively low charge, octahedral rather than tetrahedral, of the montmorillonites demonstrated by Dr. Foster in her paper. A large deficiency in potassium in a hydrous mica with high tetrahedral charge would be balanced by a high cation-exchange capacity, possibly higher than that of a montmorillonite and comparable to the capacity of the amorphous materials mentioned.