X-RAY ANALYSIS OF SOIL COLLOIDS BY A MODIFIED SALTED PASTE METHOD

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ABSTRACT

Glycerol–ethanol sodium salted clay pastes prepared from clays extracted directly from the soils and not allowed to dry were found to yield superior x-ray diffraction diagrams for the identification of the major clay minerals than pastes prepared from clays that suffered dehydration after extraction.

Prevention of drying of soil clays after their extraction from the soils is essential for proper identification of the clay minerals. This is particularly true for identification of hydrated halloysite and for differentiation between high exchange forms and low exchange forms of montmorillonite. This differentiation is based on the finding that glycerol–ethanol salted potassium-saturated montmorillonite pastes prepared from clay suspensions have a 001 spacing of 18.5 Å whenever the exchange capacity ranges between 92 and 95 meq/100 g oven-dry clay, and 14.5 Å whenever the exchange capacity ranges between 115 and 135 meq/100 g. Either both these spacings or a mixed-layer spacing appears in montmorillonites having exchange capacities between 95 and 115 meq/100 g.

Saturation of pure vermiculite minerals brings about contraction in the 001 spacing from 14.2 Å to 10.6 Å only after air drying in those forms with exchange capacities ranging between 200 and 207 meq/100 g water-free mineral, but in vermiculites with an exchange capacity of 250 meq/100 g this contraction occurs even without drying. Both of these forms of vermiculite are found in soils.

Several sets of " standardized " natural clay mineral mixtures are necessary for quantitative x-ray analysis of soil clays.

INTRODUCTION

A method (Barshad, 1954b) of preparing soil clays for x-ray analysis previously was proposed, based on the finding that the interlayer swelling of both montmorillonite and vermiculite persists in the presence of salt solutions (Barshad, 1955) and that the diffraction maxima of the 001 spacings become intensified in salted gels or pastes. The technique consists in flocculating the colloid from a suspension with sodium chloride, removing the " free " Fe_2O_3, Al_2O_3, and SiO_2 by means of a solution of sodium citrate and sodium hydrosulfite, separating the cleaned colloid from the solution as a salted paste, and as such subjecting it to x-ray analysis.

Extensive application to a large variety of California soils revealed a feature in the method which was not sufficiently emphasized previously, namely, that the clays after separation from the soils should not be allowed to dry before x-ray analysis.

Although the proposed method yielded good results it failed in many instances to distinguish between montmorillonite and vermiculite : some of

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the x-ray spacings seemed to result from interlayering of these two minerals. The necessity of placing the clay pastes in capillary tubes (to prevent precipitation of salts due to drying during x-radiation) limits the method to film x-ray analysis techniques and also reduces the intensity of the diffracted x-rays and thereby prolongs the exposure time needed for x-ray analysis. During the past 2 years, however, the method was modified to overcome these difficulties. With this modified procedure it is also possible to differentiate between montmorillonites that have high cation exchange capacities ranging from 115 to 135 meq/100 g oven dry clay and those that have lower cation exchange capacities ranging from 80 to 95 meq/100 g. Furthermore, this method revealed new features regarding the nature of vermiculite which are important for its identification. The present paper is a report of these findings.

PROCEDURE

The modification of the procedure for preparation of a clay for x-ray analysis involves the conversion of the salted clay paste to a glycerol–ethanol paste and a change in the method of preparing and mounting specimens of the clay paste for the analysis. Furthermore, the differentiation between the two forms of montmorillonite involves the preparation of two kinds of glycerol–ethanol pastes : one a sodium-salted paste and the other a potassium-salted paste.

With the modified procedure it is unnecessary to remove free iron oxide and organic matter from most clays when the x-ray analysis is carried out by the film technique ; the background scattering on the film due to the iron and organic matter does not interfere with the sharpness of the x-ray diffraction maxima. However, whenever the x-ray analysis is carried out by the diffractometer method, removal of iron and organic matter is necessary. The procedure of preparing the clay paste is outlined below.

Dispersion of Soils

Enough soil is dispersed to yield at least 0.5 g of clay ; addition of a dispersing agent such as Calgon or 0.1 N NaOH may be necessary in acid soils to obtain a stable suspension ; NaOH is preferable if the clay is to be collected for other purposes than x-ray analysis ; just enough NaOH is added to bring the suspension to a pH of about 8. A dispersing agent is not necessary whenever the soil forms a stable suspension.

Particle Size

The desired clay particle size is extracted by siphoning or pipetting from the soil suspension after the proper sedimentation time.

Preparation of Clay Pastes

The clay suspensions are treated by two alternative procedures depending on whether the film technique or the diffractometer technique of x-ray analysis is to be used :

(a) *Clay pastes for film technique.*—Two aliquots of the clay suspension each containing at least 0.2 g of clay are taken ; to one aliquot enough 5 N NaCl is added to bring the total NaCl in the suspension to a concentration in the range between 0.5 N and 1 N ; also, about 10 ml of neutral normal sodium citrate is added ; to the other aliquot KCl and potassium citrate are added instead of sodium salts. The flocculated clay in this state can be left for considerable time (up to several months) before x-ray analysis. After the clay has settled out, the supernatant liquid is decanted and the clay is transferred to a centrifuge tube and spun down using a centrifugal speed ranging from 3000–8000 rev/min for about 5 min. The supernatant liquid is decanted and the clay is resuspended in the centrifuge tubes in about 10 ml of a glycerol–ethanol solution of 1 part glycerol to 2 parts ethanol. After 5 min of centrifugation the supernatant liquid is replaced with a fresh glycerol–ethanol solution in which the clay is again suspended and again centrifuged at about 8000 rev/min for 10 min. The double treatment with glycerol–ethanol solution is necessary to replace all the interlayer water and to obtain constant 001 spacings of the clay minerals. After the last centrifugation the supernatant liquid is decanted and the clay paste in the bottom of the centrifuge tube is ready for x-ray analysis. The clay can be left in this state for a few days before the analysis without affecting the results.

(b) *Clay pastes for diffractometer method.*—The clay suspension containing about 0.5 g clay is reduced to a volume of about 30 ml over a low steam bath, or by a Chamberlain filter, and 10 ml of 30 percent H_2O_2 solution is added. The 250 ml beaker containing the clay is covered with a watchglass and let stand overnight on a low steam bath (about 50°–60°C) in order to destroy the organic matter. The suspension must not be allowed to become dry. Ten millilitres of 1 N NaCl solution is then added and the clay is transferred to a 50 ml centrifuge tube and centrifuged for 5 min. The supernatant liquid containing the unused H_2O_2 is poured out and after the walls of the centrifuge tube are rinsed with water the clay is transferred back to the beaker with distilled water and is redispersed. The suspension is divided into two aliquots ; to one of the aliquots enough 5 N NaCl and 3 N sodium citrate at pH 8.0 are added to bring the total concentration with respect to either salt to 0.5 N ; to the other aliquot KCl and potassium citrate are added instead of the sodium salts. The suspensions are then heated at about 50°C for about 1 hr and enough powdered sodium hydrosulfite is added to bleach the clays so that they are nearly white or grayish white. The amount of sodium hydrosulfite added is not critical : about 0.3 g is first added and if the clay is not entirely bleached within about 15 min, another 0.3 g is added. As soon as the clay is bleached it is transferred to a centrifuge tube and centrifuged for 5 min ; the supernatant liquid is decanted and after the walls of the tube are rinsed with water, the clay paste is converted to a glycerol–ethanol paste by the procedure described previously. The foregoing procedure, without H_2O_2 treatment, should also be used for the film x-ray technique if the clays contain a considerable free iron oxide as shown by their

color or if the x-ray diagrams of the sodium-salted pastes are too dark for observation of diffraction maxima.

Preparation of Clay Specimens for x-*Ray Analysis*

The glycerol–ethanol paste obtained by procedure (a) or (b) is transferred to a watch glass and mixed thoroughly. For the film method of x-ray analysis a specimen is prepared by the method of Brown, Dibley and Farrow (1956). This involves the placement of the paste into a squared off hypodermic needle (no. 23 or 24) and extrusion from the needle either by the device designed by Brown, Dibley and Farrow (1956), or by a regular hypodermic syringe. The former device was found to be more satisfactory because a much smaller amount of clay is needed and less effort is required to extrude the paste. The cylindrically extruded rods are placed on a 0.75 cm square piece of Mylar, $\frac{1}{4}$ mil in thickness, and mounted on specially constructed specimen holders which either fit the end of the collimator tube when the flat cassette type cameras are used or are placed in the exact center of the powder cameras. With filtered Cu radiation and a collimator having a pinhole 0.02 in. diameter and with the x-ray tube operating at 40 kV and 20 mA an exposure time of from 30 to 45 min is adequate.

For the diffractometer method of x-ray analysis a film of the clay paste is formed by spreading the clay paste on either a microscope slide or the specially constructed specimen holders for diffractometer analysis. To obtain a film with well oriented clay particles, the clay paste should have a very thick consistency and after the clay film is formed its surface should be polished with glycerol, by means of a smooth-edged instrument.

RESULTS

The importance of preparing a glycerol or a glycerol–ethanol clay paste for x-ray analysis from clay samples that are not allowed to dry after extraction from soils cannot be stressed sufficiently. The procedure relates to the following factors :

Increased Intensity and Reduction in Width of Interference Maxima

The 001 spacings of all the clay minerals are much narrower and more intense from glycerated or glycolated clay specimens that are prepared from clays which do not dry after extraction from the soil than from those which are dried before being converted to a glycerated or glycolated paste.

Dyal and Hendricks (1952), who describe measurement of surface area of clay minerals by the method of glycol adsorption, also support this conclusion.

Better Resolution

The increased sharpness and intensity of the interference maxima obtainable by this method enable a much better resolution among the 001 spacings of the montmorillonite group minerals, vermiculites, micas and hydrated

halloysite. The dimensions of the 001 spacings of the montmorillonites and of hydrated halloysite in their glycerated state are particularly favorable for resolution from the vermiculite and the mica minerals, respectively. The 001 spacing of glycerol-saturated montmorillonite clay pastes of all types in the sodium form is about 18.5 Å whereas it is only 17.7 Å (Barshad, 1950; Earley, Osthaus and Milne, 1953; MacEwan, 1948) when glycerol saturated from the dry state (Tables 1, 2); the 001 spacing of hydrated halloysite when

TABLE 1.—MOST PROMINENT SPACINGS FOR THE IDENTIFICATION OF THE CLAY MINERALS BY THE SODIUM SALTED GLYCEROL–ETHANOL CLAY PASTE METHOD

Minerals	Spacings of Most Prominent Diffraction Maxima (Å)
Montmorillonite from Bentonites and Soils	18.1–18.7
Vermiculites	14.1–14.6
Chlorites	14–14.3
	7–7.2
	4.7–4.8
Halloysite	
Hydrated	11.4–11.5
Dehydrated	7.2–7.4
Kaolinite	7.1–7.2
	4.17
	3.56–3.58
Serpentine Minerals	7.1–7.2
	3.56–3.58
Mica Minerals	10–10.1
Talc	9.1–9.4
	4.6–4.69
Palygorskite	10.5–10.7
	6.3–6.5
	5.4–5.5
Sepiolite	12.1–12.3

prepared from the wet state is 11.4 Å whereas it is 10.5 Å from the air-dry state (McEwan, 1948); the 001 spacing of about 14.3 Å of vermiculite and the 10.0 Å of illite or biotite when glycerol saturated is the same whether prepared from the wet or the dry states. Thus the 11.4 Å spacing of halloysite prepared from the wet state does not interfere with the 10.0 Å of the mica whereas a 10.5 Å line of halloysite prepared from an air-dry state may merge with the 10.0 Å spacing. Furthermore, in hundreds of soil clays containing both montmorillonite and vermiculite it was found that the 001 spacings due to interlayering of the two minerals appeared very rarely when glycerol

TABLE 2.—BASAL REFLECTIONS, d 001 (IN Å) FOR GLYCERATED MONTMORILLONITE MINERALS AS AFFECTED BY THE CATION EXCHANGE CAPACITY, THE NATURE OF THE INTERLAYER CATION AND METHOD OF SAMPLE PREPARATION FOR X-RAY ANALYSIS

| | Cation Exchange Capacity | | Interlayer Cation | | | |
| | | | Na Method of Glyceration | | K Method of Glyceration | |
Sample Source	Deter-mined[1] (meq)[3]	Calcu-lated[2] (meq)[3]	Air Dry	Paste	Air Dry	Paste
Colony, Wyo.	93	95	17.8	18.4	14.2	18.6
Rosedale, Alberta	95	95	17.7	18.5	14.2	18.1
Merritt, B.C.	68	95	17.6	18.5	14.2	18.5
Princeton, B.C.	62	95	17.7	18.5	14.2	18.4
Hector, Calif.[4]	89	92	17.7	18.1	14.2	18.5
Clay Spur, Wyo.	105	107	17.9	18.4	14.2	15.6
Belle Fourche, S.D.	103	108	17.6	18.6	14.2	15.9
Medicine Bow, Wyo.	94	100	17.7	18.5	14.1	16.1
Otay, Calif.	128	129	17.7	18.6	14.2	14.5
Goldfield, Nev.	120	122	17.7	18.6	14.1	14.3
Upton, Wyo.	121	123	17.8	18.5	14.1	14.2
Polkville, Miss.	121	125	17.6	18.5	14.2	14.6
Chambers, Ariz.	124	129	17.6	18.7	14.2	14.6
Plymouth, Utah	118	124	17.6	18.6	14.1	14.8
Los Angeles, Calif.	115	115	17.7	18.4	14.1	14.5
Death Valley Junction, Calif.	104	120	17.8	18.4	14.1	14.4
Ardmore, S.D.	114	115	17.7	18.5	14.1	14.4
Tewberry, Calif. White	135	135	17.7	18.1	14.2	14.1
Red	112	112	17.7	18.4	14.2	$\left\{\begin{array}{l}18.3\\14.1\end{array}\right.$
Garfield, Wash.[4]	116	120	17.7	18.6	14.1	14.7

[1] By the ammonium acetate method.

[2] These values were obtained by determining first the amount of impurities in the sample, either by chemical means (Earley, Osthaus and Milne, 1953) or by x-ray analysis, and then calculating the exchange capacities on the basis of the pure clay mineral present in the sample.

[3] Per 100 g sodium-saturated clay dried at 250°C.

[4] The Hector, California, sample is a saponite and the Garfield, Washington, sample is a nontronite.

saturated from the wet state but they appeared frequently either when glycerol saturated from the dry state or when the clays remained in the water-wet state as in the original method (Barshad, 1954b). In the absence of inter-layering effects, it is much easier to detect readily both vermiculite and montmorillonite when they are present in the same soil clay.

Improved Clay Particle Orientation

Preparation of clay films and clay rods with particles having preferred orientation either parallel to the surface of the film or to the axis of the extruded rods is easier from clays that have not been dried after extraction from the soil than from those that have. Preferred orientation accentuates the 001 spacings but is not desirable for the proper recording of other spacings. Furthermore, from the nature of the x-ray lines it was concluded that the extruded rods present to the x-ray beam both oriented and un-oriented clay particles. In such rods (Weymouth and Williamson, 1953) the clay particles closest to the surface of the rods appear to be preferentially oriented in the direction parallel to the axis of the rods, whereas those in the interior of the rods are unoriented.

Detection of Hydrated Halloysite

Prevention of drying before x-radiation is essential whenever hydrated halloysite is present. As a result of this procedure of clay preparation it was discovered that several California soils contain the hydrated form of halloysite.

Differentiation Between Montmorillonite Forms Having Low Exchange Capacities and those of High Exchange Capacities

Prevention of drying of the potassium saturated clays is essential for differentiating between the montmorillonite forms with high exchange capacities and those with low exchange capacities (Table 2). Whereas the 001 spacing of the glycerol-saturated clays of both forms of montmorillonite is at about 14.2 Å when the glycerated form is prepared from the air-dry state (Barshad, 1950), it differs completely when the glycerated state is prepared from the water-wet state: The 001 spacing of the montmorillonites with an exchange capacity greater than 115 meq/100 g of oven-dry clay ranges between 14.2 Å and 14.8 Å, the equivalent thickness of a monolayer of glycerol, whereas the 001 spacing of the montmorillonites with an exchange capacity of 95 meq or less ranges between 18.1 Å and 18.6 Å, the equivalent thickness of two layers of glycerol. The 001 spacing, however, of montmorillonites of exchange capacity of 95–115 meq may appear either as an inter-layered spacing of the two forms and therefore having an intermediate dimension, as the samples from Clay Spur, Wyoming; Belle Fourche, South Dakota; and Medicine Bow, Wyoming (Table 2); or having the dimensions of both forms, as the red sample from Tewberry, California.

The cation exchange capacities reported in Table 2 were determined by NH_4 adsorption and also by the sum of the cations replaced by NH_4^+. The loss of water at 250°C was also determined and the capacities were then expressed on a water- (adsorbed) free basis for a sodium-saturated state of the mineral. Some of the cation exchange capacities of the clays reported herein are different from those reported for similar clays by other investigators (Foster, 1951; Ross and Hendricks, 1945, p. 39). These differences

may be due to two factors : (a) The clays reported to be from the same source are not necessarily identical, as shown by Foster (1951). (b) The exchangeable ions in the samples from the same source during analysis may have been different and consequently the molecular weight and the water adsorption properties of the samples would be different. Unless corrections are applied for these differences the cation exchange capacity would appear to be different.

Effect of Potassium Saturation on Vermiculite

The effect of potassium saturation on the 001 spacing of pure vermiculite reported previously (Barshad, 1948), namely, a contraction from 14.3 Å to 10.5 Å, recently was discovered not to occur unless the potassium-saturated vermiculite is first air dried (Table 3). Similarly, the 001 spacing of some soil

TABLE 3.—BASAL REFLECTIONS, 001 (IN Å) FOR VERMICULITE MINERALS WITH WATER OR GLYCEROL AS AFFECTED BY THE NATURE OF THE INTERLAYER CATION AND METHOD OF SAMPLE PREPARATION FOR X-RAY ANALYSIS

Sample	Method of Preparation	Interlayer Cation			
		Na		K	
		Water	Glycerol	Water	Glycerol
Pure vermiculites : nos. 1, 2, and 3	1. Air dry samples	12.6	—	10.5	—
	2. From the air dry state to the immersed state	14.8	14.3	10.6	10.6
	3. By the salted paste method	15.0	14.2[1]	12.9	13.3(s), 10.5(w)[1]
		—	13.6[2]	—	13.3(s), 10.6(m)[2]
		—	14.2[3]	—	13.3(w), 12.7(m), and 11.9(m)[3]
Soil vermiculites (several hundred California soils)	2. From the air dry state to the immersed state	—	14.3	—	10.1–10.6
	3. By the salted paste method	—	14.1–14.6	—	14.1–14.5 and 10.1–10.4

[1] Vermiculite no. 1.   (s) = strong ; (w) = weak ; (m) = medium.
[2] Vermiculite no. 2.
[3] Vermiculite no. 3.

The cation exchange capacity of vermiculite no. 1 and no. 2 is 172 meq/100 g of the natural air dry form of the material or 207 meq/100 g of material free of adsorbed water. The cation exchange capacity of vermiculite no. 3 is 189 meq/100 g of the natural air dry form of the material or 222 meq/100 g of material free of adsorbed water (Barshad, 1948, 1954a).

clay vermiculites does not collapse to 10 Å or 10.5 Å upon potassium saturation unless first brought to air dryness—it remains at about 14 Å as with pure vermiculite. However, in many soil vermiculites and in a small portion of the pure vermiculites this contraction does occur even without drying.

If both these forms of vermiculite occur in the same sample in an interlayered manner the x-ray diagram of such a sample by the proposed method may have several 001 spacings, depending on the nature of the interlayering. Vermiculite sample no. 3 is such a sample (Table 3). Thus the 12.7 Å spacing represents a weighted mean of 22 percent of the contracted form (10.6 Å) and 78 percent of the expanded form (13.3 Å), and the 11.9 Å spacing represents a weighted mean of 52 percent of the contracted form and 48 percent of the expanded form. The significance of these differences will be discussed later. To verify, therefore, the presence of vermiculite in clays as indicated by the x-ray analysis of sodium-salted glycerated pastes, it is necessary to bring to dryness the potassium-saturated clays and then to convert them to glycerated pastes for x-ray analysis. If montmorillonite is absent, the 14.2 Å spacing will disappear and instead a 10.1 Å or a 10.5 Å spacing will appear in the x-ray diagram. If montmorillonite is present, the 14.2 Å spacing will remain but with a lowered intensity, but the 10 Å to 10.5 Å spacing will also be present. If mica minerals are also present in the clay the 10.1 Å or the 10.5 Å spacing will become intensified.

DISCUSSION

From the results presented and from extensive application of the method to a large variety of soil clays it is concluded that as a first step in the identification of the clay minerals in soils the procedure outlined in which the sodium salts are used to flocculate the clay suspension is superior to any other available method for preparing soil clays for x-ray analysis by the film technique. All the common clay minerals can be identified readily in the x-ray diffraction diagram of such pastes. If montmorillonite group minerals are present, and it is desired to differentiate between the high exchange and the low exchange forms, the procedure whereby the clay suspension is flocculated with potassium salts should be used. In fact when large amounts of impurities such as quartz or cristobalite or clay minerals with low exchange capacities such as kaolinite and illite are present in the clay fraction containing montmorillonite, the foregoing procedure is the only method by which it is possible to establish whether the montmorillonite has a high exchange capacity or a low one. If the soil clay contains both vermiculite and the high exchange form of montmorillonite, the x-ray diagram of a potassium-saturated clay paste may contain only the 14.2 Å diffraction maximum whereas that of a sodium clay paste would contain both the 14.2 Å and the 18.5 Å maxima but the intensity of the 14.2 Å spacing will be greater in the x-ray diagram of the former preparation.

The effect of the cation exchange capacity on the interlayer expansion as reported herein is most clearly shown by relating the capacity to the structural formula of a unit cell of montmorillonite (Table 4). The data of Table 2

TABLE 4.—SIMPLIFIED STRUCTURAL FORMULAS OF MONTMORILLONITES OF VARYING EXCHANGE CAPACITIES

Structural Formula	Molecular Weight (g)	Cation[1] Exchange Capacity (meq)[2]
$Na_{0.66} (Al_{3.34} Mg_{0.66}) [Si_8 O_{20}/(OH)_4]$	733.8	90.0
$Na_{0.7} (Al_{3.3} Mg_{0.7}) [Si_8 O_{20}/(OH)_4]$	734.6	95.2
$Na_{0.8} (Al_{3.2} Mg_{0.8}) [Si_8 O_{20}/(OH)_4]$	736.8	108.6
$Na_{0.85} (Al_{3.15} Mg_{0.85}) [Si_8 O_{20}/(OH)_4]$	737.7	115.4
$Na_{0.9} (Al_{3.1} Mg_{0.9}) [Si_8 O_{20}/(OH)_4]$	738.7	122.0
$Na_{1.0} (Al_{3.0} Mg_{0.0}) [Si_8 O_{20}/(OH)_4]$	740.8	133.6

[1] The cation exchange capacity was calculated by dividing the total interlayer charge by the molecular weight and multiplying by 100.

[2] meq/100 g of mineral as shown by the structural formula.

and Table 4 reveal that the double layer glycerol expansion occurs when the interlayer charge per unit cell is less than 0.7 eq whereas the single layer expansion occurs when the charge is greater than 0.85 eq per unit cell.

If soil clays contain a complex group of minerals such as montmorillonite, vermiculite, illite, chlorite, kaolinite and the serpentine minerals, it becomes necessary to obtain also x-ray diagrams of dehydrated clays at various temperatures. In the scheme of analysis proposed herein these diffracto-grams can be obtained as follows: some of the extruded glycerol–ethanol clay rods are placed on small (1 × 1 in. or 1 × 2 in.) ceramic tiles and heated gradually in a muffle to 420°C; after they have stayed at this tempera-ture a few hours one of the rods is cooled a few minutes in a desiccator and x-rayed for 30 min; the temperature is then raised to 500°C and another rod is x-rayed; the temperature is raised again to 600°C and another rod is x-rayed. The x-ray analysis of the 420°C heated clay will differentiate between vermiculite and chlorite. If both these minerals are present in the same sample together with a mica mineral (a common occurrence), then in the dehydrated pattern at 420°C the 10 Å spacing becomes intensified and the 14.2 Å spacing becomes weaker or may be replaced with a spacing any-where between 14 Å and 10 Å depending on whether the vermiculite and chlorite are interlayered. If gibbsite is present, the gibbsite spacing will disappear in the heated sample. If hydrated halloysite is present, the 11.4 Å spacing will disappear and instead a 7.3 Å spacing will appear or will become intensified if it was present in the wet sample. The montmorillonite 18.4 Å spacing also will collapse to about 10 Å upon heating. Differentiation of chlorite, kaolinite and any serpentine mineral is accomplished by heating the samples to 500°C. Differentiation between chlorite and serpentine min-erals in such heated clays will be on the basis of the presence or absence of a 14 Å spacing which is characteristic of the chlorite and not of the serpentine minerals. If both chlorite and serpentine minerals are present in the same

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sample then heating of the clay sample to 600°C would differentiate between them.

To obtain good x-ray patterns of dehydrated clays from soils which contain exchangeable " complex " aluminum ions, the clays should be treated by the same procedure as outlined for the diffractometer method and in addition they should be treated with a solution of 1 N sodium citrate at pH 10 before being converted to a glycerol–ethanol paste (Barshad, 1954b) which is subsequently dehydrated. The presence of " complex " aluminum ions may cause difficulties in the diffraction patterns of montmorillonite and vermiculite by preventing the proper contraction of the crystal lattices of those minerals to 10 Å spacings upon dehydration. A variety of spacings can be caused by " complexed " aluminum ions upon their adsorption by montmorillonite and vermiculite ; the nature of these spacings will be discussed in a separate paper.

Quantitative x-ray Analysis

The x-ray method proposed herein was found to be extremely suitable not only for qualitative analysis but also for quantitative analysis. Such an application, however, can be made only if a series of soil clays is available the mineralogical composition of which was determined, at first qualitatively by the method proposed and then quantitatively by the various methods available for this purpose—namely, differential thermal analysis, integral thermal analysis, total chemical analysis, and cation· exchange analysis. Furthermore, it was found necessary to establish several sets of " standardized " clay mineral mixtures, since the intensity of a given 001 spacing of any one mineral seems to depend not only on the amount present but also on the kind of minerals with which it is associated. For example, the intensity of the 7.2 Å spacing of a given amount of kaolinite has a different value depending on whether it is associated with montmorillonite, vermiculite or micas. The following sets of " standardized " natural clay mineral mixtures are necessary for quantitative x-ray analysis :

Kaolinite and montmorillonite generally are found together in various proportions in soil clays developed from basic igneous rocks and their derivatives and from a variety of all other types of rocks containing calcium carbonate.

Kaolinite and the mica-type clay minerals (illite and biotite) are generally found in various proportions in soils developed from granitic rocks and their derivatives and all other kinds of rocks in which the mica minerals are relatively abundant. Many of the soil clays of this group are also associated with a mixed-layer montmorillonite–vermiculite clay mineral the 001 spacing of which gives a broad and diffused diffraction maximum ranging between 18.5 Å and 14 Å. Often, however, they are also associated with either vermiculite or montmorillonite alone or with both without interlayering effects.

Kaolinite and vermiculite occur together in soils derived from a variety of lime-free sandstones and shales in large areas of California. Small amounts of montmorillonite commonly are associated with these minerals.

Halloysite and vermiculite or montmorillonite occur together in relatively young soils derived from a variety of acidic eruptive rocks, volcanic ash or breccia, and in old soils derived from basaltic and andesitic rocks developed under high winter rainfall (40–60 in.) and relatively dry summers.

Hydrated halloysite and vermiculite or montmorillonite normally are associated with halloysite and they occur in the same soils as described in the preceding paragraph, but in deeper parts of the soil profile.

Vermiculite and chlorite and commonly kaolinite occur in soils derived from metamorphosed basic igneous rocks and their derivatives.

Montmorillonite and antigorite or chrysotile are found in soils derived from serpentine rocks. The chlorite and mica minerals commonly are associated with them.

To estimate quartz, cristobalite and gibbsite quantitatively by means of x-ray analysis along with the clay minerals, suspensions of a known concentration of each of these minerals, having particle sizes in the same range as those of the clay minerals, are prepared. Various amounts of these suspended minerals are then added to known amounts of the above sets of the " standardized " minerals, which are also in a suspended state, and x-ray diffraction diagrams are made by the procedure described in this paper. Separate diagrams should be prepared for each mineral rather than for mixtures unless mixtures occur in the soil clays under investigation. Quartz was found to occur mostly in soil clays derived from acid igneous rocks, sandstones and alluvial materials derived from these rocks, whereas cristobalite occurs mostly in soil clays derived from eruptive volcanic rocks.

The wider 001 spacings reported here for glycerated montmorillonite and halloysite, i.e. 18.5 Å and 11.4 Å, instead of 17.7 Å and 10.5 Å, respectively, may result from the orientation of the glycerol molecules. The smaller spacings are believed to result when the molecules orient themselves so that the length of their carbon chains is parallel to that of the silicate sheets, whereas the larger spacings result when the molecules orient themselves so that the length of the carbon chain is perpendicular to the silicate sheets. This difference in orientation of the adsorbed glycerol or glycol molecules permits adsorption of larger amounts of these substances by montmorillonite clays which never suffered dehydration than by those which did (Dyal and Hendricks, 1952). The molecules with carbon chain oriented parallel to the silicate sheets occupy a larger surface area than those with carbon chain perpendicular to the silicate sheets.

The observation that a large proportion of the vermiculite crystal structure does not collapse upon potassium saturation until brought to air dryness leads to the conclusion that the potassium fixation properties of vermiculite depend greatly upon dehydration : fixation is less extensive than reported previously (Barshad, 1948) if the potassium vermiculite remains wet prior to measurement of the fixation capacity. Evidence that a similar condition occurs with fixation of ammonium is reported by Allison, Kefauver and Roller (1953) : ammonium fixation in soils is enhanced greatly upon drying.

*Interlayer Expansion of K-saturated Vermiculite in Relation
to the Interlayer Charge*

As with montmorillonite, an explanation for the variation among the vermiculites in their response to interlayer contraction upon potassium saturation is believed to result from differences in the magnitude of the interlayer charge as measured by the cation exchange capacity. Evidence in support of this conclusion is found in Table 3 in the data for vermiculites no. 1 and no. 3. The cation exchange capacities given in this table for these vermiculites were reported previously (Barshad, 1954a) for the natural air-dry material : 172 meq/100 g for vermiculite no. 1 and no. 2 and 188 meq for no. 3. However, in order to relate these exchange capacities to the crystal structure it is necessary to express the exchange capacity on the weight of material without adsorbed water. Since the adsorbed water of these vermiculites is known (Barshad, 1948), the exchange capacities on a water-free basis is readily calculated to be 207 meq for vermiculites no. 1 and no. 2 and 222 for vermiculite no. 3.

From the relative intensities and the magnitude of the 001 spacing of the K-saturated pastes it is concluded that vermiculite no. 1 consists almost entirely of the expanded form whereas vermiculite no. 3 consists of 65 percent expanded form and 35 percent contracted form. If we assume that the expanded form in vermiculite no. 3 has a cation exchange capacity equal to that of vermiculite no. 1, it is then possible to determine the magnitude of the cation exchange capacity of the contracted form in vermiculite no. 3 by the following equation :

$$\frac{207 \times 65}{100} + \frac{x \times 35}{100} = 222$$

where x = cation exchange capacity of the contracted form, 207 = CEC of vermiculite no. 1, and 222 = CEC of vermiculite no. 3.

Solving this equation, one finds that x, the CEC of the contracted form, is equal to 250 meq/100 g.

Since vermiculite no. 2 also contains a small amount of the contracted form and since the exchange capacity of the whole sample is the same as that of vermiculite no. 1, one must conclude that the CEC of the expanded form in this sample is a little less than that of vermiculite no. 1. If we assume that the CEC of the contracted form is equal to that of vermiculite no. 3 and that about 10 percent of vermiculite no. 2 consists of this form (an estimate from the relative intensities of the two forms) it is then possible to calculate the CEC of the expanded form by the following equation :

$$\frac{x \times 90}{100} + \frac{250 \times 10}{100} = 207$$

where x = CEC of the expanded form, 250 = CEC of the contracted form, and 207 = CEC of vermiculite no. 2.

Solving this equation one finds that x, the CEC of the expanded form, is

equal to 202 meq, which is only slightly less than that of vermiculite no. 1.

If one relates the cation exchange capacities of the vermiculites to the crystal structure and also compares them with the exchange capacities that would result if phlogopite, muscovite or biotite were converted to vermiculite (Table 5) it is seen that the interlayer charge of the contracted form of vermi-

TABLE 5.—SIMPLIFIED STRUCTURAL FORMULAS OF Mg^{2+}-SATURATED VERMICULITE, PHLOGOPITE, BIOTITE AND MUSCOVITE, AND THEIR POTENTIAL EXCHANGE CAPACITIES

Structural Formula	Molecular Weight (g)	Cation Exchange Capacity (meq)[1]
Vermiculite		
$Mg_{0.8} (Mg_{5.6} Fe^{3+}_{0.3} Al_{0.1}) [Si_6 Al_2 O_{20}/(OH)_4]$	784.4	204
$Mg (Mg_{5.6} Fe^{3+}_{0.3} Al_{0.1}) [Si_{5.6} Al_{2.4} O_{20}/(OH)_4]$	784.0	255
Phlogopite		
$Mg (Mg_6) [Si_6Al_2 O_{20}/(OH)_4]$	780.6	256
Biotite		
$Mg (Mg_4 Fe^{2+}_2) [Si_6 Al_2 O_{20}/(OH)_4]$	843.62	237
Muscovite		
$Mg (Al_4) [Si_6 Al_2 O_{20}/(OH)_4]$	742.5	269

[1] meq/100 g of mineral as shown by the structural formula.

culite is in the same range as that of phlogopite, muscovite or biotite, namely, about 2 eq per unit cell, whereas the expanded form is about 1.6 eq per unit cell.

The interlayer expansion equivalent to a monomolecular layer of glycerol is characteristic of both montmorillonite and vermiculite in their K-saturated paste form over a wide range in the interlayer charge per unit cell, namely, from 0.85 to 1.6 eq. There is, however, a small difference in the thickness of the monolayer: In the montmorillonite it is about 14.4 Å whereas in the vermiculite it is 13.3 Å. This difference is believed to result, as indicated previously, from the manner in which the glycerol molecules orient themselves on the surface: the 13.3 Å dimension results when the molecules orient themselves so that the length of the carbon chain is parallel to that of the silicate sheets, whereas the 14.4 Å thickness results when the molecules orient themselves so that the length of the carbon chain is perpendicular to the silica sheets.

REFERENCES

Allison, F. E., Kefauver, M. and Roller, E. M. (1953) Ammonium fixation in soils : *Soil Sci. Soc. Amer. Proc.*, v. 17, pp. 107–110.

Barshad, I. (1948) Vermiculite and its relation to biotite as revealed by base exchange reactions, x-ray analyses, differential thermal curves, and water content : *Amer. Min.*, v. 33, pp. 655–678.

Barshad, I. (1950) The effect of the interlayer cations on the expansion of the mica type of crystal lattice : *Amer. Min.*, v. 35, pp. 225–238.

Barshad, I. (1954a) Cation exchange in micaceous minerals. I. Replaceability of the interlayer cations of vermiculite with ammonium and potassium ions : *Soil Sci.*, v. 77, pp. 463–472.

Barshad, I. (1954b) The use of salted pastes of soil colloids for x-ray analysis : in *Clays and Clay Minerals.*, Natl. Acad. Sci.—Natl. Res. Council, pub. 327, pp. 209–217.

Barshad, I. (1955) Adsorptive and swelling properties of clay-water system : in *Clays and Clay Technology*, Calif. Div. Mines Bull. 169, pp. 70–77.

Brown, G., Dibley, G. C. and Farrow, R. (1956) An extrusion method for bonded powder specimens : *Clay Minerals Bull.*, v. 3, pp. 19–21.

Dyal, R. S. and Hendricks, S. B. (1952) Formation of mixed layer minerals by potassium fixation in montmorillonite : *Soil Sci. Soc. Amer. Proc.*, v. 16, pp. 45–48.

Earley, J. W., Osthaus, B. B. and Milne, I. H. (1953) Purification and properties of montmorillonite : *Amer. Min.*, v. 38, pp. 707–724.

Foster, M. D. (1951) The importance of exchangeable magnesium and cation-exchange capacity in the study of montmorillonitic clays : *Amer. Min.*, v. 36, pp. 717–730.

MacEwan, D. M. C. (1948) Complexes of clays with organic compounds. I : *Trans. Faraday Soc.*, v. 44, pp. 349–367.

Ross, C. S. and Hendricks, S. B. (1945) Minerals of the montmorillonite group : *U.S. Geol. Survey*, Prof. Paper 205–B, pp. 23–79.

Weymouth, J. H. and Williamson, W. O. (1953) The effects of extrusion and some other processes on the micro-structure of clay : *Amer. J. Sci.*, v. 251, pp. 89–108.