QUANTITATIVE CLAY MINERALOGICAL ANALYSIS OF SOILS AND SEDIMENTS*

by

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ABSTRACT

THE objective of this paper is to present flow sheets for a system of quantitative mineralogical analysis of clays of soils and sediments and to show representative results. Selective dissolution analysis by the $Na_2S_2O_7$–HCl–NaOH procedure yields the quartz and feldspar contents (0 to 63%) and differentiates feldspar K from mica K. The NaOH-thermal system of selective dissolution yields the allophane plus gibbsite, kaolinite plus halloysite, and dickite contents (0 to 84% for the sediments; 1 to 25% for soil clays) Mica contents (0 to 92% for the rock specimens, 7 to 43% for soil clays) are determined by nonfeldspathic K (and Na). Vermiculite contents (1 to 97% of specimens; 3 to 21% for soil clays) are measured by blocking of interlayer CEC by drying at 110°C while K saturated and replacing with NH_4Cl. Montmorillonite (and palygorskite) contents (0 to 85% of specimens; 3 to 36% of soil clays) are determined by the CEC not blocked by the K and NH_4 sequence for vermiculite. Chlorite contents (0 to 85% for specimens; 0 to 37% for soil clays) are determined by thermal gravimetric analysis, after allocation of OH water lost between 300 and 950°C to other hydrous minerals determined.

The best evidence of the accuracy of the system of analysis lies in the consistent total recovery of 24 standard mineral samples averaging 100.4 ± 1.3 ($\pm$ standard error of means) and of 22 soil clay samples averaging 99.5 ± 0.8. The different constituents were present in widely different proportions in the various samples, and were determined by independent methods. The complementary total of near 100% (maximum range 95 to 105% for specimens; 95 to 103% for soil clays) for the analyses is a significant measure of the specificity of the several determinations.

INTRODUCTION

ALTHOUGH the most powerful means for qualitative-semiquantitative study of crystalline clays is X-ray diffractometry, more accurate quantitative analytical techniques for each mineral group or species have gradually emerged. Presentation of a system for quantitative clay mineralogical analysis flow sheets (Figs. 1–5) is now opportune, since quantitative methods (as cited in

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the methods section) are now available for determination of total free iron oxides, mica, amorphous aluminous and siliceous materials, kaolinite plus halloysite, dickite, quartz and feldspars, vermiculite and montmorillonite, chlorite and talc, and anatase plus rutile. Chemical analysis for the elements present and the proportion of each (Jackson, 1956, 1958; Jackson and Mackenzie, 1964) gives an estimate of the mineral species present within each of these mineral groups.

MATERIALS

Layer silicate samples analyzed in testing the proposed scheme of analysis included three chlorites (from Cartersville, Ga., from Md., and from an unknown mineral supply house); kaolinite from Dry Branch, Ga. (Georgia Kaolin Co.); halloysite of North Gardiner Mine from Bedford, Ind. (Ward's Scientific Est., Rochester, N.Y., No. 12); dickite from Rock Springs, Wis.; nontronite from Garfield, Wash. (Ward's, No. 33A); hectorite from Hector, Calif. (Ward's, No. 34); bentonite from Cameron, Ariz. (Ward's, No. 31); the well known bentonites from Upton, Wyo., and Panther Creek, Monroe Co., Miss. (from the American Colloid Co.); muscovite from an unknown mineral supply house; glauconite from Franconia (Cambrian) sandstone near Cross Plains, Wis.; vermiculites derived from biotite occurring in granite (from S. Africa, Colo., and Wis.); vermiculite derived from phlogopite occurring in magnesite (from Texas); and vermiculite derived from biotite and augite from Libby, Mont. (Ward's).

The soil clays analyzed were from K fixing alluvial soil from the Netherlands (courtesy H. W. van der Marel); a Rendzina soil, A_{12} horizon, derived from limestone of Ireland (courtesy P. V. Kiely); a Dubuque silt loam soil, $11C_1$ horizon, residuum from dolomite in Suak County, Wis.; a clay residuum from dolomite north of Spring Green, Wis. (sampled with M. E. Ostrom); a concretionary Brown Forest soil, B_2 horizon, from Alberni, Vancouver (courtesy J. E. Brydon); a Red-yellow Podzolic soil, Tatum, A_2 horizon, from mica schist of Va. (courtesy C. I. Rich); a Rendzina soil, A horizon, derived from soft limestone of Drama, Greece; an alluvial Solometz soil, A horizon, and an alluvial Solonchak soil, C horizon, from the Agricultural Experimental Station of the University of Thessaloniki, Greece ; a Brown Forest soil, B_2 horizon, derived from sandstone of the Pertouli forest of the University of Thessaloniki, Greece; and a Terra Rossa, A horizon, derived from hard limestone of Drama, Greece. Previous work on these mineralogical and soil samples has been outlined (Alexiades and Jackson, 1965, 1966; Dixon and Jackson, 1962).

PROCEDURES

A general flow-sheet (Fig. 1) outlines the overall quantitative determination while the detailed procedures and flow sheets are given in separate sections. The mainly wet chemical system of mineralogical analysis to be presented

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was monitored qualitatively and semiquantitatively by X-ray diffraction analysis and has been tested extensively with reference to vermiculite and chlorite constituents (Alexiades and Jackson, 1965, 1966).

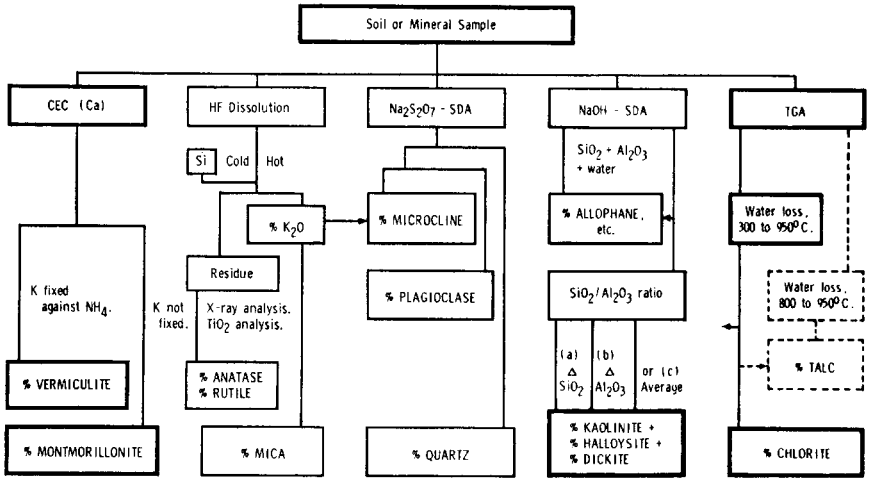


FIG. 1. General flow sheet for mineralogical analysis of soils and mineral deposits by cation exchange capacity (CEC), HF dissolution (for total K), selective dissolution analyses (SDA), and thermal gravimetric analysis (TGA). The anatase and rutile determinations are based on SDA with HF at room temperature (Raman and Jackson, 1965). Heavy boxes indicate systems newly introduced by Alexiades and Jackson (1965, 1966).

Pretreatment of Sample for Removal of Carbonates, Organic Matter, and Free Iron Oxides

For the proposed analytical methods, the mineral size fractions are obtained in suspension (Jackson, 1956), free of organic matter, carbonates and free iron oxides; they are usually cation exchange saturated with Na, and usually with Na_2CO_3 solution (pH 9.5) present. An additional dilute acid-H_2O_2 pretreatment of the samples before each of the analytical procedures is given as follows: A suitable aliquot of the suspension (Na saturated sample) containing about 100 to 200 mg of clay is placed in a 20 ml centrifuge tube. The clay is washed 3 times with N NaOAc solution of pH 5, the tube being placed for 5 min in a boiling water bath for each washing, to insure complete dissolution of the carbonates. Following this, five drops of N NaOAc solution of pH 5 and 5 ml of 30% H_2O_2 are added. The tube containing the sample is heated on a steamplate (70 to 80°C) for about 3 hr to complete the destruction of any residual organic matter such as organism growth or mineral-organic complexes. A slightly acid media enhances the oxidizing action by H_2O_2 and acetate is little attacked by H_2O_2.

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Determination of Clay Concentration (aliquot)

In the determination of the clay concentration in the suspended sample, an aliquot is saturated with either K or NH_4 to obtain the weight basis for the various quantitative determinations. Saturation with Na, Ca, Mg or H (formerly widely used) is avoided. The H saturated clay minerals decompose and release Al; also, H saturated minerals are dehydroxylated at an excessively low temperature, sometimes even lower than 100°C; the Na, Ca, or Mg saturated clay minerals introduce a high water content into the weight basis. Consequently, for the aliquot determination, an NH_4 or K saturated sample is obtained as follows: A 600 mg sample, pretreated with N NaOAc of pH 5 and 30% H_2O_2 to insure complete dissolution of carbonates and destruction of any residual organic matter as described above, is washed once with N NaCl and 5 times with N·KCl or NH_4Cl solution of pH 7. The sample is then washed free of excess salts by washing once with a limited volume of water and 5 times with 99% methanol; acetone is added in the third and subsequent washing if trouble with dispersion is encountered. These washings are carefully carried out by means of the centrifugation and decantation procedure. The sample is then suspended in a little water and is transferred quantitatively to a weighed Pt crucible and weighed after heating at 110°C for 24 hr. The difference in weights gives the aliquot weight. An NH_4 saturated sample in a Pt crucible may be used for mica K and Na determination by the HF–$HClO_4$ dissolution procedure or the $Na_2S_2O_7$ selective dissolution analysis in which the total K and Na, and often the Ca, are determined as described in later sections.

Vermiculite by Cation Exchange Capacity

Vermiculite (Table 1) is determined (Fig. 2) on the basis of the part of the cation exchange capacity (CEC) measured by Ca replaced by Mg, designated CEC (Ca/Mg), which is blocked by K fixation on oven-drying at 110°C and subsequently not exchanged by NH_4. The remaining CEC is expressed as me per 100 g of K or NH_4 saturated oven-dried clay and designated CEC K//NH_4. The calculation is by the Alexiades and Jackson (1965) equation:

$$\% \text{ Vermiculite} = \frac{\text{CEC (Ca/Mg)} - \text{CEC (K/ /NH}_4\text{)}}{154} \times 100 \qquad (1)$$

Montmorillonite by Cation Exchange Capacity

The CEC of a sample measured by the nonfixed K replaced in N NH_4Cl, designated CEC (K/ /NH_4) and expressed on the same basis as for vermiculite, represents the charge of montmorillonite plus that of other minerals such as mica, kaolinite, halloysite, chlorite, and amorphous materials, as well as of the

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external surface of vermiculite (Fig. 2). The percentage of montmorillonite is obtained by the Alexiades and Jackson (1965) equation:

$$\% \text{ Montmorillonite} = \frac{\text{CEC (K/ /NH}_4) - (5 + 105\ Amor)}{105} \times 100 \quad (2)$$

in which 5 represents the external surface CEC of the various minerals and *Amor* is the percentage of amorphous material having an SiO_2/Al_2O_3 molar ratio 3 or above. The latter ratio indicates that a montmorillonite-like component dissolved in 0.5 N NaOH treatment and is assigned (Alexiades and Jackson, 1965) the CEC value (like montmorillonite) of 110 me per 100 g (105 + 5). For amorphous materials with a ratio lower than 3, this term has been omitted, although sesquioxic allophane of SiO_2/R_2O_3 molar ratio less than 1.5 also may have a high CEC. The CEC of palygorskite (attapulgite) would cause it to be included with montmorillonite. Palygorskite can be electronoscopially identified by its fibrous particles; further work is needed on its quantitative determination.

Quartz and Feldspars by $Na_2S_2O_7$ Selective Dissolution Analysis

Quartz and feldspars are determined in the coarse clay and larger fractions of soils and mineral deposits by the pyrosulfate fusion method (Kiely and Jackson, 1965). An NH_4 sample prepared as described above is ground lightly in an agate mortar and a 0.400 g sample is transferred to a vitreous silica crucible and used for the determination of quartz and feldspars by the $Na_2S_2O_7$ selective dissolution analysis (Fig. 3). Microcline and the high Na plagioclases hold most of the K, Na and Ca in the residue. Plagioclases as high as or higher in Ca than labradorite are determined by the total Ca ("Ca minerals" in Fig. 3), with an X-ray check for the possible contents of tremolite and sphene. Quartz was found as a component of many samples studied, in a wide range from 0.8 to 63% (Table 1), while feldspars were not found in the clay of the samples. The determination of quartz and feldspars has been found to be extremely useful for a complete mineralogical analysis of the sand, silt and coarse clay fractions of soils (Kiely and Jackson, 1965).

Mica by HF Dissolution Analysis

A 0.100 g NH_4 saturated sample (e.g. the sample used for the aliquot weight determination) is used for mica determination by HF–$HClO_4$ dissolution analysis (Fig. 3). The mica determinations (Table 1) are based on the K content of mineral fractions after deduction of feldspar K (Kiely and Jackson, 1965); the content of feldspars is usually but not always small in clay fractions. Contents of 8.29% K (10% K_2O) in dioctahedral micas and 7.48% K (9% K_2O) in trioctahedral and high iron micas (Jackson, 1956, p. 543) were used (Table 1). With coarse grained aluminous dioctahedral micas, 10.6% K_2O is applicable (Raman and Jackson, 1966). Potassium contents of 48 glauconites

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TABLE 1.—MINERALS PRESENT IN FIFTY STANDARD MINERAL AND SOIL CLAY SAMPLES

Sample and source	Size fractions, microns	%								
		Am*	Kl+Hl	Qr	Mi	Mt+Nt	Vr	Chl	Tc	Total
Standard mineral samples										
Chlorite (mafic)	<20	4.1	0.0	0.8	0.0	0.0	10.0	84.9	—	99.8**
Chlorite, Ga.	<20	0.4	0.0	6.6	6.5	0.0	2.0	81.3	3.2	100.0†
Chlorite, Maryland	>100	0.0	0.0	5.6	0.0	0.0	4.9	80.3	9.2	100.0†
	100−2	0.0	0.0	4.2	0.0	11.8	10.4	64.0	9.6	100.0†
	<2	0.0	0.0	0.0	0.0	66.0	15.0	18.0	1.0	100.0†
Kaolinite, Ga.	<2	3.6	78.2	0.0	0.7	0.0	0.7	16.9	—	100.1**
Halloysite, Ind.	<2	36.5	46.6	1.4	0.8	0.0	7.9	12.1	—	105.3
Dickite, Rock Springs, Wis.	—	5.2	83.5	4.1	0.5	0.0	0.0	10.0	—	103.3
Nontronite, Washington	<2	12.7	0.0	2.0	2.9	31.8	24.5	22.7	—	96.6
Hectorite, California	<2	1.7	0.0	1.7	12.3	46.4	17.5	15.0	—	94.6††
Bentonite, Arizona	<2	4.2	0.0	0.0	14.0	48.2	26.9	7.0	—	100.3**
Bentonite, Upton, Wyoming	2−0.2	0.0	0.0	5.3	0.9	70.8	14.3	8.3	—	99.6**
	<0.2	0.0	0.0	0.0	0.0	74.4	11.8	15.6	—	101.8**
Bentonite, Panther Creek, Miss.	2−0.2	0.0	0.0	2.2	3.3	85.1	5.6	5.9	—	102.1**
	<0.2	0.0	0.0	0.0	2.2	84.2	14.8	0.0	—	101.2**
Muscovite	2−0.2	0.0	0.0	1.1	92.3	0.0	7.1	0.0	—	100.5**
Glauconite (Franconia), Wis.	2−0.2	1.1	0.0	5.8	57.3	10.0	3.4	24.5	—	102.1**
	<0.2	0.8	0.0	0.0	62.4	13.1	7.9	15.1	—	99.3**
Vermiculite, S. Africa††	<2	0.0	0.0	1.0	30.2	10.0	57.4	1.8	—	100.4**
Vermiculite, S. Africa (treat. HCl)	<2	0.0	0.0	1.3	17.9	3.6	58.4	16.3	—	97.5
Vermiculite, S. Africa (no H_2O_2)	<2	0.0	0.0	1.0	40.7	8.6	41.1	14.0	—	105.4
Vermiculite, Mont.	<2	0.0	0.0	0.5	28.4	9.1	64.5	0.0	—	102.5**
Vermiculite, Tex.	<50	0.0	0.0	0.8	1.0	2.6	97.1	0.0	—	101.5**
Vermiculite, Colo.††	2−0.2	0.0	0.0	0.0	19.6	10.5	56.4	11.3	—	97.8**
	<0.2	0.0	0.0	0.0	16.3	27.7	32.6	21.3	—	97.9**
Vermiculite, Colo. (Sediment)	2−0.2	0.0	0.0	3.9	16.9	25.6	40.5	15.1	—	102.0**
	<0.2	0.0	0.0	0.0	13.7	29.1	35.2	23.2	—	101.2**
Vermiculite, Wis.††	Flakes	0.0	0.0	2.8	70.5	2.3	12.2	10.4	—	98.2**

Standard deviation of means, $s_{\bar{x}} = 1.34$. Average $\pm s_{\bar{x}} = 100.4 \pm 1.3$

Standard deviation, $s = 2.56$. Coefficient of variation, c.v. = 2.54%

** Within the fiducial limits at the 5% level, $\pm 2.77 = 1.34 \times t$, when $t = 2.069$, for 23 degrees of freedom.

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Soil clay samples

Alluvial soil, Netherlands	2−0.2	2.4	7.1	7.7	26.2	24.5	9.4	23.4	—	100.7**
	<0.2	2.7	5.4	0.0	22.4	30.7	7.1	27.5	—	95.8
Rendzina, Kilcolgan, Ireland	2−0.2	2.6	1.3	63.0	22.1	3.0	3.2	3.2	—	98.4**
	<0.2	4.3	2.0	0.0	50.8	24.8	8.0	8.9	—	98.8**
Dubuque silt loam, Wisconsin	2−0.2	16.0	10.9	7.2	7.3	8.9	16.5	36.5	—	103.3
	<0.2	11.6	19.1	0.0	8.0	21.3	13.0	26.9	—	99.9**
Residuum from dolomite, Wis.	2−0.2	16.7	19.4	4.2	11.1	13.0	10.8	26.6	—	101.8
	<0.2	12.5	19.0	0.0	9.4	28.2	5.9	24.8	—	99.8**
Concr. Brown Forest, Alberni, Van.	<2	19.4	7.8	17.0	8.4	5.5	18.4	21.1	—	97.6
Red-Yellow Podzolic, Tatum, Va.	2−0.2	8.2	13.0	14.1	29.7	6.6	4.5	23.3	—	99.4**
Rendzina, Drama, Greece	2−0.2	8.1	12.5	8.8	42.8	12.5	9.6	3.1	—	97.4
	<0.2	14.3	10.3	0.0	35.6	10.6	20.0	7.9	—	98.7**
Solonetz, Thessaloniki, Greece	2−0.2	7.9	7.6	4.5	25.4	23.7	11.6	19.1	—	99.8**
	<0.2	7.7	8.8	0.0	12.8	36.5	13.1	20.3	—	99.2**
Solonchak, Thessaloniki, Greece	2−0.2	5.9	10.6	1.9	40.0	17.7	14.5	11.2	—	101.8
	<0.2	8.4	13.1	0.0	20.0	28.5	21.0	10.5	—	101.5
Brown Forest, Pertouli, Greece	2−0.2	2.3	2.9	17.0	41.0	13.7	6.1	20.0	—	103.0
	0.2−0.08	7.3	6.8	0.0	38.6	28.8	10.5	8.7	—	100.7**
	<0.08	8.5	7.3	0.0	28.8	35.3	11.2	7.4	—	98.5**
Terra Rossa, Drama, Greece	2−0.2	7.9	18.3	9.6	37.2	10.4	6.1	5.2	—	94.7
	0.2−0.08	19.9	25.3	0.0	21.5	19.6	14.4	−0.3‡	—	100.7**
	<0.08	22.0	23.3	0.0	16.4	22.6	15.0	−1.2‡	—	99.3**

Standard deviation of means, $s_{\bar{x}} = 0.82$. Average $\pm s_{\bar{x}} =$ 99.6±0.8

Standard deviation, $s = 1.96$. Coefficient of variation, c.v. = 1.96%

** Within the fiducial limits at the 5% level, $\pm 1.71 = 0.82 \times t$ when $t = 2.080$, for 21 degrees of freedom.

* Am = Amorphous material; Kl+Hl = Kaolinite, halloysite and dickite; Qr = quartz, Mi = mica; Mt+Nt = montmorillonite and nontronite; Vr = vermiculite; Chl = chlorite; Tc = talc.

† Formula calculation utilized 100% as a basis (Alexiades and Jackson, 1966); excluded from average.

‡ Negative values for chlorite were exluded from the total.

†† Contains F substituted for OH; hence, low OH water basis.

‡‡ These samples were treated with H_2O_2 for exfoliation and flotation separation of vermiculite flakes from weathered granite and unweathered biotite (Alexiades and Jackson, 1965).

(ferruginous micas with mixed-layer impurities) ranged (Manghnani and Hower, 1964) from 8.3 to 3.4% K_2O, and extrapolated to about 9% K_2O when no expansible layer silicates were present. Interestingly, our Franconia glauconite (Table 1) contained 15 to 24% chlorite (Alexiades and Jackson, 1965), a component which was not measured by Manghnani and Howe (1964); the presence of chlorite could cause their observed departure from the

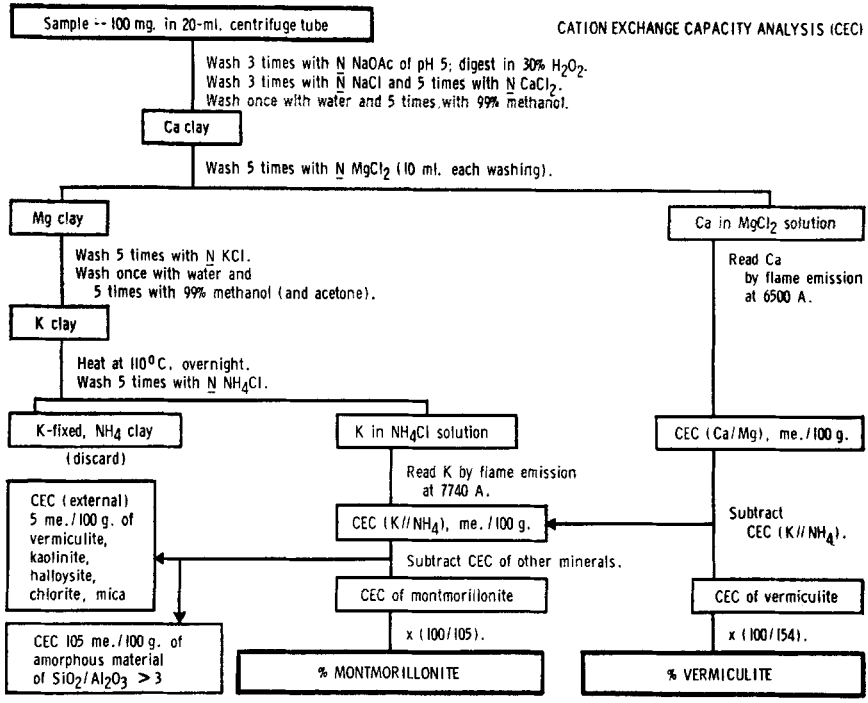


FIG. 2. Flow sheet for vermiculite and montmorillonite determinations by CEC analysis (Alexiades and Jackson, 1965)

linear regression of K_2O as a function of increase in mixed-layer components that Mehra and Jackson (1959) observed. The Na mica (paragonite), which contains 6.02% Na (8.1% Na_2O), is determined on the basis of a content of 5.02% Na (6. 77% Na_2O) based on a five-sixths retention of the theoretical interlayer cation content, a retention found applicable to K micas (Jackson, 1956; Jackson and MacKenzie, 1964; Alexiades and Jackson, 1965, 1966). The occurrence of paragonite in association with muscovite was observed in soils and their parent material in the Virginia Piedmont (Cook and Rich, 1962).

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Amorphous Material by NaOH Selective Dissolution Analysis

Amorphous material is determined by the selective dissolution method of Hashimoto and Jackson (1960) modified to include K saturation before heating (Fig. 4). A 0.100 g sample is boiled for 2.5 min in 0.5 N NaOH to dissolve the amorphous Al_2O_3 and SiO_2 (Table 2). A 0.5 N KOH solution can be used for the determination of amorphous aluminosilicates as well as for

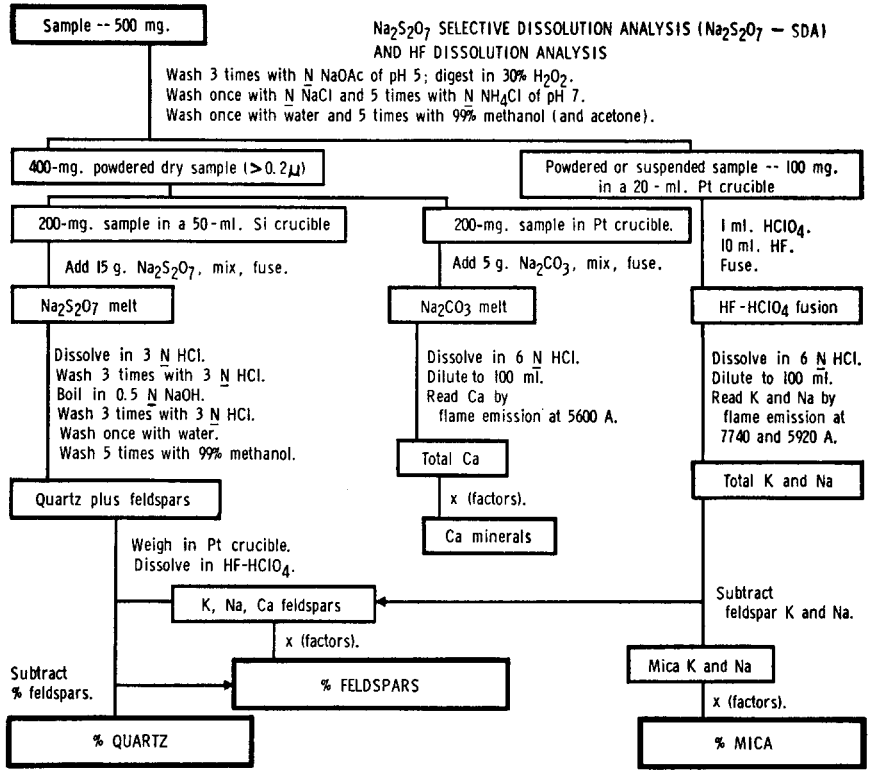


FIG. 3. Flow sheet for mica, quartz, and feldspars determinations by $Na_2S_2O_7$ SDA (Kiely and Jackson, 1965) and by HF dissolution of sample (Jackson, 1956).

kaolinite plus halloysite instead of NaOH. The KOH treatment on allophane and kaolinite samples gave amounts of Al and Si dissolved similar to those dissolved by NaOH treatment in a number of samples including one containing sesquioxic allophane.

The amorphous material (Table 1) is based on the quantity of SiO_2 plus Al_2O_3 dissolved by the above mentioned method divided by 0.9 (10% water, Table 2). This method is based on the rapid dissolution rate (high surface) of most amorphous aluminosilicates. The later silicate minerals were found to

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react only slightly with 0.5 N NaOH, as for example Georgia kaolinite (3.6%), California hectorite (1.7%), Arizona bentonite (4.2%), Wyoming bentonite (4.3%), Georgia chlorite (0.4%), and Wisconsin glauconite (1.1%). These small quantities dissolved from the most common layer silicate

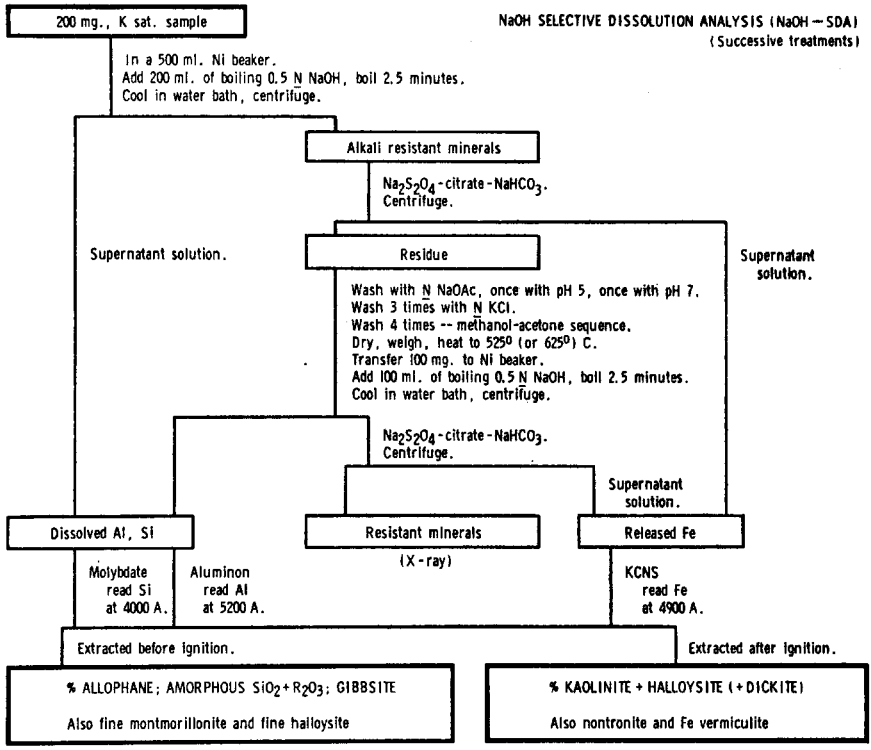


FIG. 4. Flow sheet for amorphous material, allophane and gibbsite, and kaolinite plus halloysite determinations (Hashimoto and Jackson, 1960). The sample is K saturated by KCl washings and then is washed once with water and 5 times with 99% methanol before heating. Dickite requires heating at 625°C for 24 hr as well as grinding in an agate mortar, and then it is treated in the same way as kaolinite (Alexiades and Jackson, 1966). Use of 0.5 N KOH may be substituted for 0.5 N NaOH.

minerals present in soil clays may represent amorphous impurities or a small error arising from dissolution of minerals. To obviate an error of a double calculation of a part of montmorillonite-like dissolved minerals (having a high CEC) once as amorphous materials and once as montmorillonite, a CEC of 1.1 me/g is assigned to the amorphous material which has a SiO_2/Al_2O_3 molar ratio 3 or above (marked by an asterisk, Table 2) and subtracted through equation 2.

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TABLE 2.—AMORPHOUS MATERIAL DISSOLVED FROM THE STANDARD MINERAL AND SOIL SAMPLES BY 0.5 N NaOH TREATMENT (25° OR 110°C SAMPLES)

Sample and source	Size fraction, microns	% SiO_2	% Al_2O_3	$\frac{SiO_2}{Al_2O_3}$ (Molar)	% Amorphous material
Standard mineral samples					
Chlorite (mafic)	<20	1.28	2.42	0.89	4.1
Chlorite, Ga.	<20	0.28	0.11	4.33*	0.4
Halloysite, Ind.	<2	15.66	17.18	1.55	36.5
Kaolinite, Ga.	<2	1.69	1.55	1.85	3.6
Nontronite, Wash.	<2	7.88	3.53	3.79*	12.7
Hectorite, Calif.	<2	0.90	0.66	2.47	1.7
Bentonite, Ariz.	<2	2.42	1.34	3.08*	4.2
Glauconite, Wis.	2−0.2	0.59	0.42	2.38	1.1
Glauconite, Wis.	<0.2	0.38	0.33	1.96	0.8
Soil Clay samples					
Alluvial soil, Netherlands	2−0.2	1.18	1.04	1.93	2.4
	<0.2	1.37	1.06	2.20	2.7
Rendzina, Kilcolgan, Ireland	2−0.2	1.72	0.60	4.86*	2.6
	<0.2	2.88	1.01	4.85*	4.3
Dubuque silt loam, Wis.	2−0.2	11.35	3.00	6.43*	16.0
	<0.2	6.68	3.86	2.94	11.6
Residuum from dolomite, Wis.	2−0.2	11.56	3.87	5.08*	16.7
	<0.2	7.32	4.17	2.98	12.5
Concr. Brown Forest, Alberni, Van.	<2	7.60	9.87	1.31	19.4
Red-Yellow Podzolic, Tatum, Va.	2−0.2	4.58	3.06	2.54	8.2
Rendzina, Drama, Greece	2−0.2	5.18	2.14	4.11*	8.1
	<0.2	9.24	3.59	4.38*	14.3
Solonetz, Thessaloniki, Greece	2−0.2	5.64	1.49	6.43*	7.9
	<0.2	5.44	1.48	6.25*	7.7
Solonchak, Thessaloniki, Greece	2−0.2	2.95	2.32	2.16	5.9
	<0.2	5.05	2.55	3.37*	8.4
Brown Forest, Pertouli, Greece	2−0.2	1.55	0.57	4.62*	2.3
	0.2−0.08	5.35	1.27	7.33*	7.3
	<0.08	4.50	3.12	2.45	8.5
Terra Rossa, Drama, Greece	2−0.2	3.75	3.30	1.93	7.9
	0.2−0.08	10.70	7.09	2.56	19.9
	<0.08	11.77	7.84	2.55	22.0

* In these amorphous materials with a SiO_2/Al_2O_3 ratio > 3, a CEC of 1.1 me/g was given.

Kaolinite and Halloysite by NaOH Selective Dissolution Analysis

The kaolinite plus halloysite contents (Table 1) are based on the SiO_2 and Al_2O_3 (Hashimoto and Jackson, 1960) which dissolved in 0.5 N NAOH (2.5 min boiling) of two K saturated samples, one heated at 525°C for 4 hr (625°C for 24 hr followed by agate mortar grinding, for dickite, Alexiades and Jackson, 1966) and the other at 110°C. The amounts of SiO_2 and Al_2O_3 which dissolved

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at 110°C are subtracted from those dissolved at 525°C (625°C) to obtain the ΔSiO_2 and the ΔAl_2O_3 (Fig. 4). In samples containing gibbsite, a pretreatment with NaOH to dissolve it was given by Hashimoto and Jackson (1960) before heating at 525°C because of the low solubility of Al_2O_3 from such samples after heating. Certain kaolinite samples require heating to 575°C to become soluble in NaOH (R. W. Andrew and M. L. Jackson, in manuscript).

Certain iron-rich layer silicates such as pedogenic ferruginous chlorite as well as nontronitic montmorillonites (having high substitutions of iron in the octahedral layers) have heat-instability and thus are partially dehydroxylated, together with kaolinite and halloysite. Such samples are partly dissolved in the 0.5 N NaOH solution. An extraction of iron released, by the dithionite procedure (Jackson, 1956), is used to measure the dissolution of minerals having high SiO_2/R_2O_3 molar ratios.

The heat-instability of these minerals and the effect of the 2.5–min boiling in 0.5 N NaOH in dissolving some interlayer aluminum (Dixon and Jackson, 1962) from chloritized vermiculites and montmorillonites, minerals commonly present in soil clays, result in a SiO_2/Al_2O_3 molar ratio at variance from 2 for the dissolved elements in the kaolinite plus halloysite determination (Table 3). A study of the ratios obtained with these samples shows that there is a good relationship of the ratio to the mineralogical composition. Thus, if chlorite is more abundant than montmorillonite the SiO_2/Al_2O_3 molar ratio was found to be lower than 2. For example, the residual clay from dolomite of Wisconsin, which was found to contain 27% chlorite and only 13% montmorillonite, gave a SiO_2/Al_2O_3 molar ratio 1.3 (Table 3). When montmorillonite was more abundant, this ratio was found to be higher than 2. For example, fine clay from the alluvial soil of the Netherlands, which was found to contain 31% montmorillonite and 28% chlorite, gave a SiO_2/Al_2O_3 molar ratio 4.3 Consequently, in the calculations:

(a) When the SiO_2/Al_2O_3 molar ratio is lower than 2, which indicates the existence of free alumina or dissolved interlayer aluminum, the kaolinite plus halloysite content is based on the dissolved silica by the equation:

$$\% \text{ Kaolinite plus halloysite} = \frac{\%\Delta SiO_2}{46.5} \times 100 \qquad (3)$$

(b) When the SiO_2/Al_2O_3 molar ratio is higher than 3, which indicates that some 2:1 layer silicates such as nontronitic montmorillonite were dissolved, the kaolinite plus halloysite content is calculated on the basis of the dissolved alumina by the equation:

$$\% \text{ Kaolinite plus halloysite} = \frac{\%\Delta Al_2O_3}{39.5} \times 100 \qquad (4)$$

(c) When the SiO_2/Al_2O_3 molar ratio is between 2 and 3, the kaolinite plus halloysite content is calculated on the basis of the average of the values based

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on $\%\Delta SiO_2$ and $\%\Delta Al_2O_3$ as in equations (3) and (4), or by the equation:

$$\% \text{ Kaolinite plus halloysite} = \frac{(\Delta\%SiO_2/46.5) + (\Delta\%Al_2O_3/39.5)}{2} \times 100 \quad (5)$$

The SiO_2/Al_2O_3 ratios of the samples studied as well as the calculated kaolinite plus halloysite on the basis of equations (3), (4), and (5) are given in Table 3. The minimal values for kaolinite plus halloysite are reported (Table 1) for samples involving dissolution of interlayer aluminum (equation 3) or nontronitic montmorillonite (equation 4). The average values when equation (5) was applicable (middle block of Table 3) showed a deviation of only 0.1 to 2.3% of kaolinite plus halloysite calculated from the percentages based on ΔSiO_2 or ΔAl_2O_3.

Chlorite by Thermal Gravimetric Analysis (TGA)

Chlorite is determined in the clays of soils and mineral deposits (Table 1) by the thermal gravimetric method (Alexiades and Jackson, 1966). The total OH water of K saturated samples is measured by ignition loss between 300 and 950°C (Fig. 5). The water held at 300°C, attributable to the other clay minerals present, such as mica (4% water for biotite, and 4.5% water for dioctahedral micas containing no F), montmorillonite and vermiculite (5% water), kaolinite (14% water), halloysite (16.3% water), allophane (8% water), and talc (4.75% water) is subtracted and a correction is made for the amount of FeO present and oxidized to Fe_2O_3 according to the equation:

$$\% \text{ Chlorite} = \frac{A - B}{0.14} + (\% \text{ FeO}) \times 0.79 \quad (6)$$

in which A is the ignition loss in per cent (300 to 950°C); % FeO is the percentage of ferrous oxide present, determined by HF–H_2SO_4 dissolution of the sample (Jackson, 1958) and titration with standard 0.1 N $K_2Cr_2O_7$ solution; and B is per cent water allocated to the minerals present other than chlorite, based on their content of hydroxyl water above 300°C in K saturated samples.*

An appreciable amount of chlorite is present in a number of standard layer silicate minerals, whereas pedogenic chlorite is a common constituent (3 to over 30%) of soil clays (Table 1). The Tatum soil clay has 23% chlorite, based on 3.26% OH water loss (between 300 to 950°C), after subtraction of 4.16% for the OH water attributable to mica, amorphous material, kaolinite, vermiculite, and montmorillonite). The clay was prepared with free iron oxides removed but was dispersed in distilled water for separation of the clay. The 4.5% vermiculite (Table 1) and 6.6% montmorillonite (a total CEC of 16.45 me per 100 g, Ca/Mg by the present preparation) concords with 11% expansible layer silicates found by specific surface measurement (Table 1 of Dixon and Jackson, 1962). The latter authors found a much higher CEC of 55.1 me per 100 g, after dispersion of this clay by boiling in 2% Na_2CO_3, corresponding to 29% vermiculite. Obviously, the use of the 2% Na_2CO_3

* Antiganite and other serpentine minerals are included with chlorite by this method (W. E. Wildman, M. T. Jackson and T. D. Whittig, in manuscript).

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TABLE 3.—REPRESENTATIVE KAOLINITE PLUS HALLOYSITE DETERMINATIONS IN CLAYS OF SOILS AND MINERAL DEPOSITS, LISTED IN ORDER OF INCREASING MOLAR RATIO OF $\Delta SiO_2/\Delta Al_2O_3$

Sample and source	Size fraction, microns	525°C		525–110°C			% Kaolinite		
		% SiO_2	% Al_2O_3	% ΔSiO_2	% ΔAl_2O_3	$\frac{\Delta SiO_2}{\Delta Al_2O_3}$ (Molar)	$\frac{\%\Delta SiO_2}{46.5}$ (3)	$\frac{\%\Delta Al_2O_3}{39.5}$ (4)	Average of $\%\Delta SiO_2 + \%\Delta Al_2O_3$ (5)
$\Delta SiO_2/\Delta Al_2O_3$ molar ratios less than 2, equation (3) applicable									
Residuum from dolomite, Wis.	2–0.2	20.57	15.32	9.01	11.45	1.3	19.4*	29.0	24.2
Dubuque silt loam, Wis.	2–0.2	16.41	9.24	5.06	6.24	1.4	10.9*	15.8	13.4
Halloysite, Ind.	<2	37.32	41.18	21.66	24.00	1.5	46.6*	60.8	53.7
Concr. Brown Forest, Alberni, Van.	<2	11.24	14.07	3.64	4.20	1.5	7.8*	10.6	9.2
Kaolinite, Ga.	<2	38.05	36.04	36.36	34.49	1.8	78.2*	87.3	82.8
Red-Yellow Podzolic, Tatum, Va.	2–0.2	10.61	8.44	6.03	5.38	1.9	13.0*	13.6	13.3
Residuum from dolomite, Wis.	<0.2	16.16	12.15	8.84	7.98	1.9	19.0*	20.2	19.6
$\Delta SiO_2/\Delta Al_2O_3$ molar ratios between 2 and 3, equation (5) applicable									
Terra Rossa, Drama, Greece	2–0.2	12.31	10.51	8.56	7.21	2.0	18.4	18.3	18.3*
	<0.08	23.43	16.33	11.66	8.49	2.3	25.1	21.5	23.3*
Dubuque silt loam, Wis.	<0.2	16.61	10.51	9.93	6.65	2.5	21.4	16.8	19.1*
Rendzina, Drama, Greece	2–0.2	11.98	6.27	6.80	4.13	2.8	14.6	10.5	12.5*
Solonetz, Thessaloniki, Greece	<0.2	10.20	4.37	4.76	2.89	2.8	10.2	7.3	8.8*
Brown Forest, Pertouli, Greece	<0.08	8.56	5.54	4.06	2.42	2.9	8.7	6.1	7.3*
Alluvial soil, Netherlands	2–0.2	5.05	3.35	3.87	2.31	2.9	8.3	5.8	7.1*
$\Delta SiO_2/\Delta Al_2O_3$ molar ratios higher than 3, equation (4) applicable									
Solonchak, Thessaloniki, Greece	2–0.2	11.34	6.50	8.39	4.18	3.4	18.0	10.6*	14.3
Rendzina, Drama, Greece	<0.2	17.63	7.65	8.39	4.06	3.5	18.0	10.3*	14.2
Solonchak, Thessaloniki, Greece	<0.2	16.29	7.73	11.24	5.18	3.7	24.2	13.1*	18.7
Solonetz, Thessaloniki, Greece	2–0.2	12.13	4.50	6.49	3.01	3.7	14.0	7.6*	10.8
Alluvial soil, Netherlands	<0.2	6.72	3.18	5.35	2.12	4.3	11.5	5.4*	8.5

( ) Numbers in prentheses refer to equation numbers.
* Values used in Tables 1 and 4.

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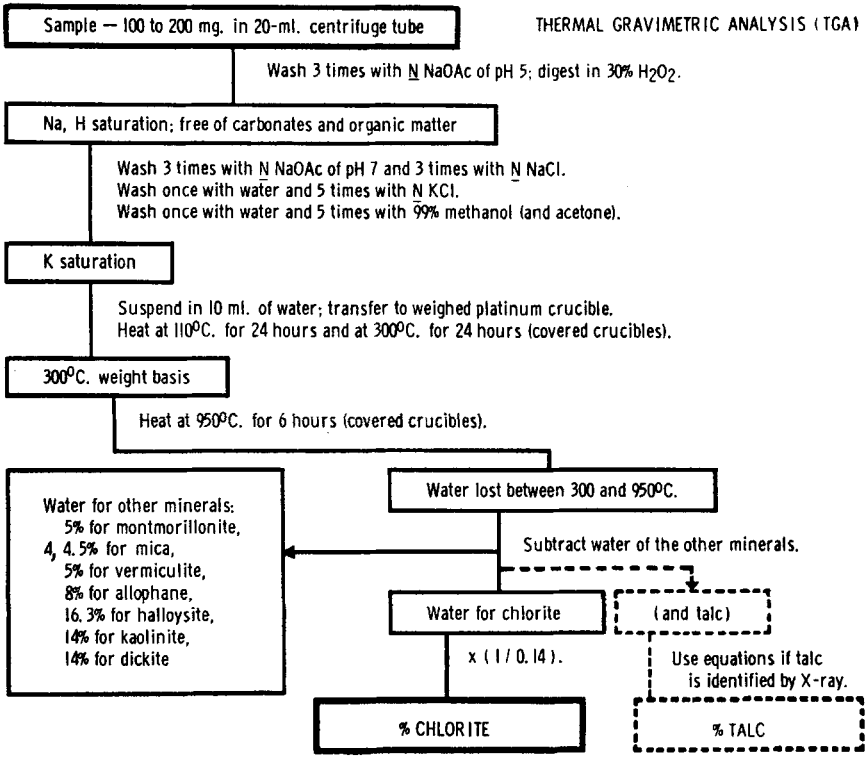


FIG. 5. Flow sheet for chlorite and talc (Alexiades and Jackson, 1966). An additional heating at 540°C for 24 hr reveals octahedral layer composition (e.g. a high Fe content gives a large ignition loss at this temperature, Jackson, 1956). Heating at 800°C for 24 hr helps in the differentiation of talc from chlorite, since talc loses most of its 4.75% hydroxyl water between 800 and 950°C while chlorite loses most of its hydroxyl water below 800°C.

boiling treatment must be avoided because of deprotization (Jackson, 1960, 1963) of highly chloritized clays such as Tatum and Alberni (Clark *et al.*, 1963). The high net negative charge (CEC) found after alkaline treatments would give an excessive vermiculite percentage in the present system of analysis without a corresponding reduction in chlorite OH water loss in the range 300 to 950°C as will be reported in detail later (J. M. deVilliers and M. L. Jackson, in manuscript).

CONSTANCY OF SUM OF MICA AND ITS WEATHERING PRODUCTS

The total mica plus vermiculite plus montmorillonite is a constant in various size fractions of each of the more micaceous of the weathered micas (Table 4). For example, in the Terra Rossa soil the sum is about 54% of the total fraction

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in all the three clay fractions. The coarse clay fraction has the highest mica content and the least vermiculite and montmorillonite. The latter two constituents increase in the finer fractions, with a corresponding weathering of mica. The same constancy holds good for the various clay fractions from the other great soil groups studied (Table 4). In a discussion of the clay transformations during the Quaternary, equations were presented (Jackson, 1965) for the replacement of K from mica and consequent production of vermiculite and montmorillonite. The process of aluminization (desilication) (Jackson, 1965) has produced varying amounts of "pedogenic" chlorite in these samples (Tables 1 and 4).

TABLE 4.—CONSTANCY OF THE SUM OF MICA AND ITS WEATHERING PRODUCTS

Sample and source	Size fraction, microns	% Mica	% Mont*	% Verm	% Sum	% Chlo	% Sum†
Clays high in mica in the coarse clay							
Terra Rossa, Greece	2—0.2	37.2	10.4	6.1	53.7	5.2	58.9
	0.2—0.08	21.5	19.6	14.4	55.5	—	55.5
	<0.08	16.4	22.6	15.0	54.0	—	54.0
Alluvial soil, Netherlands	2—0.2	26.2	24.5	9.4	60.1	23.4	83.5
	<0.2	22.4	30.7	7.1	60.2	27.5	87.7
Solonetz, Greece	2—0.2	25.4	23.7	11.6	60.7	19.1	79.8
	<0.2	12.8	36.5	13.1	62.4	20.3	82.7
Rendzina, Greece	2—0.2	42.8	12.5	9.6	64.9	3.1	68.1
	<0.2	35.6	10.6	20.0	66.2	7.9	74.1
Solonchak, Greece	2—0.2	40.0	17.7	14.5	72.2	11.2	83.4
	<0.2	20.0	28.5	21.0	69.5	10.5	80.0
Clays lower in mica							
Vermiculite, Colo.	2—0.2	19.6	10.5	56.4	86.5	11.3	97.8
	<0.2	16.3	27.7	32.6	76.6	21.3	97.9
Vermiculite (Sediment), Colo.	2—0.2	16.9	25.6	40.5	83.0	15.1	98.1
	<0.2	13.7	29.1	35.2	78.0	23.2	101.2
Residuum from dolomite, Wis.	2—0.2	11.1	13.0	10.8	34.9	26.6	61.5
	<0.2	9.4	28.2	5.9	43.5	24.8	68.3
Dubuque silt loam, Wis.	2—0.2	7.3	8.9	16.5	32.7	36.5	69.3
	<0.2	8.0	21.3	13.0	42.3	26.9	69.2

* Mont = montmorillonite, Verm = vermiculite, Chlo = chlorite.
† Sum of mica + montmorillonite + vermiculite + chlorite.

Mehra and Jackson (1959) reported that the total unit cell planar specific surface and the mica unit cell planar surface (corresponding to the K) is a constant for a number of weathered mica systems, of a specific surface averaging to about 773 m^2/g. This unit cell planar specific surface constancy shows that the mechanism of K release in the weathering of micas is by cleavage of flakes with equivalent amount of adsorption surface formed, and

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that the expandable components montmorillonite and vermiculite are produced, causing an increase in the interplanar specific surface. Constancy of the sum was also maintained in clays thought to involve pedogenesis of mica in chernozem A horizons (St. Arnaud and Mortland, 1963).

Weathering of micaceous clays can produce a complex mosaic of montmorillonite, vermiculite and chlorite crystallites mixed with mica cores of remnants (Jackson, 1964). In most of the clays, the total including chlorite with mica, montmorillonite, and vermiculite tends also to be a constant (Table 4). An influx or synthesis of 10% of montmorillonite, in the fine clay of the residuum from dolomite, independent of mica weathering, is indicated by the 10% excess of montmorillonite in the fine clay and 7% excess of the sum for this sample. With the clays from Dubuque silt loam, the greater quantity of montmorillonite in the fine fraction is balanced by a lesser quantity of chlorite, for a constant total.

The constancy principle ultimately simply reflects the soundness of the analytical methods for each component, giving total recovery of the components in the sample. The sum of the determined components of the various clays equals essentially 100% (Table 1); for the standards it averaged 100.4 $\pm$ 1.3 and for the soil clays, 99.6 $\pm$ 0.8.

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