

## CHLORITE DETERMINATION IN CLAYS OF SOILS AND MINERAL DEPOSITS

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### ABSTRACT

A thermal gravimetric method for the quantitative determination of chlorite in clays of soils and mineral deposits is based on total OH water of K-saturated samples determined between 300 and 950°C. The OH water loss attributable to other minerals such as mica, montmorillonite, vermiculite, kaolinite plus halloysite, and allophane is subtracted on the basis of system of analysis for each of these minerals. A correction is applied for the weight gain of FeO present and oxidized by the 950°C heating. Mafic chlorite samples containing relatively small amounts of impurities were used as standards. Their OH water, after subtraction of the OH water for the mineral impurities corresponded closely to 14 percent of OH water in the chlorite present. Considerable variation occurred in the temperature range of OH water loss. Magnesium chlorite lost most of its OH water above 540°C, while aluminous chlorite lost about half of its OH water below 540°C. Clays rich in ferruginous chlorite lost about five-sixths of their chlorite water below 540°C.

The best evidence of the correctness of the method for chlorite and for the other minerals lies in the close to  $100 \pm 2$  percent total recoveries obtained for the seven or eight constituents each independently determined in over 100 clay samples, representing standard mineral samples and soil clays high in the various constituents.

### INTRODUCTION

Chlorite occurs commonly as a constituent of soil clays and as an impurity in so-called reference clay minerals such as halloysite, montmorillonite, vermiculite, and mica, as indicated qualitatively by X-ray diffraction and by loss on ignition (Alexiades and Jackson, 1966; Borchardt *et al.*, 1966). The quantitative determination of chlorite has been a problem, because the X-ray diffraction peak intensities are not discrete and quantitative enough for determination of fine-grained chlorite interstratified with other phyllosilicates. Hydroxyl water should be the best quantitative analytical criterion for the chlorite component, since it is more abundant in chlorite than in most other common layer silicate clays.

Standardization of the OH water basis for chlorite is now opportune since quantitative methods (as cited in the methods section) have become available for the determination of other minerals that are common in clays such as mica, amorphous materials, kaolinite plus halloysite, vermiculite, and montmorillonite, which also contain OH water. Quantitative determinations of quartz and feldspars are now available so that chlorite can be determined in the mineralogical analysis of the sand and silt fractions as well. The present paper presents a method for quantitative determination of chlorite, based on water loss in the temperature

interval 300 to 950°C, concurrently with the determination of the other minerals commonly present.

#### REVIEW OF LITERATURE

Thermal gravimetric analysis (TGA), in which water loss between given temperature intervals is measured, has long been used to supplement elemental analysis in the allocation of chlorite in soil clays, as reviewed by Jackson (1956). Some evidence in the literature suggested that chlorite present in soil clays could be calculated on the basis of 12.3% loss of hydroxyl water from pure chlorite between 540 and 900°C, after allocation of OH water to the other minerals present. Nutting (1943) presented dehydration curves for several chlorites which indicated little water loss for mafic chlorite minerals below 500°C; a sharp loss of water occurred between 500 and 550°C. Several samples showed a gradual loss of weight from 600 to 850°C but all were completely dehydroxylated at 850 to 900°C. Predominantly magnesium chlorites (low in iron) dehydroxylate at temperatures in the range of 600 to 800°C. (Brindley, 1961). The weight-loss measurements and X-ray diffraction data show that dehydroxylation in chlorites takes place in two thermal reactions. The first reaction corresponds to loss of water from the brucite-like layers with only minor change in unit cell parameters. The second reaction corresponds to loss of water from the talc-like layers, followed by a recrystallization of new products, notably olivine,  $(Mg, Fe)_2SiO_4$ .

Montmorillonite-group minerals lost their water below 300°C, while OH water loss occurred between 300 and 800°C (Ross and Hendricks, 1945). The amount of OH water in pyrophyllite, montmorillonite and nontronite was 5.0, 4.9, and 4.5 percent, respectively, but an excessive OH water loss from some bentonites suggested to those authors the presence of chlorite impurities. An important feature in the dehydration curves of montmorillonite group minerals is an approximately 5 percent weight loss occurring between 400 to 500°C for nontronites, between 500 to 700°C for montmorillonites, and between 700 to 900°C for hectorites. The dehydration curve for vermiculite (Walker, 1951) showed that water is released in three steps corresponding to about 9.7 percent, 14.8 percent, and 20.2 percent. If each of these losses is expressed as a percentage of the total water content of the vermiculite, the values obtained (48%, 25%, and 27%, respectively) are in fair agreement with the percentages for "unbound" water (40%), Mg shell or "bound" water (30%), and hydroxyl water (30%) of vermiculite (Barshad, 1948); the loss of water between 20° and 900°C from Mg vermiculite was 21.31 percent, while from K vermiculite the loss is only 6.4 percent.

Kaolinite dehydrated at a temperature ranging from about 400 to

525°C, depending on the degree of its crystalline perfection (Ross, and Kerr, 1934; Grim, 1953; Hashimoto and Jackson, 1960). Ross and Kerr (1934) pointed out that halloysite lost its hydroxyl lattice water at a temperature 60 to 80°C lower than did kaolinite. Dickite exhibited an endotherm at 690°C as did the highly crystalline Keokuk kaolinite (Keller *et al.*, 1966), indicating that care must be exercised in the selection of a dehydroxylation temperature for these minerals.

#### MATERIALS

Layer silicate standard samples used in testing the procedure included chlorite from Cartersville, Ga.; a mafic chlorite (from an unknown mineral supply house); chlorite from Maryland (collected by the second author at Stop No. 7, National Clay Conference field trip, 1958); nontronite from Garfield, Wash. (Wards Scientific Est., Rochester, N. Y., No. 33A); hectorite from Hector, Calif. (Wards, No. 34); bentonite from Cameron, Ariz. (Wards, No. 31); the well-known bentonites from Upton, Wyo. and the Panther Creek, Monroe Co., Miss. (courtesy American Colloid Co.); muscovite (from an unknown mineral supply house); vermiculite from Colorado derived from biotite occurring in granite (Alexiades and Jackson, 1965); kaolinite from Dry Branch, Ga. (Georgia Kaolin Co., courtesy Dr. H. H. Murray); dickite from Rock Springs, Wis.; and halloysite of North Gardiner Mine, Bedford, Ind. (Wards, No. 12).

The soils used were a Concretionary Brown Forest soil, B2 horizon, from Alberni, Vancouver, well known as containing dioctahedral chlorite (Brydon *et al.*, 1961; Clark *et al.*, 1963; sample supplied through the courtesy of Dr. J. E. Brydon); a Rendzina soil, Ap horizon, derived from soft limestone from Drama, Greece; a Solonchak soil, C horizon from the Agricultural Experimental Station, University of Thessaloniki, Greece; a soil clay residual from dolomite from a quarry north of Spring Green, Wis.; and a Brown Forest soil, B2 horizon, from the Pertouli forest, University of Thessaloniki, Greece.

#### METHODS

Clay fractions of the standard samples and soils were dispersed by removal of organic matter and free iron oxides, and fractionated (Jackson, 1956) for X-ray diffraction analysis, cation exchange capacity determination, and elemental analysis. The mica content of samples containing dioctahedral mica were based on 10 percent K<sub>2</sub>O (8.29% K) and for biotite and other high iron micas, on 9 percent K<sub>2</sub>O (7.48% K) (Jackson, 1956, p. 543). Quartz and feldspars were determined by the pyrosulfate fusion method (Kiely and Jackson, 1964). The kaolinite plus halloysite contents were based on the difference in Si and Al dissolved during 2.5 minutes of boiling in 0.5 *N* NaOH from samples heated at 525°C for 4 hours and at 110°C (Hashimoto and Jackson, 1960) as slightly modified as follows: for dickite the heating was at 625°C for 24 hours, followed by moderate grinding in an agate mortar; and in the calculations (Alexiades and Jackson, 1966), (a) if the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio of the difference was lower than 2, percent SiO<sub>2</sub>/0.465 was used to obtain the 1:1 dioctahedral layer silicate; (b) if the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio was higher than 3, percent Al<sub>2</sub>O<sub>3</sub>/0.395; (c) if the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio was between 2 and 3, the average of the values based on SiO<sub>2</sub> and on Al<sub>2</sub>O<sub>3</sub> was used. The vermiculite content was based on measuring the potassium-fixing capacity (Alexiades and Jackson, 1965), by determining cation exchange capacity (CEC) in two ways: one, by saturation of the sample with Ca and exchanging the Ca with *N* MgCl<sub>2</sub> washings, CEC (Ca/Mg), and second, by saturation of the sample with K, washing out excess KCl, heating at 110°C overnight to cause vermiculite

to fix K, and exchanging the unfixed potassium with *N* NH<sub>4</sub>Cl washings, CEC (K//NH<sub>4</sub>). Then,

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

in which CEC is as meq per 100 g.

The montmorillonite content was measured by the K replaced by NH<sub>4</sub>Cl in the CEC (K//NH<sub>4</sub>) determination (Alexiades and Jackson, 1965) as follows:

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

in which 5 represents the meq per 100 g of CEC attributed to external surface of various clay minerals (excluding quartz) and *Amor* represents the percent of dissolved amorphous material of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio above 3, indicating montmorillonite- or nontronite-like material (this term is omitted if the ratio for the amorphous material is less than 3; however, for samples containing sesquioxenic allophane of ratio in the range of 0.9–1.3, a higher CEC must be employed, Jackson, 1956). The denominator is derived from the CEC of 110 meq per 100 g of montmorillonite (110–5=105). The methods used for distinguishing chlorite from talc or serpentine, and halloysite (as distinct from kaolinite plus halloysite, above) are developed in the results section below.

#### THERMAL GRAVIMETRIC ANALYSIS (TGA)

*The sample.* An aliquot containing 100 to 200 mg of Na clay (separated, above) is placed in a 15 or 20 ml centrifuge tube and washed 3 additional times with *N* NaOAc (sodium acetate) solution of pH 5 (each with a 5 minute heating in a boiling water bath) to insure complete dissolution of the Na<sub>2</sub>CO<sub>3</sub> and CaCO<sub>3</sub>. The clay is then washed free of calcium salts by 5 washings with *N* NaCl solution and then 5 drops of the NaOAc solution of pH 5 and 5 ml of 30% H<sub>2</sub>O<sub>2</sub> are added. The tube containing the clay is heated on a steamplate (70 to 80°C) for about 3 hours to complete the oxidation of any residual organic matter such as organism growth and otherwise to provide a well-oxidized sample. The sample is then washed 3 times with *N* NaOAc solution of pH 7 by means of centrifugation and decantation. The clay is washed free of NaOAc by 3 washings with *N* NaCl solution, after which the clays are saturated with K by 5 washings with *N* KCl solution. The excess KCl is removed by one washing with H<sub>2</sub>O and 1 washing with 99 percent methanol, 2 washings with methanol diluted to 50 percent with acetone and one washing with 100 percent acetone. The clays are then suspended in 10 ml of distilled water and a sample is decanted into a cleaned preweighed platinum crucible (with cover).

*The TGA.* The crucible containing the clay is heated, while uncovered, for 24 hours at 110°C. After heating, the crucible is covered, cooled and weighed immediately (within 5 minutes). To obtain the weight of the clay on a 300°C basis, the sample is then heated (the crucible must be covered) at 300°C for 24 hours, and again cooled and weighed immediately (within 5 minutes). Not more than 4 crucibles are removed from the furnace into a large desiccator at one time.

The sample is then heated (the crucible must be covered) at 540°C for 24 hours, and weighed again. The 540°C heating helps characterize the octahedral composition (Jackson, 1956, Chapter 6) of the clay minerals present, although for routine chlorite determinations the 300 to 950°C heating weight loss suffices.

The sample is then heated (the crucible must be covered) at 950°C for 6 hours. After six hours of heating, the furnace is shut off until the temperature drops to about 500°C at which time the crucible is removed from the furnace, cooled and weighed.

The total ignition loss (OH water) of the sample is calculated by dividing the difference of the weights after heating at 300°C and 950°C by the 300°C weight basis. Then the percentage of chlorite and serpentine present is calculated on the basis of the total determined OH water, by the equation:

$$\% \text{ Chlorite and Serpentine} = \frac{A - B}{0.14} + (\% \text{ FeO}) \times 0.79 \quad (3)$$

in which  $A$  is the ignition loss in percent (300 to 950°C); “% FeO” is the ferrous oxide present which is determined by HF-H<sub>2</sub>SO<sub>4</sub> dissolution of the sample and titration with standard 0.1  $N$  K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution; 0.14 represents OH water per g attributable to chlorite and serpentine; and  $B$  is percent water lost about 300°C by K saturated minerals present other than chlorite and serpentine. The most common other minerals found in soil clays and their OH water loss on the 300°C weight basis are: montmorillonite, 5 percent; vermiculite, 5 percent; amorphous material, 8 percent; kaolinite, 14 percent; and halloysite, 16.3 percent. Talc has 4.75 percent of water loss, utilized as will be shown below in equations (4) and (5). Dioctahedral micas contain 4.5 percent of OH water in absence of F substitution, while trioctahedral micas contain 4.0 percent of OH water. In calculation of the water attributable to mica present to the samples (Table 2) an assumption of 4.5 percent water was used for the soil clays (probably F-free, dioctahedral, and fairly low in Fe) and for Washington nontronite and the Arizona bentonite. Specimen muscovite frequently has considerable F substitution for OH, and thus 4 percent water was used for it and the other specimen minerals. If 4.0 percent water had been used instead of 4.5 percent for the soil clays, there would be 0.35 percent more of chlorite for each 10 percent of mica present.

## RESULTS AND DISCUSSION

*Ignition loss.* The species of exchangeable cation was found to be of great importance to the water loss percentage from expansible clay minerals. To minimize cation hydration, K-saturated clays were utilized to study the dehydroxylation curves of the clay minerals. The use of 300°C as the basis for the expression of the percent OH water determination (Table 1) was found to yield better results than the 110°C basis, concurring with the observations of Ross and Hendricks (1945) and Jackson (1956). The heating loss curves of standard minerals and soil clay samples (Fig. 1 and 2) were positioned by points determined at 110, 300, 540, and 950°C, with curve shapes taken from the literature (Jackson, 1956). Six hours of heating at 950°C were found to be required for constant weight. For example, for Maryland chlorite fractions (with montmorillonite, vermiculite, and talc, Table 2) heated at 950°C for 4, 5.5, and 8 hours, respectively, the percent ignition loss between 300 and 950°C was as follows:

Size fraction	4 hours	5.5 hours	8 hours
> 100 microns	10.83	10.94	10.92
100–2 microns	9.52	9.87	9.86
< 2 microns	4.56	6.61	6.56

The differences after 5.5 hours were within the weighing error, whereas the losses between 4 and 5.5 hours were significant.

TABLE 1. DEHYDRATION DATA FOR THE STANDARD MINERALS AND SOIL SAMPLES

Sample and source	Size fraction, $\mu$	% Water lost			
		110–300°C	300–540°C	540–950°C	300–950°C
<i>Standard mineral samples</i>					
Chlorite (mafic)	<20	0.63	4.11	8.59	12.70
Chlorite, Ga.	<20	0.20	3.71	8.21	11.92
Chlorite, Md.	>100	0.38	3.97	6.97	10.94 <sup>b</sup>
	100–2	1.07	4.62	5.28	9.90 <sup>b</sup>
	<2	2.60	4.38	2.24	6.62
Nontronite, Wash.	<2	2.84	6.97	0.12	7.09
Hectorite, Calif.	<2	1.78	1.19	4.38	5.57
Bentonite, Ariz.	<2	2.20	4.85	0.94	5.79
Bentonite, Upton, Wyo.	2–0.2	1.07	1.01	4.36	5.37
	<0.2	1.81	0.68	5.70	6.38
Bentonite, Pantner Creek, Miss.	2–0.2	1.35	0.51	5.53	6.04
	<0.2	1.85	0.42	4.33	4.75
Muscovite	2–0.2	0.76	2.03	2.05	4.08
Vermiculite, Colo. <sup>a</sup>	2–0.2	2.50	4.36	1.56	5.92
Kaolinite, Ga.	<2	0.38	12.72	0.95	13.67
Dickite, Rock Springs, Wis.		0.27	10.04	3.49 <sup>c</sup>	13.54
Halloysite, Ind.	<2	6.16	10.88	1.76	12.64
<i>Soil clay samples</i>					
Concr. Brown Forest, Van.	<2	4.98	5.73	1.43	7.16
Rendzina, A <sub>p</sub> horizon, Greece	2–0.2	2.53	4.73	1.14	5.87
	<0.2	3.90	5.22	1.59	6.81
Solonchak, C horizon, Greece	2–0.2	1.66	6.09	0.85	6.94
	<0.2	2.79	6.87	0.48	7.35
Residual from dolomite, Wis.	2–0.2	1.09	8.81	0.67	9.48
	<0.2	2.63	8.87	0.39	9.26
Brown Forest, B <sub>2</sub> horizon, Greece	2–0.2	2.75	3.97	2.25	6.22
	0.2–0.08	2.37	4.27	2.19	6.46
	<0.08	2.37	4.39	1.97	6.36

<sup>a</sup> Treated with H<sub>2</sub>O<sub>2</sub> for exfoliation and separation of vermiculite flakes from weathered biotite and chlorite (Alexiades and Jackson, 1965).

<sup>b</sup> These two numbers corrected for the FeO present, become 11.93 and 10.53 respectively.

<sup>c</sup> 540 to 625°C (6 hours) gave 1.97% loss; 625 to 800°C (18 hours) gave 1.52%; 800 to 950°C (6 hours) gave 0.008%.

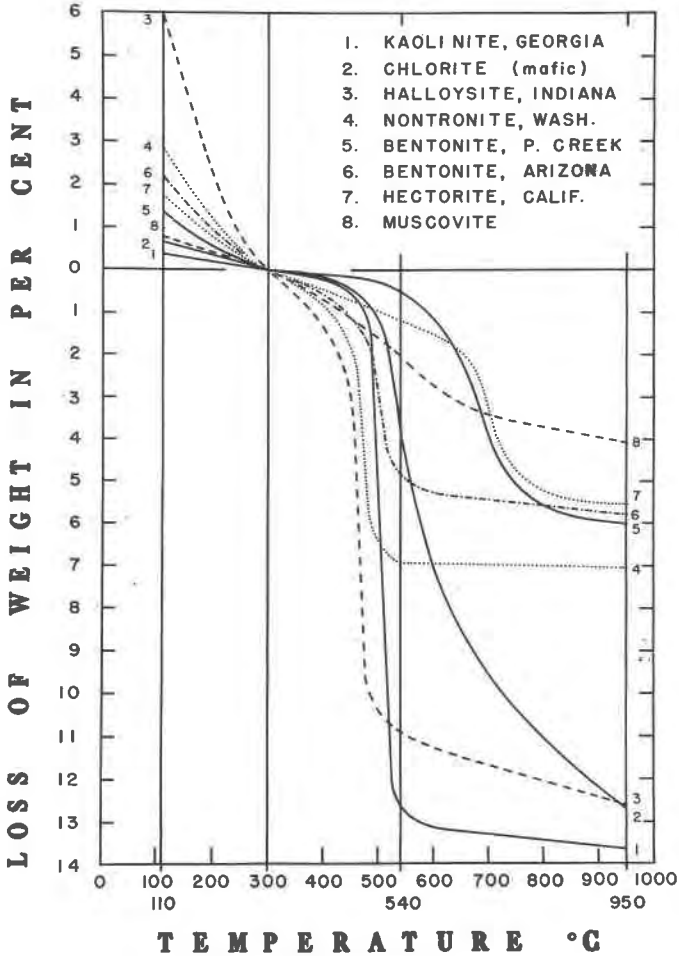


FIG. 1. Thermal dehydration curves of kaolinite (Ga.) and other reference minerals with percentage based on weight at 300°C of a K saturated sample. Size fractions in microns: 1, 3, 4, 6 and 7, <2; 2, <20; 5 and 8, 2-0.2.

The various bentonites showed wide variations of temperature for the loss of OH water. For the bentonites from Upton, Wyoming and Panther Creek, Miss., with low substitutions of iron and magnesium for aluminum, a rapid loss of hydroxyl water began at about 540°C (Fig. 1 and 2), and the dehydroxylation was practically completed at 750 to 800°C. For the Arizona bentonite and the Washington nontronite, which contain 48 and 32 percent montmorillonite and nontronite, respectively, a rapid loss of hydroxyl water had occurred below 540°C. For the California hectorite, the dehydroxylation was mostly but not entirely above 540°C.

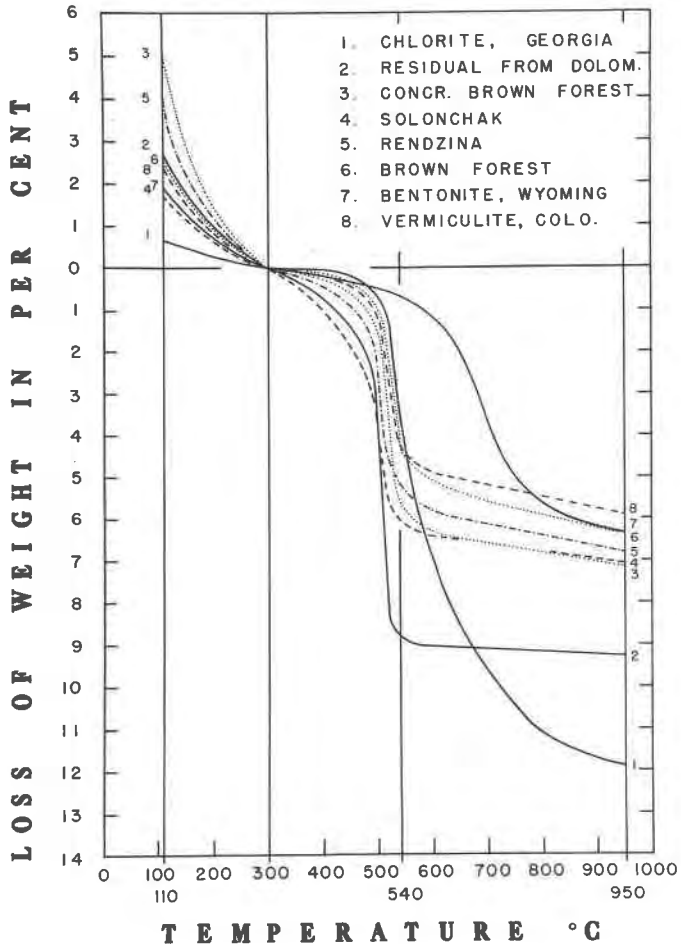


FIG. 2. Thermal dehydration curves of chlorite (Ga.) and other samples with percentages based on weight at 300°C with K saturation. Size fractions in microns: 1, <20; 2 and 7, <0.2; 3, <2; 4, 5 and 8, 2-0.2; 6, 0.2-0.08.

*X-ray diffraction data.* The presence of chlorite in the samples subjected to quantitative analysis by the proposed procedure was established qualitatively by X-ray diffraction. The peaks broadened on the low angle side of the 10 Å (001) peak and on the high angle side of the 3.33 Å (003) peak after heating of K saturated samples at 550°C, indicating interstratification of the chlorite with expansible layer silicates. The pedogenic ferruginous chlorite in the residue from dolomite clay of



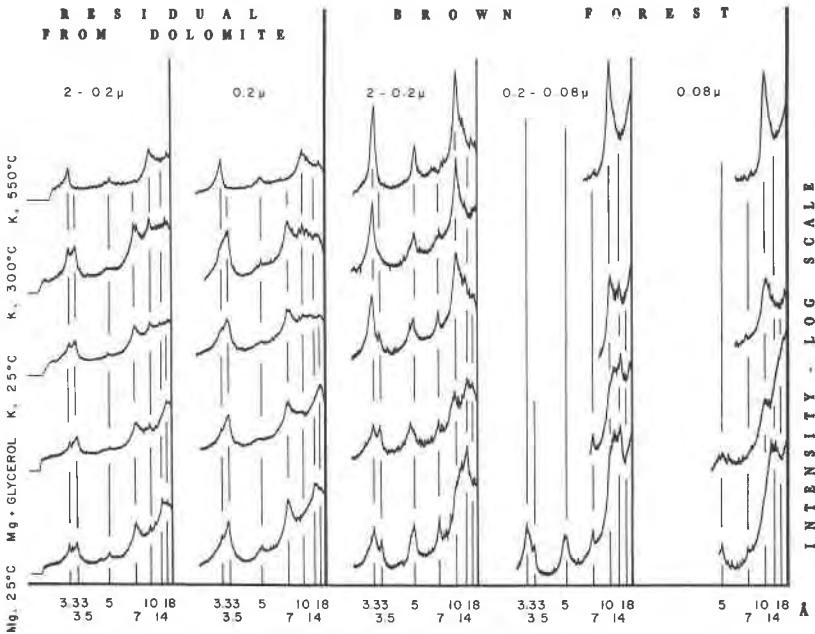


FIG. 3. X-ray diffractograms of dolomite residuum (Wis.) and Brown Forest soil clay (Greece) made with FeK alpha radiation, with the indicated cation saturations and heating temperatures.

Spring Green, Wis. was found to be largely dehydroxylated at temperatures lower than 540°C (Fig. 2). Its 10 to 11 Å peak after heating at 550°C was a broad band (Fig. 3), indicating chlorite interstratified (Jackson *et al.*, 1954) with expansible layer silicates; the 18 Å peak suggests some double interlayering (Jackson, 1963) with hydroxy sesquioxides.

*Chlorite OH water content.* The water percentage attributable to chlorite (and serpentine<sup>1</sup>) in the range of 300 to 950°C was deduced to be 14 percent. This value is a little higher than the theoretical OH water content of chlorite, of which values for chlorite and related minerals are listed as follows:

<sup>1</sup> Serpentine (identified by X-ray diffraction, differential thermal analysis, and electron microscopy) was quantitatively determined in the presence of nontronitic montmorillonite and vermiculite by this method (Wildman *et al.*, 1966).

	% H <sub>2</sub> O
Mafic chlorite (trioctahedral), (Si <sub>6</sub> Al <sub>2</sub> )(Mg <sub>8</sub> Al <sub>2</sub> Fe <sub>2</sub> )O <sub>20</sub> (OH) <sub>16</sub> .....	12.3
Serpentine or antigorite, Si <sub>4</sub> Mg <sub>6</sub> O <sub>10</sub> (OH) <sub>8</sub> .....	13.0
Chlorite (dioctahedral layers; trioctahedral interlayers), (Si <sub>6</sub> Al <sub>2</sub> )Al <sub>2</sub> O <sub>20</sub> (OH) <sub>4</sub> · Al <sub>2</sub> Mg <sub>4</sub> (OH) <sub>12</sub> .....	13.4
Chlorite (dioctahedral), (Si <sub>6.8</sub> Al <sub>1.2</sub> )Al <sub>8.4</sub> O <sub>20</sub> (OH) <sub>16</sub> .....	13.8
Chlorite (dioctahedral) with OH <sub>2</sub> for OH to make up the charge balance, (Si <sub>6.8</sub> Al <sub>1.2</sub> )Al <sub>8</sub> O <sub>20</sub> (OH) <sub>14.8</sub> (OH <sub>2</sub> ) <sub>1.2</sub> .....	15.0
Kaolinite, Si <sub>4</sub> Al <sub>4</sub> O <sub>10</sub> (OH) <sub>8</sub> .....	14.0
Chlorites and serpentines—experimental, giving 100 percent mineral recovery..	14.0

Use of 13 percent water for the mafic chlorites would give over 105 percent totals instead of approximately 100 percent found with the assumption of 14 percent (Table 2). The presence of some octahedral cation vacancies, in discontinuous hydroxyl layers with corresponding OH<sub>2</sub>, "edges" replacing some OH (Jackson, 1963), or the presence of some double interlayering, would account for a rise in the high temperature water content of chlorite materials (as represented by OH<sub>2</sub> for OH in the above list).

The total mineralogical analyses obtained for 27 samples (Table 2) provide a critical test of applicability of the chlorite factor and of the other methods used. The test of the method for each mineral comes, of course, mainly with samples high in that mineral. The approximately 100 percent recovery of minerals, even samples with 30 to 85 percent of chlorite (Table 2), supports the use of the 14 percent factor adopted as the mean value yielding the proper chlorite recovery values. In addition, 9 each of coarse, medium, and fine clay fractions of soils analyzed (Borchardt *et al.*, 1966) by the method proposed herein, with chlorite contents ranging from 2.4 to 27 percent, gave average recovery totals of 96 percent for coarse clay, 99.7 percent for medium clay, and 102 percent for fine clay. Furthermore, the results for the various clay species in the entire clay (less than 2 microns) were closely similar to those derived as weighted averages for the subfractions, with average recovery totals of 100.7 and 99.6 percent, respectively. Also, analyses of 2-micron clay from 14 micaceous sediment samples containing 16 to 33 percent chlorite and 13 to 63 percent mica yielded (Raman and Jackson, 1966) recovery totals of 97 to 102 percent.

*Vermiculitic chlorite.* One mafic chlorite sample, giving an ignition loss of 12.7 percent, was found to contain 10 percent vermiculite (Table 2). The latter was determined on the basis of its two cation exchange capacities (CEC Ca/Mg and K/ /NH<sub>4</sub>) of 19.1 meq of Ca and 3.5 meq of K (not fixed) per 100 g, respectively. The determined total of four minerals present, including 85 percent chlorite, was 99.8 percent. Another mafic

TABLE 2. MINERALS PRESENT IN STANDARD MINERAL AND SOIL SAMPLES

Sample and source	Size fraction, microns	%								
		Am	Kl+Hl	Qr	Mi	Mt+Nt	Vr	Chl	Tc	Total
<i>Standard mineral samples</i>										
Chlorite (mafic)	<20	4.1	0.0	0.8	0.0	0.0	10.0	84.9	—	99.8 <sup>a</sup>
Chlorite, Ga.	<20	0.4	0.0	6.6	6.5	0.0	2.0	81.3	3.2 <sup>b</sup>	100.0 <sup>a</sup>
Chlorite, Md.	>100	0.0	0.0	5.6	0.0	0.0	4.9	80.3	9.2 <sup>b</sup>	100.0
	100-2	0.0	0.0	4.2	0.0	11.8	10.4	64.0	9.6 <sup>b</sup>	100.0
	<2	0.0	0.0	0.0	0.0	66.0	15.0	18.0	1.0 <sup>b</sup>	100.0 <sup>a</sup>
Nontronite, Wash.	<2	12.7	0.0	2.0	2.9	31.8	24.5	22.7	—	96.6 <sup>a</sup>
Hectorite, Calif. <sup>c</sup>	<2	1.7	0.0	1.7	12.3	46.4	17.5	15.0	—	94.6
Bentonite, Ariz.	<2	4.2	0.0	0.0	14.0	48.2	26.9	7.0	—	100.3 <sup>a</sup>
Bentonite, Upton, Wyo.	2-0.2	0.0	0.0	5.3	0.9	70.8	14.3	8.3	—	99.6 <sup>a</sup>
	<0.2	0.0	0.0	0.0	0.0	74.4	11.8	15.6	—	101.8 <sup>a</sup>
Bentonite, Panther Creek, Miss.	2-0.2	0.0	0.0	2.2	3.3	85.1	5.6	5.9	—	102.1 <sup>a</sup>
	<0.2	0.0	0.0	0.0	2.2	84.2	14.8	0.0	—	101.2 <sup>a</sup>
Muscovite	2-0.2	0.0	0.0	1.1	92.3	0.0	7.1	0.0	—	100.5 <sup>a</sup>
Vermiculite, Colo. <sup>d</sup>	2-0.2	0.0	0.0	0.0	19.6	10.5	56.4	11.3	—	99.8 <sup>a</sup>
Kaolinite, Ga.	<2	3.6	78.2	0.0	0.7	0.0	0.7	16.9	—	100.1 <sup>a</sup>
Dickite, Wis.	—	5.2	83.5	4.1	0.5	0.0	0.0	10.0	—	103.3 <sup>a</sup>
Halloysite, Ind.	<2	36.5	46.6	1.4	0.8	0.0	7.9	12.1	—	105.3
Standard deviation of means, $s_{\bar{x}}=1.83$ ; standard deviation, $s=2.66$ ; c.v. = 2.66. <sup>a</sup> Average $\pm s_{\bar{x}}=100.0 \pm 1.8$										
<i>Soil clay samples</i>										
Concr. Brown Forest, Van.	<2	19.4	7.8	17.0	8.4	5.5	18.4	21.1	—	97.6 <sup>a</sup>
Rendzina, A <sub>p</sub> horizon, Greece	2-0.2	8.1	12.5	8.8	42.8	12.5	9.6	3.1	—	97.4 <sup>a</sup>
	<0.2	14.3	10.3	0.0	35.6	10.6	20.0	7.9	—	98.7 <sup>a</sup>
Solonchak, C horizon, Greece	2-0.2	5.9	10.6	1.9	40.0	17.7	14.5	11.2	—	101.8 <sup>a</sup>
	<0.2	8.4	13.1	0.0	20.0	28.5	21.0	10.5	—	101.5 <sup>a</sup>
Residual from dolomite, Wis.	2-0.2	16.7	19.4	4.2	11.1	13.0	10.8	26.6	—	101.8 <sup>a</sup>
	<0.2	12.5	19.0	0.0	9.4	28.2	5.9	24.8	—	99.8 <sup>a</sup>
Brown Forest, B <sub>2</sub> horizon, 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 <sup>a</sup>
	<0.08	8.5	7.3	0.0	28.8	35.3	11.2	7.4	—	98.5 <sup>a</sup>
Standard deviation of means, $s_{\bar{x}}=1.22$ ; standard deviation, $s=1.96$ ; c.v. = 1.96. Average $\pm s_{\bar{x}}=100.1 \pm 1.2$										

Am = amorphous material; Kl+Hl = kaolinite plus halloysite; Qr = quartz; Mi = mica; Mt+Nt = montmorillonite plus nontronite; Vr = vermiculite; Chl = chlorite; Tc = talc.

<sup>a</sup> Within the fiducial limits at the 5% level,  $\pm 3.93$  for the 15 standard minerals excluding the two high talc samples ( $1.83 \times t$  when  $t=2.145$  for 14 degrees of freedom) and  $\pm 2.76$  for 10 soil clays ( $1.22 \times t$  when  $t=2.262$  for 9 degrees of freedom).

<sup>b</sup> Calculation, given in text, utilized 100% as a basis.

<sup>c</sup> Contains F substituted for OH.

<sup>d</sup> Floated on H<sub>2</sub>O<sub>2</sub> (Alexiades and Jackson, 1965).

<sup>e</sup> Average does not include four totals of 100.0%, from which talc (<sup>b</sup>) was calculated but does include experimental totals (ignoring talc) of 97.9% and 99.3% for <2 $\mu$  Georgia and Maryland chlorites, respectively.

chlorite (Fig. 4) gave an ignition loss of 11.9 percent and contained 2 percent vermiculite, 6 percent mica, 7 percent quartz, and 81 percent chlorite (Table 2).

*Chloritic vermiculite and mica.* The Colorado vermiculite (Table 2) containing 11 percent chlorite with 56 percent vermiculite, 20 percent mica, and 10 percent montmorillonite gave a dehydroxylation curve which is

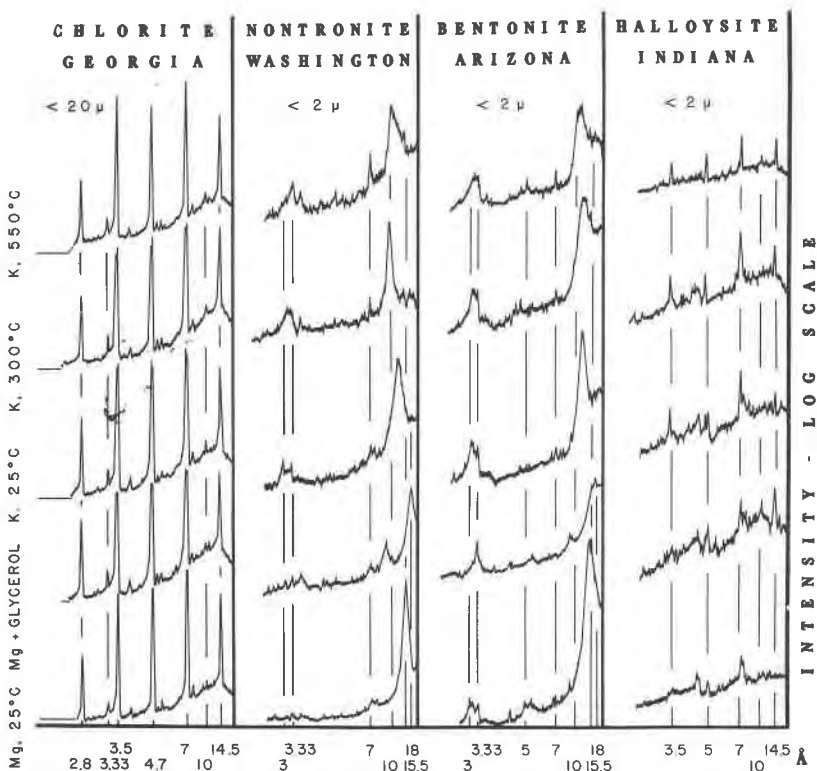


FIG. 4. X-ray diffractograms of chlorite (Ga.), clays from nontronite (Wash.), bentonite (Ariz.), and halloysite (Ind.), made with FeK alpha radiation, with the indicated cation saturations and heating temperatures.

similar in shape (Fig. 2) to that of the micaceous medium clay from the Brown Forest Soil (Greece) with a much different mineralogical composition (Table 2). The range in totals from 97 percent to 103 percent for all of the soil clays indicates the general range of cumulative errors in the determinations.

*Chloritic montmorillonite.* Montmorillonitic clays from bentonites and other deposits as well as from soils have a considerable chlorite content (Table 2), revealed also by X-ray diffraction low angle broadening of the 10 Å peak as well as by the large quantity of OH water found by TGA between 300 and 950°C; the chlorite was 27 percent for the weathering residue from dolomite (Fig. 3); 23 percent for Washington nontronite (Fig. 4); and 0 to 16 percent for Upton and Panther Creek bentonites (Table 2).

*Vermiculitic dioctahedral chlorite.* The presence of dioctahedral chlorite was identified by X-ray diffraction analysis (Brydon *et al.*, 1961) in the clay fraction of the Concretionary Brown Forest soil, B2 horizon, from Alberni, Vancouver. The presence of fairly large crystals of chlorite is clearly shown by X-ray diffraction. The analysis (Table 2) of this clay showed 21 percent chlorite, 18 percent vermiculite, 17 percent quartz, 8 percent mica, and 6 percent montmorillonite. The dehydroxylation curve of this sample showed that virtually all of the water was lost below 540°C (curve 3, Fig. 2); the curve is almost identical to that of the Solonchak soil clay (curve 4, Fig. 2) which contained more mica and montmorillonite and half as much chlorite. The reason for this equality of OH water in TGA is the dilution by 17 percent quartz in the Concretionary Brown soil clay compared with only 2 percent quartz in the Solonchak clay (Table 2).

*Talceous chlorite.* Some talc was found by X-ray diffraction analysis to be present in the Maryland chlorite as well as in the Georgia chlorite (Fig. 4; and Kiely and Jackson, 1964). The percentage of talc present in these samples was calculated on the following basis:

$$\% \text{ chlorite} + \% \text{ talc} = (100 - M) \quad (4)$$

in which the value  $M$  is the sum of minerals present other than chlorite and talc, and

$$\% \text{ talc} = \frac{W - 0.14 (\% \text{ chlorite})}{0.0475} \quad (5)$$

in which the value  $W$  is the total ignition loss found attributable to chlorite and talc. This in turn is derived from the total ignition loss of the K-saturated sample between 300 and 950°C, to which a weight correction for the FeO oxidized has been added, and the content of OH water attributable to the other minerals present has been subtracted (Table 3). The values 0.14 and 0.0475 are the OH water lost from 1 g. of chlorite and talc, respectively.

*Chloritic kaolinite.* The dehydroxylation curve of Georgia kaolinite (Fig. 1) is almost flat up to about 400°C, showing little loss of hydroxyl water at low temperatures. The main dehydroxylation of this kaolinite took place between about 400 and 540°C. The kaolinite content of this sample was found to be 78 percent on the basis of Al and Si dissolved in 0.5  $N$  NaOH after 525°C heating; the rest of the sample was made up by 4 percent amorphous material, 0.7 percent mica, 0.7 percent ver-

TABLE 3. CHLORITE AND TALC ANALYSIS, ILLUSTRATING THE COMPUTATION FOR FERROUS IRON AND OH WATER (MARYLAND SOURCE, 100 TO 2 MICRON FRACTION)

Constituent	Percentages		H <sub>2</sub> O equivalent of minerals present, %	Minerals, corrected for talc present, %	H <sub>2</sub> O equivalent of minerals present, %
	First values	Corrected <sup>a</sup>			
Ignition loss % (300–950°C)	9.90	10.53 <sup>a</sup>			
Minerals present:					
Amorphous material	0.0	0.0	0.00	0.0	0.00
Kaolinite-halloysite	0.0	0.0	0.00	0.0	0.00
Mica	0.0	0.0	0.00	0.0	0.00
Quartz	4.2	4.2	0.00	4.2	0.00
Vermiculite	10.4	10.4	0.52	10.4	0.52
Montmorillonite	11.8	11.8	0.59	11.8	0.59
Talc	—	—	—	9.6 <sup>d</sup>	0.46
Chlorite	62.6	67.4 <sup>a</sup>	9.42 = <i>W</i> <sup>c</sup>	64.0 <sup>d</sup>	8.96
Total	89.0	93.8 <sup>a</sup>	10.53	100.0	10.53

<sup>a</sup> Corrected for 5.76% FeO present in this sample on the basis of 1 g of FeO gives 1.11 g of Fe<sub>2</sub>O<sub>3</sub> and a 0.111 g correction in ignition loss, which is equivalent to 0.79 g of chlorite.

<sup>b</sup> *M* refers to minerals present other than chlorite and talc, equation (4).

<sup>c</sup> *W* refers to ignition loss between 300 and 950°C, corrected for FeO, after deduction of ignition loss attributed to the other minerals.

<sup>d</sup> Distribution of *W* between chlorite and talc by equations (4) and (5).

miculite, and 17 percent of material not dissolved in 0.5 *N* NaOH, which, in our system, shows as chlorite (Table 2). The insoluble residue, remaining after application of the NaOH selective dissolution analysis for determination of kaolinite, was found by X-ray diffraction (Fig. 5) to consist of fine-grained chlorite, in part mixed-layered with mica. The 14 Å peak was broadened and of very low intensity, which is taken to indicate an extremely fine grain size of the residual (or thermally synthesized) chlorite. Loss of additional OH water between 540 and 950°C of 0.95 percent (Table 1) is equivalent to about 7 percent chlorite left undehydroxylated; as is usual for most chlorites, some of the residual chlorite was dehydroxylated below 540°C. A similar loss pattern of OH water was shown by the standard chlorites (Fig. 1 and 2). Interlayer hydroxyl loss is responsible for the well-known reinforcement of the 14 Å peak in chlorite on heating to 540°C; the structure factor for (002) is diminished by interlayer dehydroxylation, and thus the (001) at 14 Å is strengthened. Hydrothermal synthesis of chlorite in this kaolinite during the TGA heating process is a possibility that cannot be completely

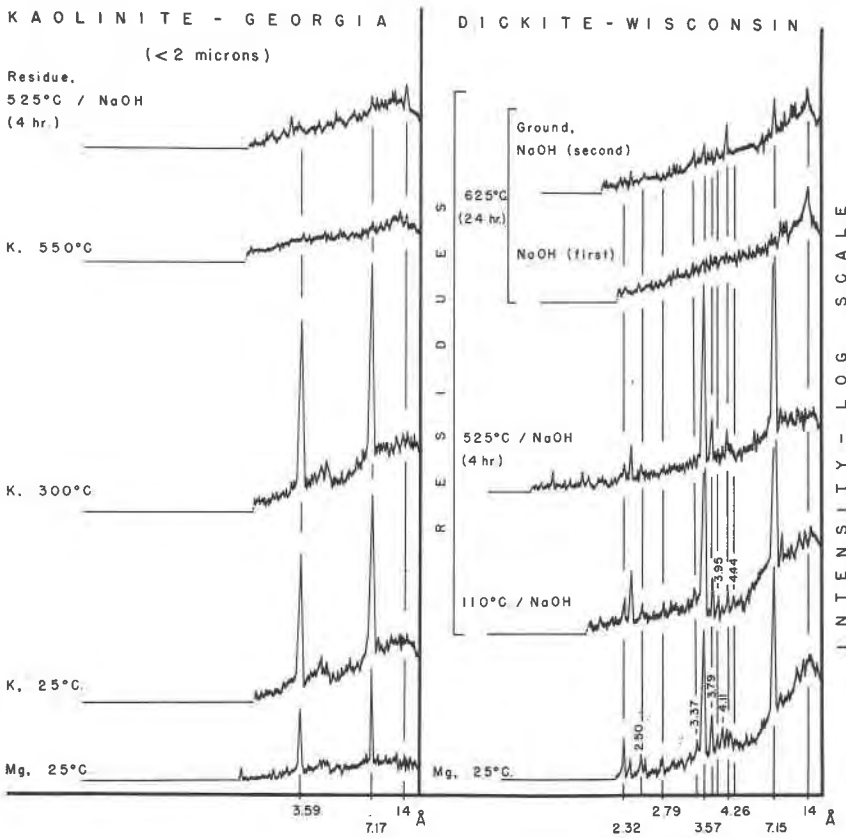


FIG. 5. X-ray diffractograms of kaolinite (Ga.) and dickite (Wis.), made with FeK alpha radiation, with the indicated heating and dissolution treatments which revealed a 14Å peak of chlorite after the kaolinite or dickite was removed. NaOH (first) shows the results with the residue from dickite after removal of only one-third of the SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> from dickite; NaOH (second) shows the results after the first residue was ground in an agate mortar and extracted again with fresh NaOH.

ruled out; however, the presence of some domains of reversed tetrahedra in the structure (giving chlorite structure) is also a distinct possibility, as will be discussed with the dickite results (following).

*Chloritic dickite.* The small X-ray diffraction peak at 14 Å before heating (Fig. 5) suggests the presence of some chlorite impurity in Wisconsin dickite. The 14 Å peak was greatly intensified in the residue after NaOH dissolution of the dehydroxylated dickite. The mineralogical analysis (Table 2) confirms the presence of some chlorite (84 percent dickite and 10 percent chlorite) by selective dissolution analysis and thermal gravi-

metric analysis. Heating for 24 hours at 625°C was required to dehydroxylate the dickite so as to render it soluble in 0.5 *N* NaOH. Moderate grinding of the heated residue in an agate mortar prior to the NaOH extraction was necessary for recovery in solution of fully two-thirds of the Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> of dehydroxylated dickite.

The water loss between 625 and 800°C from the dickite residue was 1.52 percent (footnote in Table 1), corresponding to 11 percent chlorite (compared to 10% found by the TGA analysis). This comparison indicates that no loss of OH water of chlorite in this sample occurred below 625°C, unlike the chlorite in the kaolinite (discussed above). The fact that the 10 percent chlorite residue from dickite gave a more intense peak than the indicated 17 percent chlorite in kaolinite (Ga.) simply indicates that the 14 Å crystal domains of chlorite from the dickite sample were larger and (or) better ordered than those of the residue after kaolinite dissolution.

The indication of chlorite in the Georgia kaolinite (previous section) and Wisconsin dickite may well explain two findings with intersalation analyses (Andrew *et al.*, 1960), namely (a) the persistence of some 7 Å phase in both samples when intersalated may be explained as the (002) of chlorite (since chlorite does not expand by intersalation); and (b) the need for a light grinding of the kaolinite or dickite crystals to enhance intersalation may be explained, since chlorite intergrowths (crystallographic reversal of the silica tetrahedral sheet zonally along the *a* and *b* axes) would be expected to inhibit expansion of some of the kaolinite or dickite phase until the crystals of kaolinite or dickite were detached from chlorite by the grinding. The presence of the weak, but distinct X-ray diffraction peak at 14 Å after dissolution of the kaolinite and dickite indicates the presence of small but distinct crystal zones of the chlorite phase, analogous to those found in micas (Rex, 1966), rather than the occurrence of a solid solution of the 2:1:1 and 1:1 layer silicate phases.

*Chloritic halloysite.* Halloysite (Indiana) gave 47 percent halloysite and 36 percent amorphous material, the rest of the sample being made up by other minerals such as quartz, mica, vermiculite, and chlorite (Table 2). The presence of chlorite in the sample after it was heated to 550°C is indicated by X-ray diffraction peaks at 14 Å and 7 Å (Fig. 4).

The dehydroxylation curve of Indiana halloysite (Fig. 1) shows the usual large loss of water and hydroxyl water below 540°C. The 6 percent lost between 110 and 300°C was attributed to the 36 percent amorphous material (Table 2). Analysis of another specimen from the same halloysite sample showed that it was higher still in such aluminous allophane.



Above 540°C a gradual loss of hydroxyl water occurred up to 950°C. The 300 to 950°C water remaining after allocation to determined minerals other than chlorite is 1.7 percent, corresponding to 12 percent chlorite. The 1.76 percent water loss between 540 and 950°C (Table 1) calculates to 12.5 percent of chlorite (in good agreement with the first allocation). The total of the mineralogical analysis, 105 percent (instead of 100%), may be caused by some of the halloysite being dissolved in NaOH before heating and being calculated as amorphous material as well. The halloysite content could be slightly more and the allophane slightly less; the presence of more than the standard amounts of water in the halloysite and (or) amorphous material could also cause the 5 percent excess in the analytical total.

#### SIGNIFICANCE

Chlorite is an important component of clays of diverse origin in sediments and soils. Chlorite in soils is of importance because of relationships to phosphorus fixation, potassium fixation, aluminum of soil acidity, and pH dependent cation exchange capacity. The quantitative determination of chlorite by TGA uses only simple equipment such as an analytical balance, an ignition furnace, and platinum crucibles, which makes the determination available in all laboratories.

A report at the 14th Clay Conference, August, 1965, at Berkeley, Calif. (Raman and Jackson, 1966), showed that extensive expansion of the interlayer spaces of the micas of several argillaceous sediments by treatment with Na tetraphenylboron did not release any appreciable amount of TGA water in the temperature range 300 to 650°C, in accord with the expected properties of interstratified chlorite. This finding largely excludes the possibility of the presence of trapped interlayer oxonium ( $\text{OH}_3^+$ ), or trapped interlayer  $\text{H}_2\text{O}$  (e.g., Hower and Mowatt, 1966) postulated by several workers during the past 30 years as an alternative explanation for: (1) the ignition loss in excess of the theoretical OH water for micas and (2) the X-ray diffraction on the high spacing side of the 10 Å peak of K saturated samples heated to 550°C. Detailed and extensive research by R. W. Rex and M. L. Jackson, to be published separately, shows that the thermally stable (550°C) 14 Å domains of chlorite mixed with micas and other layer silicates are indeed reproducible through high resolution X-ray diffractometry and arise from valid crystallographic entities of chlorite.

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