QUANTITATIVE ANALYSIS OF KAOLINITE AND GIBBSITE IN SOILS BY DIFFERENTIAL THERMAL AND SELECTIVE DISSOLUTION METHODS

by

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ABSTRACT

Clay fractions from four soils were analyzed for kaolinite and gibbsite by differential thermal analysis (DTA) and selective dissolution analysis (SDA). The kaolinite values by the two methods had a standard deviation of ± 0.95 for the 2–0.2 μ clay of the three most highly weathered soils. Apparently some kaolinite was dissolved with amorphous material in the 0.2–0.08 μ kaolinite standard and probably in 0.2–0.08 μ soil clays. Accuracy of kaolinite determination for the 0.2–0.08 μ soil clays by DTA was reduced because of uncertainty of exact composition of the standard. Presence of montmorillonite in Sango soil clays, particularly the 0.2–0.08 μ fraction, apparently contributed to the error in kaolinite determination by SDA. More precise values for gibbsite were obtained by DTA than by SDA because of the dissolution of alumina from sources other than gibbsite.

INTRODUCTION

The objectives of this study were: (1) to determine the relative accuracy of differential thermal analysis (DTA) and selective dissolution analysis (SDA) for determination of kaolinite and gibbsite in soil clays that contain some clay mineral assemblages important in the southeast, and (2) to estimate other minerals present for defining clay mineralogy of the samples studied. Widespread occurrence of kaolinite in soils and abundance of it and gibbsite in highly weathered soils make determination of the two minerals important.

Kaolinite and gibbsite are simpler than 2:1 layer silicates in which isomorphous substitution occurs. They should be more easily determined. If kaolinite and gibbsite can be accurately determined, estimates of other constituents will be improved.

MATERIALS AND METHODS

Soils Studied

The four soils selected for this study are representative of two major great soil groups of the southeast and are classed Ultisols in the new USDA soil classification system.

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Decatur soils are acid Reddish-brown Lateritic soils formed from limestone residuum. They are classified Typic Rhodudults (8.220) in the new USDA soil classification system. The Decatur samples reported here were taken in the Tennessee River Valley near Belle Mina, Limestone County, Alabama. The rocks of the sample area are coarsely crystalline high purity limestones of Mississippian age–Tuscumbia formation.

Sango soils are moderately well-drained, silty textured, acid, Red–yellow Podzolic soils with a fragipan. However, they are tentatively classified Aqueptic Fragiudults (8.24–3.1) in the new classification system. Sango soils were formed from cherty limestone residuum with intermittent loess cover. The Sango soil reported was sampled 11 miles north of Athens, in Limestone County, Alabama, near the Tennessee–Alabama line. The surface rock formation of the sample area is chert of Mississippian age–Fort Payne Chert.

Magnolia soils are acid Red–yellow Podzolic soils that intergrade to Reddish-brown Lateritic soils. They are classified Typic Normudults (8.230). The Magnolia samples reported were taken 3 miles south of Monroeville, Monroe County, Alabama. The sample site is in an area of acid sandy clays of Pliocene age–Citronelle formation.

Marlboro soils are Red–yellow Podzolic soils formed from unconsolidated coastal plains sediments. These soils are classified Typic Normudults (8.230). They are acid throughout the soil profile. The samples reported were taken near Fairhope, Baldwin County, Alabama. The surface deposits are mapped Citronelle formation.

Sample Preparation

Clay was fractionated from soils and reference minerals following chemical treatments used to remove organic matter, free iron oxides, and amorphous binding materials by sodium carbonate boiling (Jackson, 1956, p. 31).

Differential Thermal Analysis

The procedure followed is similar to the one proposed by Mackenzie (1957, p. 48). Samples, standards, and inert material were ground to pass a 140 mesh sieve. Clays in the 0.2–0.08 μ fraction were freeze-dried, and grinding was not necessary. Magnesium-saturated clays were diluted with three times their weight of white amphibole asbestos (Eimer and Amend American Asbestos) that had been fired at 950°C for 15 min. Standards were prepared from magnesium-saturated fractions of poorly crystalline Georgia kaolinite, Hydrite-10 kaolinite, and U.S. Bureau of Standards Bauxite No. 69A (Bryant and Dixon, 1964). The two kaolinite reference samples were provided by Dr. H. H. Murray of the Georgia Kaolin Co., Elizabeth, N.J. Mixing samples and diluent was done by transferring the material repeatedly back and forth on a glazed paper. Diluted samples were equilibrated at a constant humidity. Differential thermal analyses were made in a nitrogen furnace atmosphere with a heating rate that increased 10.3 to 11.5°C per

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minute in the range of kaolinite and gibbsite reactions employed. Gibbsite was determined in unknowns by comparison of DTA peak area with a standard curve of gibbsite peak area versus percent for the appropriate particle size range as shown in Fig. 1. The kaolinite endotherm corresponding to the loss of hydroxyl at about 565°C was evaluated by drawing two straight lines tangent to the sides of the peak and a horizontal base line at the zero reaction position as shown in Fig. 1. This method of determining kaolinite peak area was used for preparing standard curves of kaolinite and was used for determining percentage of kaolinite in unknowns. Kaolinite and gibbsite percentage values were corrected for impurities using SDA.

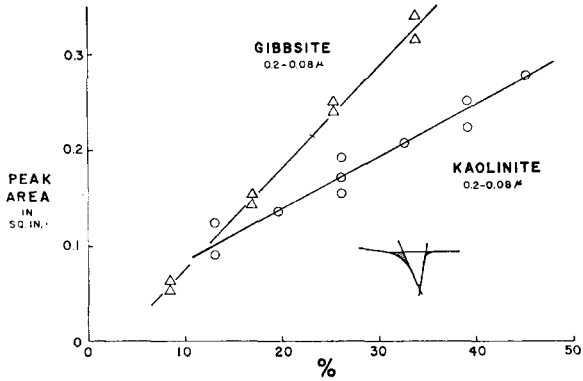


FIG. 1. Standard curves for gibbsite and kaolinite 0.2–0.08 μ fraction and kaolinite endotherm showing method of measuring peak area.

Selective Dissolution Analysis

Hydrogen saturated clay paste for SDA was frozen in liquid air for 2 min, dried at about 20 μ mercury and a maximum of 30°C. The base weight was determined by drying at 110°C. The sample was then suspended in water with a mixer, boiled 2.5 min in 0.5 N NaOH, and silica was determined as described by Hashimoto and Jackson (1960). Aluminum was determined by an Eriochrome Cyanine R. method (McLean, 1965).

RESULTS AND DISCUSSION

Quantitative Analysis of Standards

Poorly crystalline kaolinite and Hydrite-10 kaolinite were selected as standards because X-ray and DTA data indicated that the whole kaolinite samples were almost pure and had about the same endothermic peak temperature and shape as did soil kaolinites to be studied. In comparing DTA

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peak temperature of almost pure kaolinite with kaolinite in soil clays, it was necessary to make allowance for the influence of concentration on peak temperature.

The 2–0.2 μ poorly crystalline reference contained 78% kaolinite and the 2–0.2 μ Hydrite-10 sample contained 92% kaolinite by SDA. Amorphous material and residues accounted for the complement of each sample within a few per cent. X-ray analysis indicated that vermiculite and mica were present in the residues after kaolinite removal. DTA endothermic peak area per unit of kaolinite by SDA was about the same for both kaolinite standards. The DTA standard curve employed for the 2–0.2 μ clay was based on both standards and the average kaolinite composition of the two.

The 0.2–0.08 μ kaolinite standard curve (Fig. 1) was based on the poorly crystalline kaolinite and Hydrite-10 kaolinite as for the 2–0.2 μ clay. The poorly crystalline kaolinite standard contained 65% kaolinite by SDA and 19% amorphous material. The 0.2–0.08 μ Hydrite-10 standard contained 70% kaolinite by SDA and 10% amorphous material. The slope of the standard curve for the 0.2–0.08 μ kaolinite was several per cent higher than that of the 2–0.2 μ kaolinite. The slope of the 0.2–0.08 μ standard curve would have been even higher than that of the 2–0.2 μ standard curve if the whole DTA peak had been measured in both cases. The triangular area measured (Fig. 1) excludes about 8% more of the peak for 0.2–0.08 μ than 2–0.2 μ clay. The higher slope of the 0.2–0.08 μ than 2–0.2 μ kaolinite standard curve indicates that the SDA values for the finer kaolinites were too low by approximately 20%. The comparison is based on the assumption that DTA peak area of kaolinite is independent of particle size in the colloid range as suggested by Mackenzie (1957, p. 49). Some fine kaolinite apparently was dissolved in the NaOH boiling following 110°C heating, which was assumed to remove only amorphous material.

The 2–0.2 μ gibbsite standard contained 90% gibbsite and the 0.2–0.08 μ standard contained 84% gibbsite by the SDA method. Three successive NaOH boiling treatments were employed. All but 2 to 3% of the gibbsite was dissolved in the first 2.5 min of boiling. The small amounts of silica dissolved from the gibbsite samples were assumed to be from amorphous material and a kaolinite contaminant shown by DTA. Alumina values were corrected on the basis of silica dissolved using the silica: alumina ratio of kaolinite.

The gibbsite curves for both fractions were linear throughout most of the range used. There was a small increase in slope for the 2–0.2 μ fraction at 46% gibbsite.

Amorphous Material and Kaolinite in Soil Clays

The amount of silica and alumina dissolved from the 110°C heated samples (Table 1) is considered to be largely amorphous material and gibbsite (Hashimoto and Jackson, 1960). The dissolution values indicate 6 to 12% amorphous

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TABLE 1.—OXIDES DISSOLVED FROM PREHEATED CLAYS BY NaOH BOILING AND KAOLINITE BASED ON SELECTIVE DISSOLUTION ANALYSIS* AND DIFFERENTIAL THERMAL ANALYSIS

Horizon	Depth (in.)	Oxides dissolved after 110°C		Oxides dissolved after 550°C		% Kaolinite by SDA based on		DTA
		SiO_2 %	Al_2O_3 %	SiO_2 %	Al_2O_3 %	SiO_2	Al_2O_3	
				Decatur silt loam				
				2–0.2 μ				
Ap	0–7	4.41	3.50	12.0	11.0	16	19	16
B21	12–20	4.26	4.72	13.3	13.0	19	21	21
B23	31–45	5.11	5.37	15.6	14.8	23	24	25
				0.2–0.08 μ				
Ap	0–7	14.9	10.9	28.2	26.8	29	40	27
B21	12–20	14.6	10.8	28.0	26.6	29	40	30
B23	31–45	15.6	11.9	31.0	29.9	33	45	36
				Magnolia fine sandy loam				
				2–0.2 μ				
Ap	0–6	5.09	5.29	13.7	14.4	18	23	21
B22	13–19	4.77	6.43	18.0	19.7	29	34	26
B23	19–37	5.35	7.45	19.0	24.0	29	42	32
				0.2–0.08 μ				
Ap	0–6	14.7	16.2	28.5	29.3	30	33	36
B22	13–19	15.8	11.9	31.8	33.4	35	54	36
B23	19–37	15.4	11.8	31.7	33.8	35	56	42
				Marlboro loam†				
				2–0.2 μ				
Ap	0–8	4.39	8.85	5.86	7.30	13	18	15
B2	17–29	3.45	24.91	5.11	5.48	11	14	13
C	50–60	3.94	29.05	5.65	6.50	12	16	15
				0.2–0.08 μ				
Ap	0–8	12.7	22.1	9.99	9.98	21	25	28
B2	17–19	11.6	24.1	9.89	9.15	21	23	27
C	50–60	14.4	27.0	11.68	11.47	25	29	34
				Sango silt loam				
				2–0.2 μ				
A2	1–4	3.02	2.66	9.10	7.92	13	13	4
B2	11–25	3.96	4.03	11.94	12.10	17	20	14
B3X	25–41	3.21	3.02	11.38	9.98	18	18	13
				0.2–0.08 μ				
A2	1–4	12.2	12.3	27.6	24.1	33	30	19
B2	11–25	11.6	11.0	24.0	20.9	27	25	16
B3X	25–41	11.3	10.8	24.0	21.0	27	26	19

* Kaolinite values are based on the difference between silica and alumina dissolved after heating at 110°C and 550°C.

† The same samples were used for NaOH boiling after heating at 110°C and 550°C. Therefore, the 550°C values do not include amorphous material.

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material in the 2–0.2 μ fraction and 22 to 30% in the 0.2–0.08 μ fraction.

The SDA kaolinite values based on silica will be used for making comparisons between the two methods since they avoid possible error from dissolution of interlayer aluminum (Table 1). The kaolinite standards for the 2–0.2 μ fraction were pure enough to permit meaningful comparison of SDA and DTA kaolinite determinations without appreciable influence of common error because of correction of DTA standards by SDA. Kaolinite values for 2–0.2 μ clays by SDA based on silica dissolved and DTA for Decatur, Magnolia, and Marlboro soils have a standard deviation of $\pm 0.95\%$. The presence of up to 42% gibbsite in the Marlboro clays apparently did not interfere with the kaolinite determination. The agreement between SDA and DTA kaolinite values indicates that the two methods can be used with equal reliability for 2–0.2 μ clays of highly weathered soils like these. A previous report on Madison soils supports this conclusion (Bryant and Dixon, 1964).

Sango A2 2–0.2 μ clay has the largest disparity between kaolinite values by DTA and SDA for this fraction. The relative kaolinite X-ray intensity values for the 2–0.2 μ clays of this soil suggest a value for the A2 horizon between the SDA and DTA values. Some error may have been introduced in measuring the very broad DTA peak. The Sango A2 2–0.2 μ clay contains 25 per cent expansible minerals based on cation exchange capacity (Alexiades and Jackson, 1966). Part of the 14 Å component, which includes vermiculite and about 20% chlorite-like mineral, is interstratified with a small amount of montmorillonite. The expansible minerals may have been dissolved in part after 550°C heating and caused SDA kaolinite values to be too high.

Kaolinite values by SDA and DTA for 0.2–0.08 μ samples have a standard deviation of ± 2.96 for the three most highly weathered soils. Although the differences between the kaolinite values by the two methods are large enough to restrict some interpretations, they are not surprising for poorly crystalline materials in this fraction. The large correction of the 0.2–0.08 μ DTA kaolinite standard by SDA prevents a reliable comparison of the two methods.

The SDA kaolinite values for the 0.2–0.08 μ clay of Sango are appreciably higher than DTA values, indicating dissolution of other minerals following 550°C heating. Some of the montmorillonite, which is about 35 per cent of these clays, apparently was dissolved and contributed to the high SDA values for kaolinite. Hashimoto and Jackson (1960) indicated this problem with this SDA method.

The DTA method is very sensitive to gibbsite and gives a separate value for it. Dissolution of amorphous alumina and silica with gibbsite prevents determination of gibbsite independently by SDA. Presence of gibbsite is indicated where the amount of alumina dissolved following 110°C heating (Table 1) is appreciably higher than silica. Use of SDA to concentrate and determine impurities in the gibbsite DTA standard improves the accuracy of the latter method.

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Clay Mineral Analyses

The mica content of the 2–0.2 μ fraction of three soils reported was from 4 to 16% and was 24 to 30% in the Decatur soil. The mica content of 0.2–0.08 μ clays was from 2 to 11%. Mica values are based on total K_2O and Na_2O (Bryant and Dixon, 1964). There was no evidence that mica interfered with kaolinite or gibbsite determination.

The intergradient vermiculite-montmorillonite-chlorite minerals composed about 20 to 35% of both clay fractions of the soils except for Sango. Vermiculite and montmorillonite were mostly mixed layered complexes which produced broad X-ray reflections. Appreciable discrete montmorillonite was evident only in the Sango 0.2–0.08 μ clays of subsoil horizons.

Quartz content did not exceed about 20% of the clays and probably would not contribute appreciably to error in the kaolinite or amorphous material determinations.

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