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Minerology of Nipe Clay[1]

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ABSTRACT

The mineralogy of Nipe clay was characterized by means of X-ray diffraction (XRD), differential scanning calorimetry (DSC), infrared spectroscopy (FTIR), BET surface area, and chemical analysis. The major components of the clay fraction are goethite, gibbsite, hematite and kaolinite. Goethite is the predominant iron oxide as indicated by the high intensity of the XRD peaks. The unit cell dimensions of goethite, estimated from the XRD data, were a = 4.603 Å, b = 9.806 Å and c = 3.002 Å. The unit cell dimensions of hematite were a = 5.037 Å, and c = 13.735 Å. The extent of aluminum substitution in goethite and hematite was also estimated from the XRD data. The mole % Al in goethite, based on the $d_{(111)}$ value, was 15.57 mole percent, whereas when the a-dimension of the unit cell was used, a value of 12.86 mole percent was obtained. The estimated mole percent Al substitution in hematite was 0.67. The hematite/goethite ratio as estimated from the relative intensities of the 104 peak of hematite and the 110 peak of goethite was 0.51. Kaolinite showed a high capacity to absorb IR radiation as indicated by strong absorption peaks around 1000 and 3700 cm^{-1}. The surface area of the clay as determined by the BET method was 55.26 m^2/g. The ratio of Fe_{ox}/Fe_d was very low (1.17×10^{-2}), indicating that the iron oxides occur in well crystallized form.

RESUMEN

La minerología de la arcilla del suelo Nipe

La mineralogía de la arcilla del suelo Nipe se caracterizó usando difracción de rayos X, análisis termal, espectroscopía de infrarojo, área superficial (BET) y análisis químico. Los principales componentes minerales de la arcilla son goetita, gibsita, hematita y caolinita. La intensidad de los picos correspondientes a goetita, revelada mediante el análisis de rayos X, indica que este mineral es el óxido de Fe predominante en la arcilla del suelo Nipe. Los parámetros estructurales de la celda unitaria de goetita, estimados del análisis de rayos X, fueron a = 4.603 Å, b = 9.806 Å, y c = 3.002 Å. Los parámetros estructurales de hematita fueron: a = 5.037 Å y c = 13.735 Å. De los datos de rayos X también se estimó el porcentaje molar de aluminio en goetita y hematita. Para el caso particular de la

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goetita, el porcentaje de Al se estimó a base del la distancia interplanar $d_{(111)}$ y a base del tamaño de la unidad estructural-a de la celda unitaria, obteniéndose valores de 15.57 y 12.86%, respectivamente. El porcentaje de aluminio en la hematita fue de 0.67%, y se estimó a base del tamaño de la unidad estructural-a de la celda unitaria. Se obtuvo una proporción de hematita/goetita de 0.51. La caolinita demostró gran capacidad para absorber la radiación infrarroja según lo indican los picos de absorción en la cercanía de los 1000 y 3700 cm^{-1}. El área de superficie de la arcilla fue de 55.26 m^2/g. El contenido de óxidos amorfos fue muy bajo ($Fe_{ox}/F_{ed} = 1.17x10^{-2}$), lo que indica que los óxidos de hierro están mayormente en forma cristalina.

INTRODUCTION

The clay fraction of mineral soils is the most important component influencing its chemical behavior. The close relationship between mineralogy and chemistry of soils is evident from parameters like cation and anion exchange capacity, zero point of charge, delta pH, and pH. Characterization of the mineral components of the soil is essential to predict its chemical behavior with respect to nutrient adsorption, ionic equilibria reactions and nutrient reserves. For example, highly weathered soils like Oxisols and Ultisols, which are dominated by 1:1 clay minerals and iron and aluminum oxides, exhibit low CEC, low fertility level, and in many instances anion exchange capacity in the lower profiles (13). High levels of exchangeable manganese and exchangeable aluminum are often found in Oxisols and Ultisols, respectively.

Nipe (clayey, oxidic, isohyperthermic, Anionic Acrudox) is a soil of limited extent in Puerto Rico, occupying an area of 500 to 700 ha (1, 19). Its occurrence is restricted to serpentinite deposits, but is not found ubiquitously in this rock. There is no certainty as to whether the parent material is residual or transported; however, Beinroth (1) stated that without doubt the parent material of Nipe soil is derived almost exclusively from serpentinite. Jones et al. (9) studied the mineralogy of 11 highly weathered soils from Puerto Rico, including Nipe, and found that this soil contained the lowest concentration of silica and the highest amount of iron oxides. Goethite is the most common iron oxide in highly weathered soils and has been found to be determinant for phosphate adsorption characteristics of Nipe soil (5,8). The relative amount of the oxide is not the only factor influencing anion adsorption reactions. Parameters like crystal size, morphology, and chemistry also affect anion adsorption reactions. Techniques like X-ray diffraction, infrared spectroscopy and differential scanning calorimetry are useful in detecting the presence of such minerals. Also, these techniques can provide information about the degree of mineral crystallinity, ionic substitution and relative quantities of minerals.

The present study aims to evaluate the oxidic mineralogy of Nipe clay using the above mentioned techniques. Chemical and surface area analysis were also performed. X-ray diffraction data was used to estimate the degree of ionic substitution in goethite and hematite, the two major Fe oxides of the clay. The unit cell dimensions of these oxides were also determined by means of X-ray diffraction data. The results herein reported are part of a larger study to evaluate sulfate absorption on iron oxides.

MATERIALS AND METHODS

Clay fractionation

Soil samples were collected from the surface horizon of Nipe soil (clayey, oxidic, isohyperthermic, Anionic Acrudox) in western Puerto Rico. The site is located on the flat part of the Cerro Las Mesas, southeast of Mayagüez. A detailed description of the site is given by Beinroth (1). Samples were sodium-saturated and fractionated into sand (2mm-50μm), silt (50μm-2μm) and clay ($< 2\mu m$) using conventional centrifugation and gravitational techniques (7). The sand fraction was separated from the silt and clay fractions by wet sieving. Separation of silt and clay was achieved by repetitive stirring-syphoning cycles using an automatic clay separator (12). The syphoned clay was flocculated with 1*N* $MgCl_2$ solution to facilitate decanting of the supernatant liquid. The clay was then repetitively washed with deionized H_2O to remove excess of salt and then frozen, freeze dried, and stored for subsequent use.

X-ray diffraction (XRD) study

Clay samples were gently ground in an agate mortar to break up large aggregates, and then backfilled into an aluminum sample holder (15 x 20mm sample area). The material was gently pressed against filter paper to minimize preferred orientation. The random powder mounts were irradiated with Cu $K\alpha$ radiation (35 kv, 20 mA) on a Philips PW 1316/90 wide range goniometer fitted with a theta compensating slit, a 0.2 mm receiving slit and a diffracted beam graphite monochromator. The samples were step-scanned from 10 to 65°2Θ at 0.1°2Θ increments with a counting time of 40 s/increment. The digital data was stored on a floppy disc of an IBM personal computer, re-formated for compatibility with a Lotus 1-2-3 graphics package, and plotted with an IBM XY 749 plotter.

Infrared spectroscopy (FTIR) study

The IR spectrum of the clay was collected with a Bomen Model DA 310 FTIR using diffuse reflectance spectroscopy. A 4% clay dilution in KCl was finely ground in the agate capsule of a small vibratory mill. The powdered sample was placed in the diffuse reflectance cell within the sample compartment of the FTIR and evacuated to 0.2 torr before scanning. Five hundred scans (interferograms) collected at a resolution of 4/cm^{-1} were coadded to yield a primary spectrum in the range of 4000 to 400/cm^{-1}. A reference spectrum of KCl was subtracted to yield the sample spectrum.

Differential scanning calorimetry (DSC)

A 10-mg sample of clay was heated from ambient temperature to 600 °C at 10°/min under a stream of nitrogen using a Dupont 990 thermal Analyzer and a DSC cell. An empty aluminum pan was used as a reference to measure calorimetric changes in the sample.

Reductant-soluble iron, oxalate-soluble iron and surface area

The reductant-soluble Fe content of the Nipe clay was determined by the sodium dithionite citrate bicarbonate (DCB) method (11). A 1/100 dilution of the original extract (250 ml) was then analyzed for Fe by using a Varian AA-6 atomic absorption spectrophotometer. Oxalate soluble Fe was determined by shaking subsamples of clay (100 mg) with 10 ml of ammonium oxalate at pH 3 for 2 h in the dark (15). The samples were then centrifuged and 1/25 dilutions of the supernatants were used for Fe analysis. Surface area of the clay was determined by the BET method (3), using a Quantachrome Quantasorb Multipoint Instrument. This instrument measures N_2 adsorption on samples cooled to liquid nitrogen temperature. Clay samples of about 70 to 80 mg were exposed to N_2/He mixtures of 10.1, 20.5, and 30.5% N_2 and the N_2 adsorbed was converted to surface area, assuming that each molecule covers 16×10^{-20} m^2 of sample surface.

RESULTS AND DISCUSSION

X-ray diffraction analysis of Nipe clay indicates the presence of goethite and hematite in association with gibbsite and kaolinite (fig. 1). Major peaks of goethite are observed at 21.3, 33.1, 36.9 and 53.9 °2Θ. Hematite peaks were observed at 24.3, 33.1 and 53.9 °2Θ. The last two peaks of hematite overlapped with goethite peaks, thus causing a broader and less sharp appearance, than that of nearby peaks. A highly diagnostic kaolinite peak was observed at 12.2 °2Θ and a less resolved one at 24.7 °2Θ. Gibbsite peaks were observed at 18.2 and 20.2 °2Θ. Table 1 presents peak position, the corresponding interplanar spacing (d-spacing) and the lattice plane originating the diffraction.

The intensities of its peaks clearly indicate that goethite is one of the dominant minerals in the clay fraction. Jones et al. (9) reported goethite concentrations of 15 and 21% for A1 and B1 Nipe soil horizons, respec-

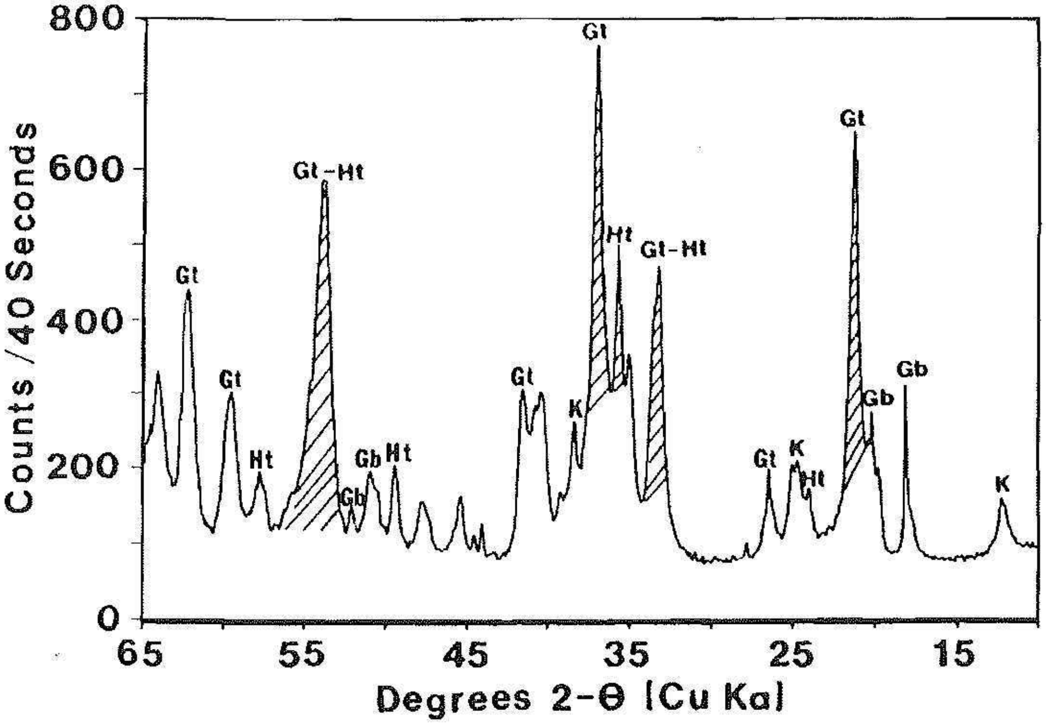

FIG. 1—X-ray diffraction pattern of Nipe clay. K = kaolinite, Gb = gibbsite, Gt = goethite and Ht = hematite.

tively. Hematite concentration for these soil horizons, in the same order, was 14 and 12%. Jones et al. (9) estimated the concentration of goethite and hematite based on the intensity of the 104 peak of hematite and the 110 peak of goethite. From the XRD pattern for the soil and the clay fraction reported by Jones et al. (9), we estimated 104/110 intensity ratios of 1.33 and 0.63, respectively. The 1.33 intensity ratio obtained for the soil corresponded to a hematite/goethite ratio of 0.93. Assuming that peak intensity is directly proportional to the concentration of the oxide, the 0.63, 104/110 intensity ratio of the clay fraction studied by Jones et al. (9) corresponds to a hematite/goethite ratio of 0.44. In the present study the intensity ratio of the 104 hematite peak and the 110 goethite peak was 0.73. Therefore, this ratio corresponds to a hematite/goethite ratio of 0.51, a value that agrees well with a 0.44 ratio obtained from Jones et al. (9) data.

Under natural conditions, goethite and hematite occur in solid solution with Al. In fact, aluminum may substitute for over 30 mole percentage of the structural iron in goethite (4) and about 12 mole percentage in hematite (6,17). Aluminum substitution results in a decrease of the unit cell dimensions of the crystals and a contraction of the spacing (d-spacing) between sets of parallel planes. This decrease is reflected in a shift of the XRD peaks to higher degree 2Θ.

TABLE 1.—*Diagnostic x-ray diffraction peaks for major mineral components of Nipe clay.*

Mineral	Peak position (Degree 2-Θ)	d-spacing (Å)	Plane[1] (hkl)
Goethite	18.2	4.8702	020
	21.3	4.1678	110
	26.5	3.3606	120
	33.1	2.7041	130
	35.0	2.5615	021
	36.9	2.4338	111
	40.3	2.2360	121
	41.5	2.1741	140
	53.9	1.6995	221
	59.5	1.5523	151
Hematite	24.3	3.6597	102
	33.1	2.7041	104
	35.6	2.5197	110
	40.7	2.2149	113
	49.4	1.8433	204
	53.9	1.6995	116
	57.8	1.5963	108
Gibbsite	18.2	4.8702	002
	20.2	4.3923	110
	27.9	3.1951	$10\bar{3}$
	50.9	1.7924	$31\bar{4}$
	52.1	1.7539	024
Kaolinite	12.2	7.2485	001
	24.7	3.6013	002
	38.3	2.3480	$20\bar{2}$

[1] Plane asignments were taken from Besoain (2)

The 111 goethite peak is the most sensitive to shifting as result of aluminum substitution. On the basis of the degree of shifting of this peak, and the decrease of the unit cell dimensions, Schulze (14) developed two equations to estimate aluminum substitution. Equation 1 relates the d_{111} value to the mole percentage aluminum substitution and equation 2 relates the c-unit cell dimension (Å):

$$\textbf{Mole \% Al} = 2086\text{-}850.7\ [(d_{(111)})]\ (r^2 = 0.96) \tag{1}$$
$$\textbf{Mole \% Al} = 1730\text{-}572.0\ c\ (r^2 = 0.98) \tag{2}$$

The position of the 111 peak of Nipe-goethite was compared to the position of the same peak for a pure goethite and an Al-substituted goethite (9.3 mole percentage Al) (fig. 2). The occurrence of the peak of Nipe-goethite at a higher degree 2Θ indicates that the aluminum content should be higher than 9.3 mole percentage. The position of 36.9 degrees 2Θ of the peak of Nipe-goethite corresponds to a d-value of 2.4338 Å. Substituting this value in the previous equation gives an estimated mole percentage Al of 15.57.

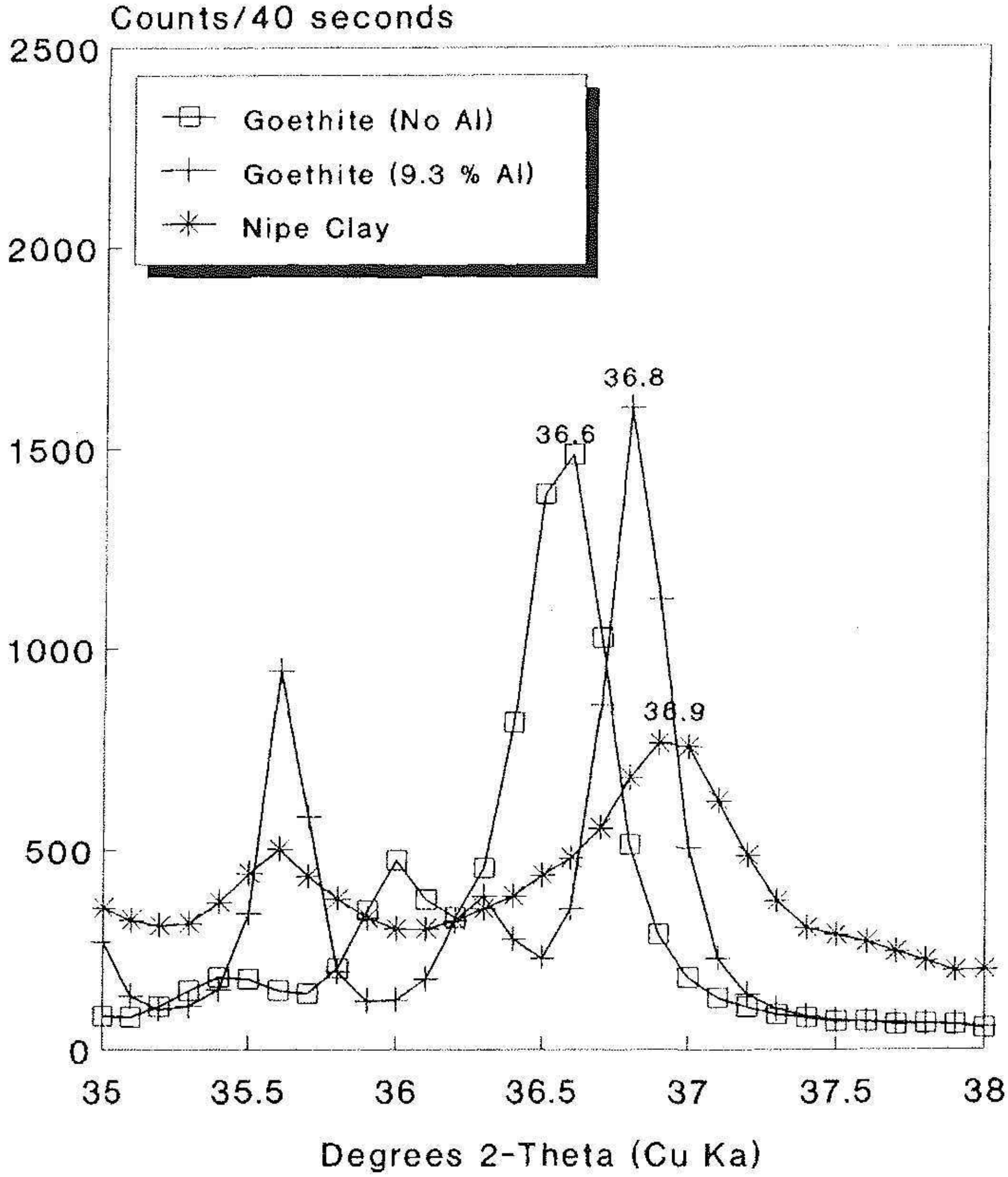

FIG. 2—Position of the 111 XRD peak of the goethite present in Nipe clay as compared to unsubstituted and Al-substituted goethites.

In order to use the second equation we have to determine the c-unit cell dimension of goethite. Goethite has an orthorhombic unit cell, and the d-value for a given line with Miller indices **hkl** is related to the cell dimensions, a, b, c by the equation:

$$\mathbf{d}_{(hkl)} = [(\mathbf{h}/\mathbf{a})^2 + (\mathbf{k}/\mathbf{b})^2 + (\mathbf{l}/\mathbf{c})^2]^{-1/2} \qquad (3)$$

Table 2 presents estimated values of the unit cell (a, b and c) dimensions of goethite. The mole percentage aluminum substitution obtained by using the c-dimension was 12.86.

A similar relationship has been developed to estimate mole percent of aluminum substitution in hematite (16). This relationship stems from data obtained for seven synthetic aluminum substituted hematites synthesized at 70 °C:

$$\textbf{Mole \% Al} = 3109\text{-}617.1\ \mathbf{a}\ (r^2 = 0.92) \qquad (4)$$

Hematite has an hexagonal crystal structure, and the d-value for a given line with Miller indices **hkl** is related to the unit cell dimensions a and c by the equation:

$$d_{(hkl)} = [4/3 \times (h^2 + hk + k^2)/a^2 + 1/c^2]^{1/2} \qquad (5)$$

The average **a-dimension** for hematite as obtained from $d_{(110)}$ and $d_{(300)}$ was 5.037 Å (table 2). Substituting this value into equation (5), gives us an estimated mole percentage Al of 0.67.

Reductant soluble iron (Fe_d), which is a measurement of the free iron oxides present in the clay, was 25.9% (37% as Fe_2O_3) (table 2). The oxalate soluble fraction (Fe_{ox}) gives an estimate of amorphous iron oxide content. The low Fe_{ox}/Fe_d ratio (1.17×10^{-2}) indicates that most of the Fe oxides exist in well-crystallized form. Similar values of Fe_{ox}/Fe_d ratios were obtained by Schwertmann and Lathan (8), for Oxisols of similar mineralogy.

The surface area of the clay was 55.26 m^2/g. This value is low when compared to surface area values reported for 2:1 dominated clays.

TABLE 2.—*Chemical, physical and minerological properties of Nipe clay and its mineral components.*

Parameter	Value
Surface area	55.26 m^2/g
Fe_d	25.9%
Fe_{ox}/Fe_d[1]	1.17×10^{-2}
Goethite	
Unit cell dimensions	
a	4.603 Å
b	9.806 Å
c	3.002 Å
Mole % Al [$d_{(111)}$]	15.57%
Mole % Al (a)	12.86%
Hematite	
Unit cell dimensions	
a	5.037 Å
c	13.735 Å
Mole % Al (a)	0.67%

[1] Fe_d = Reductant soluble iron; Fe_{ox} = Oxalate soluble iron.

Karathanasis and Hajeck (10) reported surface area values ranging from 323 to 556 m^2/g for clays of montmorillonitic mineralogy. The well-crystallized nature of the iron oxides present in Nipe clay combined with the lack of expansibility of kaolinite are responsible for the low surface area value obtained.

The DSC pattern (fig. 3), shows a broad endotherm around 95 °C, which corresponds to loss of adsorbed water. The strong endotherm around 300 °C (actually a doublet) corresponds to dehydroxylation of goethite and gibbsite. Both minerals lose their structural hydroxyls in the range of 270 to 300 °C. The last endotherm, centered at 525 °C, corresponds to the dehydroxylation of kaolinite. Differential scanning calorimetry, although used in the present study as a qualitative analytical technique, is useful for quantitative determination of clay minerals such as kaolinite, gibbsite and goethite.

The IR spectrum of the clay (fig. 4) confirms the presence of goethite, hematite, gibbsite and kaolinite in agreement with the XRD analysis. Although kaolinite is not the major mineral component of the clay, it dominates the IR spectrum with very intense absorption bands in the range of 3600 to 3700 cm^{-1} and 900 cm to 1100 cm^{-1}. Goethite peaks are observed at 3110, 894 and 789 cm^{-1}. The last two peaks overlap with gibbsite peaks. In addition, another gibbsite peak is observed at 3450 cm^{-1}. Sharp hematite peaks are observed at 502, 554 and 637/cm^{-1}.

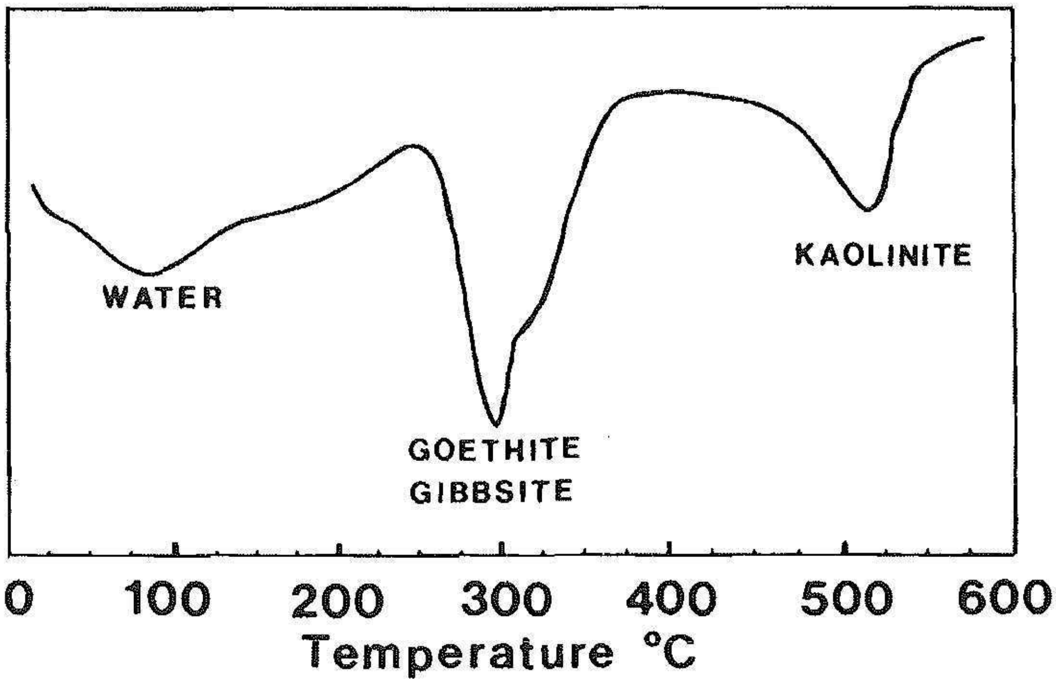

FIG. 3—Differential scanning calorimetry (DSC) pattern of Nipe clay.

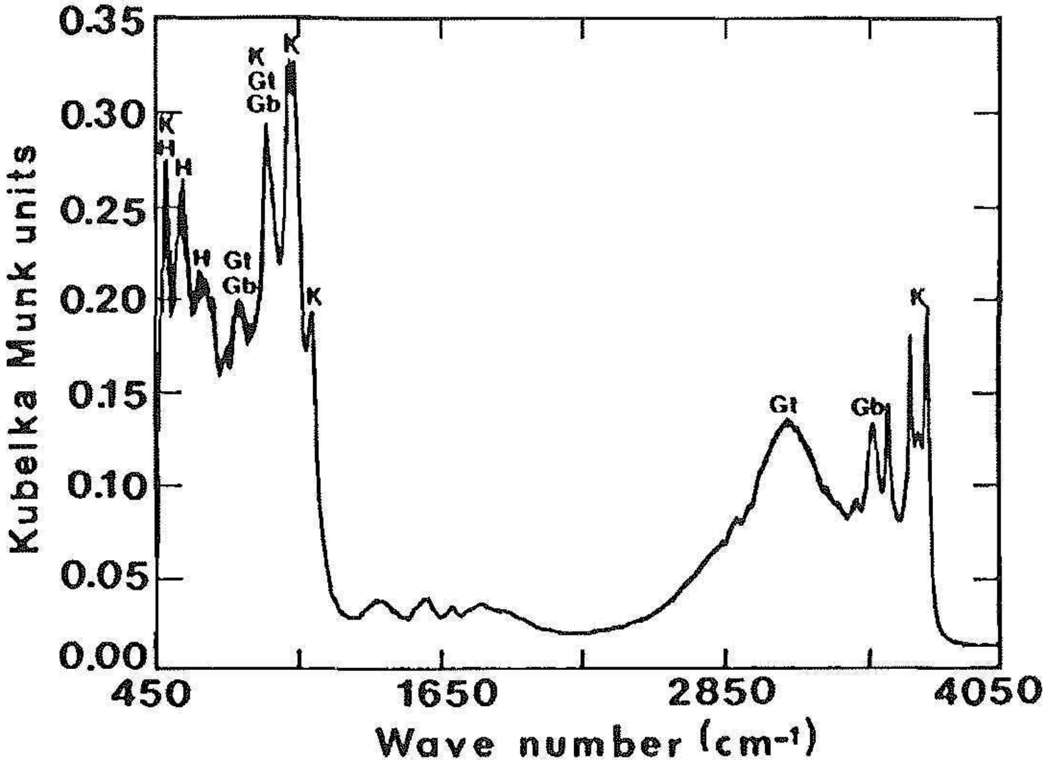

FIG. 4—FTIR spectra of Nipe clay (Diffuse reflectance). K = kaolinite, Gb = gibbsite, Gt = goethite and Ht = hematite.

Nipe soil is not a major agricultural soil in Puerto Rico. However, the typical oxidic mineralogy and well defined mineral components make this soil an excellent system for the study of anion adsorption and other surface chemistry reactions. Goethite, the major component of the clay fraction, occurs as aluminum-substituted goethite. The degree of aluminum substitution should be a significant factor in the chemical reactivity of the oxide, its crystal size and crystallinity. The analytical techniques used in the study can be used, both for qualitative and quantitative analysis of clay minerals. Their usefulness will be restricted to the heterogeneity of the clay fraction and the crystallinity of its mineral components.

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