Thermochimica Acta, 48 (1981) 277—285
Elsevier Scientific Publishing Company, Amsterdam — Printed in Belgium

DIFFERENTIAL THERMAL ANALYSIS STUDIES OF SOME SOIL-CLAYS FROM THE EASTERN CARIBBEAN, WEST INDIES. PART I. ANTIGUA, GRENADA AND TRINIDAD (MONTMORILLONITIC)

M. SWEENEY

Department of Chemistry, University of the West Indies (Trinidad)

(Received 20 February 1981)

ABSTRACT

DTA results were obtained for selected "expanding" soil/clays from the Eastern Caribbean over the temperature range 300—1400 K. The thermograms were used to identify the clay minerals present. Supporting evidence was obtained from X-ray diffraction patterns [1].

INTRODUCTION

Differential thermal analysis (DTA) has been used extensively in the study of soils and clay minerals from almost every region in the world. No such investigation has yet been initiated on soils from this region, the Eastern Caribbean, West Indies. This study was initiated as part of a continuous research program to fill this gap.

Differential thermal patterns are presented for soil-clays from different countries in this region. These analyses were run on the virgin soil (referred to as "untreated") and on these soils from which the organic matter had been degraded, free surface-adsorbed ions had been removed, and in which Mg^{2+} ions were substituted for the easily replaceable cations (referred to as "treated") samples. Each soil-clay was run in air and under an inert atmosphere, nitrogen gas.

The DTA patterns, supported by the evidence obtained from X-ray crystallographic patterns were used to identify the soil-clay constituents. This study was made on clay particles which were less than 2μ in (assumed spherical) diameter. Particles of primary minerals are usually greater than 2μ in diameter [2]. The phyllosilicates include most of the minerals commonly referred to as "clay minerals" [3].

So far as thermal characteristics are concerned, the nature of the exchangeable ion is of great importance since for minerals with a relatively high charge density (e.g. montmorillonite), it determines characteristics of the DTA curve [4]. Montmorillonite is classified as a dioctahedral smectite. It has been found that different samples of montmorillonite yield markedly different DTA curves under the same experimental conditions [4]. It shows a large low temperature endothermic peak, a medium—small endothermic peak at about 700°C and a small S-shaped endothermic—exothermic peak system at around 850—950°C. These peaks are due to the loss of sorbed interlayer moisture, dehydroxylation, and structural change, respectively. The differences must be related in some way to the lattice energy.

There have been several DTA studies on random type interstratifications of montmorillonite with other minerals [5—8].

EXPERIMENTAL

Sample preparation

"Untreated" soil

The solid samples were suspended in distilled water and unwanted materials (e.g. dried leaves, roots, etc.) removed. The air-dried samples were pulverized and $<2\mu$ particle size fractions were used.

"Treated" soil

The "untreated" soils were treated for the removal of soluble salts and exchangeable Ca^{2+}- and Mg^{2+}-carbonates [9], and the removal of the organic cementing matter [10]. Free iron oxides and aluminium oxides were removed by the method of Kittrick and Hope [11]. The soils were dispersed in water, sonified and centrifuged at a convenient speed and time for the $>2\mu$ equivalent spherical diameter particles to settle out.

The decantate containing the $<2\mu$ particles was saved, flocculated with sodium chloride and saturated with magnesium ions to ensure that expansion as a result of hydration will be uniform within all crystal lattices of a species. The soils studied were Capitol, Cunupia, Fitches, Montserrat, Princes Town and Talparo. Their origin, appearance and general composition have appeared earlier [13].

DTA method

The instrument used was the DuPont 900, differential thermal analyzer. DTA curves from 300 to 1400 K were obtained using conical platinum sample containers and platinum/platinum—13% rhodium thermocouples and a heating rate of 20°C min^{-1}. The temperature reliability of this unit is ±1°C and the calorimetric sensitivity is 0.2 mcal sec^{-1} in^{-1}.

The apparatus was calibrated using the melting point temperature of standard (pure metals), and reaction peak temperatures of standard clay minerals. DTA patterns of one-to-one intimate mixtures of the standards kaolinite—illite, vermiculite—chlorite, montmorillonite—vermiculite, montmorillonite—vermiculite—chlorite, and montmorillonite—vermiculite—illite were run. The reference material was $<2\mu$ calcined alumina. The DTA patterns were run under atmospheric conditions and with nitrogen at 2 std. ft^3 h^{-1}.

RESULTS AND DISCUSSIONS

General

The differential thermal analytical curves from these soils from Antigua, Grenada and Trinidad, West Indies, indicate that the main clay mineral present is montmorillonite. They contain, however, varying amounts of other minerals (and organic matter) existing as discrete entities or interstratified conglomerates. The thermograms from Fitches (Antigua) soil-clays are used as typical examples (Fig. 1, Table 1) of a soil-clay analyzed under the four sets of conditions.

The DTA patterns of the "untreated" soils in air all show a large low temperature exothermic reaction peak. These reaction peaks are due to the oxidation of the organic matter present in the natural soil. These large exothermic reaction peaks are absent from the "untreated" samples analyzed under the inert atmosphere, and also from the magnesium saturated samples run under atmospheric conditions. The shape and size of these low temperature exothermic reactions can be used to indicate the complexity of the reaction and the relative amount of organic matter in the soil.

Differential thermal analysis of a soil which contains organic matter can therefore be effectively run in an inert atmosphere which suppresses its oxidation, and consequently permits the changes of interests to be observed. This is particularly important in the quick identification of clay minerals in virgin soil, which will naturally contain a significant amount of organic mat-

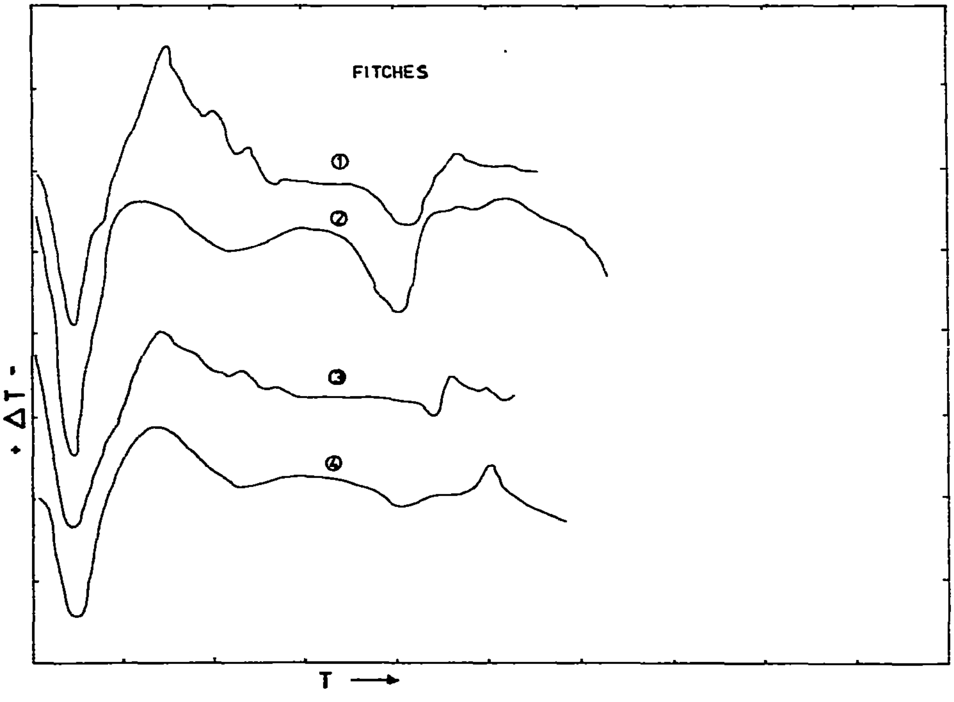

Fig. 1. DTA curves of Fitches soil-clays. 1, Untreated, air; 2, Mg^{2+} saturated, air; 3, untreated, N_2; 4, Mg^{2+} saturated, N_2.

TABLE 1

DTA reaction (peak) temperatures of Fitches soil

Conditions	Temp. (°C)(E/X) [a]
Untreated; air	140(E); 365(X); 467 and 537(X); 588 and 830(E); 912(X)
Mg^{2+}-saturated; air	140(E); 490(E); 527(E); 880(E); 906(X)
Untreated; N_2	135(E); 486—532(E); 815(E); 980—1002(X)
Mg^{2+}-saturated; N_2	140(E); 504(E); 815(E); 965(X)

[a] E = endotherm; X = exotherm.

ter. Though more time consuming, it is more advantageous to remove the organic matter and saturate the clay with a common cation.

The DTA curves of the "untreated" soils run under nitrogen show a similarity to the magnesium saturated samples run in air (Fig. 1, curves 2 and 3). An exact comparison cannot be expected since the replaceable cation will have an effect on the crystal lattice of the original clay minerals resulting in changes in the thermal patterns. Atomic absorption spectroscopic determinations of "free" iron and aluminium removed during the pretreatment process were found to vary from 0.49% to 2.17% (Fe) and 0.08% to 0.79% (Al). It has been shown that the presence of adsorbed ions influences the DTA results [12].

The thermal behaviour of these soils is shown in Fig. 2 and their similarities are summarized as follows.

(i) There are low temperature (125 ± 5°C) endothermic peaks which result from the energy requirements for the loss of water. Magnesium ion saturation and the atmospheric conditions under which the analyses were carried out have little effect on this reaction (Fig. 1).

(ii) There are marked endothermic effects in the region 510—580°C due to the loss of structural hydroxyl groups.

The differential thermograms of Fitches soil (Fig. 1) illustrate the general trend of the exothermic peaks between 300 and 540°C [Fig. 1 (1)] completely masking the more important endotherms which appear around 500°C in the other samples.

In the analyses performed under atmospheric conditions the structural water loss reaction endotherms appear at a higher temperature than those run under the inert atmosphere, indicating that more energy is required to initiate dehydroxylation of the untreated soil. More energy is also required to remove the hydroxyl ions from the untreated soils (Fig. 1: 1 and 2) than from the magnesium saturated clays (Fig. 1 (3) and (4)]. This indicates that these hydroxyls are much more strongly bonded in the untreated soils. On the other hand, the recrystallization energy released by the untreated soil is small, as observed by the small inflections. This is expected, since it has been known [5] that impurity broadens and reduces the size of a DTA peak. It has been sugggested that high temperature reactions are controlled by the chemical composition [6].

The treated soil run in air [Fig. 1 (2)] shows an S-shaped endothermic—exothermic peak between 870 and 910°C, while the analysis run under nitro-

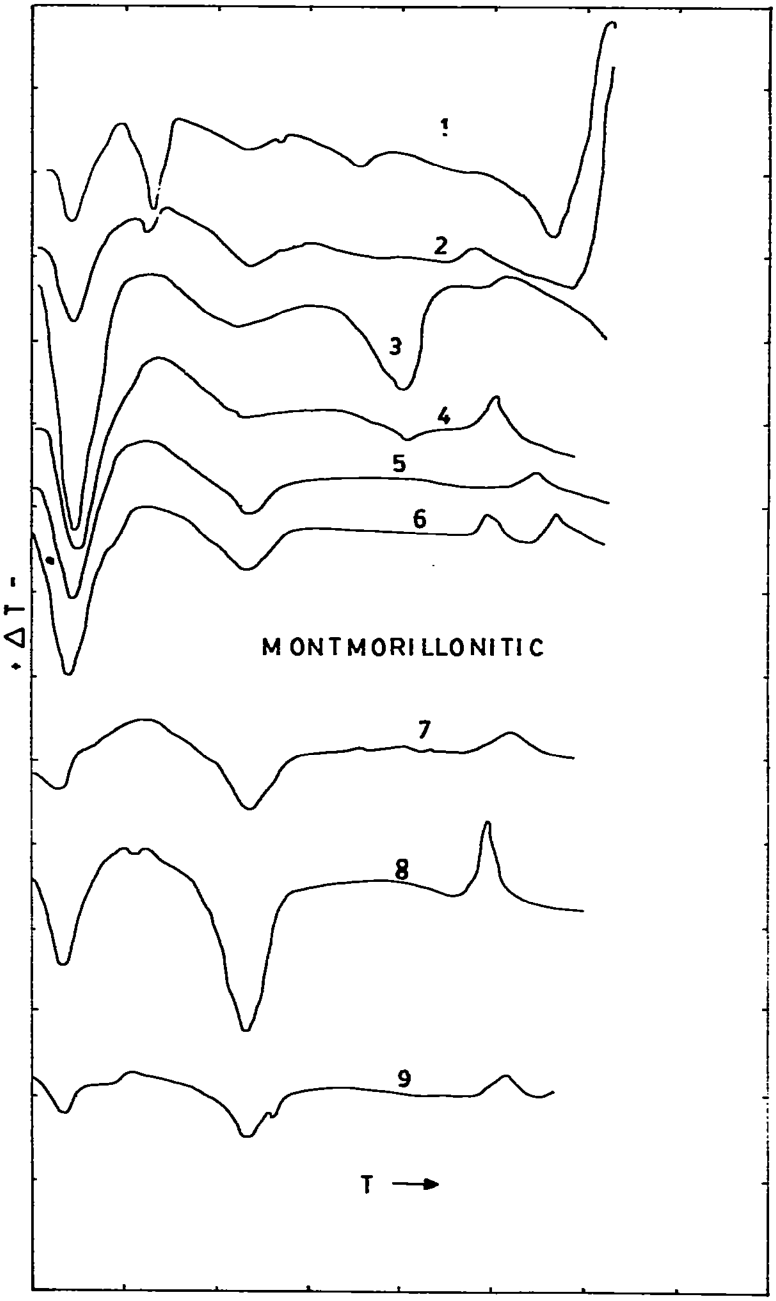

Fig. 2. DTA thermograms of some West Indian soils high in montmorillonite (run under N_2): 1 = Montserrat (untreated); 2 = Montserrat (treated); 3 = Fitches (untreated); 4 = Fitches (treated); 5 = Princes Town (untreated); 6 = Princes Town (treated); 7 = Cunupia; 8 = Capitol; 9 = Talparo.

gen [Fig. 1 (4)] shows two distinct peaks at 815 and 965°C for the endothermic and exothermic reactions, respectively. The many dissimilarities are due to the amounts and types of other clay minerals present in the different soils.

The Capitol soil is similar. The Cunupia clay shows an exothermic peak at

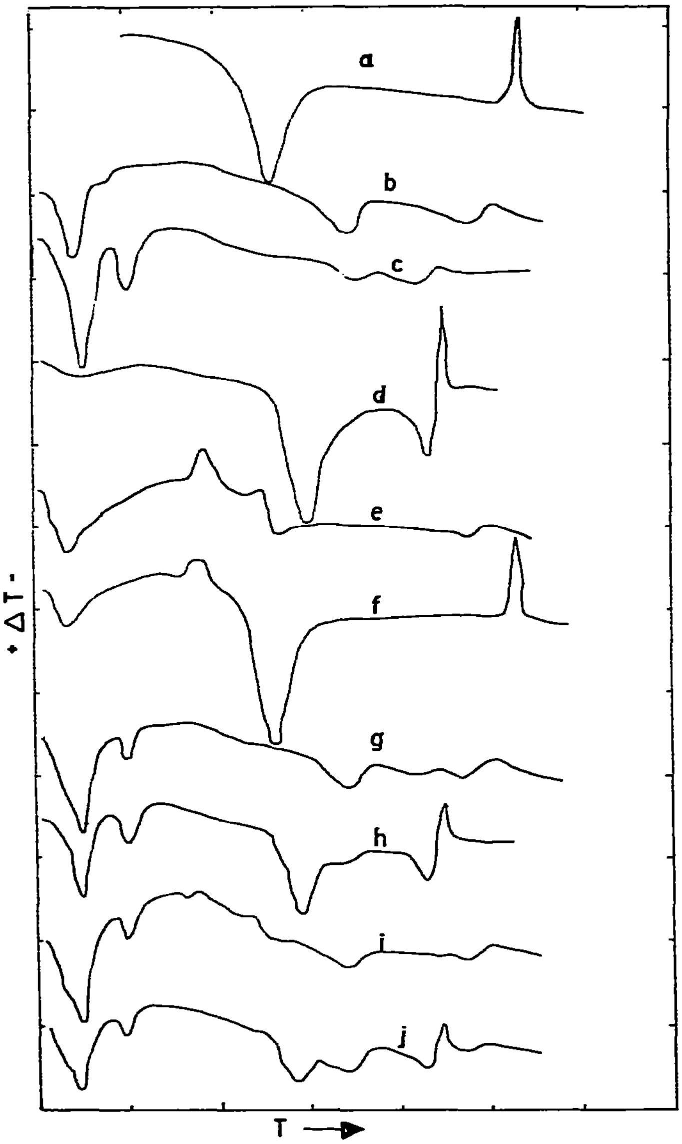

Fig. 3. DTA patterns of standard clay minerals and 1 : 1 mixtures of: a = kaolinite; b = montmorillonite; c = vermiculite; d = chlorite; e = illite; f = kaolinite—illite; g = montmorillonite—vermiculite; h = vermiculite—chlorite; i = montmorillonite—illite—vermiculite; j = montmorillonite—vermiculite—chlorite.

1000 ± 5°C in the magnesium-saturated sample only. The Mg-saturated Montserrat clay gave a small endothermic peak at 560—580°C indicating the presence of quartz; an endothermic peak at 915 ± 20°C, and an exothermic peak >1050°C. The thermogram of the Princes Town clay has an S-shaped endothermic—exothermic pattern at 890—930°C in air, but under N_2 gas the untreated soil shows a solid state (exothermic) transition at 1035 ± 2°C, while the treated clay possesses two exothermic peaks at 965 ± 2°C and 1075°C ± 2°C [Fig. 2 (6)]. It would appear that the structural change at 965°C was due to a metastable crystallite which crystallized to a more stable structure. This phenomenon is also indicative of possible interstratification of some clay minerals. In the Talparo clay there is a quartz inversion endotherm at 575° C and a rounded exotherm at 935 ± 5° C. There is also a 270° C endotherm in the untreated soil which is absent in the treated clays. It appears that the magnesium cation replaced some other cation(s) which are more readily hydrated.

Identifications

The position and shapes of the standard thermograms (Fig. 3) were used as the basis for the identification and the amounts of clay minerals present in the soils studied in this project (Fig. 2). The details of the supporting evidence of X-ray diffraction with DTA of these soils will be presented in a later paper [14].

Clays which are predominantly montmorillonitic [Fig. 3 (b)]; Fig. 2 have a single endotherm in the 100—200° C range. Consequently, these soils contain a considerable amount of montmorillonite. This conclusion is further supported by the fact that the structural hydroxyl of montmorillonite is lost in two stages, the first of which is considered to be a function of the cation—hydroxyl bond [15] and the second is considered to be due to the complete breakdown of the montmorillonite structure. These occur at 630 and 930° C [Table 2, Fig. 3 (b)] for bentonite, $<2\mu$. As expected, these peaks appear at slightly different temperatures in the soils [Fig. 2: (1)—(6)].

DTA patterns of clays which are not predominantly montmorillonitic but which contain a high proportion of montmorillonite are reproduced in Fig. 2 (7)—(9).

The montmorillonite present in both Cunupia and Talparo clays exist as montmorillonoid, i.e. interstratified montmorillonite—vermiculite. The amount is estimated to be 25 ± 2% in each case. Capitol clay, like the previous two, although essentially kaolinitic, contains enough montmorillonite to

TABLE 2

DTA reaction temperatures for standard clay minerals

Standards	Temp. (° C)
Kaolinite (1)	564(E); 1010(X)
Kaolinite (2)	568(E); 1014(X)
Montmorillonite (bentonite)	128(E); 627(E); 930(E); 964(X)
Vermiculite	153(E); 264(E); 737(E); 844(E)
Chlorite	107(E, small); 635(E); 859(E); 884(X)
Illite	107(E); 427(X); 577(E); 964(X, small)
Kaolinite—illite	106(E); 424(X); 575(E); 1010(X)
Vermiculite—chlorite	145(E); 259(E); 621(E); 862(E); 882(X)
Montmorillonite—vermiculite	151(E); 262(E); 716(E); 964(X)
Montmorillonite—vermiculite—chlorite	140(E); 250(E); 610(E); 715(E); 855(E); 881(X); 958(X)
Montmorillonite—vermiculite—Illite	143(E); 257(E); 417(X); 557(E); 710(E); 870(X); 958(X)

E = endotherm; X = exotherm.

TABLE 3

Soils, origin and clay mineral (percentage) contents

Soils	Country	Montmorillonite	Vermiculite	Others [a]
Capitol	Grenada	15 ± 5		85 ± 5(K—G); Tr(Q)
Cunupia	Trinidad	25 ± 2	5	35 ± 5(K); 20(I); 5(Go); Tr(Q)
Fitches	Antigua	75 ± 5		Tr(F); Tr(Q)
Montserrat	Trinidad	45 ± 5	15	10(K); 15(Go); Tr(I); Tr(Q)
Princes Town	Trinidad	35 ± 5		35 ± 5(K); Q
Talparo	Trinidad	25 ± 2	5	35 ± 5(K); 20(I); 4(Go); Tr(Q)

[a] F = feldspar; K = kaolinite; G = gibbsite; Q = quartz; Go = goethite; I = illinite; Tr = traces of.

merit mention (Table 3). These three soils together with other West Indian soils which are essentially kaolinitic, or mixed-minerals, will be discussed at length in a subsequent paper [16].

The Montserrat, Fitches and Princes Town clays [Fig. 2 (1)—(6)] contain small quantities of kaolinite. The X-ray diffractograms supported the presence of kaolinite in Montserrat and Princes Town clays but not in Fitches. The DTA results (Fig. 1) clearly indicate its presence. They all contain traces of quartz. Fitches clay is essentially montmorillonite, Montserrat clay is made up essentially of montmorillonite and vermiculite, while Princes Town is comprised of approximately equal amounts of montmorillonite and kaolinite and contains some quartz (Table 3).

The endothermic peak due to transformation from α- to β-quartz, which normally occurs sharply at about 573°C, is seen in Fig. 2 (1) and (2) as small humps. These peaks are interferred with by the broad endothermic effects of kaolinite and montmorillonite as seen in patterns (2)—(4). Evidence of the presence of quartz in Fitches and Princes Town clays was confirmed from X-ray diffraction study.

In addition to the more readily identifiable clay minerals, the DTA patterns (1) and (2) of Fig. 2 also show weak endothermic effects suggesting that this clay consists of weakly hydrated micas or illite, a conclusion supported by the presence of the *d* spacing for illite by X-ray diffraction technique [14]. The differential thermal pattern (1) of Fig. 2 of the treated clay in air shows the same high temperature S-shaped endothermic—exothermic reaction peaks as that obtained [pattern (e) Fig. 3] for the DTA of the standard sample of illite. This evidence cannot by itself be conclusive since it has been established that this clay is high in montmorillonite which also undergoes endothermic—exothermic reactions in a similar temperature region.

CONCLUSION

Characteristic effects of many clay minerals and organic constituents of a selected group of West Indian soils are shown in DTA patterns of the virgin soils analyzed in air and under an inert gas atmosphere. There is a marked similarity between the DTA patterns of the virgin soils run under nitrogen and the clays from which the organic constituents had been analytically degraded. As a result, the DTA patterns of the soil-clays run under N_2 were used to identify the clay mineral constituents. Supporting evidence was obtained from X-ray diffraction patterns.

ACKNOWLEDGEMENTS

The author wishes to thank the University of the West Indies for paid leave, Professor N. Ahmad, Faculty of Agriculture, University of the West Indies, Trinidad, for providing the soil samples, the Faculty of Agriculture, University of British Columbia, for use of their laboratory facilities, Marva for transcribing, and the secretarial staff of the Chemistry Department, Dalhouse University, for typing the manuscript.

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