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DIFFERENTIAL THERMAL ANALYSIS STUDIES OF SOME SOIL-CLAYS FROM THE EASTERN CARIBBEAN, WEST INDIES. PART II. DOMINICA, GRENADA AND TRINIDAD (KAOLINITIC)

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ABSTRACT

DTA results were obtained for selected "non-expanding" soil/clays from the Eastern Carribbean area over the temperature range 300—1400 K. The thermograms were used to identify the clay minerals present and to calculate the heats of reactions. Supporting evidence on the clay minerals present was gained by X-ray diffraction techniques [1].

INTRODUCTION

Differential thermal analysis (DTA) has been used extensively in the study of soils and clay minerals from almost every region of the world. No such investigation was initiated on soils from this region. This study represents Part II of this program [2]. These DTA patterns, supported by the evidence obtained from X-ray crystallographic diffractograms, were used to identify the soil-clay constituents. The clay mineral, kaolinite, which is of great importance in ceramics and other branches of technology, is particularly widespread in nature. The kaolinite sub-group minerals have essentially constant chemical composition [$Al_2Si_2O_5(OH)_4$] and differ only in the mode of stacking of the 1 : 1 silicate layers.

A typical DTA curve of kaolins has a dehydroxylation peak in the region of 500—700°C and a very sharp exothermic peak at around 1000°C; another exothermic peak at about 1200°C is also fairly typical [3]. It has been shown that the 980—1000°C exothermic peak is affected by impurities which interfere with the process occurring [4]. Because of the characteristic shape of the DTA curves of kaolinite, it is usually possible to detect their presence on DTA evidence alone. Reasonable accuracy can be obtained in the quantitative determination of minerals of the kaolinite sub-group provided the species present is known.

EXPERIMENTAL

The samples were prepared and analyzed as described previously [2]. The same methods, apparatus and techniques were employed. The soils studied, however, were Capitol from Grenada, Cunupia, Princes Town, River Estate and Talparo from Trinidad, and LaPlaine and Wood Ford Hill from Dominica.

RESULTS AND DISCUSSION

General

A considerable amount of kaolinite is present in the soils from Dominica, Grenada and Trinidad. The DTA patterns of the "untreated" soils tested in air all show a large low temperature exothermic reaction peak. The representative data for one of these soils (Capitol) is given in Table 1, and a representative thermogram is illustrated in Fig. 1 (1). These reaction peaks are due to the oxidation of the organic matter present in the natural soil. A discussion on these was presented in an earlier paper [2], which also gave the advantages of analyzing the virgin soil under N_2.

Neglecting the low temperature exothermic reaction peaks for the oxidation of organic matter, the four thermograms of Capitol soils (Fig. 1) are closely related. The obvious difference is the air oxidized organic matter exotherm being replaced by a small endotherm when the untreated sample was heated under nitrogen gas [Fig. 1 (2)]. The dehydroxylation peaks for the reaction run under atmospheric conditions appear at higher temperatures than for those run under the dynamic nitrogen flow condition by about 30°C (Table 1). The high temperature exothermic peak is small and broad for the untreated samples and the treated samples run in air, but larger and narrower for the treated sample run under nitrogen [Fig. 1 (4)].

The thermal behaviour of Cunupia, LaPlaine, Princes Town, River Estate, Talparo and Wood Ford Hill soil-clays is similar in many ways to that of Capitol soil-clay. They all exhibit the low temperature endotherm for sorbed water at around 110 ± 10°C and oxidation endotherms for the degradation of organic matter in the untreated samples run in air. Wood Ford Hill soil did not show this exotherm. Instead, the untreated soil tested in air gave a relatively large and distinct endotherm at 300°C. This soil is very low in organic matter — the temperature region representing the emission of volatile organic material is around 300 ± 50°C. They all show the characteristic dehydroxyla-

TABLE 1

DTA reaction temperature — Capitol soil-clay

Conditions	Temp. (°C)(E/X) [a]
Untreated; air	100(E); 346(X); 555(E); 950(X)
Mg^{2+}-saturated; air	105(E); 328(X); 556(E); 940(X)
Untreated; N_2	98(E); 280(E); 520(E); 940(X)
Mg^{2+}-saturated; N_2	104(E); —; 530(E); 960(X)

[a] E = endotherm; X = exotherm.

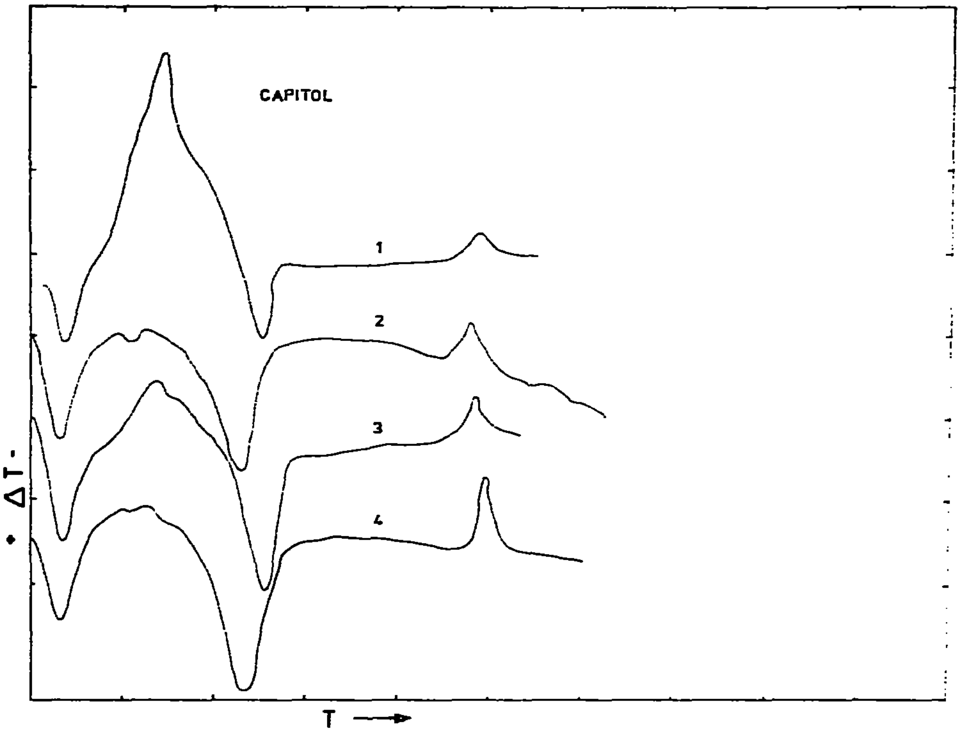

Fig. 1. DTA patterns of Capitol soil-clays from Grenada, West Indies.

tion endotherm at 540 ± 25°C, and sharp (treated sample) or rounded (untreated sample) exotherm at 980 ± 40°C. Princes Town is the only exception, which shows the solid state transition at 1035°C for the untreated soil and two distinct exotherms at 965°C and 1075°C [Fig. 2 (10)] [2]. The variations in temperature between soils are due to the other constituents present.

Identification

The DTA patterns of the seven soils run under nitrogen gas are shown in Fig. 2, and Fig. 3 shows the DTA thermograms of clay mineral standards. The position and shape of these patterns were used as the basis for identification, calculations of the heats of reaction, and amounts of kaolinite present in the soils studied (Tables 2 and 3). The details of the supporting evidence of X-ray diffraction with DTA of these soils will be presented in a later paper [5].

Loss of structural hydroxyl of kaolinite from these soil-clays usually result in an endothermic peak near 520°C when run under nitrogen gas and near 550°C when run in air. These temperatures are considerably lower than the values obtained for pure, well-crystallized kaolinite (Table 2) from Wyoming, U.S.A. This would indicate that this group of soils is comprised of an intimate mixture of clay minerals of kaolinite, high concentrations of kaolinite and not necessarily that the kaolinite is poorly crystalline.

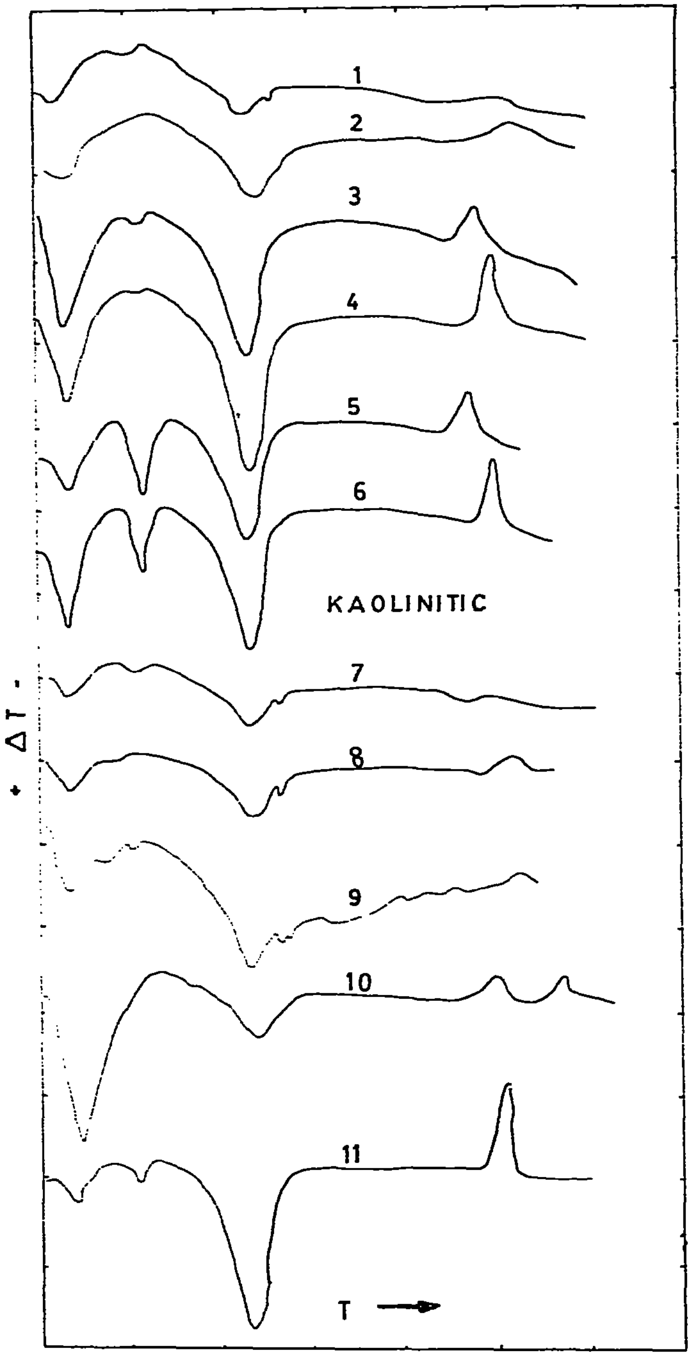

Fig. 2. DTA thermograms of some West Indian soils high in kaolinite (run under N_2 gas).

The Cunupia clay from Northern Trinidad [Fig. 2 (1) and (2)] and the Talparo clay from Central Trinidad [Fig. 2 (7) and (8)] appear to contain more poorly crystalline kaolinite than the other clays in this group. The intimacy of the mixing of the clay minerals in these clays is greater, however, as is seen from the fact that although the temperature for the loss of hydroxyl water is similar for all these soils, this loss is more gradual and is

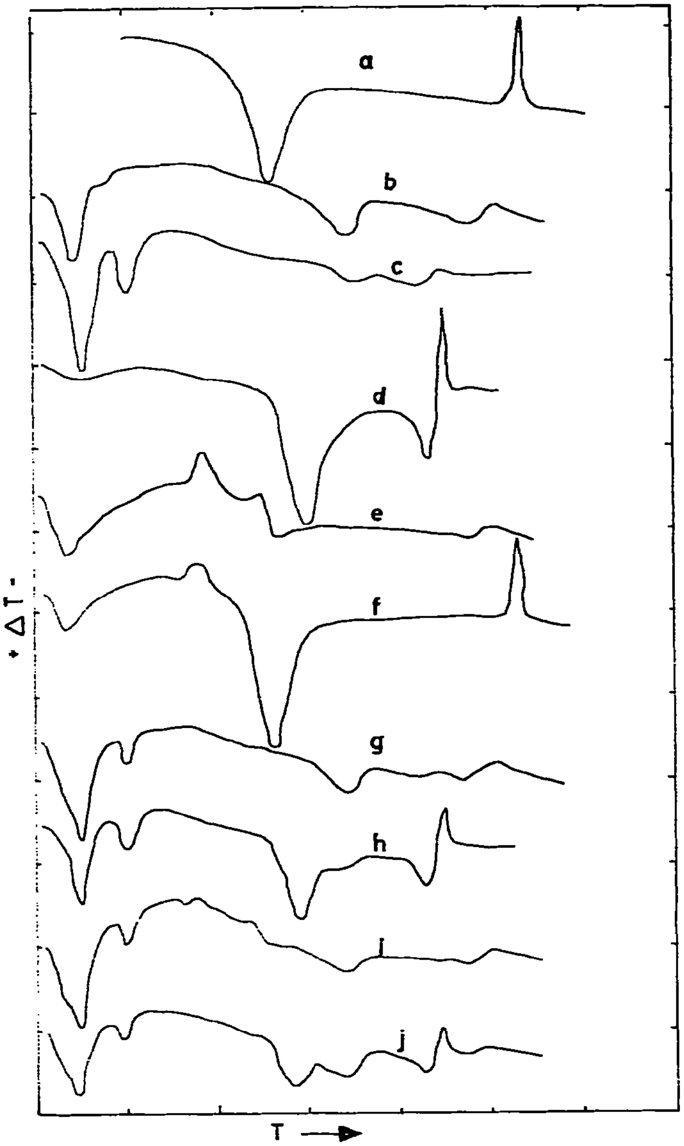

Fig. 3. DTA patterns of standard samples of clay minerals.

spread out over a wider temperature range for the Cunupia and Talparo clays. The 573°C endotherm for the α—β transition of quartz appears as a shoulder in this broad reaction endotherm. The Talparo clay contains a higher percentage of quartz and, therefore, the quartz inversion endotherm is more pronounced (larger area per weight of sample). These two soils from different areas of Trinidad are quite similar. This is clearly evident from their DTA thermograms — the thermograms of the virgin soils and those of the magnesium-treated soils are almost identical [Fig. 2 (1), (2), (7) and (8)]. They contain kaolinite, montmorillonite and quartz as their main clay minerals, with some illite and montmorillonoid.

Capitol clay from Grenada [Fig. 2 (3) and (4)] and Wood Ford Hill clay

TABLE 2

DTA reaction temperatures and heats of reaction for standards

Standards [a]	Wt. (mg)	ΔH (mcal mg^{-1})	Peak T (°C)
Pure zinc	43.9	27.0	430(E)
	56.0	27.0	434(E)
Pure tin	72.9	14.2	241(E)
Pure idium	85.3	6.79	145, 169(E, E)

Standards [b]	Peak temp. (°C)(E/X) [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 (1 : 1)	106(E); 424(X); 575(E); 1010(X)
Vermiculite—chlorite (1 : 1)	145(E); 259(E); 621(E); 862(E); 882(X)
Montmorillonite—vermiculite (1 : 1)	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)

[a] = used in quantitative calculation.
[b] = used for qualitative identification.
[c] E = endothermic; X = exothermic.

from Dominica [Fig. 2 (5) and (6)] are essentially kaolinitic with some montmorillonite and illite (Table 4). X-Ray diffraction patterns show high concentrations of kaolinite, some montmorillonite and a trace of quartz [1]. The presence of quartz was not evident from the DTA studies.

TABLE 3

Heats of reactions (kJ kg^{-1}) of some kaolinitic West Indian soils

Soils	Heats of reaction	
	Dehydroxylation	Solid state (phase) transition
Capitol	2.42 × 10^5 (U); 2.36 × 10^5 (T)	3.61 × 10^4 (U); 4.67 × 10^4 (T)
Cunupia	3.75 × 10^4 (U); 1.20 × 10^5 (T)	2.67 × 10^4 (T)
LaPlaine	1.67 × 10^5 (U); 3.17 × 10^5 (T)	2.11 × 10^4 (U); 4.0 × 10^4 (T)
Princes Town	8.79 × 10^5 (T)	1.50 × 10^4 (T)
River Estate	2.12 × 10^4 (U); 7.46 × 10^4 (T)	5.74 × 10^3 (T)
Talparo	9.97 × 10^4 (U); 1.04 × 10^5 (T)	1.52 × 10^4 (T)
Wood Ford Hill	1.84 × 10^5 (U); 2.45 × 10^5 (T)	3.75 × 10^4 (U) 4.75 × 10^4 (T)

U = Untreated; T = treated.

TABLE 4

Soils, origin and clay mineral (%) contents

Soils	Country	Kaolinite	Others [a]
Capitol	Grenada	85 ± 5 (+G)	15 ± 5(M)
Cunupia	Trinidad	35 ± 5	25 ± 5(M); 5(V); 20(I); 5(Go); Tr(Q)
LaPlaine	Dominica	45 ± 5	6(Go)
Princes Town	Trinidad	35 ± 5	35 ± 5(M); Tr(Q)
River Estate	Trinidad	25 ± 5	50(I); 8(Go); 4(M)
Talparo	Trinidad	35 ± 5	25 ± 2(M); 20(I); 4(Go); Tr(Q)
Wood Ford Hill	Dominica	85 ± 5(+G)	15 ± 5(I)

[a] G = Gibbsite; Go = goethite; I = illite; M = montmorillonite; Q = quartz; V = vermiculite; Tr = traces of.

The River Estate clay from Trinidad [Fig. 2 (9)] contains considerable amounts of both kaolinite and illite. It also contains small quantities of montmorillonite, quartz and interstratified chlorite—vermiculite.

The Princes Town soil gave DTA patterns indicative of the presence of montmorillonite but containing some kaolinite [Fig. 2 (10)]. This thermogram shows the diagnostic high temperature recrystallization exotherm for kaolinite.

The DTA thermogram of the LaPlaine soil [Fig. 2 (11)] contains features characteristic of clay kaolinite.

The soils analyzed in air required more energy to initiate the removal of structural hydroxyl groups than are required for the analyses done under nitrogen (Table 3). Except in the case of Capitol soil in which the energy of dehydroxylation is essentially the same for the untreated and treated soil-clays, the energies required for both dehydroxylations and crystalline transformations are higher for the treated clays than for the virgin soils (Table 3). This is expected since for unit mass of material, the concentration of kaolinite is greater in the treated sample.

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