STUDY OF SOME INDIGENOUS MINERALS BY DTA

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Thermal characteristics of some of the indigenous minerals such as clays, asbestos, talc, bauxite, calcite, magnesite and dolomite have been studied by means of a differential thermal analysis apparatus assembled at North Regional Laboratories.

Differential thermal method appears to have been first employed by LeChatelier[1] in 1897. With the advent of modern development in electronics there were great improvements in instrumentation. DTA has been successfully applied in the solution of problems in mineralogy, chemistry and ceramics.

Orcel[2] started his pioneering work in 1926 by using this technique in mineralogical investigations. Mlle Caillere[3] employed this technique in her studies of thermal dissociation of serpentine rocks. A review of the publications of DTA upto 1958 has been published by Smothers and Chiang.[4]

A simple DTA apparatus has been assembled in these Laboratories for studying the thermal characteristics of some of the indigenous minerals.

The schematic diagram of the apparatus used is shown in Fig. 1.

The sample powdered to pass 100 mesh sieve and ignited alumina (inert) are taken in the three holes of a stainless steel crucible (Fig. 1) and then subjected to a uniform rise of temperature (10°C/min) in a vertical furnace with nichrome wires as the heating element. Each hole of the curcible contains about 0.3 g of the material. The furnace temperature is controlled manually by a variable transformer. Chromel–alumel thermocouples (25 gauge) are used for recording temperature. The differential temperature is recorded on an automatic Cambridge recorder having a scale between +1 mV and −1 mV. The recorder driven by an electrical clock dots every 20 sec on a chart 95 mm wide with a duration of 125 min. For a given thermal reaction the recorder may be made to record either upward or downward from the base line depending on the position of the reacting sample with respect to the beads of the differential thermocouple.

DTA curves of minerals are strictly not constant due to the several factors inherent in the instrumentation. Quartz and sodium chloride were used for calibrating the instrument. Thermocouple beads were found to be attacked by sodium chloride at high temperatures. After resoldering the beads the setting was recalibrated with quartz; the results obtained were reproducible.

Fig. 2 gives the DTA curves of the above substances. In Table 1 the temperature of decomposition or inversion found is compared with that of the reported temperature.[4] The recorded temperature is within ± 3°C of the reported temperature. No attempt was made to calibrate the instrument for heat of reaction.

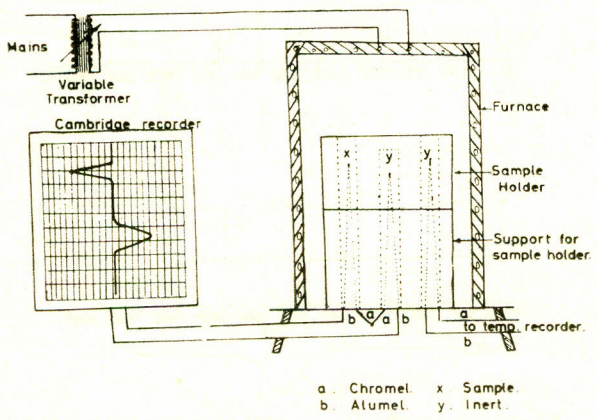

Fig.1.—Schematic diagram of the apparatus.

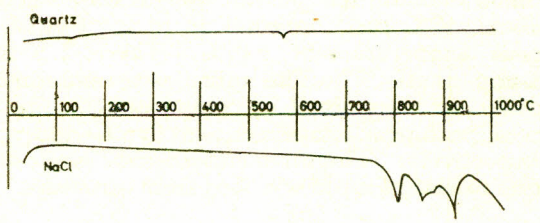

Fig. 2.—DTA curves of quartz and sodium chloride

TABLE 1.—COMPARISON BETWEEN OBSERVED AND REPORTED PEAK TEMPERATURES OF QUARTZ AND SODIUM CHLORIDE.

	Quartz	NaCl
Observed peak ..	572°C	807°C
Decomposition or inversion (reported) ..	575°C	804°C
Difference ..	−3°C	+3°C

Results and Discussion

DTA curves of some indigenous minerals have been obtained by the arrangement described above.

Clays

1. *Kaolin.*—In Fig. 3 the curve a is that of the pure kaolin from Hirshan, upper Palitanate, Baveria and is included here for comparison. The curves b, c and d are of fireclays from Khyber, Jhelum and Khewra. The endothermic (about 600°C) and exothermic (about 1000°C) peaks of fireclays from Khyber and Jhelum are comparable to that of Hirshan kaolin. The endothermic reaction occurs due to dehydration of structural water (or conversion of α-quartz to β-quartz) and the exothermic is most probably due to the formation of γ-Al_2O_3 (and/or mullite). Fireclays from Khewra (curve d) and from Swat (curve e) have small endothermic peaks with a major shift towards lower temperatures. The exothermic peaks at about 1000°C are absent in both the clays. These points suggest that the proportion of kaolin minerals is small in the two samples. Further investigation of Swat clay has shown that the bulk of the clay is quartz and plagioclase feldspars.

2. *Montmorillonite.*—Jhelum bentonite (Fig. 3, curve f) is characterized by a large and two small endothermic peaks, dehydration starts at about 35°C and continues up to 225°C, with the peak temperature at 143°C. There is a small hump at 185°C. The other two endothermic peaks are very small in comparison to the first peak, with peak temperatures at 672°C and 759°C respectively. The three endothermic peaks occur due to loss of hydroxyl ions from structure.

3. *Illite.*—The clay is from North Regional Laboratories soil. The soil is an alluvial deposit. The clay was first treated with dilute acetic acid in order ot remove carbonate minerals. The clay portion was then separated from the bulk by sedimentation.

The clay is characterized by an initial endothermic reaction (cruve g) between 70°C and 170°C corresponding to loss of adsorbed water, a second endothermic reaction beginning at about 450°C with peak at about 560°C and a third slight endothermic reaction between 865°C and 920°C.

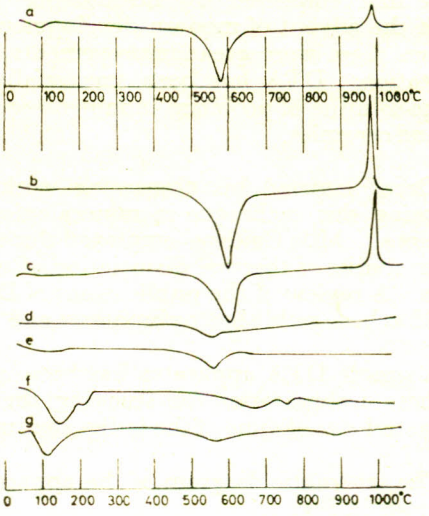

Fig. 3.—DTA curves of clay minerals, a, pure kaolin; b, fire clay from Khyber; c, fire clay from Jhelum; d, fire clay from Khewra; e, clay from Swat; f, Jhelum bentonite; g, clay from NRL soil.

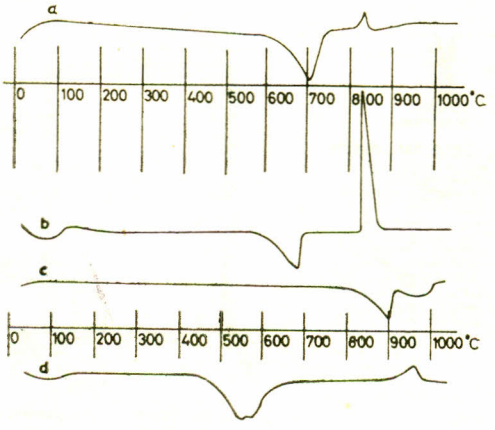

Fig. 4.—DTA curves: a, Canadian chrysotile; b, Qilla chrysotile; c, talc from Khyber Agency; d, bauxite from Margala Hills, Rawalpindi.

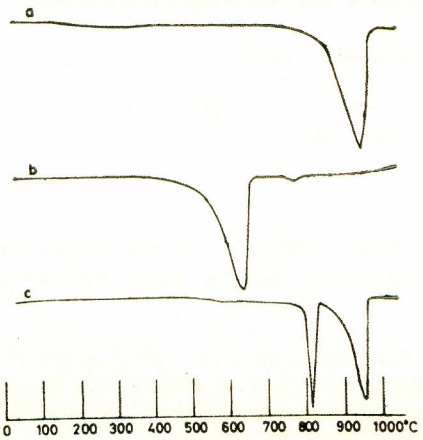

Fig. 5.—DTA curves of carbonate minerals; a, calcite from Khyber Agency; b, magnesite from Hindu Bagh; c, dolomite from Mardan.

Asbestos

Chrysotile, $H_4Mg_3Si_2O_9$.—The sample is from Qilla area of Charsadda Tehsil. The curve b (Fig. 4) is compared with that of the Canadian chrysotile (curve 1). The Qilla chrysotile is characterised by an endothermic peak, which begins at 590°C, reaches the peak at 687°C and ends at 690°C. The exothermic peak is very sharp, begins at 830°C reaches the peak at 833°C, and ends at 870°C. The endothermic peak is due to the liberation of hydroxyl ions, whereas exothermic peak is most probably due to the recrystallisation into forsterite.[5] The Qilla chrysotile could be used as heat insulating material up to a temperature of 600°C without destroying the mineral structure.

Talc, $Mg_3Si_4O_{10}(OH)_2$

The specimen is from Jamrud, Khyber Agency. The talc (Fig. 4, curve c) is marked by an endothermic peak which begins at 844°C, reaches the peak at 902°C and ends sharply at 916°C. The endothermic peak occurs due to the dehydration of structural water.

Bauxite

Hydrated oxides of iron and aluminium. The specimen is from Margala Hills, Rawalpindi. A small endothermic peak (Fig. 4, curve d) between room temperature and 140°C occurs due to the removal of adsorbed water. Decompositions of diaspore (or boehmite) begins at 450°C. Two endothermic peaks occur at 553°C and 582°C with a hump between the peaks; this hump is characteristic of bauxite. The reaction ends at 687°C. The exothermic reaction occurs between 911°C and 980°C with a peak at 956°C. This reaction is most probably due to the formation of γ-Al_2O_3. The endothermic and exothermic peaks at 582°C and 596°C are also indicative of the presence of kaolin clay mineral.

Carbonate Minerals

1. *Calcite*. $CaCO_3$.—The specimen is from Khyber Agency. The endothermic decomposition (Fig. 5, curve a) begins at 740°C, reaches a peak at 952°C, and ends rapidly at 986°C.

2. *Magnesite*. $MgCO_3$.—The specimen is from Hindu Bagh. The decomposition (Fig. 5, curve b) begins slowly at 370°C, reaches a peak at 638°C and ends rapidly at 662°C.

3. *Dolomite* $CaMg(CO_3)_2$.—The specimen is from Ghundai Tarako Hills, Swabi Tehsil, Distt. Mardan. It is essentially a dolomitic marble. The DTA curve c (Fig. 5) has two endothermic breaks: the first begins slowly at 730°C and continues to 800°C, suddenly falls at 800°C, reaches a peak at 814°C and ends rapidly at 836°C; the second begins at 836°C, reaches a peak at 954°C, and ends at 970°C. The first peak is due to the decomposition of $MgCO_3$, a part of the dolomite structure, and takes place 176 degrees higher than the peak temperature for magnesite. The second peak is due to the complete decomposition of dolomite structure, and takes place at comparable temperature to that of calcite.

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