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THERMOGRAVIMETRY OF SURFACE SILT IN THE PROVINCE OF TUCUMAN (ARGENTINA): KINETIC STUDY

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ABSTRACT

Thermogravimetry, differential thermogravimetry, differential thermal analysis and X-ray diffraction have been used to study the thermal decomposition and determination of surface silt components. Smectite and illite, as well as kaolinite and chlorite, were determined to be the major and minor components, respectively.

Dehydration, oxidation of organic matter, partial dehydroxylation, destruction of the crystalline structure and final dehydroxylation were observed in the thermogravimetric curves.

The method of Coats and Redfern was applied in the kinetics of the dehydroxylation process (420–770 °C). E_a values from 38 to 100 kJ mol^{-1} for reaction order $n = 0.5$, 1 or 2 were obtained.

INTRODUCTION

The thermal decomposition of samples of surface silt taken from a large area has been studied in order to establish the stages of dehydroxylation and their effects on the ceramic behaviour of the materials studied. The study area is a flat plain east of Sierra del Campo, Burruyacu, Tucuman, and consists of silty soils up to 2 m average depth.

Nine samples of ceramic interest were chosen from 44 control points in the field. Essential information on the geology, mineralogy, clay mineralogy and chemical composition of these silty soils can be found in Bossi et al. [1] and Vece et al. [2].

The species of argilominerals present in these samples have been identified by means of X-ray diffraction (XRD). They consist of a mixture of about 50–50% smectite and illite (with lesser proportions, 50%, of kaolinite and chlorite). Quartz and alkaline feldspar are the accessory minerals. The amount of chlorite and kaolinite is very low in all samples, except in sample

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A-60, where the presence of kaolinite (5–10% according to XRD) is shown in the differential thermal analysis (DTA) results.

METHODS

The nine samples chosen come from pits A-60, A-65, A-71, A-73, A-74, A-75, B-9 and B-10 and from a surface profile A-56. Sample A-56 is trenched in terraced silt horizon below the other nine samples. This lower horizon is rich in clay and smectite originating from the weathering of Tertiary outcrops. The shrinking rate in brick of this clay at a temperature of 950 ° C is high [2].

All samples were collected from fresh material below the hardpan (1.8–2 m depth). Samples, 5 kg in weight, were labelled and stored in plastic bags. In the laboratory, samples were reduced in size to 1 to 2 mm, and a second split was made to obtain samples approximately 200 g in weight. Sub-samples were ground slightly, oven dried, homogenized and stored through a 40 mesh tyler sieve.

For the thermogravimetric analyses (TG and DTG), 25 mg of homogenized sub-sample was used. Analyses were conducted in an oxygen atmosphere with a heating rate of 20 ° C min^{-1} (Stanton Redcroft equipment). For DTA, 75 mg of the homogenized sub-sample was used. The records were obtained in a nitrogen atmosphere with a heating rate of 15 ° C min^{-1} using Al_2O_3 as a reference (Mettler equipment).

For X-ray diffraction (XRD), a 2 micron fraction of a stable solution in distilled water was removed with a dropper, the content of which was poured on three halves of slides. The slides were left to dry under a 40 W lamp. The clay lamellae thus obtained are described as "oriented". Once dried, these lamellae were put through a Philips diffractometer with a vertical goniometer and a cobalt cathode, at a rate of 1° 2θ min^{-1} and recorded on paper at 5 mm min^{-1}. Three preparations were irradiated and analyzed: (1) dried in air, (2) heated at 250 ° C for 15 h and (3) glycerolated and heated at 250 ° C for 15 h. The relative behaviour of the three diagrams allowed a rough estimation of quantities of smectite vs. illite as defined by differences in areas under the peak of 10 Å [3]. The peaks at 3.52 Å made it possible to estimate the approximate proportion of chlorite and kaolinite respectively according to their relative heights.

RESULTS

Study of thermal decomposition

Figures 1–3 show the typical TG, DTG and DTA curves obtained through decomposition (in the range 25–950 ° C) of samples A-56, A-75 and A-60 respectively, along with the corresponding XRD results.

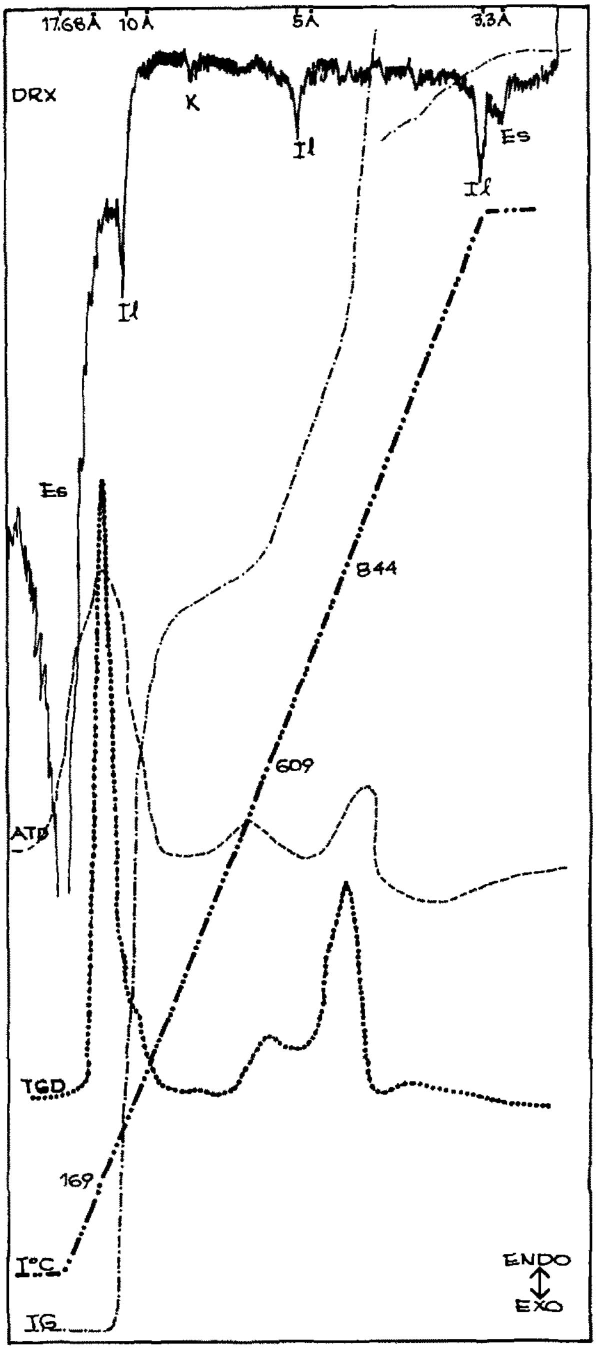

Fig. 1. Thermal behaviour (DTA and DTG) and X-ray diagram of sample A-56, rich in smectite derived from the destruction of a clay formation of the Upper Tertiary (Es, smectite; Se, sericite; Il, illite; K, kaolinite; and Q, quartz).

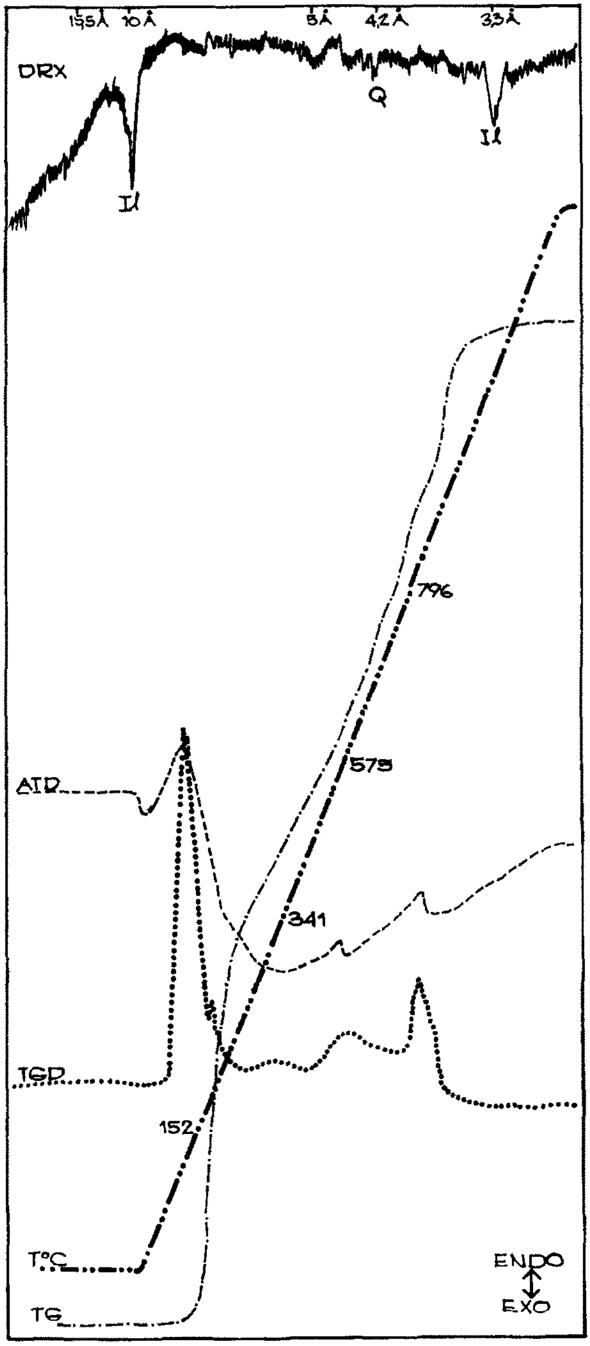

Fig. 2. Thermal behaviour (DTA and DTG) and X-ray diagram of sample A-75 which shows the typical characteristics of material derived from crystalline basement meteorization, Precambrian in recent climatic cycle.

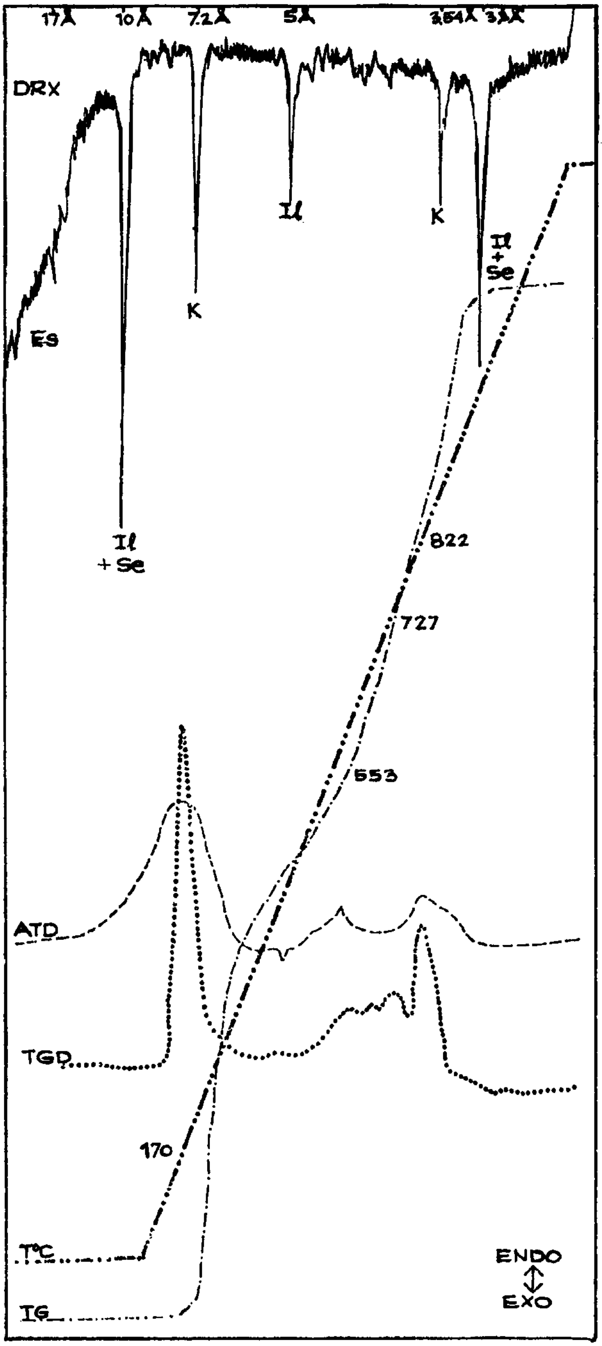

Fig. 3. Thermal behaviour (DTA and DTG) and X-ray diagram of sample A-60, which shows a significant concentration of kaolinite derived from the destruction of Lower Tertiary formation.

TABLE 1

Significant areas in the TG and DTG diagrams, temperature ranges, maximum temperatures, initial mass, final mass, cumulative mass loss percentage and mass loss percentage for each area

Sample	Zone	t_i (°C)	$t_{max.}$ (°C)	t_f (°C)	m_i (mg)	m_f (mg)	Cumul. mass loss (%)	Mass loss (%)
A-56	Zone 1	25	169	264	22.80	21.43	6.01	6.01
	Zone 2	264	609	671	21.43	21.07	7.59	1.58
	Zone 3	671	844	950	21.07	20.15	11.62	4.03
	Zone 4							
	Total				22.80	20.15	11.62	
A-75	Zone 1	25	152	249	24.25	23.37	3.63	3.63
	Zone 2	249	341	451	23.37	23.16	4.49	0.86
	Zone 3	451	575	746	23.16	22.65	6.60	2.11
	Zone 4	746	796	950	22.65	22.37	7.75	1.11
	Total				24.25	22.37	7.75	
A-60	Zone 1	25	170	246	23.95	23.17	3.26	3.26
	Zone 2	246	360	428	23.17	23.02	3.88	0.62
	Zone 3	428	553–727	772	23.02	22.37	6.59	2.71
	Zone 4	772	822	950	22.37	22.06	7.89	1.3
	Total				23.95	22.06	7.89	

The TG and DTG curves show similar behaviour in all samples, with four significant areas being defined: (1) 25–249 °C; (2) 250–470 °C; (3) 471–745 °C and (4) 746–950 °C, with a loss of mass of about 3.63%, 0.86%, 2.11% and 1.15% respectively, and a total loss of mass of 7.75%. Table 1 shows the temperature ranges for every zone, the corresponding maximum temperatures, percentage of loss of mass and cumulative loss.

The losses of mass in Zone 1 (mainly between 80 °C and 125 °C) are due to the water superficially adsorbed and to that associated to the cations $(Ca(H_2O)_6)^{2+}$ and $(Mg(H_2O)_6)^{2+}$ [4–6]. The most prominent peaks with the most loss of mass are those of the samples bearing the highest content of smectite. DTA plots show an endothermic peak with similar characteristics to those of DTG at a maximum temperature of 100 °C (Figs. 1–3) [7]. The smectite materials are characterized by an outstanding development of that endothermic peak [8].

There is a slight loss of mass in Zone 2, which in soil is attributable mainly to the oxidation of organic matter [4,6,10]. In this case the sampling excludes the A organic horizon in such a way that organic matter constitutes less than 2%. This quantity of organic matter generates an exothermic zone which is shown in DTA and DTG diagrams (Fig. 1). On the other hand, it is well known that smectite interlayers dehydrate slowly between 100 and 300 °C, so that, if the quantity of organic matter is small (lower than 1%), this can be compensated for by the loss of water in the interlayer (which would, conversely, generate endothermic reaction).

There is a loss of mass of about 2.11% in Zone 3 in the temperature range 471–745 °C, due to a process of dehydroxylation of the two species of clays present in the samples: illite, which has a small endothermic peak, the maximum of which is between 540 and 550 °C; and kaolinite, which exhibits a more prominent and characteristic endothermic peak, between 550 and 575 °C [6,7,8–10,11]. In sample A-60 (Fig. 3) where the kaolinite reaches 10% of the total volume, that peak is clearly shown at 575 °C in DTA and 563 °C in DTG. In the XRD oriented lamellae previously heated to 550 °C, the characteristic kaolinite peaks disappear at 7.2 and 3.57 Å which shows that the dehydroxylation and destruction of the crystalline structure takes place at this temperature [6–8,12–14].

Zone 4 shows an outstanding endothermic peak in DTA between 700 and 750 °C which corresponds to the generalized destruction of the crystalline structure of clays 2 : 1 in illite and smectite and final dehydroxylation (Figs. 1–3) [6–10]. As the set of analysed samples (except A-60) shows an almost constant percentage of illite, the variations of the areas of endothermic peaks are almost exclusively due to the smectite. The correlation coefficient between the area of the endothermic peak at 700–780 °C in DTA and of the 001 peak of smectite (15–17 Å) is positive and very high ($r = 0.95$). It is also evident that the crystallinity of the smectite has an influence on the development of the endothermic peak, this being several times larger in samples A-75 and A-56 (Figs. 1 and 2) with excellent crystallinity.

The quantity of chlorite in every sample analyzed is so low that its share could not be seen in the DTG and DTA.

Kinetics of the dehydroxylation process

The kinetics of the dehydroxylation process has been studied using the method of Coats and Redfern [15] for all the samples analysed within the temperature range 420–770 °C.

For a reaction of the type $a\mathrm{A(s)} \rightarrow b\mathrm{B(s)} + c\mathrm{C(g)}$ it is expressed for the values of the order of reaction n other than one thus:

$$\log(1 - (1 - \alpha)1 - n/T^2(1 - n) = \log AR/aE(1 - 2RT/E) - E/2.3RT \tag{1}$$

while when $n = 1$:

$$\log(-\log(1 - \alpha)/T^2) = \log AR/aE(1 - 2RT/E) - E/2.3RT \tag{2}$$

where α = time t, being equal to $w_\mathrm{i} - w_\mathrm{t}/w_\mathrm{i} - w_\infty$; w_i is the initial mass, w_t is the mass at time t and w_∞ is the final mass; n is the reaction order; T is the absolute temperature; A is the frequency factor; E is the activation energy; R is the gas constant.

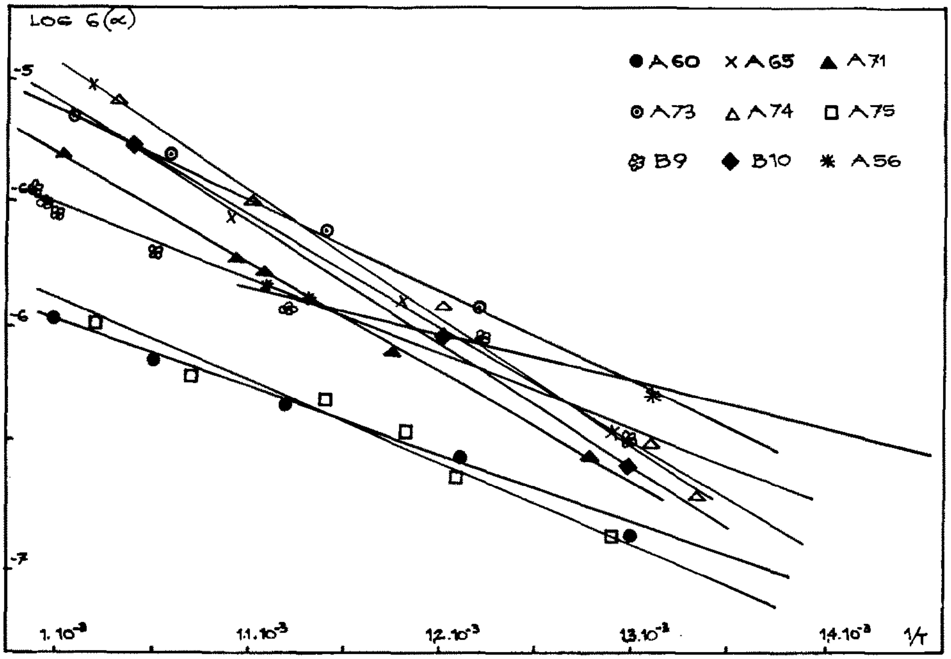

Fig. 4. Logarithmic curves of G(α) vs. $1/T$ for the samples analyzed.

If we plot the second term of eqns. (1) and (2) as a function of $1/T$, the result is a straight line, the tangent of which is $E/2.3R$ for the correct value of n. The data for each sample were plotted as a function of $1/T$ (Fig. 4). The E data obtained range between 38 and 100 kJ mol^{-1} for values of $n = 0.5$, 1 and 2 (Table 2). These values are within the range of activation energies obtained by other authors [1–16].

TABLE 2

Kinetic data summary in the dehydroxylation process of the samples analysed

Sample	Temperature range (°C)	n	E_a (kJ mol^{-1})	r [a]
A-60	428–772	1	54.472	0.99813
A-65	429–755	2	100.597	0.99315
A-71	447–763	2	86.630	0.99772
A-73	428–751	2	81.242	0.99661
A-74	444–748	2	94.132	0.99902
A-75	451–746	1	62.093	0.99301
B-9	436–950	2	47.808	0.98211
B-10	443–737	2	93.392	0.99577
A-56	264–671	0.5	38.300	0.99139

[a] Correlation coefficient.

CONCLUSIONS

(1) In a general way, the samples studied showed similar behaviour when thermally treated.

(2) The percentage loss of humidity in the first zone varies according to the mineralogical composition, specially in relation to the proportion of smectite and crystallinity.

(3) The loss of mass in Zone 2 does not exhibit outstanding peaks, partly due to the antagonism between oxidation of organic matter (exothermic) and dehydration of the interlayer of the smectite (endothermic).

(4) A loss of mass that ranges between 2 and 4% is produced in Zones 3 and 4 which is attributable mainly to the kaolinite and illite dehydroxylation (Zone 3) and clay dehydroxylation 2 : 1 in Zone 4.

(5) The greater the proportion and crystallinity of smectite, the more obvious is the dehydroxylation of structures 2 : 1 in Zone 4.

(6) There is a strong correlation between the peak area in the region 700–780 °C (endothermic) of the DTA and the 001 smectite peak in the diagrams relating to samples dried in air. Nevertheless, this effect will have to be studied in a greater number of samples in order to understand its evolution and reliability.

(7) The kinetic description of the clay dehydroxylation process as a reaction in the solid state is rendered difficult by the definition of the thermogravimetric curves which describe clays, and it is not possible to determine the physical and chemical changes involved in materials like the ones studies.

(8) The activation energy values obtained range between 38 and 100 kJ mol^{-1} for reaction orders of $n = 0.5$, 1 and 2.

(9) The E data obtained are in agreement with the results presented by Brown et al. [16] for argilominerals, and by Girgis et al. [14].

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