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QUANTITATIVE DIFFERENTIAL THERMAL ANALYSIS OF SOIL CLAYS AND SILTS

R. J. W. McLAUGHLIN

ABSTRACT. The results of a series of thermal analyses for some clays and silts from soils in varying stages of maturity and derived from an arkosic parent material are quantitatively evaluated, and are correlated with X-ray and chemical analyses. The system investigated comprises kaolinite: quartz; the thermal peaks differ in area with grain-size variation and method of specimen packing.

INTRODUCTION

The theory of differential thermal analysis is based upon the fact that if two samples, one of which undergoes a phase change at a certain temperature, are heated in separate sample holders, the material undergoing the phase change will either absorb or emit heat from or to its surroundings, and thus there will result a difference in temperature between the two materials. Should such a phase change be reversible, then upon cooling the reverse change will be observed to take place. For any one compound a phase change will take place over a temperature range peculiar to that material, and here, therefore, is the means by which qualitative estimation may be effected. The quantitative aspect may be evaluated by measuring the amount of heat involved in the change of a known weight of the material in question, and relating this to standard curves. This heat change associated with phase change is measured by a differential thermocouple, and thus for any reaction a curve may be plotted.

The literature on qualitative estimations is copious, but quantitative measurements are rarer. Le Chatelier (1887)—the originator of the method—suggested that quantitative estimations were possible, but the first apparent application was that of Matějka (1922) working with clays. Among those who have used the method as a quantitative tool in the study of clays are Hendricks and Alexander (1939), Hendricks, Nelson, and Alexander (1940), Norton (1939), Grim and Rowland (1942), Schafer and Russell (1942), Jeffries (1944), Speil et al. (1945), Dean (1947), Grimshaw, Heaton, and Roberts (1945), Kerr and Kulp (1948). These and other workers have pointed out the danger of correlation of unknown specimens with graphs drawn from synthetic mixtures.

In the materials investigated in this work the clays and silts were used as their own standards and hence their physical characteristics remain the same. The apparatus used is rather similar to those described by Norton (1940) and Berkelhamer (1945). Photograhic recording of reflecting galvanometers is employed. The sample block is of nickel and permits three samples to be investigated at one time. Thermocouples are of no. 26 S.W.G. chromel-alumel wire with junctions encased in nickel foil of known weight, and by this means the size of the thermocouple bead can be controlled. The standard used in this work was calcined analar. alumina of weighed amount (0.3000 gm). Temperature rise was linear at 10° C. per miunte up to 400° C., and then gradually increased to 12° C. per minute at 1000° C. Because of the use of nickel foil about the thermocouples, the tables compiled by Roeser, Dahl and Gowens (1935) may not be used, and therefore standardization of the instrument for temperature was absolute, and effected by using thermometrically fixed points: boiling water—100° C., quartz—573° (α - β inversion), barium carbonate—811° and 982° (α - β - γ inversions), strontium carbonate—926° (α - β inversion), lead sulphate—865° (α - β inversion). These values were taken from Kracek (1942). Thus at each of the inversions the offset of the temperature thermocouple from zero could be measured. An almost straight line graph resulted, and this is shown in figure 1. The use of nickel sheathing provided an additional temperature check, for at the magnetic transition of nickel, which Möser (1936) gives at 354° ± 1° C., there is a slight heat effect and the differential thermocouples show a slight indentation in their graph, while the slope of the temperature trace changes abruptly. Thus every record contains in itself a check on the efficiency of the thermocouples.

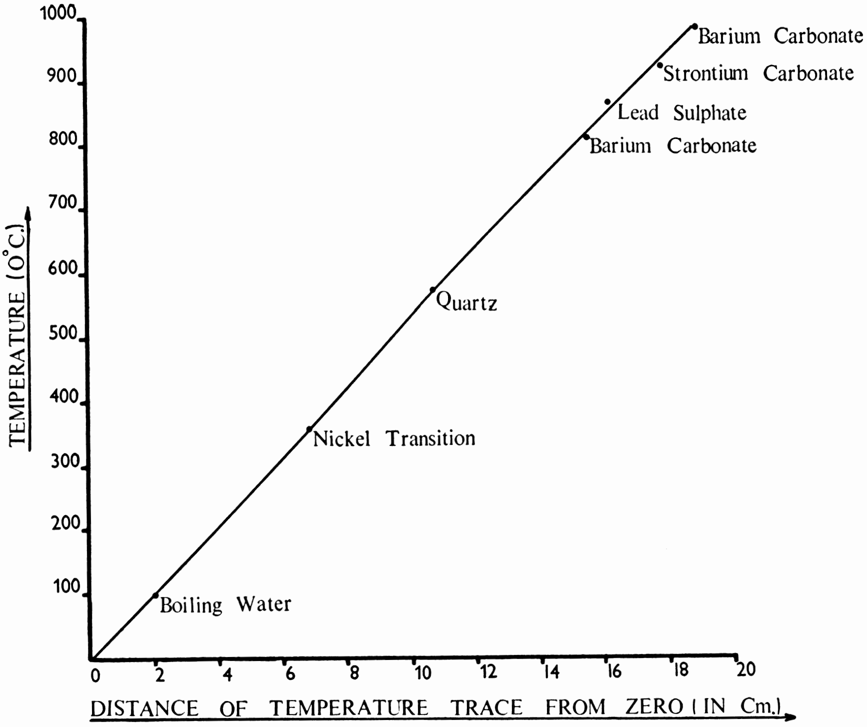

Fig. 1. Temperature of furnace as deduced from displacement of temperature trace from zero.

SAMPLE PREPARATION AND EXPERIMENTAL PROCEDURE

The soils which were investigated were from the northern region of New Zealand and were derived from an arkose. The three discussed in this work vary in stage of maturity; thus profile no. 1 is immature, profile no. 3 is a mature podzol, and profile no. 2 occupies an intermediate position.

The precise localities are: Profile no. 1—Whangarei County, Opuawhanga Survey District, 1½ miles north of Tutukaka on the Tutukaka-Matapouri bay road; Profile no. 2—Whangarei County, Opuawhanga Survey District, 2 miles northeast of Marua on Marua road; Profile no. 3—Whangarei County, Hukerenui Survey District, 2 miles northwest of Ruapekapeka trig. station 4.6 miles southeast of Kawa Kawa.

These soils were subjected to successive treatments with 20 volume hydrogen peroxide to remove organic matter. In most cases two treatments sufficed, but in some rare cases not even 100 volume peroxide would remove the last traces of humic material. The soils were dispersed by shaking in a reciprocating shaker, using ammonium hydroxide as a dispersant. After dispersion, mechanical analysis of the samples was carried out prior to their separation by sedimentation and centrifugal means. The particle size diameters separated were: sand 2 mm-0.02 mm; silt 0.02 mm-0.002 mm; clay $< .002$ mm.

The clay fractions were coagulated from suspension by lowering the pH to about 6.0 and adding a little A.R. sodium chloride. Excess soluble salts were washed from the clays by successive washing with distilled water, using centrifugal means to hasten settling. When chloride could be shown to be absent in the washings, the clays were dried using successively stronger alcohol washings, commencing at 15% and ending with absolute alcohol. To hasten drying several subsequent washings with acetone were given. This last also prevented the clay from drying as a hard cake, and usually a fairly powdery material resulted on drying the clay-acetone suspension. Silt fractions were also dried in a similar manner, but sand fractions were dried from water in an oven at 105° C.

It was found that after a little practice similar weights could be tamped into the sample holes of the thermal analysis block, provided the material remained the same. In all cases the amount of material used was weighed and a constant packing tightness was employed rather than a set weight. The effect of packing upon thermal curves has been commented upon by various workers. Thus Gruver (1948) concluded, using the same weight of sample, that the effect of packing on the type and area of the thermal curve was zero, but noted that texture could influence the reaction slightly. Schafer and Russell (1942) found that if the sample holes were not completely filled a drift of the galvanometer occurred, and that tight packing appeared to increase the area of the curve. Whitehead and Breger (1950) packed to a constant tightness of 530 psi using special tools; these workers used very small weights of material, and therefore packing could become an important factor.

As some specimens were obtainable only in very small amounts, the effects of dilution with calcined alumina were studied, and also the relationships between two methods of dilution. Thus one specimen, the clay fraction of profile 1 at a depth of 20-26 inches, was taken in various amounts. In one set of experiments the material was tamped into the sample hole and the remaining gap filled with calcined alumina. In the second set of experiments the material was tamped between alumina. The two graphs are reproduced in figure 2. For the second set of experiments there is a greater amount of reactive constituent about the thermocouple for similar weights, especially at low values, than in the first series. As a consequence the apparent energy

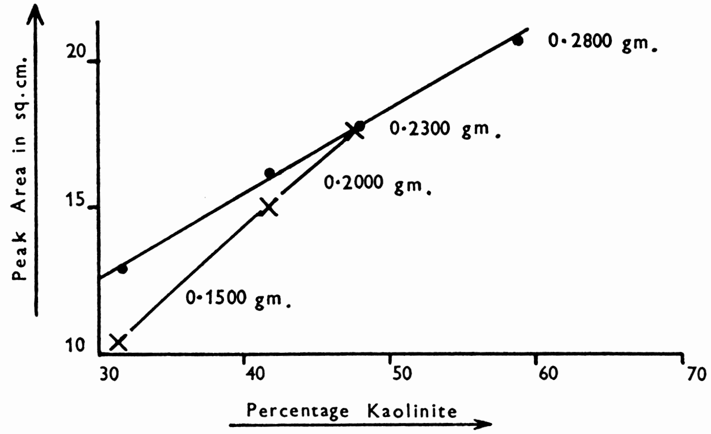

FIG 2

Peak area (570° endothermic) variation with sample dilution

● = Sample packed between Al_2O_3 X = Sample packed under Al_2O_3

intake is greater for the second series, and larger areas result. Schafer and Russell (1942) found a similar effect with kaolinite-halloysite mixtures diluted with alumina when somewhat similar experiments were conducted. Whitehead and Breger (1950) noted maximum effectiveness when the sample was packed about the thermocouple junction. Therefore, if dilution of a sample is necessary due to too violent a reaction, caking effects on heating, lack of material, etc.. care must be taken to dilute the sample in a constant fashion, or quantitative measurements may become meaningless. It will be noticed that the curve for samples packed under alumina is curved whereas that for samples between alumina is straight. Perhaps in this may lie the explanation of the differing views upon whether weight:area curves are straight or sigmoidal. But this would need proof from other samples before being accepted. On the surface, it seems a possible explanation, and, in fact, Wittels (1951) has shown marked departure from linearity in weight:reaction area curves. with variation in mass of reactive constituent.

The relationship between the three differential thermocouple groups was established by using the clay fraction of profile 1, depth 20-26 inches, in duplicate experiments. The areas of the circa 570° C. endothermic peaks were obtained by a planimeter, and the line enclosing the curve was taken as the straight line joining the two points where the curve departs from a steady unidirectional tendency. These points are readily obtainable by laying a straight edge along the photographic record. They are quite arbitrary but they do serve as standard points, and the areas so measured are reproducible with great accuracy. Using the averaged values for the different thermocouple groups, a factorial arrangement was arrived at, and by using the requisite factor a sample run in, say, thermocouple group no. 3 could readily have its curve area converted in terms of thermocouple group no. 2.

TABLE 1
Chemical Analyses of Clay and Silt Fractions

Profile no. and depth in inches	SiO2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	K_2O	Na_2O	Ign. Loss	Total
CLAYS											
No. 1 0-2	46.10	1.66	25.08	9.70	0.06	1.26	0.52	0.96	0.08	15.20	100.62
8-12	48.23	1.45	24.29	9.78	0.01	0.72	0.31	0.68	0.09	14.23	99.79
20-26	46.96	2.71	23.00	12.52	0.05	0.69	0.60	0.41	0.04	13.72	100.70
66-72	41.16	1.30	27.31	12.89	0.01	0.21	0.08	0.13	0.09	16.10	99.28
156-162	40.97	1.50	28.34	11.03	0.06	N.D.	0.29	0.34	0.03	16.82	99.38
No. 2 0-4	44.36	1.50	29.20	6.84	0.02	1.56	0.28	0.44	0.34	16.62	101.16
29-32	38.18	1.69	28.97	13.14	Ab.	0.24	0.28	0.47	0.26	16.84	100.07
No. 3 12-14½	37.95	2.74	21.61	18.25	Ab.	0.30	0.45	0.20	0.18	18.40	100.08
24-28	36.58	1.66	28.86	14.36	Ab.	0.16	0.22	1.63	0.26	15.80	99.53
SILTS											
No. 1 0-2	71.48	0.66	10.53	5.22	0.04	0.23	0.65	0.48	0.24	10.14	99.67
8-12	80.62	0.73	7.07	4.22	0.01	0.03	0.59	0.37	0.27	6.04	99.95
20-26	75.31	0.73	10.71	5.62	0.01	0.20	0.35	0.36	0.20	6.68	100.17
66-72	52.86	1.11	24.31	8.20	0.01	0.28	0.56	0.30	0.11	12.54	100.28
156-162	48.47	1.30	25.57	8.79	0.06	0.12	0.15	0.48	0.14	14.26	99.34
No. 3 0-6	95.91	0.73	0.50	0.28	Ab.	0.09	0.30	0.19	0.18	1.43	99.61
7-9	96.85	0.48	0.61	0.31	Ab.	0.08	0.34	0.09	0.10	0.87	99.73
9-11½	97.07	0.65	0.77	0.34	Ab.	0.10	0.23	0.14	0.14	0.80	100.24
12-14½	90.97	0.64	2.56	3.14	Ab.	0.13	0.26	0.07	0.08	2.36	100.21
24-28	49.70	0.41	30.29	5.86	Ab.	0.06	0.12	0.66	0.16	13.45	100.71
42-48	48.51	0.89	30.56	5.79	Ab.	0.14	0.11	1.72	0.23	12.85	100.80

The efficiency of the thermocouples was checked from time to time, using the same standard sample mentioned above. Thermocouple replacement, due to embrittlement after prolonged use, did not necessarily change the areas (and therefore the factors) very greatly, but the size of the nickel sheath on the thermocouple must be rigidly controlled, or different heat absorption rates by thermocouple junctions result, and in such cases the areas can vary by about 20%.

TABLE 2

Thermal Analysis Data

Profile no. and depth in inches	Weight taken	Area of endothermic peak in sq. cm.	Observed temperature of peak.	Area of endothermic peak corrected to 0.2800 gm.	Al_2O_3%	Al_2O_3% converted to kaolinite%	Number used in figure 3.
			CLAYS				
No. 1 0-2	0.2800	22.4	572° C.	22.4	25.08	63.3	1.
	"	22.5	570	22.5			
8-12	"	20.85	572	20.85	24.29	61.5	2.
	"	20.25	570	20.25			
20-26	"	20.7	572	20.7	23.00	58.3	3.
	"	20.7	572	20.7			
66-72	"	23.2	589	23.2	27.31	69.1	4.
	"	23.4	578	23.2			
156-162	0.2404	23.4	578	27.3	28.34	71.7	5.
	0.2300	22.8	580	26.8			
No. 2 0-4	0.2306	21.85	583	26.5	29.20	73.9	6.
	0.2300	21.7	589	26.4			
29-32	0.2300	22.15	578	27.0	28.97	73.3	7.
		22.65	589	27.6			
No. 3 12-14½	0.1860	11.5	552	17.3	21.61	54.7	8.
	0.1900	11.2	547	16.5			
24-28	0.2042	19.05	578	26.1	28.86	73.1	9.
	0.2100	19.3	572	25.8			
			SILTS				
No. 1 0-2	0.3000	12.2	540 & 572	11.4	10.53	26.7	10.
8-12	0.3500	8.1	540 & 572	6.5	7.07	17.9	11.
20-26	0.3300	11.7	547 & 572	9.9	10.71	27.1	12.
66-72	0.3000	29.8	565	27.8	24.31	61.5	13.
156-162	0.2540	24.1	565	26.6	25.57	64.7	14.
No. 3 0-6	0.3710	1.55	498 & 570	1.2	0.50	1.3	15.
7-9	0.3920	1.2	498 & 570	0.9	0.61	1.3	16.
9-11½	0.3800	2.2	498 & 570	1.6	0.77	2.0	17.
12-14½	0.3500	4.0	521 & 575	3.2	2.56	6.5	18.
24-28	0.2500	27.2	572	30.4	30.29	76.7	19.
42.48	0.2580	30.2	575	35.0	30.56	77.4	20.

The three profiles had selected clay fractions analyzed by X-ray powder diffraction methods. The lines present fell into a general kaolinite-quartz pattern, with one or two very weak or enhanced lines which could be attributed to other oxides reported on later. Selected clay fractions were chemically analyzed; their results appear in table 1. The thermal curves for the series show no signs of other clay minerals such as illite or montmorillonite, and therefore it seems highly reasonable to place all the alumina as kaolinitic alumina. This is further substantiated by the chemical analyses in table 1. Chemical analysis of various pure kaolinites has revealed that the percentage of alumina in the molecule varies (Ross and Kerr, 1931). In this investigation, the idealized lattice value of 39.5% Al_2O_3 has been chosen, and it will be seen that good agreement has been obtained.

In the thermal curves there are two indentations, both being the characteristic kaolinitic pattern, viz. the large endothermic with peak temperatures at about 570-580°-C., and the exothermic with peak temperatures varying considerably about a temperature of 950°. It is inadvisable to use this latter peak in quantitative estimations, for it has been shown by various workers that the iron content alters the peak temperatures and lowers the areas of such curves (Caillère and Hénin, 1947; Grim and Rowland, 1942; Saunders and Giedroyc, 1950). Attention has therefore been confined to the endothermic peak.

Taking the ideal value of 39.5% Al_2O_3 in kaolinite, the alumina figure obtained by chemical analysis (table 1) is converted to kaolinite percentage, and this figure is plotted against the corresponding area of the endothermic peak for that sample. The various data relating to percentage alumina and kaolinite and to the thermal curves have been tabulated in table 2. The remaining silica in the chemical analysis, after sufficient has been taken for kaolinite, would be quartz.

DISCUSSION OF RESULTS

Because of voltage fluctuation of the power supply, the energy input into the furnace was not always the same, hence the variation of peak temperatures on duplicate samples of the same material (table 2). This fluctuation does not affect the peak areas (Speil et al., 1945), and the agreement of these between duplicates is excellent, when the various inherent difficulties of area measurement are considered. It will be noticed, however, that the peak temperature rises with the rise in percentage of kaolinite present, and this property gives therefore an approximation of the amount present. The weights of sample which fit into the holes also reflect the percentage kaolinite in the samples. Thus the maximum area of endothermic peak corresponds with a value of about 0.21 gm; with decrease in percentage kaolinite and therefore decrease in area of the endothermic peak, the weights needed to fill the sample hole rise. This is an expression of the differences in specific gravity and specific volume between kaolinite and quartz. There is one exception to this rule, namely profile 3, depth 12-14½ inches, clay, for this sample contained light organic matter, which could not be removed by the hydrogen peroxide treatment, and therefore the resultant specific gravity is lower than it should be for a simple mixture, and small weights fill the sample hole. As the percentage of kaolinite falls, the quartz peak becomes first of all just discernible as a slight indentation on the up-slope of the kaolinite peak. With a smaller percentage it becomes more visible, and eventually at a very low percentage, less than about 18%, the peak divides into two, and at a value less than about 9% kaolinite there are two well-separated curves.

In plotting the graphs in figure 3 it was necessary to compare a constant weight of sample, and therefore the areas obtained from the graphs have

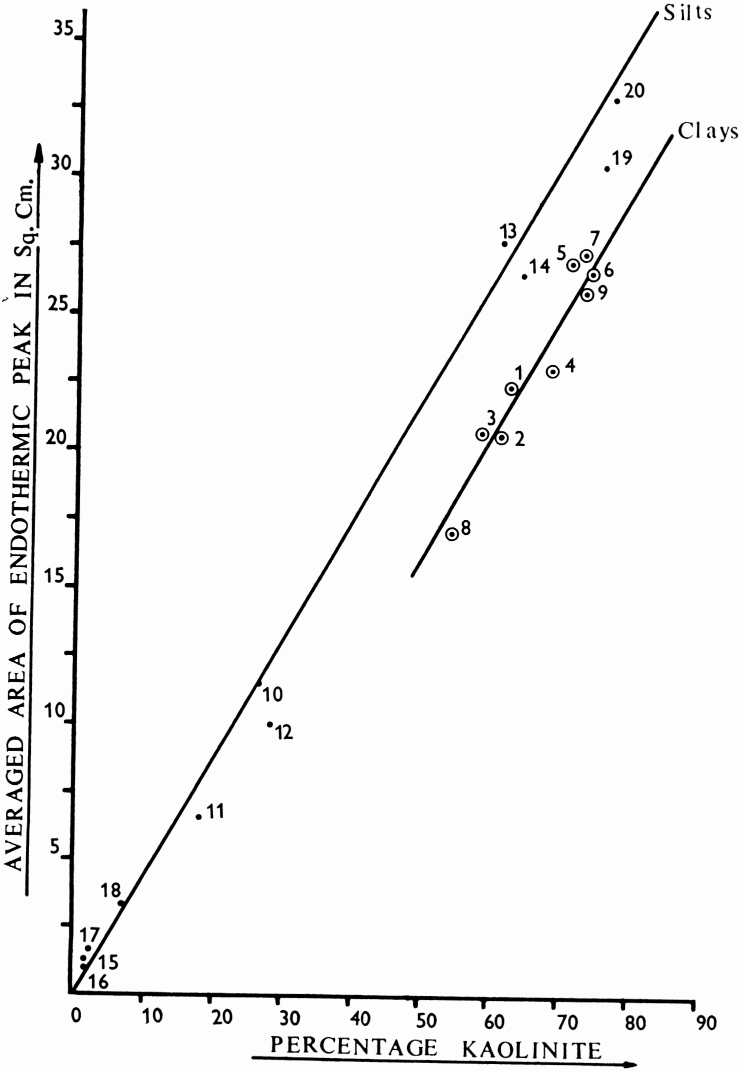

Fig. 3. Relation between endothermic peak area and percentage kaolinite for silts and clays.

been corrected to a value of 0.2800 gm. This value is arbitrary and was chosen because it is an average weight for these and other clay samples investigated. The validity of this correction finds substantiation in the graph of samples of differing weights packed between alumina and shown in figure 2.

The agreement among the clays plotted in figure 3 is surprisingly good when consideration is taken of the various inherent difficulties of the method. Furthermore, some samples such as profile 3, depth 12-14½ inches, clay, contained organic matter which even 100 vol. H_2O_2 would not remove, and the exothermic dome caused by the oxidation of this material interferes with accurate measurements of the kaolinite endothermic peak area. For the accurate quantitative determination of such contaminated samples, either a vacuum or inert atmosphere is required in the furnace; with the application of such apparatus to the problem, the scatter observed in figure 3 would be much reduced.

Agreement among the silt fractions is not so marked. The reason here is found if attention is directed to the alkali figures for these samples in table 1. It will be observed that the alkali contents are, generally speaking, much higher than for the clays. Consequently, some portion of the alumina which has been calculated as kaolinitic alumina must be in combination with the alkali as an alumino-silicate. It is for this reason that scatter is more pronounced, and also that the graph has been placed in a position which is not the most geometrically advantageous if the points are taken by themselves and alkali contents are neglected. When it is realized that 1% of Na_2O and/or K_2O will utilize approximately 2% Al_2O_3 in feldspar or micaceous structures, and that this in turn corresponds to an amount of approximately 5% kaolinite which should be subtracted from the calculated amounts of figure 3 and table 2, the scatter is readily explained. The impurity present in these samples is probably either feldspar or the sericitic decomposition product of feldspar, but positive data as to which is present is lacking.

Direct agreement between X-ray powder photographs, thermal analysis (table 2), and chemical analysis (table 1) is exhibited by a consideration of samples no. 1, depth 20-26 inches, clay, and no. 2, depth 29-32 inches, clay. The line strengths of these and pure kaolinite and pure quartz are tabulated in table 3.

Taking the two samples, calculating all the alumina as kaolinite, and allowing the ideal value of 39.5% Al_2O_3 to 46.5% SiO2, the amounts of SiO_2 needed for the kaolinite molecule can be calculated and the remainder placed as quartz.

Sample	Total Al_2O_3	Total SiO_2	SiO_2 needed for Ka. lattice	Remainder
No. 1, 20-26 inches, clay	23.00	46.96	27.07	19.89
No. 2, 29-32 inches, clay	28.97	38.18	34.10	4.08

In the powder photographs, which were obtained keeping conditions as constant as possible, the values obtained by chemical and thermal analysis are closely parallelled. In no. 1, depth 20-26 inches, clay, almost all the quartz lines are present, whereas in no. 2, depth 29-32 inches, clay, only the very

TABLE 3

Line Strengths of X-ray Powder Photographs (in Ångstrom Units)

Quartz	Kaolinite	Strength	Profile 1, depth 20-26 inches clay	Profile 2, depth 29-32 inches clay	Unmatched Lines
	7.19	s	m	s	
	4.41	ms	m	ms	
4.28		s	m		
	4.16	ms	w	s	
	3.57	s	m	ms	
3.35		vs	s	ms	
			vw	w	2.68
	2.56	ms	m	ms	
	2.49	ms	m	vw	
2.46		m	w	w	
	2.34	ms	vw	w	
2.28	2.29	m, m	w	vw	
2.23		w	w	w	
	2.19	vw		vw	
2.13		m	vw		
1.97	1.99	m, m	vw	vw	
	1.89	vw		w	
1.81		s	ms	w	
	1.78	m		vw	
			w	m	1.70
1.67	1.66	w, ms	w	vw	
1.54		s	m	w	
	1.49	ms	m	m	
1.45	1.45	w, vw	m		
1.38		s	w		
1.37		s	w		
1.29		m	vw		
1.25	1.25	m, vw	w		
1.23	1.23	w, vw	vw		
1.20		ms	w		
1.18		s	vw		
1.15		m	w		
1.08		ms	w		
1.05		m	w		
1.03		m	w		
1.01		m	w		
0.988		m	w		
0.986		m	vw		

Intensities: s = strong, m = moderate, w = weak, v = very.

strongest of the quartz lines appear (see table 3). The lines appearing at 2.68 Å and 1.70 Å are placed as due to hematite, for there is a large amount of iron oxide in the samples, as shown by chemical analysis (table 1). The thermal curves in the 290-350° region would tend to substantiate this result. It is believed that the 1.89 Å kaolinite reflection, very faint in pure kaolinite and yet appearing slightly stronger in no. 2, depth 29-32 inches, clay, is due to anatase, and this mineral would also reinforce the 1.70 Å reflection placed as a hematite reflection. Although the titanium content is low (1.69%) it might be expected to show, for titanium is a heavy atom and X-ray exposures were for 12 hours. Nagelschmidt (1949) has recorded anatase from sedimentary kaolins. The high iron content of the samples, with appearance of only the very strongest hematite lines, points to this mineral's being in a very fine state of division and practically amorphous, a condition frequently encountered in soil clays (Hendricks and Alexander, 1939).

The two different curves obtained for silts and clays show quite clearly that in evaluation of minerals in soil clays by thermal analysis an individual curve must be established for each fraction. Agreement between fractions of the same size and from different depths of the same profile is good and, in the case investigated, so also is correlated between three profiles, in different states of maturity and weathering but from the same parent material. The last is an important conclusion, for if it can be shown to hold for other samples, then standardization of the instrument need only be effected for each soil group and fairly rapid measurements might then be undertaken.

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Department of Mineralogy and Petrology
University of Cambridge
Cambridge, England