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EVALUATION OF KAOLINITE AND QUARTZ DIFFERENTIAL THERMAL CURVES WITH A NEW HIGH TEMPERATURE CELL

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ABSTRACT

A Dupont Model 900 Differential Thermal Analyzer equipped with a 1200°C high temperature cell was evaluated with kaolinite and quartz as representative of three common mineral reactions: dehydroxylization, recrystallization and reversible phase change. The two minerals were separately analyzed, using a range of sample weights, particle-sizes, and packing densities.

In the dehydroxylization and recrystallization of kaolinite, peak temperatures, areas, shapes, and baseline slopes deviate systematically but in differing degrees from well-established standard values. Systematic changes of reaction peaks are great in the dehydroxylization reaction, small to negligible in the recrystallization reaction, and nil for the quartz high-low phase change. The reference material was varied in the same manner and systematic changes in the baseline slope were observed. Heating rate and instrumental sensitivity changed kaolinite thermograms but no changes were observed for quartz.

Some reaction types are sensitive to specific conditions of environment before, during and after completion of the reaction. Dehydroxylization reaction rate, involving the generation of a vapor phase, is particularly sensitive to these conditions.

INTRODUCTION

Kaolinite and quartz were chosen to evaluate instrumental and experimental variations of peak temperature (maximum deflection from baseline), peak shape and area, and baseline slope.

Kaolinite undergoes dehydroxylization and recrystallization when heated. Dehydroxylization produces a broad endothermic reaction in the 500°–600°C range, while recrystallization of the resulting metakaolinite to cristobalite and γAl_2O_3 or mullite produces a sharply defined exothermic reaction between 950° and 1050°C (Holderidge and Vaughn, 1957). Quartz undergoes an $\alpha \rightleftharpoons \beta$ phase change at 573°C (Grimshaw and Roberts, 1957, p. 278). These three reaction types are commonly observed in the thermal analysis of minerals.

Materials used. The clay mineral used in all thermal runs is Clay 9a from Columbia University's American Petroleum Institute clay mineral collection, kaolinite from Mesa Alta, New Mexico. X-ray and chemical data are given in Molloy and Kerr (1961, p. 586–587) and thermal data in Kerr, Kulp and Hamilton (1949). The quartz was furnished by the Pennsylvania Glass Sand Company and represents their most pure 95 percent −5 micron quartz.

Instrument. The instrument used in this study is the Dupont DTA Model 900 equipped with a high temperature 1200°C cell. This relatively new instrument is described in Vassalo and Harden (1962, p. 132) and Muller (1962). Essentially, the emf potential of differential pair of Pt/Pt 13 percent Rh thermocouples is preamplified by a Philbrick amplifier and fed into the Y-axis of a Moseley X-Y potential recorder.

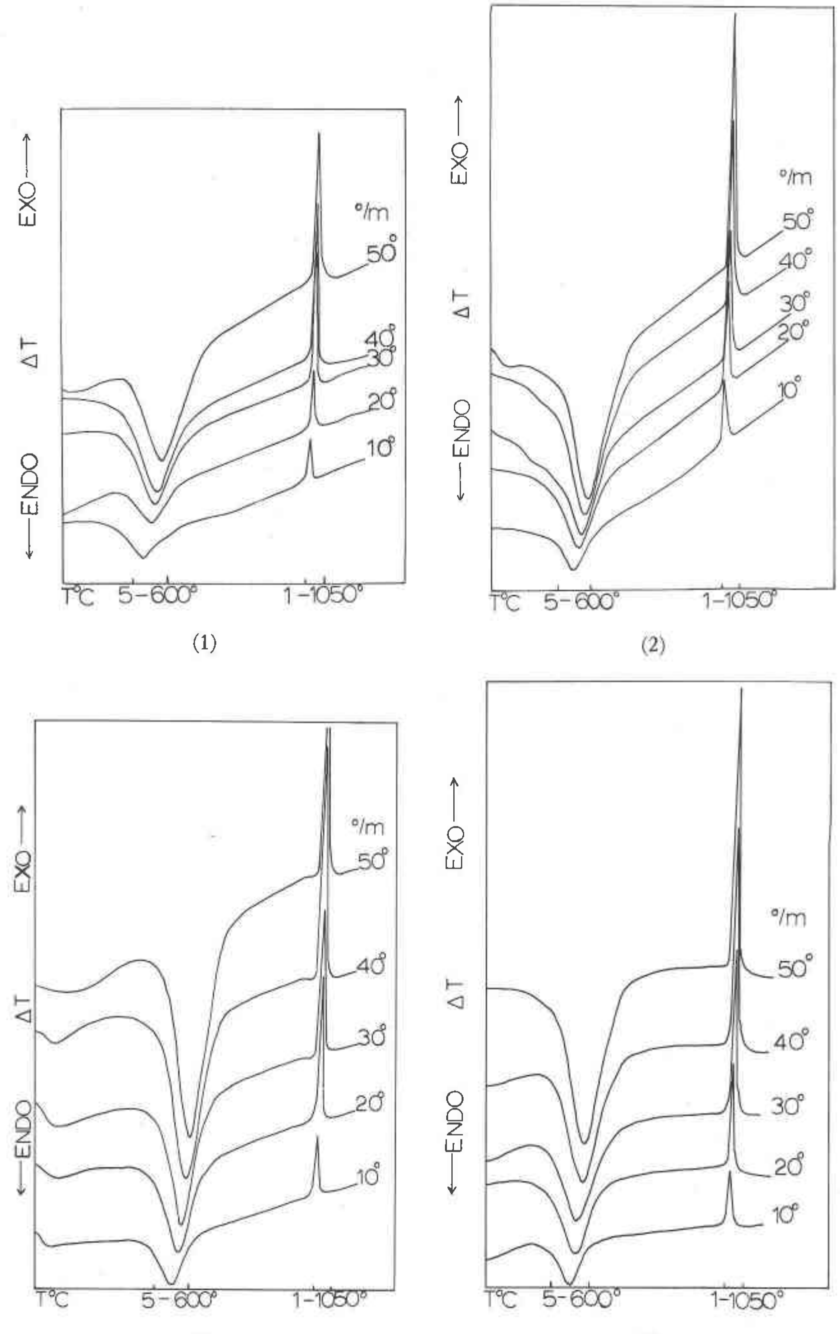
The instrument was temperature-checked with the melting point and inversion of sulphur, the low-high quartz inversion and the melting point of silver. Heating rates of 10°C/minute approached established temperature values of the reactions within 2°C. Reproducibility of peak location, shape and area on repeated runs was excellent when experimental conditions were reproduced.

A general review of theory, historical development, application and methods of instrumentation is given in Mackenzie (1957), Smothers and Chiang (1958) and Murphy (1958; 1960; 1962).

Conditions of Experimentation. It is not always possible to separate sample, reference and instrumental variables during heating cycles, hence much of the data are obtained from interdependent variables simultaneously examined. Sample variables include weight, particle-size, and packing. Reference materials were similarly varied. Instrumental variables examined include heating rate and sensitivity.

THERMAL ANALYSIS OF KAOLINITE

Curve configuration of kaolinite as influenced by sample and reference factors and heating rate. In Figures 1–4, which represent 20 DTA curves obtained under slightly different experimental conditions, the peak temperature of both the dehydroxylization (endothermic) and the recrystallization (exothermic) peak shifts upward on the temperature scale with a corresponding increase of the heating rate. Whereas the dehydroxylization temperature shift is marked, the recrystallization increases only slightly. The former effect was observed by Samoilov in 1915 (Smothers and Chiang, 1958, p. 45). Many factors may control peak temperature: (a) the increase in heating rate effectively causes an increasingly rapid buildup of the partial pressure of water vapor which may inhibit or halt the reaction until some vapor is diffused from the site (Kingery, 1959). An increase in the amount of sample, and its degree of packing, also shifts completion to higher temperatures by increasing the number of hydroxyl groups involved in the diffusion and by restricting available avenues of escape (Bollin, 1961). This feature is indicated by the differences in peak temperatures observed in Figures 1 and 3; but a time lag may occur between the start and end of a reaction so that the longer its duration, the



(1)

(2)

(3)

(4)

FIG. 1–4. Kaolinite thermal curves as influenced by sample, reference, and heating rate. Heating rate (marked as °/m), 10-50°C/min in increments of 10°C; ΔT Sensitivity, .04 mv/in; T axis, 2.0 mv/in.

(1) Sample 15–20 mg, unpacked; reference compartment empty.
(2) Sample ~32 mg, packed; reference compartment empty.
(3) Sample ~35 mg, packed; reference granular alundum, unpacked.
(4) Sample 32 mg, packed; reference 38 mg alundum, ground to clay size and packed.

more its peak tends to extend into a higher temperature range (Murphy, 1958, p. 869). Dehydroxylization reactions may be kinetically slow and may be influenced by such physical factors as particle-size and number of nucleation centers developed. Therefore, peak temperature shift may be brought about by environment-sensitive factors, dependent upon reaction type.

Furthermore, instrument design may profoundly influence thermograms. An increase in the heating rate tends to increase the difference in temperature between the sample and the heating head, and thus the recorded temperature may not always be the temperature at which the reaction is taking place. In the Dupont high temperature cell, the reference and sample thermocouples are positioned vertically in the center of the heating element in the furnace. The thermocouple set is "shielded" by a silica glass tube. Heating rates in excess of 10°C/min appear to initiate thermal gradients from the head to the thermocouple set. Heating rates less than 10°C/minute approach isothermal conditions, with little temperature difference between furnace, sample and reference thermocouples, and are recommended for accurate peak temperature determination. At these low heating rates, however, the reaction peaks tend to become rounded and ill-defined as the temperature differences in the system are minimized.

Peak temperatures and heating rates for each set of thermograms in Figures 1–4 were graphically plotted and an ideal line calculated for each point distribution by least-square regression analysis. Each equation (Table 1) represents the ideal change of peak temperature and heating rate for each thermogram set. Incremental differences in peak temperatures were calculated for each 10°C/min rise in heating rate. A comparison of the data for the different runs indicates that the temperature shifts recorded fall within narrow ranges. Incremental rise for the dehydroxylization peak is more pronounced than it is for the recrystallization peak in the same thermogram. Both temperatures decrease with increasing heating rate, by about two-thirds for each interval of 10°C/min. This general relationship, which exists regardless of differences in sample and reference preparation, is apparently related in part to the geometry of the system.

The peak areas and amplitudes as shown in Figures 1–4 increase with the heating rate as the reaction angles decrease (Table 1). Greater sample masses produce larger peak areas, sharper peaks and higher reaction peak temperatures. Peak areas of the dehydroxylization reactions (Fig. 4) are linearly related to heating rates less than 40°C/min (Fig. 5), but at 50°C/min the reactions are ill-defined (Fig. 4). This relationship may be related to head design and, depending on reaction type, vapor pressure

Table 1. Thermal Data for Kaolinite as Derived from Thermograms in Figures 1–4

	Dehydroxylization Peak Temperature and Peak Angle										Heating Rate and Dehydroxylization Temperature	$\bar{X}$ Slope mv/2.0mv*
Heating Rate:	10°	∡	20°	∡	30°	∡	40°	∡	50°	∡		
Figure 1	535	80	555	68	568	44	574	36	589	34	$Td = 460.8 + 73.0 \log_{10} B$	0.015
Figure 2	549	54	564	38	572	33	584	27	596	23	$Td = 448.5 + 87.9 \log_{10} B$	0.029
Figure 3	561	—	584	—	596	—	601	—	608	—	$Td = 496.3 + 66.2 \log_{10} B$	—
Figure 4	549	49	566	34	572	24	589	26	596	20	$Td = 480.5 + 66.3 \log_{10} B$	0.006

	Recrystallization Peak Temperature and Peak Angle										Heating Rate and Recrystallization Temperature	$\bar{X}$ Slope mv/2.0mv*
Heating Rate:	10°	∡	20°	∡	30°	∡	40°	∡	50°	∡		
Figure 1	1013	10	1023	8	1035	3	1040	3	1045	2	$T_r = 973.6 + 40.7 \log_{10} B$	As above
Figure 2	1018	7	1031	3	1036	3	1040	2	1049	1	$T_r = 985.5 + 34.7 \log_{10} B$	As above
Figure 3	1013	—	1023	—	1033	—	1035	—	1040	—	$T_r = 975.5 + 37.6 \log_{10} B$	As above
Figure 4	1015	8	1028	4	1033	3	1047	2	1049	1	$T_r = 963.0 + 50.4 \log_{10} B$	As above

Heating Rate:	10°	20°	30°	40°	50°
Figure 4:					
Peak Area (in^2)	0.31	0.63	0.93	1.25	1.99
Peak Displacement (T°C)	2.6	4.3	5.2	7.4	10.2

*all slopes endothermic

Change of reaction temperature at various heating rates, 10°/min intervals. Based on equations for heating rate and reaction temperature.

	10–20°/min	20–30°/min	30–40°/min	40–50°/min
Dehydroxylization				
Figure 1	22.0	12.8	9.2	7.0
Figure 2	26.5	15.4	11.0	8.5
Figure 3	19.9	11.7	8.3	6.4
Figure 4	20.0	11.6	8.3	6.4
	$\bar{X}$=22.1	12.9	9.2	6.6
Recrystallization:				
Figure 1	12.3	7.1	5.1	3.9
Figure 2	10.4	6.1	4.4	3.3
Figure 3	11.3	6.6	4.7	3.6
Figure 4	15.2	8.9	6.2	4.9
	$\bar{X}$=12.3	7.2	5.1	3.9

buildup (Sewell, 1955; Mackenzie 1957). The reaction angle, like the peak area is related to heating rate, and this may be related to the design of the X-Y recorder (Bollin, 1966). Peak intensity and area is also related to type of sample holder and block, in that metals invariably allow rapid heat transfer, producing comparatively smaller peaks (Mackenzie and Mitchell, 1957).

The baseline slope of thermal curves may be related to the following factors: relative mass (M), heat capacity (C_s), and thermal diffusivity (K) of the sample and reference materials; instrumental heating rate (β);

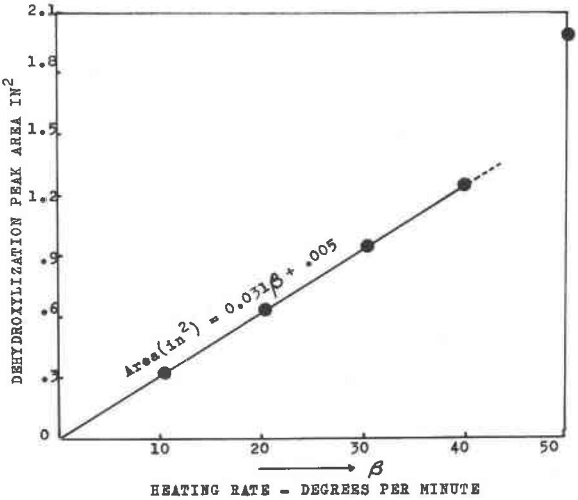


FIG. 5. Relationship between endothermic peak area in kaolinite and heating rate (Fig. 4). Equation of slope excludes 50°C determination.

and the temperature relationships (T) among the heating blocks (B), sample wells (S) and reference well (R). With environmental conditions and sample-reference preparation closely controlled, and the geometry of the system such that the sample and reference are equally heated and are at the same temperature, base line slope would be nil and expressed as follows:

$$\beta_R(MC_s/K)_R = \beta_S(MC_s/K)_S$$

Marked, positive, linear base line slopes are observed in Figures 1–3, and their values in millivolts are given in Table 1. Air at 500°C has a thermal diffusivity of 5.7×10^{-5} cal cm^{-1} sec^{-1} whereas kaolinite's diffusivity is 0.7×10^{-3} cal cm^{-1} sec^{-1}. The sample compartment is always slightly "hotter" than the reference compartment, so that a positive or exothermic base line slope results. Slope was markedly reduced by grinding the reference alundum to clay-size and packing 38 mg of it to 32 mg of sample (Fig. 4). The product of (mC_s) for kaolinite (32 mg$\times$0.22 cal gm^{-1} °C^{-1}) is of the same order of magnitude as the product for alundum (38 mg$\times$0.174 cal gm^{-1} °C^{-1}). This method for reduction of base line slope was suggested by Jeffries (1944).

Curve configuration of kaolinite as influenced by instrumental sensitivity. Kaolinite was thermally analyzed with simultaneous variation of both heating rate and sensitivity. For all curves at constant heating rate, dehydroxylization peak temperatures decreased up to 11°C as the sensitiviy of the instrument was increased from 0.40 mv/in to 0.008 mv/in. The effect was most pronounced at low heating rates and high sensitivities (Figs. 6 and 7). Recrystallization peak temperatures were little affected by change in sensitivity.

For a given sensitivity setting, as the heating rate increases the magnitude of the dehydroxylization peak increases, the reaction angle decreases, and the peak area increases.

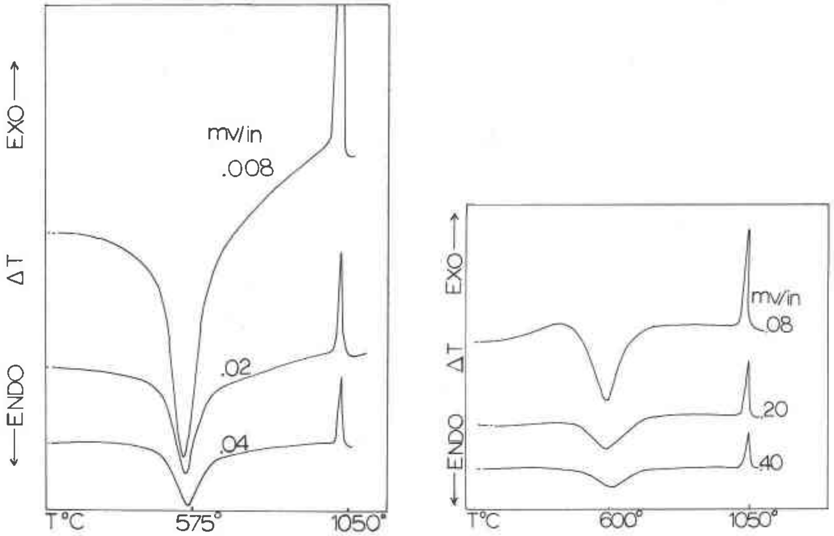


FIG. 6–7. Kaolinite thermal curves as influenced by instrumental sensitivity (marked as mv/in) and heating rate.

(6) Sample ~32–35 mg, packed; reference as in Fig. 4; heating rate 10°/min; ΔT as marked.

(7) Sample 32–35 mg, packed; reference as in Fig. 4; heating rate 50°/min; ΔT as marked.

For each set of curves produced under the same heating rate there is an apparent increase of slope with increase in sensitivity. Conversion of millivolts to degrees centigrade indicates that the thermal drift is the same within the limits of the determination. It was noted, however, that heating rates at 50°C/min produced greater thermal drift than did the lower rates, which may indicate heat loss in the system. The base lines for heating rates above 30°C/min are reproducible and without excess drift.

Most of the above observations concerning the change in thermograms with instrumental sensitivity are related primarily to instrument design, *e.g.* the apparent shift of the dehydroxylization peak with increased sensitivity (R. Baxter, 1965, personal communication). The increase in reaction magnitude with heating rate may be related to vapor pressure-reaction rate relationships.

Peak temperature, peak area and base line configuration as influenced by sample weight. Thermal curves for kaolinite were determined for a weight range of 12–43 mg, using the same experimental and environmental conditions in each case. The resulting thermograms are shown in Figure 8 and the data are given in Table 2. The dehydroxylization peak temperature increases markedly (Fig. 8) and linearly (Fig. 9) as the sample weight increases. The shift of the recrystallization peak temperature shows that it is little affected by increased sample weight. For the range of weights studied, a 45°C range in temperature is observed for the dehydroxylization reaction, as compared to a 5°C range for the peak temperature of recrystallization. As previously reported, the dehydroxylization reaction peak temperature is significantly affected by an increase in the number of reactive moles present and increased packing of the sample. The recrystallization of metakaolinite may peak at higher temperatures because of the increase of the number of reactive moles involved in the reaction and the thermal lag in the system at this elevated temperature.

TABLE 2. SAMPLE MASS AND REACTION TEMPERATURES FOR MESA ALTA KAOLINITE—CONFIGURATION OF DEHYDROXYLIZATION ENDOTHERMS*

Mass (mg)	Dehydroxylization Temp.	Recrystallization Temp.	Peak Angle Dehydroxylization	°C Deflection	Peak Area (in²)
12	562	1026	62	2.3	.33
15	566	1026	42	3.3	.44
21	574	1029	39	3.5	.43
25	579	1030	27	5.6	.73
29	590	1030	22	7.3	1.08
36	599	1931	18	8.0	1.11
43	607	1031	17	9.2	1.35
		$\bar{X}=1029+2$			

* Heating rate: 25°C/minute.

Peak area, magnitude and reaction angle for dehydroxylization endotherms are given in Table 2. Peak areas increase with weight in a linear manner (Fig. 10). Speil (1945), Kerr and Kulp (1948), Murray and White (1949) and Sewell and Honeyborne (1957) observed that the area of the reaction peak and curve slope were a measure of the total heat effect and, under similar experimental conditions, are proportional to the amount of

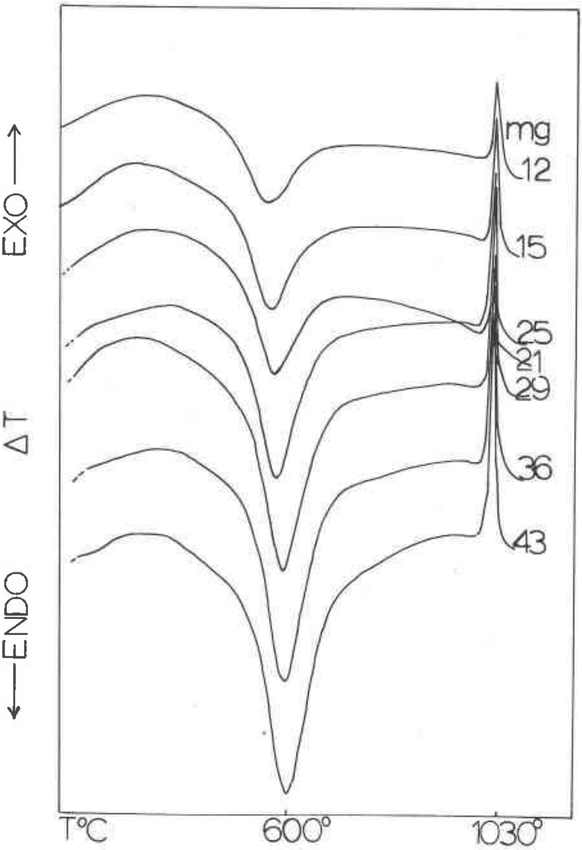


FIG. 8. Kaolinite thermal curves as influenced by sample weight (marked as mg). All samples packed; reference as in Fig. 4: heating rate 25°/min; sensitivity .04 mv/in.; T axis 2.0 mv/in.

thermally active material. However, this simple relationship between peak area and reactive mass may not yield meaningful thermal values when environmental factors are not considered. This may be the case when vapors are generated in a reaction.

Using the data obtained from Figure 10 and the quantitative relationship given in Kerr and Kulp (1948):

$$T_s = \frac{m(\Delta H)}{MC_s} = \int_a^c \frac{dh}{dt}\,dt = m\Delta H$$

The change in body temperature of kaolinite during dehydroxylization was calculated at about 94.9 cal/gm; reported values range from 90–140 cal/gm. The high temperature cell did not yield reproducible values for a

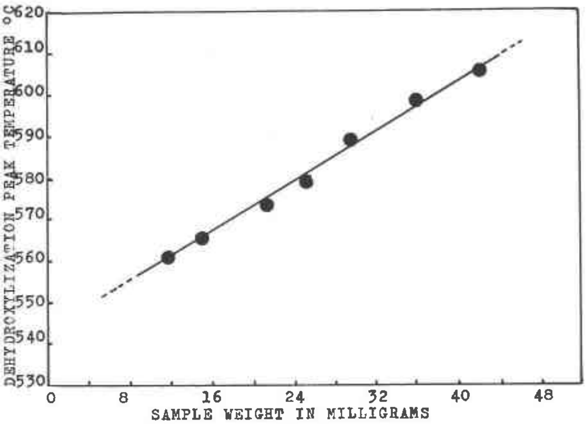


FIG. 9. Temperature shift kaolinite dehydroxylization peak, as influenced by sample weight. Experimental conditions as in Fig. 8.

range of instrumental sensitivities (Fig. 11). Differences in peak area and magnitude for different sensitivities indicate that the head was designed for a particular range of experimental conditions which may vary for the material being examined.

Reaction angles and base line slope were observed to change as a function of sample weight. The reaction angle decreases because the reaction is more pronounced with an addition of reactive moles of material, and change in base line slope is primarily related to the mass ratio of sample and reference. The thermal diffusivity is also markedly increased when packed clay replaces air pockets, producing an apparent exothermic drift (Holderidge and Vaughn, 1957).

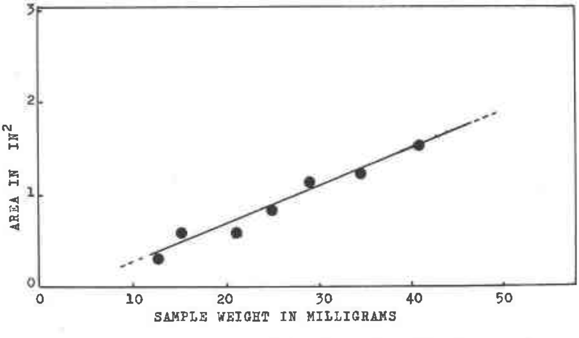


FIG. 10. Rate of change in area of kaolinite dehydroxylization peak, as influenced by change in sample weight. Experimental conditions as in Fig. 8.

Particle-size of kaolinite and its effect on thermal curves. Kaolinite was ground and size fractions were separated by standard sedimentation techniques. No deflocculating agent was used so that these fractions may represent aggregates. However, they are in the approximate size range desired. These fractions were oven-dried at 80°C and then thermally analyzed under similar experimental and environmental controls. The resulting thermograms are shown in Figure 12.

The thermal curves representing the <1 micron fraction of kaolinite were reproducible within narrow margins. The dehydroxylization reaction ranges only some three degrees from a mean of 593°C, while the recrystallization reaction ranges less than one degree from a mean of 1030°C. As the mean grain size of the sample increased, the dehydroxylization reaction shifted upward to 602°C (curve B) and to 609°C (curve A). There was no observable shift for the recrystallization reaction. The dehydroxylization shift was reported by Speil (1945) to depend on size, and therefore surface area.

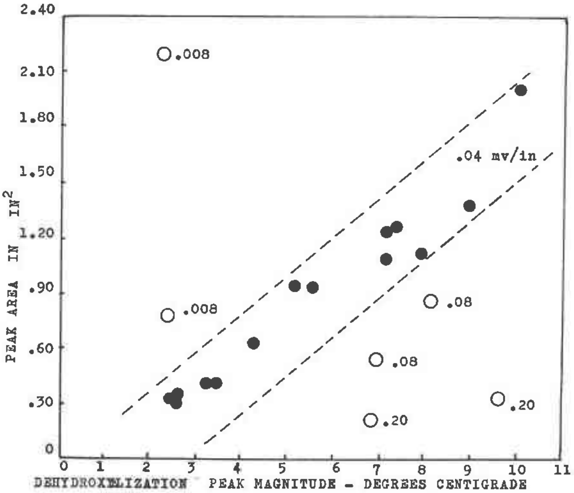


FIG. 11. Relationship of peak shape and area in kaolinite dehydroxylization, as a function of instrumental sensitivity. Sample weights 30–35 mg; heating rate 25°C/min.

THERMAL ANALYSIS OF QUARTZ

The high-low transformation temperature of quartz appears to be unaffected by change in heating rate (Fig. 13), sample weight (Fig. 14), instrumental sensitivity and particle-size. These factors apparently do not influence this reversible phase change, within limits. Low heating rates

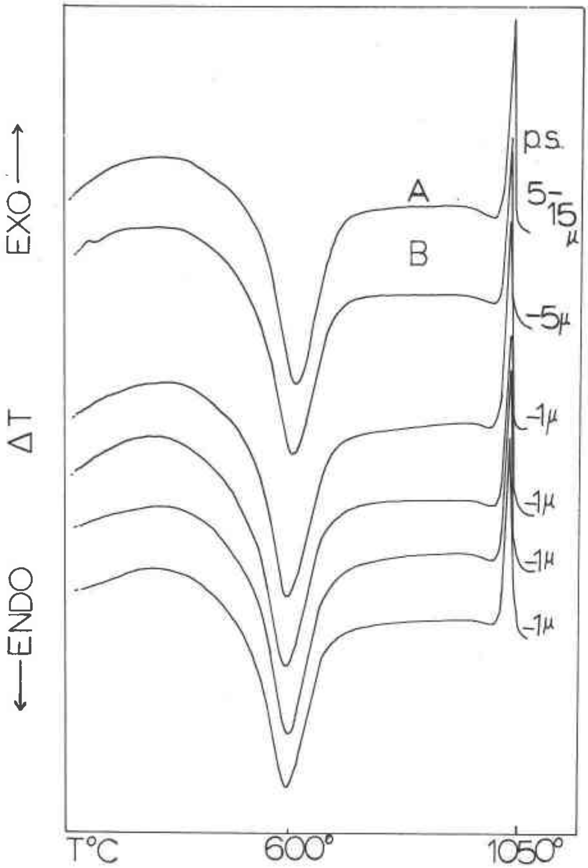


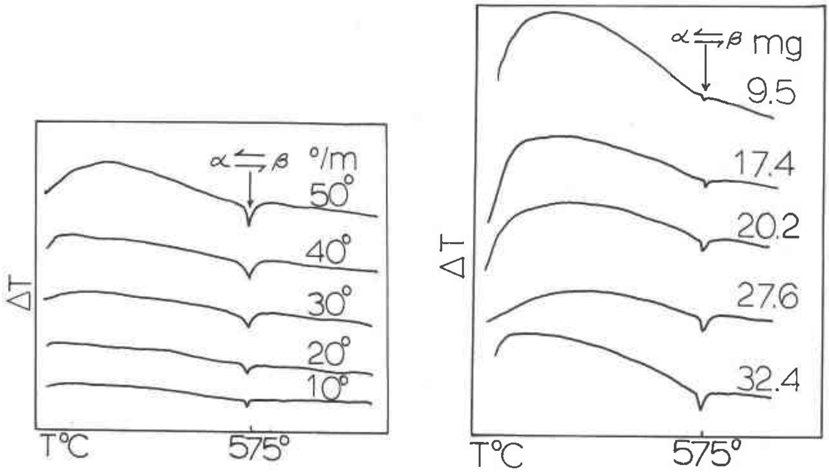
FIG. 12. Shift of kaolinite dehydroxylization peak as influenced by particle-size. Sample 31–33 mg, packed. Reference alundum, 38 mg, reduced to clay-size, packed. Heating rate 25°/min; sensitivity .04 mv/in.; T axis 2.0 mv/in.; particle size as marked.

tend to produce smooth base lines with small and "sharp" peaks. Small samples tend to sharpen the reaction, minimizing temperature lag across the sample. Increased instrumental sensitivity produces larger peak areas and greater apparent drift in base line slopes. Increase in particle-size tends to broaden the reaction temperature range because of thermal gradients within the particles themselves and within the sample compartment because of packing differences.

CONCLUSIONS

Differential thermal curves obtained with the Dupont Model 900 instrument and its high temperature cell vary systematically with sample, reference, instrumental and environmental variables. Kaolinite and quartz were chosen for analysis because of their well-defined and contrasting reactions. Their responses were affected in the following manner:

Sample weight. As the sample weight per unit volume of kaolinite increases, areas of dehydroxylization and recrystallization peaks increase and peak temperatures shift upward, the former reaction being far more affected than the latter. The quartz inversion peak area increases although the reaction temperature is unaffected by sample weight. These effects are related to the type of reaction, reaction rate and instrument design. Peak area may be related to sample weight, if proper environmental and instrumental variables are employed. Heating rate and instrumental sensitivity apparently affect reaction peak area, indicating that the head design functions best at specific instrumental settings.



FIGS. 13, 14. Quartz thermal curves as influenced by heating rate (Fig. 13); sample weight (Fig. 14). Reference in all cases alundum, 38 mg, reduced to clay-size and packed

(13) Heating rate as marked; bulk samples; weight 32–34 mg; sensitivity 0.4 mv/in.; T axis 2.0 mv.

(14) Heating rate 50°/min; bulk samples; weights as given; sensitivity 0.4 mv/in.; T axis 2.0 mv.

Sample particle-size. As the particle-size of kaolinite decreases, the dehydroxylization temperature decreases correspondingly. The shifts in peak temperature of metakaolinite recrystallization and of the quartz inversion were negligible.

Sample preparation. Packing of samples increases heat diffusivity through the sample compartment, resulting in a general sharpening of reactions. The upward temperature shift observed for the dehydroxylization peak is related in part to the increased partial water vapor pressure, which tends to extend the reaction until vapor is diffused from the reaction site.

Reference material. The nature of the reference material may affect the base line. It is recommended that the reference material be comparable in particle-size to the sample examined and that its weight be such that its mass-specific heat product is equal to that of the sample. In this manner base line slope may be significantly controlled.

Instrumental controls. Heating rates have produced a marked effect on the area and temperature of the dehydroxylization peak. Incremental differences between successively determined peak temperatures are greatest at the lower heating rates (10–20°C/min) and tend to decrease with higher (40–50°C/min) heating rates. Dehydroxylization is particularly sensitive to a change in heating rate because of the relationship between the buildup of vapor pressure and the reaction rate. The temperature for metakaolinite recrystallization is slightly higher than reported in the literature, suggesting that at these elevated temperautres, high heating rates may initiate high heat loss from the head, or that thermal lag is pronounced. Heating rate change did not produce any observable temperature shift for the quartz inversion temperature. It is noteworthy that heating rates, some 20°C greater than those recommended for the instrument, produce both reproducible and well-defined base lines without appreciable thermal drift.

With increased instrumental sensitivity, the dehydroxylization of kaolinite was recorded at lower temperatures, whereas the recrystallization of metakaolinite and the inversion of quartz were unchanged.

For DTA curves to be reproducible rigid experimental controls are necessary. In this manner it may be possible to compare qualitative data obtained from similar materials using the same instrument. Quantitative thermal data must be viewed with extreme caution, as each material may be best analyzed under a completely different set of instrumental controls. Reliability of the data also may be a function of the reaction type. Many of the observed systematic variations may be instrumental, and not directly applicable to other instruments.

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