

# *SLOPE RATIOS OF DIFFERENTIAL THERMAL CURVES OF DICKITE*

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## ABSTRACT

The relationships between the shapes of kaolinite and dickite differential thermal curves are described. The slope ratios of dickite are distinctly greater than those of kaolinite of equivalent particle size for the endothermic peak at about 550°C and the same effect is observed for the exothermic peak at about 980°C, especially in diluted samples. The packing density of dickite does not differ markedly from that of kaolinite and the curve obtained for weight *vs.* area of the endothermic peak is in agreement with this. The dickite samples, however, give slightly lower areas than those of kaolinite, an effect that is dependent on the shape of the particles. The exothermic peak is shown to be influenced considerably in shape and size by thermal gradients.

## INTRODUCTION

Although considerable research has been carried out on the less well-ordered kandites, not so much attention has been paid to dickite and nacrite, especially as regards the mathematical relationships and shapes of the curves resulting from differential thermal analysis. In view of the restricted natural occurrence of these members of the group, the smaller amount of attention is not surprising. In this paper comparison is made between dickite and kaolinite and the relative shapes of the curves are utilised to gain an insight into the actual mechanism of the dehydroxylation reactions occurring on heating.

## EXPERIMENTAL

The apparatus used had a temperature rise of 10°C/min, nickel block and cover, chromel-alumel thermocouples, and recording was by means of electronic recorders. The samples investigated were those used as standard clay samples by Kerr (1951) and were as follows, the number in brackets referring to the A.P.I. number: dickite, on U.S.550, near Red Mountain Pass, south of Ouray, Colorado, U.S.A. (No. 14); dickite, Bull Valley, 40 miles north-west of St. George, Washington Co., Utah, U.S.A. (No. 16); kaolinite, from Twin Knobs, Murfreesboro, Pike Co., Arkansas, U.S.A.

(No. 1); kaolinite, from O'Neal pit 8.8 miles south-east Macon railway station, Georgia, U.S.A. (No. 4). The  $2\text{-}20\mu$  equivalent spherical diameter (e.s.d.) fraction was separated from the samples by centrifugal means, this fraction comprising almost the entire sample in the case of the dickite samples. X-ray examination and chemical analysis of these fractions revealed no foreign minerals and from the figures for the latter (Table 1) it will be seen that chemically the specimens are almost identical, so that any differences in behaviour must be largely due to morphological effects. The general chemical relationships between these and other kandites have been reported elsewhere (McLaughlin, 1959).

TABLE 1—Chemical analyses of  $2\text{-}20\mu$  e.s.d. fraction of various kandites (in per cent.)

Element	Dickite Colorado	Dickite Utah	Kaolinite Arkansas	Kaolinite Georgia
Si <sup>4+</sup>	21.24	21.32	22.21	21.22
Al <sup>3+</sup>	19.98	20.88	20.19	20.65
Ti <sup>4+</sup>	0.11	0.01	0.40	0.69
Fe <sup>3+</sup>	0.27	0.17	0.52	0.74
Mg <sup>2+</sup>	0.68	0.60	0.08	0.17
Na <sup>+</sup>	0.13	0.01	0.01	0.02
Ca <sup>2+</sup>	0.07	0.10	0.27	0.31
K <sup>+</sup>	0.28	0.05	0.14	0.12
Si/Al	1.06	1.02	1.10	1.03

The procedure in investigating these samples has been to tamp the kandite into the sample well of the block to finger tightness. The inert material was ignited alumina of  $10\text{-}15\mu$  e.s.d. and this same material was used as diluent. Where small quantities of kandite were involved, a pre-amplifier was used to enlarge the curves and these were later corrected to the scale of the unamplified curves.

The results obtained from the thermal curves are reported in Table 2, for both endothermic and exothermic peaks. The values given for the slope ratio are derived using the technique of Bramão *et al.* (1952), *i.e.*, from tangents drawn to the curve from the lowest point on the trough. It has been found that the trends with these do not differ greatly from those using the slope of the sides of the curves (Dean, 1947).

TABLE 2—Results obtained from differential thermal curves of kandite fractions (2-20 $\mu$  e.s.d.) expressed in C.G.S. units.

Sample	Kandite (%)	Weight of kandite (g)	Endothermic Peak					Exothermic Peak				
			Tan $\alpha$ / Tan $\beta$	Ampli- tude	W*	A*	A/W	Tan $\alpha$ / Tan $\beta$	Ampli- tude	W*	A*	A/W
Dickite Colorado	100	0.2877	4.0	4.7	1.0	5.43	5.4	1.4	4.4	0.2	1.16	5.8
	75	0.2292	3.6	3.9	1.0	4.16	4.2	1.6	2.8	0.3	0.86	2.9
	50	0.1691	3.5	2.6	0.8	2.23	2.8	2.3	1.5	0.4	0.55	1.4
	25	0.0863	3.1	1.2	0.8	1.05	1.3	3.0	0.7	0.4	0.23	0.6
	10	0.0334	2.5	0.4	0.8	0.40	0.5	2.8	0.2	0.6	0.06	0.1
Dickite Utah	100	0.3185	3.5	5.2	1.5	9.30	6.2	1.2	5.2	0.3	1.73	5.8
	75	0.2614	2.6	3.9	1.5	7.85	4.6	1.5	3.1	0.3	1.13	3.8
	50	0.1846	2.0	2.2	1.5	4.30	2.9	3.7	1.5	0.4	0.57	1.4
	25	0.0971	1.8	1.1	1.4	1.83	1.3	3.7	0.6	0.4	0.30	0.9
	10	0.0384	1.3	0.3	1.1	0.50	0.5	4.0	0.1	0.5	0.06	0.1
Kaolinite Arkansas	100	0.2624	0.98	4.1	1.8	8.23	4.6	—	—	—	—	—
	75	0.2374	0.96	3.5	1.7	6.03	3.5	0.70	6.1	0.2	1.16	5.8
	50	0.1722	0.79	2.3	2.0	4.13	2.1	0.65	3.4	0.2	0.73	3.7
	25	0.0940	0.86	0.9	1.6	1.77	1.1	1.8	1.1	0.3	0.28	0.9
	10	0.0371	0.20	0.2	1.8	0.45	0.3	2.5	0.3	0.5	0.09	0.2
Kaolinite Georgia	100	0.2902	1.9	7.0	1.5	11.53	7.7	1.9	( $>8.5$ )†	0.2	(2.33)†	11.7
	75	0.2418	1.8	5.2	1.4	8.57	6.1	0.67	(8.6)†	0.2	(2.00)†	10.0
	50	0.1752	1.8	3.4	1.4	5.40	3.9	1.5	4.2	0.2	0.97	4.9
	25	0.0982	1.5	1.2	1.7	2.17	1.3	1.7	1.3	0.3	0.39	1.3
	10	0.0394	1.3	0.4	1.7	0.68	0.4	2.1	0.3	0.4	0.11	0.3

\*A—area of peak; W—width of the peak at half the amplitude. †Extrapolated results.

## DISCUSSION

The weights of kandite packed into the sample well (Table 2) are interesting as they reveal the packing density of the minerals in question. This is shown graphically in Fig. 1, which indicates that the packing densities of kaolinite and dickite are not greatly different, but that in all specimens there is marked departure from linearity—as would be expected, for the maximum packing density of such mixtures should occur at low percentages of clay mineral (Martin and Lambe, 1957). The lowest part of the curve might, from theory, be expected to be convex upwards and the reason why this is not so is probably connected with experimental difficulties of tamping at

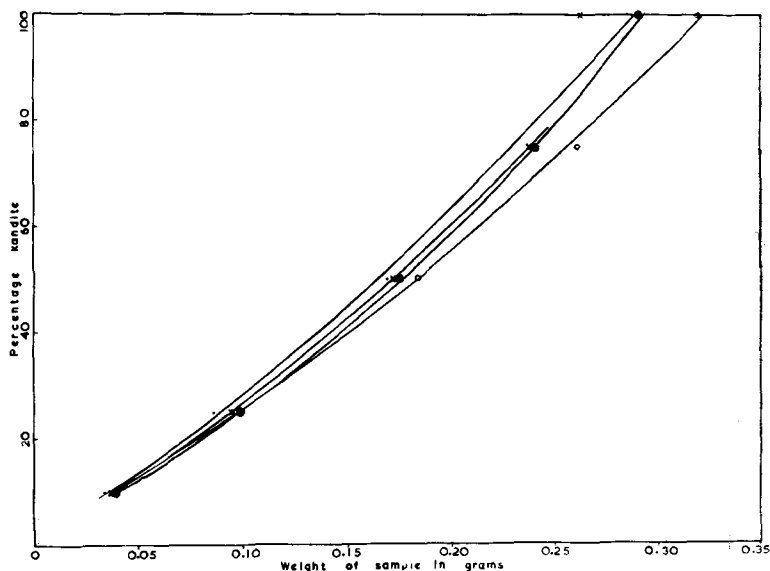


FIG. 1.—Relationship between weight of material packed into sample well and percentage reactive constituent; —Colorado dickite; o—Utah dickite; x—Arkansas kaolinite; ●—Georgia kaolinite.

amounts lower than about 20 per cent. clay mineral, since lack of coherence renders the exclusion of voids very difficult.

As most workers have found that it is normally possible to reproduce the same sample weight by tamping to uniform tightness, all figures derived from differential thermal curves involving weight data should show some curvature rather than exact linearity. In Fig. 2 have been plotted the results for weight of kandite against area of the endothermic peak at about 550°C, and the similarity to the curves in Fig. 1 is quite striking. It will also be observed that although the areas enclosed by the peaks on the dickite curves are

smaller than those on the kaolinite curves, the curve for Arkansas kaolinite is close to that for Utah dickite. Electron microscopy has shown that the particle size of the Arkansas kaolinite, although small, is uniform, with elongated particles. The morphology of this sample, therefore, more closely approximates to that of the dickites and hence the energies associated with dehydroxylation, as expressed by the areas under the endothermic peaks, are somewhat similar—a conclusion in accord with the findings of Roy and Osborne (1954). Fig. 2 also illustrates that for dickite, as well as for kaolinite, packing density and thermal conductivity of diluent, have similar

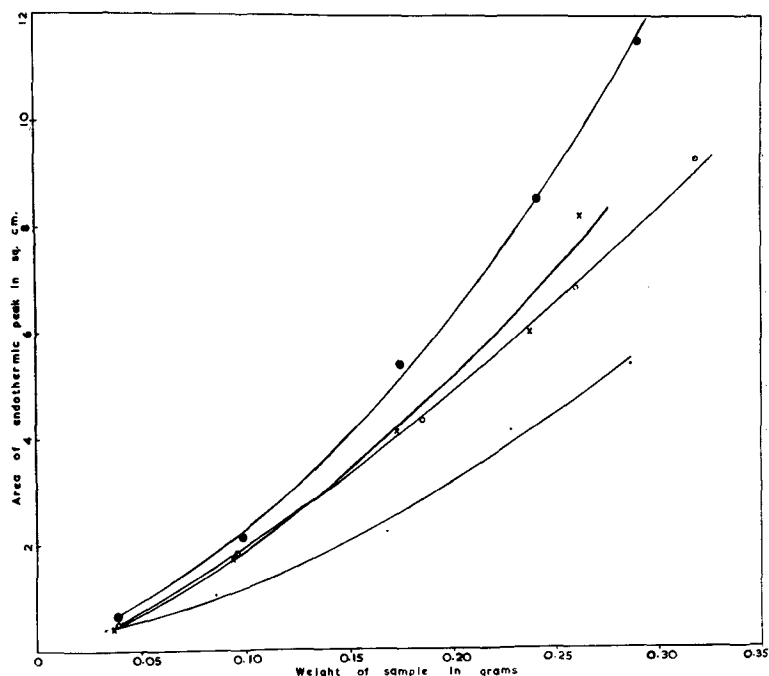


FIG. 2—Relationship between area of endothermic peak of kandite and weight of reactive constituent. Symbols as in Fig. 1.

effects, increase in the former tending to increase and in the latter to decrease areas at the lower concentrations. This effect on kaolinite curves has been more fully considered elsewhere (McLaughlin, 1961).

The values derived for slope ratios are interesting. Those for kaolinite require little or no comment, but those for dickites are considerably greater than those for equivalent weight, or percentage, of kaolinite. Bramão *et al.* (1952) found slope ratios to rise with degree of disorder in the kandite structure and also with decrease

in particle size: thus, halloysite had higher slope ratios than kaolinite. The dickite values, however, lie well above those of kaolinite (Table 2), yet dickite is more ordered in crystal structure than kaolinite. This apparent contradiction can be resolved by a closer study of the peak shapes. Whereas in halloysite the higher slope ratios are caused by a rise in  $\alpha$  and a drop in  $\beta$ , corresponding to a broadening of the peak on the downslope and sharpening on the upslope, in dickite the upslope (*i.e.*, the return to zero) is always sharp, and higher slope ratios are due largely to change in  $\beta$ . Even at quite considerable dilutions the curve returns to zero comparatively sharply for dickite as compared with kaolinite, indicating that once dehydroxylation has commenced in dickites the reaction proceeds extremely rapidly and is evidently faster than in kaolinite of similar morphology. This might perhaps be expected from the conclusions of Roy and Osborne (1954), that differences in the thermodynamic constants of the kandite minerals under equilibrium conditions would be slight, since the elevated peak temperature for dickite, as compared with kaolinite, would probably demand more rapid dehydroxylation. The rapid spread of this would result in the early completion of the reaction, with a quick return of the thermal conditions to equilibrium. An additional factor, which may lead to increased rate of decomposition, is the initial reaction, occurring in some samples of dickite which gives rise to a step on the dehydroxylation peak. This initial reaction probably triggers the later and faster reaction. It is believed by Schmidt and Heckroodt (1959) to represent loss of hydroxyl from surfaces and edges of particles and this appears to be substantiated by the observation of the author that the effect becomes more marked on dilution with calcined alumina, because of the lower thermal conductivity of the resultant mixture. In Fig. 3 may be observed the rapid fall in slope ratio at dilution less than the optimum packing density at about 25-30 per cent. clay. This rapid fall is due to greater permeability of sample and differences in thermal diffusivity (McLaughlin, 1961). There is some slight indication of increased asymmetry in the region about 25 per cent. clay, especially for the dickite samples, but the evidence is not sufficiently conclusive, although theoretically some such increased asymmetry might be expected in this region of maximum packing density.

The area divided by the width of the peak at half the amplitude (Carthew, 1955) has been plotted against the slope ratio in Fig. 4. It is quite obvious that the dickite field lies well outside that for the kaolinites. When areas are reduced to a common weight basis there is a distinct trend for points at any dilution to lie on a narrow belt (*cf.* Carthew, 1955), the best alignment being at low values of clay concentration. The values at 25 per cent. clay are a good example and this indeed was the approximate concentration recommended by Grimshaw and Roberts (1953) for accurate quantitative evaluation of peaks.

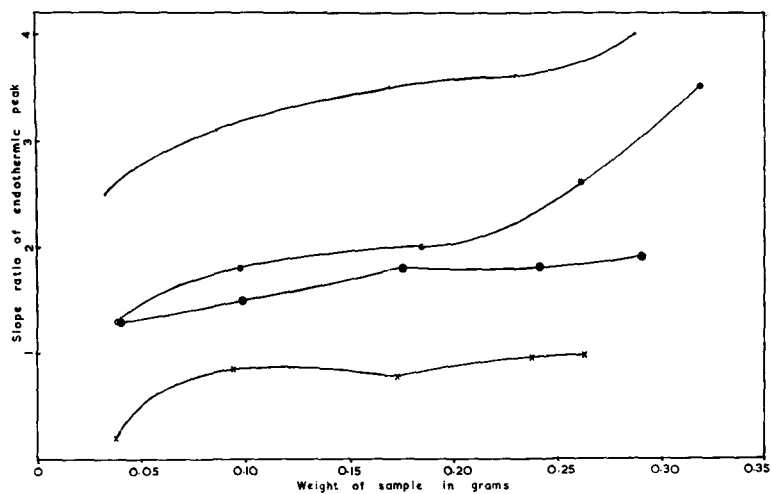


FIG. 3—Relationship between the slope ratio of the endothermic peak of kandites ( $\tan\alpha/\tan\beta$ ) and weight of reactive constituents. Symbols as in Fig. 1.

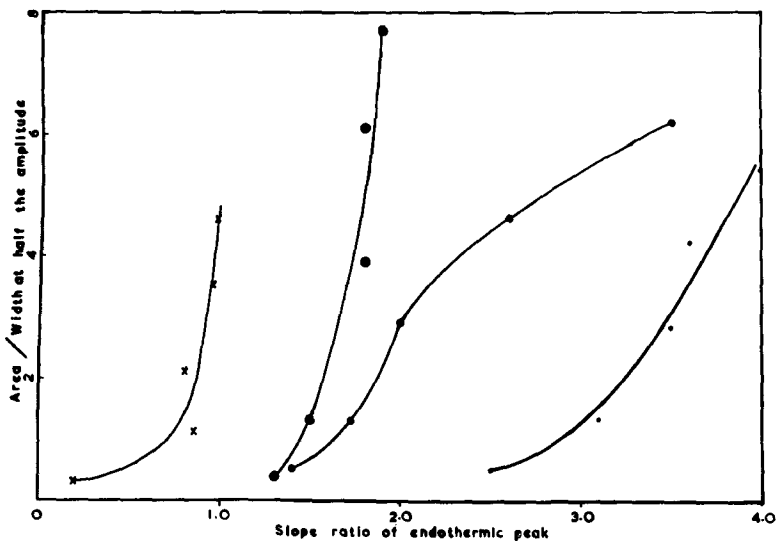


FIG. 4—Relationship between slope ratio and area divided by width at half height for the endothermic peak of kandites at varying dilutions. Symbols as in Fig. 1.

The results for the exothermic peak at about  $980^{\circ}\text{C}$  are also interesting. The areas of peaks for dickite are lower than those for the kaolinite, and the relationship between peak area and sample weight is shown in Fig. 5. Curves drawn using amplitude instead of peak area closely parallel in shape those in Fig. 5, but the separation between the dickite and kaolinite fields is enhanced. The curves in Fig. 5 show increase in curvature with increase in weight of reactant, the lower areas tending more nearly to linearity. Similar effects have been noted for amphiboles (Wittels, 1951) and for other kaolinite fractions (McLaughlin, 1961) and are believed related to thermal gradients within the samples. The greater the clay content the greater the shrinkage, and hence the greater the difference in temperature between sample and inert material.

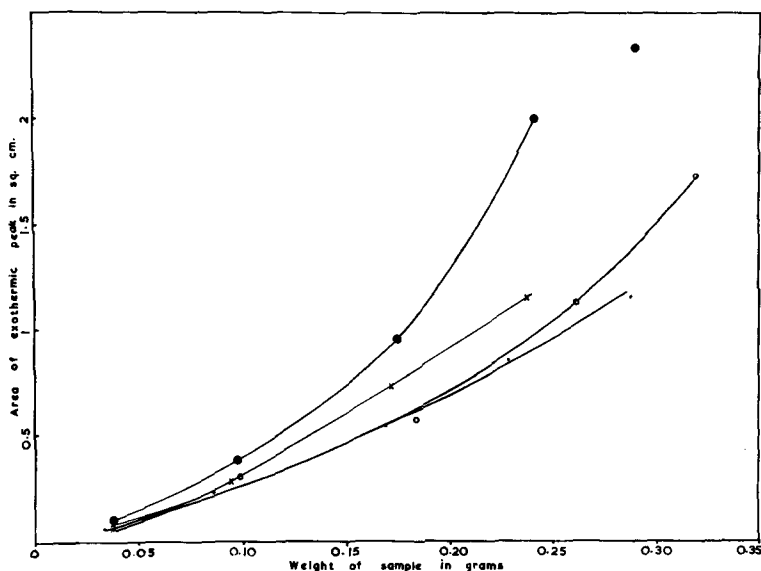


FIG. 5—Effects of dilution on the area of the exothermic peak of kaolinites. Symbols as in Fig. 1.

The values for the slope ratio of the exothermic peak rise with dilution for both dickite and kaolinite, but the dickite field lies well above that of the kaolinite. This is rather surprising, as the endothermic reaction might well be assumed to have destroyed any original morphological differences and this certainly appears to happen with kaolinite samples of different particle size (McLaughlin, 1961). An examination of the shapes of both sides of these exothermic peaks shows that with kaolinite the up-slope, *i.e.*, the initial reaction, is always sharp until very low dilutions are reached (10



per cent.). The return to zero, *i.e.*, the down-slope, behaves similarly. With dickite the up-slope is never so sharp as with the kaolinite and on dilution the asymmetry is increased, for only at low dilutions is the down-slope not sharp. Furthermore, at low dilutions the down-slope is more gradual than for kaolinite. This exothermic reaction is not broken in any way as is the endothermic peak for some samples of dickite: on the contrary it is quite sharp but not so steep as for kaolinite. The only explanation which can be offered for this difference in behaviour is that during dehydroxylation the dickite reacts slowly at first but more violently later (Schmidt and Heckroodt, 1959). This violent loss of water causes a certain intumescence and hence on the initiation of the high temperature change there could be more resistance to the spread of the reaction. Once initiated, the reaction is almost complete at the peak, and hence the rapid return of the difference trace to zero giving a higher slope ratio for the peak than for kaolinite. This hypothesis finds some substantiation in the shapes of the curves in Fig. 5 where the curves for dickite appear flatter than those for kaolinite, corresponding to a greater thermal gradient in the latter because of uniform shrinkage. It should, however, be pointed out that more experimental work would be required to substantiate the hypothesis.

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