

A dickite with an elongated crystal habit and its dehydroxylation.

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Summary. Dickite from a new occurrence at Barkly East, Cape Province, is described and compared with a previously unreported dickite from Postmasburg and a dickite from Ouray, Colorado. The Barkly East dickite crystals are elongated in the direction of the *a*-axis; the ratio of length to width of crystals varies from 3:1 to 16:1. Optical, electron microscopic, X-ray, and thermal data and a chemical analysis are given. The thermogram of the fraction smaller than $2\ \mu$ e.s.d.¹ is characterized by a single peak at 600° C., while that of fractions larger than $2\ \mu$ e.s.d. shows a double endothermal effect. This two-stage dehydroxylation of dickite on heating is attributed to a particle size effect.

THE only dickite occurrences so far reported in South Africa are those in the Witwatersrand system (Whiteside, 1941; Frankel, 1949). In the latter paper mention is also made of a dickite from the Middelburg district, Transvaal, but only refractive indices are given.

In this paper a dickite occurring near Barkly East in the Eastern Cape Province is described and compared with a dickite from Postmasburg in the northern Cape Province as well as with the dickite from Ouray, Colorado (Clay Mineral Standard, H-14).

The sample received from *Barkly East* is a white glittering powder. Large calcite crystals and portions of vugs lined with calcite crystals were found in the material. Although nothing more is known of the geological associations it is assumed that the dickite is closely associated with the vugs found in the sample bag and that it is, therefore, of hydrothermal origin. The most outstanding feature of this dickite is the fact that the particles have a very pronounced elongated crystal habit. Except for slightly elongated particles shown in electron micrographs (Davis *et al.*, 1950), dickites with such a pronounced elongation have not yet been described in the literature. According to Grim (1953, p. 108) dickite occurs in well-formed, six-sided, flake-shaped particles,

¹ e.s.d.—effective spherical diameter.

frequently showing a definite elongation in one direction, but in the electron micrograph of dickite (Grim, 1953, p. 114) elongation is not very marked. The only other reference to elongated dickite crystals which could be found in the literature is that by Mezösi (1957) who described a dickite occurrence from Mád, Hungary. This dickite is closely associated with kaolinite in cavities in porous rhyolite tuffs. The crystals are from 15 to 20 μ long and 3 to 8 μ wide and the elongation is in the direction of the *a*-axis. As will be seen below, this elongation is much less than that of the Barkly East dickite.

The *Postmasburg* specimen is in the form of a lump with quartz crystals and specularite adhering to it. The dickite in a hand specimen is very light greenish in colour and is slightly transparent. When pulverized, the material is pure white. According to Dr. L. G. Boardman,¹ from whom the sample was received, it occurs in the highly altered Gamagara shales associated with iron ores, especially where diaspore and zunyite have also been found. It is found as fillings in cavities in the ore bodies on Kapstewel although some cavities contain only quartz or calcite crystals. According to Boardman, the iron ore bodies have been formed by the replacement of the Gamagara shales which were infolded in the lower Griquastad beds. Remnants of the original shales are often found in the quarries.

In view of the fact that this dickite occurs in cavities associated with the iron ore bodies, one must conclude that it also was formed as a result of hydrothermal activity.

Microscopical examination.

The Barkly East dickite was sieved through a 200-mesh (74 μ) Tyler sieve, without grinding, to eliminate all the coarse calcite crystals and other contaminants. This sieved material, when examined under the microscope, was found to be exceptionally free from contaminants and was fractionated into three sizes of fractions by sedimentation in water, viz. < 2 μ , 2 to 6.3 μ , and 6.3 to 20 μ . It did not contain any particles larger than 20 μ equivalent spherical diameter (e.s.d.) and only a very small percentage (1.3 %) less than 2 μ .

In fig. 1 the elongated habit of the particles can be clearly seen. The length:width ratio of the plates varied from 3:1 to 16:1. The width of the particles varied from 6.6 to 13.2 μ and the length from 33 to 105 μ . The plates were elongated in the direction of the *a*-axis. Refractive indices were determined in sodium light at 23° C. using phase contrast

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equipment. Plates lying on (001) gave α' 1.566 and γ 1.569. Fig. 2 is an electron micrograph of the dickite. Here again the elongated habit of the plates can be clearly seen.

The Postmasburg sample was ground to pass a 200-mesh (74μ) screen. Under the microscope some plates were more or less regular hexagons but most had rounded outlines, which was probably due to the grinding. Plates lying on (001) gave α' 1.565' and γ 1.568.

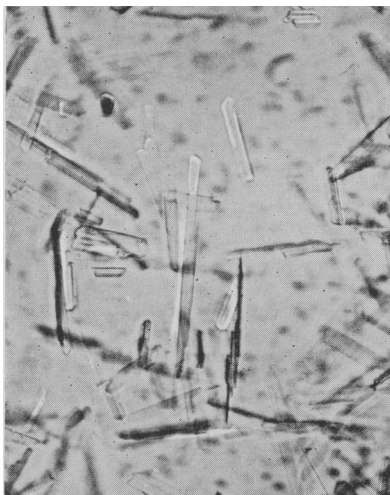


FIG. 1

FIG. 1. Dickite in 6.3 to 20 μ fraction from Barkly East ($\times 400$).

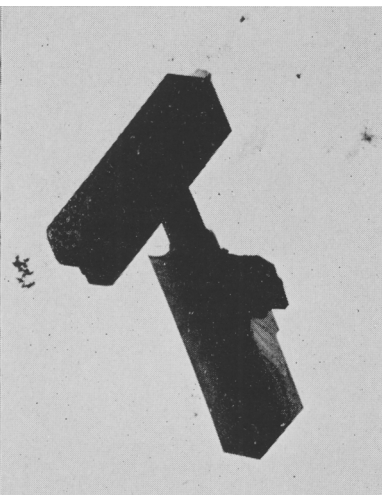


FIG. 2

FIG. 2. Electron micrograph of Barkly East dickite showing euhedral crystals with elongated outlines ($\times 3000$). (Electron micrograph by Dr. J. T. Fourie, National Physical Research Laboratory, South African Council for Scientific and Industrial Research.)

A chemical analysis of the 6.3 to 20 μ fraction of the dickite from Barkly East gave: SiO_2 46.43, Al_2O_3 39.54, Fe_2O_3 0.15, MgO 0.17, CaO nil, K_2O 0.02, Na_2O 0.03, TiO_2 nil, loss on ignition 14.20, total 100.54 (Analyst: Miss R. Rethemeyer, National Chemical Research Laboratory, C.S.I.R.). No impurities were detected by X-rays, and the $\text{SiO}_2:\text{Al}_2\text{O}_3$ ratio, 1.996, confirms the purity of the material.

X-ray examination.

X-ray powder diffraction patterns were obtained with a Phillips high-angle goniometer, using $\text{Cu-K}\alpha$ radiation and a speed of one degree 2θ

per minute. To minimize preferred orientation the samples were first mixed with an equal volume of fine cork powder before loading the aluminium sample holders. One side of the sample holder was cut away so that the samples could be loaded from the side according to the method described by von Engelhardt (1955). The spacings and intensities of the two South African dickites were compared with those of dickite from Ouray, Colorado (Clay Mineral Standard H-14), obtained under the same conditions, and with the spacings published by Smithson and Brown (1957).

The average values of the first five basal spacings are 7·152, 7·156, and 7·152 for the dickites from Barkly East, Ouray, and Postmasburg respectively. These values compare well with the average value of 7·154 found by Smithson and Brown (1957).

The intensities of the basal reflections of the Barkly East dickite were lower relative to those of the other two dickites, but it is possible that there could still have been some preferred orientation in the latter samples. The long needle-like plates of the Barkly East sample would not show such a strong tendency to orientate themselves parallel to {001} as would plates with equant outlines. Apart from slight variations in the intensities of the reflections, the spacings are identical, within experimental error, and correspond very well with the values of Smithson and Brown (1957).

The Barkly East dickite also developed a 14 Å. reflection after heating at 600° C. and 650° C. for one hour and therefore shows the same phenomenon as that reported by Hill (1955) for the dickite from Ouray. The 2 to 6·3 μ and 6·3 to 20 μ fractions both developed a 14 Å. reflection after heating at 600° C. and 650° C. for one hour. For material heated to 550° C. this reflection did not form and for material heated at 700° C. it disappeared. After heating at 600° C. the reflections at 7·2, 3·57, and 2·33 Å. had not completely disappeared. According to Roy and Brindley (1955) these reflections must not be regarded as the higher orders of the 14 Å. line, since they are almost certainly due to incomplete conversion of the ordinary dickite structure and indicate only a mixture of phases.

Differential thermal analysis.

Differential thermal analysis curves were obtained using a two-well nickel block and a heating rate of 10° C. per minute. The temperature was measured in the inert material (calcined α -alumina, -74 μ).

In fig. 3 the curves for the various dickites are shown. These curves were made using the sieved materials. The curves for the Ouray and

Postmasburg dickites are nearly identical and correspond closely to the published curve for dickite from Ouray (Kerr *et al.*, 1949). In the Ouray and Postmasburg dickites, dehydration starts at about 500° C., taking place slowly at first as indicated by the shallow inflexion between about

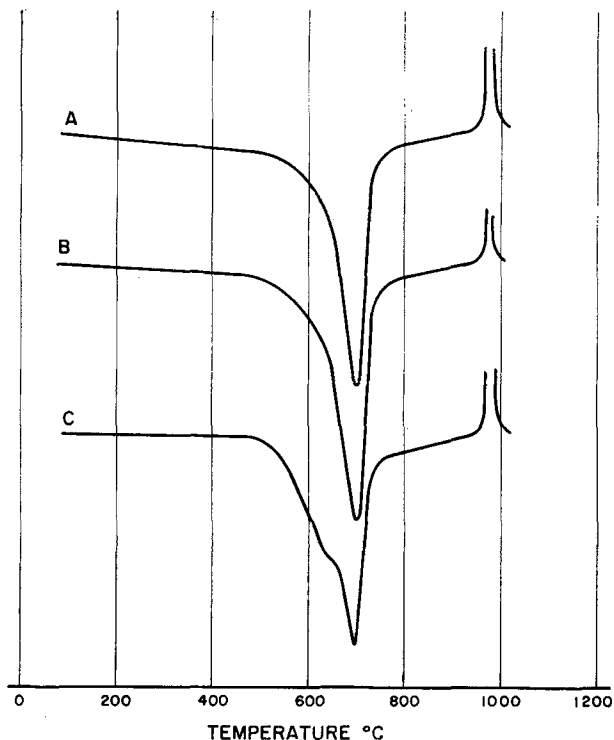


FIG. 3. Differential thermal analysis curves of various dickites. A. Ouray, Colorado (C.M.S. H.14). Amplification $\times 5$. B. Postmasburg, Northern Cape Province. Amplification $\times 5$. C. Barkly East, Eastern Cape Province. Amplification $\times 5$.

500° C. and 610° C. At the latter temperature the curve turns down sharply. The curve for the Barkly East dickite shows a better defined, although only partially resolved, double endothermic peak, similar to the curve for dickite from Anglesey (Kerr *et al.*, 1950, p. 66) and the curve published by Smithson and Brown (1957). In the Barkly East dickite, dehydration also starts at about 500° C. but takes place more rapidly than in the Ouray and Postmasburg dickites.

According to Smithson and Brown (1957) there are two possible reasons for the double peak in dickite; either both peaks are due to

dickite and are shown because of the particular conditions, e.g. small ranges of crystal size with well-developed crystals, or the first peak is due to an impurity, the most likely being kaolinite. On the basis of X-ray and optical evidence, Smithson and Brown decided that the double endothermic peak must be tentatively attributed to dickite only.

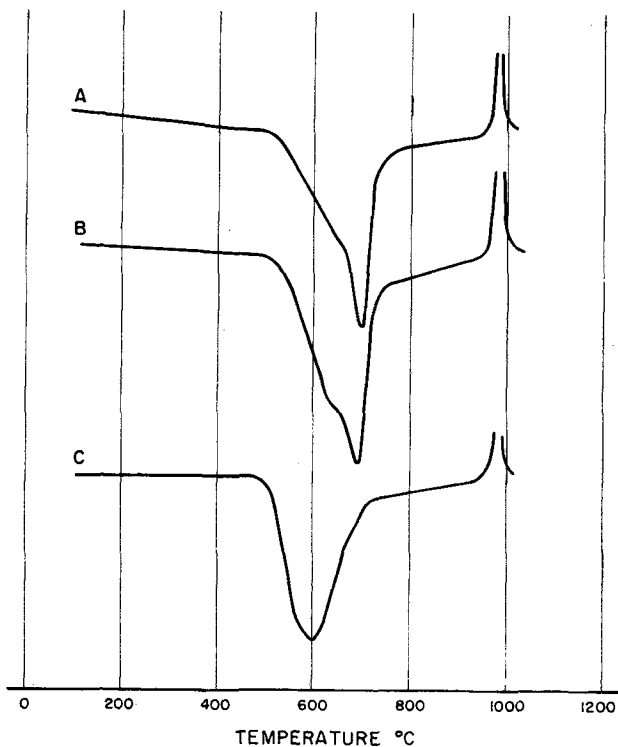


FIG. 4. Differential thermal analysis curves of various size fractions of the Barkly East dickite. A. 6.3–20 μ . Amplification $\times 5$. B. 2–6.3 μ . Amplification $\times 5$. C. $< 2 \mu$ (Sandwich). Amplification $\times 20$.

In fig. 4 the differential thermal analysis curves of the fractionated Barkly East dickite are shown. The high-temperature portion of the double peak becomes smaller with a decrease in particle size. In the $< 2 \mu$ fraction, only a slight inflexion remains on the high-temperature side of the peak. The curve for the $< 2 \mu$ fraction in fig. 4 cannot be directly compared with that of the coarser fractions because insufficient material was available to fill the well in the sample holder. In this case the material was sandwiched between calcined alumina and the ampli-

fication was increased. In fig. 5, however, the curves are directly comparable; these curves were obtained for samples which were diluted with calcined α -alumina (10% dickite, 90% Al_2O_3). For the $< 2 \mu$ fraction the main peak is at about 600°C . instead of 690°C . for the coarser

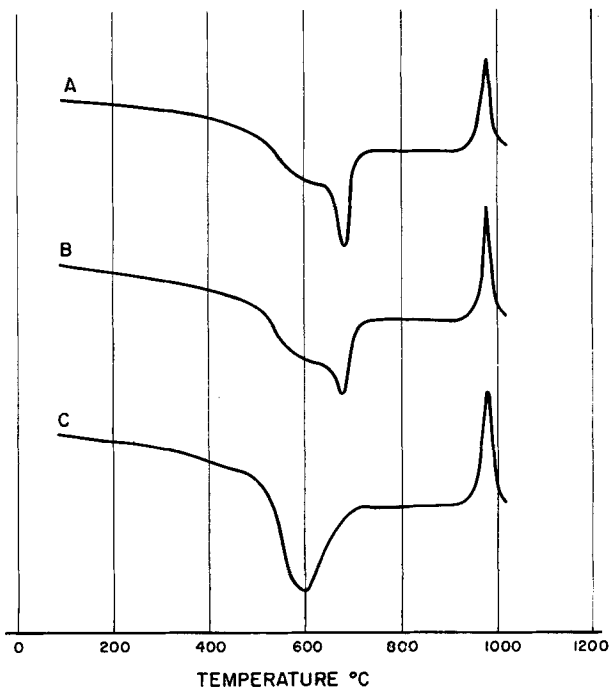


FIG. 5. Differential thermal analysis curves of various size fractions of the Barkly East dickite diluted with calcined alumina (10% dickite, 90% alumina). A. $6.3\text{--}20 \mu$. Amplification $\times 20$. B. $2\text{--}6.3 \mu$. Amplification $\times 20$. C. $< 2 \mu$. Amplification $\times 20$.

particle size fractions. As would be expected, the effect of the dilution was to improve the resolution of the two poorly-resolved peaks of the undiluted samples. Microscopical examination of the $< 2 \mu$ fraction showed that it consisted of very fine elongated dickite particles only. No contaminants could be detected.

Discussion and conclusions.

With coarse-grained dickites such as those from Ouray and Postmasburg it would be very difficult to obtain a size fraction $< 2 \mu$ e.s.d.

without resorting to grinding, but it is assumed that similar results will be found with these materials. McLaughlin (1955) studied the effects of grinding on the Ouray dickite. After two hours dry grinding he obtained a material which yielded a double endothermic peak. After 60 hours wet grinding, only one peak remained at a temperature lower than 600° C. McLaughlin states that the double peak is probably due to differences in reactivity between ground and unground material. It is, however, more probable that the particle size distribution of the sample after dry grinding for two hours was such that a double peak was formed. Unfortunately, McLaughlin did not report the particle size after 60 hours wet grinding but his curve is similar to the $< 2 \mu$ fraction in fig. 4, although the peak temperature is somewhat lower. According to Murray and White (1955, p. 147), when fine particle size is produced by grinding it is not certain that the lowering of decomposition temperature is due to particle size alone, since fine grinding causes considerable disturbance in the surface layers of minerals, particularly if they are soft. It must be pointed out, however, that the actual temperature where decomposition started in the wet-ground material is not significantly lower than the corresponding temperature in the unground material, viz. 500° C.

The evidence presented shows that the double peak for some dickites must be ascribed to dickite only and not to the presence of contaminants. Furthermore, it is clear that in the particular dickite with elongated habit examined, the double peak is a particle size effect which practically disappears if all the particles are $< 2 \mu$ e.s.d.

The mechanism of dehydroxylation in dickite.

The results of the present study enable some conclusions to be drawn as to the mechanism of dehydroxylation in dickite. Apart from the elongated habit of the Barkly East dickite, the only obvious difference between it and the Ouray and Postmasburg dickites appeared to be their different ranges of crystal sizes. It was also noticed that the latter dickites intumesced in the differential thermal analysis sample holder whereas the Barkly East dickite did not. In the Ouray and Postmasburg dickites, which have well-developed basal planes and equant outlines, one would expect the final dehydration to take place violently when the OH-groups in the interior of the particles escape, so that a portion of the material would be ejected from the holder, especially if the particles had acquired a preferred orientation as a result of being tamped into the holder. Roy and Osborn (1954), in a study of the temperatures of formation and temperature limits of stability of certain clay minerals, found

that kaolinite, halloysite, dickite, and nacrite all decomposed under equilibrium conditions at the same temperature of 405° C. They state (p. 863): 'The main difference in decomposition behaviour is the rate of decomposition with the larger particles of dickite and nacrite requiring longer periods of time to effect significant decomposition. Differences in the thermodynamic constants among these four phases must be slight.' Roy and Osborn conclude (p. 885): 'Thus the data from the present study would indicate that differential thermal analysis curves of dickite would approach more and more closely those of kaolinite as the particle shape and size were made more and more equal.'

For the Barkly East $< 2 \mu$ fraction the peak temperature of about 600° C. corresponds to a peak temperature of 610° C. for well-crystallized kaolinite from Macon, Georgia (Clay Mineral Standard H4), obtained with the same differential thermal analysis apparatus under the same conditions. These findings support the conclusions of Roy and Osborn (1954) and confirm their deductions which were based on indirect evidence.

It is clear from the curves that the loss of water begins at a constant temperature of about 500° C. for different dickite samples and irrespective of particle size. It is thus reasonable to explain the double peak of dickite as follows: The first portion of the double peak is due to the loss of OH-groups from the surfaces and edges of the particles and the second to the loss of OH-groups situated in the interior of the particles. The intumescence noticed with the Ouray and Postmasburg dickites is especially indicative of the loss of OH-groups from the interior of the relatively large particles. In the Barkly East dickite the loss of such OH-groups does not take place so violently because they can escape more easily, owing to the thin elongated habit of the crystals. A higher temperature is, however, still necessary to eliminate them from the coarser particles as indicated by the curves. As the particle size diminishes, the number of OH-groups in the interior of the crystals decreases relative to the more loosely bound OH-groups on the surfaces and edges of the particles, and therefore less energy is needed for their elimination (see fig. 5). In the particle size fraction $< 2 \mu$ e.s.d., practically all the OH-groups can escape easily, so that only one peak occurring at a relatively low temperature is registered on the differential thermal analysis curve.

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