Dickite from sandstones in northern England and North Wales.

(With Plate XIII.)

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Summary. The occurrence of dickite as a rock-forming mineral in sandstones of the Lower Carboniferous Series, the Millstone Grit, and the Middle Jurassic has been reported previously by the authors. In view of the paucity of data on this mineral, six samples were purified and examined optically, by staining tests, and by the X-ray powder method. In addition, a chemical analysis, a differential thermal analysis, and a thermal weight-loss curve were made on the purest sample. The investigations confirm the identity of the material.

As a result of his microscopic studies, Dick believed that there were two varieties of kaolinite and recorded that the optically positive and 'better crystallized type', now known as dickite, occurred at Amlwch, Anglesey (Dick, 1888; Miers, 1888, 1890), at Bolton Abbey, Yorkshire, at Newcastle upon Tyne, and at Congleton, Cheshire (Dick, 1908). Ross and Kerr (1931) have suggested that the earliest observation of this mineral was that by Knop (1859) who described 'orthorhombic' crystals of kaolin occurring at Schneckenstein. Of these early examples only the Amlwch material appears to have been still available when Ross and Kerr made their X-ray studies that led them to propose a specific name for it. Other dickite localities they name are in the U.S.A. (Arkansas, Colorado, Iowa, and Oklahoma), Mexico, Peru, and Silesia. Dickite has been subsequently proved by X-ray methods in Pennsylvania (Honess and Williams, 1935), Missouri (Tarr and Keller, 1936), Utah and New Mexico (Kerr *et al.*, 1950), at Newcastle upon Tyne (mentioned by Boswell, 1933, when abstracting Tomkieff, 1927), in County Durham (Dunham, Claringbull, and Bannister, 1948), in Yorkshire (Hemingway and Brindley, 1948, Brindley, 1951), and in South Africa (Frankel, 1949).

In all the above cases the mineral is apparently restricted to veins, pockets, cavities, &c., and does not enter into the composition of the rock as a rock-forming mineral except at Congleton, where Dick found that in the Millstone Grit 'the mineral fills the spaces between the grains of the grit'. Although this example has not been tested by X-ray methods, proved dickite occurs in this manner in parts of North Wales and northern England (Brown and Smithson, 1953; Smithson, with appendix by Brown, 1954) and from these occurrences the samples described in the present paper have been taken. Our earlier papers dealt chiefly with the petrography of the kaolin-bearing sandstones and, in the Middle Jurassic, indicated the geographical boundary between dickite- and kaolinite-bearing strata, showing that the former were characterized by more severe diagenesis than the latter. The present paper gives a detailed account of the X-ray identification and results of some optical tests on six representative samples, enumerated in the next section.

Without entering into details concerning the origin of dickite it may be pointed out that whereas hydrothermal activity has often been regarded as the sole or major cause of the formation of dickite, the present examples are not associated with ore-bearing veins nor with any known or probable magmas.

The source rocks (F. S.).

The stratigraphical horizons, localities, and general appearance of the six dickite sandstones are as follows:

No. 1. Carboniferous, Carboniferous Limestone Series, Bangor, Caernarvonshire, about 1000 yards north-east of Menai suspension bridge. Fissile sandstones with coaly plant remains, much limonitic matter and inconspicuous dickite.

No. 2. Carboniferous, Millstone Grit, Bodorgan Shore, Anglesey, about 1500 yards south-west of the bridge, Pont Malldraeth. Very coarse sandstone speckled white with dickite and brown with limonitic matter (pl. XIII, fig. 1).

No. 3. Carboniferous, Millstone Grit, about ½ mile west of Ellingstring, near Masham, Yorkshire. Coarse sandstone with some large felspar grains; interstitial dickite white to buff.

No. 4. Jurassic, Lower Estuarine Series (Lower Deltaic Series),[1] cliff near West Pier, Whitby, Yorkshire. Soft sandstone slightly mottled yellow and white.

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[1] The Lower Estuarine Series (Geol. Surv.) includes the Lower Deltaic Series of Hemingway (1949) and part of his Middle Deltaic Series.

No. 5. Jurassic, Lower Estuarine Series (Lower Deltaic Series), escarpment above Crag Pond, Farndale, Yorkshire. Yellow sandstone faintly speckled with dickite.

No. 6. Jurassic, Lower Estuarine Series (Middle Deltaic Series), 200 yards below road-bridge, Bondfield Gill, about 6 miles north of Helmsley, Yorkshire. Yellow sandstone with vertical carbonaceous markings (stems of Equisetum (?)). The rock is speckled with dickite particularly in the fossil stems, which also contain limonitic matter.

Microscopical examination (F. S.).

Examination of thin sections of the sandstones shows interstices packed with dickite in the form of rouleaux (pl. XIII, fig. 2). Such bodies are often regarded as piles of platy crystals, though it may be more accurate to interpret them as columnar crystals, which, owing to flexibility and ready basal cleavage, have suffered distortion and dislocation as they jostled one another during growth.

The separated material (pl. XIII, figs. 3–6) contains both rouleaux and plates, the latter ranging from almost regular hexagons to elongated and rhombic shapes or complex figures with re-entrant angles (Smithson, 1954, fig. 1). Plates with diameters from 5μ to 50μ were encountered, but most lay well within those limits. All but the thinnest plates showed changes of colour on rotation when using a sensitive purple gypsum plate and crossed polars, and this test showed the fast-ray vibration direction to be parallel to two sides of the hexagon. The birefringence is sufficient to give slight 'twinkling' if phase-contrast equipment, a single polar, and an appropriate immersion liquid are used (Smithson, 1948). This arrangement was adopted for determining the refractive indices for sodium light, using a series of liquids with intervals of 0·001 as measured on an Abbé refractometer at 20° C. Dickite plates adhered flat on the glass, but rouleaux were variously oriented and liable to movement. With plates the slow vibration direction (γ) gave values 1·567–1·568, and the fast direction 1·564–1·565. Since rouleaux appropriately oriented will give a correct value of α a number were tested in each sample and the lowest values, 1·562–1·563, were taken as a measure of this index.

With appropriate stains the plates become coloured, though feebly and with little or no pleochroism, i.e. the absorptions for Y and Z are practically identical. With the same stains the rouleaux are more strongly coloured and pleochroic, the absorptions for X being distinct from those for Y and Z (table I).

TABLE I. Pleochroism of stained dickite.

Stain.	*X*.	*Y*.	*Z*.
Safranin	Yellow	Pink	Pink
Thionin	Yellow	Bluish-violet	Pinkish violet
Crystal Violet	Yellow or brown	Violet	Violet
Malachite Green	Violet	Blue-green	Blue-green
Nile Blue	Violet	Pale blue	Pale blue
Methylene Blue	Almost colourless	Blue	Blue

In the dickite separations, particularly nos. 5 and 6, there are what appear to be aggregates of a cryptocrystalline clay mineral (pl. XIII, fig. 6) that have a mean refractive index about 1·565 and take a deep stain with malachite green.

Non-clay minerals. Of the other minerals present in the source rocks only the following were recognized contaminating the dickite separations: quartz, felspars, and white mica, together with minute particles of the heavy minerals anatase, leucoxene, brookite, rutile, tourmaline, and zircon.

X-ray examination (G. B.).

For X-ray examination the separates obtained from the sandstones by crushing and sieving were purified further. Optical examination had shown that the diameter of the bulk of the hexagonal plates lay well within the range 5 to 50μ but also that in this range of particle size were many aggregates cemented by iron oxides or clay. To disperse these aggregates the separates were warmed in dilute hydrochloric acid for about a minute and washed free of acid immediately. After treatment the powders were white except no. 1, which was grey owing to carbonaceous impurities. No sign of attack by acid on the edges of the delicate hexagonal plates could be seen. Two size-fractions, 5 to 20μ and 20 to 40μ (ideally), were separated by repeated sedimentation giving twelve 10 to 20 mg. samples which were used without further crushing or grinding for X-ray examination. In addition a further one-gram sample of 5 to 40μ material was obtained from no. 2 (which proved to be the purest) by the method outlined above, and this was used for differential thermal analysis, chemical analysis, and thermal weight loss analysis. About 75 % of this 5 to 40μ fraction had diameters in the range 10 to 20μ and the diameters of most of the remainder were in the range 20 to 30μ. As this fraction consists chiefly of hexagonal plates with only a few rouleaux it can be taken that its physical behaviour will be determined almost exclusively by the former.

Powder photographs of unground material were taken in a 9·0 cm. diameter Bradley type evacuated powder camera with filtered Co-$K\alpha$ radiation; a few photographs were also taken with a Cu-$K\alpha$ radiation. The specimens were rotated during exposure. For flaky minerals of low symmetry two particular requirements are good resolution and random orientation of crystallites in the specimen. Narrow specimens were prepared from aggregates obtained by drying viscous slurries of the powders with gum arabic and water on slides, and specimens about $1{\cdot}5 \times 0{\cdot}1 \times 0{\cdot}1$ mm. were cut from the aggregates. The gum arabic acts as binder for the powder and also as a spacer, and if the slurry is viscous it tends to prevent preferred orientation by hindering the settling of the flaky particles on the slide. Narrow specimens have the additional advantage of low absorption and thus line-displacement errors due to absorption can be neglected. Photographs were taken of both coarse and fine fractions and the dominant mineral in all fractions was found to be dickite.

The spacings and visually estimated intensities of lines due to dickite in the different samples have been tabulated and the tables deposited in the library, Rothamsted Experimental Station. Copies may be obtained from the Librarian. Although the patterns were measured only to $d = 1{\cdot}2$ Å., reflections occur to $d = 0{\cdot}8$ Å. Despite the apparent perfection of the microscopically observed crystals (pl. XIII) the α_1, α_2 doublet was not resolved even at the highest θ values.

The powder data for dickite appear to be incomplete (compare Gruner, 1932; Brindley, 1951). The observed reflections from our materials were allocated to dickite or impurities on the basis of Gruner's and Brindley's data and from a knowledge of the microscopically observed impurities in each sample. The impurities detected by X-rays were quartz and anatase in all specimens, mica and feldspar in some. Sample no. 2, 5 to 40μ, is estimated to contain more than 95 % dickite.

All the dickite patterns were identical within experimental error and the average spacings derived from all the measurements are given in table II where they can be compared with Gruner's (1932) and Brindley's (1951) data. The accuracy of the average spacings was estimated to be ±0·1 % by comparing the quartz spacings with A.S.T.M. card 5–0490. The observed reflections all fit Gruner's cell, the differences in lattice constants being within experimental error. For example, the layer thickness, d (002), is given as 7·160 Å. by Gruner (1932). Using the first four visible (00l) spacings we obtain 7·153, 7·156, 7·149, 7·156 Å., and the average 7·154 Å. The observed reflections coincide with the reflections

TABLE II. X-ray powder data for dickite. Col. 2, spacings in Å. and visually estimated intensities, averaged from the detailed data deposited at Rothamsted. Col. 1, indices calculated for Gruner's (1932) unit cell. Cols. 3 and 4, spacings recorded by Gruner (1932) and Brindley (1951) respectively.

1.	2.		3.	4.
002	7·153	vs	7·12	7·17
020, 110	4·451	ms	4·43	4·452
$11\bar{1}$	4·366	ms		4·374
021	4·254	mw		4·273
111	4·118	s	4·15	4·129
$11\bar{2}$	3·953	mw	3·95	3·962
022	3·790	ms	3·79	3·798
004, 112	3·578	vvs	3·578	3·582
$11\bar{3}$	3·428	m	3·439	3·432
023	3·262	w		3·253
113	3·094	mw	3·011	3·103
$11\bar{4}$	2·936	mw		2·937
024	2·794	mw		2·796
114	2·650	vvw	2·634	2·656
$13\bar{1}$, 200 130	2·558	ms	2·566	2·565
$11\bar{5}$	2·524	vvw	2·514	2·523
131, $20\bar{2}$	2·503	s		2·506
006, 132	2·383	m	2·384	2·388
$13\bar{3}$, 202	2·322	vs	2·328	2·323
220, 133 204, 041	2·210	mw	2·180	2·211
026, 223	2·105	w	2·099	2·103
$22\bar{4}$, $13\bar{5}$ 204	1·974	ms	1·976	
223, $11\bar{7}$	1·935	vvw		
044	1·896	mw	1·895	
027, 135 $20\bar{6}$	1·862	mw	1·859	
$22\bar{5}$	1·850	w		
$13\bar{6}$, 224	1·803	w		
008, 117	1·789	mw	1·792	
045	1·761	vw		
$22\bar{6}$, 118	1·717	vw	1·718	
150, $24\bar{1}$ $31\bar{1}$, $15\bar{1}$ 240	1·686	mw		
310, $31\bar{2}$ 225, 151 $24\bar{2}$, 028	1·669	mw		

1.	2.		3.
$15\bar{2}$, $13\bar{7}$ 206, 241	1·651	ms	1·649
311, $31\bar{3}$	1·644	w	
046, 152 $24\bar{3}$	1·626	w	
$15\bar{3}$, 242	1·610	mw	
312, $31\bar{4}$ $22\bar{7}$	1·589	vw	
153, $24\bar{4}$	1·574	vw	
137, $20\bar{8}$	1·558	mw	1·555
$15\bar{4}$, $11\bar{9}$ 243, 226	1·548	vw	
313, $31\bar{5}$	1·525	vw	
047, $13\bar{8}$	1·509	vw	
154, $24\bar{5}$ 029	1·502	vw	
060, $33\bar{1}$	1·488	ms	1·490
$22\bar{8}$	1·469	vw	
062, $33\bar{3}$ 331, $31\bar{6}$ 314, 119	1·457	mw	1·455
227, 138 155, $24\bar{6}$ 0.0.10	1·433	w	1·431
$15\bar{6}$, 245 048, $1.1.\overline{10}$ $13\bar{9}$, 208	1·402 1·392	vw w	1·391
315, $31\bar{7}$ 064, $33\bar{5}$ 333	1·376	mw	1·374
065, $33\bar{6}$ 139, 1.1.10 $2.0.\overline{10}$	1·319	ms	1·317
	1·296	vvw	
	1·289	mw	
	1·279	w	
	1·264	w	
	1·254	mw	
	1·238	mw	

of higher calculated intensity (Gruner, 1932) except for a few of spacing less than 1·5 Å. which would be more sensitive than those of higher spacing.

Chemical analysis (G. B.).

A partial chemical analysis was carried out on about 0·3 g. of the 5 to 40μ separate of no. 2 referred to previously and gave SiO_2 47·4, Al_2O_3 38·0, TiO_2 0·2, H_2O- 0·0, H_2O+ 13·7 = 99·3. Alumina was determined using aluminon (Chenery, 1948) and is the value most likely to be in error. The impurities detected by X-rays in this fraction were quartz and traces of anatase and mica. Assuming these to be the only impurities present in appreciable amounts, calculation from the H_2O+ value leads to a content of approximately 98 % $Al_2O_3.2SiO_2.2H_2O$, the remainder being quartz 1·8 % and anatase 0·2 %.

Thermal examination (G. B.).

The material used for the thermal examination was part of the 5 to 40μ separate from no. 2. Optical examination of this sample showed that about 75 % of the plates had major diameters in the range 10 to 20μ. The largest plates seen were about $40 \times 30\mu$, the smallest $4 \times 3\mu$. For the thermal studies the samples were used in the unground condition.

Weight loss. For this determination duplicate 0·3 g. samples were heated in small platinum boats in a furnace controlled within $\pm 5°$ C. of the recorded value. The specimens were weighed after heating at 50° temperature intervals between 100° and 850° C.; they were held at each temperature for 14 hours which allowed an approach to equilibrium. The resultant curve is shown in fig. 1. The crystals retain their hexagonal shape after heating. Ross and Kerr (1931) gave an equilibrium weight loss curve for dickite from Chihuahua, Mexico, which they describe as vermicular with the average diameter of the crystals about 30μ. Their curve is similar in shape to fig. 1, but the main weight loss occurs in the range 500° to 600° C. in which about 90 % of the water is lost, as opposed to 400° to 550° C. for our material; no explanation can be offered at the moment for the different temperature at which the weight loss occurs. Neither the curve in fig. 1 nor that given by Ross and Kerr (1931) for dickite shows the second break at about 675° C. recorded by Ross and Kerr (1931) and by von Knorring, Brindley, and Hunter (1952) for nacrite, the other mineral of the kaolin group that forms large crystals.

Differential thermal analysis. A curve covering the ranges 200° to 800° C. was made using 0·25 g. with calcined kaolinite as the inert material. The samples were heated in ceramic crucibles suspended in a cavity in a nickel block in an atmosphere of dry nitrogen at a heating rate of 10° per minute. The curve (fig. 2) shows what appear to be two

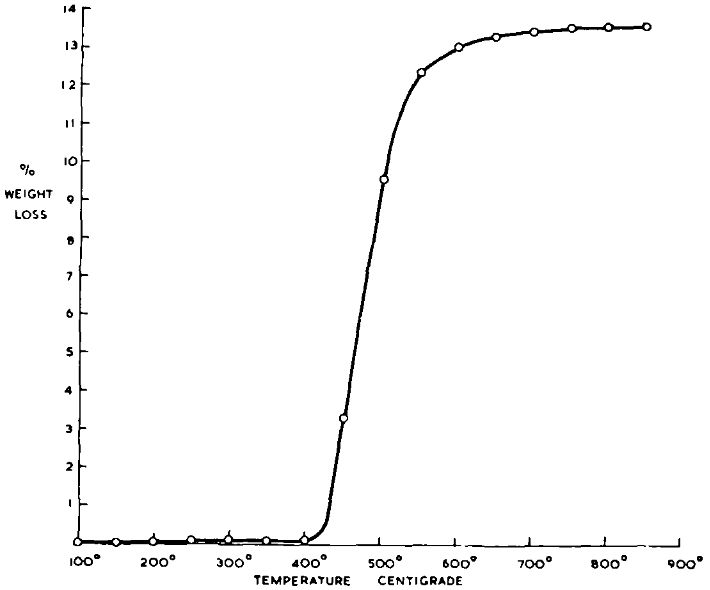

FIG. 1. Thermal weight loss curve for dickite no. 2, 5 to 40μ. 14 hours at each temperature.

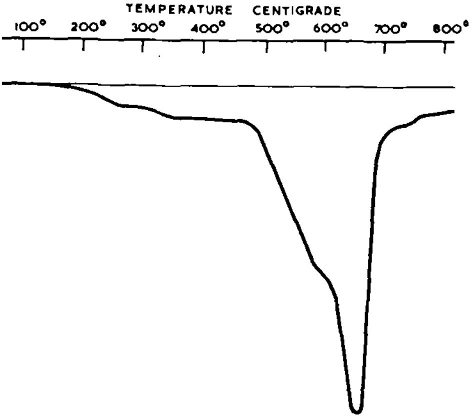

FIG. 2. Differential thermal analysis curve for dickite no. 2, 5 to 40μ.

partially resolved endothermic peaks at about 590° and 670° C. The differential thermal analysis curves given in the literature for dickite often show an asymmetric endothermic peak with a slow approach to the maximum. Kerr and Kulp (1948) show curves of this type and others in which the endothermic peak is symmetrical, but unfortunately they give no evidence for either identity or purity of the samples. Kerr *et al.* (1950, p. 66) give the differential thermal analysis curve of a dickite from Anglesey (not the type locality) which resembles the curve in fig. 2 although the double endothermic peak is less marked; they suggest that nacrite is present in this material, but give insufficient data to support this.

There are two possible sources for the double peak. Either both peaks are due to dickite and are shown here because of the particular conditions, for example, small range of crystal size with well-developed crystals, or the first peak is due to impurity, the most likely being kaolinite. No X-ray reflections other than those that can be attributed to dickite, quartz, anatase, and mica (see the tables deposited at Rothamsted) were observed from no. 2. In view of the large number of dickite reflections observed, many of them very weak, if kaolinite is present in this material then its detection in the presence of major amounts of dickite must be difficult. The impurities revealed by microscopical examination were minute amounts of quartz, anatase, zircon, muscovite, and unidentifiable particles similar to those shown stained in pl. XIII, fig. 6, and although these may be a cryptocrystalline clay mineral other than dickite, their amount (<1 %) is probably too small to affect the thermal results. On the basis of the X-ray and optical evidence the double endotherm must be tentatively attributed to dickite but it must be borne in mind that it is very difficult to establish purity with fine grained materials.

Discussion of thermal studies. The thermal studies reported above were merely carried out as an adjunct to other methods of identification and lay no claim to completeness. It is interesting to note the difference between the differential thermal analysis curve obtained directly and the differential curve obtained from the weight loss curve. The former shows two unresolved peaks and the peak as a whole is asymmetric with the steeper slope on the high-temperature side, the latter shows only one peak much less asymmetrical with the steeper slope on the low-temperature side. The non-correspondence of the curves emphasizes the dynamic character of the differential thermal curve.

It appears from the literature that kaolinite, dickite, and nacrite differ in their differential thermal and weight loss curves. It is not known how far these differences may be due to differences in crystal structure leading to variations in hydroxyl binding or to factors such as crystal size and perfection, which may affect the reactions. The results of the present limited study suggest that combined X-ray, weight loss, and differential thermal analyses, made on well-characterized materials with varied narrow ranges of crystal size and with varied rates of heating, might throw considerable light on the mechanism of the dehydroxylation reactions. Until such a study is made, interpretations based on differences in the differential thermal analysis endothermic peaks of clay minerals in the region 500° to 800° C. must be made with caution.

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EXPLANATION OF PLATE XIII.

Fig. 1. Broken surface of dickite-bearing Millstone Grit, Bodorgan shore, Anglesey (source rock no. 2). ×9.

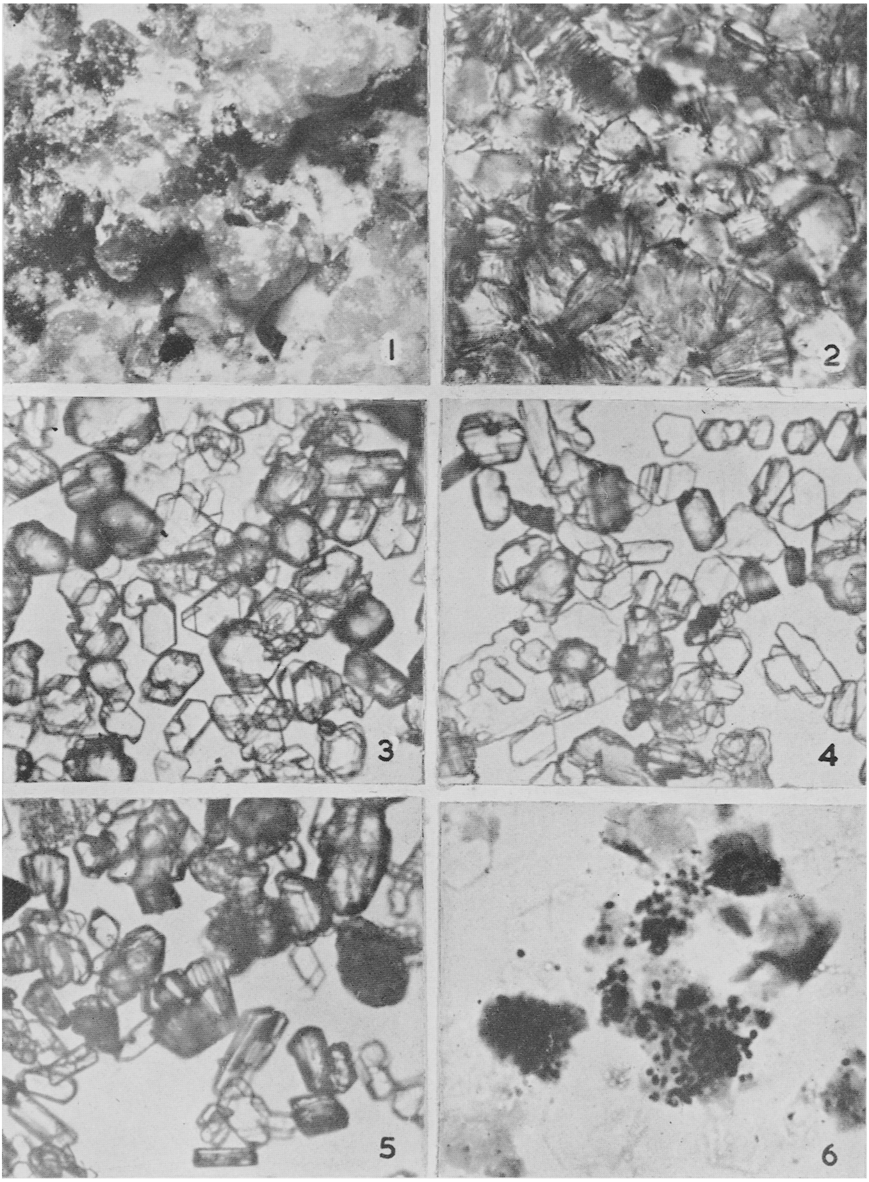
Fig. 2. Dickite in thin section of above. ×500.

FIG. 3. Dickite in coarse silt fraction from source rock no. 2. In air. ×432.

FIG. 4. Dickite in coarse silt fraction from Lower Estuarine sandstone, Whitby, Yorks. (source rock no. 4). The large flake is muscovite. In air. ×432.

FIG. 5. Dickite in coarse silt fraction from Lower Estuarine sandstone, Farndale, Yorks. (source rock no. 5). Particle near centre shows splitting along cleavage planes. In air. ×432.

FIG. 6. As no. 5, stained with malachite green to show the associated cryptocrystalline clay mineral (?) and mounted in Canada balsam. ×1025.



F. SMITHSON AND G. BROWN: DICKITE