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DICKITE IN THE HAWKESBURY SANDSTONE OF THE SYDNEY BASIN, AUSTRALIA[1]

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Abstract

The widespread occurrence of dickite in the freshwater Triassic Hawkesbury Sandstone of the Sydney Basin is recorded. The dickite is associated with kaolinite, illite and mixed-layered minerals and is concentrated in the $>2\mu$ fraction. It appears as rouleaux and vermicular crystals which yield hexagonal plates on dispersion. The absence of any evidence of hydrothermal activity indicates that the dickite is authigenic, although the mechanism of formation is still conjectural.

Introduction

Dickite was first recognized as a distinct member of the kaolin group of clay minerals by Dick (1888, 1908) on the basis of its optical and chemical properties and was subsequently confirmed and named by Ross and Kerr (1931) from the *x*-ray diffraction data. The material originally examined by Dick came from Amlwch, Isle of Anglesey, where it occurred in a hydrothermal environment. However, in his 1908 paper, the same author described three new occurrences of the mineral, all of which were apparently of authigenic or sedimentary origin. The origin of dickite was also considered by Ross and Kerr (1931) who concluded that it "is commonly formed by hydrothermal solutions and occasionally by cool solutions, although nowhere, as far as is known, is evidence presented that clearly shows the origin through a process of weathering."

Since the investigation of Ross and Kerr there have been many references to the occurrence of dickite, particularly as cavity fillings in rocks (Sohlberg, 1933; Miser, 1943; Allen, 1945; Frankel, 1949; Schmidt and Heckroodt, 1959). Each of these authors attributed the origin to hydrothermal activity.

Tarr and Keller (1936) considered the deposits of dickite in the uppermost beds of the Mississippian in Missouri were also hydrothermal in origin but a more recent investigation by Keller (priv. comm.) indicates the mineral is the product of intense chemical weathering.

Minor occurrences of dickite for which no evidence of a hydrothermal origin was found and hence presumed to be authigenic, have been described by Honess and Williams (1935) from coal-bearing strata in Pennsylvania; Hemingway and Brindley (1948) from Jurassic sediments in Yorkshire; and Loughnan (1962) in a tonstein from New South Wales.

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[1] This work describes one facet of a comprehensive study of the Hawkesbury Sandstone presented to Sydney University as a Ph.D. thesis by Standard.

References to the more widespread distribution of dickite as a rock-forming mineral in sediments have been restricted to Carboniferous and Jurassic sandstones of northern England and northern Wales (Dick, 1908; Brammall and Leech, 1943; Smithson, 1954; Smithson and Brown, 1957) and to Narrabeen sandstones of the Sydney Basin (Loughnan, *et al.*, 1964). Smithson (1954) investigated the origin of the dickite in sandstones of England and Wales and found that the sediments had not been disturbed by hydrothermal activity. He believed that the soft and friable nature of the dickite crystals indicated an authigenic development.

It is the purpose of the present paper to describe a further occurrence of the widespread distribution of authenic dickite in sandstones.

THE HAWKESBURY SANDSTONE

The Hawkesbury Sandstone forms the middle unit in the three-fold subdivision of the Triassic freshwater sediments of the Sydney Basin. It overlies the Narrabeen Group and in turn is succeeded by the Wianamatta Group. The formation outcrops over an area of several thousand square miles and attains a maximum thickness of 800 to 1,000 feet in the central portion of the basin. Current-bedded, quartzose sandstone is the dominant rock type although shale lenses, which range up to 40 feet in thickness, occur in places. Fossil fish and poorly preserved plant remains have been found in the shales. The sandstone has suffered secondary silicification which has rendered it relatively resistant to erosion and, in consequence, outcrops of the formation give rise to spectacular canyon-like scenery.

The sandstones vary in quartz content between 45 and 95 per cent although few samples contain outside the range of 70 to 85 per cent. The grains are well-sorted and originally possessed a high degree of roundness but silicification has yielded secondary outgrowths and sutured contacts while some have developed crystal outlines. Frequently the original grain boundary is marked by fine dust inclusions. According to Golding (1956), the extent of secondary silicification increases with the original quartz content of the rock. Feldspar is rare, and the heavy mineral assemblage consists only of stable species (McElroy, 1954). Carbonates, principally calcite with a little siderite, may be present to the extent of 10 per cent but rarely exceed 1 per cent and commonly are absent. The rock differs from a true quartzose sandstone, as defined by Pettijohn (1957), in that the clay matrix generally exceeds 15 per cent and in places 50 per cent by volume. Thin sections of the rock show that much of the clay is an intermix of low-birefringent material, presumed to be a kaolin mineral, and fine illite flakes. In the larger interstices between the quartz grains there is a tendency for illite to occur marginal to the low-birefringent areas. Vermicular crystals, rouleaux and wisps of a well-cleaved kaolin mineral have been recorded previously by Smith (1891), McElroy (1954) and Golding (1956) and can be observed in most thin sections.

CLAY MINERALOGY

Samples of sandstone were obtained from outcrop and bore cores over widely separated sections of the Sydney Basin in order to gain both vertical and lateral representation. From the initial program, 50 samples were selected for detailed mineralogical examination.

Each of the selected samples was gently crushed with a rubber pestle to free the particles and the material passing through a 325 mesh B.S. sieve (43μ) collected. Examination of this material under the microscope, using high magnification, revealed the presence of hexagonal plates, principally in the size range of 2 to 10μ, with other clay material (Fig. 1). The plates, which vary in abundance from sample to sample, are not quite isotropic and have a mean refractive index of 1.56. However, because of the fine particle size, the remaining optical properties were not obtainable.

Portion of the $<43\mu$ material was further fractionated into $>2\mu$ and $<2\mu$ sizes by standard settling procedures. From the smaller size fraction, oriented aggregates were prepared and subjected to x-ray analysis without further treatment, after glycolation for a period of 24 hours and after heating to 450° C. for half an hour. From the data obtained, quantitative estimations of the clay mineral composition of the $<2\mu$ fraction were made. In Fig. 2 the results have been plotted on a triangular dia-

FIG. 1. Electron micrograph of hexagonal plates.

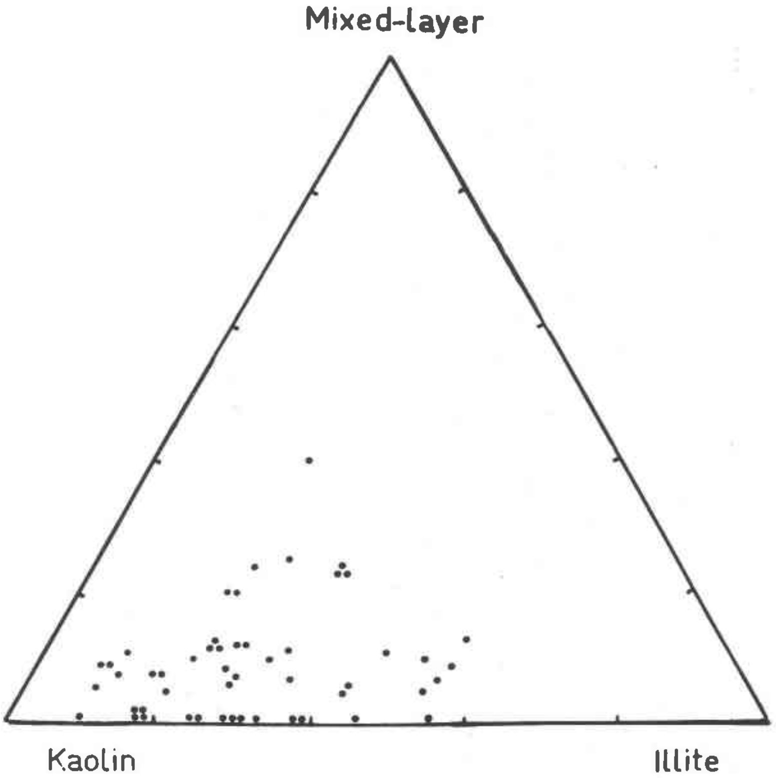

FIG. 2. Composition of $<2\mu$ fraction determined by x-ray diffraction.

gram in which kaolin, illite and mixed-layered clay minerals are the end-members. It will be observed that the kaolin minerals predominate although illite is invariably present and in several it is the most abundant component. Mixed-layered minerals, generally in the form of degraded illite, are a minor constituent.

Differential thermal analyses were made of the 2–43μ and $<2\mu$ fractions and it was found that the curve for the $<2\mu$ fraction showed only one endothermic peak, coincident with that of kaolinite at 600° C., whereas the 2–43μ fraction gave two endothermic peaks, one at 600° C. and the other 700° C. (Fig. 3). The relative size of the two peaks obtained for the 2–43μ fraction varied considerably as shown in Fig. 4 which represents a histogram of the ratio of the 700° C. endothermic area to the total endothermic area against the number of samples.

To determine the mineral responsible for the reaction at 700° C., the samples were heated at the rate of 15° C. per minute to a temperature of

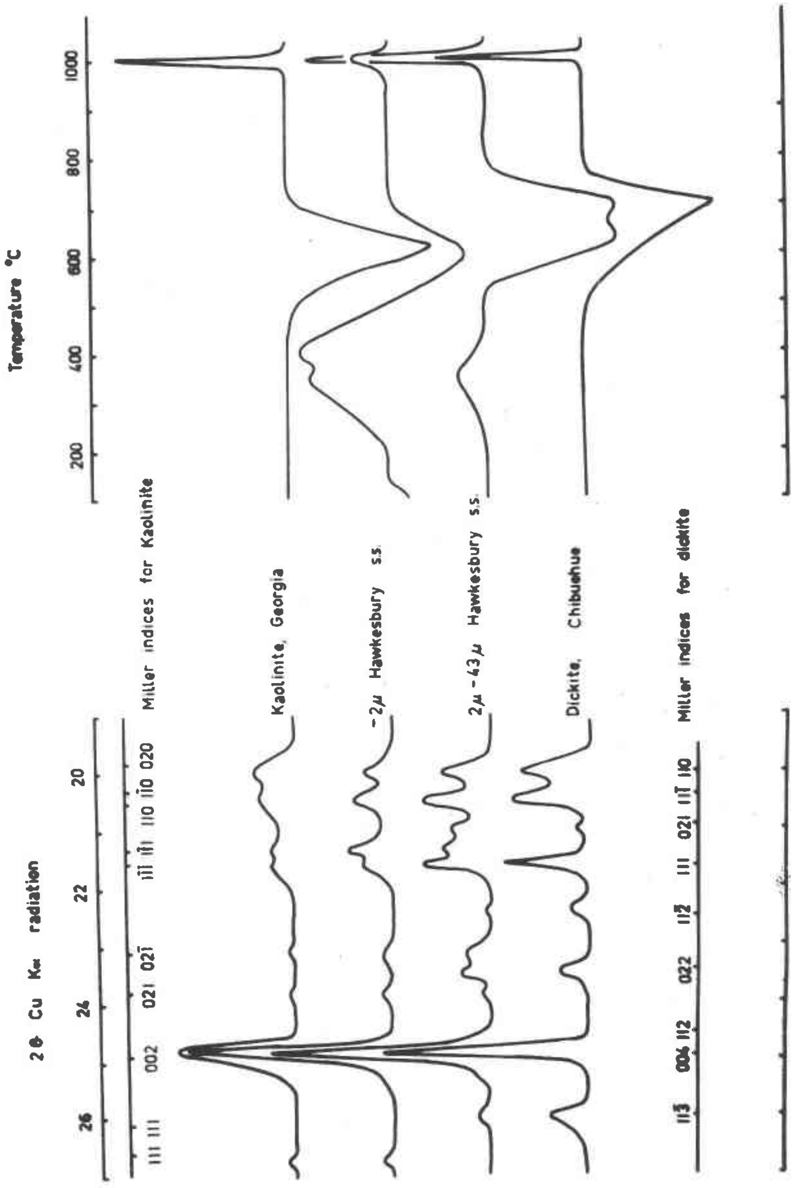

FIG. 3. Differential thermal and x-ray diffraction curves.

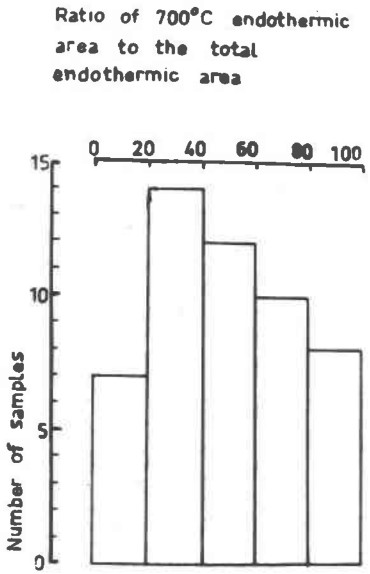

FIG. 4. Differential thermal data.

600° C. and then held at that temperature for a further 15 minutes. Subsequent x-ray examination showed the presence of a kaolin mineral. Since the x-ray pattern of kaolinite is destroyed by this thermal treatment (Grim, 1953), it was concluded that dickite is present and was responsible for the 700° C. endothermic reaction.

Smithson and Brown (1957), in their investigation of dickite from sandstones of northern England and northern Wales, also obtained a double endothermic peak on the differential thermal curve which they attributed to two possible causes: "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." Since they failed to obtain x-ray diffraction data for clay minerals other than dickite and mica, they concluded that the two peaks were caused by a variation in the particle size of the dickite. Moreover, Schmidt and Heckroodt (1959) fractionated dickite from Cape Province, South Africa and also obtained a double endothermic peak for the fine separations. They considered the development of the earlier 600° C. endothermic peak was due to the fine size of the dickite and could not be attributed to kaolinite contamination.

Previously, McLaughlin (1955) studied the effect of grinding dickite from Ouray, Colorado, on the differential thermal curve. He found after two hours dry treatment a second endothermic peak appeared at 600° C. and after 6 hours the original 700° C. peak vanished entirely.

The work of these authors suggests that the differential thermal curve for dickite varies with the particle size. The failure to obtain a 700° C. endotherm on curves of the $<2\mu$ fraction of the Hawkesbury Sandstone, therefore, does not necessarily imply the absence of dickite in this fraction nor does the existence of a 600° C. endotherm prove the presence of kaolinite. In short, the differential thermal data are inconclusive.

The positive differentiation between the polymorphs, kaolinite and dickite, is possible by *x*-ray diffraction if accurate resolution of the non-basal reflections is obtained (Brindley, 1951). In consequence, examination of the $2\text{–}43\mu$ and $<2\mu$ separations of the Hawkesbury Sandstone were made using scanning speeds of $\frac{1}{8}$ degree 2θ/minute, and particular attention was paid to the presence of a reflection at 23.4 degrees 2θ with Cu kα radiation (d=3.80) which corresponds to the 022 spacing of dickite. It was observed that, although the $2\text{–}43\mu$ separations of all samples gave reflections at this angle (Fig. 3), the intensities varied considerably. On the other hand, only a few of the $<2\mu$ separations recorded reflections at the specific angle and these were from samples which yielded the maximum intensities for the $2\text{–}43\mu$ size range.

On the basis of the *x*-ray diffraction data therefore, it must be concluded that both dickite and kaolinite are present in the matrix of the sandstone and that the dickite is concentrated in the $2\text{–}43\mu$ fraction. Since the hexagonal plates are also virtually restricted to the same size range it would appear that these are, in fact, dickite crystals.

The mineralogy of the interbedded shales has been shown by Ferguson and Hosking (1955) and Loughnan (1958) to contain approximately equal amounts of quartz, kaolinite and illite with a little degraded material. Dickite has not been detected by either *x*-ray or differential thermal techniques and vermicular crystals and hexagonal plates have not been observed in these sediments.

ORIGIN OF THE DICKITE

Despite a considerable number of independent investigations of the Hawkesbury Sandstone and associated Triassic sediments of the Sydney Basin, there has not been any evidence presented to suggest that the rocks have formed by processes other than those generally considered sedimentary. Mineralization, apart from one or two isolated curios, is absent, and indications of hydrothermal activity are lacking. On the other hand, the soft and friable nature of the rouleaux and vermicular crystals attests to their development *in situ*, for transportation would have surely destroyed these delicate structures. It would appear that an authigenic origin is the only possible solution, and this contention is supported by the fact that the crystals are restricted to the more permeable sandstones and are not encountered in the associated shales.

The actual mechanism of formation of the dickite, however, is more conjectural. Possibly groundwater leaching of feldspar and/or illite in the sandstones has removed the alkalies and alkaline earths and resulted in a residual concentration of alumina and silica which ultimately crystallized as dickite. However, as noted previously feldspar is relatively deficient in these rocks, and illite generally shows only a slight degree of degradation while the partial transformation of either mineral to vermicular forms or rouleaux has not been observed in thin section. Moreover, this mechanism also fails to account for the formation of dickite in preference to kaolinite, the normal alteration product of these minerals.

It is obvious more data will be necessary before the problem of the mechanism can be solved. However, an interesting point arising out of the discovery of the widespread distribution of authigenic dickite in the Hawkesbury Sandstone is that it offers an explanation for the high matrix content in an otherwise well-sorted, quartzose sandstone.

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