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DICKITE IN LANSING GROUP (PENNSYLVANIAN) LIMESTONES,
WILSON AND MONTGOMERY COUNTIES, KANSAS

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INTRODUCTION

Previously undescribed dickite is a conspicuous void-filling mineral in limestones of the Lansing Group (Missourian, Pennsylvanian) of southeast Kansas, particularly in Wilson and Montgomery counties. No other reported occurrence of dickite is similar to that in Kansas, so a short description seems appropriate.

Dickite, an uncommon clay mineral, is one of three well crystallized polytypes of the kaolin composition, $Al_4(Si_4O_{10})(OH)_8$; kaolinite is by far the most abundant, whereas nacrite is rare. Kaolinite has a one-layer stacking sequence and triclinic symmetry; dickite and nacrite represent two different two-layer stacking sequences with monoclinic symmetry. Dickite and nacrite typically are better crystallized than many kaolinites, and appear as well formed pseudohexagonal plates up to 1 mm across. A recent summary of kaolin polymorphism was given by Bailey (1963).

Most reported occurrences of dickite (and nacrite) are in direct and obvious association with veins of metallic sulfides and common gangue minerals, apparently of hydrothermal origin. This usual paragenesis, together with laboratory synthesis at elevated temperatures (Ewell and Insley, 1935), suggests the value of dickite as a geothermometer. In contrast are more widespread occurrences of dickite where no source of hydrothermal solutions is apparent. For example, Bayliss *et al* (1965) reported authigenic dickite in pore spaces of Triassic sandstones of Australia; that paper contains an extended bibliography on the dickite problem. Because clear evidence of hydrothermal activity is unrecognized, genesis of the Kansas dickite is yet unknown, but some speculations are offered.

DESCRIPTION OF DICKITE AND MODE OF OCCURRENCE

While participating in a Geological Society of America 1965 field trip to study algal limestones in the Lansing Group of southeast Kansas (Harbaugh *et al.*, 1965), the writer collected limestones containing small pockets of snow-white powder at four of the scheduled stops. Upon X-ray examination, the powders from stops 2, 4, and 6 proved to be dickite, whereas that from stop 7 is kaolinite. Figure 1 shows locations of the exposures. Dickite is especially abundant at stop 4. Figure 2 gives the

stratigraphic positions of the mineral specimens. Dickite and kaolinite probably are to be found many other places in the area, for the field trip localities were merely representative. In the field it was faintly suspected the powder might be dickite, judging from the bright reflections from cleavage or crystal faces observable through a hand lens. This glistening appearance is characteristic of dickite.

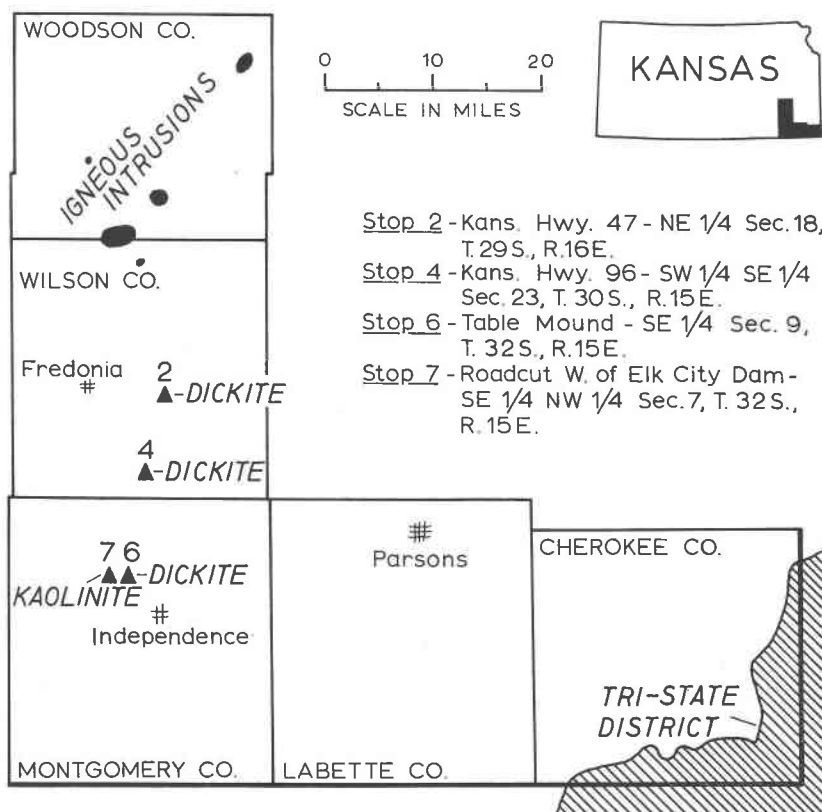


FIG. 1. Map of five southeast Kansas counties to show dickite and kaolinite localities, igneous intrusions, and northwest margin of Tri-State lead-zinc district (Harbaugh *et al.*, 1965).

Limestones in which the dickite is found have been admirably described in a series of papers by Harbaugh (1959, 1960, 1961, 1962). Leaf-like calcareous algae were dominant and locally built up abnormal thicknesses of porous carbonate sediment as marine banks miles in length and width. Much of the present porosity is interpreted by Harbaugh to be original, though secondary solution porosity also is recognized. Void-fill-

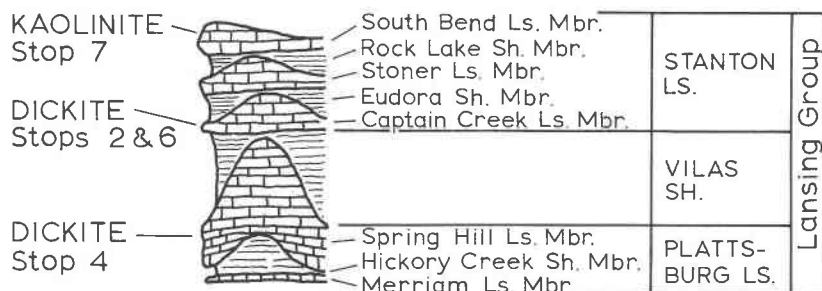


FIG. 2. Stratigraphic classification of Lansing Group (Pennsylvanian) in southeast Kansas (after Harbaugh, 1962, p. 14). Dickite and kaolinite occurrences are indicated. Limestone units with algal bank development are accentuated.

ing calcite and ferroan dolomite are abundant, as is sparry calcite said to be recrystallized carbonate mud. Dickite was found in these porous algal limestones and associated biocalcarenites, but not in the interbedded shales or fine-grained limestones.

Dickite-filled pores range in size from a fraction of a millimeter to a centimeter across. Dickite is a loose fluffy powder in some pores, but in others it forms a hard compacted mass. Fluffy dickite appears as discrete pseudo-hexagonal plates 30–40 μ across and 5–10 μ thick (Fig. 3), whereas compact dickite is made up of strongly intergrown vermicular aggregates or rouleaux (Fig. 4). The one example of kaolinite, in the South Bend Limestone Member at stop 7, shows only poorly developed plates and rouleaux, with individual grains about one-third the size of those of dickite (Fig. 5).

Specimens to be X-rayed were prepared by jamming the open end of a

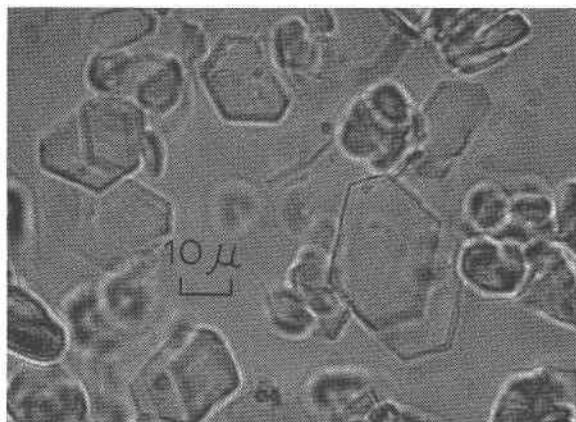


FIG. 3. Photomicrograph of fluffy dickite, from Spring Hill Limestone Member, Plattsburg Limestone, stop 4. Figures 3, 4, and 5 are of the same magnification.

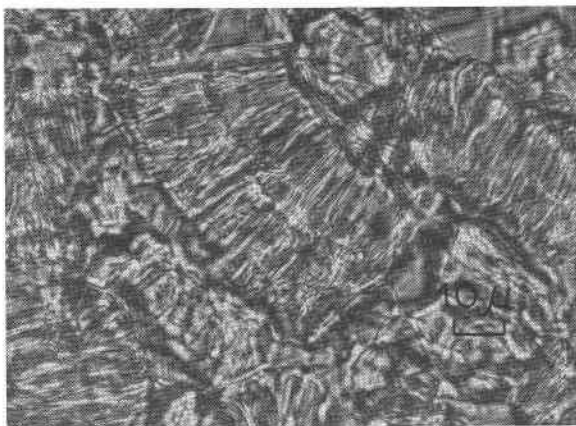


FIG. 4. Photomicrograph of compact dickite developed as intergrown rouleaux, from Captain Creek Limestone Member, Stanton Limestone, stop 6.

glass capillary tube into a pocket of dickite and withdrawing a core of mineral in the end of the tube. Presumably, such a mount consisted mainly of unbroken crystals in original orientation. The resulting powder patterns ($\text{FeK}\alpha$ radiation, 114.6 mm Debye-Scherrer camera) show no preferred orientation effects, suggesting random orientation of dickite crystals in place. Relative intensities, spacings, number, and resolution of reflections of Kansas dickite agree more closely with the calculated data of Bailey (1963, p. 1203) than do those of Michigan dickite observed by Bailey. The Kansas dickite is exceptionally well crystallized. On most films a direct correlation exists between sharpness of reflections, particularly back reflections, and grain size as measured microscopically.

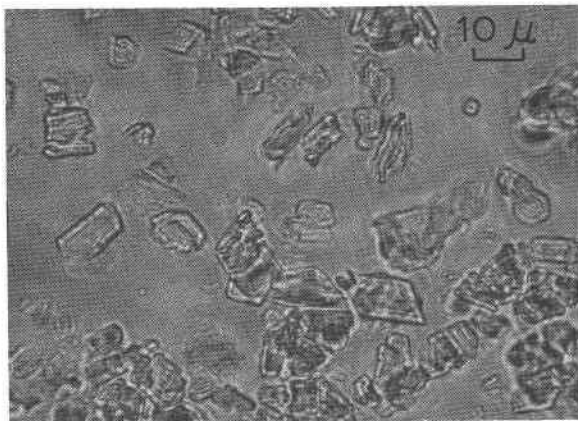


FIG. 5. Photomicrograph of kaolinite, from South Bend Limestone Member, Stanton Limestone, stop 7.

A few dickite films display line broadening, weakened back reflections, and darkened background which cannot be explained merely by fine grain size. Possibly a slight degree of stacking disorder exists, analogous to the well known *b*-axis disorder of kaolinite. The specimen of kaolinite from stop 7 shows a small amount of *b*-axis disorder on the film pattern.

Infrared and DTA patterns, kindly provided by W. D. Keller, conform to previously published data for dickite. See, for example, the DTA curve of Bundy and Murray (1959, p. 350), and the infrared spectrum of Ser-ratosa *et al.* (1963, p. 25).

Along with dickite are void-filling ferroan dolomite, void-filling calcite, and a few tiny pyrite crystals in pores and cavities of Lansing limestones. The ferroan dolomite is especially significant, for it probably is genetically related to dickite. Typically, a cavity is lined with curved rhombs of dolomite, and the rest of the cavity is filled with dickite. Dolomite precipitation preceded that of dickite, for no example could be found of dolomite which ingested dickite. The ability of dolomite and calcite to ingest kaolinite was demonstrated by Hayes (1963, p. 264). Unit-cell dimensions and relative intensities of X-ray reflections indicate about 14 mole percent FeCO_3 in place of MgCO_3 in the ferroan dolomite, by comparison with data of Goldsmith *et al.* (1962).

The ferroan dolomite is white where unweathered, but upon weathering it becomes stained from light yellow to dark red-brown with progressive oxidation of the ferrous iron. Dickite may become superficially iron-stained as a result. If ferroan dolomite and dickite are genetically related, the environment of dickite crystallization must have had abundant ferrous iron and alkaline pH. It may be significant that the kaolinite from stop 7 has no associated ferroan dolomite.

GENESIS OF KANSAS DICKITE

Field and laboratory studies in progress hopefully will reveal the origin of Kansas dickite, but a few comments about genesis can be made now. The dickite is authigenic, not detrital, as evidenced by localization in cavities, and by perfect pseudo-hexagonal crystal plates and delicate rouleaux. Almost certainly, the dickite is not the product of weathering, modern or ancient. Stop 6 was in an active quarry in the Captain Creek Limestone Member of the Stanton Limestone where fresh limestone is abundant. Pockets of dickite in typical association with ferroan dolomite are numerous. Unweathered dolomite is milky-white, with no hint of the yellow, orange, and brown oxidation stains the dolomite shows in older parts of the same quarry and in road cuts. Because dickite is the same age or younger than dolomite and because dolomite is unweathered, the dickite cannot be the result of weathering.

Though far from conclusive, the relationship of dickite to igneous intrusions shown on Figure 1 suggests a kind of hydrothermal origin for the dickite. In Woodson County and northern Wilson County are acidic, basic, and ultrabasic intrusive igneous bodies of probable Cretaceous age, some exposed and others known from wells. Papers by Knight and Landes (1932), Wagner (1954), Hambleton and Merriam (1955), and Franks (1959) document these bodies and include numerous references. Pennsylvanian rocks adjacent to the intrusions suffered contact metamorphism; hydrothermal veins of quartz, magnetite, and sulfides extend outward into the country rock. Kaolin was identified microscopically in an early report by Twenhofel (1917); this might have been dickite.

Dickite localities described herein lie on a line extending some thirty miles south from the igneous intrusions; further away kaolinite appears. This distribution of dickite versus kaolinite could reflect cooling of magmatic water or heated groundwater below the temperature of dickite formation away from the proposed igneous source. The highly porous Lansing limestones could have conducted significant volumes of water rapidly for miles to give the widespread distribution of dickite.

ACKNOWLEDGMENTS

S. W. Bailey of the University of Wisconsin and W. D. Keller of the University of Missouri kindly read the manuscript and made useful suggestions. Professor Keller also provided DTA and infrared analyses of the dickite. Staff members of the State Geological Survey of Kansas are offering continuing advice and encouragement. The assistance of all is truly appreciated.

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EFFECT OF pH AND SOLUTION CONCENTRATION ON THE
COMPOSITION OF CARBONATE APATITE

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INTRODUCTION

Carbonate substitutions for phosphate in the apatite structure have been indicated by many investigations (McConnell, 1952; Ames, 1959; Le Geros, 1965; Simpson, 1964, 1965). The reported quantities of carbonate substituting in natural and synthetic apatite range from a fraction of a percent to more than 22 weight percent. Because many of the experiments were performed under conditions conducive to the formation of metastable crystals, the effect of extrinsic variables on carbonate substitution in apatite cannot be gleaned from the studies. It is the purpose of this study to present data on the effects of pH and concentration of other ions on the composition of apatite.

EXPERIMENTS

Apatite can be formed by the slow interaction between sodium phosphate solution and calcite, as described by Ames (1959). Although it takes from several months to a year for the reaction to go to completion,