

KANSAS GEOLOGICAL SURVEY
OPEN-FILE REPORT 67-5

Dickite and Kaolinite in Pennsylvanian
Rocks of Southeast Kansas

by

Richard John Schroeder

Disclaimer

The Kansas Geological Survey does not guarantee this document to be free from errors or inaccuracies and disclaims any responsibility or liability for interpretations based on data used in the production of this document or decisions based thereon. This report is intended to make results of research available at the earliest possible data, but is not intended to constitute final or formal publications.

KANSAS GEOLOGICAL SURVEY
1930 Constant Avenue
University of Kansas
Lawrence, KS 66047

KGS
OF
67-5

DICKITE AND KAOLINITE IN PENNSYLVANIAN
ROCKS OF SOUTHEAST KANSAS

by

Richard John Schroeder

A thesis submitted in partial fulfillment of the requirements
for the degree of Master of Science, in the Department
of Geology in the Graduate College of the
University of Iowa

June 1967

Thesis supervisor: Associate Professor John B. Hayes

LIBRARY
USE ONLY

TABLE OF CONTENTS

Abstract	1
Introduction	3
Acknowledgments	5
Geologic setting	6
Mound complexes	13
Fragment-pellet limestone subdivision	19
Crystalline limestone subdivision	19
Calcarenite subdivision	22
Porosity and permeability	23
Igneous intrusions	24
Methods of study	27
Occurrence of dickite, kaolinite, and related minerals	28
Stratigraphic and areal distribution of dickite and kaolinite	53
Crystallinity of dickite and kaolinite	54
Genesis of dickite	65
Genesis of Kansas dickite	68
Conclusions	72
References	74
Appendix A Mound complexes	77
Appendix B Sample localities	80

LIST OF FIGURES

Figure 1. Index map for reported dickite localities in the Mid-Continent region 8

Figure 2. Locality numbers in southeast Kansas and Washington County, Oklahoma 10

Figure 3. Stratigraphic column for Pennsylvanian rocks sampled in Kansas (adapted from Moore, 1949) 12

Figure 4. Dickite localities in southeast Kansas 16

Figure 5. Kaolinite localities in southeast Kansas 18

Figure 6. Idealized northeast-southwest cross-section of an algal-mound (after Harbaugh, 1959, pp. 318-319) 21

Figure 7. Photomicrographs of dickite grain mounts 30

Figure 8. Photomicrographs of dickite grain mounts 32

Figure 9. Photomicrographs of kaolinite grain mounts 34

Figure 10. Photomicrographs of kaolinite grain mounts 36

Figure 11. Dickite in cavity beneath algal leaf 38

Figure 12. Dickite on stylolite surface 40

Figure 13. Dickite in solution cavity of biomicrite 42

Figure 14. Dickite interstitial in sandstone 44

Figure 15. Dickite in shell fragment 46

Figure 16. Kaolinite interstitial in sandstone 48

Figure 17. X-ray diffraction films of dickite from southeast Kansas 56

Figure 18. X-ray diffraction films of kaolinite from southeast Kansas 59

Figure 19. Differential thermograms of kaolinite and dickite 61

Figure 20. Infrared spectra of kaolinite and dickite 64

ABSTRACT

Dickite and kaolinite are polymorphs of $\text{Al}_4(\text{Si}_4\text{O}_{10})(\text{OH})_8$. Based on field and laboratory evidence dickite is traditionally regarded as hydrothermal. In southeast Kansas dickite and kaolinite are consanguineous and occur in cavities in algal-mound limestones, and along joints, fractures, and stylolite surfaces in Pennsylvanian rocks throughout 9600 square miles. The stratigraphic interval of approximately 1100 feet extends from the Fort Scott Limestone (Desmoinesian) through the Lecompton Limestone (Virgilian). Dickite appears as glistening white powder composed of, at best, well developed pseudo-hexagonal plates up to 40 μ wide. Variations in crystal size and morphological perfection are genetically significant.

The distribution of dickite and kaolinite is related to (1) igneous intrusions (early Tertiary?) in Woodson and Wilson counties, (2) gentle regional westward dip, (3) stratigraphic alternation of limestones and impervious shales, and (4) thick mound-like buildups of highly porous algal limestones, miles in length and width. Dickite is confined to an elliptical area 125 miles long northeast-southwest, and extending 60 miles eastward from the intrusions. Dickite is preferentially associated with algal-mounds inside the area. Kaolinite occurs in less porous rock units within the dickite area, and is most abundant well beyond. Meteoric waters were heated by and mixed with magmatic solutions emanating from the intrusions. These heated waters moved along strike

and up-dip outward from the source along easy avenues such as the conduit-like algal-mounds, fractures, veins, and stylolites. Dickite was deposited along with ferroan dolomite as long as the waters remained heated. However, after travelling tens of miles the waters cooled; ferroan dolomite and kaolinite were deposited instead. Where heated waters became stagnant inside the dickite area, they first deposited dickite; as they cooled kaolinite was precipitated in the same place. Kansas dickite, unlike other dickites, formed in rocks which were neither deeply buried nor extensively altered hydrothermally.

INTRODUCTION

The mineral dickite was first recognized as a distinct member of the kaolin group by Dick (1908), because its optical properties differed from ordinary kaolinite. However, not until 1931 did Ross and Kerr confirm the findings of Dick and name the mineral after him.

The kaolin minerals, kaolinite, dickite, and nacrite are chemically identical, $\text{Al}_4(\text{Si}_4\text{O}_{10})(\text{OH})_8$, and differ only in the stacking sequence of the structural unit layer. Kaolinite is a one-layer stacking sequence and has triclinic symmetry. Dickite and nacrite are monoclinic and represent two different two-layer stacking sequences. Dickite and nacrite generally form larger crystals which appear as pseudo-hexagonal plates up to 1mm across. Bailey (1963) presented a recent summary of kaolin polymorphism.

Kaolinite is by far the most abundant kaolin mineral. Dickite and nacrite, on the other hand, are less widespread and generally are associated with veins of metallic sulfides and gangue minerals, presumably of hydrothermal origin. Laboratory synthesis of dickite by Ewell and Insley (1935) at elevated temperatures supports the field relationships and suggests the value of dickite as a geothermometer. However, there are some occurrences of dickite which do not show evidence of hydrothermal solutions. Among these, Bayliss *et al.* (1965) described authigenic dickite in pore spaces in fresh water sandstones of Australia. Keller (1964) attributed dickite formation in north-

central Missouri to extensive leaching at an unconformity.

The widespread occurrence of dickite in Upper Pennsylvanian strata of southeast Kansas does not concur entirely with the hydrothermal concept, or any other proposed origin. A modification of the hydrothermal concept is suggested, whereby dickite was deposited from meteoric waters which were heated by and mixed with magmatic solutions from local igneous intrusions. Evidence for intense hydrothermal activity is absent in most of the Pennsylvanian rocks of southeast Kansas; therefore, this alternate explanation is offered.

ACKNOWLEDGMENTS

The writer wishes to express sincere appreciation and thanks to Dr. J. B. Hayes for suggesting the problem, for assisting in the field and laboratory, and for critically editing the manuscript. He also wishes to thank Dr. P. H. Heckel of the Kansas Geological Survey for providing an unpublished map of the algal-mound complexes and also for his excellent advice in the field. The writer's appreciation is extended to the Kansas Geological Survey and Dr. D. F. Merriam in particular for supplying publications and maps. Discussions with, and a number of kaolinite localities furnished by Mr. W. E. Hill are greatly appreciated. Special thanks are due Dr. W. D. Keller, University of Missouri, for DTA and IR patterns, and Mr. M. K. Bateman, University of Iowa, for diffractometer analyses.

GEOLOGIC SETTING

The area of study includes 16 counties in southeast Kansas and one county in northeast Oklahoma (Figures 1 and 2). Total area covered is approximately 9600 square miles. Over 100 localities were sampled, but some contained neither dickite nor kaolinite (Figure 2).

The Pennsylvanian sequence of Kansas is composed primarily of alternating limestones and shales with a number of sandstone channel cuts throughout the sequence (Figure 3).

The interval sampled extends from the Fort Scott Limestone (Marmaton Group) through the Biel Limestone Member of the Lecompton Limestone (Wabaunsee Group). The entire sequence sampled covers approximately 1125 feet of Middle and Upper Pennsylvanian strata. The total outcrop width of these Pennsylvanian rocks is about 90 miles and extends diagonally across the state from Osage and Johnson counties in the north to Cherokee and Chautauqua counties in the south. The beds dip very gently westward, forming cuestas with steep east faces.

The nature of the Pennsylvanian strata of Kansas has been treated in detail by Moore (1949). He summarized thus (p. 9):

"The Kansas Pennsylvanian rocks may be compared to a small stack of many-colored sheets of paper ranging in weights from thinnest onion-skin to cardboard. Each sheet of some specified color represents a certain kind of rock, such as black platy shale, light-gray calcareous shale, coal, a particular sort of limestone, and so on. The extreme

Figure 1. Index map for reported dickite localities in the Mid-

Continent region. Occurrences 2-4 are of uncertain origin, whereas occurrences 5-8 are the result of magmatic hydrothermal deposition.

(1) This report, dickite in Kansas. The heavy line encloses the area investigated, as shown in Figure 2.

(2) Tarr and Keller (1936), dickite and sulfides in limestones near Columbia, Missouri.

(3) Keller (1947), dickite and sulfides in Pennsylvanian plant fossils near Eldon, Missouri.

(4) Allen (1936), dickite in single geode specimen from St. Louis County, Missouri.

(5) Tarr (1936), dickite and sulfides in the southeast Missouri lead district, along veins and in solution cavities in Ordovician dolomite.

(6) Grohskopf and Hundhausen (1937), dickite, fluorite, and sulfides in subsurface Cambrian and Ordovician rocks of Perry County, Missouri.

(7) Ross and Kerr (1931), Miser (1943), Stone (1966), dickite in veins in Pennsylvanian rocks of the Arkansas valley.

(8) Sohlberg (1933), Miser (1943), Miser and Milton (1964), Stone (1966), dickite in the famous quartz veins in the more intensely deformed and metamorphosed portions of the Ouachita Mountain Region and the eastern portion of the Frontal Ouachitas.

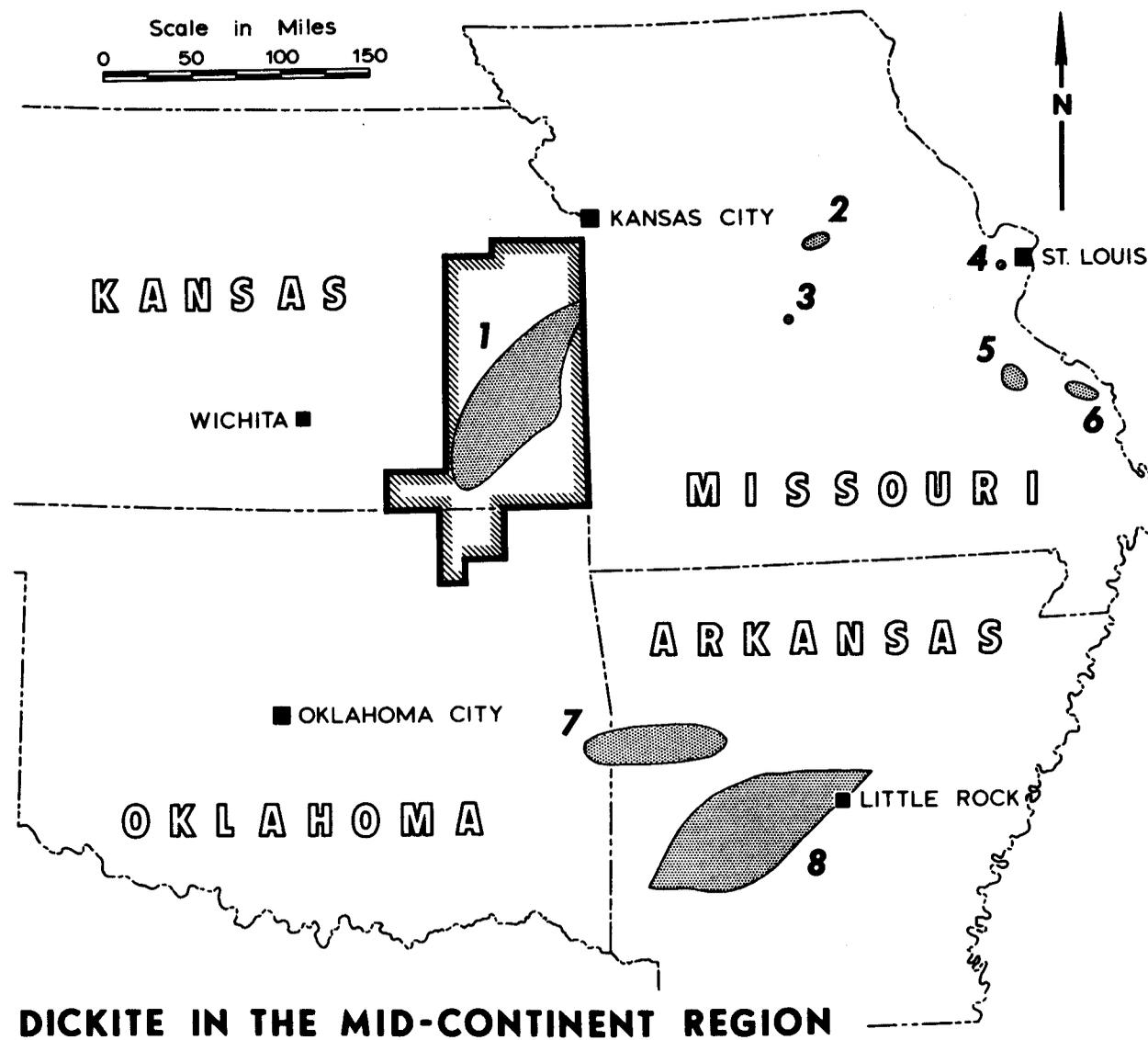


Figure 1

Figure 2. Locality numbers in southeast Kansas and Washington County,
Oklahoma. For township, range, and sample numbers see Appendix B.

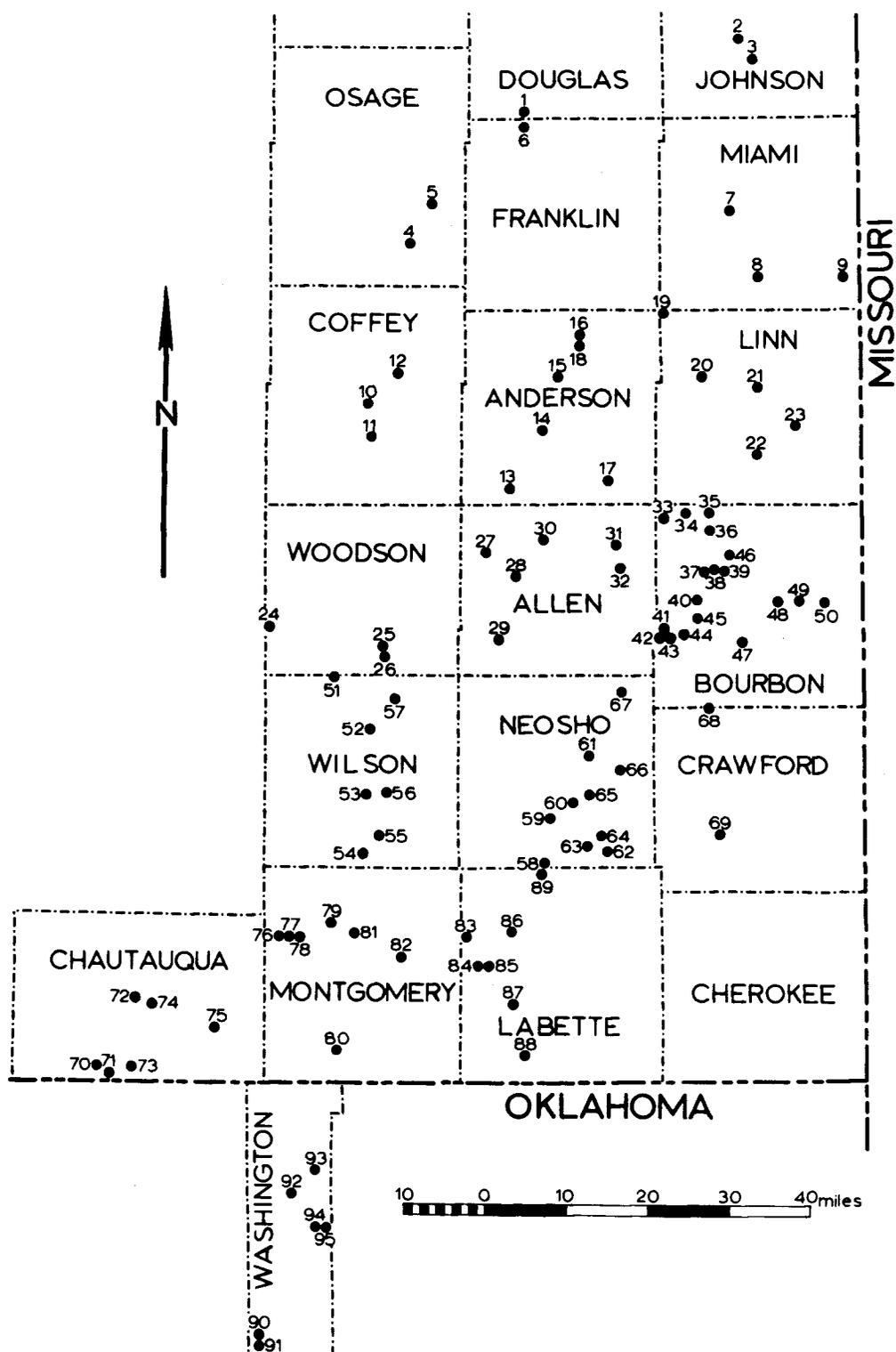


Figure 2

11

Figure 3. Stratigraphic column for Pennsylvanian rocks sampled in Kansas (adapted from Moore, 1949). (D) indicates dickite was found in the member or formation. (K) indicates kaolinite was found in the member or formation. Numbers 1-12 indicate limestone units in which there are algal-mounds. For areal extent of the algal-mound complexes see Appendix A.

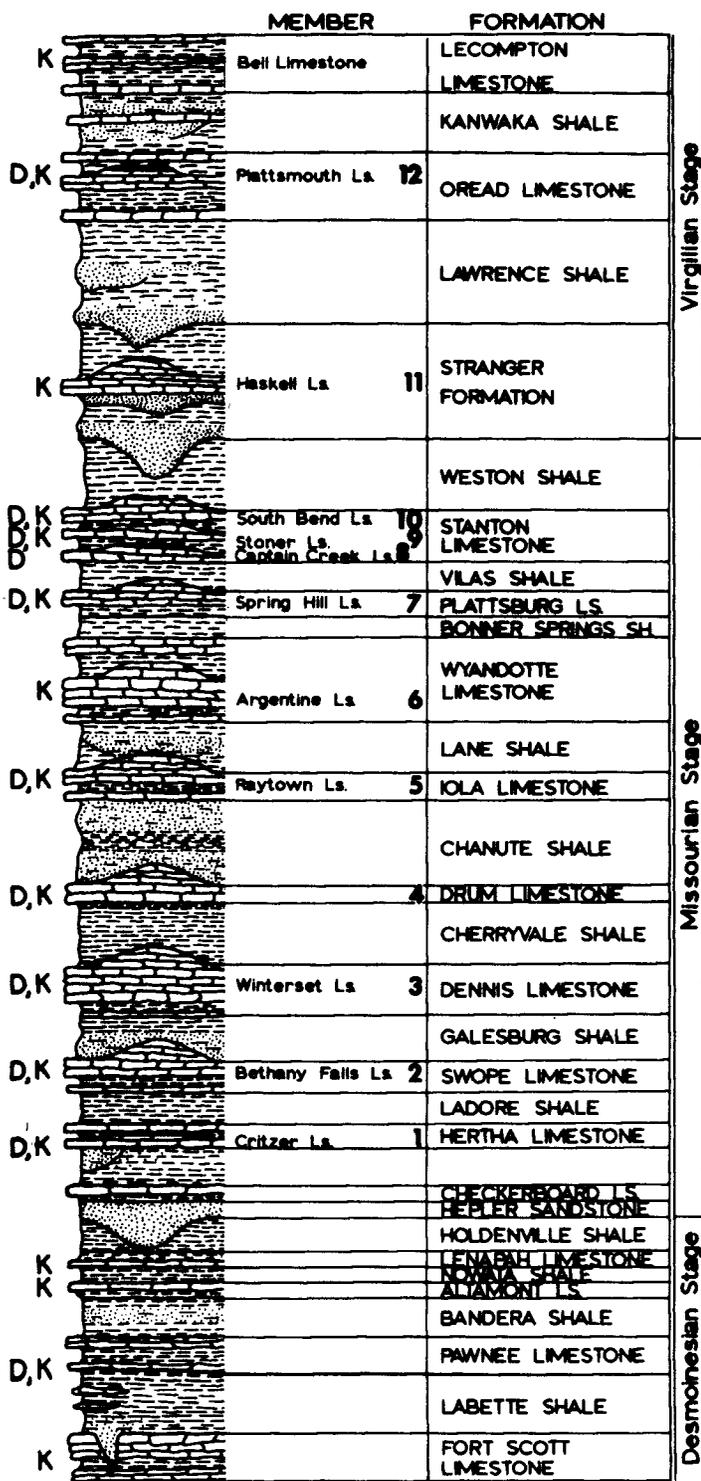


Figure 3

relative thinness of the sheets as compared to their lateral dimensions suggests the small vertical measurements (ranging from less than 1 foot to not more than 25 feet generally) of Pennsylvanian rock units which can be traced 100 to 400 miles along the outcrop and similar distances at right angles to the outcrop underground. Of course, there are irregularities. Some layers vanish here and there, and they may show local pinching or swelling in the area where they persist. These are features which we should expect to find. The outstanding character of the Pennsylvanian rocks north of Oklahoma, never the less, is stratigraphic regularity and this makes possible application of the same classification and nomenclature of divisions (with very minor variations) throughout the States of Kansas, Missouri, Iowa and Nebraska."

Mound Complexes

Local pinching and swelling of units noted by Moore (1949) is characteristic of a number of limestones in southeast Kansas. The swelling or thickening of these units typically represents local build-ups of algae formed in a shallow submerged area rising above the surrounding sea floor (Harbaugh, 1959).

The abnormal thickness of the Plattsburg Limestone near Neodesha was first noted by Newell (1933). Since then eleven other abnormally thick units from the Upper Pennsylvanian of Kansas and Oklahoma have been reported (Heckel, personal communication, 1966) (Figure 3 and Appendix A). Wilson (1957) interpreted these abnormally thick portions as barrier reefs. However, Harbaugh (1960) argued that these are not necessarily wave resistant and therefore cannot rightfully be called

reefs. Thereupon he introduced the term marine bank (Harbaugh, 1960, p. 192). More recently, Heckel (1966) coined the terms algal mound or algal-mound complex. In this paper Heckel's terminology will be used.

The algal mounds formed parallel to the Pennsylvanian shoreline; Harbaugh (1959) considered them somewhat analogous to barrier reefs, in as much as they lay between the land and the open sea. The increase in sandstones and shales in Pennsylvanian rocks southward from the mounds suggests that the shoreline was to the south with shallow seas to the north (Harbaugh, 1959). The total east-west length of the mounds is not known because of erosion up-dip to the east and insufficient well data down-dip to the west. However, the width of the mounds is known from north east-southwest outcrop patterns, as portrayed in Figures 4 and 5. It is not uncommon for the units to pinch and swell perpendicular to the Pennsylvanian shoreline and thereby produce a series of mounds outward from the shore. Heckel (1966) used the term mound complex for units with more than one mound. An example of a mound complex is seen in the Raytown Limestone Member of the Iola Limestone. The Raytown Limestone thickens or mounds in Allen and Neosho counties and is of normal thickness in Montgomery County (Figures 4 and 5). However, in Washington County, Oklahoma, the Raytown Limestone (called the Avant Limestone in Oklahoma) once again mounds to abnormal thickness. This phenomenon can also be seen in the Winterset Limestone Member, the Captain Creek Limestone Member and the Spring Hill Limestone Member (Figures 4 and 5).

The thickness of a unit containing a mound is variable. For

25

Figure 4. Dickite localities in southeast Kansas. Triangles indicate dickite localities in the crystalline limestone subdivision of the algal mounds, (dickite is extremely well crystallized). Dots indicate dickite localities in other subdivisions of the mounds and also in other limestone and sandstone units (crystals are not as well developed). Stippled pattern indicates outcrop patterns for the algal mounds. Solid diagonal lines indicate the portion of the Tri-State district in Kansas. Crosshatched pattern indicates the igneous intrusions in Woodson and Wilson counties. Numbers 1-12 refer to stratigraphic position of algal-mounds; see Figure 3 for member and formation names.

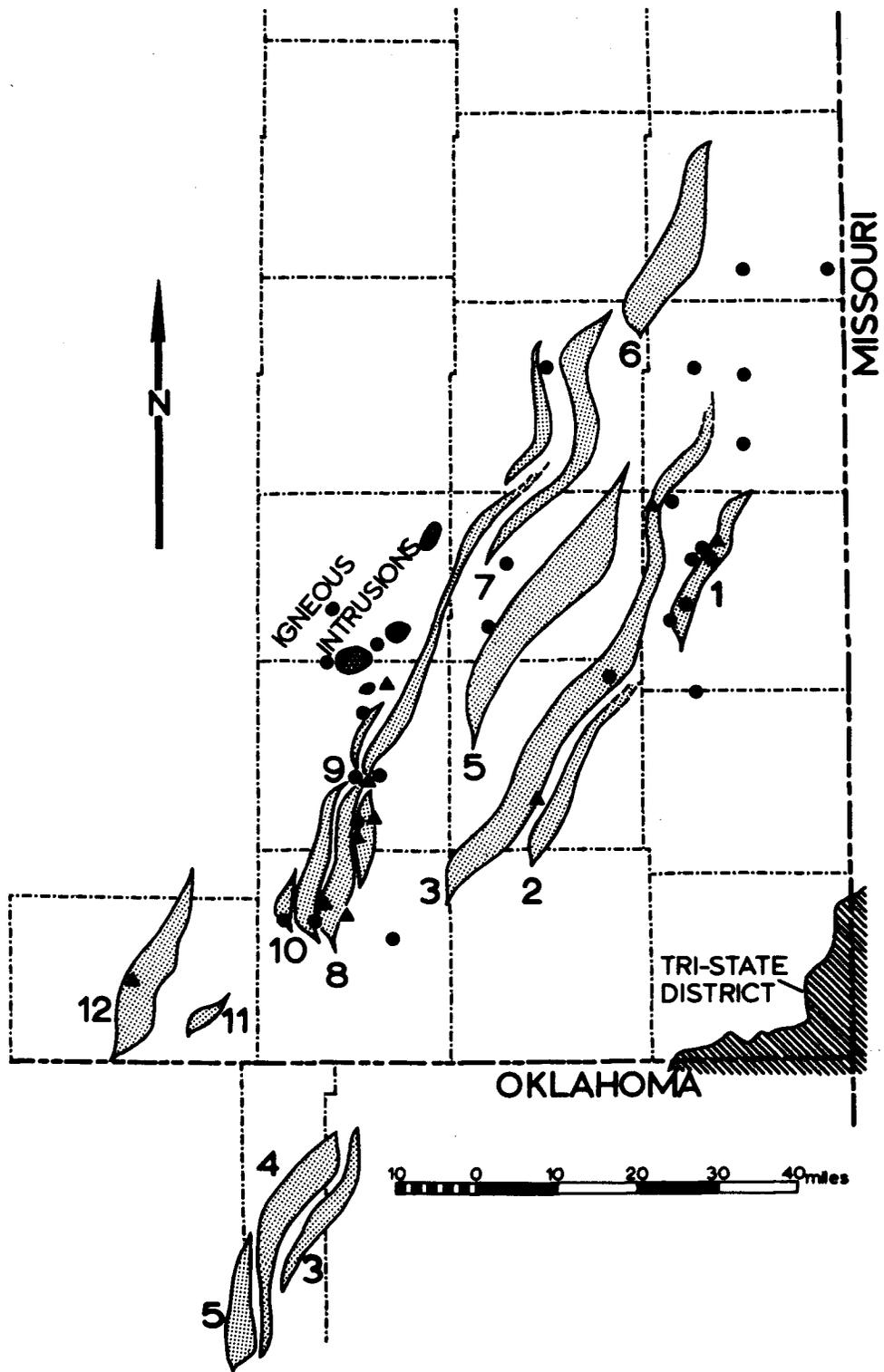


Figure 4

Figure 5. Kaolinite localities in southeast Kansas. Dots indicate kaolinite localities in all limestone and sandstone types. Other symbolism same as in Figure 4.

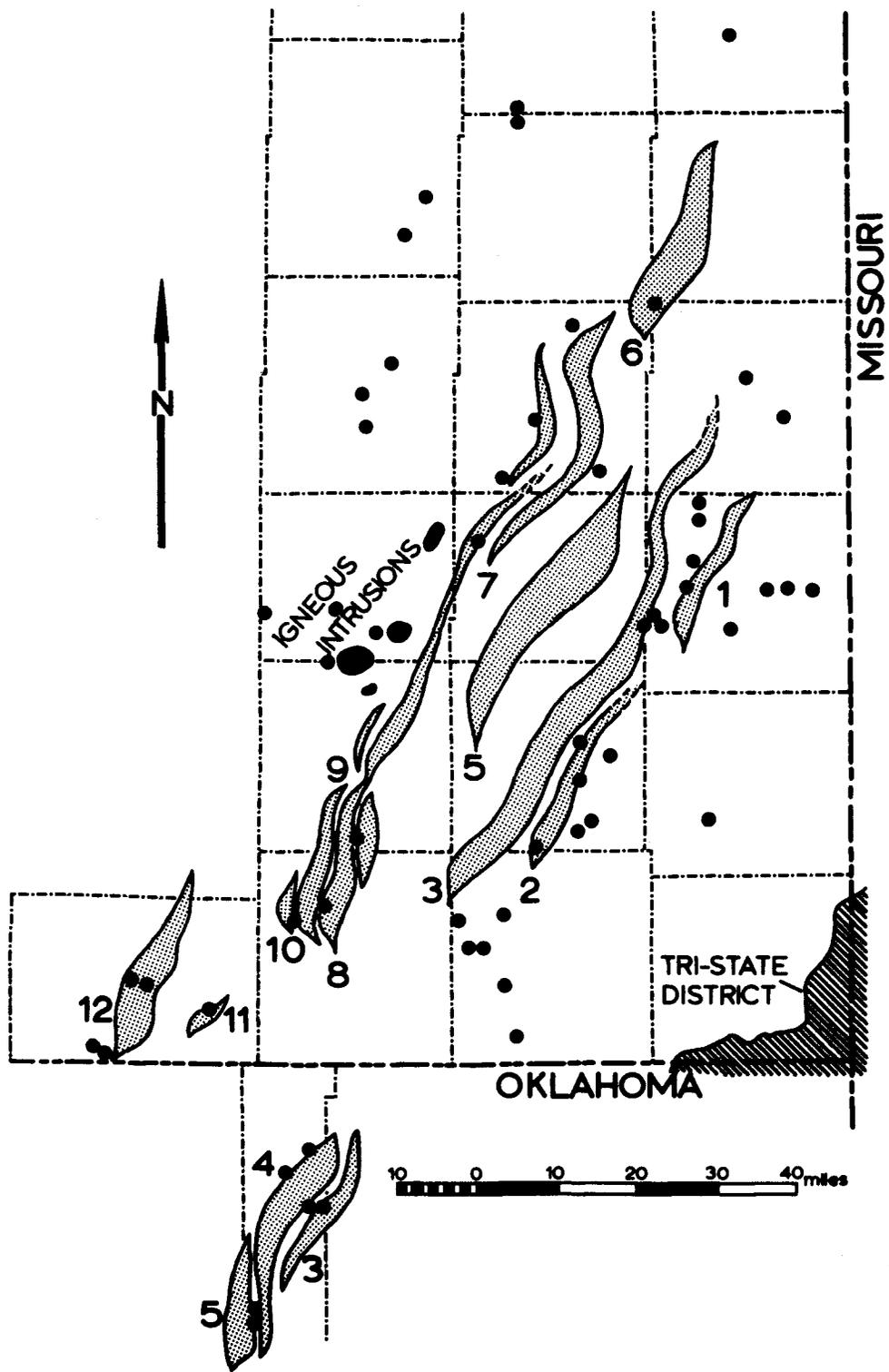


Figure 5

example, minimum thickness of the Spring Hill Member of the Plattsburg Limestone is about three feet and maximum thickness about 88 feet.

Ideally, each of the mounds is made up of three lithologic subdivisions. In ascending order these are (1) fragment-pellet limestone subdivision, (2) crystalline limestone subdivision and (3) calcarenite subdivision (Harbaugh, 1959). The subdivisions are intergradational in any one mound and also vary slightly in lithologic characteristics between mounds (Figure 6).

Fragment-pellet limestone subdivision--Fragment-pellet limestone is the lowest subdivision in the mound and forms a tabular mass ranging in thickness from 3 to 35 feet. The limestone is composed of fragments of calcareous algae, invertebrate fossils such as mollusks, brachiopods, sponges, crinoid fragments, and bryozoans. Also there are numerous irregularly shaped small pellets, possibly of algal origin. These pellets are smaller than the algal fragments and range in size from 1/4 to 3/4mm and are round to oval in shape.

The matrix material in the fragment-pellet limestone is micro-crystalline calcite and offers very low porosity and permeability. Visibly-crystalline calcite is completely absent from this subdivision.

Crystalline limestone subdivision--The middle lithologic subdivision is characterized by an abundance of calcareous algal leaves. The algae are of two principal types: (1) encrusted thin blades or fronds, which represent broken portions of upright-growing algal forms, and (2) encrusting prostrate algae which are believed to be in growth position (Harbaugh, 1959). Though algae are the dominant fossils in this

Figure 6. Idealized northeast-southwest cross section of an algal mound (after Harbaugh, 1959, pp. 318-319). Dashed lines indicate shales; heavy stippled pattern indicates fragment-pellet-limestone subdivision; "cauliflower" pattern indicates crystalline limestone subdivision; fine stippled pattern indicates calcarenite subdivision.

Note vertical and horizontal scales. Most mounds in southeast Kansas are much wider than the one idealized here.

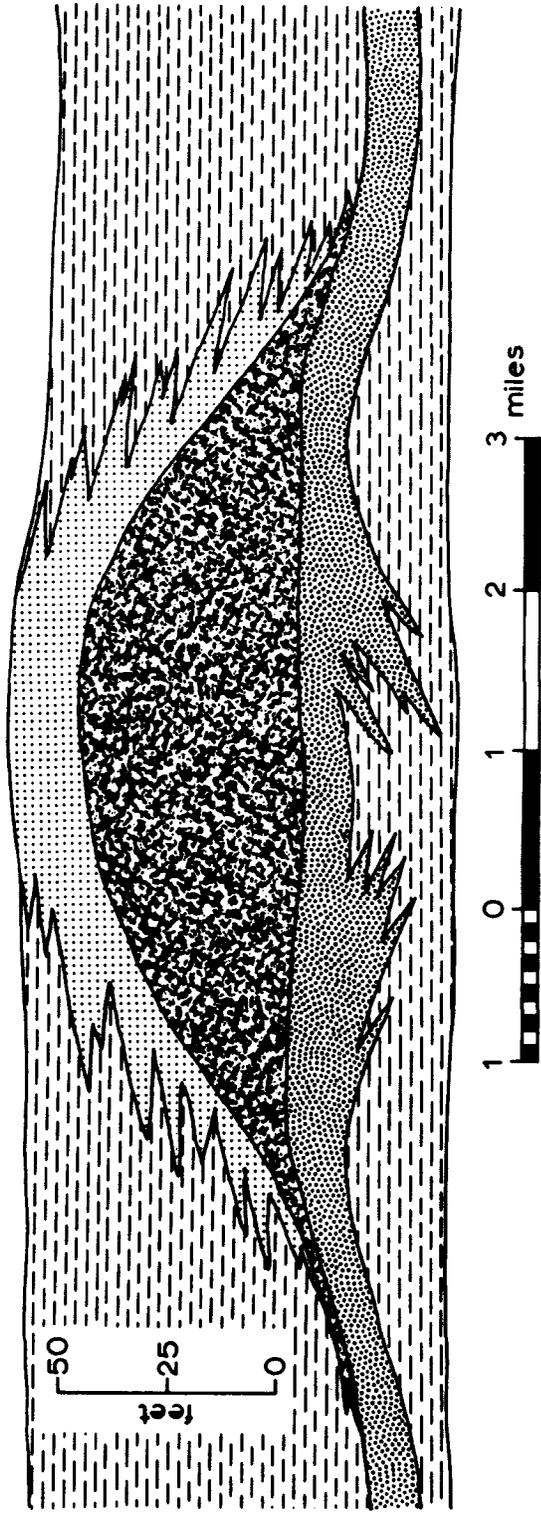


Figure 6

subdivision, there are also brachiopods, mollusks, bryozoans, and crinoids. The thickness of the crystalline limestone subdivision ranges from a featheredge to about 45 feet.

Sparry or visibly-crystalline calcite is conspicuous and of two types: (1) recrystallized fine lime mud and (2) sparry, void-filling calcite cement. Algal leaves acted as umbrellas to fine micro-crystalline material which filtered down from above. The area beneath the algal leaves formed an open cavity into which sparry calcite cement later was precipitated.

The mounds which are composed of algae in the position of growth, termed "cauliflower crusts" by Harbaugh (1959), contain the most sparry calcite cement. The porosity and permeability is relatively greater in these mounds than in those containing abundant micro-crystalline material and thin blades and fronds of the broken upright-growing algal forms.

The voids formed beneath the "cauliflower crusts" were not, in all instances, filled completely by the sparry calcite cement; thus, other minerals such as dickite, kaolinite, ferroan dolomite, and barite could be precipitated in the cavities.

Calcarenite subdivision--The uppermost subdivision of the mounds is composed of a calcarenite bed, typically cross-laminated, with interbedded shales. The calcarenite subdivision varies considerably in thickness over short horizontal distances. Thickness ranges from a featheredge to about 35 feet.

The calcarenite is composed of organic debris showing variations

in size, rounding, and sorting. The grains consist of fusulinids, crinoid fragments, algae, gastropods, brachiopods, sponges, and bryozoans.

The matrix of the calcarenites is microcrystalline calcite of low porosity and permeability, relative to the sparry calcite-cemented crystalline limestones. Minor amounts of sparry calcite formed from recrystallization of microcrystalline calcite may be present.

Porosity and Permeability

Porosity and permeability of the Pennsylvanian limestones increase with the percentage of visibly-crystalline calcite; though much of the present porosity is original, Harbaugh (1960) attributed some to secondary solutions. The permeability and porosity of limestone types varies, and Harbaugh (1959, pp. 315-316) arranged them in order of decreasing porosity.

- (1) Limestone containing thick algal crusts. In most places the individual algal crusts are recrystallized, and material between crusts is coarsely crystalline. Porosity is greatest.
- (2) Limestone containing cauliflower-shaped crusts. The cauliflower crusts are generally recrystallized, but debris filling the space between the crusts is not. Porosity is moderate.
- (3) Limestone containing thin algal crusts. The crusts are crystalline, and material between crusts is generally crystalline. Porosity is moderate.
- (4) Fragment-pellet limestone. This limestone type is generally only slightly recrystallized and exhibits only slight development

of porosity.

(5) Calcarenite. Recrystallization is confined to small patches and porosity is low.

Porosity and permeability of all other limestone types in the Pennsylvanian sequence is generally low. Such limestones are composed predominately of microcrystalline calcite matrix with very little sparry calcite.

The sandstones and channel sands have moderate porosity and permeability and may act as oil reservoirs. Shale beds between the limestones have low porosity and permeability, and for this reason act as barriers to circulating fluids. Fluid movement is restricted to the more permeable limestones or sandstones by the overlying and underlying shales.

Igneous Intrusions

The igneous and metamorphic rocks of Kansas are described by Merriam (1963). In this report we are concerned only with the intrusions in Woodson and Wilson counties (Figure 4).

Rose Dome, in southern Woodson County (sec. 13, T. 26., R. 15 E.) reveals coarse grained granitic boulders on the surface and in shallow wells. Missourian rocks surrounding the dome are slightly arched. Twenhofel (1917) suggested the boulders were ice rafted to their present position in Pennsylvanian time. However, in 1926 he reported that exposures of shales in contact with the granite showed alteration, and, therefore, he concluded the granite was intrusive. He also noted that wells drilled on the dome encountered peridotite and this was in

some way associated with the granite. Recent Rb/Sr dating by the United States Geological Survey indicates the granite to be 1200 million years old. Merriam (1963) suggested that the granite represents blocks of Precambrian basement which were incorporated as xenoliths in a peridotite intrusive plug. Granite boulders on the present surface are residual from weathering of the peridotite (Merriam, 1963, p. 154).

The Hills Pond Peridotite is exposed in NE sec. 32 and NW sec. 33, T. 26 S., R. 15 E. Here the largest exposures of peridotite and contact metamorphic rocks follow a west-northwest-trending high angle fault dipping north. Wagner (1954) suggested that the doming is due to the lateral injection by the intrusive peridotite into the layers of Pennsylvanian rocks, increasing the thickness of the stratigraphic interval. The injected magma cooled rather slowly, forming a medium grained mica peridotite composed of biotite, olivine, augite, hypersthene, apatite and titanite (Wagner, 1954).

The Neosho Falls Dome (SW sec. 8, T. 24 S., R. 17 E.) in Woodson County does not expose igneous rocks but metamorphosed post-Cambrian sediments found in wells suggests the presence of igneous intrusions.

Two other localities showing metamorphosed strata in the subsurface are described by Knight and Landes (1932). The Curtis well (SE sec. 26, T. 25 S., R. 14 E.) in Woodson County revealed highly silicified sedimentary rock with some disseminated magnetite. In northern Wilson County another well (NW sec. 15, T. 27 S., R. 15 E.) encountered sedimentary rock containing large mica flakes.

The age of the igneous rocks in Kansas is somewhat open to question, but they are believed to be about the same age as the

volcanism in Arkansas and Texas. This would put the date sometime in the Cretaceous Period. Thermoluminescence studies by Pearn (1959) on the Silver City intrusives (Hills Pond Peridotite) indicate an early Tertiary age. More recent work by Pearn with Potassium-Argon has put the date at 65 ± 5 million years, suggesting a very early Tertiary date.

Wheeler (1965) suggested that the igneous rocks in Kansas are klippen of a late Permian thrust sheet which originated in the Ouachita geosynclinal belt. However, because of the Tertiary dates by Pearn (1965) on the peridotites, it is unlikely that this is the case. Further evidence in this report will also suggest that the igneous rocks are of magmatic origin formed in situ.

METHODS OF STUDY

Two or more samples containing supposed dickite or kaolinite were collected from 91 localities in Kansas and Oklahoma (Figure 2). Specimens of the white powder were prepared for X-ray analysis by jamming a 0.3mm capillary tube into the white powder and withdrawing a core of mineral. Presumably, this gave a sample of dickite or kaolinite crystals in original orientation. The sample was then placed in a 114.6mm or 57.3mm Debye-Scherrer camera and X-rayed using $\text{FeK}\alpha$ radiation with Mn filtration.

Thin sections of a number of the limestones containing dickite or kaolinite were cut in order to determine the mode of occurrence for the two minerals in question. The calcite in the thin sections was stained with alizarine-red S and the ferroan dolomite with potassium ferricyanide (Dickson, 1966).

Diffraction analyses of detrital clay minerals from two of the low porosity, slightly argillaceous limestones were run. A modified version of the Jackson method (1956) was used to separate the clay minerals.

DTA and IR patterns were run by W. D. Keller.

OCCURRENCE OF DICKITE, KAOLINITE, AND RELATED MINERALS

Crystal size and morphological development of dickite and kaolinite grains (Figures 7-10) are related to the several modes of occurrence of the two minerals (Figures 11-16). Dickite and kaolinite in southeast Kansas are consanguineous and therefore the modes of occurrence are the same for both minerals. Mixtures of dickite and kaolinite are rare; in most cases the samples proved to be either pure kaolinite or pure dickite. Several modes of occurrence are now described.

(1) Dickite was first reported in southeast Kansas (Hayes, in press, 1967) from cavities in algal-mound limestones of the Spring Hill Limestone Member of the Plattsburg Limestone (Figure 3). The cavities range from a fraction of a millimeter to a centimeter or more in diameter. These cavities represent original voids which were not completely filled by earlier sparry calcite cement or microcrystalline calcite (Figure 11). Dickite in many of these cavities is a loose, white, fluffy powder, whereas in others it forms a hard compact mass. The fluffy dickite is composed of discrete pseudo-hexagonal plates 20-40 μ across and 5-10 μ thick (Figure 7a and b). X-ray powder patterns of the fluffy white dickite indicate it is extremely well crystallized.

Kaolinite in cavities in algal limestone also appears as white fluffy powder or as a compact mass. The pseudo-hexagonal crystals of fluffy kaolinite are about 1/3 as large as those of dickite (Figure 9);

Figure 7. Photomicrographs of dickite grain mounts. (a) Extremely well crystallized fluffy dickite from cavity in crystalline limestone subdivision in algal-mound limestone. Spring Hill Limestone member, locality 54. (b) Very well crystallized semi-fluffy dickite from cavity in algal-mound limestone. Winterset Limestone Member, locality 46. (c) Well crystallized compact dickite from shale parting. Raytown Limestone Member, locality 28.

The qualitative crystallinity of dickite was determined from x-ray powder patterns.

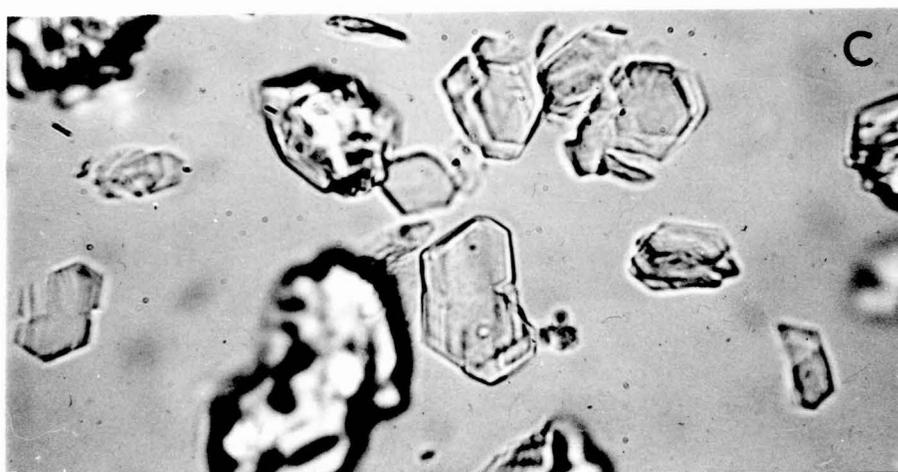
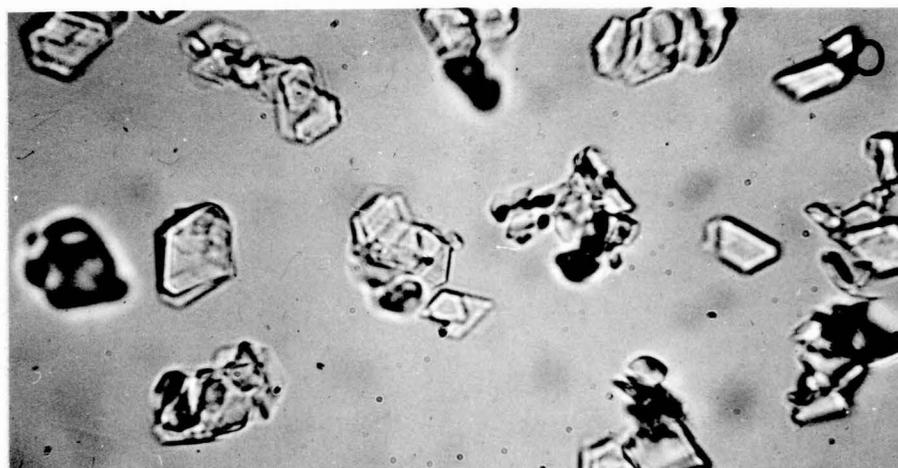
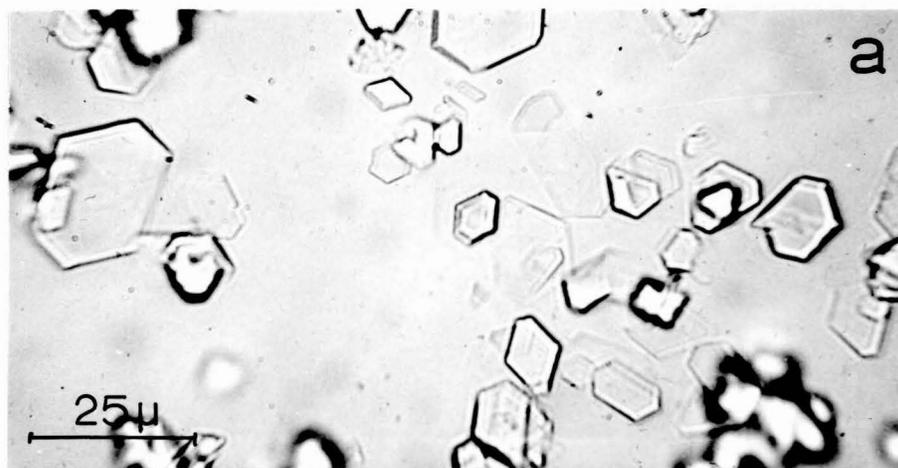


Figure 7

Figure 8. Photomicrographs of dickite grain mounts. (a) Well crystallized semi-fluffy dickite from shale parting. Raytown Limestone Member, locality 29. (b) Fairly well crystallized compact dickite from shale parting. Captain Creek Limestone Member, locality 52. (c) Poorly crystallized compact dickite from stylolite surface. Captain Creek Limestone Member, locality 79.

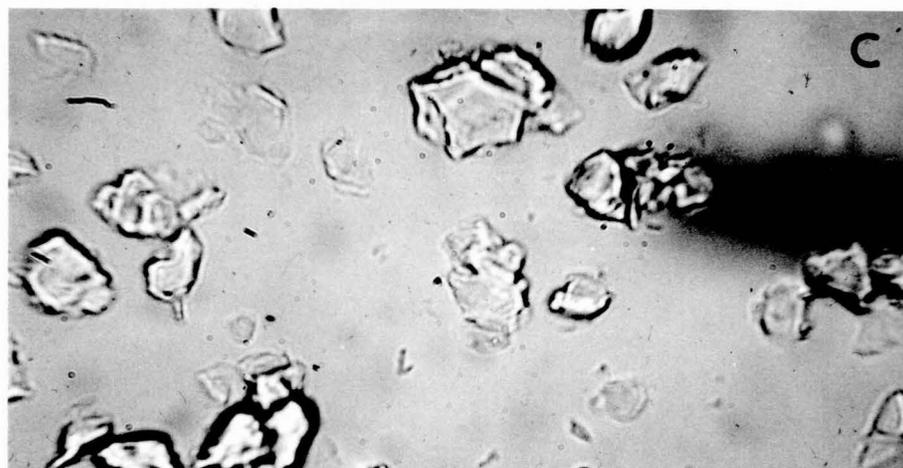
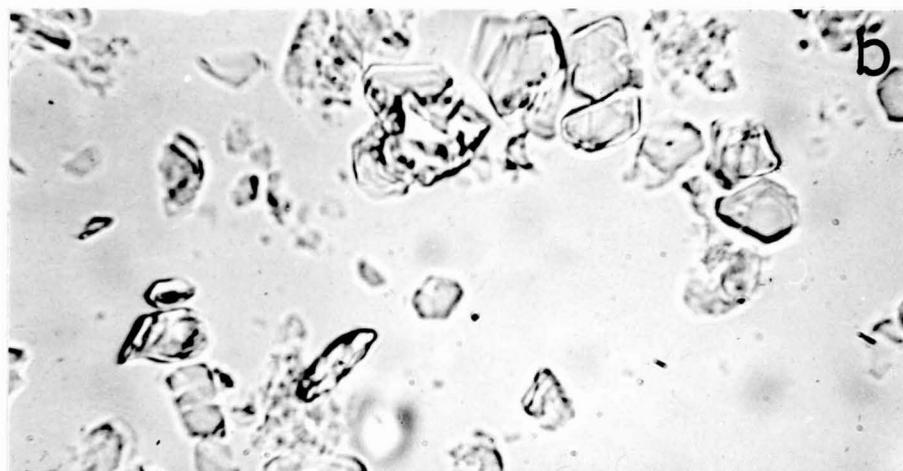
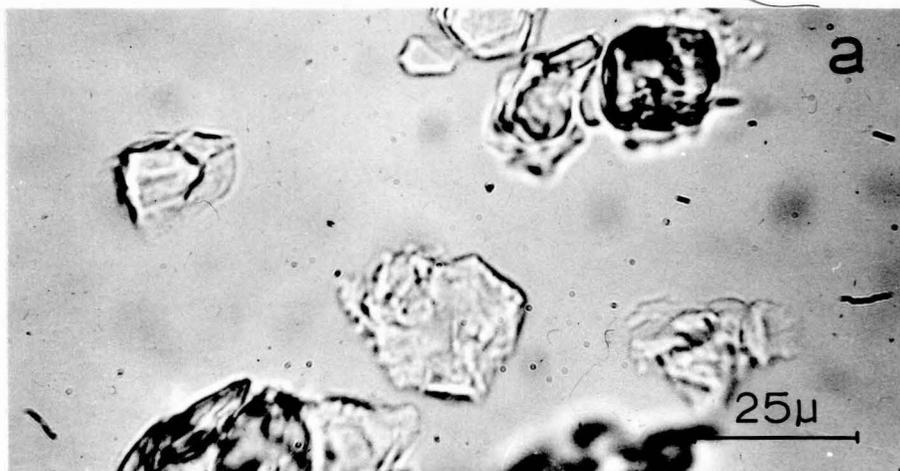


Figure 8

Figure 9. Photomicrographs of kaolinite grain mounts. (a) Very well crystallized semi-fluffy kaolinite from algal-mound limestone. Argentine Limestone Member, locality 19. (b) Extremely well crystallized fluffy kaolinite from Keokuk geode (Hayes, 1963). (c) Well crystallized compact kaolinite from cavity in algal-mound. Argentine Limestone Member, locality 2. The qualitative crystallinity of kaolinite was determined from X-ray powder patterns.

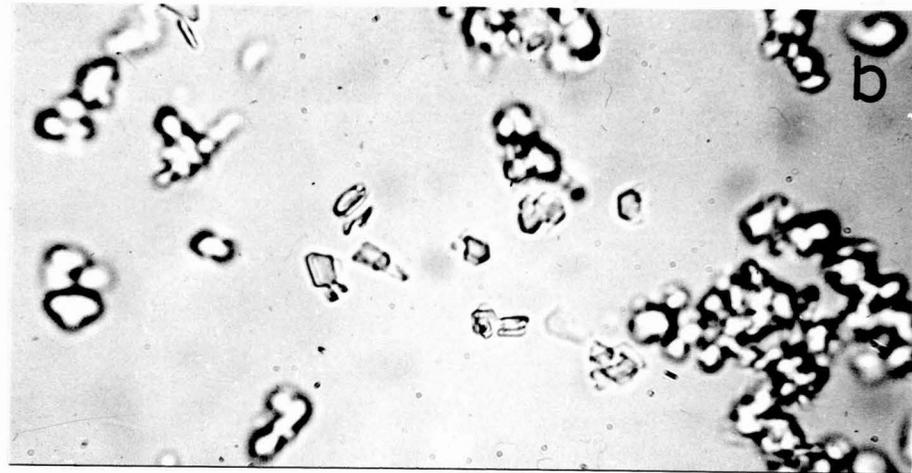


Figure 9

28

Figure 10. Photomicrographs of kaolinite grain mounts. (a) Well crystallized compact kaolinite from the interior of a brachiopod shell. Dewey Limestone (Oklahoma), locality 93. (b) Poorly crystallized compact kaolinite from shale parting. Raytown Limestone Member, locality 27. (c) Poorly crystallized compact kaolinite from solution cavity in a biomicrite. Hogshooter Limestone Member (Oklahoma), locality 95.

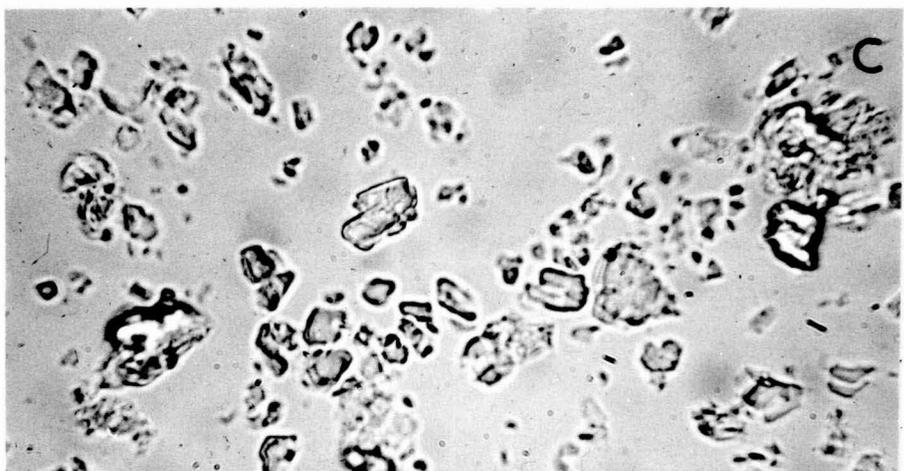


Figure 10

76

Figure 11. Dickite in cavity beneath algal leaf. (a) Dickite, D, algal leaf, A, ferroan dolomite, F, and void-filling calcite, C (plane polarized light). Spring Hill Limestone Member, locality 54. (b) Same as (a) except polarizers crossed.

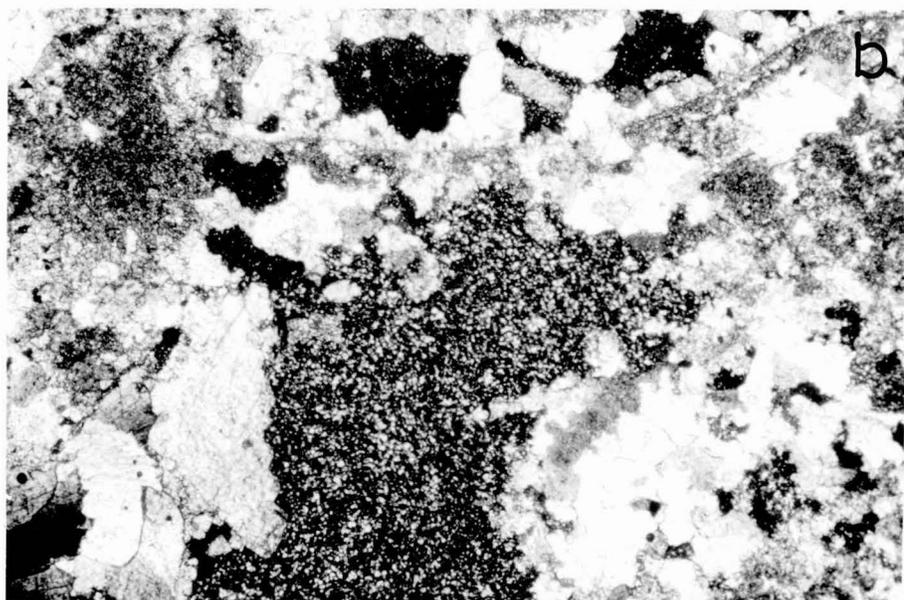
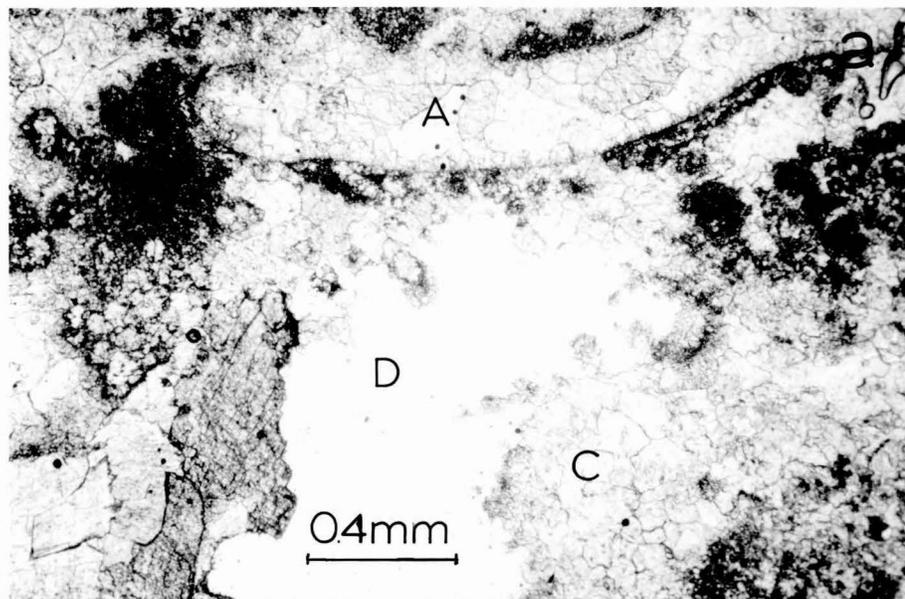


Figure 11

Figure 12. Dickite on stylolite surface. (a) Dickite, D (plane polarized light). Captain Creek Limestone Member, locality 52.
(b) Same as (a) except polarizers crossed.

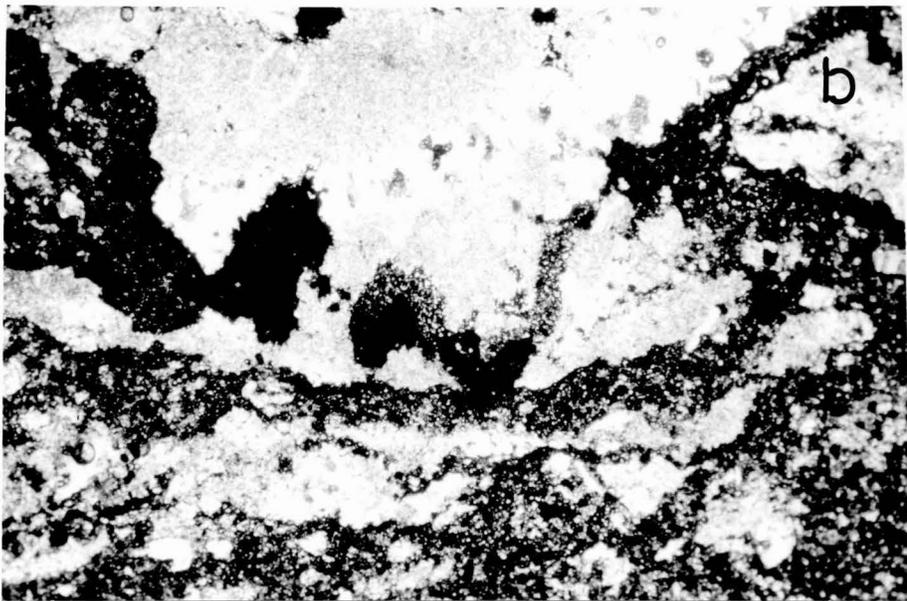
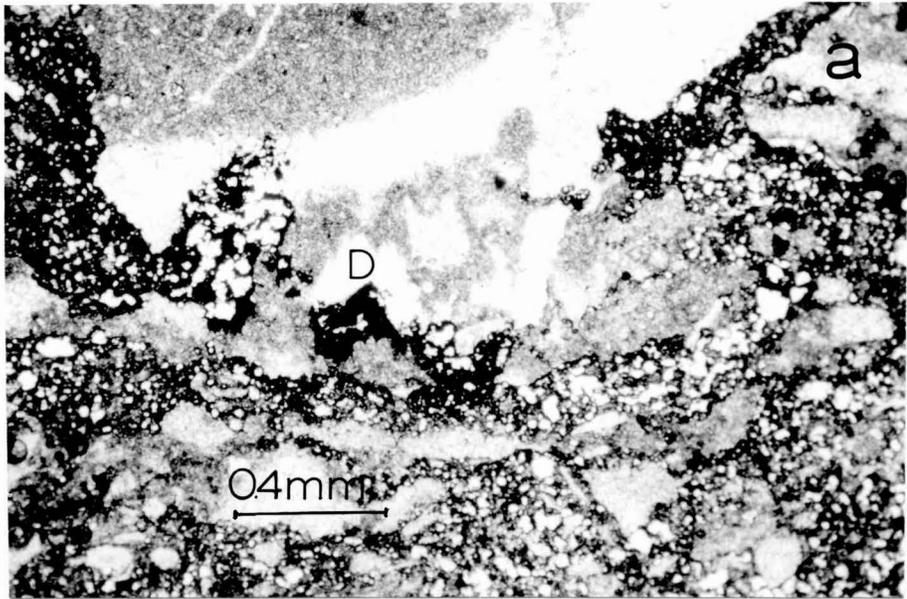


Figure 12

Figure 13. Dickite in solution cavity of biomicrite. (a) Dickite, D
(plane polarized light). Line on the right of the thin section is
a scratch. (b) Same as (a) except polarizers crossed. Bethany
Falls Limestone, locality 34.

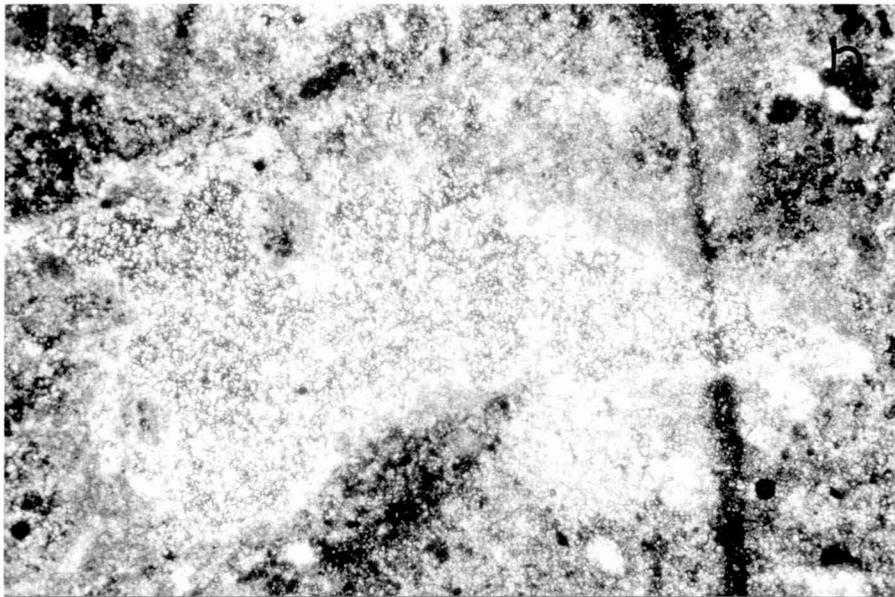
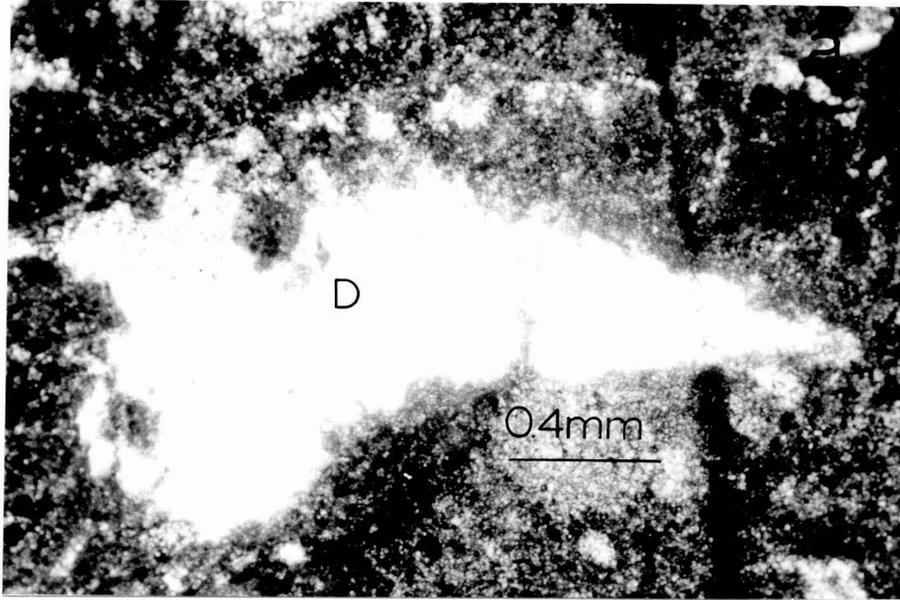


Figure 13

Figure 14. Dickite interstitial in sandstone. (a) Dickite, D, ferroan dolomite, F, (plane polarized light). Stanton Limestone, locality 77. (b) Same as (a) except polarizers crossed.

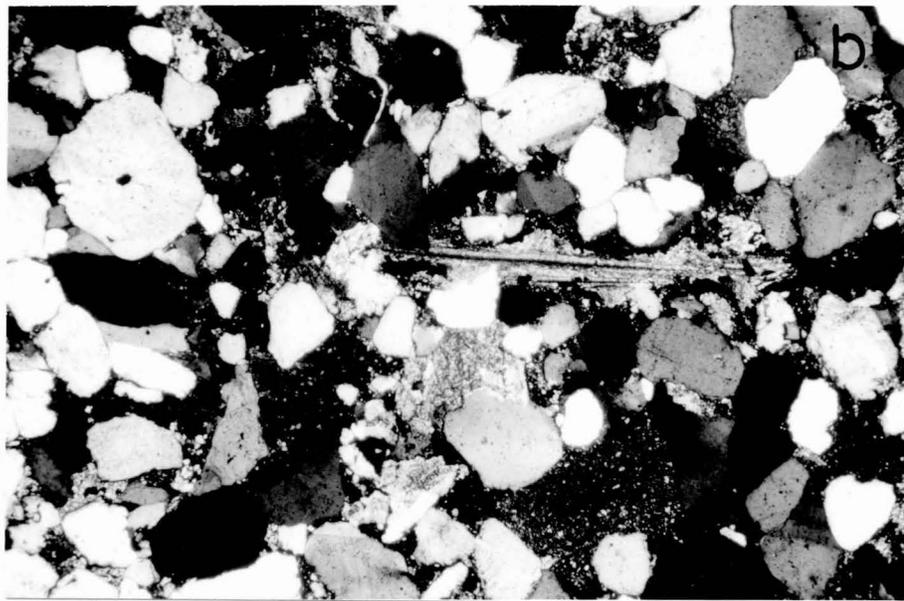
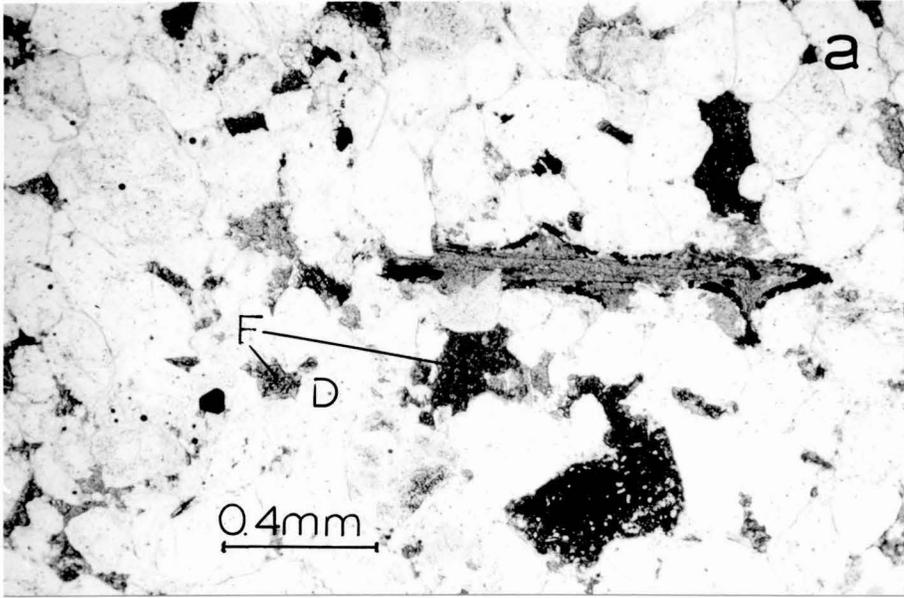


Figure 14

Figure 15. Dickite in shell fragment. (a) Dickite, D, (plane polarized light). Stanton Limestone, locality 26. (b) Same as (a) except polarizers crossed.

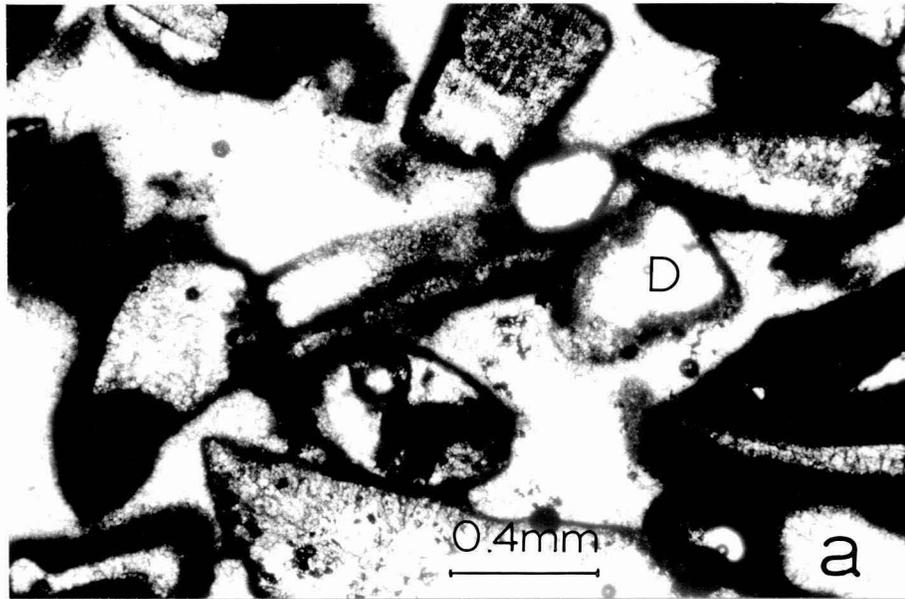


Figure 15

Figure 16. Kaolinite interstitial in sandstone. (a) Kaolinite, K
(plane polarized light). South Bend Limestone, locality 25.
(b) Same as (a) except polarizers crossed.

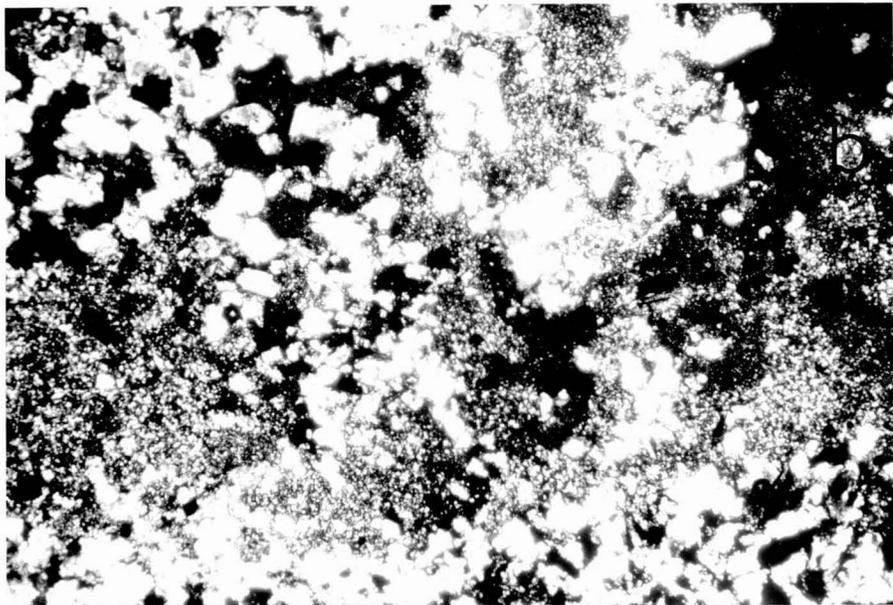
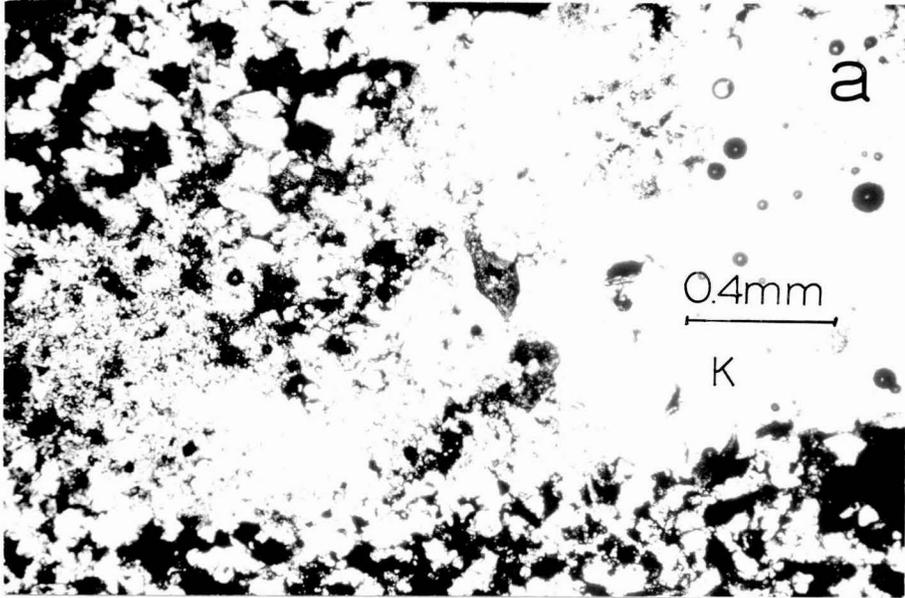


Figure 16

X-ray powder patterns indicate the kaolinite is also extremely well crystallized.

The crystalline limestone subdivision of the algal-mound limestones described by Harbaugh (1959) contains many of the cavities mentioned above. The porosity and permeability of these limestones is moderate to high and dickite and kaolinite are found to be relatively most abundant in this mode of occurrence. Ferroan dolomite is commonly associated with dickite or kaolinite in the cavities (Figure 11).

(2) A second mode of occurrence is along stylolite surfaces (Figure 12). Dickite or kaolinite crystals are not as well developed nor are they as large as those found in the cavities of algal-mound limestones (Figure 8c). The stylolites cut across low porosity, low permeability limestone units and furnish avenues for solutions moving through these limestones.

(3) Dickite and kaolinite are found along shale partings in low porosity limestones. These shale partings are not extensive but do form interfaces for solutions moving through the unit. It is possible that these shales also provided a source for some of the silica and alumina which were later used in forming dickite or kaolinite. Crystals of dickite and kaolinite along shale partings are small and poorly to moderately developed (Figures 7c, 8a & b, 10b).

(4) The interiors of brachiopod shells commonly are filled with kaolinite or dickite if they have not been previously filled with some other material such as sparry calcite cement or microcrystalline calcite (Figure 15). The grains are relatively small and crystals are moderately well developed. In some instances where the matrix material is micro-

crystalline calcite, kaolinite or dickite may be deposited in tiny pores localized along the contact between the fossil fragment and the microcrystalline calcite.

(5) Interstitial areas between grains in calcarenites and sandstones are sites for deposition of dickite or kaolinite. Either the interstitial areas were not filled by sparry calcite cement or microcrystalline calcite, or solutions removed the original calcite, leaving a void which was later filled with dickite or kaolinite (Figures 13, 14 & 16). Crystals had very little space in which to grow and therefore are small and poorly developed.

(6) Joint surfaces and fractures form a site of deposition for dickite or kaolinite. Joints and fractures serve as avenues for migrating solutions from which the clay minerals may be precipitated. Crystals are small and poorly developed.

Ferroan dolomite is intimately associated with the dickite or kaolinite (Figures 11 & 14). Unit cell dimensions and relative intensities of X-ray reflections indicate about 15 mole percent FeCO_3 $\text{Ca}_{55}\text{Mg}_{30}\text{Fe}^{++}_{15}(\text{CO})_3$ 100 in the ferroan dolomite. This mineral is identical to ferroan dolomite (Hayes, 1961) in Keokuk geodes of Iowa. Chemical analyses and X-ray data for geode dolomite are given by Goldsmith, et al. (1962, p. 683). In weathered outcrop the ferroan dolomite is red, brown, or yellow, depending on the degree of oxidation of the iron. In fresh samples the ferroan dolomite is milky white or translucent. Samples of dolomite in contact with dickite were washed, crushed, and X-rayed. There was no evidence of dickite incorporated in the dolomite, indicating the deposition of ferroan dolomite preceded the deposition of dickite.

The ferroan dolomite is significant in as much as it indicates depositing solutions which were slightly alkaline and reducing.

Harbaugh (1961) has outlined a sequence of events for the visibly crystalline calcite in late Paleozoic limestones. Much of his study has come from the Spring Hill Limestone Member of the Plattsburg Limestone in southeast Kansas. The relative ages of dickite, kaolinite, and ferroan dolomite are incorporated into Harbaugh's findings.

(1) Encrusting calcite most likely formed during deposition of the sediment. (Harbaugh, 1961, p. 125).

(2) Void-filling calcite formed early in the history of the limestone. (Harbaugh, 1961, p. 125).

(3) Grain growth calcite is not older than the adjacent void-filling calcite. (Harbaugh, 1961, p. 125).

(4) The age of ferroan dolomite relative to the grain growth calcite is poorly known but it is definitely post void-filling calcite. Evidence for this is suggested by the ferroan dolomite growing into cavities not completely filled by void-filling calcite.

(5) Soon after formation of the ferroan dolomite dickite or kaolinite was precipitated in the remaining portion of the cavity. The presence of dickite or kaolinite in contact with and not incorporated in ferroan dolomite suggests this to be the case.

(6) A final period of void-filling calcite precipitation has filled post-lithification fractures. (Harbaugh, 1961, p. 125). A milky white calcite scalenohedron was dissolved with HCl, and X-ray analysis proved the residue to be dickite. This later period of calcitization injected previously deposited dickite or kaolinite.

Hayes (1963) noted this same injection of kaolinite by calcite in the Keokuk geodes of Iowa.

STRATIGRAPHIC AND AREAL DISTRIBUTION OF DICKITE AND KAOLINITE

The dickite in southeast Kansas is confined to an elliptical area 125 miles in length northeast-southwest, and 60 miles wide with the intrusions in Woodson County (Figures 1, 4 and 5) on the westernmost border. The area is about 3000 square miles. Inside the elliptical area, dickite is preferentially associated with porous algal-mounds, joints, fractures, stylolite surfaces and interstitial voids in calcarenites and sandstones. Kaolinite may also occur within the dickite area, but it is found in the less porous rocks. Mixtures of kaolinite and dickite in the same sample are uncommon. Kaolinite is abundant outside the area of dickite.

Stratigraphically, dickite occurs in limestones ranging in age from the Pawnee Limestone (Desmoinesian) to the Plattsmouth Limestone Member (Virgilian) (Figure 3). This accounts for approximately 1000 feet of Middle and Upper Pennsylvanian rocks.

Dickite and kaolinite are abundant in porous and permeable rock units such as the algal mound limestones. There is a direct correlation between the percentage of sparry calcite cement and abundance of dickite or kaolinite in these limestones. The more sparry units are more porous and permeable and therefore contain more dickite or kaolinite. The porosity and permeability of the sandstones and calcarenites is less; they include only moderate amounts of dickite or kaolinite. There is no evidence of dickite or kaolinite having formed in any of the interbedded shales.

CRYSTALLINITY OF DICKITE AND KAOLINITE

The crystallinity of dickite and kaolinite is a function of the stacking of structural unit layers. Brindley and Robinson (1946) and Hayes (1963) have done extensive work on the crystallinity of kaolinite. Those kaolinites which are well crystallized also are well ordered as to the stacking of structural unit layers. Disordered stacking produces poorly crystallized kaolinite. Hayes (1963) discussed the value of diffraction bands where $k \neq 3n$. Other differences in X-ray powder patterns in regard to crystallinity of kaolinite are discussed by Murray (1954) as: (1) sharpness of reflections, (2) number of reflections, (3) resolution of closely spaced reflections, (4) d spacings of reflections.

Although little work has been done on the crystallinity of dickite, X-ray powder patterns show similar characteristics in regard to crystallinity as do kaolinite X-ray powder patterns.

The crystallinity of dickite and kaolinite in southeast Kansas varies with the mode of occurrence. This is evidenced by the study of fragment mounts and X-ray powder patterns. Fluffy dickite, which fills cavities in algal mound limestones appears as discrete pseudo-hexagonal plates 20-40 μ long (Figure 7a & b). The X-ray powder patterns suggest the large grain size and perfect crystallinity of the fluffy dickite by exhibiting sharp back reflections (Figure 17a). The fluffy dickite is exceptionally well crystallized. Relative intensities, d spacings,

Figure 17. X-ray diffraction films of dickite from southeast Kansas.

(a) Extremely well crystallized fluffy dickite from a cavity in the crystalline limestone subdivision of the algal-mound limestone (see Figures 7a & 11). Crystals are large. Back reflections are well developed and diffraction bands are intense with good resolution. (b) Well crystallized compact dickite from a fracture surface (see Figure 7c). Crystals are smaller than in (a). Back reflections are not as well resolved nor are the diffraction bands as intense as in (a). (c) Fairly well crystallized compact dickite from interstitial area in a biocalcarenite (see Figure 8b). Back reflections are weak and indistinct. (d) Poorly crystallized compact dickite from joint surface (see Figure 8c). Crystals are small. Back reflections are almost non-existent, resolution and intensity of diffraction bands is poor.

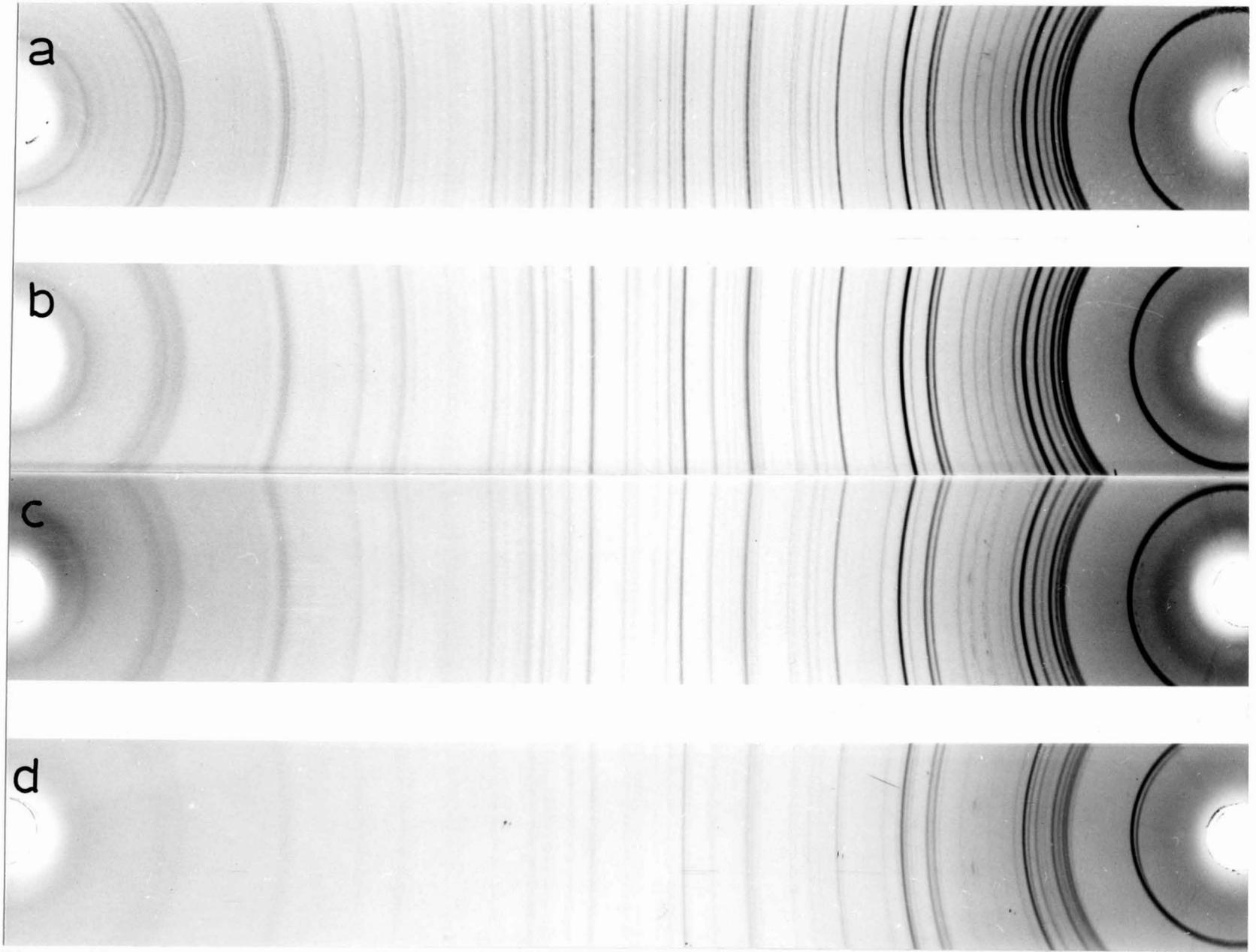


Figure 17

number, and resolution of reflections of Kansas dickite agree more closely with the calculated data of Bailey (1963, p. 1203) than does that of observed Michigan dickite presented by Bailey.

Fluffy kaolinite found in algal limestone cavities exhibit similar properties. Crystals are extremely well developed and compare favorably with the Keokuk geode kaolinite (Figure 9a & b). Back reflections on X-ray powder patterns are sharp (Figure 18a). However, the kaolinite crystals are about 1/3 the size of the dickite crystals.

In places where dickite is compact such as on stylolite surfaces, fractures, joints and shale partings the crystals are smaller, less well developed and typically form rouleaux (Figures 7c, 8a, b, & c). X-ray powder patterns display line broadening of lines and loss of intensity of back reflections (Figure 18b, c, d). Also, b-axis disorder is evidenced by disappearance of reflections where $k \neq 3n$ (Hayes, 1963).

A series of specimens of decreasing crystal size and morphological perfection can be assembled from X-ray powder patterns of dickite and kaolinite (Figures 17 and 18). X-ray patterns of well crystallized kaolinite and dickite show sharp diffraction bands and resolution of back reflections. Poorly crystallized dickite exhibits line broadening, weakened back reflections and darkened background. These cannot be merely explained by decrease in grain size but also possibly a slight b-axis disorder analogous to the well known b-axis disorder of kaolinite (Hayes, 1963).

The differential thermogram for Kansas dickite is very similar to that of Keokuk geode kaolinite (Figure 19). Keller, et al. (1966) also showed this similarity and attributed the parallelism to the well

Figure 18. X-ray diffraction films of kaolinite from southeast Kansas.

(a) Very well crystallized fluffy kaolinite from cavity in algal-mound limestone (see Figure 9a). Crystals are large. Back reflections are good and diffraction bands are well resolved and intense; $k \neq 3n$ diffraction bands are present. (Minor calcite present). (b) Well crystallized compact kaolinite from joint surface (see Figure 9c). Back reflections are not as strong as in (a). There is broadening of diffraction bands and $k \neq 3n$ diffraction bands are weaker. (c) Fairly well crystallized compact kaolinite from joint surface (see Figure 10a). Back reflections are extremely weak. Intensity of diffraction bands is poor; $k \neq 3n$ diffraction bands are extremely weak. (d) Poorly crystallized compact kaolinite from solution cavity in biomicrite (see Figure 10c). Back reflections are non-existent as are the $k \neq 3n$ diffraction bands.

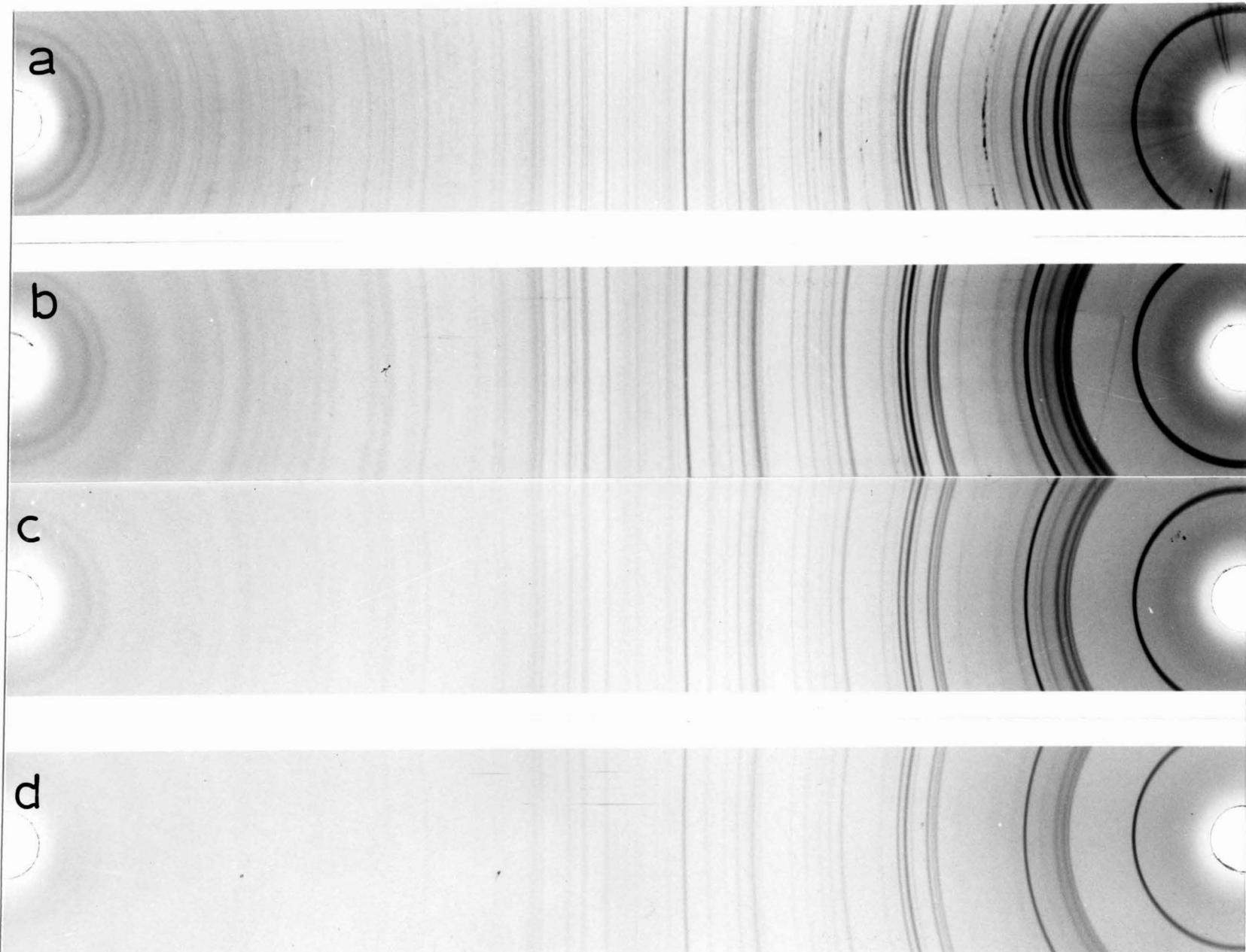


Figure 18

88

Figure 19. Differential thermograms of kaolinite and dickite. Keokuk geode kaolinite (top) and Kansas dickite (bottom). These samples show the similarity in DTA patterns for well crystallized kaolinite and dickite. Samples run by W. D. Keller.

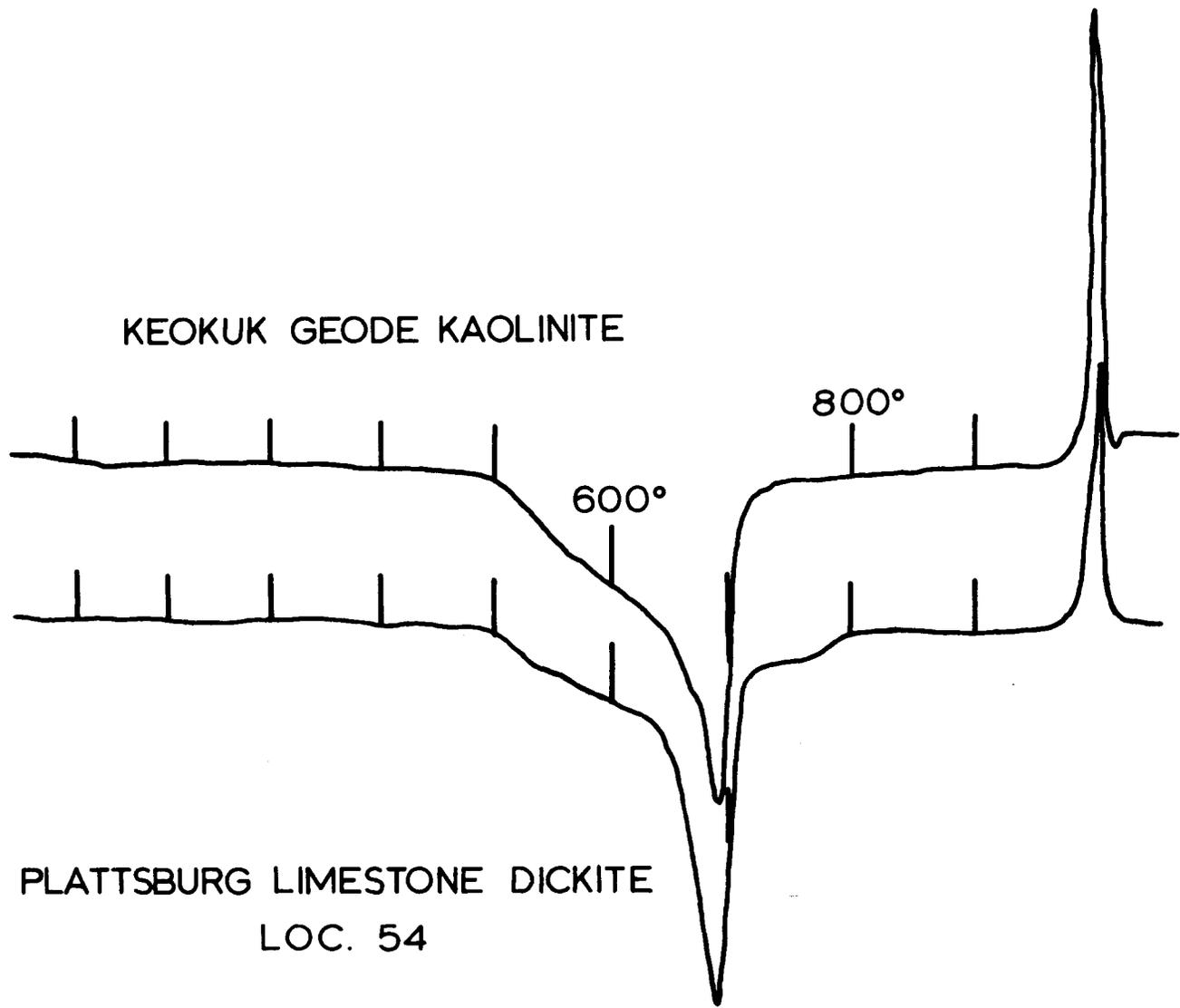


Figure 19

ordered and crystallized nature of the kaolinite. However, infrared patterns of Kansas dickite and Keokuk geode kaolinite show the dissimilarities of the two kaolin minerals (Figure 20). These IR patterns conform to those published by Serratosa, et al. (1963).

Figure 20. Infrared spectra of kaolinite and dickite. Keokuk geode kaolinite (top) and Kansas dickite (bottom). Wave numbers, cm^{-1} , along base. Wave lengths in microns along top. Samples run by W. D. Keller.

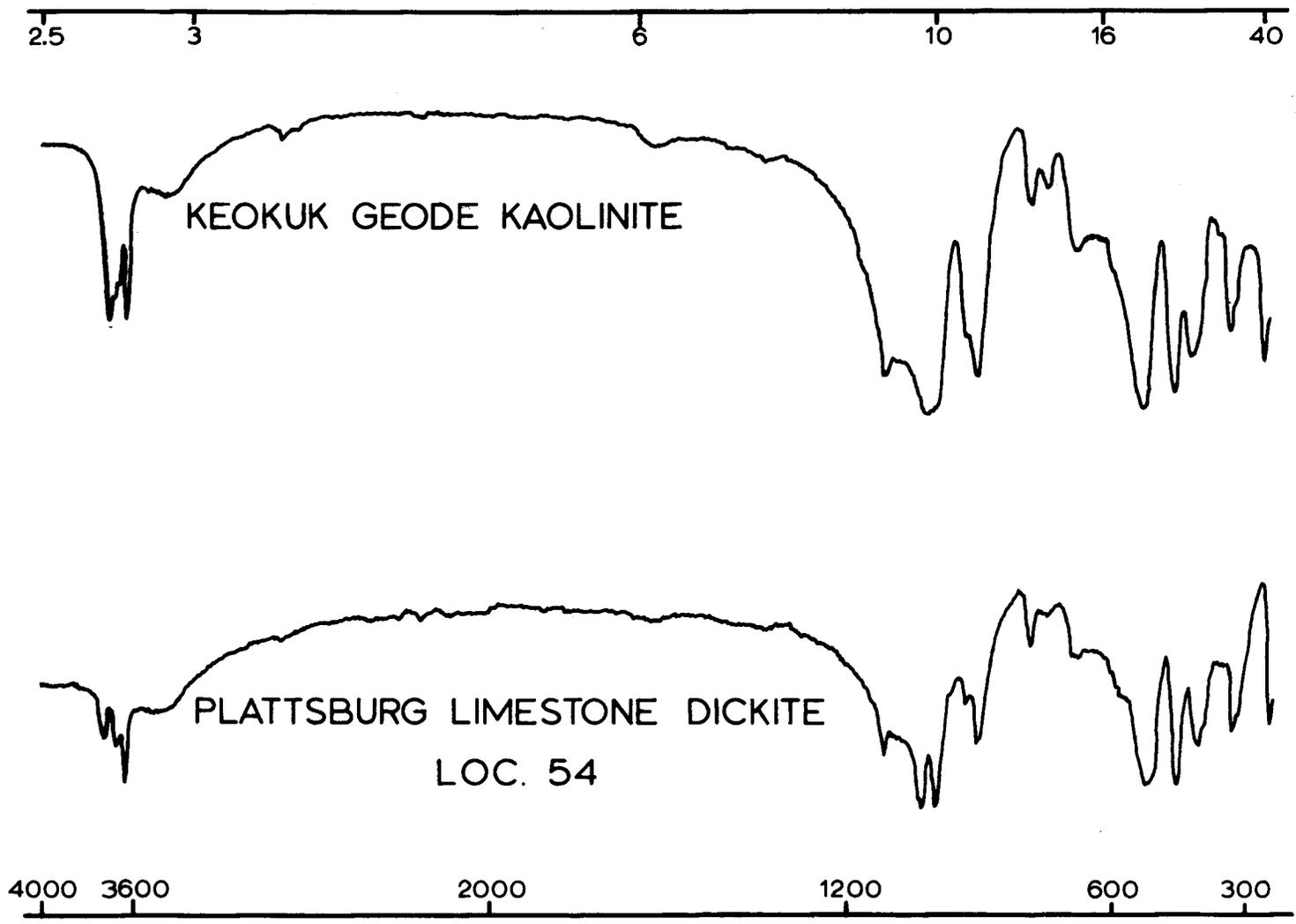


Figure 20

GENESIS OF DICKITE

Most of the reported occurrences of dickite are localized about fractures, cavities, or hydrothermally altered zones in association with sulfides, carbonates, or oxides. This has led many to conclude that dickite is a hydrothermal mineral. Supporting laboratory evidence for the hydrothermal origin of dickite comes from Ewell and Insley (1935) who synthesized dickite at elevated temperature and pressure.

Traditionally, hydrothermal refers to hot solutions emanating from magma and travelling upward along easy avenues through older rocks, locally altering pre-existing minerals and depositing new minerals. To other geologists it may have a broader and more literal meaning, that of mineralization by any waters at temperatures and pressures higher than those at the earth's surface. In this sense, most dickite could be hydrothermal, but not necessarily under magmatic influence.

Bailey and Tyler (1960) found agreement with the hydrothermal origin of dickite when they were working with the clay minerals of the Marquette, Gogebic, and Iron River districts of Michigan. Associated with dickite are other hydrothermal minerals such as nacrite, talc, pyrophyllite and $2M_1$ muscovite.

Kerr (1955, p. 530) stated: "Field relationships suggest that among the clay minerals dickite is usually formed under deep seated conditions. It is usually, if not always, hydrothermal in origin."

Others have proposed alternative origins for the genesis of dickite. Among these is Keller (1964, p. 5) who suggested that

"...long, intensive leaching substituted chemical energy for thermal energy,..." to precipitate dickite in Burlington chert at or near the unconformity which exists between the Burlington Limestone and the overlying Pennsylvanian rocks.

Earlier, Keller (1947, p. 470) questioned the validity of a hydrothermal origin for dickite in otherwise unaltered sediments when he asked, "...is it reasonable that sedimentary rocks which are fairly deeply buried may be heated high enough by conduction in establishing a normal geothermal gradient so that dickite is deposited in them instead of, or along with kaolinite? Water in them might be warm (hydrothermal?) over a wide area without necessarily emanating from a magma which otherwise would have to be postulated as being disturbingly widespread."

Following this thought Smithson and Brown (1954, 1957) have attributed the formation of authigenic dickite in the Middle Jurassic sandstones of Yorkshire to depth of burial and not magmatic hydrothermal solutions.

Shutov (1964) has established a thermal alteration curve for the recrystallization of kaolinite to dickite with increased depth of burial in kaolinite-cemented rocks in Paleozoic strata on the Russian platform. According to Shutov, kaolinite which is isolated in sediment and then subject to higher temperature or greater depths "'improves' its crystalline lattice and changes to dickite." (Shutov, 1964, p. 523)

Most of the occurrences of dickite in the Mid-Continent region are attributed to a hydrothermal origin (Figure 1). These are generally associated with sulfides and quartz veins. However, dickite in Missouri at localities 2, 3, and 4 on Figure 1 cannot be explained by the

hydrothermal concept (Tarr & Keller, 1936; Keller, 1947; Allen, 1936).

GENESIS OF KANSAS DICKITE

The foregoing discussion brings to point the question of origin of dickite in southeast Kansas. (1) The dickite in Kansas is present in cavities and veins as discrete pseudo-hexagonal crystal plates and delicate rouleaux suggesting an authigenic and not detrital origin. Diffractometer analyses of detrital clay minerals from two of the low porosity, slightly argillaceous limestones indicated illite, kaolinite, quartz and mixed layer chlorite-vermiculites, but no dickite. This further suggests a non-detrital origin for the dickite.

(2) It did not appear, in any instance, that dickite was a replacement or recrystallization phenomenon. Though there are no precise figures as to the depth of burial for Upper Pennsylvanian strata in southeast Kansas it is highly improbable that they were ever as deeply buried as the Paleozoic sequence described by Shutov (1964), and therefore recrystallization of kaolinite to dickite is unlikely.

(3) The dickite is in association with unweathered ferroan dolomite. In as much as the dolomite is unweathered and the dickite is younger than the dolomite it is most unlikely that dickite is a weathering product.

(4) The igneous intrusions in Woodson and Wilson counties could produce a source for hydrothermal solutions. Sulfide alterations, silicification, and contact metamorphism are found near the intrusions. However, as one travels away from the intrusions there is very little evidence to suggest any form of hydrothermal alteration.

(5) A remaining possibility is that dickite is precipitated from meteoric waters which have been heated by and mixed with magmatic solutions. Gruner (1937, p. 130) proposed a modified hydrothermal oxidation and leaching theory for the origin of the Mesabi iron ores in the Lake Superior district. His theory suggests that meteoric "...waters mingled with gaseous emanations which rose from large intrusives." These active solvents followed joints and fractures in the rock and dissolved silica which was later deposited as sinter on the top of the ore. The system continued by influx of surrounding meteoric waters and ceased when the gaseous emanations stopped.

There are two possible sources for such solutions in Kansas. The first, the Tri-State zinc-lead district covering about 2000 square miles in southwest Missouri, northeast Oklahoma, and southeast Kansas poses a possible origin for solutions which could deposit dickite in southeast Kansas (Figures 4 and 5). However, there are a number of objections to the Tri-State district as a source.

(a) Hagni (1962) described 51 minerals from the Tri-State district but dickite is not in the group. Kaolinite however, has been reported from the district by Tarr and Keller (1937) at Oronogo, Missouri.

(b) The majority of the zinc-lead deposits are in Mississippian strata and only minor mineralization has taken place in the Pennsylvanian strata.

(c) Any solutions originating in the Tri-State district would have to travel up stratigraphically across impervious shale beds in order to deposit dickite in Middle and Upper Pennsylvanian rocks of Kansas. This seems highly unlikely.

(d) Hagni (1962) suggested that solutions which deposited ores in the Tri-State district were cold meteoric downward-moving waters and not upward-moving, cooling, hydrothermal solutions.

(e) The areal extent of dickite and kaolinite is shown in Figures 4 and 5. Dickite, being the more sensitive of the two clay minerals, forms in a more restricted environment. The waters which precipitate dickite in favor of kaolinite must be warm solutions. Most of the localities in eastern Bourbon, Neosho and Labette counties contain kaolinite and not dickite. These localities form a distinct line between the Tri-State district to the east and the major occurrences of dickite to the west. If the Tri-State district were the source area for dickite in southeast Kansas one would expect to find it in the porous algal limestones of Washington County, Oklahoma, but this is not the case. All samples of white powder collected from the algal limestones in Oklahoma proved to be kaolinite.

The second possible source for the magmatic solutions is the peridotite intrusions in Woodson and Wilson counties. These igneous rocks were injected into and through Pennsylvanian strata causing doming as described by Wagner (1954) and also silicifying and metamorphosing nearby limestones, sandstones and shales. Merriam (1963, p. 157) believed that the pre-Cretaceous and early Cretaceous land surface was at about the same position as the present surface in relation to the Permian strata. Hence, only a possible few hundred feet of Cretaceous sediment lay above the intrusions. Meteoric waters circulating in the area were heated by and mixed with magmatic solutions emanating from the igneous intrusions. These waters then migrated along easy avenues such as

joints, fractures, veins and stylolite surfaces. They also travelled through highly porous and permeable rock units such as the algal-mound limestones. Shale beds above and below the limestones acted as barriers to waters moving upward stratigraphically. The waters were forced up-dip to the east and along strike to the northeast and southwest. Iron and magnesium ions were very possibly derived from the parent magmatic solutions whereas aluminum and silicon ions were dissolved from neighboring shales. Ferroan dolomite was precipitated from alkaline reducing solutions along the avenues which they travelled. Dickite was precipitated soon afterward from acid solutions (Hayes, 1963) in the same areas. The more easily the waters could travel, the further they moved from the intrusions. Provided the solutions maintained a high temperature dickite precipitated; however, those solutions which cooled deposited kaolinite instead. In areas where warm waters became stagnant first dickite precipitated; then as the solutions cooled kaolinite was deposited.

The above process for dickite formation in southeast Kansas suggests a means by which dickite is deposited in rocks which have neither been deeply buried nor have undergone major alteration by hydrothermal solutions.

The supposition that dickite is deposited from migrating waters which have been heated by and mixed with magmatic solutions from the intrusions in Woodson and Wilson counties casts doubt upon Wheeler's (1965) hypothesis that the igneous rocks are klippen of Precambrian rock implaced by a thrust sheet originating in the Ouachita geosynclinal belt.

CONCLUSIONS

Dickite in southeast Kansas is precipitated from meteoric waters which have been heated by and mixed with magmatic solutions derived from peridotite intrusions (early Tertiary?) in Woodson and Wilson counties. These heated waters, under pressure, moved up-dip and along the strike of the gently westward dipping Pennsylvanian strata. Near the intrusions the country rocks were metamorphosed and minor amounts of sulfides were deposited. As the warm waters moved outward from the vicinity of the intrusions dickite was deposited in cavities of porous and permeable algal-mound limestones, stylolites, joints, veins and fractures. In areas where the waters became stagnant, kaolinite was deposited. The warm waters which travelled along easy avenues moved farther from the intrusions and deposited dickite some distance from the source. After travelling tens of miles the waters cooled and kaolinite was deposited instead. Associated closely with the deposition of dickite and kaolinite is ferroan dolomite which formed slightly before the clay minerals. The mode of occurrence governs the crystallinity of dickite and kaolinite. Cavities in the highly porous and permeable algal limestones provide a site of deposition with ample space for crystals to grow. In these cavities fluffy dickite or kaolinite may be deposited which shows a high degree of crystallinity and, in the case of dickite large crystals up to 40 μ long. In areas where growth of crystals was prohibited by insufficient space, such as in veins, stylolites and fractures, they became compacted; crystals are small and

poorly developed. X-ray powder patterns for dickite often display line broadening, weakened back reflections, and darkened background which cannot be entirely explained by small grain size. Possibly there is a slight degree of stacking disorder analogous to the well-known b-axis disorder of kaolinite.

REFERENCES

- Allen, V. T. (1936) Dickite from St. Louis County, Missouri: Am. Mineral, 21, 457-459.
- Bailey, S. W. (1963) Polymorphism of the kaolin minerals: Am. Mineral, 48, 1196-1209.
- Bailey, S. W. and S. A. Tyler (1960) Clay minerals associated with the Lake Superior iron ores: Econ. Geol. 55, 150-175.
- Bayliss, P., F. C. Loughnan and J. C. Standard (1965) Dickite in the Hawkesbury Sandstone of the Sydney Basin, Australia. Am. Mineral, 50, 418-426.
- Brindley, G. W. and Robinson, K. (1946) The structure of kaolinite: Mineralog. Mag. 27, 242-253.
- Dick, A. B. (1908) Supplementary notes on the mineral kaolinite: Mineral. Mag. 15, 124-127.
- Dickson, J. A. D. (1966) Carbonate identification and genesis as revealed by staining: Jour. Sed. Pet. 36, 491-505.
- Ewell, R. H. and H. Insley (1935) Hydrothermal synthesis of kaolinite, dickite, beidellite, and nontronite: Jour. Research U. S. Bur. Standards 15, 173-186.
- Goldsmith, J. R., D. L. Graf, J. Witters and D. A. Northrop (1962) Studies in the system $\text{CaCO}_3\text{-MgCO}_3\text{-FeCO}_3$: 1. Phase relations; 2. A method for major-element spectrochemical analysis; 3. Compositions of some ferroan dolomites: Jour. Geology 70, 659-688.
- Grohskopf, J. G. and Hundhausen, M. (1937) Occurrence of dickite and fluorite: Missouri Geol. Survey and Water Res. 59th Bienn. Rept., 1-13.
- Gruner, J. W. (1937) Hydrothermal leaching of iron ores of the Lake Superior type--a modified theory: Econ. Geol. 32, 121-130.
- Hagni, R. D. (1962) Mineral paragenesis and trace element distribution in the Tri-State zinc-lead district, Missouri, Kansas, Oklahoma: Unpub. Ph.D. thesis, Univ. of Missouri.

- Harbaugh, J. W. (1959) Marine bank development in Plattsburg Limestone (Pennsylvanian), Neodesha-Fredonia area, Kansas: Kansas Geol. Survey Bull. 134, 289-331.
- Harbaugh, J. W. (1960) Petrology of marine bank limestones of Lansing Group (Pennsylvanian), southeast Kansas: Kansas Geol. Survey Bull. 142, 189-234.
- Harbaugh, J. W. (1961) Relative ages of visibly crystalline calcite in late Paleozoic limestones: Kansas Geol. Survey Bull. 152, 91-126.
- Hayes, J. B. (in press, 1967) Dickite in Lansing Group (Pennsylvanian) limestones, Wilson and Montgomery counties, Kansas: Am. Mineral. 52.
- Hayes, J. B. (1963) Kaolinite from Warsaw geodes, Keokuk region, Iowa. Proc. Iowa Acad. Sci. 70, 261-272.
- Hayes, J. B. (1961) Mississippian geodes of the Keokuk, Iowa, region: Ph.D. thesis, University of Wisconsin.
- Heckel, P. H. (1966) Relationship of carbonate facies in an algal-mound complex in Upper Pennsylvanian of Kansas: Program, 1966 Annual Meeting, Geol. Soc. America, San Francisco, Calif., 90-91.
- Jackson, M. L. (1956) Soil chemical analysis--advanced course. Published by the author, University of Wisconsin, Madison, 991 p.
- Keller, W. D. (1964) Processes of origin and alteration of clay minerals: Soil Clay Mineralogy, Univ. of North Carolina Press, Chapel Hill, 3-76.
- Keller, W. D. (1947) Sulfide replacements of a Trigonocarpus fossil fern fruit: Am. Mineral. 32, 468-470.
- Kerr, P. F. (1955) Hydrothermal alteration and weathering: in Poldervaart, A., Editor, Crust of the earth: Geol. Soc. America Spec. Paper 62, 525-543.
- Knight, G. L. and K. K. Landes (1932) Kansas laccoliths: Jour. Geology 40, 1-15.
- Merriam, D. F. (1963) The geologic history of Kansas: Kansas Geol. Survey Bull. 162, 317 p.
- Moore, R. C. (1949) Divisions of the Pennsylvanian System in Kansas: Kansas Geol. Survey Bull. 83, 203 p.
- Miser, H. D. (1943) Quartz veins in the Ouachita Mountains of Arkansas and Oklahoma, their relations to structure, metamorphism, and metalliferous deposits: Econ. Geol. 38, 91-118.

- Miser, H. D. and Milton C. (1964) Quartz, rectorite, and cookeite from the Jeffrey Quarry, near North Little Rock, Pulaski County, Arkansas: Arkansas Geol. Commission Bull. 21, 1-29.
- Murray, H. H. (1954) Structural variations of some kaolinites in relation to dehydrated halloysite: Am. Mineral. 39, 97-108.
- Newell, N. D. (1933) The Stratigraphy and paleontology of the upper part of the Missourian Series in eastern Kansas: Unpub. doctoral dissertation, Yale Univ., 247 p.
- Pearn, W. C. (1959) Thermoluminescence applied to the dating of certain tectonic events: Unpub. master's thesis, Kansas Univ., 74 p.
- Ross, C. S. and P. F. Kerr (1931) The Kaolin minerals: U.S. Geol. Survey Prof. Paper 165E, 151-180.
- Serratos, J. M., A. Hidalgo and J. M. Vinas (1963) Infrared study of the OH groups in kaolin minerals: Inter. Clay Conf. 1963, Vol. 1, 17-26.
- Shutov, V. D. (1964) Epigenetic zones in terrigenous deposits of the platform mantle: International Geology Review 6, 519-530.
- Smithson, F. and G. Brown (1957) Dickite from sandstones in northern England and North Wales: Mineral Mag. 31, 381-391.
- Smithson, F. and G. Brown (1954) The petrography of dickitic sandstones in North Wales and northern England: Geol. Mag. 91, 177-188.
- Sohlberg, R. G. (1933) Cinnabar and associated minerals from Pike County, Ark.: Am. Mineral. 18, 1-8.
- Stone, C. G. (1966) General geology of the eastern Frontal Ouachita Mountains and southeastern Arkansas Valley: Kansas Geol. Soc., Wichita, Guidebook, 29th Field Conf., 195-221.
- Tarr, W. A. and Keller, W. D. (1936) Dickite in Missouri: Am. Mineral. 21, 109-114.
- Twenhofel, W. H. (1917) The Silver City quartzites: Geol. Soc. Am. Bull. 37, 403-412.
- Wagner, H. C. (1954) Geology of the Fredonia Quadrangle, Kansas: U.S. Geol. Survey Map GQ49.
- Wheeler, H. E. (1965) Ozark Pre-Cambrian-Paleozoic relations: Am. Assoc. Petroleum Geologists Bull. 49, 1647-1665.
- Wilson, F. W. (1957) Barrier reefs of the Stanton Formation (Missourian) in southeastern Kansas: Kansas Acad. Sci. Trans. 60, 429-436.

Appendix A. Mound complexes

APPENDIX A

MOUND COMPLEXES

There are 12 major algal-mound complexes in southeast Kansas and northeast Oklahoma with which this paper is concerned. These are listed below in stratigraphically ascending order (Figures 4 and 5).

- 1) The stratigraphically lowest mound is the Critzer Limestone Member of the Hertha Limestone. It outcrops solely in Bourbon County.
- 2) The Bethany Falls Limestone Member of the Swope Limestone is the next stratigraphically higher mound and outcrops in eastern Neosho County.
- 3) The Winterset Limestone Member of the Dennis Limestone extends southwestward from Linn County through Bourbon, Allen and Neosho counties into the northwest corner of Labette County. South of this area it thins to normal thickness but in Nowata County, Oklahoma it mounds again and extends into Washington County, Oklahoma. (The Winterset Limestone is known as the Hogshooter Limestone in Oklahoma).
- 4) The Drum Limestone in Kansas is of normal thickness, however, in Washington County, Oklahoma the Drum Limestone (in Oklahoma the Drum Limestone is called the Dewey Limestone) thickens and forms a mound.
- 5) The Raytown Limestone Member of the Iola Limestone mounds in central Allen and northern Neosho counties, then resumes normal thickness until it once again mounds in the western portion of Washington County,

Oklahoma. (The Raytown Limestone is called the Avant Limestone in Oklahoma).

6) The Argentine Limestone Member of the Wyandotte Limestone forms a mound in Miami County.

7) The Spring Hill Limestone Member of the Plattsburg Limestone forms two mounds, the larger in central Anderson and northern Allen counties and the smaller in southern Wilson and northern Montgomery counties.

8) The Captain Creek Limestone Member of the Stanton Limestone forms a narrow mound extending from the southern boarder of Anderson County through Allen, Woodson and Wilson counties and ending in central Montgomery County.

9) The Stoner Limestone Member of the Stanton Limestone mounds in Wilson and Montgomery counties.

10) The South Bend Limestone Member of the Stanton Limestone forms a small mound in western Montgomery County.

11) In eastern Chautauqua County the Haskel Limestone Member of the Stranger Limestone forms a small mound.

12) The Plattsmouth Limestone Member of the Oread Limestone also mounds in central Chautauqua County.

Appendix B. Sample localities

APPENDIX B

SAMPLE LOCALITIES

LOCALITY	LOCATION	SAMPLE NUMBERS
1	NE sec. 15, T. 15 S., R. 18 E.	*
2	SW sec. 29, T. 13 S., R. 23 E.	205
3	SE sec. 9, T. 14 S., R. 23 E.	206
4	E2 sec. 4, T. 18 S., R. 16 E.	*
5	SW sec. 7, T. 17 S., R. 17 E.	*
6	C sec. 22, T. 15 S., R. 18 E.	*
7	SE NE sec. 7, T. 17 S., R. 23 E.	207
8	SE sec. 27, T. 18 S., R. 23 E.	208
9	SE SW sec. 28, T. 18 S., R. 25 E.	209
10	SW sec. 14, T. 21 S., R. 15 E.	*
11	SE sec. 2, T. 22 S., R. 15 E.	*
12	NE sec. 32, T. 20 S., R. 16 E.	*
13	NE sec. 27, T. 23 S., R. 18 E.	189
14	SE NE sec. 1, T. 21 S., R. 18 E.	188
15	SW sec. 34, T. 20 S., R. 19 E.	187
16	NE sec. 1, T. 20 S., R. 19 E.	186
17	SW sec. 35, T. 22 S., R. 20 E.	171
18	NW sec. 7, T. 20 S., R. 20 E.	164
19	C sec. 23, T. 19 S., R. 17 E.	167
20	SW sec. 28, T. 20 S., R. 22 E.	168, 220
21	SE NW sec. 2, T. 21 S., R. 23 E.	169, 211
22	C sec. 23, T. 22 S., R. 23 E.	170, 213
23	NW sec. 34, T. 21 S., R. 24 E.	212
24	NW sec. 35, T. 25 S., R. 13 E.	185
25	SE SW sec. 18, T. 26 S., R. 16 E.	184
26	NE sec. 19, T. 26 S., R. 16 E.	183
27	NE sec. 19, T. 24 S., R. 18 E.	200
28	NE sec. 2, T. 25 S., R. 18 E.	191
29	SE sec. 9, T. 26 S., R. 18 E.	163
30	SE sec. 5, T. 24 S., R. 19 E.	190
31	NW sec. 13, T. 24 S., R. 20 E.	172
32	C sec. 25, T. 24 S., R. 20 E.	201
33	NW sec. 36, T. 23 S., R. 21 E.	202
34	SE sec. 20, T. 23 S., R. 22 E.	227, 228
35	SE sec. 23, T. 23 S., R. 22 E.	226
36	SW sec. 36, T. 23 S., R. 22 E.	225
37	NW sec. 35, T. 24 S., R. 22 E.	229
38	SW sec. 30, T. 24 S., R. 23 E.	222
39	NE sec. 31, T. 24 S., R. 23 E.	223

LOCALITY	LOCATION	SAMPLE NUMBERS
40	SW sec. 15, T. 25 S., R. 22 E.	230
41	NE NE sec. 12, T. 26 S., R. 21 E.	220, 221
42	C sec. 12, T. 26 S., R. 21 E.	219
43	C sec. 7, T. 26 S., R. 22 E.	218
44	NE SE sec. 8, T. 26 S., R. 22 E.	217
45	C sec. 34, T. 25 S., R. 22 E.	216
46	SE sec. 17, T. 24 S., R. 23 E.	224
47	SE sec. 16, T. 26 S., R. 23 E.	198
48	SE SW sec. 17, T. 25 S., R. 23 E.	215
49	SE sec. 15, T. 25 S., R. 24 E.	214
50	C N2 sec. 19, T. 25 S., R. 25 E.	197
51	SE NW sec. 6, T. 27 S., R. 15 E.	162, 166
52	SE SE sec. 2, T. 28 S., R. 15 E.	158, 159
53	NW NW sec. 23, T. 29 S., R. 15 E.	154, 155
54	NW sec. 26, T. 30 S., R. 15 E.	104-109, 151-153, 165
55	SE NW sec. 18, T. 30 S., R. 16 E.	156, 157
56	NW NE sec. 18, T. 29 S., R. 16 E.	100-103
57	SW sec. 17, T. 27 S., R. 16 E.	160, 161
58	NE NW sec. 33, T. 30 S., R. 19 E.	174
59	SW sec. 34, T. 29 S., R. 19 E.	193
60	NW sec. 30, T. 29 S., R. 20 E.	194
61	NW sec. 20, T. 28 S., R. 20 E.	195, 232
62	SE sec. 22, T. 29 S., R. 20 E.	192
63	NW NE sec. 20, T. 30 S., R. 20 E.	236
64	SW sec. 10, T. 30 S., R. 20 E.	235
65	SE sec. 17, T. 29 S., R. 20 E.	231
66	NW sec. 36, T. 28 S., R. 20 E.	233
67	SE sec. 12, T. 27 S., R. 20 E.	173
68	SW sec. 31, T. 27 S., R. 24 E.	196
69	SE sec. 12, T. 30 S., R. 22 E.	234
70	NE sec. 8, T. 35 S., R. 10 E.	147
71	NE sec. 16, T. 35 S., R. 10 E.	146
72	NW SW sec. 30, T. 33 S., R. 11 E.	148, 149
73	C N2 sec. 12, T. 35 S., R. 10 E.	143-145
74	C sec. 33, T. 33 S., R. 11 E.	150
75	SE sec. 10, T. 34 S., R. 12 E.	175
76	SE sec. 18, T. 32 S., R. 14 E.	130-132
77	SW sec. 17, T. 32 S., R. 14 E.	133-136
78	C sec. 16, T. 32 S., R. 14 E.	114, 115
79	NW sec. 7, T. 32 S., R. 15 E.	117-129
80	SW SE sec. 30, T. 34 S., R. 15 E.	182
81	SW sec. 10, T. 32 S., R. 15 E.	110-113
82	NW sec. 33, T. 32 S., R. 16 E.	137-142
83	NE NW sec. 24, T. 32 S., R. 17 E.	239
84	SW sec. 31, T. 32 S., R. 18 E.	238
85	SE sec. 31, T. 32 S., R. 18 E.	237
86	SW sec. 11, T. 32 S., R. 18 E.	199
87	NW sec. 35, T. 33 S., R. 18 E.	240

<u>LOCALITY</u>	<u>LOCATION</u>	<u>SAMPLE NUMBERS</u>
88	SE sec. 36, T. 34 S., R. 18 E.	241
89	SE sec. 8, T. 31 S., R. 19 E.	204
90	**E2 sec. 25, T. 24 N., R. 12 E.	178
91	**SE sec. 17, T. 24 N., R. 12 E.	179
92	**SW sec. 23, T. 27 N., R. 13 E.	177
93	**CW2 sec. 5, T. 27 N., R. 14 E.	176
94	**NE sec. 17, T. 26 N., R. 14 E.	180
95	**NW sec. 16, T. 26 N., R. 14 E.	181

** Localities in Oklahoma

* No sample numbers. Kaolinite localities obtained from Walter Hill, Kansas Geological Survey.