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Petrology and diagenesis of the cyclic Maquoketa Formation (Upper Ordovician) Pike County, Missouri

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Title

PETROLOGY AND DIAGENESIS OF THE CYCLIC MAQUOKETA FORMATION (UPPER ORDOVICIAN) PIKE COUNTY, MISSOURI

BY

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THESIS

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ABSTRACT

The Maquoketa Formation (Upper Ordovician-Cincinnatian Series) has been extensively studied for over one hundred years, but a petrographic study of its cyclic lithologies has been neglected. The following six distinct Maquoketa lithologies have been recognized in this study in Pike County, Missouri: 1) phosphatic biosparite, 2) phosphorite, 3) micrite-microsparite, 4) dolomitic shale, 5) dolomitic marlstone, and 6) dolomitic quartz siltstone.

Three cycle types are present in the Maquoketa. They are expressed as thin beds (1-20 inches) of alternating micrite-shale, micrite-marlstone, and shale-siltstone. Contacts between different lithologies are sharp, indicating a primary sedimentological origin for the cycles. Precisely what mechanism was responsible for these rapid and repetitive changes in sedimentation is undetermined.

All Maquoketa sediments have experienced extensive diagenesis, the most widespread of which were dolomitization, neomorphism of calcium carbonate and formation of syngenetic pyrite. Minor development of authigenic silica, fluorite, and sphalerite were found in selected examples. The formation of sedimentary boudinages, cone-in-cone structures, and minor intrastratal folds is interpreted as having taken place in some micritic sediments before consolidation was completed.

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TABLE

I. Introduction

A. General

The Maquoketa Formation (Upper Ordovician-Cincinnatian Series) has been extensively studied for over one hundred years with the literature encompassing more than fifty authors. But a study of the Maquoketa cycles has been totally neglected. The cyclic nature may vary laterally over relatively short distances, but locally it is very conspicuous, notably in Pike County, northeastern Missouri. The cyclic pattern is best perceived on weathered outcrops as an alternation of thin beds (1 to 8 inches) of resistant lithographic to sublithographic limestones with thin beds (1 to 20 inches) of nonresistant dolomitic shale (Figs. 1, 2, and 3). The shale grades into dolomitic marlstone, but this change is not apparent on weathered outcrops. Bedding of the limestones varies from very regular to nodular. Some limestones have highly irregular, continuous, hummocky surfaces (Fig. 38). Generally this cyclic pattern is found in the lower 50 to 70 feet of the formation. A minor siltstone-shale cyclic sequence may be recognized in the upper Maquoketa that is similar in appearance to the limestone-shale sequence.

The term "cyclic" has been applied to repetitive vertical variations in sedimentary rocks. The following have been used as criteria for cyclicity: change in gross lithology (i.e. limestone to shale, shale to sandstone, etc.), mineralogical changes (i.e. calcite-dolomite ratio,

Fig. 1. Weathered outcrop of the cyclic limestone-shale sequence exposed on the Dundee Quarry property. About 20 feet of the Maquoketa is exposed. Limestone weathers in relief and exhibits very regular bedding planes. The base of this outcrop is about 40 feet above the base of the formation.

Fig. 2. Fresh unweathered cyclic Maquoketa outcrop in the "shale pit" at the Dundee Quarry. Light colored rock is limestone, darker rock is shale. Note the blocky subconchoidal fracture exhibited by both lithologies at this outcrop. About 6 feet of the Maquoketa is shown in picture. Base of this exposure is about 10 feet above the base of the formation.

Fig. 1.

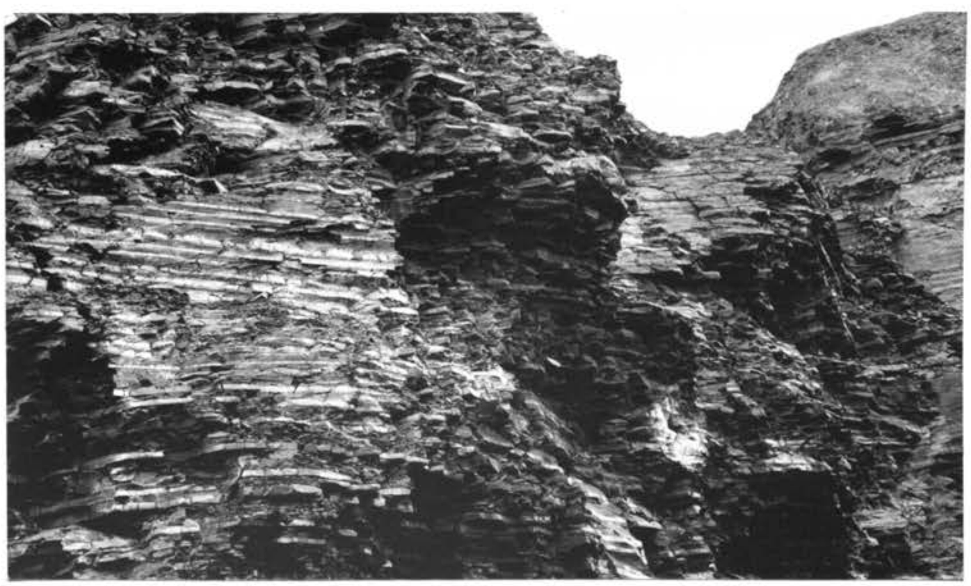

Fig. 2.

Fig. 3. Weathered outcrop of the cyclic limestone-shale sequence at the Stark Nursery (ST) section. Here the limestones exhibit irregular hummocky bedding surfaces that are thought to be the results of minor intrastratal flowage. About 6 feet of the Maquoketa is shown in picture.

Fig. 4. Irregular limestone bedding surface showing rectangular fracture pattern, exposed in Noix Creek at the Stark Nursery (ST) section.

Fig. 3.

Fig. 4.

percentage of clay minerals, etc.), change between marine and non-marine rocks, and changes in the number and types of fossils in successive layers. Unfortunately, no general agreement exists as to what constitutes a cyclic sedimentary unit. The terms cycle, rhythm, and cyclothem have been used interchangeably by different authors. Some authors have restricted these terms by adding genetic connotations, thickness and time requirements, confinement to Pennsylvanian rocks and specifications of the number and sequence of units involved. Duff et al. (1967) are the first to discuss systematically all types of cyclic sedimentation and their terminology is followed in this paper. They state:

> "In our opinion the three terms, rhythm, cycle, and cyclothem should be regarded as synonymous except that the latter always refers to sedimentary deposits. Cycle or rhythm, though referring on most occasions to the deposits, might also denote the period of time during which certain sediments formed. The use of the terms will be clear from their context...We see no prospect of general agreement on, nor any particular advantage in, the usage of these terms according to arbitrary, restrictive definitions." (Duff et al., 1967, p. 2-3.)

Spreng (1953) further clarified the use of the term cycle as intended in this paper:

> "A cycle, as used in this paper, is the sedimentary evidence of an environment of sedimentation which changes from an original condition only to return to that same condition. It is a general term in the sense that there are no strict requirements for the pattern of the occurrence or the duration of the pattern. The comparable parts must be

> equal in expression only; not necessarily in thickness. Thus the only requirement is that there be a recognizable pattern of recurrence. A change in sedimentary layers from shale to limestone, which repeats itself, is considered a cycle." (Spreng, 1953, p. 676.)

Some authors (notably Zeller, 1964) have objected to applying the term cyclic to simple, two component systems (ABAB type) similar to those of the Maquoketa. Zeller has argued that a random arrangement of lithologies in a two component system would give the false appearance of perfect cyclicity, and that a rigorous definition of the term cycle would include time as a parameter. He (Zeller, 1964, p. 634) states: "Thus, in the strictest sense, each sedimentary cycle would have to be completed in the same amount of time." However, the equality of time as a geologic parameter would seem to be very rarely fulfilled, and could seldom be adequately demonstrated. Cyclic is used in this paper to describe the alternating lithologies of the Maquoketa Formation. No specific genetic or time implications are intended by the use of this term.

Maquoketa samples from four outcrops and five cores are considered in the present study. The sample locations were spaced as evenly as possible along the length of the exposed Maquoketa in Pike County (Fig. 5). An interpretation of the environment of deposition and post-depositional history of these cyclic units is proposed on the basis of relationships and thin section analysis.

There are several serious obstacles to a study of the

TABLE I. Sample Localities

OUTCROPS

LOCATIONS (Geographical)	(Township and Range)	LOCATION CODE
Stark Nursery on Noix Creek Louisiana, Mo.	NE¼, SW¼, Sec. 25, T.54 N., R.2 W.	ST
Dundee Quarry "Shale Pit" Clarksville, Mo.	SE¼, SE¼, Sec. 24, T.53 N., R.1 W.	DD
Ramsey Creek near County Road WW, Pike County, Missouri.	SE¼, SW¼, Sec. 12, T.52 N., R.1 W.	WW
Grassy Creek, Pike County, Missouri.	NW¼, SE¼, Sec. 19, T.54 N., R.2 W.	GC

CORES

Dundee Designations	Locations	Maquoketa Thickness
1. CDH # 63	Sec. 18, T.53 N., R.1 E.	104.8 feet
2. CDH # 72	Sec. 13, T.53 N., R.1 W.	15.0 feet
3. CDH # 73	Sec. 13, T.53 N., R.1 W.	39.0 feet
4. CDH # 76	Sec. 13, T.53 N., R.1 W.	43.0 feet
5. PQ # 7	Sec. 13, T.53 N., R.1 W.	107.0 feet

Maquoketa Formation. The most serious of these is the lack of fresh exposures. Due to the abundance of clay minerals and clay-sized particles, outcrops weather rapidly with subsequent slumping. The interpretation of textures is complicated by the fine grain size of the clays and carbonates. The presence of fine-grained constituents, and the sparceness of fossils, yields a monotonous sequence of alternating shales and limestones, which are difficult to correlate even locally. Correlations in Pike County are further complicated by the absence of a single exposed continuous section. Regional correlation with the type Cincinnatian Series has been debated due to unconformities at the top and the bottom of the Maquoketa. (Gutstadt, 1958; Rooney, 1966.)

B. Sample Locations and Designations

The representation of measured stratigraphic sections of thin beds of alternating limestone and shale presents problems. Some workers have measured great thicknesses of these interbedded units as "calcareous shales" or "shale interbedded with thin limestone flags." This imprecise type of stratigraphic description is too general to be of value for locating sample positions in a meaningful petrographic study of cyclic units. Other workers have recorded one and two inch units as individual beds. Although many of the units considered in this study are of the magnitude of one or two inches in thickness, graphic presentation of sample positions was found to be cumbersome.

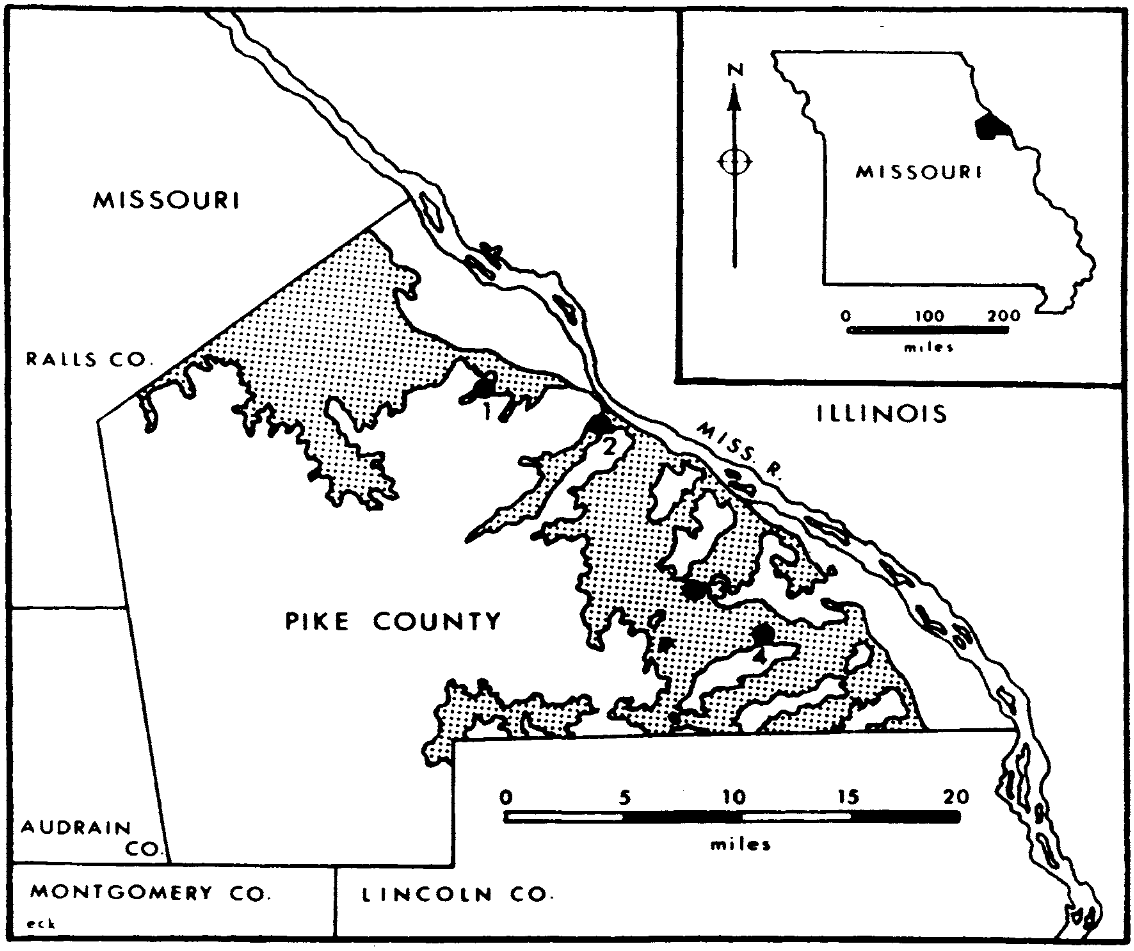

FIG. 5. MAP OF PIKE COUNTY, MISSOURI, SHOWING MAQUOKETA OUTCROP PATTERN (STIPPLED AREA) AND SAMPLE LOCALITIES — (1.) GRASSY CREEK SECTION; (2.) NOIX CREEK SECTION; (3.) DUNDEE QUARRY SECTION (1 OUTCROP AND 5 CORES); (4.) RAMSEY CREEK SECTION.

Instead, sample positions for outcrops are conveniently recorded in chart form in Appendix B.

The shales on all outcrops, except at the Dundee Quarry, were so well weathered and friable that only the limestones and siltstones were thin-sectioned. Each sample was assigned a letter designation based on geographical location, and limestones were numbered consecutively from the base of the outcrop upward. Representative and unusual lithologies were collected.

Five cores from Dundee Cement Company Quarry of Clarksville, Missouri, were used. All lithologic types were thin-sectioned in these samples. Sample positions were located by Dundee's core designation followed by the letter "L" or "S" designating limestone or shale respectively. The letter was followed by consecutive numbers for both the limestone and shale with number one starting for each lithology at the bottom of the hole.

C. Acknowledgements

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This work could not have been completed without the cores that were generously supplied by the Dundee Cement Company of Clarksville, Missouri. Through the cooperation of Erwin K. Pennington, Production Engineer, Dundee Cement also allowed free access to their quarry and supplied valuable geologic and analytic data.

Dr. Keene Swett, University of Iowa, critically read portions of this thesis and offered suggestions concerning petrographic interpretations.

John S. Trapp, graduate student at the University of Missouri-Rolla, accompanied the author into the field. Trapp supplied some chemical data and many interesting discussions of Maquoketa problems.

My wife Gail was of great assistance and offered helpful suggestions during all phases of this investigation.

II. Previous Work

A. Maquoketa Formation

Only a very brief historical sketch of Maquoketa studies will be presented. An extensive annotated bibliography concerning Maquoketa problems can be found in Appendix I of this report. As previously indicated, a great deal of work has been done on this formation by numerous authors for many years. Unfortunately many of the original problems are still unsolved. Concerning Maquoketa studies, Calvin and Bain in 1900 had the following to say:

> "Scarcely any formation in this geological province has been written about more persistently; scarcely any has been more misunderstood; with respect to no other has there been a greater diversity of judgement and interpretation; in no case is it more obvious that some of the latest attempts to harmonize discrepant opinions have involved the whole subject in more inextricable confusion." (Calvin and Bain, 1900, p. 431-432.)

During the seventy years that have intervened between the writing of the above passage and this study the literature has more than doubled, with an increasing diversity of opinions.

Most of the previous work on the Maquoketa Formation is comprised of stratigraphic and paleontologic studies. Apparently the first mention of rocks now assigned to the Maquoketa Formation was made by John Locke in 1840 in a report on "mineral lands" to David Owen. Locke gave a generalized geologic section for northeast Iowa and grouped what is now known as the Galena and Maquoketa Formations into the "Cliff Limestone." Foster and Whitney (1851) first applied the name Hudson River Group to Maquoketa rocks and correlated them with Ordovician rocks of the same name in New York.

White (1870) named the Maquoketa Formation and described a type section from exposures of bluish-gray shale along the Little Maquoketa River about twelve miles west of Dubuque, Dubuque County, Iowa. He correlated the Maquoketa with the type Cincinnatian Series in Ohio. James (1890) confirmed White's correlation with the type Cincinnatian Series. Between 1896 and 1897 Sardeson authored a series of five papers on the Galena and Maquoketa Formations which illustrates the chaotic nomenclature concerning these formations.

Calvin (1906) divided the Maquoketa into four members with the type localities in Fayette and Winneshiek Counties, Iowa. Calvin's descriptions of these members from the base of the formation upward are as follows:

> "1. Elgin Shaly Limestone-Limestones, dolomites and shaly limestones with beds of calcareous clays; quite variable in character and fossil contents, but generally yellowish, decidedly calcareous and more indurated than the blue, plastic shales of 2 and 4...Near Elgin the Isotelus beds at the base of the member are largely blue, hard, fine grained limestones. Thickness of entire member 70 feet.
>
> 2. Clermont Shale-Bluish colored, plastic, fine grained shale, well

developed below the Fort Atkinson limestone at Clermont in Fayette county...Thickness 15 feet.

3. Fort Atkinson Limestone-Massive, yellow, cherty, dolomite and associated beds of limestone... best exposures occurring at Fort Atkinson. Thickness 40 feet.

4. Brainard Shales-Blue and bluish-gray shale, with some intimately associated beds of limestone at the top and bottom of the division... It is proposed to designate this member by the name of the small railway station in Fayette county near to which it has its most typical development. Thickness about 120 feet." (Calvin, 1906, p. 332-339.)

In Missouri, Rowley (1907) used the name Hudson River Shale for the Maquoketa Formation. He investigated the stratigraphy and paleontology of the Maquoketa in Pike County.

Ladd (1929) published the most complete study on the stratigraphy and paleontology of the Maquoketa Formation. He described a number of faunal zones; the so-called "depauperate zone" at the base of the formation; the *Isotelus iowensis* zone, associated with graptolites in the lower Elgin member; the *Vogdesia vigilans* zone found locally in the Elgin member; an upper faunal zone of the Elgin member; faunal zones characteristic of the Clermont and Fort Atkinson members; and the *Cornulites* zone of the upper Brainard member. Most of Ladd's work concerned the Iowa section, but he did reconnaissance work in Michigan, Wisconsin, Illinois, and Missouri.

Johnson (1939) investigated the stratigraphy and paleontology of the Maquoketa Formation in Missouri and Illinois. Much of his work was done in Pike County, Missouri, and his paper proved to be a useful guide in this study. He correlated the Missouri section with the Maquoketa type section in Iowa.

Comprehensive faunal lists for the Maquoketa Formation can be found in Rowley (1907), Ladd (1928), Johnson (1939) and Branson (1944).

Agnew (1955) published a comprehensive stratigraphic study of the Middle and Upper Ordovician rocks of Iowa. His study was based on outcrop and subsurface data. Gutstadt (1958), in a regional study, attempted to correlate the Maquoketa Formation with its time equivalents in the Eastern Interior region. Laswell (1957) considered some aspects of Maquoketa stratigraphy in Pike County, Missouri, but added no new information.

Bromberger (1965, 1968) studied the mineralogy of the basal phosphate beds of the Maquoketa Formation. Bromberger apparently was the first person to undertake any thin-section study of Maquoketa rocks. His work was limited to the phosphate-bearing horizons.

Further references to previous Maquoketa studies will be made in appropriate sections of this report.

B. Cyclic Limestone-Shale Sequences

As no previous investigation of cyclic units in the Maquoketa Formation has been undertaken, examples of other cyclic units having similar lithologies will be reviewed.

Only minor cycles composed of limestone and argillaceous beds will be considered. Duff *et al*. (1967, p. 163) define this type minor cycle as "Regular cyclic alteration of shale (and/or marl) and fine-grained argillaceous limestone of the order of a few decimeters per cycle..." The origin of these cycles has been interpreted by various authors as 1) primary, 2) secondary, and 3) secondary accentuation of primary features. Evidence appears to exist favoring both a primary and secondary origin. However, the results of most studies favor a primary origin.

The Blue Lias Formation, Lower Jurassic of England and Wales, is perhaps the best studied cyclic formation of this type, and its lithology is very similar to that of the Maquoketa. All three origins of cyclicity, primary, secondary, and secondary accentuation of primary features, have been proposed for this formation. The lithology consists of argillaceous calcilutites (2 to 12 inches thick) separated by marlstones and shales of somewhat greater thickness. The bedding of the limestones varies from very regular to nodular.

Richardson (1923) made the first significant study of the Blue Lias. He observed that limestones progressing upward stratigraphically were separated by increasing amounts of shales. From this observation he concluded that the Blue Lias cycles were secondary. He thought the cycles formed essentially contemporaneously, by a downward migration of calcareous solutions, a process he termed "rhythmic precipitation."

Kent (1936) and Shurko (1942), using more sophisticated criteria, also concluded a secondary origin for the Blue Lias cycles.

Hallam (1957, 1960, 1961, 1964) has published a number of recent papers on the origin of the cycles in the Blue Lias. In 1957 he concluded a primary origin for the cycles in the Blue Lias. In 1960 Hallam accepted the possibility of a small amount of carbonate segregation but considered the cycles of the Blue Lias to have an essentially primary origin. In 1964 he revised his ideas again with a composite theory of secondary accentuation of primary features which includes primary precipitation of calcium carbonate and clay. Hallam considered mottling, resulting from the burrowing of various organisms, as the single strongest piece of evidence favoring a primary origin. Shale (or marl) is seen to penetrate underlying limestone and vice versa depending on lithologic sequence. According to Hallam (1964, p. 158): "The fine preservation of these trace fossils can only be due to the original deposition of alternating layers of lighter, more calcareous, and darker, more argillaceous, mud." Very thin, finely laminated bituminous shales with a benthonic fauna occur in the midst of the normal shales and marls in several parts of the section. Hallam considered this distinctive lithology in the midst of typical cyclic units to be good evidence for a primary origin.

A number of the Blue Lias limestone beds are concretionary and may pass into bands of ellipsoidal nodules symmetrical to bedding planes which suggested to Hallam a secondary origin. Hallam considered the constant thickness of beds, regardless of the rock succession, to be the most decisive evidence favoring large scale segregation of carbonates. The thicker the sequence, the more limestone beds it contains in proportion. Hallam recognized that evidence existed favoring both a primary and secondary origin for the cycles in the Blue Lias Formation. He resolved conflicting evidence by proposing the following theory:

> "At some time subsequent to the deposition of the Blue Lias sediments, the $CaCO_3$ was subjected to rhythmic unmixing with respect to the clay (Sujkowski, 1958), so differentiating the more marly sediments into alternating thin bands of lime-rich and lime-poor mud. This process served to accentuate primary carbonate rhythms and to create other secondary ones. Where the succession is highly condensed...it is quite likely that diagenetic unmixing has actually obliterated small-scale primary changes." (Hallam, 1964, p. 166.)

Sujkowski (1958) has noted that most sediments are mixtures of heterogeneous compounds that are chemically unstable, and that diagenetic processes may lead to the chemical unmixing of the primary components. He has suggested diagenetic models for unmixing for the following three types of heterogeneous, two component sedimentary rocks: 1) a carbonate-free silica mixture; 2) a free silica-clay mixture; and 3) a clay-carbonate mixture. Only the latter will be considered. For the clay-carbonate unmixing Sujkowski suggested:

> "1. It is not the auxiliary but the main

components (i.e. carbonates) which migrate.
2. Migration never progresses to completeness and the parts impoverished may still contain 35 percent carbonates.
3. Diagenetic nodules are rare, the normal product consisting of well defined beds of limestone, in many places several feet thick." (Sujkowski, 1958, p. 2709.)

Cyclic hard and soft beds would result from this process, with the soft layers resembling marls. Preservation of calcareous fossils is much better in the limestone than in the shale, and calcite cement only exists in the hard limestone beds. Soft marl beds may show traces of corrosion. The contact between beds is very sharp. Sujkowski cited evidence supporting his theory from the Jurassic Oxfordian limestones of Poland. Sea water acting shortly after deposition and percolating ground water after consolidation are considered to be the agents responsible for "diagenetic unmixing."

Although Sujkowski did not think that all cyclic limestone-shale sequences developed during diagenesis, he did believe that primary cyclic sequences of this type are rarer than usually believed.

Schwarzacher (1964) applied a statistical time-series analysis to a cyclic limestone-shale sequence. The units studied were the Lower Carboniferous Bebbulbin shale, and Darty limestone of northwest Ireland. Schwarzacher, following a mathematical definition of cycle (cyclic repetition must be regular in time), applied the term "sedimentary oscillations" to this limestone-shale sequence.

Rather than interpret the various environments suggested by the cyclic lithologies, Schwarzacher has statistically investigated the nature of the lithologic variations. He suggested that a study such as his should be supplementary to detailed sedimentological and paleontological investigations. Schwarzacher found small scale fluctuations between thin beds of limestone and shale superimposed on a long-range trend. He assumed these cycles were primary in origin but cited no petrographic or paleontological evidence to support his assumption. Schwarzacher states:

> "The analysis makes it likely that the environmental changes which led to the sediment variation have been strictly cyclical in time. Periodic variations in the earth's orbit could be suggested as the ultimate cause of the oscillation. The trend variation can be described by a stochastic process of a moving average. Linked random disturbances such as irregular tectonic uplifts would be responsible for this type of change." (Schwarzacher, 1964, p. 195.)

Spreng (1953) studied several limestone-shale sequences in the Mississippian Banff Formation, Alberta, Canada. The entire Banff section studied was cyclic, although some cycles were larger than the minor cycles considered here. The purpose of his study was to determine if the cycles could be used for detailed stratigraphic correlation. Although simple cycles did not correlate, it was found that they were variable components of larger cycles (termed "megacycles") which persistently recurred throughout the entire section. Spreng observed that faunal changes in the Banff were closely related to lithologic changes. He interpreted the origin of these cycles as primary with deposition occurring on an unstable shelf edge environment. Lithologic changes were probably controlled by periodic downward tectonic movement of the sea bottom.

According to Bruckner (1953), cyclic variation in the carbonate content of rocks in many regions is due chiefly to climatic fluctuations. Bruckner reasoned that calcium carbonate precipitated on the sea bottom may be partly or completely redissolved if the sea water is undersaturated with calcium carbonate. He stated:

> "As a general rule, cold sea water is more or less undersaturated, and warm sea water is saturated or sometimes over-saturated. The formation of calcareous sediments is therefore greatly favored in warm, tropical, shallow seas, and hindered or even prevented in the cold water of higher latitudes and of greater depth." (Bruckner, 1953, p. 237.)

Bruckner explained the formation of both major and minor cycles by this process. He considered long range temperature fluctuations on the order of magnitude of those of the Pleistocene (2°C to 5°C) to be sufficient to shift sedimentation from limestone to shale. This theory is based mainly on Bruckner's observations of rocks of the Helvetic zone (Cretaceous) of the Swiss Alps.

Carozzi (1955) also studied the Helvetic zone of the Swiss Alps and has objected to Bruckner's climatic theory. He maintained that tectonics were the controlling factor in the formation of the cyclic sequence. He has pointed out that the number of cycles in the complete sequence varies from point to point in the basin, and that they are not necessarily related to facies changes. Such a situation, according to Carozzi, would require unreasonable climatic fluctuations over short distances.

The cyclic Silurian Rochester Formation of West Virginia has been investigated by Folk (1962). Approximately 85% of the Rochester Formation is composed of gray to black, fissile shale. Thin (one to three inches), dark gray calcilutite interbeds comprise the remaining 15% of the formation. Individual beds are generally separated by about one foot of shale. Unresolvable organic matter imparts a uniform brown color to the limestones. A well-winnowed biosparite bed, one foot thick, occurs at the base of the formation. No fossils were found in the shale; however, the limestones have an abundant ostracode fauna. Many of the limestone beds have an irregular nodular surface. Folk believes these nodules (three to six inches long and one half inch thick) may have existed as low carbonate mud mounds on the black mud sea bottom. Folk has interpreted the depositional environment as one of prevalent quiet waters and strongly reducing conditions. He believed that it probably represented a barrier bar-stagnant lagoon couplet with the cyclic lithologies due to shifting positions of the bar-lagoon margin. Folk also considered it likely that the same lithologic sequence could have developed in a deep water basin, beyond the littoral and neritic zone.

In a later study, Folk (1965) noted a bimodal grain-size distribution of micrites in the limestone beds of certain cyclic limestone-shale sequences. According to Folk, the normal micrite has a unimodal grain-size distribution. He considered this bimodal distribution the result of incomplete recrystallization of micrite to microspar. Although Folk did not elaborate on this observation, further study might lend support to Sujkowski's (1958) theory of "diagenetic unmixing."

Recent sediments of the Black Sea more closely resemble cyclic limestone-shale sequences in ancient rocks than any other modern analog. Three main sediment types exist: 1) a gray clay, 2) a transitional mud and 3) a calcareous mud. These lithologies differ in the amount of clay, calcium carbonate and organic material they contain (Chilingar, 1956). These sediment types are found in alternating beds several inches thick. Individual beds commonly exhibit fine bituminous laminations. Archanguelsky (1927) suggested that these laminations represented annual varves. The Black Sea has a low density, low salinity surface layer and hydrogen-sulfide rich anaerobic water below 150 meters. These conditions are partially due to the fact that the rate of precipitation and runoff exceeds the rate of evaporation and to limited water circulation through the Straits of Bosporus.

Most authors (Archanguelsky, 1927, Casper, 1957, and Chilingar, 1956) agree that most of the calcium carbonate in the Black Sea was precipitated by anaerobic sulfate reducing bacteria. Some calcium carbonate may have been chemically precipitated in shallow water and carried to deeper parts of the basin. Colloidal ferrous sulfide is commonly found in all three sediment types. The carbonate mud occurs at a greater distance from land than either the gray clay or transitional mud, suggesting a relatively small amount of dilution by terrigenous mud seaward.

Several authors (Hallam, 1964, Hemmingway, 1951) have suggested that similarities may have existed between the environment of deposition of recent Black Sea sediments and ancient cyclic limestone-shale sequences. Duff et al. (1967) agree that it is reasonable to hypothesize a special chemical environment (similar to that of the Black Sea) to explain the environment of deposition of certain cyclic sequences.

A more detailed comparison of certain petrographic similarities between Maquoketa rocks and the preceding examples of other cyclic limestone-shale sequences can be found in later sections of this paper.

III. Geologic Setting

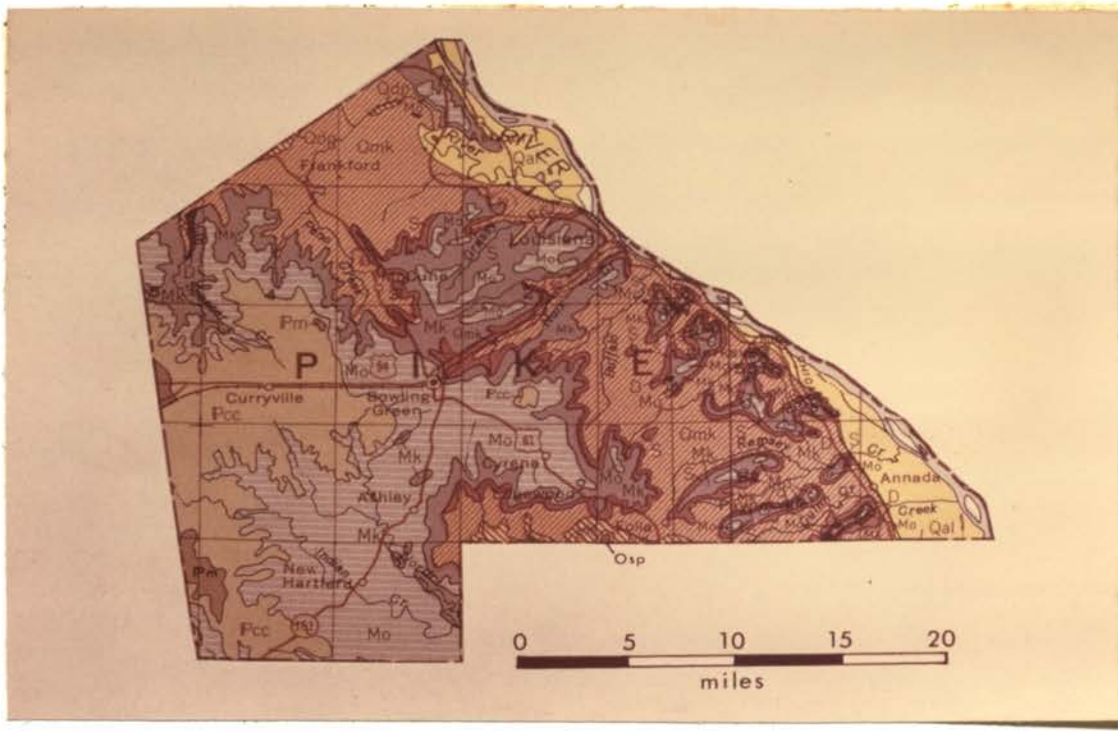
A. Introduction

Pike County is located in northeastern Missouri. It occupies an area of 620 square miles and is bounded on the east by the Mississippi River, on the north by Ralls County, on the west by Ralls and Audrain counties, and on the south by Lincoln and Montgomery counties (Fig. 5).

R. R. Rowley (1907) divided Pike County into two physiographic provinces, an eastern hilly region, dissected by small tributaries of the Mississippi River, and a western, level prairie region. The Maquoketa Formation forms a gentle rolling topography and many of the knobs in the eastern hilly region are underlain by this formation. Alluvial plains of the Mississippi River cover parts of the eastern region.

B. General Stratigraphy

Within Pike County, sixteen stratigraphic units are exposed. Fourteen of these are pre-Pennsylvanian formations and two are undifferentiated Pennsylvanian groups. All are sedimentary and they range in age from Middle Ordovician, Champlainian Series (St. Peter Sandstone) to Middle Pennsylvanian, Desmoinesian Series (Marmaton Group). Four pre-Kimmswick Ordovician formations (St. Peter, Joachim, Plattin, and Decorah) are exposed in Pike County. They crop out because they are on or near the crest of the Lincoln Fold. Their outcrop areas are small and the maximum



LEGEND

ORDOVICIAN

Osp--St. Peter Fm.
Ojd--Joachim Fm.
Odp--Decorah and Plattin Fms.
Omk--Maquoketa and Kimmswick Fms.

SILURIAN

S--Edgewood Fm.

DEVONIAN

D--Callaway Fm.

MISSISSIPPIAN

Mk:
Grassy Creek Fm.*
Saverton Fm.*
Louisiana Fm.*
Hannibal Fm.
Chouteau Fm.

Mo--Burlington Fm.

PENNSYLVANIAN

IPcc--Cherokee Gp. Cabaniss Subgp.
IPm --Marmaton Gp.

PLEISTOCENE

Qal--Alluvium

*Uncertain Miss.-Dev.

Fig. 6. Geologic map of Pike County, Missouri. (After McCracken, 1961.)

SYSTEM	FORMATION	LITHOLOGY	FEET	DESCRIPTION
PLEIST.			0–100	Loess, glacial drift and recent alluvium
PENN.	MARMATON GP.		0–20	Cyclic ls.–sh., with some coal
	CHEROKEE GP.		0–20	Cyclic ss.–sh. with some coal
MISS.	BURLINGTON		0–60	Thin to massive bedded coarse gn. cherty ls.
	CHOUTEAU		0–25	Thin-bedded fine-gn. ls.
	HANNIBAL		90-120	Silty, sandy bluish sh. with upper ss.
MISS.–DEV.	LOUISIANA		0–40	Thin irregularly bedded fine-gn. ls.
	SAVERTON		1–14	Silty olive-gray sh.
	GRASSY CREEK		1–44	Brown sh. with basal congl.
DEV.	CALLAWAY		0–20?	Massive-bedded medium-gn. ls.
SIL.	EDGEWOOD		0–40	Fine-gn. dolomite with minor ls.
ORD.	MAQUOKETA		80-125	Lower cyclic ls.-sh., upper olive-gray sh.
	KIMMSWICK		85–145	Thin to massive-bedded fine to coarse-gn. ls.
	DECORAH		0–25?	Fine-gn. ls. with clay partings
	PLATTIN		0–80	Thin-bedded, fine-gn. ls.
	JOACHIM		0–65	Sandy fine-gn. dolomite
eck	ST PETER		0–15?	Medium-gn. pure quartz ss.

FIG. 7. GENERALIZED STATIGRAPHIC SECTION FOR PIKE CO., MO. (COMPILED FROM LASWELL, 1957, MARTIN *et al.*, 1961, McCRACKEN, 1961, McQUEEN *et al.*, 1941).

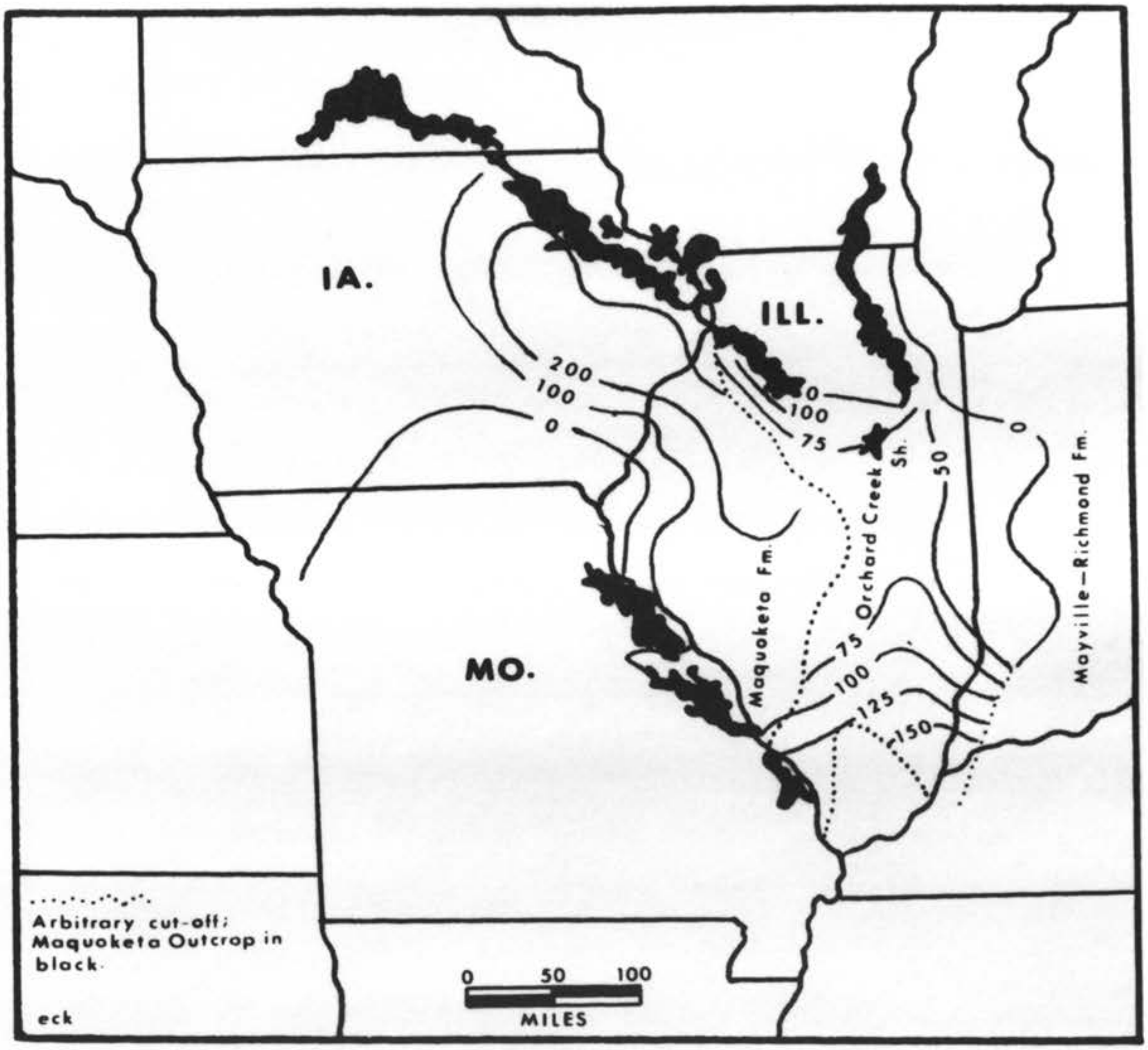


FIG.8. ISOPACH MAP OF THE MAQUOKETA FORMATION AND LITHOLOGIC EQUIVALENTS (AFTER SLOSS, DAPPLES, AND KRUMBEIN, 1960).

thicknesses shown on the generalized stratigraphic section (Fig. 7) are very approximate. These formations have been included in Fig. 7 for the sake of completeness. Undifferentiated Pleistocene loess and drift mantle much of the county.

Ordovician and Mississippian rocks comprise most of the exposed Pike County section. Pennsylvanian, Silurian, and Devonian rocks occur in relatively smaller areas. The dominant lithology is limestone, then shale, with lesser amounts of siltstone, sandstone, chert, conglomerate, and coal. The type section for three formations, Edgewood (Silurian), Grassy Creek (Devonian-Mississippian), and Louisiana (Devonian-Mississippian) are located in Pike County. Geologic investigations have centered around these diverse lithologies in Pike County for more than seventy-five years.

More detailed aspects of the stratigraphy and paleontology of the rocks in Pike County are discussed in the Kansas Geological Society field guide Northwestern Missouri and West-Central Illinois (1961) and in works by Laswell (1957), Rowley (1907), McQueen (1941) and Buehler (1937). A summary of the stratigraphy of Pike County is presented in a generalized stratigraphic section (Fig. 7) and a geologic map (Fig. 6).

C. Maquoketa Stratigraphy

The Maquoketa Formation is extensively exposed at a number of separated localities in the Upper Mississippi

Valley (Fig. 8). Gutstadt (1958a, p. 513-514) states in a regional study:

> "The Upper Ordovician Maquoketa shale is exposed in fragmentary outcrops in two belts: in northwestern Illinois, northern Iowa, southwestern Wisconsin, and southeastern Minnesota; and along the Mississippi River in Missouri and southern Illinois. Another belt of equivalent rocks crop out in eastern Wisconsin, but...it is mostly covered by glacial drift...The outcrop belts are associated with mild post-Ordovician structural highs."

Maquoketa rocks have been correlated with the Upper Ordovician rocks in Michigan (Ladd, 1928, Ostrom, 1967, and Bromberger, 1968), with the Orchard Creek Shale of western Illinois (DuBois, 1945, and Gutstadt, 1958a), and with the type Cincinnatian Series (Eden and Maysville Stages) in Ohio by numerous authors.

Some workers (Savage and Ross, 1916, Ladd, 1928, Twenhofel et al., 1954, and Brown and Whitlow, 1960) have considered the Neda "formation" (a thin, discontinuous red hematitic oolitic shale) as part of the very uppermost Maquoketa. The Neda has been referred to as the "Clinton Formation" in some older papers (Howell, 1916). The Neda is restricted to local occurrences, but beds of the same lithology in a similar stratigraphic position have been recognized in isolated outcrops in Iowa, Illinois, Kansas, Missouri, and Wisconsin. Although no general agreement exists as to the age or exact stratigraphic position of the Neda, its presence is believed to indicate an erosional unconformity at the top of the Maquoketa (Ladd, 1928, Agnew, 1955). Brown and Whitlow (1960) believed that the Neda is only found where the Maquoketa Formation has a maximum thickness.

The Thebes Formation of southeastern Missouri and adjacent Illinois is a thin (5 to 25 feet) quartzose sandstone with varying amounts of silt. It has been considered by some to be a southern sandy facies of the lower Maquoketa (Rowley, 1907, Martin et al., 1961, Gutstadt, 1958a, and Bromberger, 1968).

In 1870, when White named the Maquoketa as a new formation in northeastern Iowa, he described the lithology as follows:

> "...largely composed of bluish and brownish shales which weather into a tenaceous clay upon the surface, and the soil derived from it is usually stiff and clayey. The shales are sometimes slightly arenaceous, and sometimes calcareous bands compose a considerable part of its bulk." (White, 1870, p. 180.)

White's original description of the lithologies remains a valid generalization for the Maquoketa in Iowa, Illinois, Missouri and for equivalent rocks in adjacent states.

An examination of described sections and well logs for the Iowa-Illinois-Missouri area discloses a great variability of Maquoketa lithologies. Certain generalizations about Maquoketa lithologies are suggested from this data. The Maquoketa is more calcareous in the lower half of the section and more argillaceous in the upper half, with some lenses of silt or sand.

In Iowa and Illinois the Maquoketa Formation unconformably overlies the Galena Limestone (Champlainian), whereas in Missouri, the same relationship exists with the Kimmswick Formation (Champlainian-Galena equivalent). Both the Galena and the Kimmswick are massive carbonates. According to Ladd (1928) the erosional unconformity between the Galena (or Kimmswick) becomes less pronounced northward from Missouri. A thin horizon of phosphatic pellets and diminutive pyritized and phosphatized fossils occurs within several feet above this erosional contact. Ladd (1928) coined the term "depauperate zone" in describing this horizon. This basal phosphatic horizon has been used by a number of later workers as a datum plane for correlating the Maquoketa. Recently, Bromberger (1965, 1968) has pointed out that the phosphate in the Maquoketa is not restricted to the so-called "depauperate zone," but can be found in a number of other horizons in the formation. Gutstadt (1958a) has found "depauperate" fossils and phosphatic pellets in several horizons in the type Cincinnatian Series rocks in the Indiana and Ohio area. Based on scanty paleontological evidence, the Maquoketa has been assigned to the Cincinnatian Series, Richmondian Stage. Gutstadt (1958a) believed that insufficient work has been done to consider a Maquoketa correlation with the type Cincinnatian well established. However, Templeton and Willman (1963, p. 27) believed that the Maquoketa represents all of the Upper Ordovician (Cincinnatian Series). The Maquoketa correlation and age problem will remain unsolved until more detailed studies are made on Upper Ordovician faunas and physical stratigraphy.

In Missouri, the Maquoketa is exposed in most of the counties which border on the Mississippi River from Scott County, in southeastern Missouri, to Marion County, in northeastern Missouri. It thickens to the north, ranging in thickness from 10 to 60 feet in southeastern Missouri and 30 to 140 feet in northwestern Missouri (Martin et al., 1961). Parker et al. (1959) gave a maximum thickness of 320 feet in the type area of Iowa. The Maquoketa also thickens to the east into the Illinois Basin (Fig. 8). The Maquoketa is recorded in the subsurface north of Marion County in northeastern Missouri and in the Forest City Basin of northwestern Missouri. In the Forest City Basin, it ranges in thickness from 20 to 70 feet. Koenig (1966) attributes this incomplete section in northwestern Missouri to extensive erosion in Silurian or Devonian time.

In Missouri, the most complete and best exposed Maquoketa outcrops are in Pike County. Johnson (1939, p. 123) gave an average thickness of 119 feet for the Maquoketa in this county. Rowley (1907, p. 16-17), one of the first persons to study the Maquoketa in Pike County, described it as follows:

> "The shale is light blue in color and sandy in places on Sulphur Creek. It is usually rather argillaceous and composed of softer shales separated by hard beds from an inch to six inches in thickness. In perpendicular bluffs, these alternate beds of softer and harder material look much like artificial walls. Of all the shales in the county, the Hudson Valley [Maquoketa] is the most durable, resisting longer

> the action of the weather. Wherever found in the county the flags are persistent and are the chief characteristic of the formation...There are very few fossils anywhere in this formation and it would be difficult to separate it into horizons on paleontologic ground."

The distribution in Missouri of thin calcareous units, called "limestone flags" by most workers, is quite variable. Krey (1924) believed that the amount of calcareous material increases to the north from Lincoln County, Missouri. In Pike County, the thin limestone beds are restricted to the lower 50 to 70 feet of the formation, with the aggregate thickness of the shale generally exceeding that of the limestone. In northeastern Missouri the Maquoketa lies unconformably upon the Kimmswick Formation and it is overlain unconformably either by the Lower Silurian Edgewood Formation or more rarely by the Middle Devonian Callaway Formation. In areas where the Edgewood and Callaway formations have been removed by erosion, the Grassy Creek Formation (Devonian-Mississippian) appears as a thin (10 to 15 feet) black shale with a basal phosphatic conglomerate, unconformably overlying the Maquoketa. The phosphatic conglomerate is absent where the Grassy Creek Formation overlies rocks younger than the Maquoketa. Laswell (1957) has suggested that this phosphatic conglomerate is reworked Maquoketa. Several authors, notably Keyes (1913), Branson and Mehl (1933), and Johnson (1939) have overlooked this unconformity and placed these black shales in the Maquoketa. The age of these black shales has recently been substantiated as Devonian by the presence of the spore-like Tasmanites (Mehl and Shaffer, 1961).

Johnson (1939) divided the Maquoketa in Pike County into three members, based on lithology and paleontology, and attempted a correlation with Calvin's (1905) original members in the type area. In this correlation Johnson erroneously included the basal black shales of the Grassy Creek as a new member of the Maquoketa in Missouri. Johnson found a trilobite-graptolite zone (mainly Isotelus iowensis and Diplograptus peosta) about 10 feet above the base of the formation, which corresponds to the Isotelus zone of the Elgin member in Iowa. The Elgin Member of Iowa and the Lower Maquoketa in Missouri are both composed of alternating thin beds of limestone and shale. The basal phosphatic "depauperate zone" is found in both areas. Johnson recognized that the upper half of the Maquoketa in Pike County was similar to the Clermont Member of Iowa. Both are blue-green shales and their general lack of limestone beds and calcareous fossils is distinctive. Johnson's correlation is reproduced with minor modifications in Fig. 9.

D. Structure

The Lincoln Fold, Cap au Gres Fault, Forest City Basin, and the Illinois Basin comprise the major structural features of the Northern Missouri-Central Illinois region (Fig. 10).

The Lincoln Fold is a northwest-southeast trending

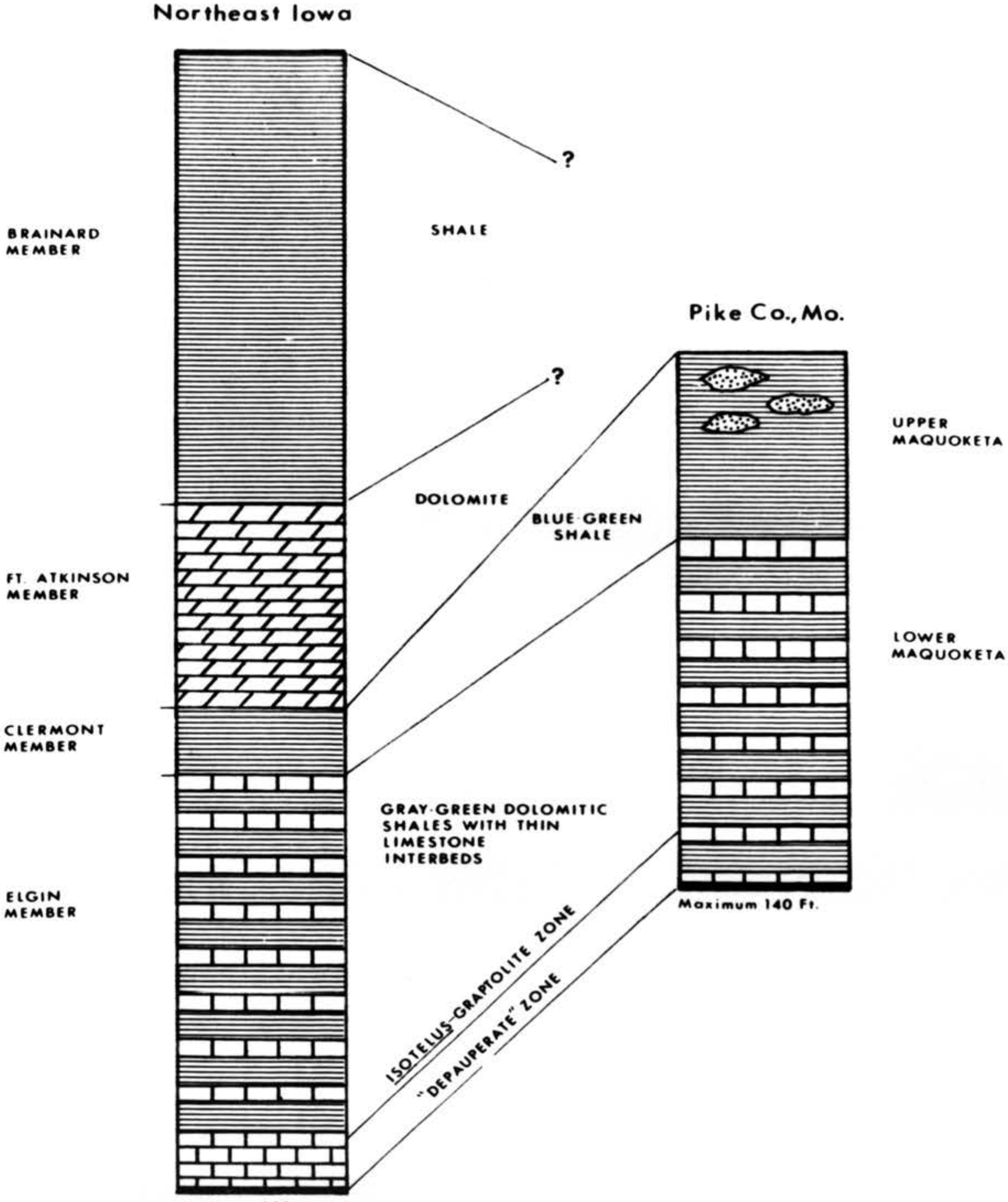


FIG. 9. H.N. JOHNSON'S (1939) CORRELATION OF THE MAQUOKETA IN IOWA AND MISSOURI—WITH MODIFICATIONS AFTER MARTIN et al. (1961) AND PARKER et al. (1959).

anticlinal structure. It can be traced for approximately 165 miles north from Winfield, Missouri (Lincoln County), where it is truncated by the Cape au Gres Fault, to southern Iowa where it plunges into the subsurface. This fold has been of major importance in the tectonic history in the central Mid-continent area. The Illinois and Forest City Basins were separated by the Lincoln Fold (Fig. 10). Koenig (1961, p. 65) states, "It [the Lincoln Fold] also, with the Mississippi and Wisconsin Arches, forms a discontinuous arcuate succession of highs between the Wisconsin uplift to the north and the Ozark uplift to the South."

Potter (1872, p. 221), who was one of the first workers to mention the fold but did not name it, described it as an anticlinal arch with a "general direction of W 30°N" (*sic*) in northeastern Missouri. Rowley (1907) studied this structure in detail in Pike County and applied the name "Trenton Backbone." Krey (1924) in a regional study first applied the term Lincoln Fold to this structure. He recognized that the Lincoln Fold was not a simple symmetrical anticline, but an uplifted linear area with many minor structures superimposed. McQueen *et al*. (1941, p. 100) have given perhaps the best description of this structure. They state as follows:

> "The Lincoln Fold may be described as an asymmetrical anticline with a general axial strike of N 45°W. The southwest side of the fold is marked by steep dips, and in some localities faulting. The northeast flank of the fold is marked by comparatively gentle dips and faulting is not known to occur on that flank."

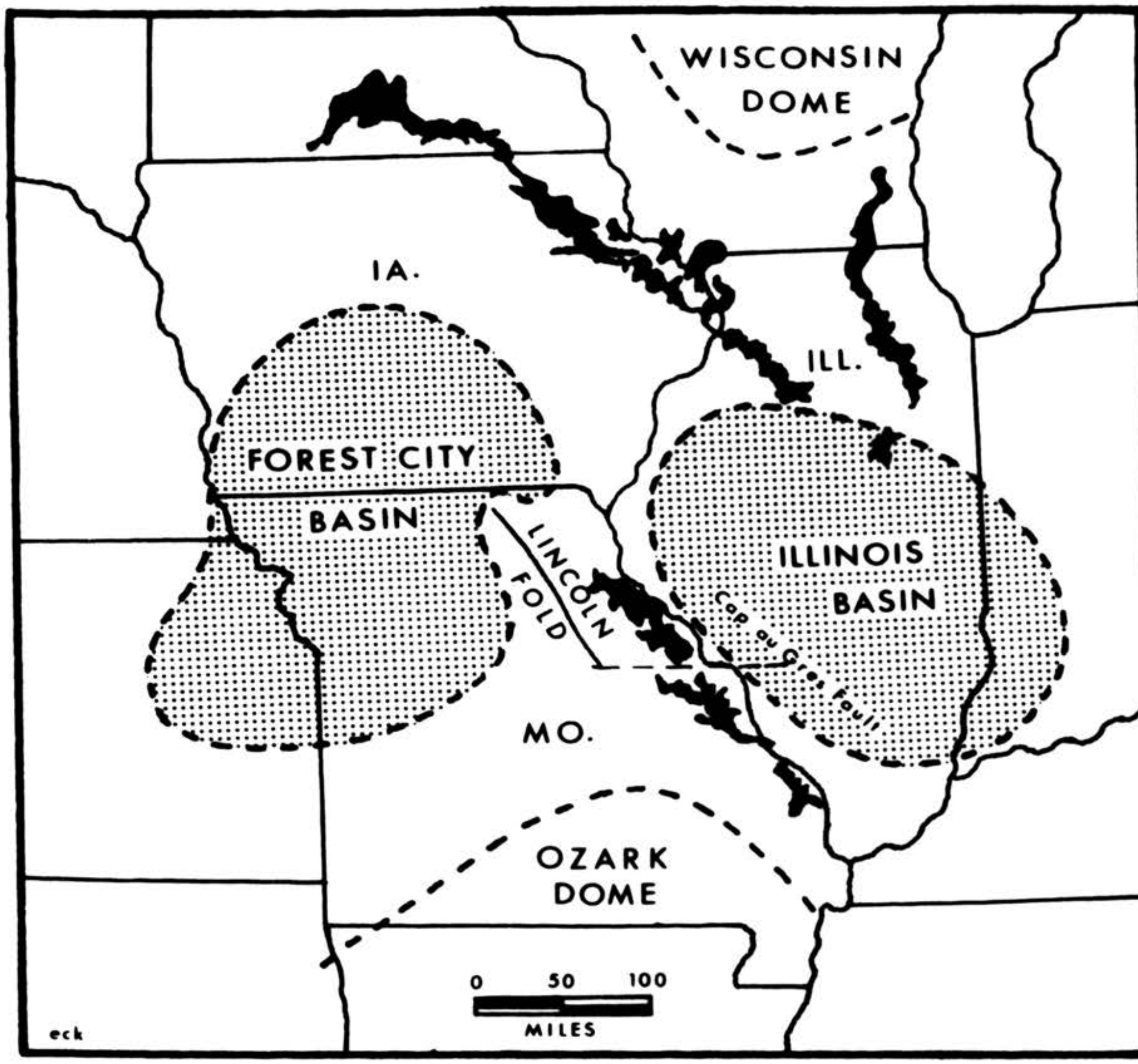


FIG.10. GENERALIZED LOWER PALEOZOIC TECTONIC SETTING WITH REGIONAL MAQUOKETA OUTCROP PATTERN (AFTER GUTSTADT, 1958, KOENIG, 1961, AND SNYDER, 1968).

Based on subsurface data, McQueen et al. (1941) gave the maximum structural relief of the fold as 100 feet. They also reported high angle normal faulting with small slightly overturned blocks associated with the fold in faulted zones. In the Bowling Green Quadrangle (Pike County), Laswell (1957) measured maximum dips of 5°30' on the eastern flank of the fold with maximum dips of 10°30' on the western flank. This substantiates the asymmetrical nature of the fold in Pike County. Laswell also cited examples of more localized doming and folding in Pike County.

The Cap au Gres Fault, trending east-west, is observed only in the southwestern part of Pike County. It is mentioned only because it truncates the southern end of the Lincoln Fold. Magnetics indicate this fault may extend into the Precambrian basement, and it is probably related to both the Lincoln Fold and the Ozark Dome. Magnetics further suggest that there is a vertical displacement of over 1000 feet on this fault with the upthrown side to the north. Based on geophysical, structural, and stratigraphic information, Cole (1961) has suggested that the Cap au Gres Fault is a left lateral fault with a movement of approximately 30 miles, offsetting the Lincoln Fold of Missouri and the Dupo-Waterloo anticline of eastern Illinois.

E. Tectonic History

Much of the early Paleozoic history of the central Mid-continent is obscured because the Paleozoic sediments are covered by glacial drift and alluvium, and further hidden due to a lack of subsurface data. Snyder (1968) believes that slow epeirogenic movements beginning at the end of Late Cambrian time led to the formation of basins and arches in the Mid-continent region. He considered the transition from a positive area during Late Precambrian to a slowly subsiding negative area in the Paleozoic as a major tectonic change of the mid-continent. The reasons for this reversal are not clear. Snyder lists the following events that accompanied this transition:

> "1) Slow subsidence of the entire mid-continent
> 2) development of the major arches and basins with intermittent subsidence and uplift
> 3) fragmentation of the region through subdivision of the basins by short-lived or minor arches
> 4) oscillation leading to cyclic deposition and
> 5) final uplift and stability."
> (Snyder, 1968, p. 71.)

The appearance of the Cincinnati Arch, Ozark Dome and Wisconsin Dome led to a basin-arch relationship. A number of smaller arches and basins were intermittently active. Snyder (1968, p. 71) has suggested that many of these smaller structures "were short-lived and influenced the sedimentary record for a brief time." The development of the Illinois and Forest City Basins was initiated in Late Cambrian time. By the end of Pennsylvanian time the Illinois Basin had accumulated over 12,000 feet of sediments while the Forest City Basin had accumulated roughly 4,000 feet of sediments. Gutstadt (1958a) believed that the Illinois Basin, as defined, did not exist until post-Ordovician time. He based his argument on thickness and facies relationships. Most of the above described structural elements had ceased to be active by the end of the Paleozoic.

Koenig (1961, p. 75) believed that the inception of the Lincoln Fold was "related to the initial uplift of the Ozark Dome in post-Canadian time," and that "...prior to this time, a thick succession of upper Cambrian and lower Ordovician sediments had been deposited in a deep syncline that extended north from the central Ozark region."

Doming is known to have occurred in Pike County at the end of Kimmswick time and prior to the deposition of the Maquoketa (McQueen _et al_., 1941). Erwin Pennington (personal communication, 1968) has shown that structure contours on the top of the Kimmswick Formation exhibit a relief of over 30 feet in Pike County (possibly due to doming or pre-Maquoketa erosion). Movement during late Silurian or early Devonian time initiated the development of the Lincoln Fold as a unique structural feature. "Subsequent stages of the fold's development involved recurrent episodes of erosion and deposition through Devonian and Mississippian time" (Koenig, 1960, p. 75). The fold probably reached its maximum structural development by the close of Mississippian time. Due to the sparceness of Pennsylvanian rocks exposed in the fold area, little is known about tectonics during Pennsylvanian time. Evidence does suggest some gentle Pennsylvanian folding, and it is thought that the Cap au Gres Fault transected the Lincoln

Fold at the end of Mississippian or early in Pennsylvanian time.

IV. Petrography

A. Introduction and Procedure

A detailed petrographic study was made in order that it might reveal the genesis of the Maquoketa cyclic sequence. In this investigation six distinct Maquoketa lithologies have been recognized:

1) phosphatic biosparite
2) phosphorite
3) micrite-microsparite
4) dolomitic shale
5) dolomitic marlstone
6) dolomitic quartz siltstone

Petrographic interpretations are based primarily on a study of approximately 125 thin sections. Megascopic textural relationships were studied with the binocular microscope on polished slabs and split cores. The Geological Society of America Rock Color Chart (Goddard et al., 1948) was used in applying Munsell color designations to hand specimens. Stained acetate peels (Lane, 1963; Frank, 1965) were extensively used on polished slabs. Alizarin-red S stain differentiated calcite from dolomite. Ferroan carbonates were distinguished from non-ferroan carbonates by potassium ferricyanide stain.

Due to the extreme friability of weathered materials, the shale thin sections made in this study were solely from the cores and outcrop at the Dundee Quarry. All shales and most of the marlstones from the cores were too friable to thin-section without impregnation. The shales also proved to be reactive to water, splitting and flaking on wetting.

Cores had to be cut dry using a hacksaw, as even diamond saw coolant caused splitting and spalling of the shaly units. Two impregnation methods were used: a methyl methacrylate "lucite" procedure (Bell, 1939) and a method employing "Scotchcast electrical resin" (Dobell and Day, 1966). Both procedures proved to be satisfactory, but the "Scotchcast" method was faster and more convenient. Supplementary x-ray analyses were performed on a General Electric XRD-5 diffractometer.

B. Phosphatic "Limestones"

Two distinct phosphate-rich rocks, both from the Dundee Quarry, were recognized in this study. Both occur at or near the base of the formation. One, a phosphatic biosparite, is quite local, restricted to certain parts of the quarry. The other, a "calcite-cemented phosphorite" of the so-called "depauperate zone," is quite thin but is found over a considerable area at approximately the same stratigraphic horizon.

At the Dundee Quarry, a thin phosphatic limestone directly below the "depauperate zone" was located on outcrop and in cores. The limestone is massive and dark brown (10 YR 3/2) in color with visible phosphate pebbles up to 1.0 cm. in diameter. Large orthocone cephalopods, up to 1 foot in length and tentatively identified as _Endoceras_ sp. (Bromberger, 1968), were also rather common. Thickness of this unit varies from 0.5-1.5 feet. A well-defined erosional unconformity exists between this unit and the

Fig. 11. Biosparite from the lowermost Maquoketa exhibiting relatively abundant trilobite and echinoderm allochems. Note clear euhedral dolomite crystals. Black areas are authigenic pyrite and sphalerite. Sample from outcrop at the Dundee Quarry, X28.

Fig. 12. Thin section of phosphorite from the so-called "depauperate zone." Darker colored pellets are phosphate. Most are structureless and many exhibit replacement "dust rims" of syngenetic pyrite. Cement is a coarse-grained calcite spar. (CDH # 63, L-1), X28.

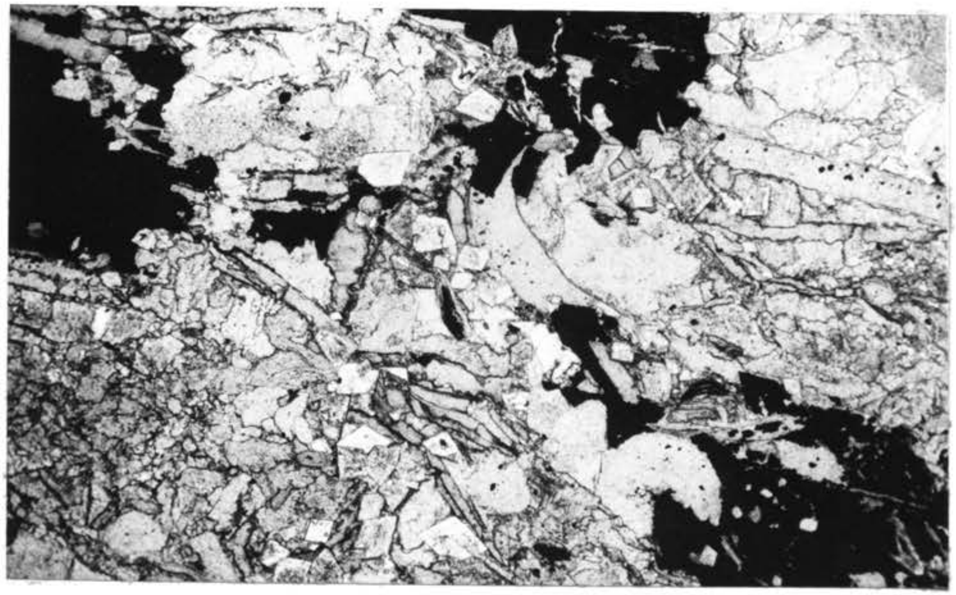


Fig. 11.

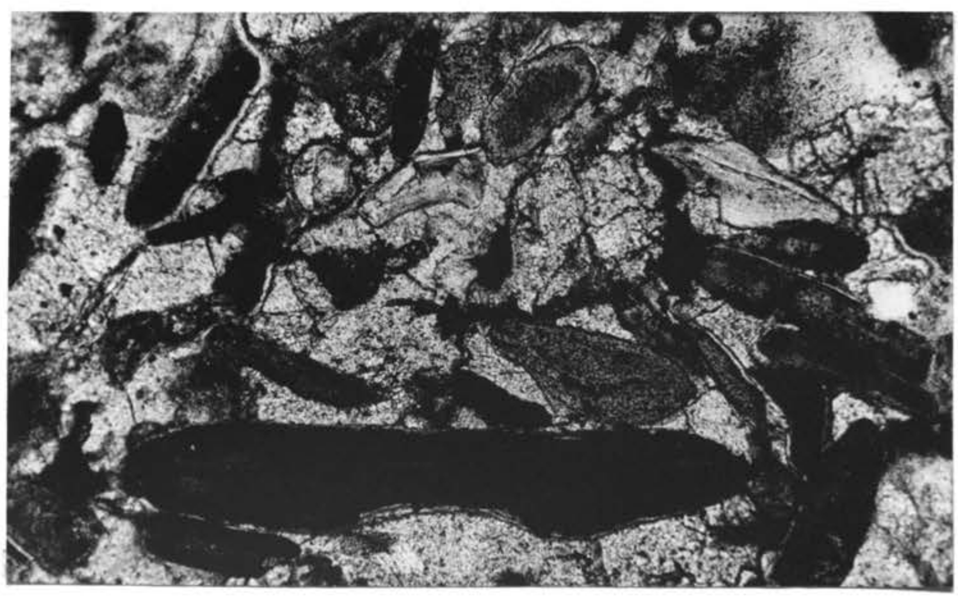


Fig. 12.

Fig. 13. Calcite spar cemented phosphorite from the so-called "depauperate zone." Interior of gastropod in center of photo is filled with fine-grained phosphate and its shell replaced by ferroan calcite. (CDH # 76, L-2), X80.

Fig. 14. Echinoderm stereome structure partially replaced by phosphate. Specimen from the so-called "depauperate zone." (CDH # 76, L-1), X80.

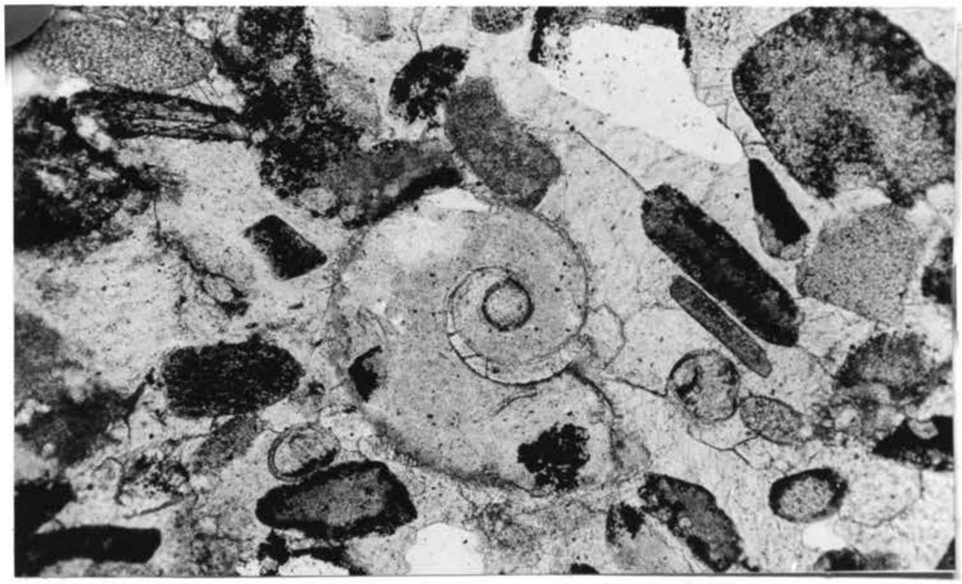


Fig. 13.

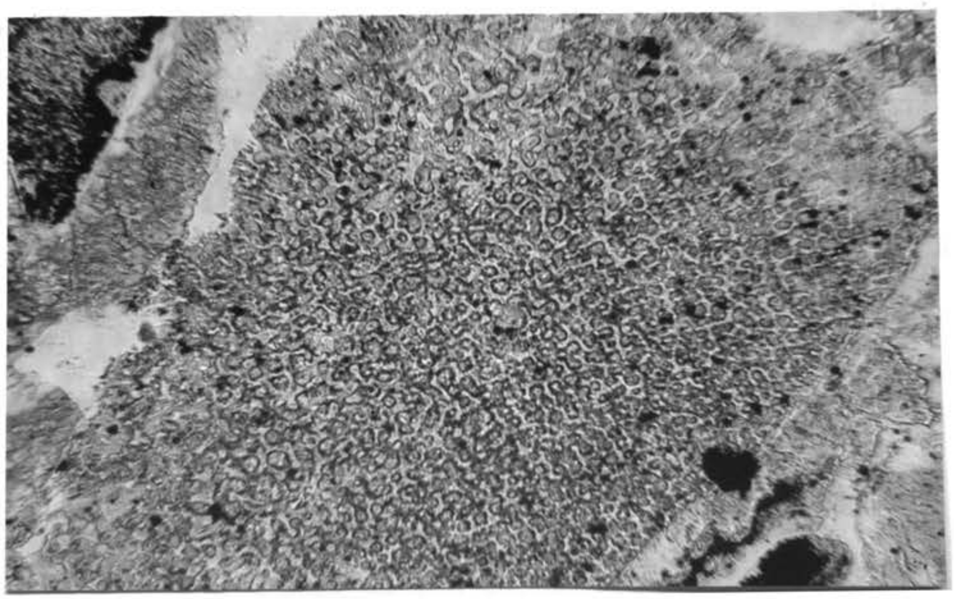


Fig. 14.

underlying Kimmswick Formation. This limestone is quite local, being absent in some parts of the Dundee Quarry (Erwin Pennington, personal communications, 1968). Problems exist in assigning this limestone to a formal stratigraphic unit. In Missouri the base of the "depauperate zone" is usually considered to mark the basal contact of the Maquoketa. Bromberger (1968) in a regional analysis of the phosphate-bearing horizons of the Maquoketa assigned the unit in question to the basal Maquoketa. He based his decision on the following: 1) lack of any phosphate in the underlying Upper Kimmswick, 2) presence of an erosional unconformity at the base of the phosphatic limestone, and 3) a description of a similar unit assigned to the Maquoketa by McQueen et al. (1941). McQueen et al. (1941, p. 106) described this similar unit as follows:

> "In northwestern Pike county, west of Frankfort, Mo., the Maquoketa includes a coarsely granular impure reddish-brown limestone which contains the depauperate fauna that is locally characteristic of the formation."

Although McQueen et al. (1941) did not give a thickness, it seems likely that they refer to the same unit or an equivalent of the one present in the Dundee Quarry since the lithology of the normal "depauperate zone" would not fit their description.

Thin section analysis of this rock type (Fig. 11) indicates that it would be best categorized as a "poorly washed fossiliferous phosphatic biosparite" (terminology after Folk, 1962). Allochems include phosphatic pellets and fossil fragments. The principal allochems are elongated calcareous fossil fragments, 1 to 3 mm. long, that probably represent trilobites. Echinoderm fragments are also common and some exhibit syntaxial spar overgrowths. A few gastropods were also observed. Calcareous fossils comprise between 40 and 60 percent of this lithology. All calcareous fossils show some abrasion, and they are moderately well-sorted. Internal structure of most fossils has been obliterated by recrystallization. The rock contains between 8 and 15 percent light yellow, structureless, isotropic microcrystalline phosphate pellets which average 0.8 mm. in diameter. A few laminated phosphatic fossil fragments probably representing trilobites are also present. The rock contains rare fine sand-size grains of detrital quartz.

Some areas having a high concentration of fossils contain original unwinnowed micrite matrix in protected areas. Micrite content never exceeds 20 percent of the rock. Also 5 to 10 percent of a clay mineral, probably illite, is distributed in irregular patches and concentrated along microstylolites. According to Folk (1962), this "poorly washed" micrite and clay is indicative of moderate or sporadic current action in the depositional environment. However, fragmented and abraded fossil fragments would seem to indicate a somewhat higher energy level.

Cementation has been accomplished in these rocks by the precipitation of coarse polyhedral spar crystals up to 2.0 mm. in diameter, which exhibit regular interlocking grain boundaries. Pyrite and sphalerite are the next most common authigenic minerals, constituting 10 to 15 percent of the rock. Pyrite is probably syngenetic, whereas cross-cutting relationships indicate that sphalerite is rather late in the diagenetic sequence. Average grain size of these sulfides is 0.05 mm., although masses several centimeters in diameter were seen on the outcrop. Approximately 10 percent of the rock is composed of clear euhedral dolomite crystals, averaging 0.5 mm. in diameter. These crystals are not nucleated or zoned as the Maquoketa dolomites generally are. There is nothing to suggest that these crystals are not authigenic as is the rest of the Maquoketa dolomite. Small patches of ferroan calcite replacing calcite spar and fossil fragments were also observed.

The "depauperate zone" is thin, 1½ to 2 inches, at the Dundee Quarry. According to Johnson (1939), it never exceeds 3 inches in thickness. The principal constituent of the rocks of this zone is phosphatic pellets (Fig. 12). Point counts of 1000 points for 5 thin sections indicate a phosphate content of 63 percent for this unit. It is likely that this phosphate developed as a grain supported sediment. Authigenic minerals compose approximately 15 percent and spar accounts for no more than 30 percent of these rocks.

By definition, a limestone should contain at least 50 percent $CaCO_3$ by volume. If the samples studied are representative, the rocks of the "depauperate zone" would not be classed as limestones. The nomenclature of phosphate bearing rocks has not been rigorously defined (Pettijohn, 1957, p. 470). However, the term "calcite spar cemented phosphorite" is suggested for these rocks in this study.

The phosphate pellets are similar to those of the subjacent limestones, averaging 0.5 mm. in diameter. Phosphate pellets, 1.0 cm. in diameter, are not uncommon on the outcrop. These larger pellets usually have included calcareous fossil fragments, most of which have been replaced by ferroan calcite. A few isolated calcareous fossils are present, but many have been completely or partially replaced by phosphate (Fig. 13). The partial replacement of calcareous fossils by phosphate is particularly well demonstrated by echinoderm stereome structures (Fig. 14). It appears that minor phosphatization of spar cement adjacent to phosphate pellets may have taken place. An x-ray study by Bromberger (1968) showed that the Maquoketa phosphate is in the form of francolite (apatite with appreciable CO_2 and more than 1 percent fluorine).

Transportation of phosphate pellets and fossil fragments is clearly indicated by rounding and abrasion. These rocks are very cleanly washed with no clay or micrite matrix present, indicating fairly strong current action.

Cement in these rocks is a coarse spar with individual crystals up to 1.0 mm. in diameter. Pyrite occurs most frequently as small disseminated crystals in phosphate pellets and fragments and as "dust rims" on pellets and fossils. In some cases the "dust rims" are so thick that they have almost completely replaced the clast which they have coated. Rarely a small grain of sphalerite was noted. Minor silicification of clasts and cement has occurred.

Bromberger (1968) suggested that the Maquoketa phosphate was a primary chemical precipitate in areas of shallow water carbonate subaerial erosion. He thought that replacment of the carbonate substrata took place in areas of most intense phosphate precipitation. And "Following a period of phosphate accumulation the sites of precipitation acted as sources of phosphatic sediments for the remainder of the basin" (Bromberger, 1968, p. 191).

No new evidence concerning the origin of the Maquoketa phosphate can be added by this study. Until new evidence is discovered, Bromberger's (1968) hypothesis seems to be a plausible explanation of this occurrence.

C. Micrites-Microsparites

Thin limestone units, one half to sixteen inches in thickness, interbedded with somewhat thicker shale beds, were found at all the localities visited in this study. The limestone beds weather in relief rendering the limestone-shale cycles conspicuous on outcrops. On outcrops these limestones would be categorized as lithographic or sublithographic. The color of these rocks is medium gray (5 GY 5/1) on fresh surfaces. Weathered material is lighter in color with a somewhat bluish cast. Rocks break with a subconchoidal fracture. Normally hand specimens of these rocks show few structures or distinctive textures.

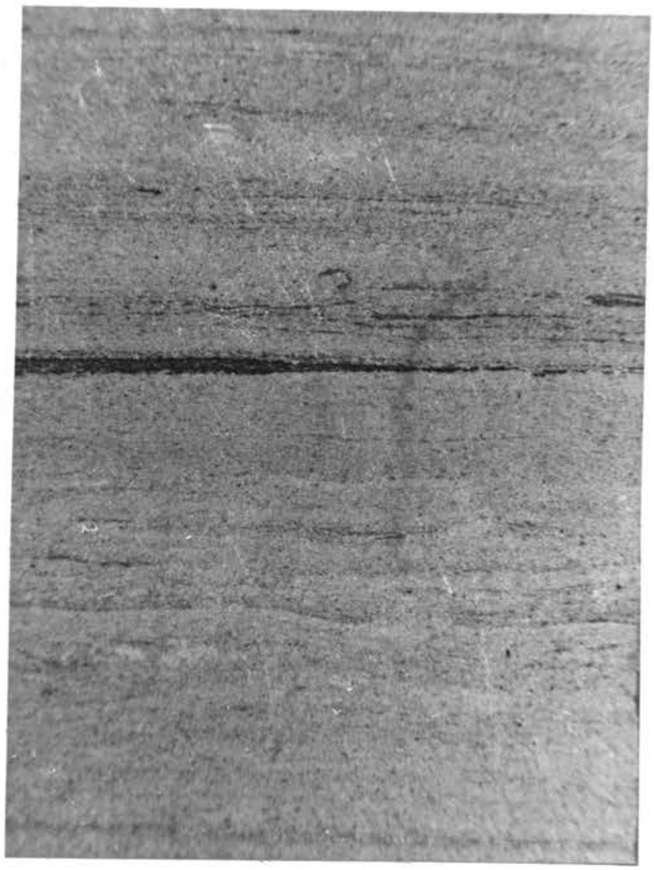


Fig. 15. Polished slab of micrite from a core from the Dundee Quarry. Limestone exhibits pyrite laminations. (PQ # 7, L-17) X3.

However, limestone blocks etched in dilute HCl acid revealed small scale (on the order of several millimeters) laminations parallel to the bedding. Limestone bedding planes vary from irregular and hummocky to extremely regular. Irregular bedding planes are more of an exception than are the regular bedding planes. Limestones commonly exhibit vertical fractures that appear as a rectangular pattern in plan view (Fig. 4). Rectangular limestone slabs several feet in length commonly accumulate in stream beds downstream from Maquoketa exposures. These weathered slabs are particularly common along Ramsey Creek in Pike County.

Probably the most conspicuous feature in thin section of the Maquoketa limestones is their fine grain size. Following Dunham's (1962) classification, the Maquoketa limestones would all be classed as lime mudstones. These rocks may also be assigned to four categories in Folk's (1962) classification. They are as follows:

1. dolomitic clayey micrite
2. dolomitic clayey fossiliferous micrite
3. dolomitic clayey microsparite
4. dolomitic clayey fossiliferous microsparite

A few rare examples of dolomitic clayey biomicrite were also encountered.

However, problems were encountered in applying Folk's (1962) classification to the Maquoketa limestones. Differentiation between micrite and microspar was difficult. Folk (1962) defined micrite as calcite grains 1 to 4 microns (0.001 to 0.004 mm.) in diameter. Micrite grains are generally equant and irregularly rounded, and subtranslucent with a faint brownish cast in thin section (Folk, 1965). Folk (1962, 1965) considered most of this material to represent a "normal" chemical or biochemical precipitate which is supposedly the slightly altered lithified equivalent of an original carbonate mud. However, much of this material, particularly that initially deposited as aragonite, has already suffered volumetrically important diagenetic changes during the inversion from aragonite to calcite. Microspar, a product of more extreme calcite recrystallization, occurs in grains 5 to 30 microns (0.005 to 0.030 mm.) in diameter (Folk, 1965). Microspar is usually very uniform in size, although gradations from micrite to microspar are common. Commonly individual grains are clearer than micrite grains. In microspar, clay and other impurities have commonly been removed and have been pushed into interstitial corners by recrystallization. Although Folk (1962, 1965) admitted that drawing the boundary between micrite and microspar on grain size alone is not very satisfactory, he believed that genetically these two calcite types were different. The grain size of the calcite in the Maquoketa limestones varies from 2 to 35 microns (0.002 to 0.035 mm.), with the average near 12 microns (0.012 mm.). The habit of these grains is usually equant. Following Folk's (1965) size criteria the majority of these calcite grains would be classified as microspar. However, most of these grains are subtranslucent with a brownish cast and they commonly contain numerous clay size inclusions. These observed characteristics are more

Fig. 16. Void filling by spar inside partially enrolled trilobite carapace. Matrix is micrite. Trilobite carapace has been replaced by calcite, but an indication of the original wall structure has been preserved as a slightly darker color zone. Sample from the outcrop at the Stark Nursery (ST) section. X28.

Fig. 17. Another view of the trilobite section that is illustrated above. Orientation of the photo is the same as field orientation. Micrite had fallen to the bottom of the cavity before void filling occurred, producing a geopetal structure. X 28.

Fig. 16.

Fig. 17.

commonly found in micrite grains. Concerning this type of calcite and its abundance in limestones, Folk (1968), in a later work, had the following comments:

> "These rocks would be classified as micrites...or biomicrites...were it not for the fact that the grains are still equidimensional and uniform in size but microcrystalline calcite is coarser than normal-average 5 to 15 microns instead of 2 to 5 microns. Because this relatively coarser material occupies large areas or makes up the entire specimen, it cannot have formed as a cement and probably represents aggrading recrystallization of a 'normal' microcrystalline ooze matrix." (Folk, 1968, p. 159.)

Also in the Maquoketa, larger calcite grains, approximately 15 microns and greater, normally exhibit features thought to be typical of microspar. Identification of this material was no problem. Problems were only encountered in the calcite with a smaller grain size between 5 and 15 microns. Not all workers think that a universal upper limit for carbonate muds exists at 4 microns as Folk (1962, 1965, 1968) believed. Leighton and Pendexter (1962) set the upper diameter of carbonate mud at 31 microns. Baars (1963) did not believe an exact size limitation for micrite was critical. In view of the fact that the 5 to 15 micron calcite grains in the Maquoketa exhibit characteristics thought to be indicative of a slightly altered original carbonate mud, they are referred to as "micrite," even though they exceed Folk's (1962) size limit. The term "microspar" is reserved for those larger calcite grains (greater than 15 microns) that exhibit

Fig. 18. Bryozoan, partially replaced by pyrite (black crust around edges and openings). Note that some internal structure of this fossil has been preserved. From the micrite at the Stark Nursery (ST) section. X80.

Fig. 19. Bryozoan colony with much internal structure preserved. Small areas of this colony (which do not show up well in this photo) have been selectively replaced by silica. From the micrite at the Stark Nursery (ST) section. X28.

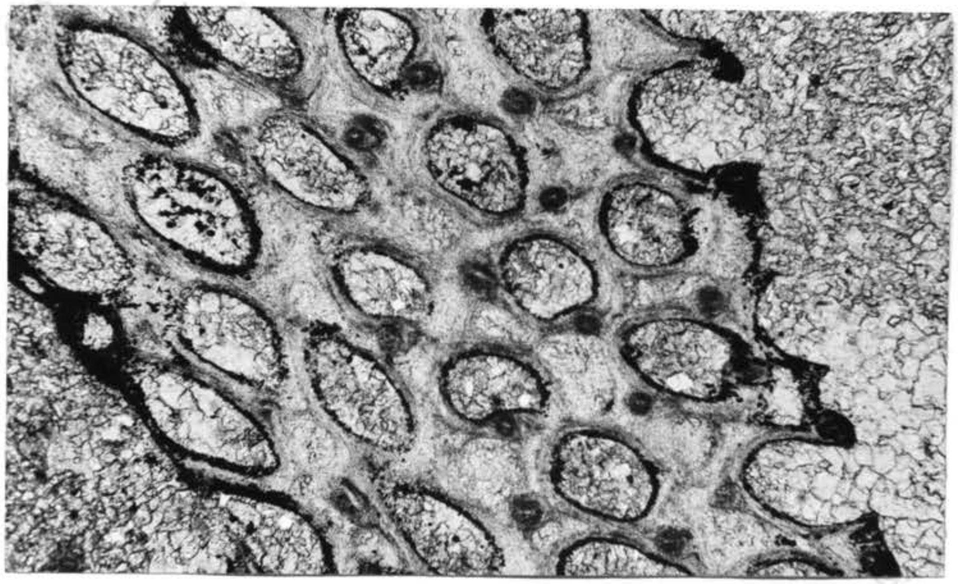


Fig. 18.

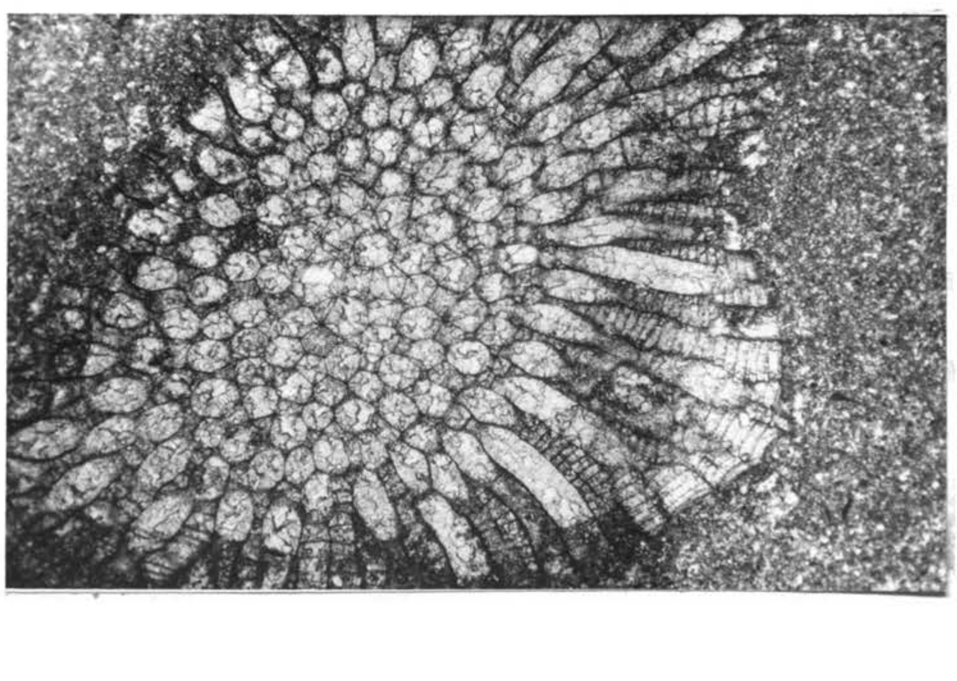


Fig. 19.

Fig. 20.

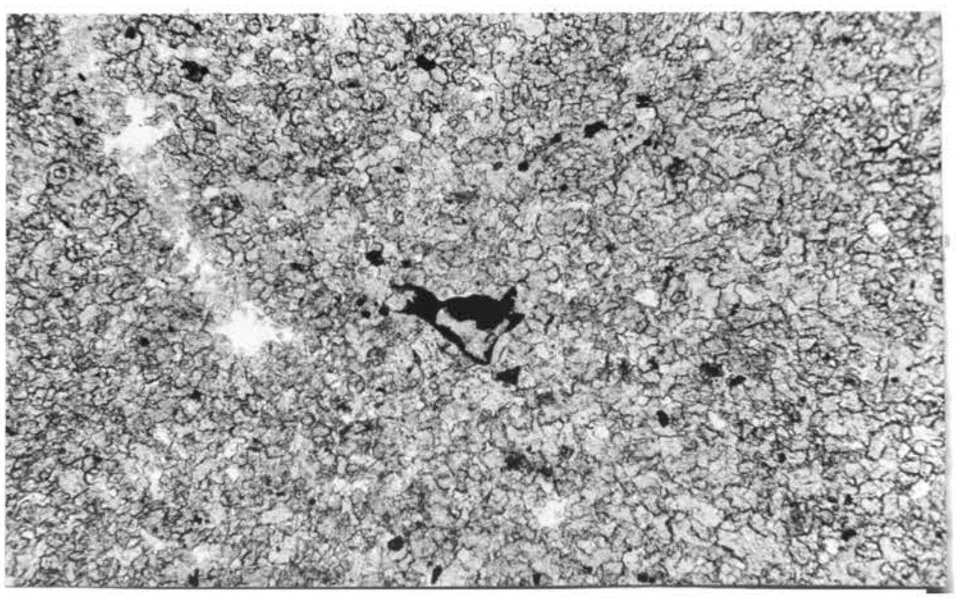


Fig. 21.

characteristics other than size that are indicative of recrystallization following criteria cited by Bathurst (1958) and Folk (1965). The micrite-microspar problem is considered in more detail in this paper in a later section covering diagenesis (Chapter VI).

Careful examination revealed a few allochemical constituents in all limestones thin-sectioned. In only a few rare examples did allochems exceed amounts greater than 10 percent of the total constituents in the rock. The allochems consisted primarily of trilobites (Fig. 16, Fig. 17), ostracodes (Fig. 22), brachiopods, pelecypods, and bryozoans (Fig. 18, Fig. 19). Most of these fossils were fragmented, but a few complete specimens of each type were found. The fossil fragments were small, the majority less than 0.01 mm., and many were unidentifiable. In the fragmented fossils the breaks were usually very sharp and angular showing little or no evidence of rounding or abrasion. This lack of abrasion may indicate that these allochems originated close to the site of deposition. A few thin sections included structures that have been interpreted as recrystallized calcareous sponge spicules (Fig. 25). Non-calcareous fossil fragments included graptolites and unidentified sapropel-like organic material (Fig. 21). Insoluble residues from the Stark Nursery (ST) section yielded somewhat "dehydrated" three-dimensional graptolites, conodonts, and sponge spicules. The sponge spicules, several millimeters in length, are a siliceous triaxon type consisting of six rays at right angles to one

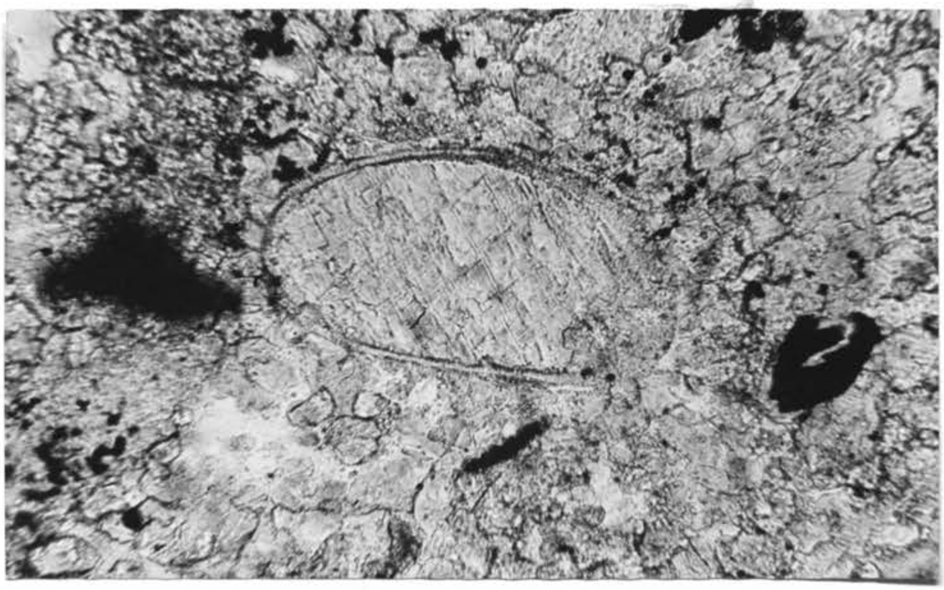


Fig. 22.

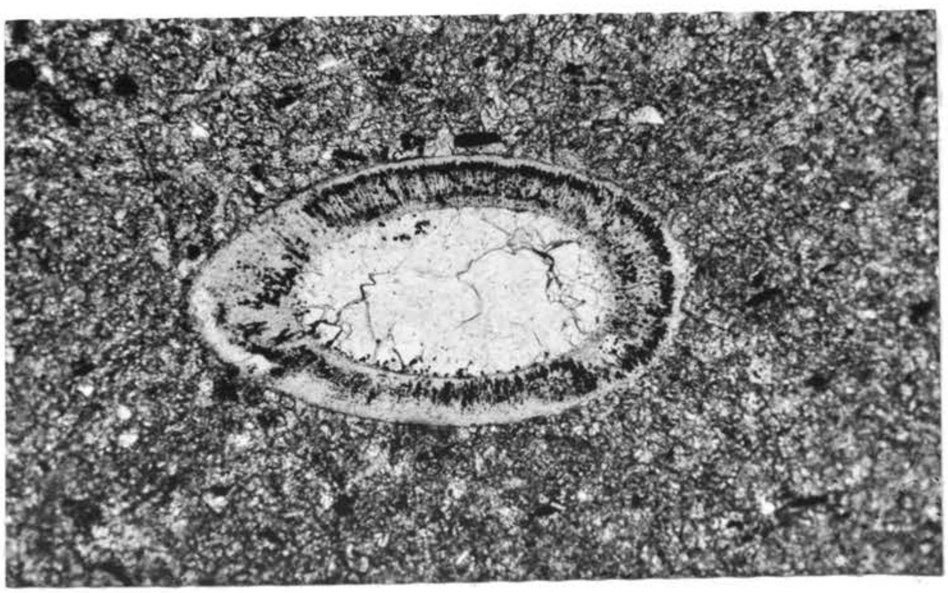


Fig. 23.

Fig. 24. This micrite specimen has an unusually high dolomite content, approximately 20 percent. Fossil fragment in the center of the photo has been cross-cut by dolomite rhombohedra. Note the sharp, angular broken edges on this fossil fragment. (ST-1), X80.

Fig. 25. The clear cross-shaped structures in this micrite are thought to be recrystallized calcareous sponge spicules. (ST-14), X29.

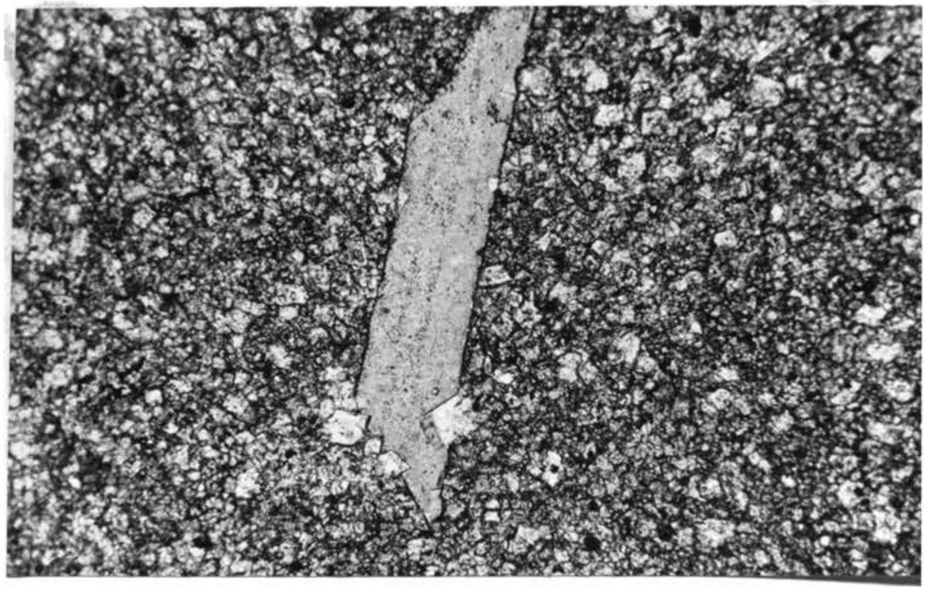


Fig. 24.

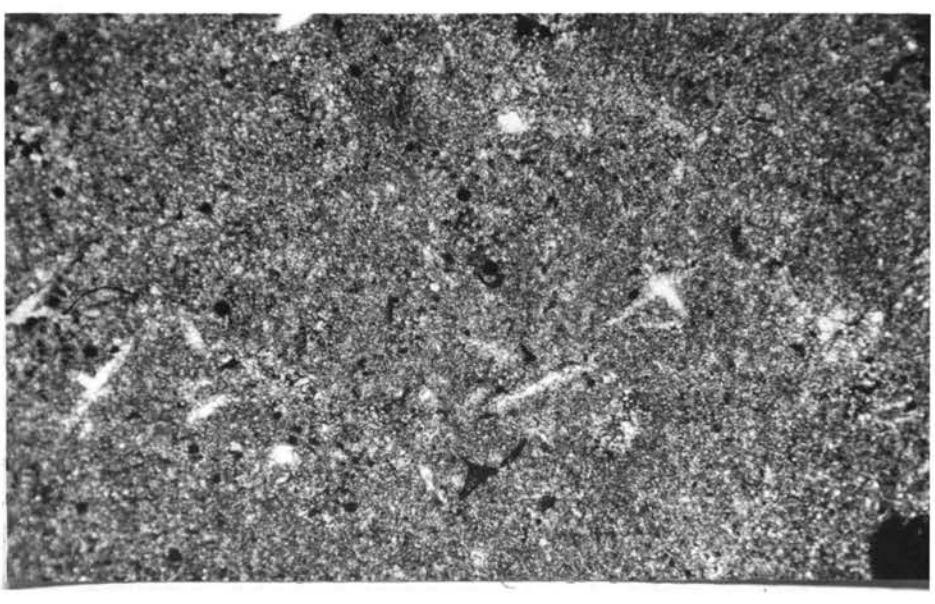


Fig. 25.

another.

Void filling calcite spar which is usually scarce in these rocks due to the small amount of available pore space has been found in articulated ostracode valves (Fig. 22), in brachiopod spines (?) (Fig. 23) and under partially enrolled trilobite carapaces (Fig. 16, Fig. 17). In one of these examples (Fig. 17) a geopetal feature consisting of internal sediments with an attitude consistent with the bedding was encountered. A few other examples that probably represent void filling calcite spar were also observed (Fig. 58, Fig. 67). In these examples not associated with fossil filling, the origin of the original cavity is not obvious.

Some of the limestones exhibit a "clotted" or mottled texture due to patches of calcite crystals of different size and different degrees of clarity. These patches are usually very irregular. At first this texture was thought to be caused by burrows or pellets similar to those described by Beales (1965). Serial peels and thin sections through the clotted areas failed to reveal a three-dimensional form that could be attributed to either burrows or pellets. It seems likely that this grumous texture has been produced by incomplete recrystallization of micrite to microspar.

All of the limestones contain some clay. Most of the clay is well dispersed throughout the rocks occurring as inclusions in calcite crystals and between individual crystals. Larger isolated lenses of clay, usually oriented parallel to the bedding are also present. Laswell (1957) gave a range of insolubles for these limestones between 20 and 30 percent. Much of these insolubles is composed of "dolomoldic shale" (Grohskopf _et al._, 1949).

Between 5 and 10 percent of the limestones is composed of sapropel-like organic fragments. Most particles are small, less than 0.01 mm. in diameter, and disseminated throughout the rocks. Larger, elongated shreds of organic material, which may represent graptolites, are oriented parallel to the bedding. A few small, less than 0.05 mm. in diameter, randomly distributed structureless phosphate pellets were also encountered.

Silt-size grains of well rounded quartz are sporadically distributed through the limestones and vary from rare to uncommon. In no example did quartz account for more than a fraction of one percent of the total constituents of the rock.

Dolomite is the most abundant authigenic mineral in the limestones. Dolomite content varies from 5 to 10 percent with rare examples containing over 20 percent. The habit of the dolomite is always that of euhedral crystals. All dolomite present in the limestones is the non-ferroan variety. The crystals average 0.07 mm. in diameter, and have no preferred crystallographic orientation in the rocks. Only about 30 percent of all dolomites present show zoning or distinct nucleation. The authigenic origin of this mineral is clearly indicated by its euhedral crystal form and its common transection of allochems and void filling calcite (Fig. 24).

Pyrite, though not as abundant as dolomite, is ubiquitous in the limestones. It usually occurs as very small (0.005 mm. average) euhedral cubes and pyritohedra. Larger euhedral cubic crystals several millimeters in diameter were also present in the limestones. Pyrite has in many cases partially replaced calcareous fossil fragments. Perhaps the most unusual occurrence of this mineral is its concentration in zones parallel to the bedding. These zones vary from thin laminations a fraction of a millimeter in thickness (Fig. 15) to zones over ¼ inch in thickness (Fig. 26, Fig. 41). The thin pyrite laminations may commonly be close spaced as in Fig. 15. Most of the limestones show some of these pyrite laminations and they are best observed on polished slabs. These pyrite laminations and zones may be indicative of poor circulation in the depositional environment. Also, the laminations would seem to preclude the existence of burrowing organisms in the original Maquoketa carbonate mud. Thin sections through the thicker pyrite zones reveal a greater concentration of calcareous fossils than in any other part of the limestones. The fossils are small and are primarily ostracodes. Many of the fossils have been partially or completely replaced by pyrite (Fig. 20, Fig. 26). Recent ostracodes are known to have a high tolerance for foul water. A similar situation may have existed for Paleozoic forms.

A few "calcispheres" composed of single crystal crystals of clear calcite were observed in the pyrite-rich

Fig. 26. This section represents one of the thicker pyrite-rich zones in the micrite. Pyrite has partially or completely replaced abundant ostracodes. Matrix is a clear sparry calcite. (CDH # 76, L-10), X80.

Fig. 27. The origin of this "calcisphere," composed of a single crystal of clear calcite, is uncertain. Note that adjacent pyrite is replacive to the "calcisphere." The "calcispheres" were only found in pyrite-rich zones in the micrite. (CDH # 76, L-10), X200.

Fig. 26.

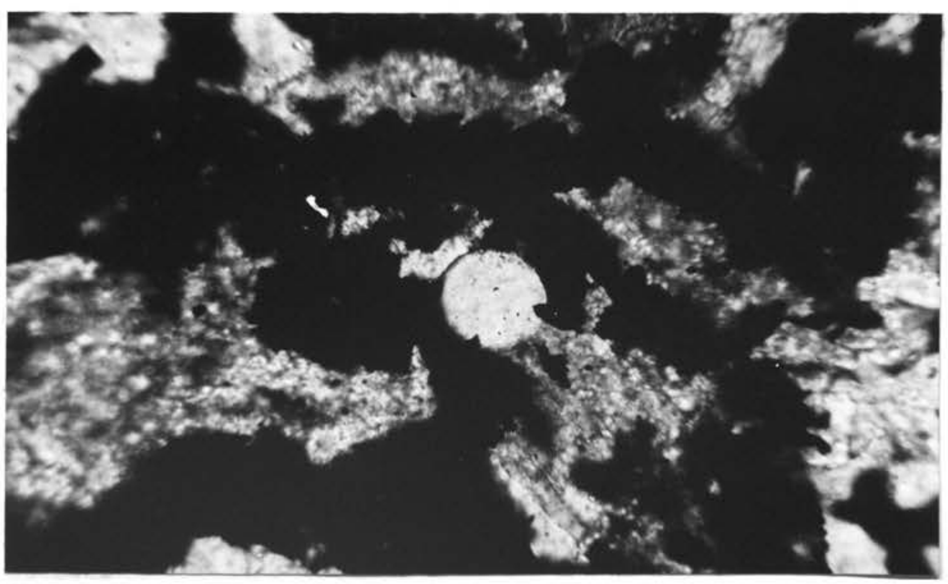


Fig. 27.

in the micrite (Fig. 27). They average 0.080 mm. in diameter. No internal structure was apparent. Nor is any exterior shell structure visible to suggest that these structures are void filling of fossils, such as ostracodes. Monogram and Lytte (1958) have figured and described aragonite spherulites that are similar in appearance and comparable in size to the Maquoketa "calcispheres." These structures were produced by sulfate-reducing bacteria in an anaerobic environment both naturally in recent sediments and in the laboratory. Sulfate-reducing bacteria are capable of raising the alkalinity of the medium in which they grow, and pH values as high as 10 have been recorded. The presence of iron appears to increase the rate of growth of bacteria (Monogram and Lytte, 1958). The Maquoketa "calcispheres" are always intimately associated with pyrite. However, crosscutting relationships indicate that the pyrite is replacing the "calcispheres." This situation suggests that the "calcispheres" were present before the formation of pyrite, which in most cases can be demonstrated to be a product of early diagenesis (syngenesis). It is thought that bacteria may have played a role in the production of the Maquoketa "calcispheres," but without further evidence their origin will remain problematical.

D. Dolomitic Shales

Little is known about the petrology of shales. They have been largely ignored by petrographers because of their fine grain-size. In the Maquoketa, shales are the dominant lithology. Shales and marlstones, which exhibit an imperceptible intergradation, comprise greater than 60 percent of the entire formation. Unfortunately, shales probably reveal less about environment of deposition than any other rock type.

Because of the unsatisfactory state of the present classifications of argillaceous rocks no formal nomenclature has been followed. The term "shale" has been retained to indicate that these rocks possess some degree of fissility. The following discussion of mineralogy and textures should suffice to "classify" these rocks.

The detrital fraction of the Maquoketa shales is almost completely composed of clay-size material. Probably no more than 5 percent of the total detritals are silt-size or larger. However, silt-size and larger authigenic minerals (i.e. dolomite and pyrite) comprise between 5 and 50 percent of the total mineralogy of the shales and marlstones. Laswell (1957, p. 15) gave a range of insolubles from 66 to 87 percent for the shales.

The shales vary from olive gray (5Y 4/2) to bluish gray (5B 6/1) in color, assuming lighter shades with an increase in the amount of dolomite. Weathered material is usually light bluish gray (5B 7/1) in color and forms a very sticky tenaceous clay. Most of the shales do not exhibit conspicuous laminations in hand specimen.

Following Ingram's (1953) division of breaking characteristics of mudstones, the Maquoketa shales would be classified as flaggy and flaky. The flaggy shales split into fragments of varying length many times greater than their thickness, and the two essentially flat sides approximately parallel. None of the flaggy shales exhibits the high degree of fissility of the so-called "paper-shales." The flaky shales split into uneven flakes along irregular surfaces approximately parallel to the bedding, and their length seldom exceeds several inches. The flaky shales are much more common than the flaggy varieties. As carbonate content increases to the point that the shales approach a marlstone, little fissility is apparent. At this point the rock breaks into irregular blocky fragments, with a subconchoidal fracture, and has only a slight preference for splitting parallel to bedding planes.

In thin section, the clay minerals are oriented parallel to the bedding. Individual clay minerals are too small to be seen with the microscope but the mass orientation of the shales goes to extinction simultaneously in a position approximately parallel to the bedding. Some authors have considered the parallel orientation of clay minerals to be entirely a direct response to compaction due to the weight of overlying sediments. However, argillaceous rocks with randomly oriented clay minerals have been found at very great depths and rocks with a high degree of parallel orientation of clays have been found in rocks with almost no overburden (Odom, 1967, Folk, 1968). Odom (1967) has found a great variation in the degree of preferred clay orientation in Pennsylvanian shales separated by only a few inches stratigraphically. He has suggested that fabric variation not only reflects gravitational compaction but more importantly also the physico-chemical conditions in the depositional environment.

Clay minerals were analyzed by x-ray diffraction. Nine samples, one from near the top, middle and bottom from three different cores, were used (CDH # 76, CDH # 72, and CDH # 73). Identification was made by comparison with A.P.I. standard diffractometer patterns for clay minerals (Mollay and Kerr, 1961). Illite was the only clay mineral determined. The environmental significance of illite is slight. It is the most commonly occurring clay mineral in Paleozoic rocks and is thought to be both detrital and authigenic in origin. Bromberger (1965, 1968) found most of the clay fraction in the Iowa Maquoketa to be the $2M_1$ polymorph of illite, indicative of high temperature of formation. Hence, he considered the illite to be detrital. Both Bromberger (1965, 1968) and Ostrum (1961) have reported small amounts of chlorite in the Maquoketa of Iowa and Illinois. Chlorite is considered by many workers to represent near-shore, estuarian, deltaic and lagoonal environments (Hayes, 1963). No chlorite was found in the Missouri Maquoketa, but it is possible that small amounts of this mineral were overlooked due to the small number of samples analyzed.

Dolomite is the second most abundant mineral in the shales. Concentrations range from 5 to 10 percent in the lower part of the formation and gradually increase to subequal amounts of illite and dolomite in the marlstones.

Fig. 28. Dolomitic shale exhibiting numerous nucleated dolomite crystals. Dark colored lenticular masses are pyrite crystals and unidentified sapropel-like organic materials. Note the discontinuous laminations exhibited by this specimen. Orientation of photo is normal to bedding. (CDH # 63, S-7), X80.

Fig. 29. Dolomitic marlstone, composed of approximately equal amounts of euhedral dolomite crystals and clay minerals. Note that dolomitization, in this specimen, has obliterated all indications of primary textures. (CDH # 76, S-32), X220.

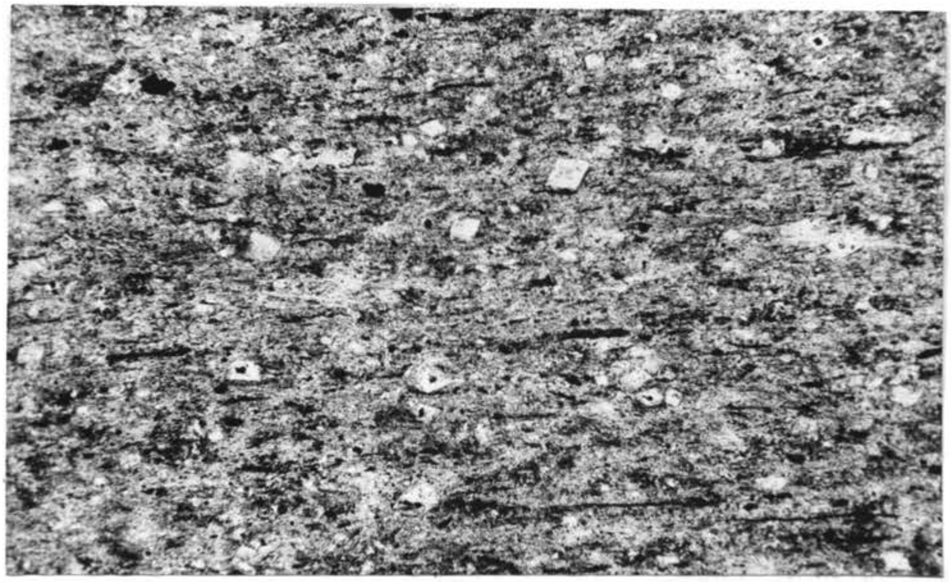


Fig. 28.

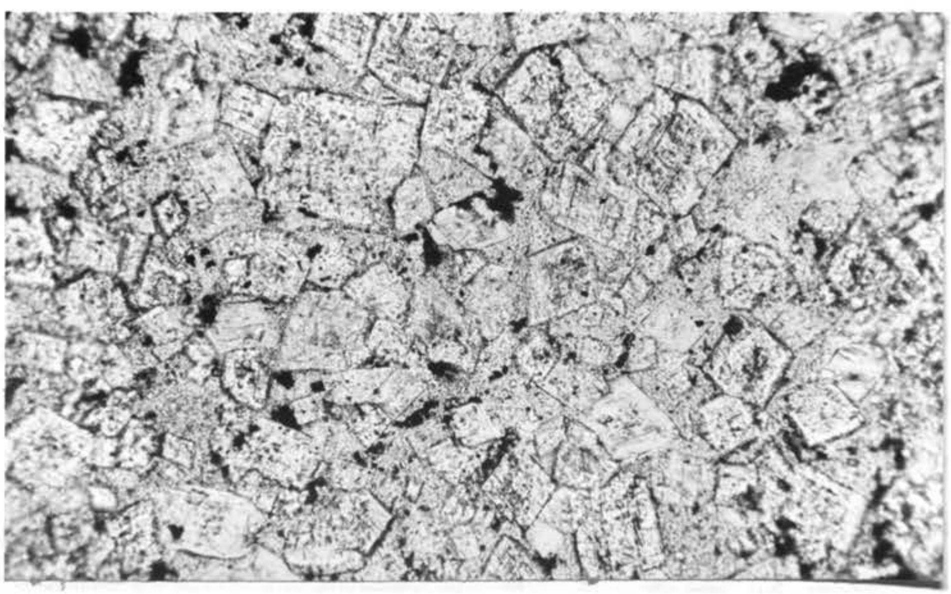


Fig. 29.

The dolomite occurs as euhedral rhombic crystals averaging 0.025 mm. in length. They are commonly zoned and many are nucleated by small pyrite crystals and very fine unresolvable organic material (Fig. 51, Fig. 52). Some of the zoned crystals show cloudy centers and clear rims, similar to those described by Murray (1964). There does not seem to be any particular trend toward a parallel alignment of the long axis of the dolomite crystals to the bedding. The euhedral habit of the crystals, the lack of preferred orientation, and the pyrite and organic nuclei strongly suggest a secondary origin for the dolomite.

Calcite is rare in the shales, never comprising more than a fraction of one percent of the total mineralogy. It occurs exclusively in the form of ferroan calcite in small (less than 0.01 mm.) structureless masses. Its irregular form does not indicate a detrital origin. This occurrence may represent pore filling and cementation by ferroan calcite. No calcareous fossils were observed in any of the shales or marlstones.

All of the shales contain some sapropel-like (carbonaceous and/or phosphatic) organic material. The average organic content is between 5 and 10 percent. Some of this material occurs as elongated shreds orientated parallel to the bedding, producing discontinuous irregular laminations. The bulk of the organics is in the form of very small (0.001 mm. or less) particles disseminated throughout the rock. Most of this material is unidentifiable, but occasionally a graptolite fragment can be recognized. The organic material accounts for the majority of the silt-size detrital fraction of the shales.

Pyrite is found in all of the shales and it is commonly associated with the sapropel. It usually occurs as elliptical masses of crystals with the major axis parallel to the bedding, and as small (0.01 mm. average) disseminated single crystals. Larger euhedral crystals and aggregates of small crystals up to 1.0 cm. in diameter were observed. The elliptical masses of crystals form irregular and discontinuous laminations similar to those produced by the organic material. Larger pyrite crystals have inevitably disrupted the parallel orientation of the adjacent clay minerals (Fig. 63). This deformation probably represents compaction of soft shale around the more rigid pyrite crystals and crystal growth in a soft sediment. Both processes indicate an early diagenetic (syngenetic) origin for the pyrite.

Small structureless phosphate pellets were randomly distributed and scarce in the shales. No detrital quartz was observed in either the shales or marlstones.

E. Dolomitic Marlstone

The A.G.I. Glossary of Geology and Related Sciences (1960, p. 178) defines "marlstone" as "an indurated mixture of clay material and calcium carbonate (rarely dolomite) normally containing 25% to 75% clays." Pettijohn (1957, p. 411) has added, "The marlstones are less fissile than the shales, and like mudstones have a blocky subconchoidal fracture." In this study the term "marlstone" is applied to those rocks that exhibit little fissility and in which the amounts of clay and dolomite are approximately equal.

Although the main difference between the shales and marlstones is in the amount of dolomite they contain, other differences do exist. Practically all of the original texture of these marlstones has disappeared and been replaced by a mosaic of euhedral dolomite crystals (Fig. 29). The dolomite in all of the marlstones examined was entirely the ferroan variety as determined by the potassium ferrocyanide staining technique described by Dickson (1965, 1966). On application of the stain, the entire dolomite crystal assumed the color of Turnbull's blue. However, sharply defined darker blue zones indicated higher concentrations of ferroan iron parallel to the rhombic crystal faces. Nucleated crystals, though present, were not as abundant proportionally as in the shales.

Pyrite appears to be approximately equally abundant in both the shales and marlstones. Abundant pyritized invertebrates, generally altered to limonite, were found on several bedding planes in the upper part of the marlstone at the Dundee Quarry (Fig. 31). Sapropel-like organic material was not as common as in the shales. No ferroan calcite was observed in the marlstones. In hand specimen, the marlstones do not usually exhibit distinct laminations; however, several notable exceptions were observed (Fig. 30). In samples such as the one in Fig. 30, laminations were observed as color banding caused by the concentration of

Fig. 30. Hand specimen of the dolomitic marlstone from the upper Maquoketa. Note the well developed subconchoidal fracture and distinct laminations. Sample from the outcrop at the Dundee Quarry. X½.

Fig. 31. Hand specimen of dolomitic marlstone with pyritized invertebrate fossils from the upper Maquoketa. The bright metallic areas on the fossils are portions of pyrite which has not been oxidized to limonite. Sample from the outcrop at the Dundee Quarry. X½.

Fig. 30.

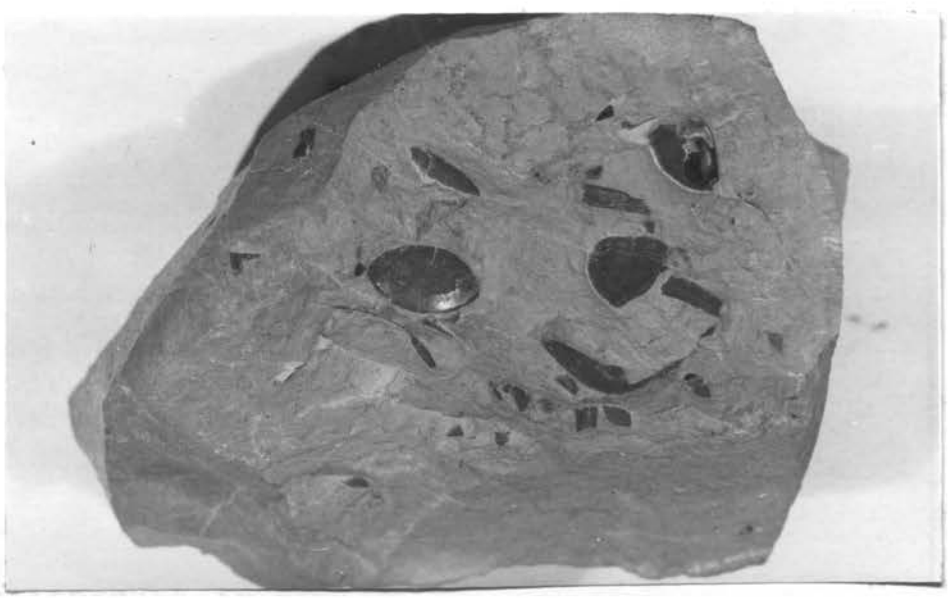


Fig. 31.

organic material (sapropel) and clays. Fewer small scale laminations caused by elongated masses of pyrite and sapropel were observed in thin section. This may represent greater disruption of the parallel orientation of smaller particles by the growth of numerous dolomite crystals. Several examples of sparry calcite and quartz replacement of marlstone were encountered.

The dolomitic marlstone is the most abundant single lithology of the Maquoketa. The marlstone completely succeeds the shales approximately 50 feet above the lower contact of the formation. The thickness of the marlstone between limestone units is generally greater than that of intervening shales. Probably all of the upper blue-green "shales" of Johnson's (1939) stratigraphic section of the Maquoketa in Pike County are in reality dolomitic marlstones (Fig. 9). In this study the marlstones were easily recognized due to the advantage of having the fresh unweathered samples from the Dundee Quarry. It is likely that these marlstones would develop a higher degree of fissility on weathered outcrops and could be easily identified as shales (Ingram, 1953).

F. Dolomitic Quartz Siltstone

By general agreement (Pettijohn, 1957, Folk, 1968) the term "siltstone" is applied to non-fissile clastic rocks containing greater than two-thirds silt-size detrital particles by volume. No separate siltstone classification scheme has been attempted, although Folk (1968) has applied his sandstone classification to siltstones.

Dolomitic quartz siltstone was found only at the Grassy Creek (GC) outcrop during this study. It occurs near the top of the formation. Laswell (1957) has noted the occurrence of a dolomitic siltstone near the top of the Maquoketa at a number of outcrops in Pike County. However, at the Grassy Creek (GC) locality he misidentified the siltstone as a "silty shaly limestone" (Laswell, 1957, p. 24). Although Martin *et al*. (1961) reported local lenses of sandstone in the upper Maquoketa, this siltstone was the coarsest clastic discovered during this investigation.

At the Grassy Creek (GC) locality ten individual siltstone beds ranging in thickness from one-half to two inches alternate with somewhat thicker shale beds. Only one thin (one and one half inch) badly weathered limestone unit was found near the base of the outcrop. The siltstones weather in relief on the outcrop and the cyclic sequence appears very similar superficially to the limestone-shale sequence in the lower part of the formation. Although the outcrop is badly weathered, the contact between the two lithologies appears to be sharp. The siltstones are yellowish gray (average 5 Y 7/2) in color and exhibit no fissility. These rocks are well indurated and very hard, breaking with a subconchoidal fracture. Bedding planes are irregular and locally siltstone beds may pass into bands of elliptical nodules with their long axis parallel to the bedding.

In thin section these rocks are composed primarily of

Fig. 32. Dolomitic quartz siltstone from the upper Maquoketa along Grassy Creek. Note euhedral dolomite rhombohedra (clear) and organic fragments (black). (GC-8), X80. Plane polarized light.

Fig. 33. Same as above. Crossed nicols.

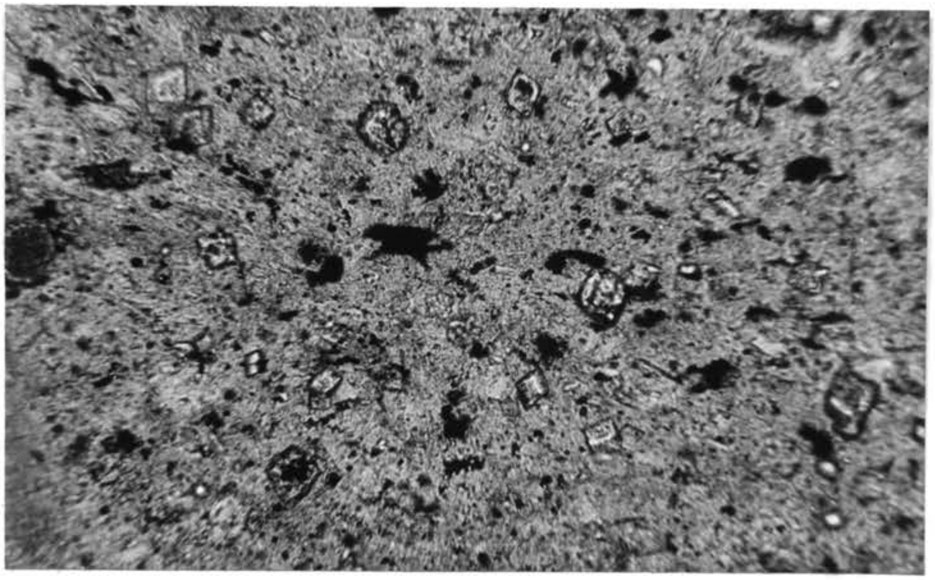


Fig. 32.

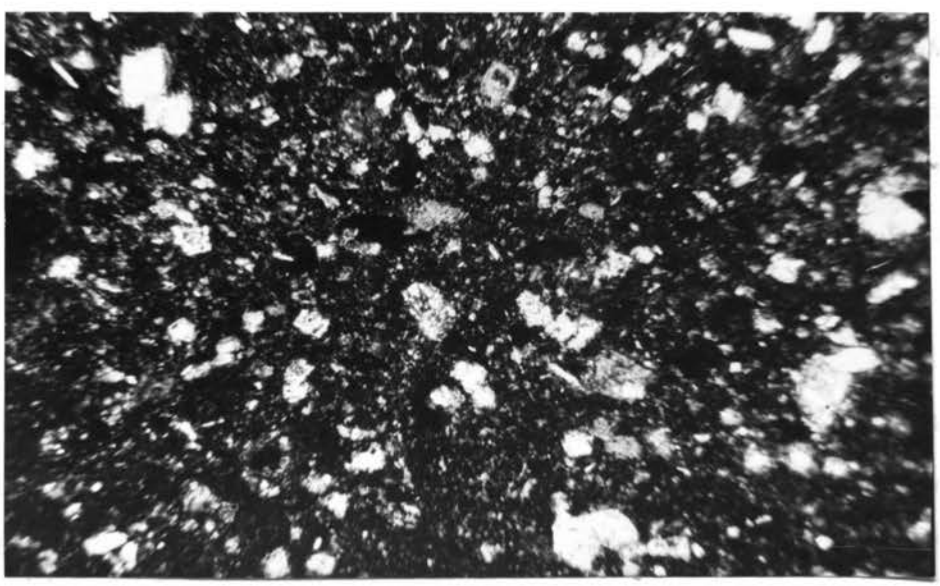


Fig. 33.

silt-size quartz grains, clay minerals, and authigenic dolomite. Other minor constituents are present. Mineralogy, textures, and percentage of constituents are not readily resolved under the microscope due to the extremely small grain size. Quartz grains are angular and range from very fine silt-size (0.0039 mm.) to medium silt-size (0.031 mm.). The bulk of the quartz is near the smaller grain size. Very fine silt-size and smaller quartz grains in most cases are impossible to distinguish from clay minerals. Small areas of irregular-shaped authigenic quartz particles (up to 0.01 mm.) also complicate the determination of the percentage of detrital quartz. However, in most cases quartz probably represents greater than two-thirds of the detritals.

Clay minerals with no preferred orientation account for the bulk of the remaining detritals. Fragments of organic sapropel-like material were present in all the thin sections examined. Sapropel may comprise up to 10 percent of the rock. Most fragments are small (0.01 mm. or less) but a few graptolite fragments up to 0.5 mm. in length were observed. Identification of fragments as graptolites was confirmed by comparison with acetate peels of documented three-dimensional graptolites from the Maquoketa of Iowa, supplied by Steven R. Herr, University of Iowa. The graptolite fragments from the siltstone show the best preservation of any found in this study with the internal structure of individual rhabdsomes clearly visible (Fig. 36, Fig. 37). One phosphatic tooth-like fossil, probably a conodont,

Fig. 34. Phosphatic tooth-like fossil, probably a conodont. From the siltstone in the upper part of the Maquoketa along Grassy Creek. (GC-2A) X80.

Fig. 35. Linear structure in the center of the photograph is probably a siliceous sponge spicule. From the siltstone in the upper part of the Maquoketa along Grassy Creek. (GC-6) X80.

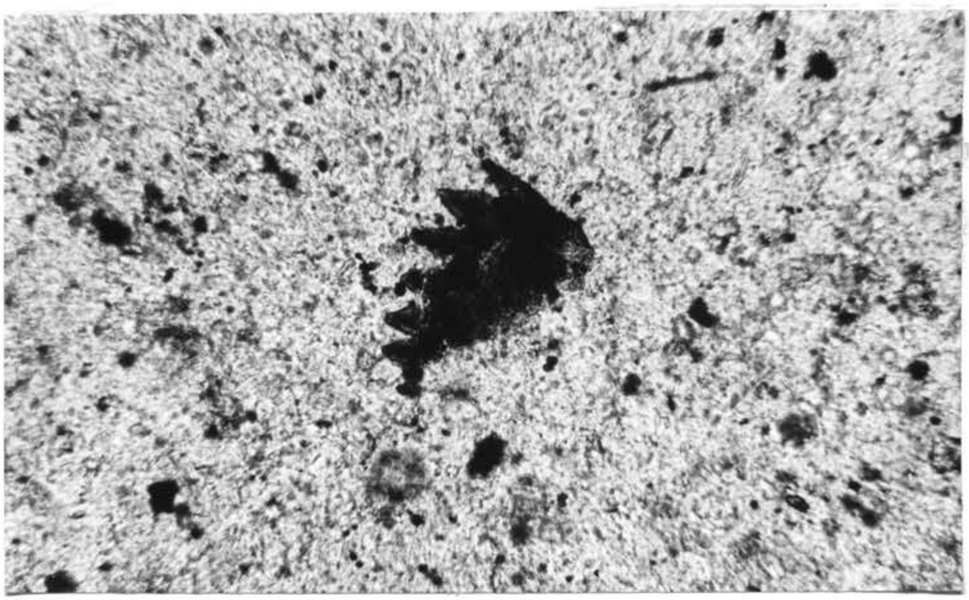


Fig. 34.

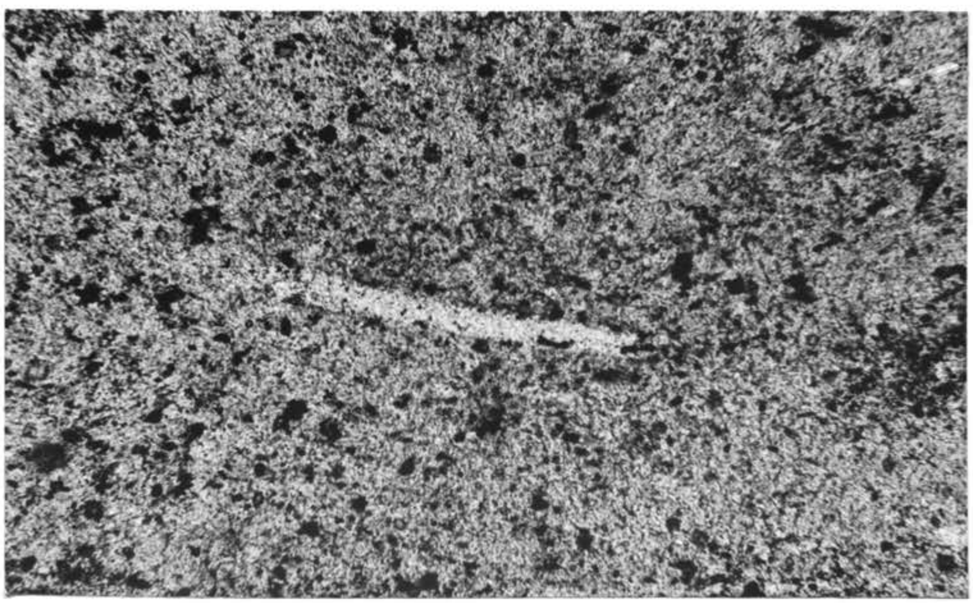


Fig. 35.

Fig. 36. Graptolite fragment, in the siltstone, showing the internal structure of the rhabdosome. (GC-7), X80.

Fig. 37. Graptolite fragments in the siltstone. These fragments show some indication of internal structure, but not as distinct as in the specimen figured above. (GC-4), X80.

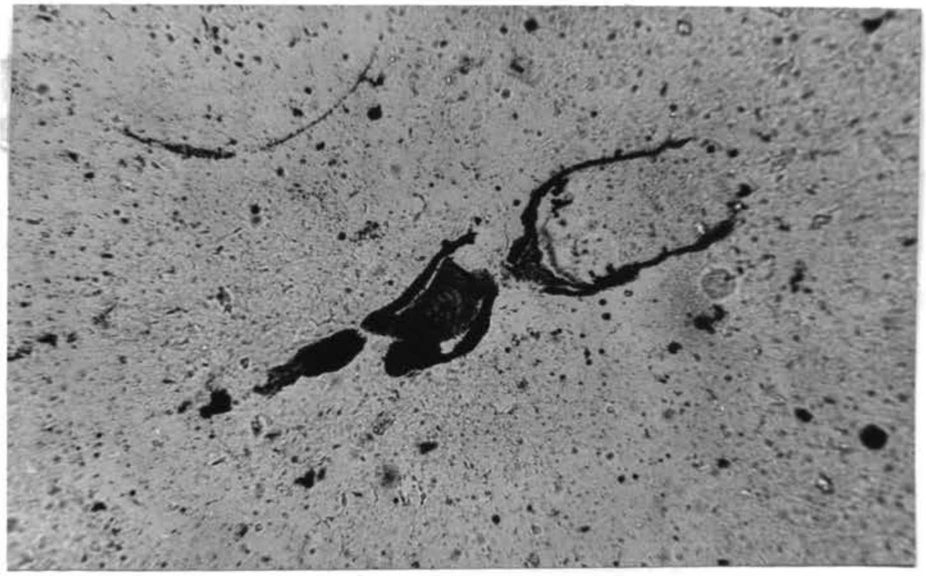


Fig. 36.

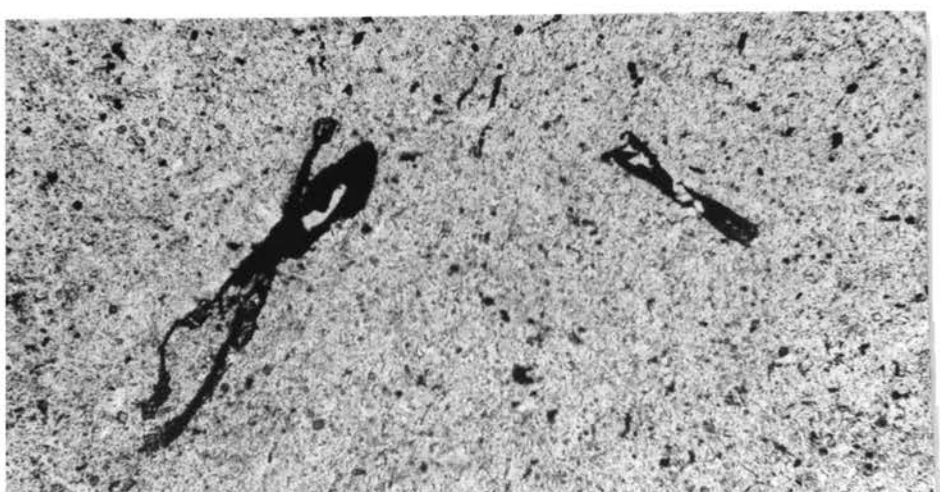


Fig. 37.

was seen in thin section (Fig. 34). No calcareous fossils were found in these rocks. Some thin sections contained a few siliceous linear structures (Fig. 35). They are approximately 0.5 mm. in length and composed of microcrystalline mosaic quartz grains. Individual grains are only slightly larger than the surrounding matrix. Some of these structures exhibit poorly defined right angle junctions with similar siliceous structures. It is thought that these structures represent sponge spicules. Several rare problematical structures observed may represent silicified calcareous fossils, but conclusive evidence is lacking (Fig. 73, Fig. 74). Some very irregular small-scale disturbed laminations produced by varying amounts of fine organic material are present in some units.

Authigenic dolomite constitutes 25 to 35 percent of the siltstones. Crystals are small (0.025 mm. average) and euhedral (Fig. 32, Fig. 33). They usually show no zoning or nucleation. Commonly crystal faces are irregular as if they had been subjected to chemical corrosion. Vertical fractures, probably produced by tension and filled with ferroan calcite, are common features (Fig. 61). Approximately 5 percent of the rocks are composed of pyrite. Usually it occurs as very small (less than 0.001 mm.) disseminated crystals but a few unusual pyrite spherulites approximately 0.01 mm. in diameter were observed. A number of vugs, up to 1/8 inch in diameter, completely filled with quartz, ferroan calcite, and fluorite were discovered in thin section (Fig. 71, Fig. 72, Fig. 75). The difficulty in cutting and grinding thin sections, along with the corroded edges of quartz grains and dolomite crystals, suggests that some very fine microcrystalline quartz cement may be present.

G. Contact Relationships

Special effort was made to thin-section samples across the contacts of the cyclic lithologies (i.e. limestone-shale, marlstone-limestone, and siltstone-shale). It was thought that these contact relationships might reveal evidence concerning the genesis of the cycles. All of the above mentioned cyclic contacts were thin-sectioned. However, because of the badly weathered condition of the Grassy Creek (GC) outcrop, only two samples were obtained of the siltstone-shale contact. In all cases the contacts were similar: microgradational, with the change from one lithology to the other accomplished over a distance of approximately 2 millimeters. Both the upper and lower boundaries of each individual bed showed this same type of microgradational contact. In hand specimens and outcrops the contacts appear to be very sharp. No evidence of a diastem or period of erosion was observed at the contact between differing lithologies. From the contact relationships, it appears that the Maquoketa cycles were caused by repetitive rapid changes in environment accompanied by subsequent changes in sedimentation.

V. Structures

A. Introduction

The lack of any unequivocable primary sedimentary structures in the Maquoketa is distinctive. Those structures that are present probably formed shortly after deposition and should be regarded as early diagenetic. For convenience, these structures will be considered separately instead of in the section on diagenesis.

B. "Sedimentary Boudinage" (Pinch and Swell)

The limestones in the lower 15 to 20 feet of the Maquoketa at the Stark Nursery (ST) exposure on Noix Creek exhibit irregular, hummocky bedding planes. These beds pinch and swell and may pass locally into bands of irregular "nodular" bodies (Fig. 3). Such bands of "nodules" are generally uncommon at the Stark Nursery locality. Bands of "nodules" were also rarely observed in the siltstone in the upper part of the Maquoketa at the Grassy Creek (GC) section. These siltstones were also irregularly bedded. The highly weathered state of the shales at the Stark Nursery outcrop rendered it impossible to determine the exact nature of the contact relationship between most of the limestones and shales. A section of core (Fig. 39) taken from several feet above the base of the formation at the Dundee Quarry also exhibited an irregular pinch and swell structure between the limestone and shale beds. Fortunately, at the Stark Nursery section, Noix Creek flows for several hundred feet over one of these limestone bedding planes, exposing its irregular surface (Fig. 38). In plan view these "bedding-plane nodules" are expressed as irregular circular or elliptical mound-like bodies, with gently sloping edges, 5 to 9 inches in longest diameter and rising 1 to 2 inches above the surface of the bed. Individual "nodules" are spaced 6 inches to 2 feet apart. There is an indication of a N-S orientation of these "nodules." However, it is ill-defined. The configuration of these "nodules" in plan view would seem to eliminate the possibility of their being ripple marks. These "nodules" do not display distinct laminations or any concentric or radial structure. Nor is there an intimate relationship between "bedding-plane nodules" and fossil content. They are structureless except for fine fractures (up to 1.0 mm. in width) which are filled with ferroan calcite spar. The fractures are oriented perpendicular to the bedding. Several very distinct calcite-filled cracks occurring at the very tops of beds were observed in the irregularly bedded siltstones. It is thought that these cracks were produced by tensional forces.

Folk (1962) has reported similar mound-like protuberances on the upper surfaces of limestones in the cyclic Rochester Formation (Silurian) of West Virginia. He interpreted these as primary carbonate mud mounds. A similar interpretation does not seem appropriate for the Maquoketa structures. A cross section of these "nodules" as seen on the outcrop (Fig. 3) and in cores (Fig. 29) reveals that

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Fig. 38. Irregular hummocky limestone bedding plane in Noix Creek at the Stark Nursery (ST) section. Mound-like structures are thought to be "sedimentary boudinage" structures seen in plan view. Hammer, for scale, is approximately 12 inches long and oriented approximately N-S. Note the ill-defined N-S orientation of the "sedimentary boudinages."

Fig. 39. Section of core from the Dundee Quarry showing "pinch and swell" structure. This feature is believed to represent a cross-section through one of the "sedimentary boudinages." (CDH # 63, L-3) X1.

Fig. 38.

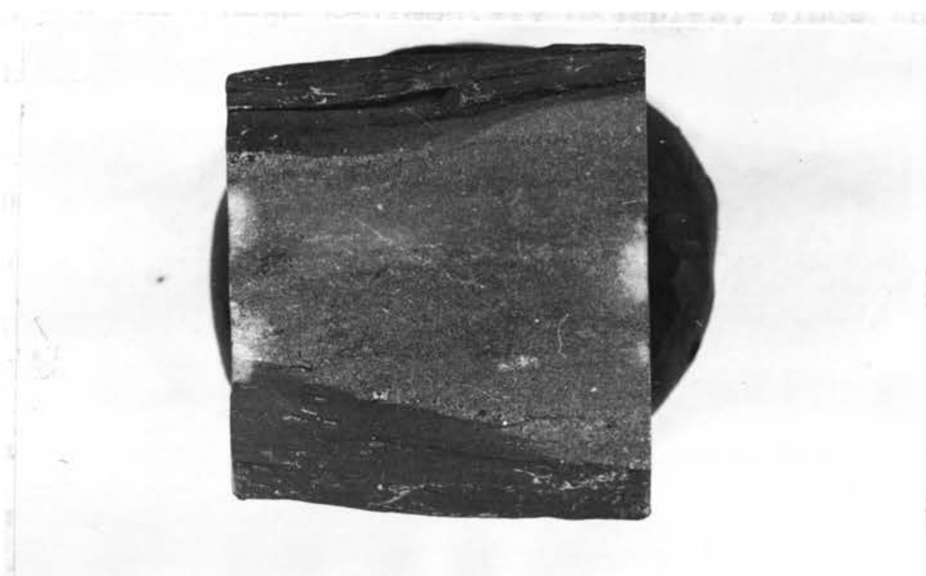

Fig. 39.

these structures protrude both upward and downward into the adjoining shale beds. One would not expect such a small primary carbonate mud mound to protrude into the underlying bed.

It seems more feasible that these structures were produced by intrastratal flowage of unconsolidated or weakly consolidated sediments. Comparative structures produced by intrastratal flowage have been reported from thin-bedded cyclic sequences from the Devonian Ireton Formation in Alberta, Canada, by McCrossan (1958), from the Jurassic Blue Lias Formation in England and Wales by Wobber (1967) and by Rich (1950) from Silurian rocks from Aberystwth, Wales. Both Pettijohn (1957) and McCrossan (1958) have called these structures "sedimentary boudinages." Hills (1963, p. 132) suggested the term "pull-apart" rather than boudinage for these sedimentary examples, since the term "boudinage" carries the implication of tectonic deformation. However, from a descriptive point of view "boudinage" seems to be a better designation, particularly if prefaced by the term "sedimentary," so that no confusion may arise.

"It is generally accepted that the basic reason for boudinage structures is difference in competency between boudin layers and the adjacent rock" (Ramberg, 1955, p. 512). The boudin layers are always more competent and brittle than the surrounding layers. The application of a stress promotes flowage in the incompetent layer from the center toward the margin. The friction produced by plastic flowage creates tensile stresses in the competent layer causing elongation and eventual rupture. In the simplest case this elongation is probably caused by compressive stresses perpendicular to the bedding. Differential loading of overlying sediments may be sufficient to produce the required stress. According to the experiments of Ramberg (1955) a tensile stress or a stress couple at an angle of 45 degrees to the elongation could also produce boudinage structures. McCrossan (1958) suggested that a tensile stress could be created by the lateral spreading of soft sediments. This lateral spreading of sediments would require a slightly irregular depositional surface or a slight lateral variation in the density of the sediments (McCrossan, 1958).

McCrossan (1958) cited the following characteristics as criteria in recognizing sedimentary boudinages:

> "1) The 'boudinage' structures should be coarser grained and hence less plastic at the time of deposition than the sediment surrounding them;
> 2) they may show evidence of tensional stresses such as fine peripheral cracks;
> 3) they may have thread-like connections;
> 4) nodules in the same plane should show similarities suggesting that they originated from the same bed and dissimilarities to the matrix;
> 5) there may be all gradations from undeformed laminations to isolated scattered nodules." (McCrossan, 1958, p. 319.)

The Maquoketa boudinages appear to be consistent with McCrossan's criteria with the exception that no thread-like connections were observed between "nodules." The Maquoketa was deposited on the irregular erosional surface of the Kimmswick Formation. This unconformable surface may have promoted a lateral spreading of soft sediments as McCrossan (1958) has suggested. These sedimentary boudinages are found in the lower part of the Maquoketa where the difference in clay content between the limestones and shales is the greatest. Hence, the difference in competency between these beds is greatest. Going stratigraphically upward in the section the clay content of the limestones and the carbonate content of the shales increases. This results in a much smaller difference in the competency of these beds. Boudinages were not observed in these units. At the very top of the Maquoketa where thin siltstone beds, instead of limestone, alternate with the shales, the difference in competency between the beds is again greater and boudinage structures are again found.

C. Minor Intrastratal Folding

Several of the thin pyrite zones in the micrite exhibit microfolds (Fig. 40, Fig. 41). It is not thought that the pyrite is related genetically to the folding, but rather that the pyrite emphasized these structures that would have otherwise been virtually indistinguishable. Lenticular masses of pyrite which are usually observed oriented parallel to the bedding in these rocks have been folded with the limestone. It is thought that these folds represent a form of soft sediment deformation. The folding was confined to the central portion of individual

Fig. 40. Photomicrograph of sigmoidal intrastratal fold. Note that pyrite has been folded along with the micrite. This photo illustrates the same fold which is figured and circled below. However, this figure is a mirror image of the fold below due to the manner in which the thin-section was made. (CDH # 76, L-10), X24.

Fig. 41. Polished section of core showing intrastratal folding of a pyrite-rich zone in micrite. Note that the folding was confined to the central portion of this individual bed and died out near the margins. It is not thought that the pyrite was related genetically to the folding, but rather, that it emphasized this structure that could have been easily overlooked. (CDH # 76, L-10), X2.

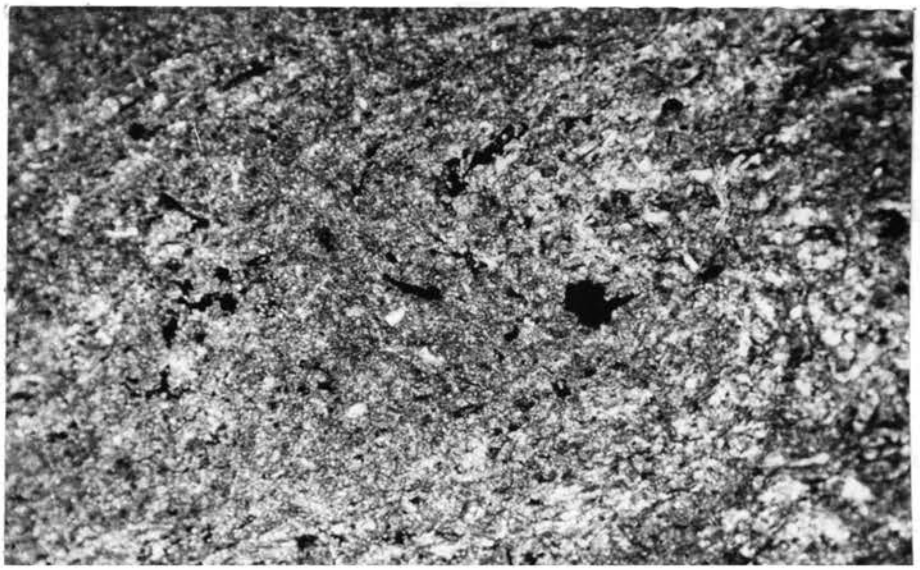

Fig. 40.

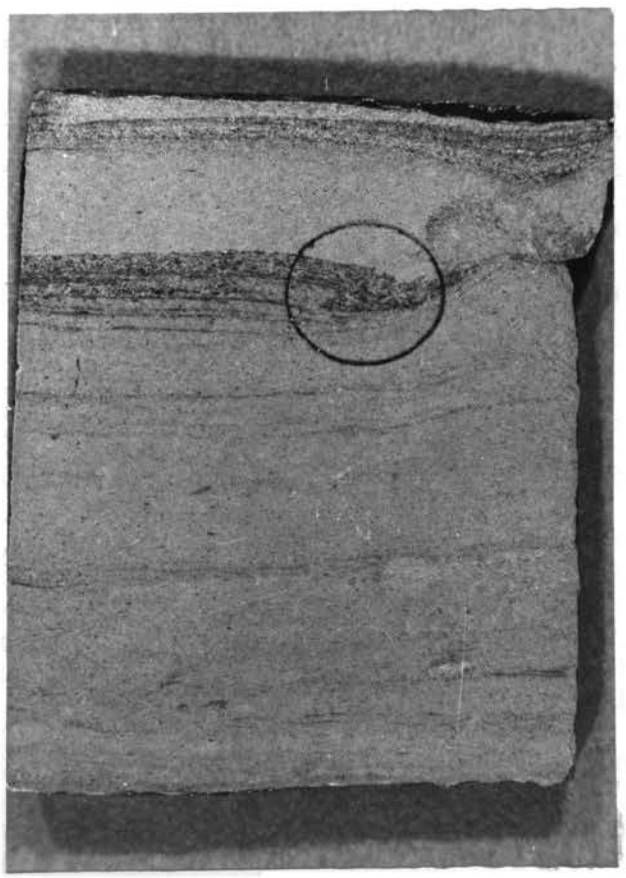

Fig. 41.

limestone beds and died out near the margins. These folds are similar to folds attributed to intrastratal flowage as described by Pettijohn (1957, p. 190). Rich (1950, p. 730) figured similar folds of a slightly larger size which he also attributed to intrastratal flowage. The genesis of these folds is probably similar to that of the sedimentary boudinages.

D. Cone-in-Cone Structures

Cone-in-cone structures were found in the five cores and in the open pit at the Dundee Quarry, distributed over a distance of about one mile. These structures occur in a layer from three to six inches above the top of the phosphatic "depauperate zone." The cone-in-cone varies from one quarter to two inches in thickness. Several other reports of cone-in-cone in the Maquoketa of Pike County have been made. Ladd (1929) noted a similar cone-in-cone zone, one inch thick, at the same stratigraphic position, about 3 inches above the contact with the "McCune Limestone" (Kimmswick Fm.) in the center of section 15, T.54 N., R.3 W., Pike County. He described it as follows:

> "Limestone, slightly phosphatic, with large pyrite crystals showing 'cone-in-cone' structure in section. Bedding planes show botryoidal structure with swelling downward." (Ladd, 1929, p. 381, unit 5 of Ladd's section 13.)

Ladd's locality had either been mislocated or completely obliterated by weathering, as it could not be found. This occurrence is more than 17 miles from the Dundee locality.

Laswell (1957, p. 14) noted another cone-in-cone exposure in the SE¼, SW¼, section 16, T.53 N., R.2 W., Pike County, more than 8 miles from the Dundee Quarry. He did not give the stratigraphic position of the cone-in-cone with regard to the base of the Maquoketa. Due to this lack of information it is uncertain if this occurrence is in the same stratigraphic position as the preceding two examples.

Some cone-in-cone layers extend over a large area and are regular enough to be used as stratigraphic datum planes. Tarr (1932) reported a cone-in-cone zone in the Comanchean rocks of Kansas that covered an area of over 1000 square miles. This same cone-in-cone layer had been used cautiously by Twenhofel and Tester (1926) for local stratigraphic correlations. In other cases multiple horizons of cone-in-cone occur in the same formation. Tarr (1932, p. 724) has reported as many as 25 persistent individual "shale with beef" (cone-in-cone) layers in the Blue Lias of Wales. It is uncertain if the three cone-in-cone occurrences in the Maquoketa are continuous. It appears that they are continuous in the Dundee Quarry. The continuity of the other two cone-in-cone exposures with the Dundee occurrence is unknown. Detailed field work might resolve this question, possibly adding another tool for the physical correlation of the Maquoketa in Pike County.

The Maquoketa cone-in-cone consists principally of a more or less continuous horizontal layer of right circular cones. The cone-in-cone layer is surrounded on both top and bottom by thin beds of dolomitic shale. The cones are

Fig. 42. Plan view of upper surface of hand specimen showing cone-in-cone structure. The circular structures represent the bases of individual cones. At higher magnification these structures give the appearance of overlapping circular rosettes of terminated calcite crystals. Sample from outcrop at the Dundee Quarry. X½.

Fig. 43. Polished section of core showing vertical section of cone-in-cone structure. Orientation of photo is the same as field orientation. Note the flared bases of the larger cones at the top of the picture. This specimen is unusual as it shows a double cone structure with cone sets on the top and bottom of the intervening zone of microcones. However, note that the lower layer of cones is greatly reduced in size. (CDH # 73, L-3) X1½.

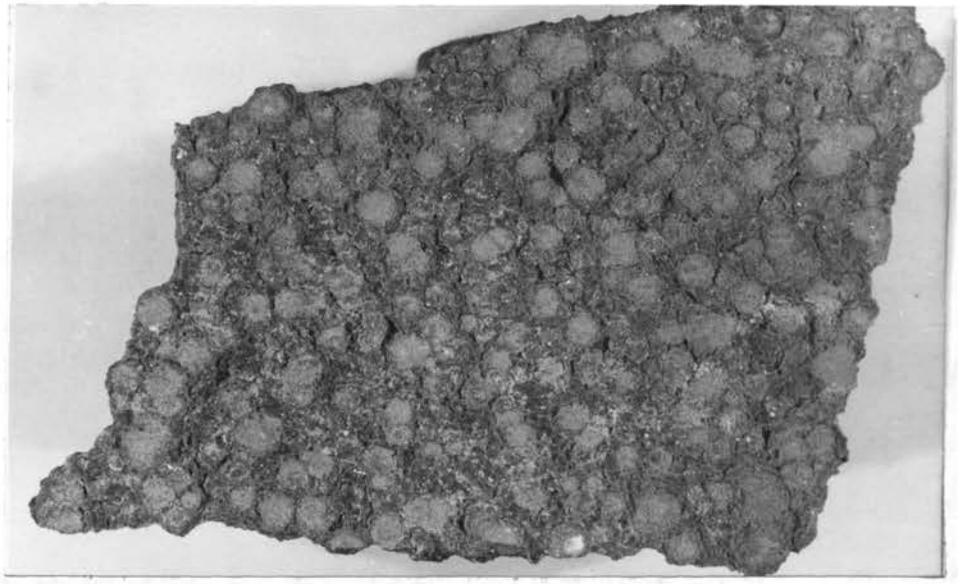

Fig. 42.

Fig. 43.

composed of fibrous calcite with individual crystals up to 1.0 cm. in length. The well defined cone-in-cone structure (Fig. 42, Fig. 43) may grade laterally into a zone of poorly defined patches of microcones (average 0.1 mm.) associated with small lenses of clay (Fig. 44, Fig. 45). In this paper, the term "microcone" refers to small, poorly defined cone-in-cone structures which are not visible to the naked eye. Generally the cone-in-cone structures are composed of a single layer of cones with their apices pointing downward. The microcones may show a double cone structure with cones on either side of intervening clay lenses pointing in opposite directions (Fig. 44). Only one example of the larger better developed cone-in-cone structures exhibited a double layer of cones (Fig. 43), with the lower layer of cones greatly diminished in size. Individual cones may be so crowded together as to interfere with one another and form overlapping conical structures. In the well-defined examples, larger cones extend from one side of the calcite layer to the other with the intervening space near the apices filled with smaller cones.

Individual calcite crystals are oriented approximately parallel to the cone axis with their c-axis in a vertical position. The cones exhibit axial angles between 20 and 35 degrees. Cones usually have straight sides, but some may have slightly flared bases. The apices of individual cones are terminated by an aggregate of small, elongated calcite crystals with rounded ends (Fig. 49). These small crystals are commonly associated with a relatively large amount of

Fig. 44. "Microcone" zone, exhibiting double cone structures, with cones on both sides of compacted clay lenses pointing in opposite directions. Note that the largest cones in this example are nucleated on clay lenses. (CDH # 72, L-3), X80.

Fig. 45. Group of authigenic pyrite crystals (black) in the Maquoketa "microcone" zone. Linear light gray area above pyrite is a clay lense. (CDH # 76, L-3), X80.

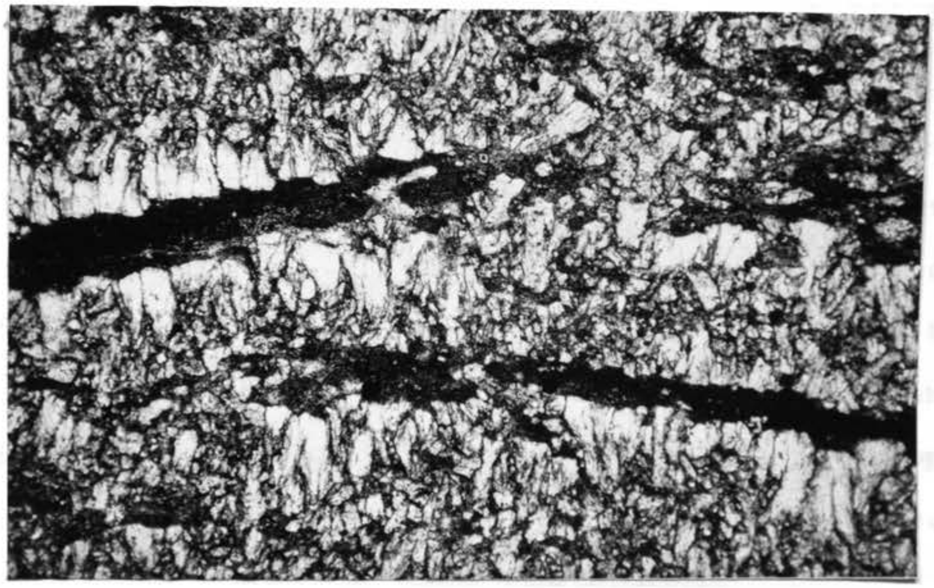

Fig. 44.

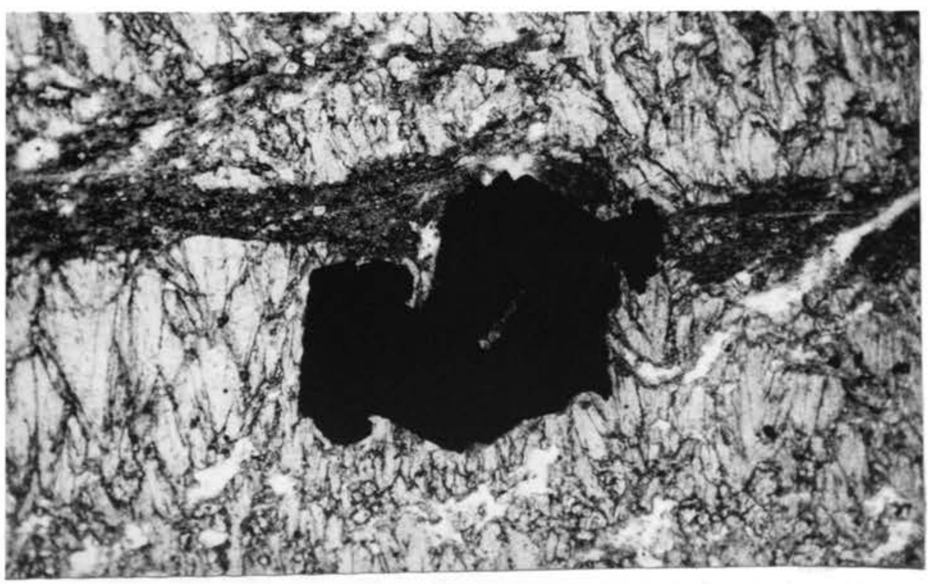

Fig. 45.

clay. Cones are seen to be grooved horizontally in thin section but do not show prominent annular depressions or ridges in hand specimen. These horizontal grooves have been called "chatter marks" by Shaub (1937) and "corrugations" by Woodland (1964). They form a discontinuous ledge around the cones and exhibit a triangular cross section (Fig. 50). Thin sheaths of clay may surround the long calcite crystals and clay is commonly concentrated in the "corrugations." The included clay in many cases can be identified as fragments of dolomitic shale which appear to have been ripped apart by the growth of the calcite.

Pettijohn (1957, p. 210) has stated:

> "The fibrous material antedates the formation of the cones inasmuch as the cone structure transgresses the fibers and normally extends across the fibrous seam."

Richardson (1923) made a similar observation on the cone-in-cone in the Blue Lias of Wales. However, this situation is not true for the Maquoketa cone-in-cone structures. In none of the specimens studied did the cone structure transgress the fibrous calcite layer.

The well-developed Maquoketa cone-in-cone can be divided into three distinct parts. The upper part, composed of larger crystals of fibrous calcite, shows the largest, best developed cone structures. Directly below the plane on which the apices of the larger cones terminate is a zone of microcones associated with minute lenses of shale. This zone in most cases is about 1/8 inch thick. The height of most microcones averages 0.1 mm. The composition of this zone is approximately 50 percent calcite and 50 percent shale, the greatest concentration of shale in any part of the cone-in-cone structure. Staining reveals the unusual fact that the calcite in this zone is exclusively the ferroan variety (Fig. 48). This zone is extremely regular and it is the only portion of the cone-in-cone structure that is composed of ferroan calcite. Even in the poorly developed layers where the larger cone-in-cone structure has been superceded by an aggregate of microcones, staining reveals a similar ferroan calcite zone. This ferroan zone may correspond to the "central parting" described by Richardson (1923) in the Blue Lias cone-in-cone structures. Richardson (1923) considered this "central parting" to represent the plane of weakness from which the development of the cone-in-cone proceeeded in both an upward and downward direction. No adequate explanation can be offered that would account for the concentration of ferroan calcite in this particular zone. However, because of the high clay concentration in this zone, one may speculate that the clay mineral (presumably illite) supplied the ferroan iron to the calcite lattice under some specialized and unknown conditions. Directly below the ferroan zone is an aggregate of extremely small, poorly oriented microcones (about one tenth the size of those in the ferroan zone) with subordinate amounts of clay. The contact between the ferroan zone and the extremely small microcones is also very abrupt.

One specimen thought to be typical of the well-developed cone-in-cone structures yielded an HCl acid

Fig. 46. Plan view of cone-in-cone structure. This specimen has been thin-sectioned in the region where the larger cones are terminated by smaller rounded calcite crystals. Sample from the outcrop at the Dundee Quarry. X24.

Fig. 47. This unusual sulfide mineral, thought to be pyrite, was only found in the cone-in-cone structure. The acicular habit of this mineral may be a reflection of the stress field in which the cone-in-cone structure is thought to have formed. (CDH # 76, L-3), X80.

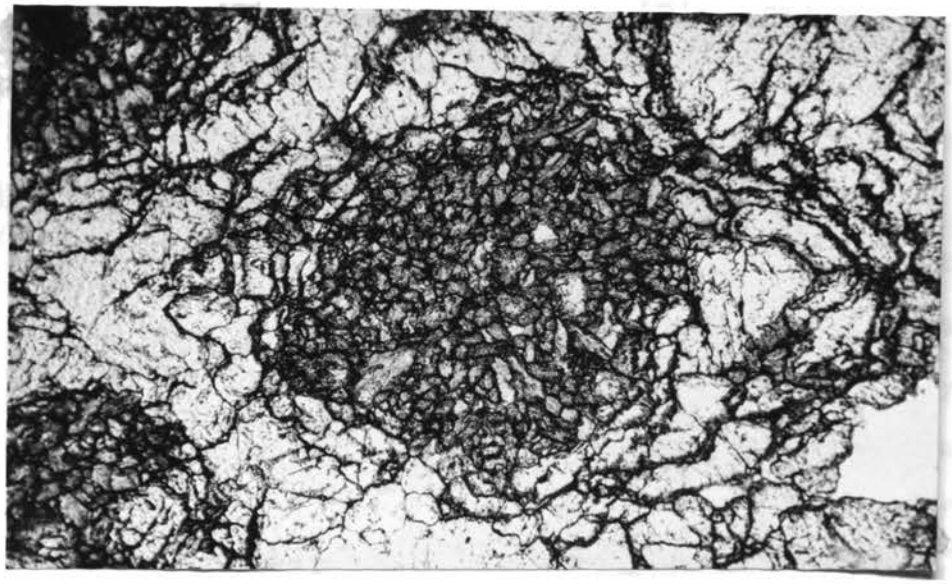

Fig. 46.

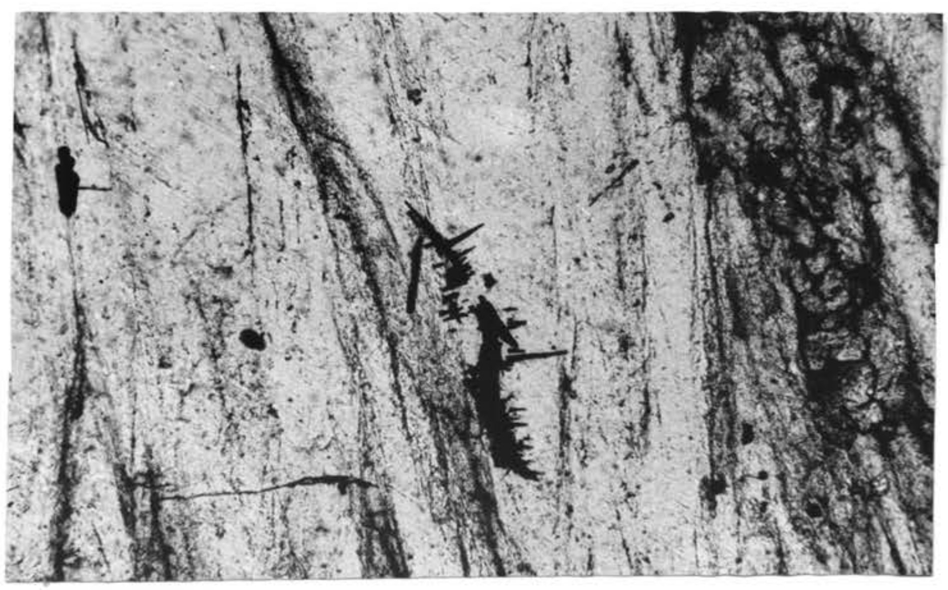

Fig. 47.

insoluble residue of 18.7 percent. Most of the insolubles consisted of clay but other minor minerals were present. In thin section, authigenic pyrite (Fig. 45) is common and a few included phosphate pellets were observed in the cone-in-cone. A sulfide mineral with an unusual acicular habit was seen in most of the cone-in-cone thin sections (Fig. 47). In no case was this mineral abundant enough to extract a large enough sample from insoluble residues for x-ray analysis. It is tentatively identified as pyrite which sometimes shows a similar habit. The acicular habit of this mineral may be a reflection of the stress field in which the cone-in-cone structure is thought to have formed.

A hosizontal view of the upper surface of the cone-in-cone layers gives the appearance of overlapping circular rosettes of terminated calcite crystals (Fig. 42). Under the binocular microscope the habit of these crystals appears to be a prismatic with elongated and distorted prisms, and rhombohedral terminations. In horizontally oriented thin sections the individual nature of the cones can also be observed (Fig. 46). The specimen illustrated in Fig. 46 has been sectioned in the region where the larger cones are terminated by the smaller rounded calcite crystals.

The origin of cone-in-cone structures has been a subject of much debate. The earliest workers in the early nineteenth century considered cone-in-cone structures to represent organic remains and applied such names as "Petrificato derbiensia" and "Cophinus dubius" to them

Fig. 48. Polished slab showing cone-in-cone structure. Specimen has been stained with alizarin red S (red areas-indicating calcite) and potassium ferricyanide (blue zone through center of specimen-indicating ferroan calcite). Specimen is from the Dundee Quarry (CDH # 76, L-2). X2.

(Tarr, 1932, p. 716). Recent workers however have recognized cone-in-cone as inorganic sedimentary structures. Most have considered them to be diagenetic, with their origin involving pressure-solution phenomena. Some workers, notably Shaub (1937), have hypothesized a primary origin for cone-in-cone structures. Shaub's (1937) theory involving settling and volume shrinkage during the slow dewatering of highly saturated and loosely packed sediments has not been generally accepted.

The carbonate in the Maquoketa cone-in-cone could have been supplied by diffusion of dissolved material from the original enclosing sediment, which was probably a marl, or perhaps from circulating interstitial water. The decay of organic material has been cited as a possible initiator for the deposition of calcite at localized centers (Woodland, 1964). However, in the Maquoketa no fossils were observed in the cone-in-cone layer. But the common occurrence of pyrite in the Maquoketa specimens would seem to favor a reducing environment. The apparent physical displacement of dolomitic shale by the growth of calcite crystals suggests that formation of the cone-in-cone structures took place before the sediments were completely consolidated. Woodland (1964, p. 290) has suggested that the original sediment probably still had a high water content when the cone-in-cone development was initiated.

True cone-in-cone structures are always restricted to cyclic limestone-shale sequences, limey shales and to the peripheral zone of carbonate concretions in shales. Clay

Fig. 49. The apex of this individual cone (central portion of photo) has been terminated by an aggregate of smaller, elongated calcite crystals with rounded ends. These smaller crystals are associated with relatively large amounts of clay minerals. Sample from the outcrop at the Dundee Quarry, X28.

Fig. 50. The vertical zone of triangular areas in this photo represent a higher magnification of the corrugations that are localized at edges of the individual cone that is illustrated above. The corrugations are filled with clay minerals and they represent a pressure-solution feature. Sample from the outcrop at the Dundee Quarry, X390.

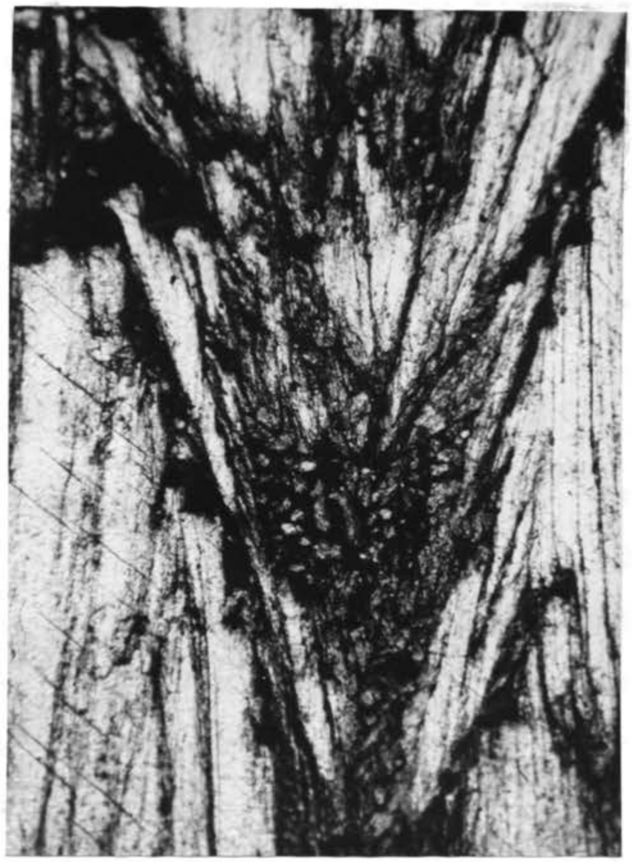

Fig. 49.

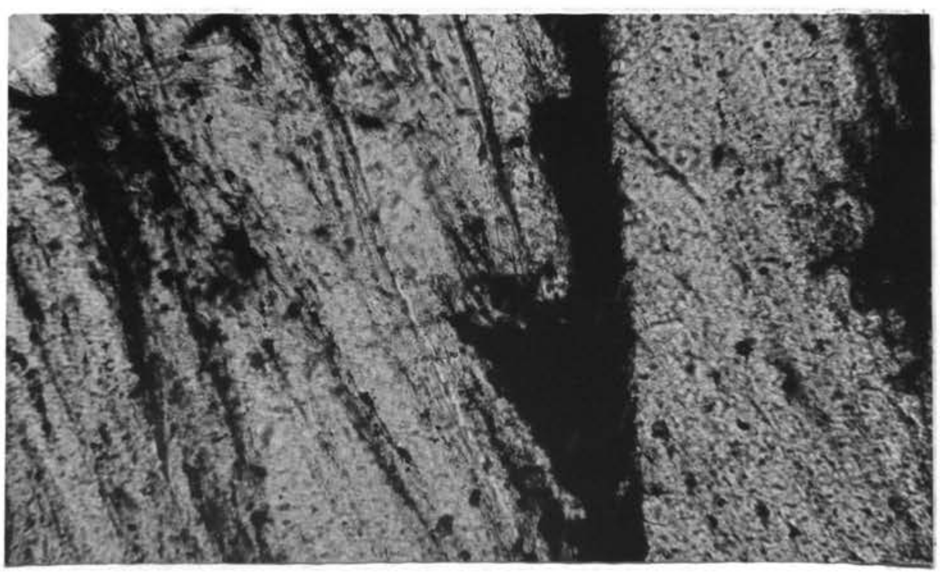

Fig. 50.

minerals are important in the formation of these structures.

The theory of origin postulated by Woodland (1964) in his monograph on cone-in-cone structures seems to be the most consistent with the evidence shown by the Maquoketa specimens. He visualized the original sediment in which the cone-in-cone formed as a fine meshwork of water-filled spaces between somewhat compacted lenses of clay and carbonate grains. Nucleation of calcite occurred on the surface of the clay lenses. Subsequent crystal growth was responsible for forcing the lenses apart. Although locally the small clay lenses were somewhat compacted, the overall sediment was still rather "loose." Much of the clay was incorporated between calcite crystals as growth proceeded. Woodland (1964) considered that crystal growth away from the clay lenses would have been favored because lateral growth would have been competitive, with interference by neighboring nuclei. Theoretical thermodynamic considerations by Kamb (1959) would seem to favor this type of crystal growth. He has shown that in a hydrostatic stress field the weakest axis of a crystal will tend to align with the greatest principal pressure axis. In calcite the weakest direction is parallel to the c-axis. The weight of overlying sediments may have been sufficient to produce a stress field in which the cone-in-cone layer formed. Following Woodland's (1964) theory, the lateral gradation of well-developed cone-in-cone structures to a less well defined zone of microcones associated with clay lenses could be explained by differences in the compaction of the original sediment. Well-defined larger cones developed where layers and lenses of clay were larger and more coherent. During calcite crystallization these more compacted clay layers and lenses were physically deformed. The microcones developed in sediments less compacted, and where there was a more uniform dispersion of smaller clay aggregates and lenses. The dispersed clay particles acted as shields which discouraged the growth of larger calcite crystals. The clay lenses also served as stable "substrata" required for the growth of larger calcite crystals. Fig. 44, a section through the microcone zone, exhibits the largest calcite crystals growing on included clay lenses. The area between included clay lenses has a high content of smaller clay particles and subsequent calcite development was inhibited. In the Maquoketa specimens the upward vertical gradation from microcones to well developed cones can probably also be explained by a similar differential compaction between adjacent horizons. Orientation of cones in predominantly one direction may be related to the direction and mode of supply of ions in the early stages of nucleation (Woodland, 1964). Woodland's (1964, p. 299) explanation of the formation of the cone structure involves calcite growth in a stress field:

> "It may be, however, that the stress state existing in the environment of crystallization controls not only the lattice orientation of the fibrous calcite but also the differential growth of the calcite that produces the macrocones; for example, the growth may be influenced by cylindrical zones of varying rates of calcite deposition

> concentric to random axes which become the eventual macrocone axes...If the cone axes are parallel to the direction of maximum stress, cylindrical zones around the axes will parallel potential tensional surfaces. Orientation of macrocones around a common axis...arises from a control of the axial position determined by original differences in the clay medium at the time of initiation of crystallization."

The annular corrugations around cones can probably be explained by solution of calcite due to pressure caused by the weight of overlying sediments (Pettijohn, 1957, p. 210). It may be that the orientation of the outer edge of the corrugation conforms to the $(11\bar{2}0)$ crystallographic direction in which calcite is most soluble (Honess, 1927, p. 21).

VI. Diagenesis

A. General Statements

Reconstruction of ancient environments of deposition requires more exact knowledge of the post-depositional changes that have taken place in sediments. This is especially true for carbonate rocks. The majority of carbonate rocks were originally chemically or biochemically precipitated in the form of thermodynamically unstable compounds (i.e. aragonite, Mg-rich calcite, and vaterite). An examination of the geologic record reveals a decreasing amount of these unstable carbonates with increasing age. Hence we conclude that certain replacements or transformations of these unstable compounds by stable carbonates has taken place. Likewise clastic sediments are subject to extensive but usually more subtle diagenetic changes. These sediments were derived from preexisting rocks and were subject to varying degrees of alteration in response to weathering, transportation, and the depositional environment. Logically we would expect certain changes in texture, porosity, and the preservation of organic and sedimentary structures to accompany these mineralogical changes. Also, authigenic minerals replacing the original constituents are a very common feature in rocks of both a chemical and clastic origin. The interpretation of secondary features as primary textures and structures may lead to erroneous environmental conclusions. In order to confidently suggest an environment of deposition, one must consider the diagenetic changes, both chemical and physical, that have taken place when hypothesizing the nature of the original sediment.

There is no generally accepted definition of the term "diagenesis." Krumbein (1942) cited more than 30 processes that have been included under the name "diagenesis." Many confusing and burdensome terms as epigenesis, katagenesis, neogenesis, syndiagenesis, andiagenesis, aquatolysis, epidiagenesis, halmyrolysis, metaharmosis, etc. have been coined to denote special types and phases of diagenesis. Most of these terms seem superfluous since the physical and chemical conditions for many diagenetic processes are not well understood. The more generalized, and all encompassing, definition of Twenhofel (1939) would seem to better express the term "diagenesis" as used in this paper:

> "Diagenesis includes all modification that sediments undergo between deposition and lithification under conditions of pressure and temperature that are normal to the surface or outer part of the crust, and in addition, those changes that take place after lithification under the same conditions of temperature and pressure, which are not katamorphic in character so that the effect is delithification." (Twenhofel, 1939, p. 254.)

In the Maquoketa rocks, the most important diagenetic changes are those involving the recrystallization of calcite and the formation of other authigenic minerals. Guest-host relationships were determined by criteria cited by Swett (1965, p. 931). These include cross-cutting relationships of authigenic minerals to structural and textural features, syntaxial overgrowths, relic mineral inclusions, euhedral crystals in an otherwise clastic texture, loss of structural details resulting in "ghost structures," mineral incompatability with structures such as silicified fossils, and mineral pseudomorphs. In this paper, diagenesis is first considered in order of approximate abundance of authigenic minerals and not, for the moment, in their order of appearance.

B. Dolomite

Dolomite is the most abundant authigenic mineral in the Maquoketa. It has been found in all Maquoketa lithologies, and individual occurrences have been discussed previously in the section on petrography. Much of the dolomite encountered was the non-ferroan variety. However, in the marlstones, much, perhaps all, of the dolomite was the ferroan type. Considerable disagreement exists concerning the nomenclature of iron-bearing dolomites. Dickson (1966) has considered this problem and it will not be discussed here. In this study, the term "ferroan dolomite" is applied to all dolomites that were stained blue by potassium ferricyanide.

According to Friedman and Sanders (1967), all dolomites owe their origin to hypersaline brines, either in the depositional or post-depositional environment. The following observed characteristics of the Maquoketa dolomites are offered as evidence of an authigenic origin:

1) euhedral crystals, more or less uniform in size in an otherwise clastic

matrix (Fig. 28, Fig. 29). Friedman and Sanders (1967) have considered small grain size and euhedral crystals as indicators of a syngenetic origin;

2) dolomite rhombohedra cross-cutting allochems (Fig. 24);
3) dolomite crystals commonly nucleated by syngenetic pyrite and/or fine organic material (Fig. 51, Fig. 52). Taft and Harbaugh (1964, p. 43) have figured dolomites with similar nuclei from recent carbonate sediments of Florida. They have considered these dolomites to be authigenic;
4) zoned dolomite crystals with cloudy centers and clear rims (Fig. 51) indicating subsequent enlargement of original dolomite crystals as optically continuous overgrowths.

The formation of dolomite was an early diagenetic event, having taken place before consolidation of sediments was completed. Dolomitization was preceeded by the formation of syngenetic pyrite and by neomorphism of calcite mud, as indicated by included pyrite nuclei and cross-cutting relationships. Included fragments of shale in the cone-in-cone structures yield some evidence as to the relative time of dolomitization. The cone-in-cone

Fig. 51. Euhedral dolomite crystals exhibiting a nucleated and cloudy center with relatively clear outer rim. This type dolomite crystal is very common in the shales. (CDH # 76, S-12), X440.

Fig. 52. Euhedral dolomite crystal, from the shale, nucleated by finely disseminated pyrite grains. This type crystal is also very common in the shale. (CDH # 76, S-7), X440.

Fig. 51.

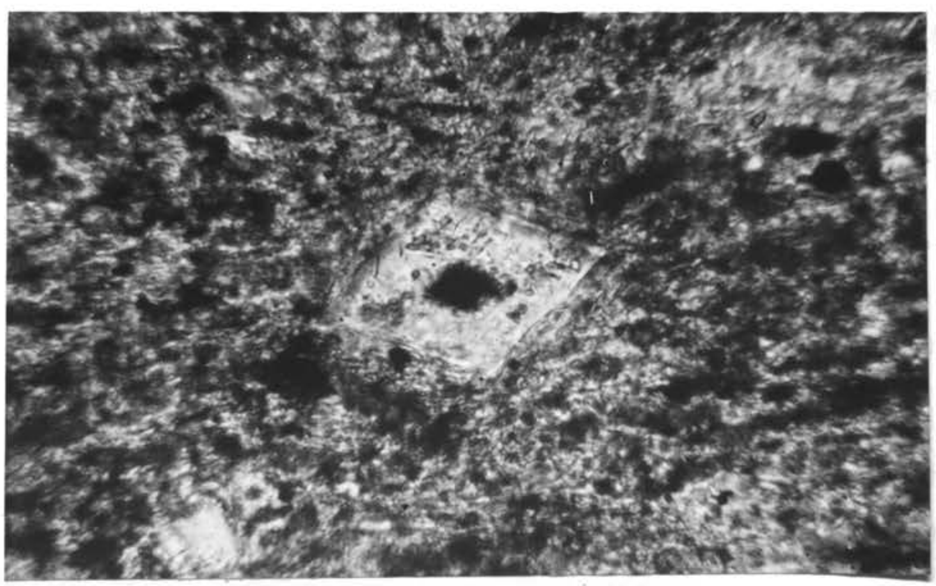

Fig. 52.

structures commonly contain included fragments of shale that were apparently ripped apart by the crystallization of the fibrous calcite. The included shale fragments contain small euhedral dolomite crystals identical to those found in the surrounding limestones and shales. Dolomite was not found in any other part of the cone-in-cone structure (i.e. as dolomite cross-cutting calcite fibers). Therefore, it is believed that dolomitization preceeded cone-in-cone formation, which has been demonstrated to have been an early diagenetic event accomplished in loosely consolidated sediments. An early diagenetic origin for the Maquoketa dolomite would be consistent with observations made in recent sediments by Shinn et al. (1965) and Illing et al. (1965).

Fairbridge (1957) concluded that dolomite (both primary and replacement types) was formed relatively close to land. More recent studies do not lend much support to Fairbridge's (1957) hypothesis. Kahle (1965) has demonstrated that, with the exception of dolomite-evaporite sequences, dolomitization is not always associated with shallow water or shoaling conditions. Most workers agree that dolomitization took place by the addition of Mg ions to Mg-rich calcite or aragonite with a subsequent change in crystal structure (Fairbridge, 1957, Friedman and Sanders, 1967, Kahle, 1965, and Shinn et al., 1965). Fairbridge (1957, p. 149) has suggested that "the metasomatic change-over to dolomite requires a special environment of the marine realm, under moderate pressure and sufficiently in contact with the ocean to receive adequate Mg^{++} ions but sufficiently isolated to permit elevated alkalinity and concentration." Friedman and Sanders (1967) and Muller (1967) also considered elevated salinity necessary for dolomitization to take place. A chemical environment identical to the one described above could be accomplished in the pore space of freshly deposited sediments by the concentration of interstitial waters. Lalou (1957) has demonstrated that bacteria can aid precipitation of dolomite in freshly deposited sediments. Abundant organic material, elevated temperatures, shallow water, maximum light and sunshine are required for the formation of dolomite by bacteria. Zobell (1942) measured pH, caused by sulfate reducing bacteria, up to 8.9 in marine cores. However, dolomite produced by bacterial action would be restricted to water depths less than 100 meters (Friedman and Sanders, 1967). Friedman and Sanders (1967) concluded that conditions required for the formation of authigenic dolomite were best fulfilled in tropical lagoons which were isolated from the open marine environment.

Seawater has been frequently suggested as the source of the Mg ions required for the formation of dolomite. Kahle (1965) has pointed out that seawater probably could not have provided sufficient Mg ions for extensive dolomitization (as in the Maquoketa marlstones). He, Kahle, suggested that ion exchange of Mg ions between clay minerals and interstitial waters could have supplemented Mg ions supplied by sea water. The greater amount of dolomite in the Maquoketa marlstones and shales than in the limestones seems to lend support to Kahle's (1965) argument. However, the increase in dolomite content in the shales and marlstones going upward stratigraphically probably represents favorable chemical conditions other than the availability of Mg ions.

The concept of "seepage reflux" (Adams and Rhodes, 1960) does not seem to be the most appropriate explanation for the Maquoketa dolomite. Dolomite produced by seepage reflux, a downward migration of denser supersaline sea water, is usually associated with evaporite minerals. No evaporite minerals or evidence of previous evaporite minerals since removed (i.e. breccia caused by solution of evaporites between limestone or shale beds, crystal molds of evaporite minerals, etc.) was discovered in the Maquoketa rocks. Instead, it seems more likely that dolomite precipitated out of supersaline water that had been concentrated in pore spaces in the limestone and shale. Concentration of Mg ions in the interstitial water may have been supplemented by ion exchange with clay minerals. In the limestones, dolomitization may have selectively taken place on original Mg-rich calcite grains. In the shales, evidence for any primary carbonate minerals is lacking and dolomite is thought to have precipitated directly into pore spaces from interstitial solutions. Small pyrite crystals and organic fragments produced micro-reducing environments favorable to the initiation of dolomite precipitation. These fragments served as nuclei for growth of the dolomite crystals.

The source of iron for the ferroan dolomites in the marlstone could possibly have been supplied to the dolomite lattice during precipitation by clay minerals. Carroll (1958) has demonstrated that clay minerals are capable of transporting iron, in several different ways, which in turn may be removed by a change in chemical conditions in the post depositional environment.

C. Calcite

Neomorphism of carbonate mud to micrite is an early diagenetic change in the Maquoketa rocks. Although direct evidence is lacking concerning the time of this event, cross-cutting relationships suggest that only pyrite formed before neomorphism took place. As the mineralogical composition of the original mud is unknown, Folk's (1965) term "neomorphism" is preferred to the term "recrystallization." Agrading neomorphism of micrite produced microspar and small amounts of pseudospar. Folk (1965) considered neomorphism, a special type of replacement between the same mineral or polymorphs, to have taken place in the solid state with the aid of interstitial solutions. Folk (1965) also considered the change from micrite to microspar to have been a volumetrically important change with approximately nine-tenths of the original grains (assumed to have been no more than 4 microns in diameter) consumed. The patchy gradation from micrite to microspar, shown in most thin sections, suggests that recrystallization took place by a process Folk (1965) has

Fig. 53. Higher magnification of a typical microsparite. Note that crystals are relatively clear and grain boundaries are interlocking. (WW-6), X200.

Fig. 54. Central portion of photo represents a patch of microspar in a micritic matrix. Note the gradation between micrite and microspar. Euhedral dolomite crystals are moderately abundant. (ST-11), X80.

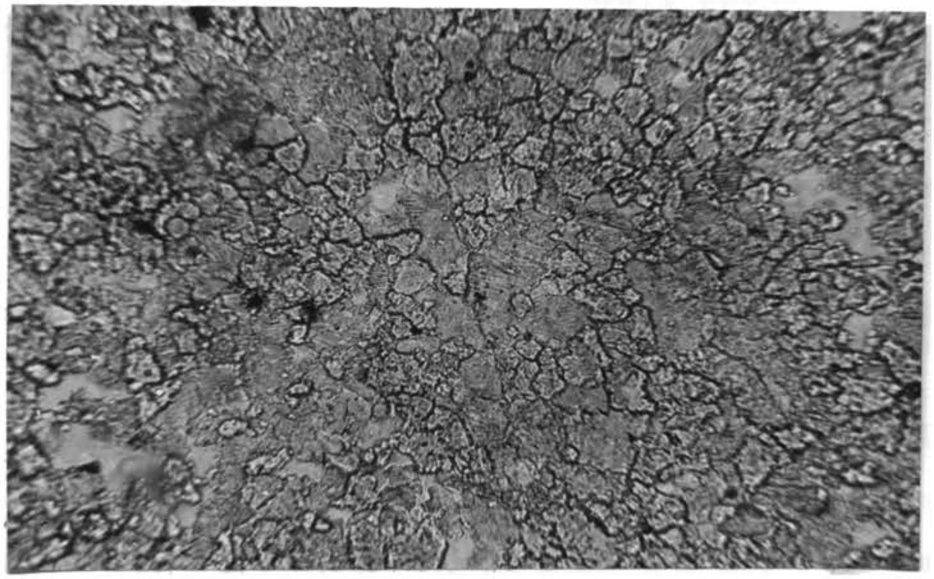

Fig. 53.

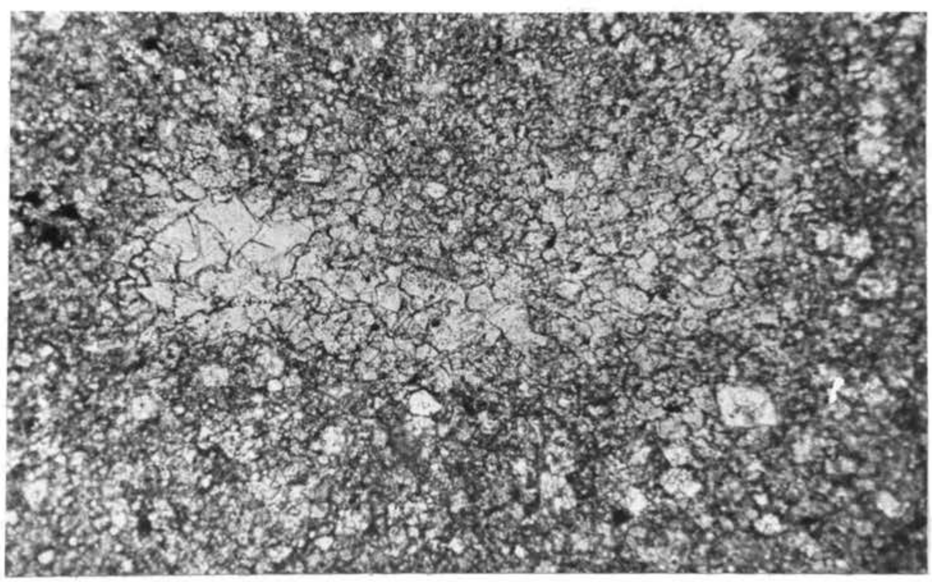

Fig. 54.

termed "porphyroid neomorphism" (Fig. 54, Fig. 56, Fig. 58, Fig. 59). Recrystallization has started at spaced centers instead of preceeding uniformly throughout the entire rock. The cause of the incipient recrystallization which caused this "clotted" texture is not clear. Carozzi (1960) has suggested that this texture may be due to the recrystallization of a mud composed of a mixture of calcite and aragonite, with the aragonite more susceptible to diagenetic changes.

The difference in diaphaneity between the micrite and microspar is shown particularly well by the specimen in Fig. 58. Most microspar grains were equant, but some larger grains exhibited a "loaf-like" form which Folk (1965) considered to be characteristic of certain microspar crystals.

Generally the microspar crystals in the Maquoketa exhibited less tendency to form interlocking grain boundaries than did void filling calcite spar. It also seemed as if the void filling calcite spar exhibited a greater degree of clarity than did the microspar.

Patches of microspar had no preferred orientation to the bedding. Microspar often formed fringes around fossil fragments and clay lenses (Fig. 56).

The processes involved in the recrystallization of $CaCO_3$ are not well known. Both Bathurst (1958) and Folk (1965) have advanced some theories and reviewed much of the earlier ideas on the subject. Folk (1965) discovered that all of the microspar that he had studied either

Fig. 55. Although the calcite in this specimen resembles the gradational micrite-microspar, it is another view of the void filling under the partially enrolled trilobite carapace illustrated in Fig. 16 and Fig. 17. The areas of included micrite represent sections of the cavity wall that protrude into the spar. Note that the void filling spar exhibits a greater degree of clarity than any of the neomorphic calcite types observed in the Maquoketa. Sample from the outcrop at the Stark Nursery (ST) section. X28.

Fig. 56. This rock also exhibits a patchy gradation between micrite and microspar. Note in particular the fringe of microspar crystals around the lense of clay (black area) in the upper left hand quadrant of the photo. (ST-13), X80.

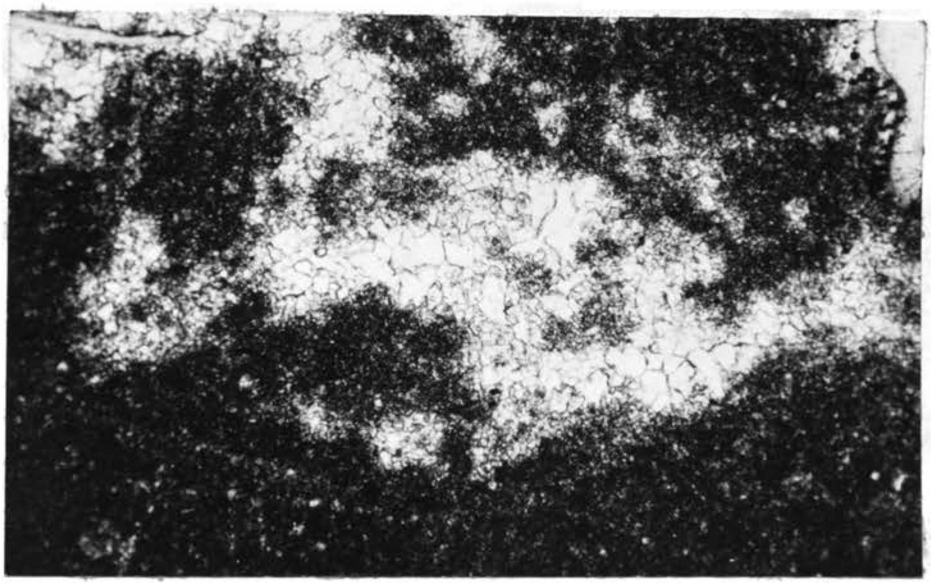

Fig. 55.

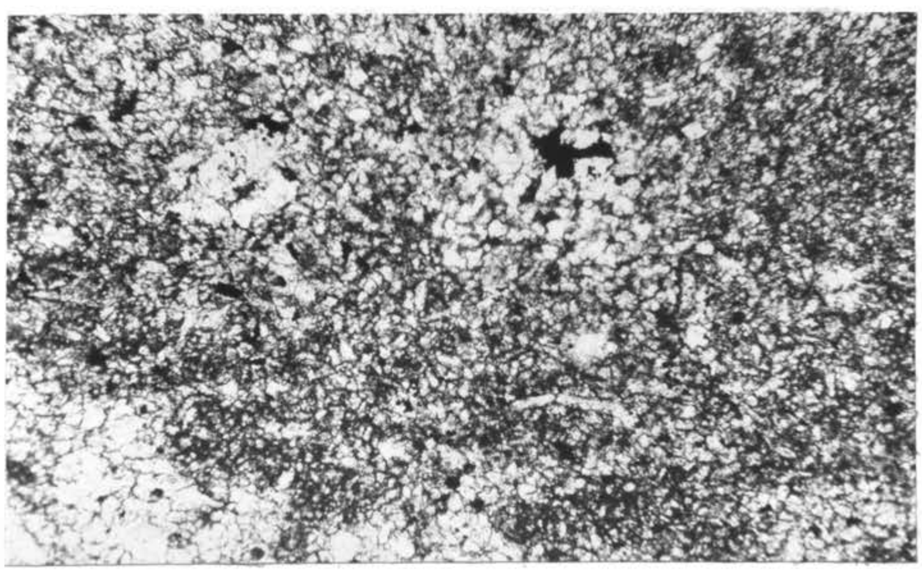

Fig. 56.

Fig. 57. The large area of spar in the center of this marlstone is thought to represent void filling. However, the origin of this cavity is problematical. (CDH # 76, S-14), X28.

Fig. 58. This limestone also exhibits a patchy gradation between micrite and micro-spar. Areas of microspar are clearer, since clay minerals have been excluded during neomorphism. (ST-28), X80.

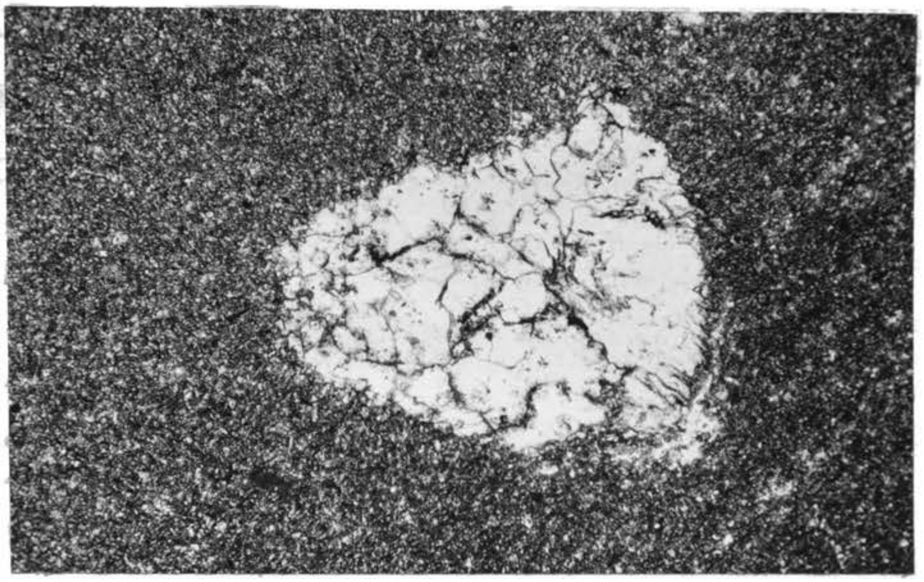

Fig. 57.

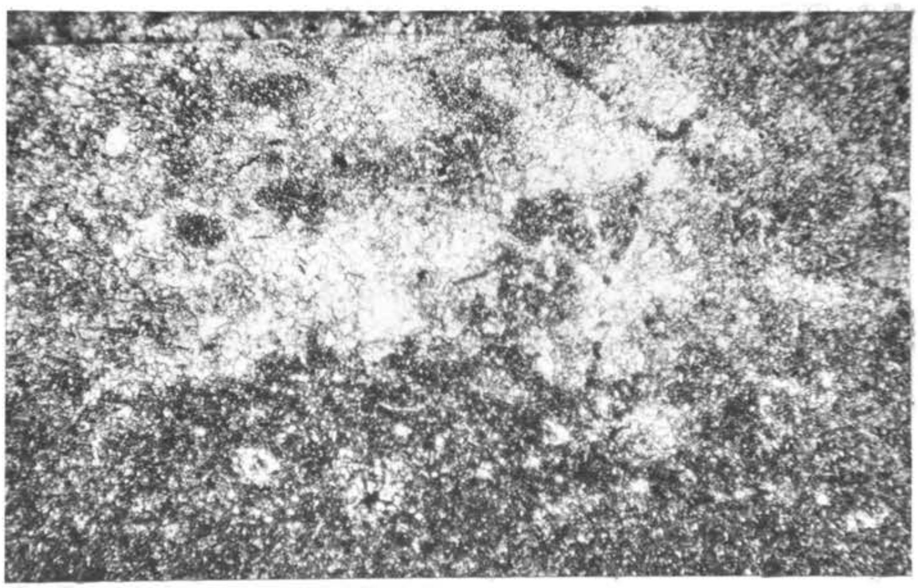

Fig. 58.

changed facies into clay beds or were interbedded with shales. Most of the Maquoketa limestones would fit into the microspar category using Folk's (1962, 1965, 1968) size criteria in differentiating micrite from microspar. Folk was unable to explain this association between clay minerals and microspar adequately.

Although microspar occasionally grades into pseudospar (Fig. 58), most grains of neomorphic calcite do not attain a diameter greater than 25 microns. Some original aragonitic and calcitic fossils have recrystallized to pseudospar. Fig. 66, thought to be a pelecypod fragment, exhibits fine zones of pyrite along what was probably original zones of organic material between fibrous crystals of the original shell material (Brown, 1966). The shell material is now composed of pseudospar and the pyrite is still arranged in parallel zones. This evidence strongly suggests a neomorphic origin for the calcite. Had the original shell material been dissolved and the cavity later filled by void-filling sparry calcite, the pyrite would have been redistributed.

Fig. 65 illustrates a bryozoan that has been almost completely obliterated by degrading recrystallization. Were it not for the small areas of pyrite replacement, this "ghost fossil" probably would have been overlooked. A careful search revealed a number of other partially recrystallized calcareous fossils. Those which had been partially replaced by pyrite were easily detected. Those which had not been replaced by any pyrite were difficult

Fig. 59. Patches of clear microspar in darker colored matrix of micrite. These irregularly distributed patches of microspar in micrite produce a "clotted" texture. (ST-23) X24.

Fig. 60. Higher magnification of above, showing "loaf-like" microspar crystals which Folk (1965) considered characteristic of certain microspar crystals. Note that clay and other impurities have been removed and pushed into interstitial corners by recrystallization. (ST-23) X150.

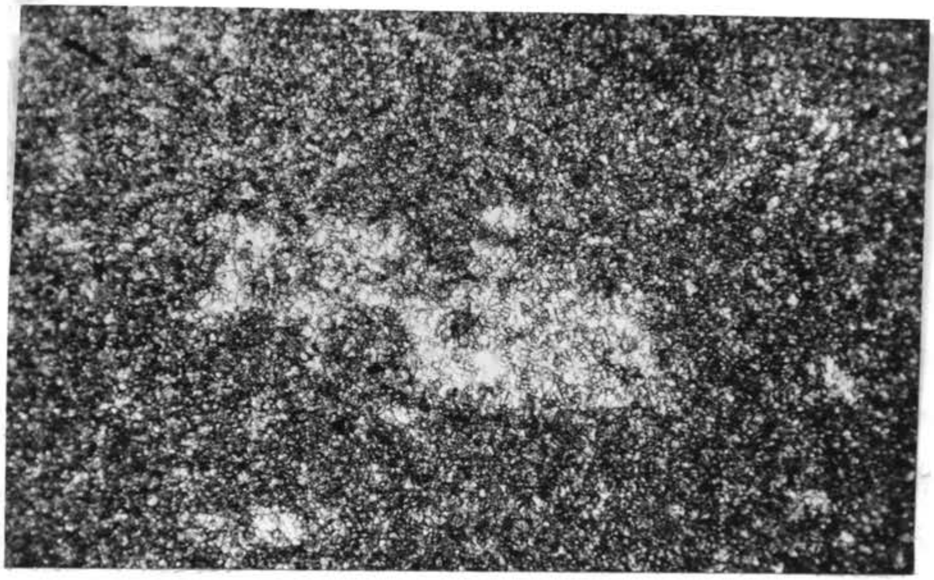

Fig. 59.

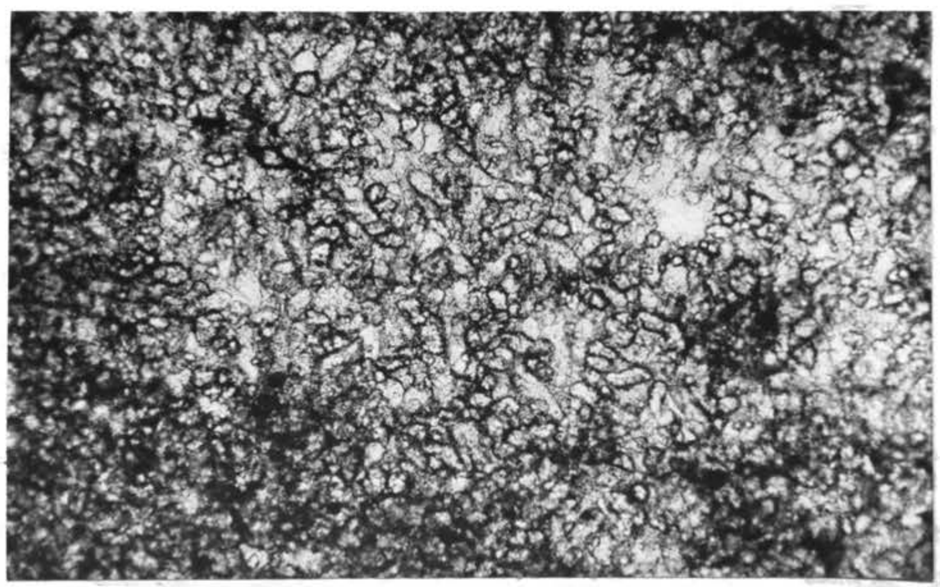

Fig. 60.

to discern. Banner and Wood (1964, p. 21) have demonstrated that microfossils are recrystallized in a "constant order related to the biological affinities of the fossil genera." This selective recrystallization is probably a function of the original crystal structure and mineralogy of the organisms' skeletal material. Although not enough fossils are present in the Maquoketa to predict an order of recrystallization, it appears that certain bryozoa and ostracodes were most affected by this selective recrystallization. The Maquoketa was probably never very fossiliferous, but these "ghost fossils" demonstrate that part of the original fauna has been obliterated by calcite recrystallization.

The occurrence of void filling calcite spar has previously been discussed. The formation of this mineral is probably also an early diagenetic event, following neomorphism and based on scanty petrographic evidence, probably after dolomitization.

Ferroan calcite occurs predominantly as pore filling cement (in the shales) and as fracture filling (in the limestones and siltstone). It was probably one of the last authigenic minerals to form, and in no example was it very abundant. The presence of fractures implies that the rocks possessed some degree of induration at the time of fracture filling (Fig. 61, Fig. 62). Also, ferroan calcite was not observed replaced by any other minerals. Oldershaw and Scoffin (1967) have also noted ferroan calcite to occur as pore fillings in their study. They

Fig. 61. Fractures filled by ferroan calcite in the dolomitic quartz siltstone. The presences of fractures implies that this rock possessed some degree of induration at the time of fracturing. (GC-2), X24. Plane polarized light.

Fig. 62. Same as above. Crossed nicols.

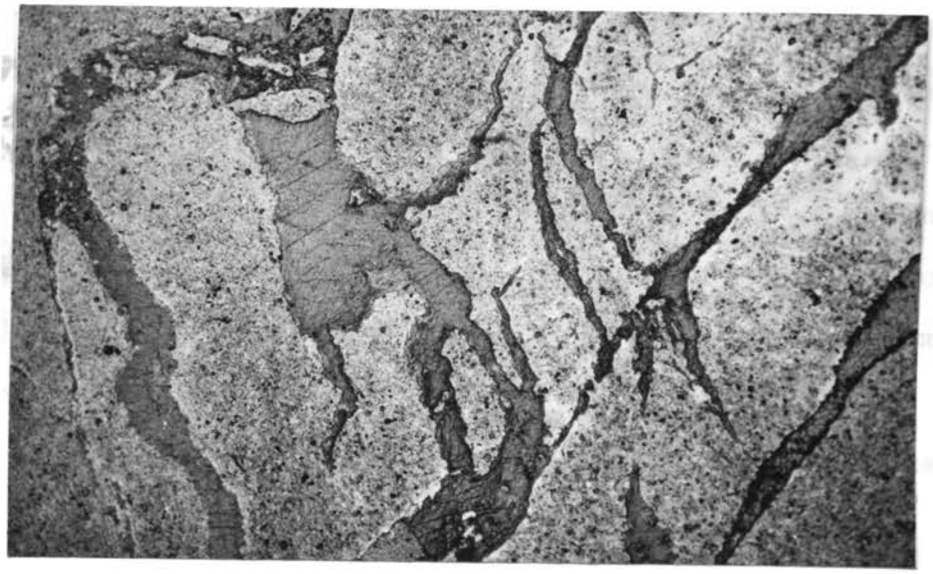

Fig. 61.

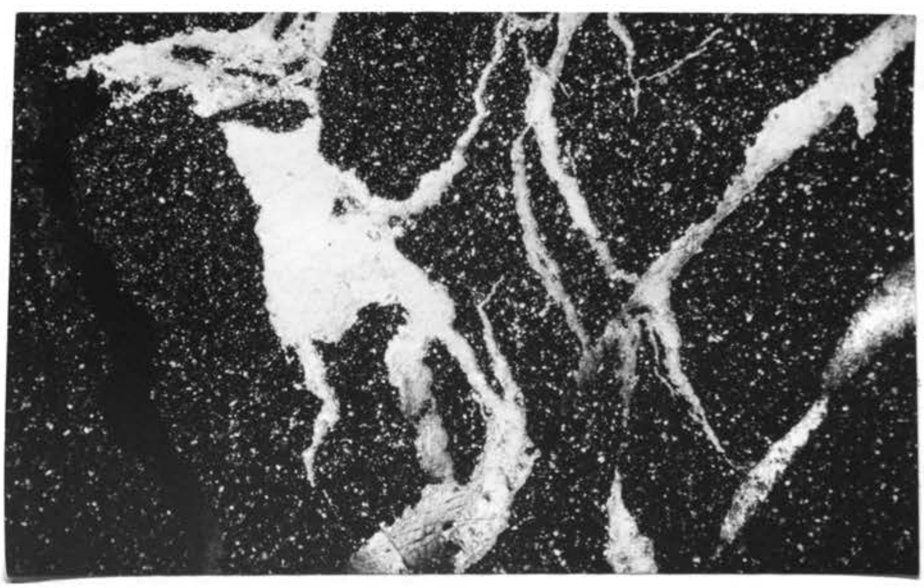

Fig. 62.

observed that ferroan calcite was only found in argillaceous limestones or where thin limestone beds were directly in contact with shale beds. A similar situation exists concerning the distribution of ferroan calcite in the Maquoketa rocks. Oldershaw and Scoffin's (1967) observations seem to lend support to the suggestion made earlier in this paper that clay minerals might have provided the ferroan ion to the calcite lattice in some unknown manner.

In addition, a few rare examples of coarse-grained calcite crystals replacing the dolomitic marlstone were also encountered (Fig. 68).

D. Pyrite

Pyrite is also a very common authigenic mineral in Maquoketa rocks of all lithologies. Most commonly it occurs as small disseminated single crystals (Fig. 64). Larger euhedral cubic crystals and crystal aggregates are also present (Fig. 26, Fig. 40, Fig. 63). Pyrite partially replacing calcareous fossils was frequently encountered (Fig. 18, Fig. 65, Fig. 66, Fig. 69).

The formation of pyrite requires an alkaline reducing environment and the presence of a supply of sulfur and iron ions. The presence of this mineral reflects chemical conditions in the post-depositional environment. Implications concerning the environment of deposition can be made in certain instances. Bathurst (1964, p. 333) has pointed out that "It is now generally realized that the presence

Fig. 63. Growth of this large pyrite crystal (black area) and compaction of soft clays has disrupted the parallel laminations of this particular shale specimen. Smaller black areas in this photo are also pyrite. (CDH # 63, S-4), X28.

Fig. 64. Note the high concentration of closely spaced small pyrite crystals in this sample of micrite. A higher magnification of these small rounded pyrite crystals reveals that they are not spherulites, but euhedral pyritohedra. (ST-18), X80.

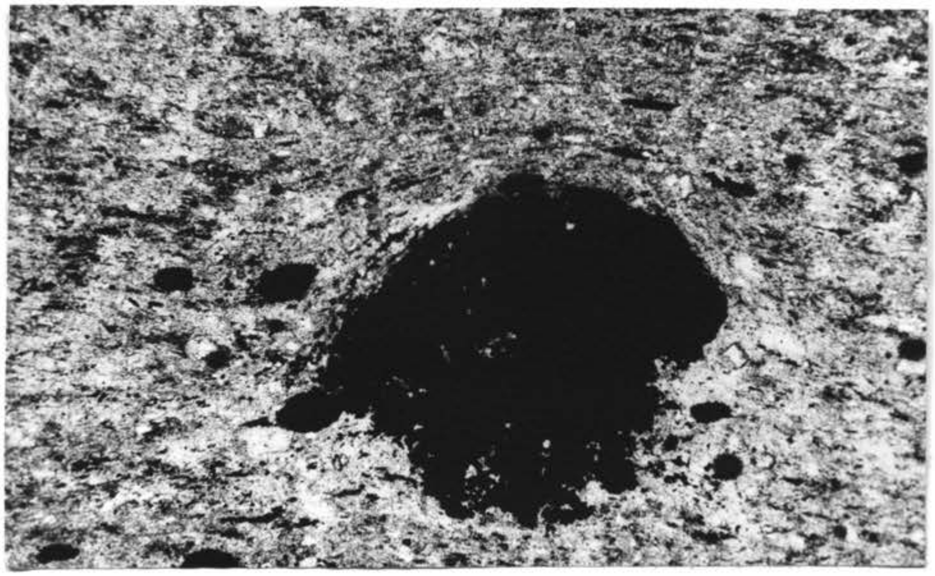

Fig. 63.

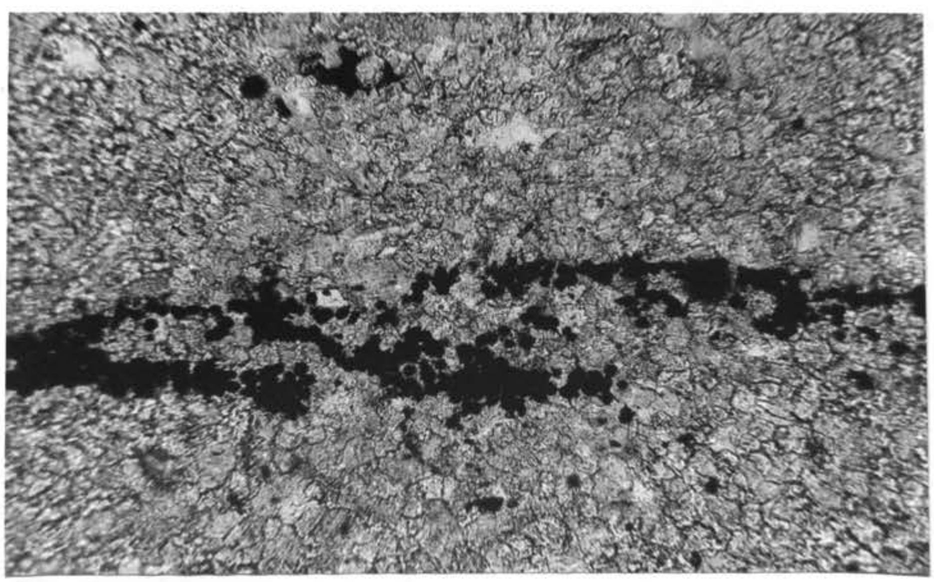

Fig. 64.

of pyrite in a sediment is by itself no indication that the water above the sediment was poorly oxygenated or that benthonic life was impeded." Ginsburg (1957) has reported the occurrence of iron sulfides less than one inch below the sediment-water interface in the shallow water carbonate muds of Florida Bay. He concluded that "...shallow Florida Bay acts like a barred or stagnant basin where... the environment of early diagenesis leaves perhaps a permanent record, and its recognition might prevent a deep-water basinal interpretation for sediments deposited in a few feet of water" (Ginsburg, 1957, p. 88). Petrographic evidence indicates that the Maquoketa pyrite was a product of early diagenesis, produced in an alkaline reducing environment. An early diagenetic origin for the Maquoketa pyrite is indicated by the deformation of soft shale by crystal growth (Fig. 63), partial replacement of calcareous fossils by pyrite before neomorphism (Fig. 65, Fig. 66) and by small pyrite crystals nucleating dolomite crystals (Fig. 28, Fig. 52). The lack of organic burrows and pellets, along with the preservation of fine pyrite laminations and organic material, indicates a strongly reducing post-depositional environment. The sparseness of fossils, if not just a matter of non-preservation, seems to lend support to a somewhat alkaline reducing environment of deposition inhospitable to most forms of life.

Recent experimental studies by Berner (1969) have provided insight into the formation of authigenic pyrite. He has shown that variability in the content of organic

Fig. 65. "Ghost" bryozoan has been almost completely obliterated by degrading calcite recrystallization. Presence of fossil is emphasized by the small pyrite crystals (black spots) that have partially replaced it. (ST-23), X80.

Fig. 66. This fossil fragment, thought to be a pelecypod, exhibits fine zones of pyrite along what was probably original zones of organic material between fibrous aragonite crystals of the original shell material. The shell material is now composed of pseudospar, a product of neomorphism. (WW-6), X80.

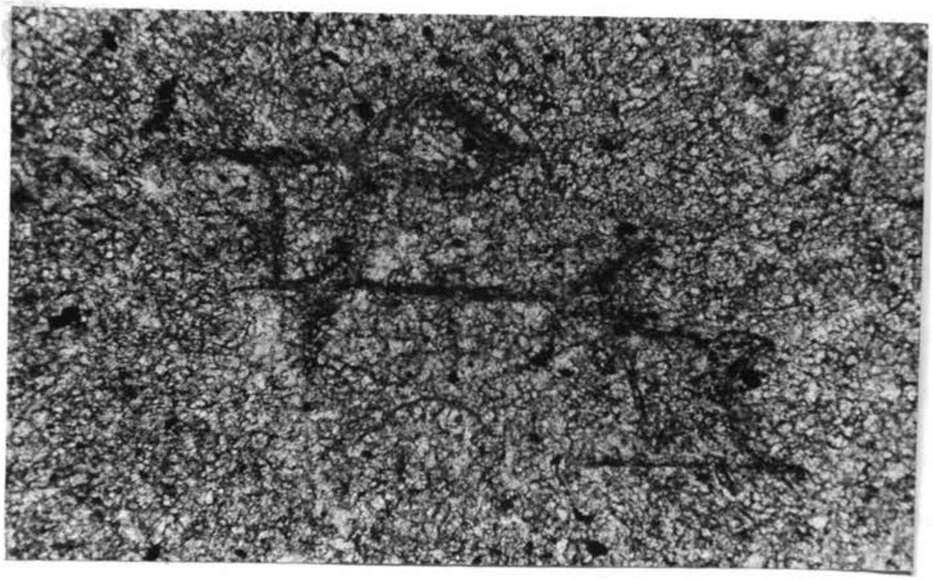

Fig. 65.

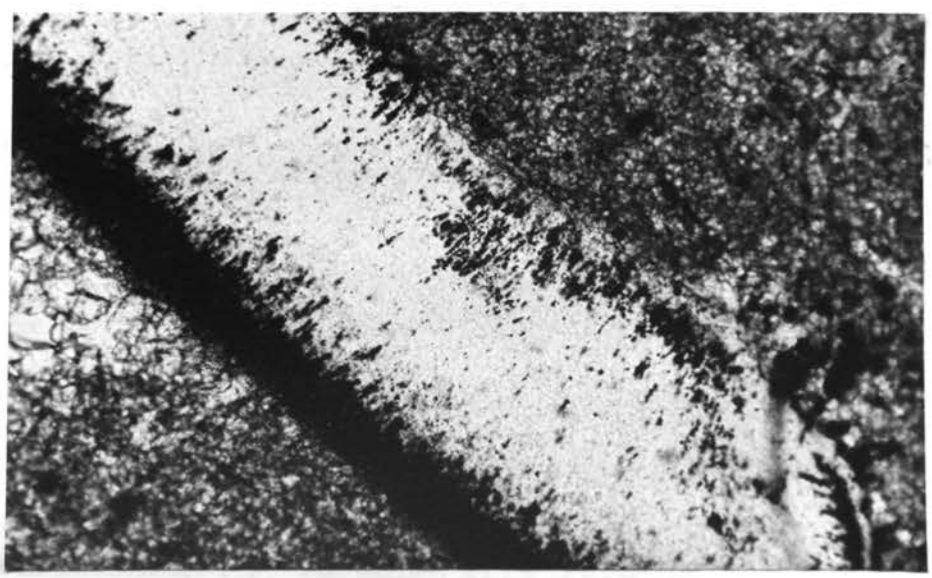

Fig. 66.

material in an otherwise homogeneous anaerobic sediment can bring about migration of iron and sulfur ions which is followed in some cases by localized concentrations of iron sulfides. Thin pyrite laminations and thicker pyrite zones (Fig. 15, Fig. 26) probably represent areas that originally had a higher content of organic material and therefore were more susceptible to pyritization. Sulfur ions were probably produced by bacterial reduction and the breakdown of sulfur-containing organic compounds within organic rich zones which resulted in the formation of H_2S which in turn reacted with iron to form iron sulfides. Iron could have been supplied to these localized zones of high sulfur content by the upward migration of Fe ions, derived from detritals (Berner, 1969). The same reasoning may also be applied to the origin of the pyritized fossils in the upper marlstone (Fig. 77, Fig. 78). A similar origin for syngenetic pyrite not intimately associated with organic remains is also suggested. Berner (1969) has shown that the bacterial generation of H_2S in an organic-rich region can lead to darkening and iron sulfide formation in the surrounding organic-poor sediment to a distance much greater than the size of the organic region.

E. Silica

Silicification is generally rare in the Maquoketa. Examples were found in the micrite, marlstone and siltstone. Authigenic silica was most abundant and showed a greater diversity of forms in the siltstones. The silica

Fig. 67. Section of void, filled with sparry calcite (light gray area at left side of photo) in a micritic matrix. Mosaic quartz (white area) has begun to replace calcite spar along margin of void. Sample from the outcrop at the Stark Nursery (ST) section, X28.

Fig. 68. Dolomitic marlstone (darkest gray areas showing euhedral dolomite crystals) has been partially replaced by calcite spar (light gray areas) which in turn has been partially replaced by mosaic quartz (white areas). It appears that silicification was restricted to those areas that had previously been replaced by calcite spar. Sample from the outcrop at the Dundee Quarry, X28.

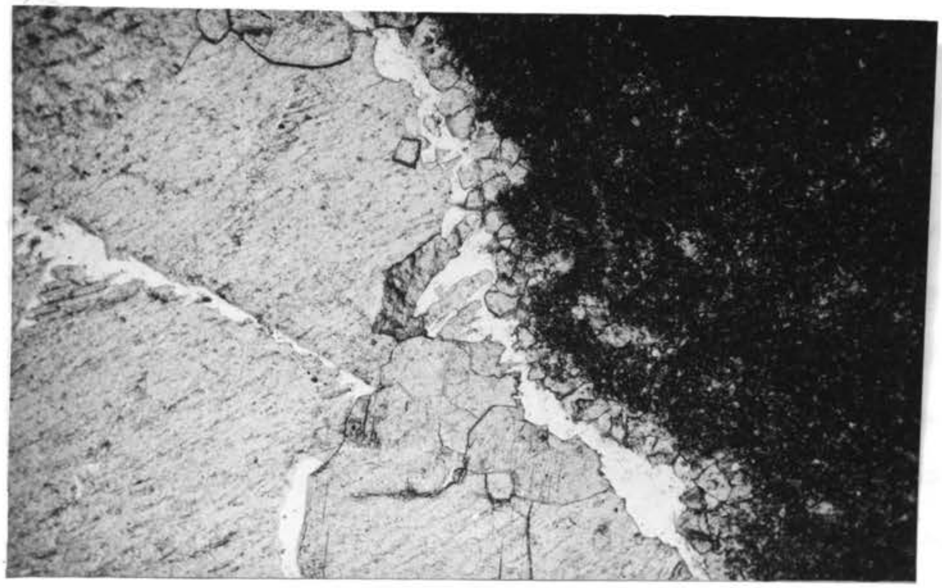

Fig. 67.

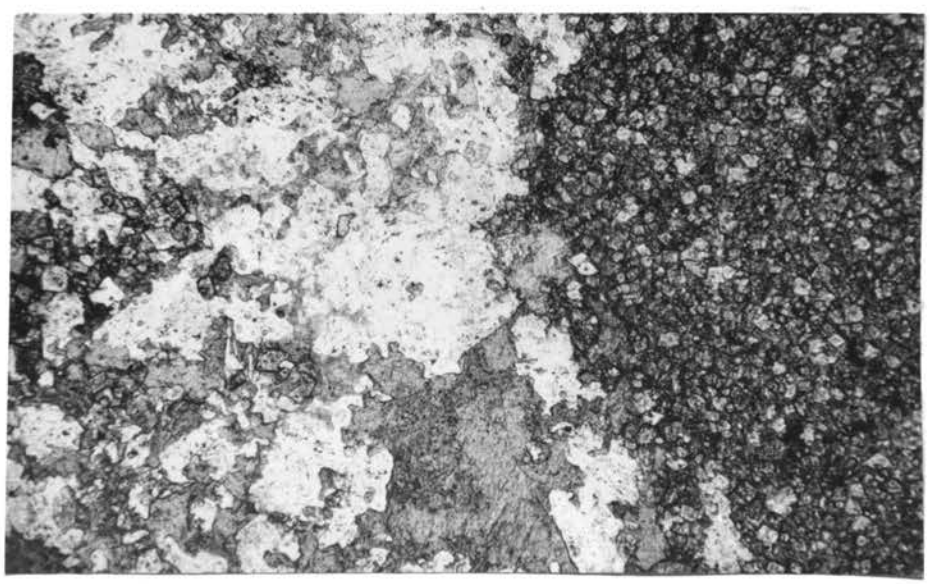

Fig. 68.

is predominantly in the form of mosaic quartz (terminology after R. C. L. Wilson, 1966) with minor gradations to chalcedony.

In the micrite, mosaic quartz has partially replaced calcareous fossil fragments and void-filling calcite spar. In thin section silicified areas were seldom observed greater than 0.3 mm. in diameter. Quartz grains were a uniform size and showed no marked size gradation toward the edges of the replacement areas. Silicification has obliterated original textures in all cases. Insoluble residues from the Stark Nursery (ST) samples yielded fragments of completely silicified brachiopods up to 1.0 mm. in diameter. Euhedral doubly terminated milky white quartz crystals and crystal aggregates up to 2.0 mm. in diameter were found in the same residues (Fig. 70). Examples of silica replacement of void-filling calcite spar are shown in Fig. 67 and Fig. 69.

Only one example of silicification was found in the marlstone (Fig. 68). Calcite spar has replaced parts of the marlstone and in turn has been replaced by mosaic quartz. The quartz has a "dirty" appearance and contains numerous tiny inclusions of calcite. Individual crystals of mosaic quartz attain a diameter of 0.8 mm. It appears that silicification in this example was restricted to those areas that had previously been replaced by calcite spar.

It has been previously mentioned that part of the cement in the siltstone is thought to be very fine-grained

Fig. 69. Oval-shaped object in the center of the photo is an ostracode. The shell has been completely replaced by pyrite. The interior has been filled by void-filling calcite spar, which in turn has been replaced in part by mosaic quartz. Sample is from one of the pyrite-rich zones in the micrite. Other black areas shown in photo also represent pyrite. (CDH # 76, L-10), X150.

Fig. 70. Euhedral doubly terminated authigenic quartz crystal approximately 2 mm. in length, from insoluble residue from the micrite collected at the Stark Nursery (ST) section. Photographed with a combination of transmitted and reflected light. X24.

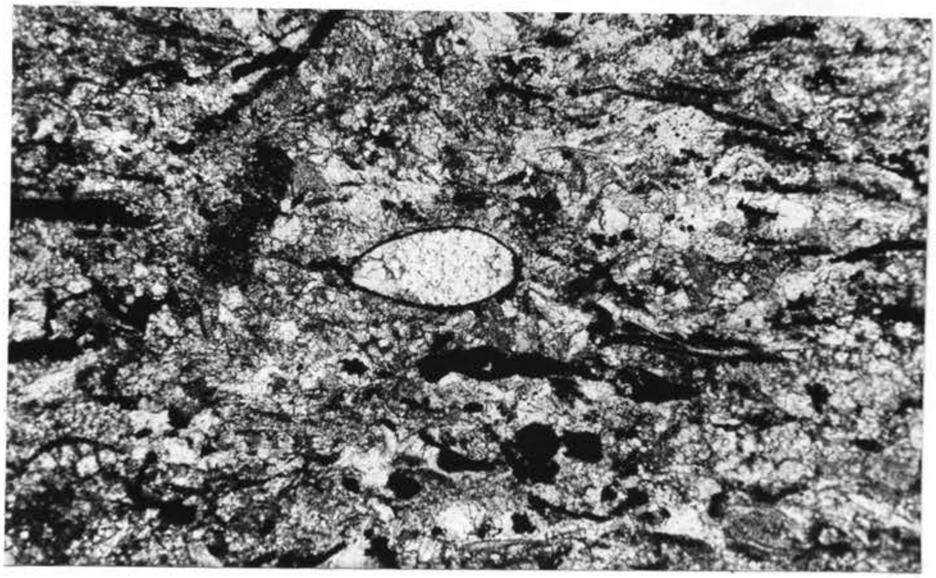

Fig. 69.

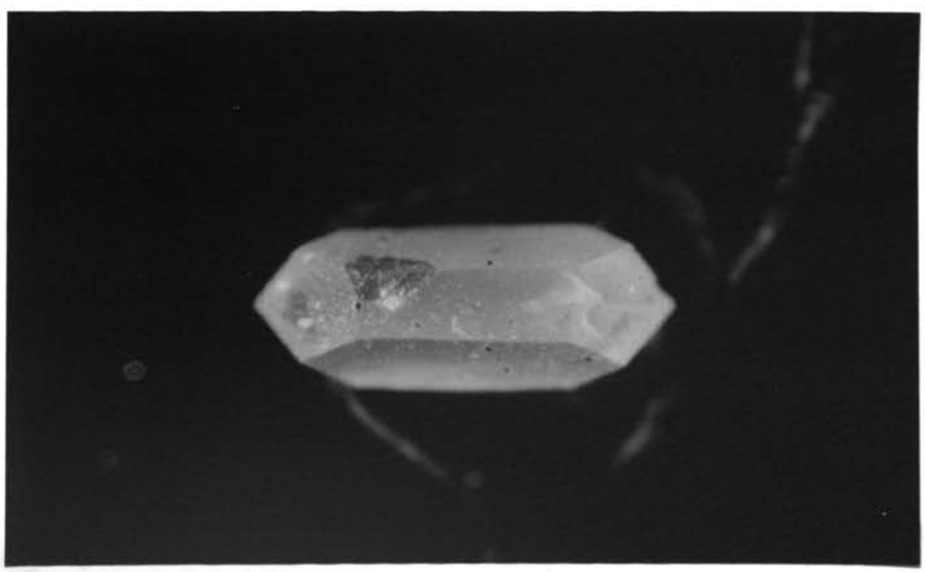

Fig. 70.

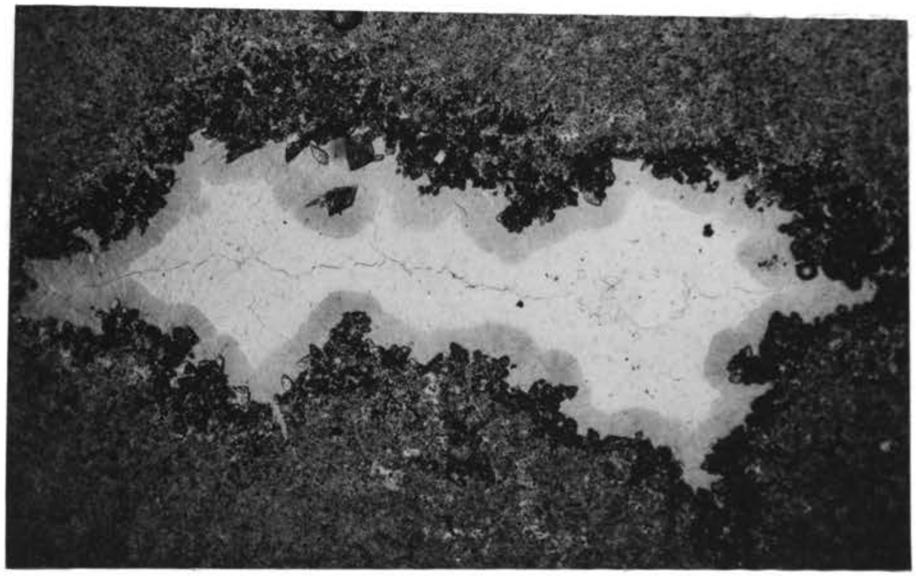

Fig. 71.

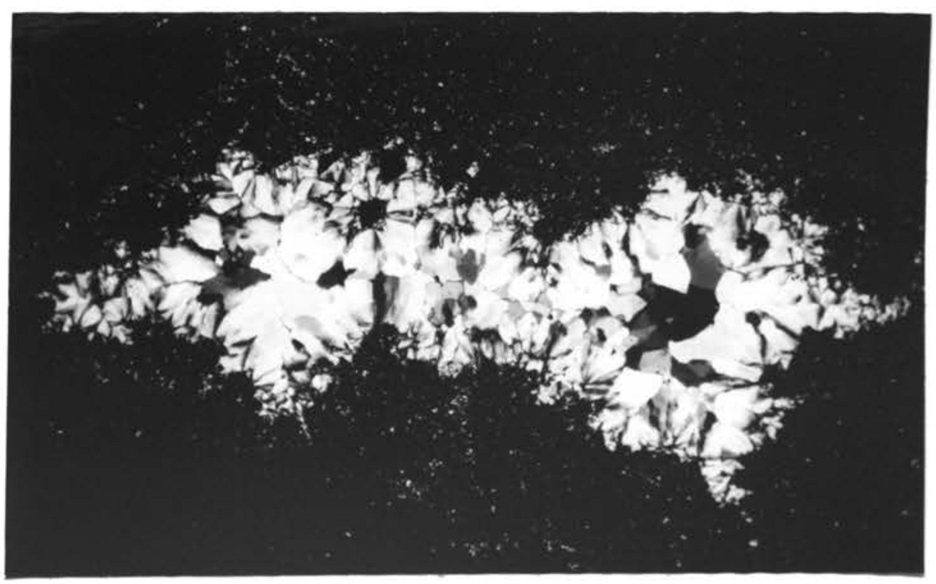

Fig. 72.

Fig. 73. This problematic structure, found in the siltstone, may have formed by replacement of an ostracode or as a void filling. Note that this structure exhibits the same chalcedony-mosaic quartz gradation shown by most examples of void filling quartz. (GC-6), X80. Plane polarized light.

Fig. 74. Same as above. Crossed nicols.

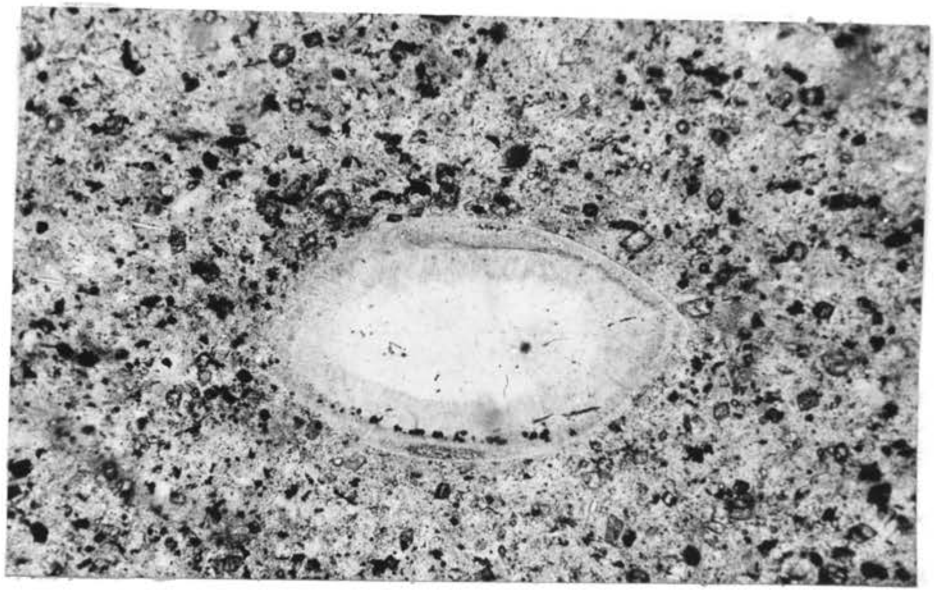

Fig. 73.

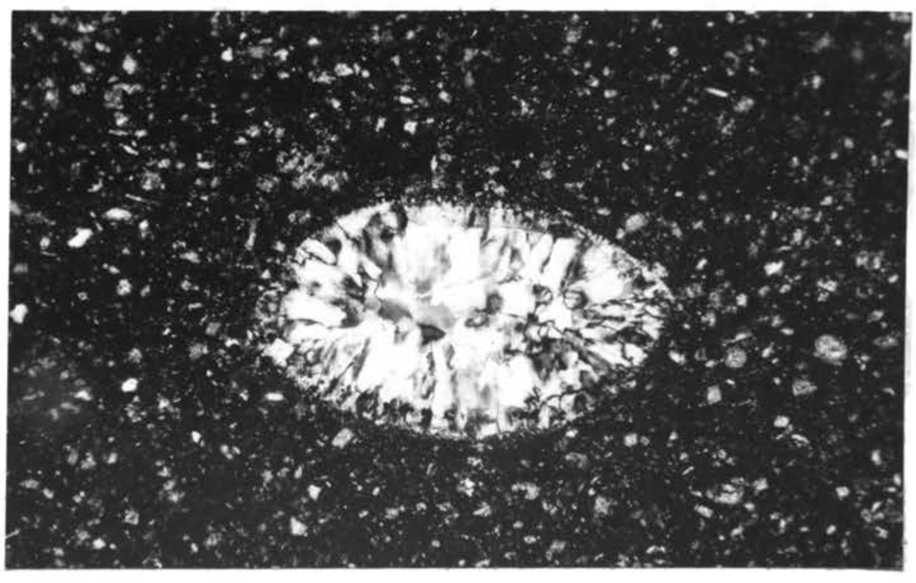

Fig. 74.

authigenic quartz. Larger individual grains of authigenic quartz with irregular etched edges up to 0.1 mm. in diameter were also seen. Several quartz filled vugs lined with euhedral crystals of ferroan calcite were observed (Fig. 71, Fig. 72). The faces of the calcite crystals appear to have been etched by the initially precipitated chalcedony. The quartz consists of a fibrous brownish colored chalcedony near the edges which grades to progressively larger grains of mosaic quartz near the center of the vug. Folk and Weaver (1952) have shown that the brownish color of chalcedony in most cases is due to numerous inclusions of submicroscopic water-filled cavities. This situation probably represents a rapid rate of silica precipitation. Using the petrographic criteria cited by Folk (1962) for carbonate rocks, the progressive increase in the grain size of mosaic quartz toward the center of the vugs suggests a void-filling origin. Folk and Weaver (1952, p. 501) have noted similar chalcedony-mosaic quartz gradations and explained them as "due to a decreasing rate of precipitation because of the diminished rate of supply of solution as consolidation proceeds." The problematic structure shown in Fig. 73 and Fig. 74 exhibits the same chalcedony-mosaic quartz gradation and it may also represent a void filling. However, the regular shape and smooth outside edges of this structure are difficult to explain with a void filling origin.

The discovery of siliceous sponge spicules in the micrite, which is notably deficient in detrital quartz grains, lends support to a biologic source for the small amount of authigenic silica in the limestones. In the siltstones both sponge spicules and detrital quartz grains could have served as a source of silica. The solution, concentration and redeposition of silica by alkaline interstitial waters has been invoked to explain many examples of silicification in sedimentary rocks (Dapples, 1959, 1967; Taylor, 1964). A similar process is probably responsible for the silicification in the Maquoketa. Cross-cutting relationships indicate that the silicification took place late in the diagenetic sequence.

F. Fluorite

The occurrence of fluorite, although a very minor constituent, is sufficiently unusual to merit individual consideration. The fluorine ion content of sedimentary rocks is usually low, and is normally only detected by chemical analysis. Krauskoph (1967, p. 592) gives the following average fluorine contents: shales 740 ppm., sandstone 270 ppm., and carbonates 330 ppm. Usually the small amount of fluorine in sedimentary rocks is substituted in apatite grains and phosphatic fossil fragments. Occasionally fluorine is concentrated enough to form crystals of authigenetic fluorite (Bagg, 1918, Bushinsky, 1936, Graf, 1960, and Teodorvich, 1961). Many sedimentary fluorite occurrences have been attributed to hydrothermal activity. Others are far removed from any known hydrothermal source. In cases where hydrothermal activity is not evident the genesis of fluorite is difficult to explain.

Brown (1967) has reported well formed crystals of color-zoned fluorite associated with calcite, sphalerite, and pyrite in the lowermost phosphatic horizons of the Maquoketa Formation at Volga, Iowa. He has suggested that this mineralization may have resulted from residual hydrothermal fluids from the Upper Mississippi Valley zinc-lead district 20 miles to the east. The Volga location was previously the only known occurrence of fluorite in the Maquoketa. During this study fluorite was discovered in the dolomitic quartz siltstone of the upper Maquoketa at the Grassy Creek (GC) section in Pike County. Fluorite was identified in four individual siltstone units (Appendix II shows the fluorite distribution).

The fluorite was found in irregular vugs up to 1/8 inch in diameter. Vugs were completely filled and showed no evidence of collapse or distortion, nor were they situated along fractures. The origin of these vugs is undetermined. The fluorite consisted of dark purple and yellow color-zoned crystal units. Identification was based on the characteristic colors and zoning, along with the isotropic nature and index of refraction of 1.43 for this material. In each occurrence the fluorite was surrounded by clear mosaic quartz. Quartz is replacive to the adjacent siltstone (Fig. 75). The etched fluorite edges, and the projection of euhedral quartz crystals into the fluorite, suggests that quartz may also be replacing fluorite.

Fig. 75. Color-zoned purple (dark area) and yellow (light area) authigenic fluorite from the dolomitic quartz siltstone. White area around the fluorite is authigenic quartz which has replaced both the siltstone and fluorite. Several larger euhedral quartz crystals are shown near the lower part of the photo. (GC-4), X24.

Fig. 76. Irregular-shaped mass of sphalerite (black) in the lowermost phosphatic biosparite. Sphalerite has replaced calcite spar, calcareous fossils and, to a lesser extent, dolomite crystals. (CDH # 63, L-1), X24.

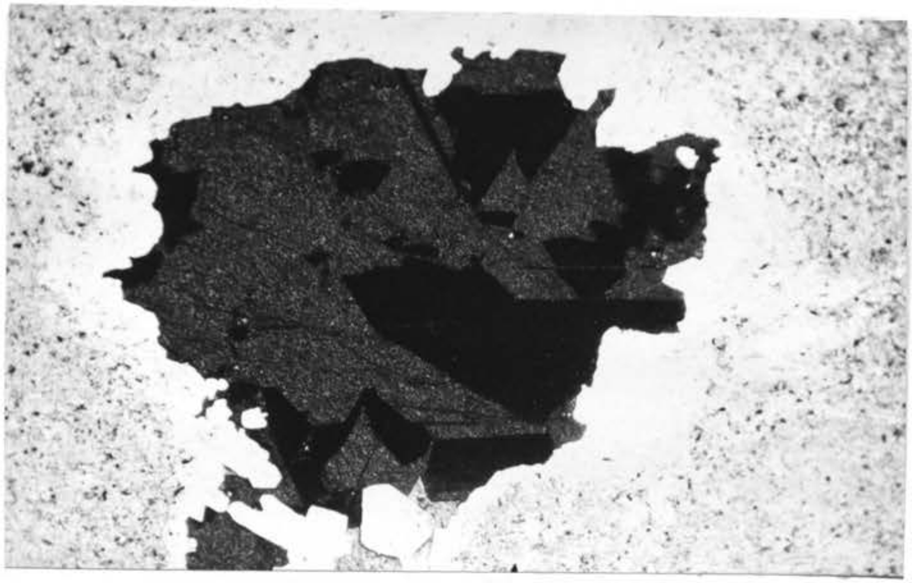

Fig. 75.

Fig. 76.

Evidence for this relationship is not conclusive and the fluorite might also be interpreted as a void filling. Several small areas of ferroan calcite adjacent to the fluorite were noted, and are thought to have been void fillings.

The origin of this fluorite is uncertain. The occurrence of color-zoned crystals would seem to eliminate a primary origin. The closest site of known hydrothermal activity is greater than 100 miles away. Phosphate pellets and phosphatic fossil fragments, a possible source of fluorine, are scarce in this part of the Maquoketa. Recent work of Lowenstam and McConnell (1968) suggests another possible source for this fluorite. They have been able to demonstrate the biologic precipitation of crystalline fluorite by certain recent marine crustaceans and gastropods. The results of their study indicate that significant amounts of fluorite are concentrated in the skeletal material of these organisms. The fixation of fluorite in organic tissue seems to be mainly limited to shallow shelf seaways with only minor amounts in the deeper parts of the ocean. They suggest that fluorite crystals could be freed from their organic matrices and incorporated in the clay-size fraction of sediments by the action of both scavengers and deposit feeders. Possibly Paleozoic invertebrates had this same capacity to precipitate fluorite. If this were the case, invertebrates in the Maquoketa Sea may have precipitated fluorite that was later concentrated by diagenetic processes.

G. Clay Minerals

The only observable diagenetic changes in the clay minerals are those produced by physical forces (i.e. compaction of soft sediments). The differential compaction of soft clay around more rigid grains of pyrite has previously been mentioned. With the exception of physical processes and probably minor ion exchange, it would be hazardous to postulate any other diagenetic changes. The literature shows a diversity of opinion concerning the importance of authigenesis in the formation of clay minerals. Some workers (Weaver, 1958, Milne and Earley, 1958) think that very little alteration of clay minerals takes place after deposition. Others (Grim, 1953, Muller, 1967, Taylor, 1964) consider authigenesis of prime importance in determining the type of clay mineral present. No evidence was observed that would support an authigenic origin for the Maquoketa clays. Nor were any of the clay minerals observed replacing any other minerals.

H. Sphalerite

Small amounts of sphalerite were found in the phosphatic biosparite of the lowermost Maquoketa at the Dundee Quarry. Sphalerite had previously been noted in the lower Maquoketa of Pike County by Rowley (1907, p. 52). The sphalerite occurs in very irregular dark yellow to brown masses 0.10 to 3.0 mm. in diameter (Fig. 76). It is commonly accompanied by pyrite which it is replacing in part.

Sphalerite has replaced some fossil fragments. Krauskopf (1955) has suggested that Zn substituted in the aragonite lattice may have been freed during the transformation of aragonite to calcite and combined with sulfur from organic material to form sphalerite, indicating a syngenetic origin. However, cross-cutting relationships indicate that the Maquoketa sphalerite was one of the last minerals to form. Graf (1960) has suggested that clay minerals in which Zn is readily accommodated in interlayer positions are likely hosts for Zn in impure limestones. In the Maquoketa, phosphates, which are well-known for their concentration of metallic cations, seem to be the most likely source of Zn in the sphalerite.

I. Limonite

Limonite is exclusively a product of oxidation caused by weathering. It may occur as pseudomorphs after pyrite crystals or as light yellow to dark brown stains coating the surface of weathered rocks. This staining is particularly common on some of the rocks at the Stark Nursery (ST) outcrop. In thin section some ferroan dolomite crystals (in the marlstone) exhibit a thin surface layer of limonite which is also due to weathering. Hayes (1967) has demonstrated the alteration of ferroan dolomite to limonite by the progressive oxidation of the included ferroan iron.

J. Gypsum, var. Selenite

Selenite crystals up to one inch in length have been found on weathered outcrops of the lower Maquoketa on Noix Creek near the Mississippi River by A. C. Spreng (personal communications, 1969). Similar crystals had been reported by Ladd (1928) from weathered outcrops of the Brainard Member of the Maquoketa of Iowa. Abundant sulfate ions, produced by the oxidation of pyrite during weathering, combined with soluble calcium salts in the near surface ground water are probably responsible for the formation of this mineral. No selenite crystals were collected during this study, nor was any form of gypsum observed in any of the thin sections studied.

K. Diagenetic Sequence

In summary, the following diagenetic sequence, constructed utilizing Ockham's Razor, is offered as a possible explanation for the relative chronologic order of the formation of authigenic minerals and of the diagenetic events in all lithologies. Evidence in support of this paragenetic sequence has been cited previously in appropriate sections of this report and needs not be reviewed:

1. Compaction of sediments was initiated penecontemporaneously with deposition and continued to some undetermined point when lithification was completed.
2. Pyrite, the first authigenic mineral, formed as

small crystals at localized sites of high pH and negative Eh throughout the sediment and selectively on decaying organic material. It is probable that sulfate-reducing bacteria aided the formation of this mineral.

3. Intrastratal flowage of unconsolidated or weakly consolidated sediments produced microfolds and sedimentary boudinage structures. Some uncertainty exists as to whether this event took place before or after neomorphism.
4. Neomorphism of calcium carbonate mud to micrite with gradations to microspar and pseudospar took place next. The mineralogical composition of this mud is unknown, but it seems likely that both aragonite and calcite were present. Recrystallization of calcareous fossils probably also took place at this time.
5. Dolomitization, based on cross-cutting relationships of dolomite rhombohedra to micrite and microspar, followed neomorphism. Formation of both ferroan and non-ferroan varieties is thought to have occurred at the same time.
6. Void-filling of open pores and cavities by sparry calcite probably followed dolomitization. At approximately the same time (possibly earlier or later) the growth of the

fibrous calcite which comprises the bulk of the cone-in-cone structure was initiated. The unusual acicular sulfide mineral found only in the cone-in-cone structures developed simultaneously with the fibrous calcite. Sediments were still not completely consolidated at this time.

7. The formation of fluorite in the siltstone of the upper Maquoketa probably preceeded silicification.
8. Minor silica replacement of fossils, all rock types, void filling calcite spar, fluorite and dolomite occurred next.
9. An exact relationship is uncertain, but sphalerite was one of the last authigenic minerals to form.
10. Minor amounts of ferroan calcite developed as pore filling and fracture filling after consolidation of sediments was completed or almost completed.
11. Two minerals, selenite and limonite, are recent additions to the Maquoketa rocks. Both are products of weathering formed after the outcrops were exposed by erosion.

VII. Paleoecological Observations

Although fossils are generally scarce in the Maquoketa Formation in Pike County, they may be valuable environmental indicators when present. Locally fossils may be moderately abundant, as in the "depauperate zone" and Isotelus zone. An unusual occurrence of pyritized fossils completely covering several bedding planes was discovered in the upper part of the formation at the Dundee Quarry.

An attempt was made to observe and to record the distribution of fossils in the field. However, fossils were too scarce to permit the collection of much data. Complete specimens or fragments of megascopic fossils were collected from all the outcrops studied (Table I.), with the exception of the Grassy Creek (GC) exposure. Fossils were most abundant, but still relatively rare, at the Stark Nursery section (ST). Here fossils were randomly distributed in the limestones. Usually fossils were found as isolated individuals. However, it was not too uncommon upon splitting a rock to find a number of associated individuals. There was no preferential orientation of fossils. Fossils, trilobite parts in particular, were oriented at all angles to the bedding. This would seem to substantiate petrographic evidence, indicating a very low energy environment. Dead organisms would either remain in the position in which they died or in which they landed on the soft mud bottom.

The fossils of the "depauperate zone" are different from those of the remainder of the formation. The fauna consist of minute, phosphatized and pyritized invertebrates (e.g., gastropods, pelecypods, and echinoid fragments). Agnew (1955) has interpreted this assemblage as evidence of widespread foul water at the beginning of Maquoketa time. Orthocone cephalopods up to six inches in length were observed on the outcrop. The paleoecological significance of the "depauperate zone" has been considered in detail by Ladd (1925, 1928), Ojakangas (1959), Ralls (1951), and Tasch (1953, 1958).

No calcareous or calcareochitinous fossils (such as trilobites) were found in the shales or marlstone of the Maquoketa in Pike County. A microscopic examination of these rocks reveals only a few graptolite and unidentified sapropel-like organic fossil fragments. No other fossils were found. Johnson (1939) states that generally the shales are barren of fossils except conodonts, but that he had found several very small calcareous gastropods and pelecypods at one locality in Pike County. As Johnson's locality is no longer accessible, his observation could not be checked. It is impossible, in Pike County, to determine if this lack of calcareous fossils in the shales and marlstones is a primary or a secondary feature. Bayer (1967) noted a similar faunal distribution in the cyclic Maquoketa of Minnesota. The lithology of the Maquoketa in Minnesota is somewhat different than it is in Missouri. In Minnesota the limestones are much more fossiliferous.

Bayer believed the difference in fauna between the limestones and shales was due primarily to repetitive shoaling and non-shoaling conditions, with the periods of shale sedimentation unfavorable for invertebrate life.

In the limestones on outcrop, trilobites are the most commonly observed fossil. Brachiopods, badly weathered graptolites, and a few bryozoans, pelecypods, and small orthocone cephalopods were collected. In thin section, ostracodes and trilobite fragments were the most abundant fossils. Fragments of mollusks, brachiopods, bryozoans, graptolites, conodonts and calcareous and siliceous sponge spicules were observed in smaller number in thin section. It should be noted that the fossil content of thin sections was biased in favor of the smaller fossils and fragments.

Trilobites are considered to have been exclusively marine organisms. They were supposed to have been vagrant bottom dwellers, although some delicate spiny forms may have been planktonic. The most commonly occurring trilobite in the Maquoketa, Isotelus, a smooth-carapace form, was probably benthonic. Most trilobites are thought to have been scavengers; others may have been filter feeders (Shrock and Twenhofel, 1953). Shrock and Twenhofel (1953) have pointed out that many of the trilobite parts commonly found represent molts with low specific gravity and large surface area that could easily be transported by slow moving currents over long distances without breakage. Many of the trilobite parts of the Maquoketa Formation probably represent molts. A number of complete trilobite carapaces have been found in the Maquoketa during the course of this study and by others (Johnson, 1939, Laswell, 1957, and Rowley, 1907). The presences of complete articulated trilobite carapaces indicates these organisms died at or near the environment in which they lived, since these carapaces were probably much too delicate to survive any appreciable amount of transportation without disarticulation.

Ostracodes are relatively abundant in thin section. Single valves are most commonly observed, although a smaller number of individuals with articulated valves have been found. The small size, streamlined shape, and low specific gravity of ostracodes probably makes them very amenable to transportation as Agnew (1957) has suggested. Modern ostracodes are both marine and non-marine, living in environments ranging from shallow ditches and tidal pools to depths exceeding 9000 feet (Sohn, 1957). The paleoecology of Paleozoic ostracodes is not well known. However, it seems likely that water conditions favorable to trilobites would also be suitable for ostracodes, and that the ostracodes are probably part of the original _in situ_ Maquoketa fauna.

Graptolites are most abundant in the limestones of the Lower Maquoketa. In thin section graptolite fragments have been observed in all of the Maquoketa lithologies. Their epiplanktonic nature and mode of life has been investigated by Lapworth:

"Graptolites are commonest in shales,

> particularly black, carbonaceous shales, where their abundance is related to carbon content, fineness of grain, and lack of quartz and feldspar. The abundance of graptolites is thus in some way related to carbon content of the rocks, quietness of the sea-bottom and slow accumulation. That they are so well preserved shows that the graptolites themselves cannot have supplied the carbon: this must have some other, probably vegetable, origin. That they constituted a sessile benthos is unlikely, as their remains never traverse the bedding planes, but invariably lie parallel to them, as though they had sunk through tranquil water to come slowly to rest upon the surface of fine muds." (Lapworth, 1897, quoted in Bulman, 1957, p. 987.)

According to Bulman (1957), graptolites have drifted into and sunk into almost every type of sedimentary environment. He also mentions that graptolite seas have been compared with the recent Black Sea.

The remaining Maquoketa fauna is generally too scarce to make specific mention, although it may be noteworthy that several pelecypods complete with both valves were found. Possibly this occurrence indicates that these particular mollusks were not transported, but were found in the environment in which they lived.

The pyritized fossils of the Upper Maquoketa from the Dundee Quarry are previously unreported. They are not known to occur at any other Maquoketa locality. A number of bedding planes completely covered by pyritized bryozoans, brachiopods, trilobites, and cephalopods were observed (Fig. 77). Most fossils have been flattened by the compaction of overlying sediments. One unusually large

Fig. 77. Bedding plane covered with numerous pyritized invertebrates (most have altered to limonite). These fossils are found in the dolomitic marlstone in the upper part of the Maquoketa in the Dundee Quarry.

Fig. 78. Large flattened orthocone cephalopod (28 inches in length) from the dolomitic marlstone from the upper part of the Maquoketa in the Dundee Quarry.

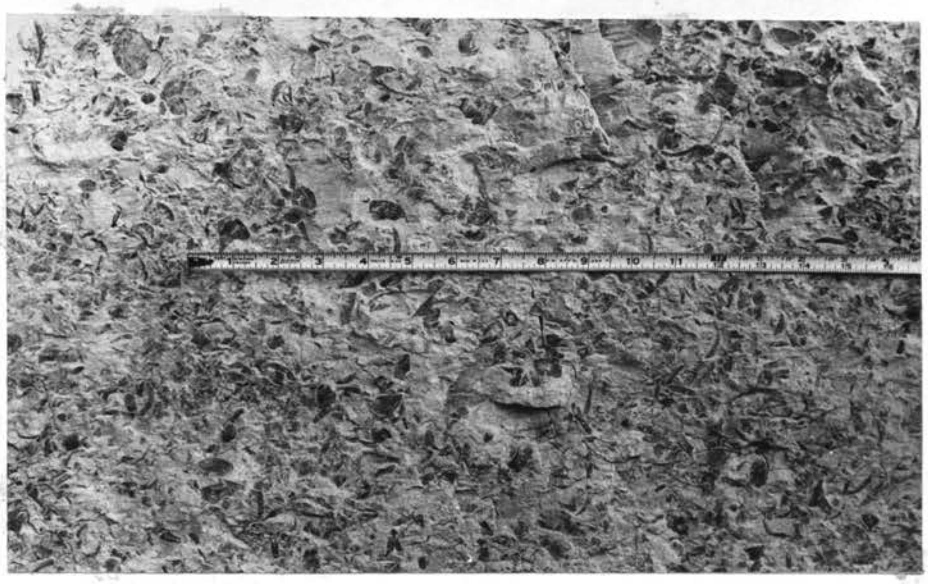

Fig. 77.

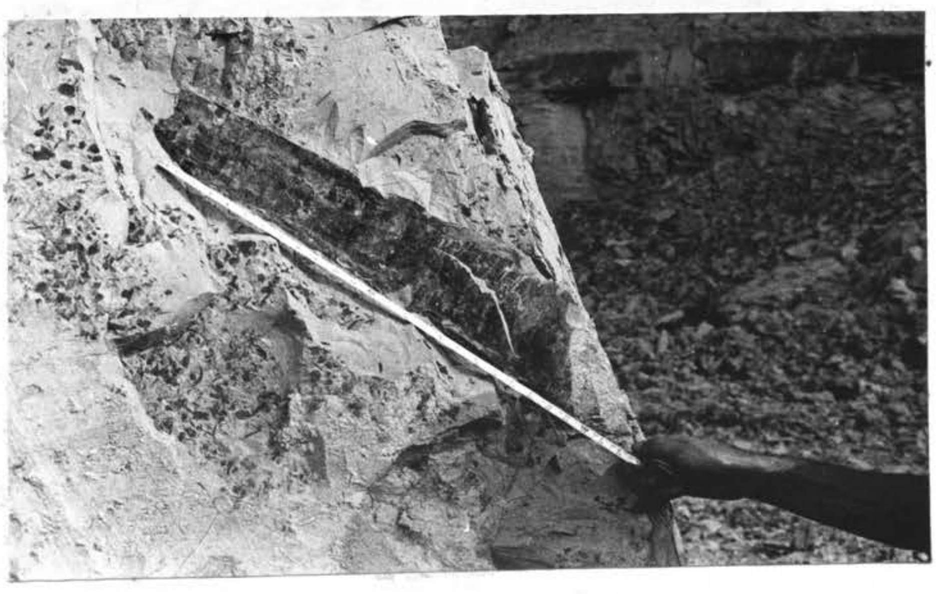

Fig. 78.

(28 inches in length) orthocone cephalopod was found (Fig. 78). A greater number, and a greater variety, of fossils was seen on these bedding planes than anywhere else in the Maquoketa Formation in Pike County. These fossiliferous bedding planes were separated by one to two feet of barren dolomitic marlstone. It is hypothesized that these fossils may represent a death assemblage caused by the periodic upwelling of hydrogen sulfide-bearing waters. The hydrogen sulfide would provide a mechanism for mass mortality and a source of sulfur ions for the replacement of the fossils by pyrite. Similar mass mortalities caused by the upwelling of hydrogen sulfide have been observed in the recent environment (Brongersma-Sanders, 1957). It is also recognized that the presence of these fossils may be more a matter of preservation than of occurrence. As illustrated in a previous section, some calcareous fossils of the Maquoketa have been obliterated by recrystallization. Perhaps fossils completely replaced by syngenetic pyrite were less subject to destruction by diagenetic processes.

Fossils of the Maquoketa Formation indicate a low energy environment of deposition with waters that were probably poorly oxygenated. The lack of fossil orientation and the presence of articulated trilobite carapaces and articulated pelecypods and ostracode valves suggest a low energy environment of deposition below wave base with little current action. Unfortunately, the paleoecology of the fauna present in the Maquoketa is not well enough known to suggest a water depth in which they lived.

Recent ostracodes are known to live in foul water (Sohn, 1957). Paleozoic ostracodes probably lived in the same type of environment (Agnew, 1957). By analogy with recent crustaceans and from geologic evidence, it is thought that trilobites also existed in anaerobic environments, which were unfavorable to most other forms of life (Wilson, 1969). The lack of burrowing organisms, as indicated by laminations that are preserved, also lends support to an environment inhospitable to most forms of marine life. The relative scarceness of the two most abundant forms, trilobites and ostracodes, may suggest that Maquoketa seas did not contain enough food to support a prolific fauna. This suggestion might lend further support to a somewhat anaerobic environment generally unfavorable to life forms other than trilobites and ostracodes. Graptolites are not good indicators of environment of deposition because they were epiplanktonic. However, since they are preserved, and were not carbonized on the sea floor, their presence may further suggest a slightly anaerobic environment of deposition.

VIII. Environmental Interpretations

The problems in hypothesizing an environment of deposition for the Maquoketa are twofold. First, one must interpret the environment in which individual lithologies were deposited. Second, one must hypothesize a mechanism or process responsible for a repeatedly changed environment which resulted in the cyclic lithologies.

The origins of the two lower Maquoketa lithologies, the phosphatic biosparite and phosphorite, are relatively easy to explain. The biosparite, with the exception of the phosphate pellets, is similar paleontologically and petrographically to the underlying Kimmswick Formation. Abraded fossils in an incompletely winnowed lime mud matrix suggest that deposition took place in shallow water, probably above wave base, by moderately strong currents (Folk, 1965). The very local occurrence of this rock type may be due to a slow rate of deposition, with those materials that were deposited being moved by currents into erosional depressions on the unconformable Kimmswick surface. The thin phosphorite of the so-called "depauperate zone" contains abraded fossils similar to those of the biosparite. This also suggests shallow water deposition above wave base for the phosphorite. However, in this rock type, the lack of mud (micrite and clay minerals) indicates somewhat stronger current action. Both Agnew (1955) and Bromberger (1968) have interpreted the abundance of phosphate as indicative of widespread foul, shallow water at the beginning of Maquoketa time. If Bromberger's (1968) theory of primary phosphate precipitation with replacement in areas of intense precipitation is correct, this lithology probably represents a very slow rate of sedimentation.

The environmental interpretation of lime mud (micrite) is much more difficult. Folk (1965) has given as a hypothetical example sixteen different environmental interpretations for a biomicrite. Unfortunately, petrographic criteria cannot usually differentiate between micrites of different origins. Prior to 1955, most micrites were considered to represent inorganic chemical precipitates. In 1955, Lowenstam demonstrated the biologic precipitation of clay size aragonite needles by certain recent red algae. Since that time it has been discovered that several other genera of recent red and green algae precipitate aragonite needles (Baars, 1963). After death, these algae disintegrate and the aragonite needles in their tissues produce carbonate mud. These aragonite needles are particularly subject to diagenetic changes. These plants are important sources of carbonate mud because of their great abundance and their short life cycle. It seems likely that these same algal processes are responsible for some of the micrite found in ancient sediments. However, in the Maquoketa it is impossible to determine if any of the micrite was produced by algae. Paleoecological observations indicate a depositional environment unfavorable to most forms of life, and the lack of organisms which are characteristically abundantly associated with algae cast doubt on an algal origin for the Maquoketa micrite.

A carbonate "dust" formed by the abrasion of fossil debris and grinding by deposit feeders has been suggested as a source for some micrite (Wood, 1941, Folk, 1965, Carozzi, 1960). This explanation does not seem appropriate for the Maquoketa micrite for a number of reasons: 1) Petrographic evidence indicates a very low energy level, not sufficient for extensive abrasion required to produce carbonate "dust;" 2) Those larger fossil fragments present exhibit sharp angular breaks with little or no evidence of abrasion. The grinding of fossil debris by deposit feeders (which might explain angular fossil fragments) is ruled out because of the preservation of fine pyrite laminations in the micrite. If abundant deposit feeders had been present in the Maquoketa, their burrowing would have destroyed these laminations; 3) The general lack of fauna in the Maquoketa suggests that shell debris is quantitatively unimportant to the production of micrite.

Due to the sparcity of fossil remains in the Maquoketa, primary chemical precipitation is tentatively suggested as the most plausible origin for the bulk of the micrite. Taft and Harbaugh (1964) in their work on recent sediments have suggested 0.01 mm. as a rough upper size limit for carbonates that have originated through direct inorganic precipitation. If it is permissible to apply this reasoning to ancient sediments, essentially all of the Maquoketa micrite-microspar would fall below this upper limit. Most authors (Cloud, 1962, Krauskopf, 1967, Hallam, 1964, and Lalou, 1957) have suggested that the precipitation of $CaCO_3$ in seawater is favored by warm, slightly alkaline water and a sufficient supply of Ca. In addition, CO_2 must be lost through evaporation or photosynthesis.

Evidence previously introduced suggests that the Maquoketa environment of deposition was reducing. Several authors, Lalou (1957) in particular, have demonstrated the importance of sulfate-reducing bacteria in the precipitation of $CaCO_3$ in a reducing environment. Lalou (1957, p. 195) concluded that the importance of bacteria in the formation of carbonates was "only to change the physico-chemical conditions of the medium, increasing its concentration of CO_2 up to saturation, enriching it in calcium and giving an escape of H_2S by reducing sulfates." It seems possible that sulfate-reducing bacteria may be responsible for the Maquoketa micrite. Three separate pieces of evidence (although admittedly weak) are offered in support of this hypothesis: 1) The bacterially precipitated aragonite spherulites, reported by both Lalou (1957) and Monogram and Lytte (1958) are similar (with the exception of mineralogy) to the Maquoketa "calcispheres." However, one would not expect to find aragonite preserved in Ordovician sediments, and the Maquoketa "calcispheres" may have originally been aragonite. Reference to Fig. 27 shows that the Maquoketa "calcispheres" had been partially replaced by early diagenetic pyrite, which is consistent with Lalou's (1957) experimental studies. In Lalou's experiment, bacterially precipitated iron monosulfide appeared after $CaCO_3$ crystals and spherulites formed; 2) The presence of abundant pyrite in the Maquoketa limestones has been demonstrated petrographically to have been a very early diagenetic event. It is thought that sulfate-reducing bacteria were largely responsible for the formation of this mineral. This would seem to indicate an abundance of sulfate reducing bacteria in the Maquoketa sediments shortly after deposition; 3) Carozzi (1960) has suggested that the "clotted" (or micromottled) texture in certain micritic limestones might be due to recrystallization of a mud originally composed of both calcite and aragonite, with the aragonite more subject to later diagenetic alterations. In Lalou's (1957) experiments, bacteria were responsible for the precipitation of calcite, aragonite and dolomite. However, calcite and aragonite were volumetrically the most important, with more calcite than aragonite precipitated. If Carozzi's (1960) suggestion is valid, a bacterial origin of both calcite and aragonite mud would seem to explain the "clotted" texture due to differential recrystallization in the Maquoketa micrites. Lalou (1957) cited the following conditions required for the bacterial precipitation of carbonates:

> "1.) Presence of assimilable organic matter in sufficient quantity.
> 2.) Temperature sufficiently high.
> 3.) Maximum light and sunshine; it appears that the phenomenon must take place in shallow waters.
> 4.) Quiet and very seldom renewed

> waters. Those conditions are to be found in the lagoons and the portions of sea water most isolated from the open in the tropical seas." (Lalou, 1957, p. 195.)

Most of Lalou's criteria appear to have been met by the Maquoketa environment.

The virtually complete lack of silt-size or larger detrital constituents in the Maquoketa shales and marlstones is noteworthy. Most shales contain a significant quantity of silt-size or larger detrital particles (Pettijohn, 1957). The extremely fine-grained size of these rocks would seem to indicate a source area with very low relief. Laminations (although disrupted by growth of authigenic minerals) in both the shales and marlstones indicate deposition in quiet water below wave base. Current strength was low, since fine-grained muds were able to remain at the sites at which they were deposited. The shales and marlstones are interpreted as having been deposited farther from the shore (and probably in deeper water) than the limestones. Although this interpretation differs from the traditional view, Sheppard (1963, p. 480) cites examples in the recent environment where carbonates are being deposited closer to shore and detritals farther out. This interpretation for the Maquoketa rocks is favored for the following reasons:

1.) Individual clay minerals in the shale are much smaller than the calcite grains of the micrites. Based on hydrodynamic principles, clay minerals, because of their smaller size, could have been transported farther seaward, assuming equal current strengths during periods of carbonate and shale sedimentation. The micrites commonly contain disseminated particles and small lenses of clay minerals. According to Laswell (1957) the micrites average 20 to 30 percent clay minerals. It is suggested that this situation was produced when currents loaded with clay particles in suspension passed over the area of carbonate deposition and some of the coarser detritals were deposited with the limestones. Credibility is lent to this suggestion by the lack of any primary calcite in the shales or marlstones.

2.) The lack of benthonic calcareous fossils in the shales and marlstones is conspicuous. Generally, near shore, shallower water sediments contain more benthonic organisms than those of deeper water.

With one rare exception, the only fossils found in the shales and marlstones were graptolites, which were epiplanktonic. These fossils have no environmental significance since they could have floated in from some other environment. The interpretation of the pyritized benthonic fossils in the upper marlstone presents problems. Possibly this occurrence represents short periods of non-deposition which were favorable to invertebrate life. These favorable conditions may have been suddenly replaced by conditions unfavorable to life, possibly due to upwelling of hydrogen sulfide, resulting in mass mortality of the organisms.

The siltstone near the top of the Maquoketa sequence, which is also lacking in benthonic fossils, is thought to have been deposited further from the shore and in deeper water than the limestones. Based on hydrodynamic considerations, the siltstones are thought to have been deposited closer to the shore and in shallower water than the shales because of their coarser grain size.

The marlstones are located stratigraphically between the shales and the siltstones. It seems possible that the marlstones represent sediments that had been deposited at a distance from the shore and in water depths intermediate between those of the shales and siltstones. If this suggestion is true, possibly Fairbridge's (1957) suggestion that dolomitization is more extensive in shallower water has more validity than later workers have thought.

The absence of ripple marks, mud cracks or any other recognizable primary structures in the volumetrically important Maquoketa lithologies (micrite, shale, and marlstone) suggests that deposition took place below wavebase. However, in a very shallow epicontinental sea of the type prevalent during the Ordovician (Dunbar, 1962), wavebase was surely a great deal shallower than in the present oceans. It seems likely that the maximum depths of the epicontinental Maquoketa Sea may have been measured in tens of meters. The paleogeography of the midcontinent does not indicate a deep Illinois Basin during Maquoketa time (Gutstadt, 1958, Sloss et al., 1960).

It is tempting to apply Sujkowski's (1958) hypothesis of "diagenetic unmixing" to the origin of many enigmatic cyclic sequences including those of the Maquoketa. However, this hypothesis is largely unproven with no experimental studies as a followup. Although calcite recrystallization and the formation of authigenic minerals are widespread events in the Maquoketa, it seems doubtful that these processes significantly accentuated the cyclic lithologies. If the Maquoketa cycles had been produced by "diagenetic unmixing," it is difficult to understand why any of the fine laminations, composed of pyrite and organic fragments, had been preserved. For these reasons the hypothesis of "diagenetic unmixing" is considered to be one of the less feasible explanations of the origin of the Maquoketa cycles. Based on petrographic evidence previously cited (particularly that concerning cyclic contacts), the Maquoketa cycles are believed to have been produced by primary differences in sedimentation.

Some cyclic sedimentary sequences have been explained by oscillatory tectonic activity (Spreng, 1953, Carozzi, 1955). According to Koenig (1961), the Lincoln Fold had experienced periodic uplifts and downwarps from Canadian through Late Mississippian or Early Pennsylvanian time. In cycles produced by oscillatory uplifts and downwarps, one would expect to find cycles with gradational lithologies. It is difficult to conceive of any type of tectonic activity that could have produced repetitive cycles with the sharp contacts that the Maquoketa rocks exhibit. For this reason, tectonic activity does not seem to be a likely mechanism for the Maquoketa cycles.

It is believed that the Maquoketa cycles were produced as a result of a rapid change in sedimentation. Precisely what mechanism was responsible for this rapid change in sedimentation is impossible to determine. The exposure and stratigraphic control of the Maquoketa in Pike County is not adequate to determine facies changes which might suggest a specific interpretation. However, two interpretations which seem reasonable are 1) a barrier bar-stagnant lagoon couplet with the cyclic lithologies due to shifting positions of the bar-lagoon margin (similar to interpretations made by Folk, 1962) and 2) a deltaic sequence along the margin of the Illinois Basin with changes in lithology due to variations in the rate of supply of terrigenous material or to a "wandering delta."

IX. Conclusions

The results of this study indicate the following:

1). Six distinct Maquoketa lithologies have been recognized in this study:

1. phosphatic biosparite
2. phosphorite
3. micrite-microsparite
4. dolomitic shale
5. dolomitic marlstone
6. dolomitic quartz siltstone

2). The phosphatic biosparite and phosphorite is a minor lithologic constituent and occurs only at the base of the Maquoketa. These two rock types were deposited in shallow, foul water in a zone of moderately high energy with a slow rate of sedimentation.

3). The micrite-microsparite, restricted to the lower 50 to 70 feet of the formation, was also deposited in shallow water in a slightly reducing environment in a zone of very low energy with few or no benthonic organisms. Tentatively, this rock type is thought to be the result of primary chemical precipitation with precipitation possibly initiated by sulfate-reducing bacteria.

4). The dolomitic shale and dolomitic marlstone, which exhibit an imperceptible intergradation, comprise greater than 60 percent of the entire formation. These rocks were deposited in quiet, undisturbed water which was chemically unfavorable to a benthonic fauna. The extremely small grain-size of the detrital material present indicates a depositional environment in somewhat deeper water and farther from the shore than that of the micrite-microsparite. The increase in dolomite content, upward stratigraphically, may represent conditions of increased shallowing of water depth.

5). The dolomitic quartz siltstone, with a relatively coarse grain-size, found only in the upper Maquoketa, was deposited closest to the shore line and in the shallowest water of all the detrital Maquoketa lithogenic environments.

6). Bedding of the Maquoketa micrite-microsparite and dolomitic quartz siltstone varies from irregular and hummocky to extremely regular. The beds exhibiting irregular hummocky surfaces have suffered varying degrees of intrastratal flowage prior to total lithification.

7). The cone-in-cone layer found in the lower two feet of the Maquoketa is the result of pressure-solution phenomenon during early diagenesis in weakly consolidated water saturated sediments. Clay minerals, although their exact function is uncertain, were essential for the development of this structure.

8). Even though the average grain size of the Maquoketa rocks is small, extensive diagenetic changes have taken place: 1. aggrading neomorphism of calcium carbonate in the limestones, 2. growth of euhedral authigenic dolomite crystals in all rock types, 3. formation of authigenic pyrite in all rock types and 4. minor and selective development of authigenic silica, fluorite, and sphalerite.

9). Microscopic examination of all three cycle types (limestone-shale, limestone-marlstone, and siltstone-shale) revealed microgradational contacts between different lithologies. This type of cyclic contact is indicative of a primary origin for the Maquoketa cycles with rapid changes in environment accomplished by subsequent changes in sedimentation.

10). Precisely what mechanism produced the rapid environmental changes which resulted in the Maquoketa cycles is impossible to determine. Both a barrier bar-stagnant lagoon couplet and a "wandering delta" along the margin of the Illinois Basin would be feasible suggestions.

X. Appendices

A. Annotated Maquoketa Bibliography

During the course of this investigation many references concerning Maquoketa studies were consulted. Some of these references were directly concerned with problems considered in this paper; others were not. A number of these references were published in old or obscure journals, and were difficult to locate. It was thought that assembling these references into a single bibliography might be of benefit to future investigators. Articles in which the subject matter is clearly indicated by the title have not been annotated. A brief annotation occurs where the title does not sufficiently reveal connection with Maquoketa problems. State geological survey publications and unpublished theses are concerned with the stratigraphy and general geology of the Maquoketa Formation in the region on which they report, unless noted otherwise.

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B. Outcrop Sample Positions

Grassy Creek Section (GC), NE¼, SE¼, Sec. 19, T. 54 N., R. 2 W., Pike County, Missouri.

Shale was too friable to be collected. Only siltstone and limestone units were collected and numbered.

GC-1	12"	Shaley phosphatic conglomerate of the basal Grassy Creek Fm., section covered above this point
-	66"	shale
GC-2	2"	siltstone
-	3"	shale
GC-6	2"	siltstone
-	2"	shale
GC-5	1"	siltstone
-	3"	shale
*GC-4	1"	siltstone
-	2"	shale
GC-3	1"	nodular siltstone
-	22½"	shale
GC-8	½"	nodular siltstone, very shaley
-	15"	shale
GC-7	1"	nodular siltstone
-	9"	shale
GC-9	1"	nodular siltstone
-	12"	shale
*GC-10	1"	nodular siltstone
-	95"	shale
*GC-11	1"	calcareous siltstone
-	64½"	shale
GC-12	1½"	fine-grained limestone
-	62"	shale, exposed above the base of the outcrop

*denotes that fluorite was found in thin section.

Ramsey Creek Section (WW), SE¼, SW¼, Sec. 12, T. 52 N., R. 1 W., near county road WW, Pike County, Missouri.

Shale was too friable to be collected. Only limestone units were collected and numbered.

-	6"	shale, section covered by alluvium above the base of the outcrop
WW-5	2"	fine-grained limestone
-	6"	shale
WW-4	3"	fine-grained limestone
-	14"	shale

WW-3	1½"	fine-grained limestone
-	6"	shale
WW-6	22"	fine-grained limestone
-	18"	shale
WW-1	2"	fine-grained limestone
-	6"	shale
WW-2	2"	fine-grained limestone
-	188"	shale, exposed above the base of the outcrop

Stark Nursery Section (ST), NE¼, SW¼, Sec. 25, T. 54 N., R. 2 W., on Noix Creek, Louisiana, Missouri.

Shale was too friable to be collected. Only limestone units were collected and numbered.

-	10"	shale, section covered above this point
L-31	2"	fine-grained limestone
-	2"	shale
L-30	2"	fine-grained limestone
-	2"	shale
L-29	2"	fine-grained limestone
-	2"	shale
L-28	2"	fine-grained limestone
-	4"	shale
L-27	2"	fine-grained limestone
-	2"	shale
L-26	2"	fine-grained limestone
-	2"	shale
L-25	2"	fine-grained limestone
-	4"	shale
L-24	3"	fine-grained limestone
-	4"	shale
L-23	1"	fine-grained limestone
-	2"	shale
L-22	2"	fine-grained limestone
-	2"	shale
L-21	2"	fine-grained limestone
-	3"	shale
L-20	4"	fine-grained limestone
-	5"	shale
L-19	2"	fine-grained limestone
-	1"	shale
L-18	2"	fine-grained limestone
-	3"	shale
L-17	2"	fine-grained limestone
-	3"	shale
L-16	2"	fine-grained limestone
-	2"	shale
L-15	2"	fine-grained limestone
-	1"	shale
L-14	2"	fine-grained limestone
-	8"	shale

L-13	3"	fine-grained limestone
-	5"	shale
L-12	1"	fine-grained limestone
-	1"	shale
L-11	2½"	fine-grained limestone
-	½"	shale
L-10	3"	fine-grained limestone
-	4"	shale
L-9	2"	fine-grained limestone
-	4"	shale
L-8	2"	fine-grained limestone
-	2"	shale
L-7	2"	fine-grained limestone
-	2"	shale
L-6	1½"	fine-grained limestone
-	1½"	shale
L-5	2"	fine-grained limestone
-	2"	shale
L-4	2"	fine-grained limestone
-	1"	shale
L-3	2"	fine-grained limestone
-	1"	shale
L-2	5"	fine-grained limestone
-	12"	shale
L-1	12"	fine-grained limestone exposed, top of this bed is 16' above creek

<u>Dundee Quarry "Shale Pit" Section (DD)</u>, SE¼, SE¼, Sec. 24, T. 53 N., R. 1 W. Samples collected from south side of working face, June 1968.

All lithologies at this locality were fresh. Both shales and limestones were collected and numbered.

DD-26	2"	fine-grained limestone, higher samples could not be obtained
DD-25	4"	shale
DD-24	27"	fine-grained limestone
DD-23	16"	shale
DD-22	3"	fine-grained limestone
DD-21	6"	shale
DD-20	2"	fine-grained limestone
DD-19	3"	shale
DD-18	2"	fine-grained limestone
DD-17	4"	shale
DD-16	2"	fine-grained limestone
DD-15	2"	shale
DD-14	3"	fine-grained limestone
DD-13	6"	shale
DD-12	1"	fine-grained limestone
DD-11	1"	shale
DD-10	2"	fine-grained limestone

DD-9	2½"	shale
DD-8	1"	fine-grained limestone
DD-7	5"	shale
DD-6	2"	fine-grained limestone
DD-5	1½"	shale
DD-4	1"	fine-grained limestone
DD-3	6"	shale
DD-2	2"	fine-grained limestone
DD-1	5½"	shale, exposed at quarry floor

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XII. Vita

Edwin Carl Kettenbrink, Jr., was born on November 12, 1944, in St. Louis, Missouri. He received his primary and secondary education in the public school system of St. Louis and St. Louis County, Missouri. He received a Bachelor of Science degree in geology in June, 1967, from the University of Missouri-Rolla. During the school year 1967-1968 he was a graduate student and teaching assistant at the University of Missouri-Rolla. At present he is enrolled in a Ph.D. program in geology at the University of Iowa while completing a Master's thesis from the University of Missouri-Rolla. He married the former Gail Kathleen Davidge, a geologist-classmate, June 15, 1968. He is at present an N.D.E.A. fellow at the University of Iowa. He is a member of Sigma Gamma Epsilon and the Society of Economic Paleontologists and Mineralogists.