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## DIAGENETIC HISTORY OF THE CARBONATE MEMBERS OF THE DENNIS FORMATION (MISSOURIAN, UPPER PENNSYLVANIAN) IN IOWA, MISSOURI, AND KANSAS

**by**

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Loren Bruce Railsback

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Thesis supervisor: Professor Philip H. Heckel

Graduate College
The University of Iowa
Iowa City, Iowa

CERTIFICATE OF APPROVAL

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MASTER'S THESIS

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This is to certify that the Master's thesis of

Loren Bruce Railsback

has been approved by the examining committee for the thesis requirement for the Master of Science degree in Geology at the May, 1983 graduation

Thesis Committee: ______________________
Thesis supervisor

______________________
Member

______________________
Member

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Finally, I must thank my family for many years of financial and moral support of my education.

# ABSTRACT

The carbonate members of the cyclothemic Dennis Formation can be divided into five objective diagenetic facies that are distinguished by differing preservation of relict structures in originally unstable grains. The upper three of these facies contain fabrics suggestive of diagenesis in meteoric environments, whereas the lower two show little meteoric influence. The distribution of these facies suggests that isotopically light fresh water unsaturated with respect to $CaCO_3$ entered the Winterset Member during regression and dissolved unstable carbonate grains until a lens of saturated meteoric water formed. Further invasion by fresh water transferred $CaCO_3$ southward and downward in the formation, allowing early neomorphism and calcite cementation there. Unsaturated meteoric water penetrated the top of the transgressive Canville Member during maximum regression before subsequent transgression caused saturated meteoric water to rise back up through the formation. This allowed further calcite cementation, followed by later void filling by ferroan dolomite. Irregularities in the distribution of diagenetic facies occur in beds that occupied anomalous paleohydrologic positions.

The transfer of $CaCO_3$ caused by movement of meteoric lenses led to greater cementation in middle diagenetic facies than in uppermost or lowermost facies. This distribution of early cement governed later patterns of pressure solution and void filling by ferroan dolomite. Two other kinds of dolomite resulted from mixing of fresh and marine waters and from transfer of Mg from adjacent thick shales.

Chemical trends in ferroan dolomite and cathodoluminescent calcite may be explained by temporal and spatial changes in oxygenation during diagenesis. The organic-rich Stark Shale may have decreased oxygenation greatly.

Derivation of silica from intraformational biogenic sources allowed silicification of carbonate grains by chalcedony very early in diagenesis and permitted later void filling by megaquartz.

The distribution of Dennis diagenetic facies suggests a paleotopography and depositional history consistent with previously recognized depositional evidence. This agreement of diagenetic interpretations with established depositional evidence suggests that the concepts of diagenetic environments and resulting diagenetic facies may be useful in studying carbonate diagenesis.

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# INTRODUCTION

## Pennsylvanian Cyclothems

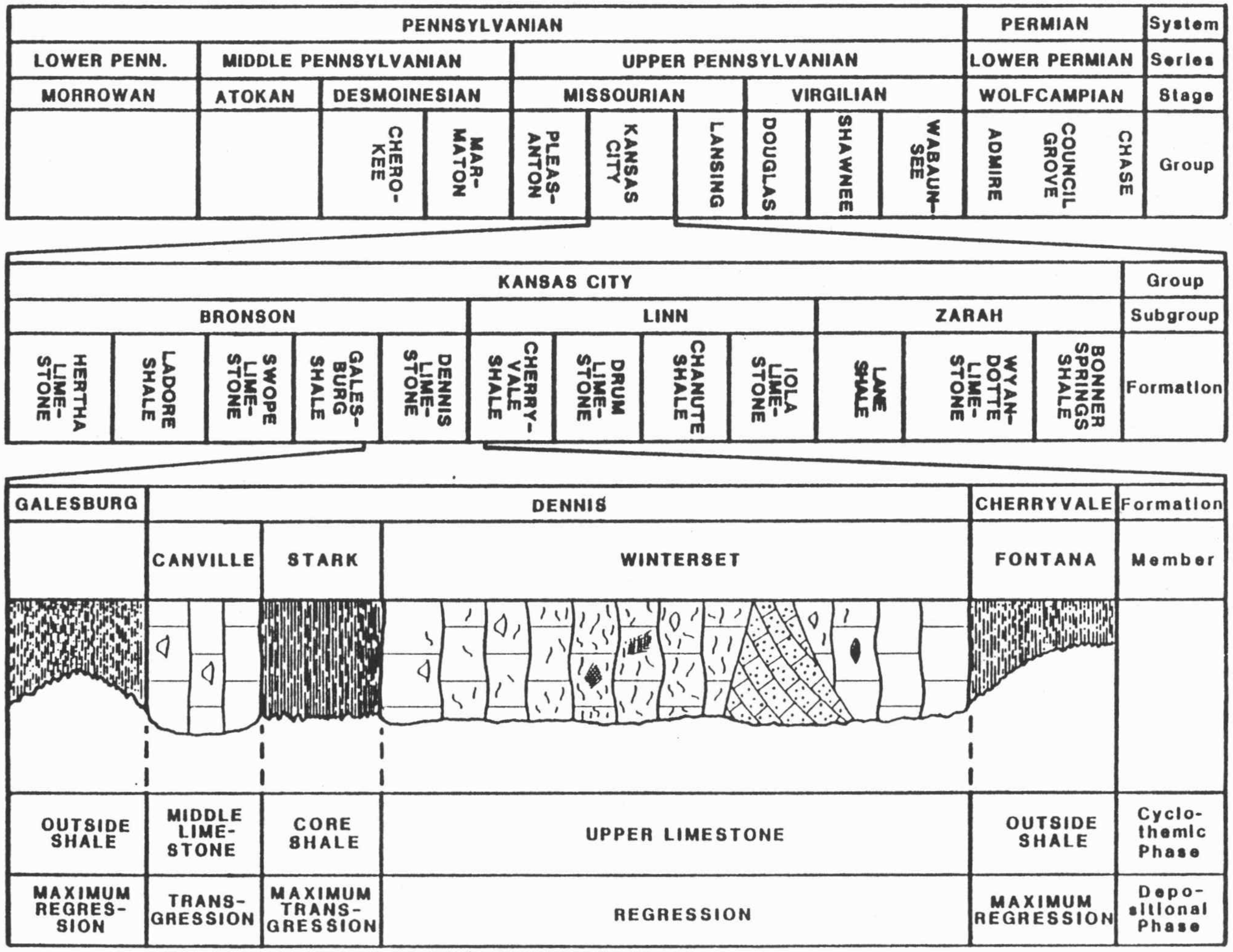
### Stratigraphy

Upper Pennsylvanian strata of the Mid-Continent United States are, in general, alternations of laterally extensive limestone and shale deposits (Fig. 1). These strata extend from Iowa and Nebraska through Missouri and Kansas into Oklahoma (Fig. 2). Moore (1931) recognized that these alternating deposits form cycles that ideally consist of seven phases in Virgilian sediments. Heckel (1977, 1978) has divided such cycles into just four phases, from top to bottom:

1) A thick sandy "outside" shale.
2) A thick "upper" limestone.
3) A thin and often black "core" shale.
4) A thin "middle" limestone.

This sequence is called a "cyclothem" (Fig. 3). Heckel's scheme emphasizes the difference between the black non-sandy "core" shale and the gray sandy "outside" shales, and ignores Moore's (1931) "lower" and "super" limestones, which are rare in

Figure 1 -- Stratigraphic terminology of Mid-Continent Pennsylvanian cyclic strata. Center column shows strata in Kansas City Group; right column gives details of Dennis Formation. Compiled from Moore et al. (1944), Moore (1949), Dunbar et al. (1960), and Heckel (1977). Cyclothemic and depositional phases adapted from Heckel (1977).



| PENNSYLVANIAN | | | | | | | | | | PERMIAN | | | System |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| LOWER PENN. | MIDDLE PENNSYLVANIAN | | | UPPER PENNSYLVANIAN | | | | | | LOWER PERMIAN | | | Series |
| MORROWAN | ATOKAN | DESMOINESIAN | | MISSOURIAN | | | VIRGILIAN | | | WOLFCAMPIAN | | | Stage |
| | | CHEROKEE | MARMATON | PLEASANTON | KANSAS CITY | LANSING | DOUGLAS | SHAWNEE | WABAUNSEE | ADMIRE | COUNCIL GROVE | CHASE | Group |

| KANSAS CITY | | | | | | | | | | | | Group |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| BRONSON | | | | | LINN | | | | ZARAH | | | Subgroup |
| HERTHA LIMESTONE | LADORE SHALE | SWOPE LIMESTONE | GALESBURG SHALE | DENNIS LIMESTONE | CHERRYVALE SHALE | DRUM LIMESTONE | CHANUTE SHALE | IOLA LIMESTONE | LANE SHALE | WYANDOTTE LIMESTONE | BONNER SPRINGS SHALE | Formation |

| GALESBURG | DENNIS | | | CHERRYVALE | Formation |
|---|---|---|---|---|---|
| | CANVILLE | STARK | WINTERSET | FONTANA | Member |
| OUTSIDE SHALE | MIDDLE LIMESTONE | CORE SHALE | UPPER LIMESTONE | OUTSIDE SHALE | Cyclothemic Phase |
| MAXIMUM REGRESSION | TRANSGRESSION | MAXIMUM TRANSGRESSION | REGRESSION | MAXIMUM REGRESSION | Depositional Phase |

Figure 1

Figure 2 -- Pennsylvanian outcrop belt in northern Mid-Continent. Stage boundaries are shown by solid lines; boundaries between depositional facies belts (Heckel, 1968) are shown by diamond symbols; Bourbon Arch is shown by double line. Modified from Heckel (1978) and Huffman (1959).

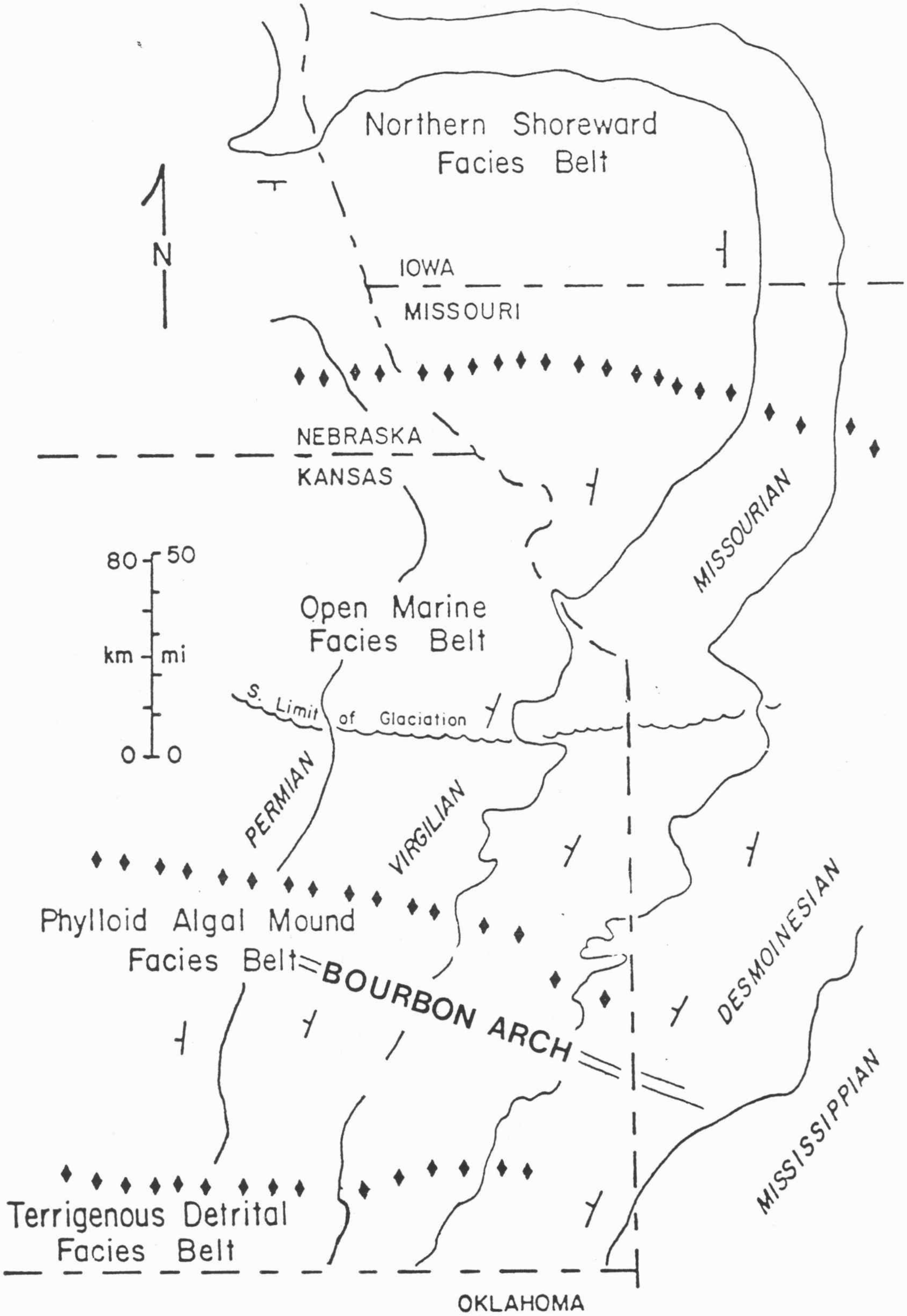

Northern Shoreward Facies Belt
N
IOWA
MISSOURI
NEBRASKA
KANSAS
80 km 0
50 mi 0
Open Marine Facies Belt
MISSOURIAN
S. Limit of Glaciation
PERMIAN
VIRGILIAN
Phylloid Algal Mound Facies Belt
BOURBON ARCH
DESMOINESIAN
MISSISSIPPIAN
Terrigenous Detrital Facies Belt
OKLAHOMA

Figure 2

Figure 3 -- Basic Upper Pennsylvanian Kansas cyclothem. Positional members, depositional environments, and phases of deposition presented according to Heckel (1977). Modified from Heckel (1977).

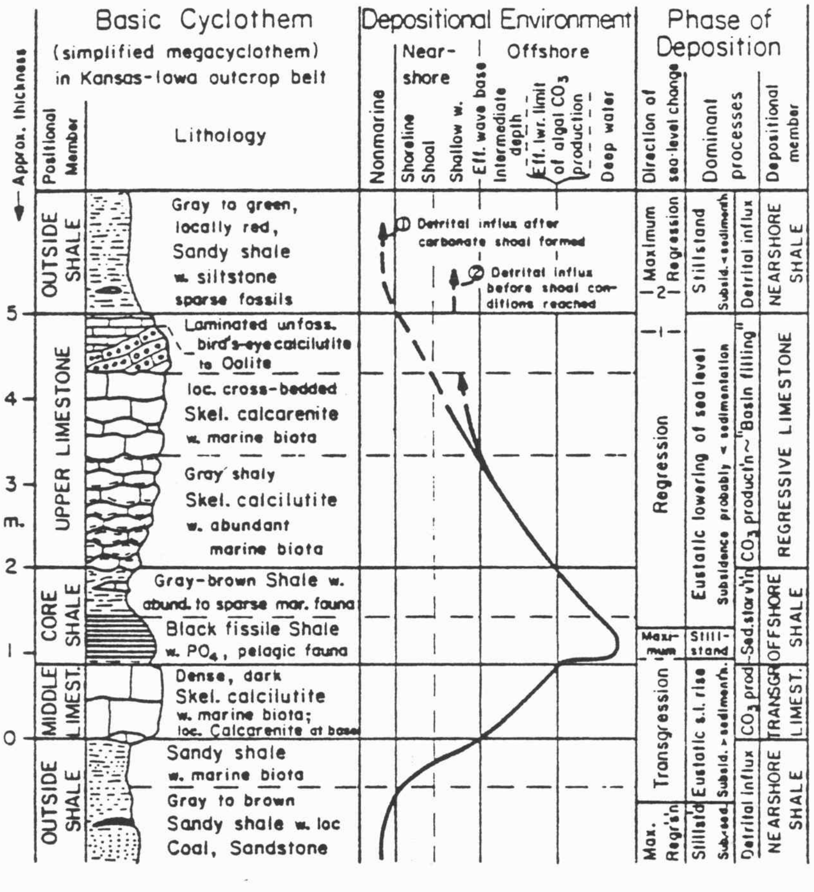

Basic Cyclothem
(simplified megacyclothem)
in Kansas-Iowa outcrop belt
Approx. thickness
Positional Member
Lithology
Depositional Environment
Nonmarine
Near-shore
Offshore
Shoreline
Shoal
Shallow w.
Eff. wave base
Intermediate depth
Eff. lwr. limit of algal $CO_3$ production
Deep water
Phase of Deposition
Direction of sea-level change
Dominant processes
Depositional member
OUTSIDE SHALE
Gray to green, locally red, Sandy shale w. siltstone sparse fossils
① Detrital influx after carbonate shoal formed
② Detrital influx before shoal conditions reached
Maximum Regression
2
1
Stillstand
Subsid.<sedimen'n
Detrital influx
NEARSHORE SHALE
5
UPPER LIMESTONE
Laminated unfoss. bird's-eye calcilutite to Oolite
loc. cross-bedded Skel. calcarenite w. marine biota
4
Gray shaly Skel. calcilutite w. abundant marine biota
3
m.
Regression
Eustatic lowering of sea level
Subsidence probably < sedimentation
$CO_3$ producti'n ~ "Basin filling"
REGRESSIVE LIMESTONE
2
CORE SHALE
Gray-brown Shale w. abund. to sparse mar. fauna
Black fissile Shale w. $PO_4$, pelagic fauna
1
Maximum
Stillstand
Sed. starv'n
OFFSHORE SHALE
MIDDLE LIMEST.
Dense, dark Skel. calcilutite w. marine biota; loc. Calcarenite at base
0
Transgression
Eustatic s.l. rise
Subsid.>sedimen'n
$CO_3$ prod.
TRANSGR. LIMEST.
OUTSIDE SHALE
Sandy shale w. marine biota
Gray to brown Sandy shale w. loc Coal, Sandstone
Max. Regr'n
Stillst'd
Subsid.≈sed.
Detrital influx
NEARSHORE SHALE

Figure 3

Missourian cyclothems. Therefore, Heckel's (1977) terminology will be used in this study.

## Depositional Models

Moore (1929) recognized that the interbedding of marine (limestone) and non-marine (gray shale) strata in cyclothems represents repeated transgression and regression, and concluded that "the seas were not only very shallow but they were also excessively fluctuating." Wanless and Shepard (1936) attributed such fluctuations to late Paleozoic glaciation, and more recently Crowell (1978) has supported that explanation.

Moore was uncertain about the deposition of the black shales, referring to them as the "least well understood" phase in the depositional cycle (Moore, 1950). He concluded that they were deposited under a "marine swamp" that restricted water circulation over the sediments and which may have resulted from the flooding of coal swamps (Moore, 1929, 1950, 1964). Zangerl and Richardson (1963) and Merrill (1975) proposed that the black shales were deposited in shallow water beneath dense floating mats or "flotants" of vegetation in nearshore or non-marine settings. According to this model, the vegetation prevented disturbance of the underlying sediment and created an anoxic bottom.

Heckel (1977) proposed an offshore environment of deposition for the black shales during maximum transgression (see also Heckel and Baesemann, 1975). Heckel's model calls for an anoxic sea bottom below a thermocline, which prohibited vertical water circulation (Heckel, 1977). This suggests deposition of the middle limestone during transgression, the core shale during maximum transgression, and the upper limestone during regression (Fig. 3). This model accounts for the great lateral extent of the black shales, and it requires fewer transgressions and regressions for the deposition of one cyclothem than do the flotant models, which treat all shales as products of nearshore environments.

## Depositional Facies Belts

Heckel (1968) recognized four depositional facies belts in Missourian cyclothems (Fig. 2). In Iowa, Nebraska, and northern Missouri, the "northern shoreward" facies belt is dominated by _Osagia_ calcarenites and laminated calcilutites. In Missouri and northeastern Kansas the "open marine" facies belt consists largely of skeletal calcilutites with scattered calcarenites. The "algal mound facies belt" in southeastern Kansas consists of thick algal mound complexes, with calcarenites in their upper reaches. In southernmost Kansas and Oklahoma the "detrital" facies belt contains thin skeletal calcarenites and calcilutites between thick outside shales. The boundary between the detrital and algal mound facies belts is sharp; boundaries between facies belts become less distinct northward (Heckel, 1977).

## Carbonate Diagenesis

The diagenesis of marine carbonate sediments involves the stabilization of sediments to chemical and physical conditions differing from those present at deposition. This process includes the recrystallization or removal of unstable minerals and the reduction of primary porosity, in response to changed pore-water chemistries and greater hydrostatic pressures.

Physical and chemical conditions at the time of deposition are altered most readily by burial of the sediment or by exposure to non-marine waters. Burial increases hydrostatic pressure and allows the chemistry of the waters within the sediment to change slowly in a closed chemical system. Exposure of the sediment to non-marine water, such as meteoric water encountered during regression of seas, changes the water chemistry greatly in a more open system and causes most marine sediments to be out of equilibrium (unstable) in their new chemical environments. Any combination or sequence of burial and exposure to meteoric water can occur after deposition.

### Processes

Grains of unstable mineralogies (generally aragonite and very high-Mg calcite in meteoric water) are believed to be eliminated either by complete dissolution of the grain and subsequent filling of the resulting void by stable minerals (generally low Mg calcite), or by a more gradual transformation of unstable mineralogies to stable ones with only a small resultant void at any one time. The former process ("void filling") would destroy original structures within the grains, and the resulting spar would have textures like those of a cement (see below). In contrast, the latter process ("neomorphism") would allow preservation of original structures.

These processes result from differing chemical environments. Water unsaturated with respect to $CaCO_3$ would dissolve grains completely to leave voids, and because aragonite is more soluble than calcite, aragonite grains would be preferentially dissolved. Water saturated with respect to $CaCO_3$ would also dissolve aragonite but would precipitate calcite at the same time, perhaps within the same grain to allow neomorphism.

Bathurst (1975) proposed criteria for the recognition of the two types of spar resulting from these processes. In general, coarse clear calcite spar with straight crystal boundaries, no remnant internal structures, geopetal sediment fabrics, and multigenerational textures is interpreted as resulting from void filling. In contrast, fine-grained or cloudy inclusion-rich spar with jagged crystal boundaries and relict ("ghost") structure is taken to result from neomorphism. Saller

(1982) argued, however, that these two processes are only ideal end members and that processes intermediate between the two give rise to textures intermediate between complete preservation and complete destruction of original structure in carbonate grains. Steinen (1982) found evidence of such intermediate processes in Bahaman Holocene carbonate mud.

Porosity in carbonate sediments is reduced by filling of voids with spar, by compaction, or by both. Folk (1974) found that needle-like aragonite and high-Mg calcite are the phases most likely to precipitate into voids from Mg-rich marine water, whereas drusy or blocky low Mg calcite is most likely to precipitate from meteoric water, or connate water from which Mg has been removed. Crystals precipitated in primary voids early in diagenesis may become unstable as conditions change and be modified by one of the processes discussed above in relation to carbonate grains; Lohmann and Meyers (1977) have discussed this modification of high-Mg calcite cements.

Porosity can also be reduced by compaction and/or pressure solution; the latter involves the dissolution of carbonate material. Meyers (1980) listed petrographic characteristics of compaction, and Wanless (1979) and Buxton and Sibley (1981) classified fabrics resulting from pressure solution.

Diagenesis may also increase porosity through dissolution of grains, cements, or both. Choquette and Pray (1970) classified the porosity of carbonate rocks resulting from all known diagenetic processes.

## Diagenetic Environments

Longman (1980) outlined diagenetic environments that might result from subaerial exposure of carbonates and invasion by fresh water, and he summarized the petrographic characteristics of each, as interpreted from Recent or Pleistocene examples. Wilkinson, Janecke, and Brett (1982) have suggested that strict uniformitarian application of these characteristics to the interpretation of ancient carbonate sediments may be faulty. Longman (1980) classified environments according to the nature of the water present within the sediment and by the presence or absence of air in the pores. The environments, in order from the surface of subaerial exposure to the non-meteorically affected sediments, are meteoric vadose, meteoric phreatic, mixed meteoric-marine phreatic, and marine phreatic (Fig. 4). Because fresh water enters the system at the surface of subaerial exposure, water undersaturated with respect to calcium carbonate will exist in much of the meteoric vadose environment and may exist in the meteoric phreatic environment, allowing delineation of zones within environments. Zones are defined also by whether or not calcium carbonate precipitates rapidly (in the "active" zone) or only very slowly (in the "stagnant" zone). Longman (1980) pointed out that the presence

Figure 4 -- Nearshore diagenetic environments (upper case) and zones (lower case). Zones of major cement precipitation are shown with oblique lines. Positions and presence of many environments depend on climate, hydrology, and variations in lithology. Adapted from Heckel (ms. in press).

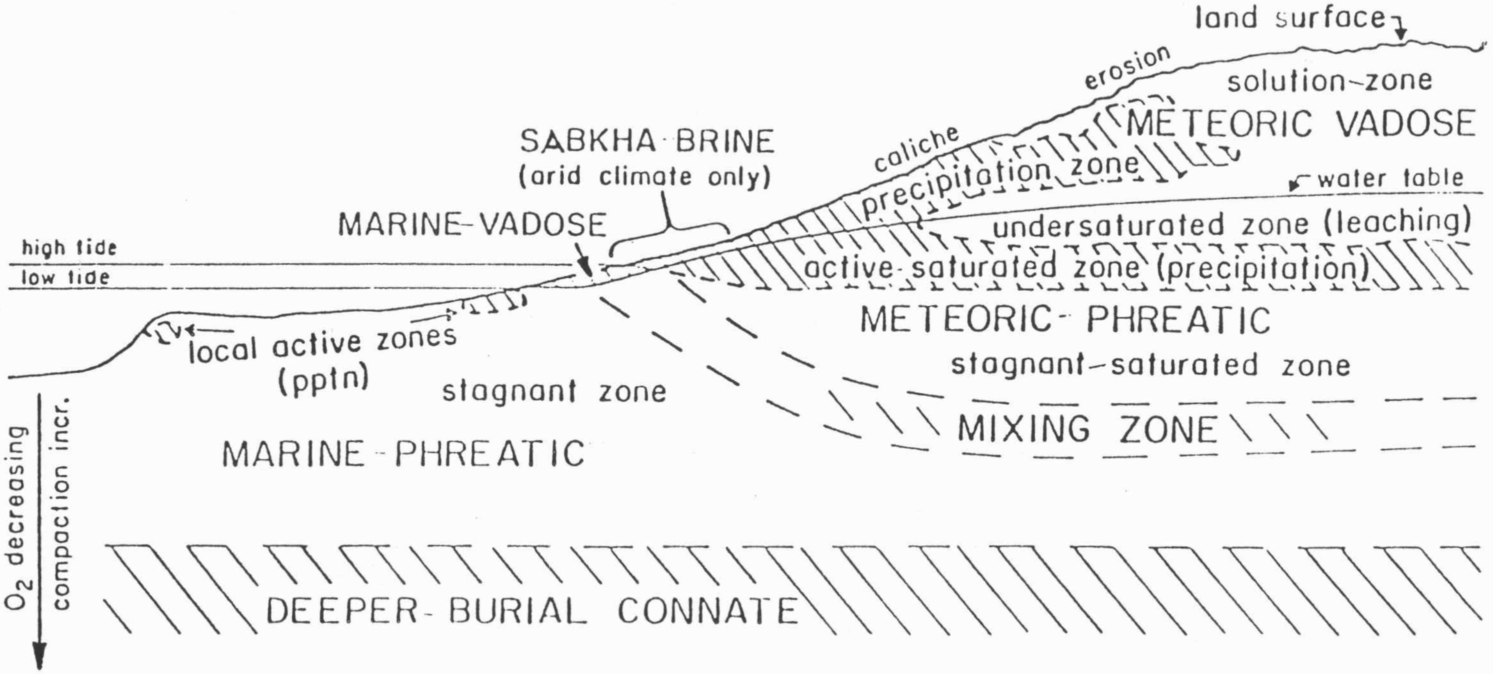

land surface
erosion
solution-zone
caliche
METEORIC VADOSE
precipitation zone
water table
SABKHA BRINE
(arid climate only)
MARINE-VADOSE
high tide
low tide
undersaturated zone (leaching)
active-saturated zone (precipitation)
METEORIC-PHREATIC
local active zones
(pptn)
stagnant zone
stagnant-saturated zone
MIXING ZONE
MARINE-PHREATIC
$O_2$ decreasing
compaction incr.
DEEPER-BURIAL CONNATE

Figure 4

and configuration of the various environments may vary greatly with hydrologic conditions and climate.

Many of Longman's (1980) diagenetic environments and zones have distinct processes and resultant textures. The active marine phreatic zone is characterized by fibrous to granular aragonite and high-Mg calcite cements. Precipitation of dolomite and silica (and replacement of carbonate grains by these minerals) may occur in the meteoric-marine mixing zone (Hanshaw et al., 1971; Badiozamani, 1973; Land, 1973; Knauth, 1979). Neomorphism and little cementation occur in the stagnant meteoric phreatic zone, whereas widespread neomorphism and cementation by low-Mg calcite occur in the active saturated meteoric phreatic zone. Leaching occurs in the unsaturated meteoric phreatic zone, and extensive leaching and weathering occur in the unsaturated meteoric vadose zone. Caliche forms in the saturated meteoric vadose zone.

With extensive exposure of carbonate sediments above sea level, any given portion of the sediment may be exposed to different diagenetic environments with time. Longman (1980) pointed out that continued regression could cause passage from the marine phreatic environment to mixing zone, meteoric phreatic, and meteoric vadose environemnts. He concluded that a sequence of diagenetic environments may be deduced from petrographic evidence, although both he and Saller (1982) stress that petrographic textures, such as preservation of a particular grain type, may vary greatly within one environment.

## Diagenesis of Pennsylvanian Cyclothems

Heckel (1982; ms. in press) has applied the work of Longman (1980) and other authors to develop a model for the diagenesis of Mid-Continent Pennsylvanian cyclothems. From study of diagenetic patterns within many Pennsylvanian cyclothems, Heckel has generalized that middle limestones are overpacked, late-cemented, and show excellent preservation of original structures in unstable grains. Upper limestones, in contrast, show much more early cementation, less overpacking, and much more variable preservation of original structure. These diagenetic trends follow logically from the depositional model established by Heckel (1977). The transgessive middle limestones should have been buried under the seal-like core shales without encountering meteoric water, whereas the upper limestones should have been flushed to varying degrees with meteoric water as the seas withdrew (Heckel, 1980).

Other diagenetic studies of Mid-Continent Pennsylvanian cyclothems include Mossler (1971) on the Swope Formation in southeastern Kansas, Watney and Ebanks (1978) on subaerial freshwater diagenesis of cyclothems in the subsurface of southern Nebraska and northern Kansas, Ravn and Heckel (1978) on early cements in algal sparites, and Dubois (1979) on porosity in the subsurface "E" zone in southwestern Nebraska. Watney (1980) has discussed the diagenesis of cyclothems in the subsurface of northwestern Kansas and southwestern Nebraska.

## Description of Study

### Dennis Formation

This study examines the diagenesis of the Canville and Winterset Members of the Missourian (Upper Pennsylvanian) Dennis Formation in Iowa, Missouri, and Kansas (Fig. 1). The Winterset and Canville Members are the upper and lower limestone members of the Dennis Formation, respectively, and are separated by the Stark Shale Member. Above the Dennis Formation is the Cherryvale Shale, and below it is the Galesburg Shale. The Dennis Formation is at the top of the Bronson Subgroup of the Kansas City Group (Moore, 1948).

The Canville Member is, in the terminology of Heckel (1977), the middle or transgressive limestone of the Dennis cyclothem. It is generally less than three feet thick and is developed typically only in southeastern Kansas (Jewett, 1932; Moore, 1935). The Winterset Member is the upper or regressive limestone and is generally up to fifty feet thick, although in one area it reaches a thickness of ninety feet (Frost, 1975).

The Winterset extends through all four of Heckel's (1968) facies belts from Iowa to Oklahoma. In Iowa and northern

Missouri it consists of skeletal calcilutites, with a skeletal calcarenite in its upper portion (Fig. 5). In southeastern Kansas it consists largely of algal calcilutites with oolitic calcarenites in its upper reaches.

Previous workers have discussed thoroughly the stratigraphy and deposition of the Dennis Formation. Adams, Girty, and White (1903) named the Dennis Formation; Jewett (1932) named the Canville Member, and Tilton and Bain (1897) named the Winterset Member. Lane (1939) studied the Winterset Member in Jackson County, Missouri, and Hanson (1957) studied the Winterset in southernmost Kansas and northern Oklahoma. Horne (1965) studied the Dennis Formation throughout the outcrop belt, Payton (1964, 1966) studied the Dennis in Iowa and Missouri, and Frost (1968, 1975) studied the Winterset Member in southeastern Kansas. Dubois (1979) studied the development of porosity in the Winterset Member (subsurface "E" zone) in southwestern Nebraska. Siebels (1981) studied the overlying Cherryvale shale, and Schutter (1983) studied the Galesburg and Stark Shales.

## Objectives

This study attempts to establish objective diagenetic facies within the Canville and Winterset Limestone Members, to relate these facies to interpreted diagenetic environments or sequences of environments, and from such sequences to interpret

Figure 5 -- Stratigraphic cross-section of Dennis Formation showing major depositional facies. Datum is top of Stark Shale Member. Vertical lines show extent of vertical control at each locality. Compiled from Payton (1964, 1966), Frost (1968, 1975) and author's field notes.

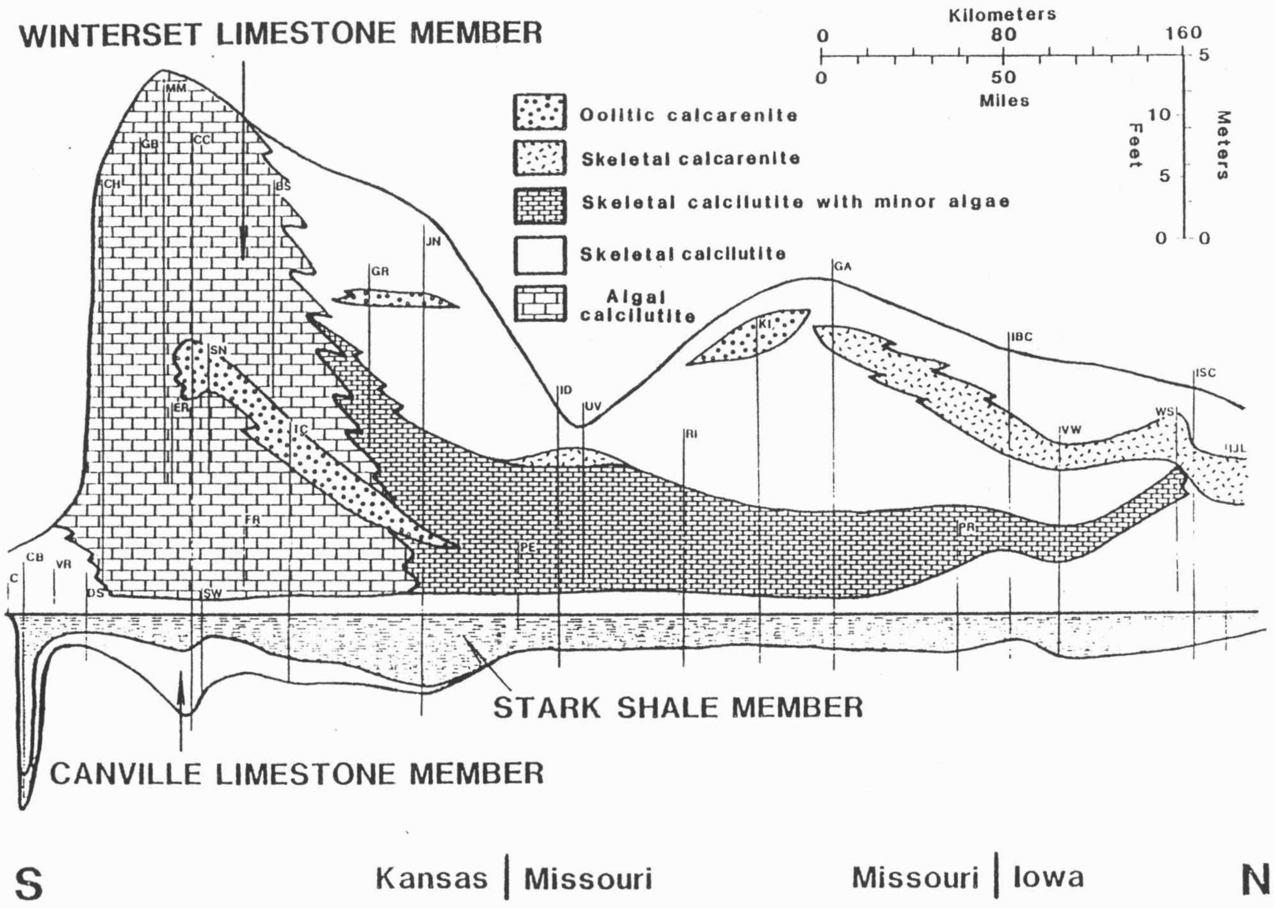

WINTERSET LIMESTONE MEMBER
Kilometers
0
80
160
0
50
Miles
Feet
10
5
0
Meters
5
0
Oolitic calcarenite
Skeletal calcarenite
Skeletal calcilutite with minor algae
Skeletal calcilutite
Algal calcilutite
MM
GB
CC
CH
BS
JN
GR
SN
ER
TC
FR
C
CB
VR
DS
SW
PE
ID
UV
RI
KI
GA
IBC
ISC
WS
VW
IJL
PR
STARK SHALE MEMBER
CANVILLE LIMESTONE MEMBER
S
Kansas | Missouri
Missouri | Iowa
N

Figure 5

the diagenetic history of both units. The study attempts to relate that diagenetic history to previous depositional and paleogeographic interpretations, and, by systematically studying one cyclothem, will test the models of Heckel (1977, 1982) for deposition and diagenesis of Mid-Continent cyclothems. In addition to examining carbonate diagenetic textures, the study examines diagenetic silica and opaque minerals and integrates these into the diagenetic history. It examines also some aspects of the chemistry of carbonate diagenesis, but does not concentrate on the diagenesis of carbonate mud.

## Methods

Thirty-three outcrop localities of the Dennis Formation in Iowa, Missouri, and Kansas were measured and sampled, and 159 thin sections were prepared from 28 of those localities (Fig. 6). In addition, 28 thin sections were prepared from three cores in Iowa. All thin sections were examined petrographically and with a Nuclide ELM-2A cathodoluminoscope operated at 12 kilovolts, 0.5 milliamps and 50 to 70 millitorr. Selected samples were stained with alizarin red S and potassium ferricyanide in accordance with Dickson (1965). Chemical analyses of selected samples were obtained by wavelength dispersive spectrometry (WDS) using an ARL EMX-SM electron microprobe with Tracor Northern TN-2000 software. Whole-rock

Figure 6 -- Outcrops and cores used in study. Exact locations are given in Appendix A.

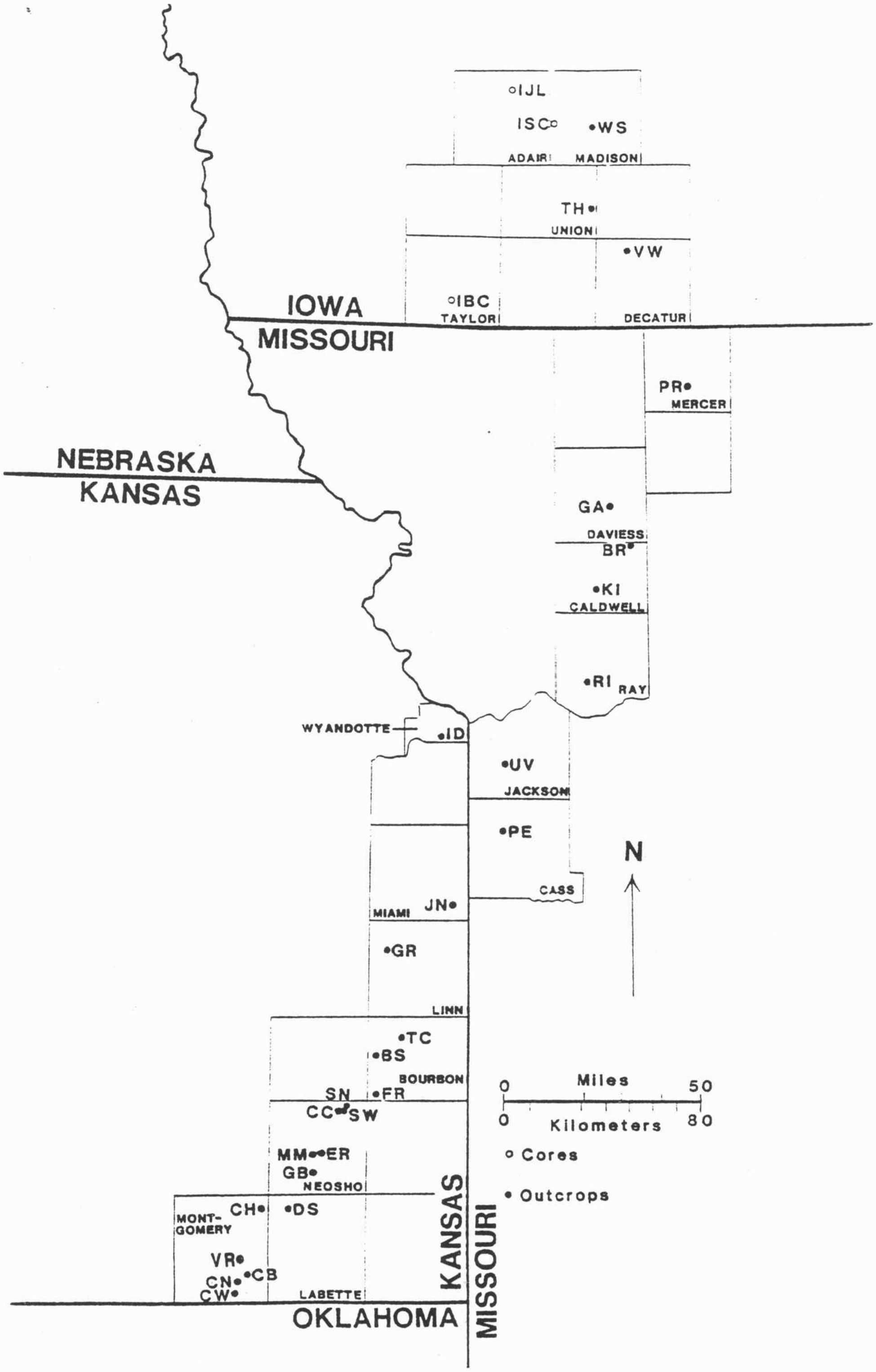

IJL
ISC
WS
ADAIR
MADISON
TH
UNION
VW
IBC
TAYLOR
DECATUR
IOWA
MISSOURI
PR
MERCER
NEBRASKA
KANSAS
GA
DAVIESS
BR
KI
CALDWELL
RI
RAY
WYANDOTTE
ID
UV
JACKSON
PE
N
JN
CASS
MIAMI
GR
LINN
TC
BS
BOURBON
SN
FR
CC
SW
Miles
0
50
0
80
Kilometers
○ Cores
● Outcrops
MM
ER
GB
NEOSHO
CH
DS
MONT-GOMERY
VR
CB
CN
CW
LABETTE
KANSAS
MISSOURI
OKLAHOMA

Figure 6

analyses of carbon and oxygen isotopes of a limited number of samples were performed by Mr. Ken Schmitz of Northern Illinois University.

# CHAPTER 2

# CARBONATE DIAGENETIC FACIES IN THE DENNIS FORMATION

## Diagenetic Facies

Diagenetic facies are rock bodies that possess distinctive diagenetic textures. They are, therefore, objectively defined units and are not based on an interpretation of diagenetic history. However, the heterogeneous nature of diagenetic textures (as noted in this study) causes most facies boundaries to be gradational. In this study, diagenetic facies are determined by the degree of preservation or destruction of original structures within carbonate grains usually interpreted as having unstable original mineralogies. In the Dennis Formation molluscs, algae, and ooids are the major grain types reasonably interpreted as having such original mineralogies. The only carbonate strata in the Dennis completely lacking such grains are characterized by a distinctive dolomitic microspar fabric, and they are delineated as a separate facies.

The naming of diagenetic facies is problematic. Purely descriptive names, such as "clams, algae, and ooids with clear blocky spar" facies, are too awkward to be useful. Interpretive names, such as "leached" facies, prejudge interpretation and mask the objective nature of the facies. Geographic or stratigraphic names, such as "northern" or "upper", conceal the complexity of facies distributions. Therefore, in this study facies will be designated by arbitrary letters (A, B, C, D, and E) to avoid these problems.

The distribution of five diagenetic facies within the carbonate members of the Dennis Formation is shown in Figure 7. This chapter describes the diagenetic fabrics characteristic of each of these facies, makes basic interpretations regarding void-filling, neomorphic, and compactional processes, and determines the relative timing of events. Some facies overlap into Facies E because it locally contains molluscs, ooids, and algae, which allow recognition of the other facies. It should be noted that the diagenetic facies are generally independent of depositional facies and cut across Heckel's (1968) depositional facies belts except at the boundary between the detrital and algal mound facies belts.

## Facies A

Facies A consists of those rocks in which all originally unstable grains lack any relict internal structure. The facies extends through almost the entire Winterset Member in Iowa and northernmost Missouri. South of Mercer County, Missouri, this facies extends only through the uppermost Winterset, and south

Figure 7 -- Stratigraphic cross-section of Dennis Formation showing diagenetic facies. Datum is top of Stark Shale Member. Facies A consists of rocks in which originally unstable grains contain no trace of original structure; Facies B consists of rocks in which such grains have little or no preservation of structure; Facies C consists of rocks in which such grains commonly contain preserved structure but some do not; Facies D consists of rocks in which all such grains contain some preserved structure; Facies E consists of rocks devoid of originally unstable grains and characterized by a dolomitic microspar matrix. Vertical lines show extent of vertical control at each locality.

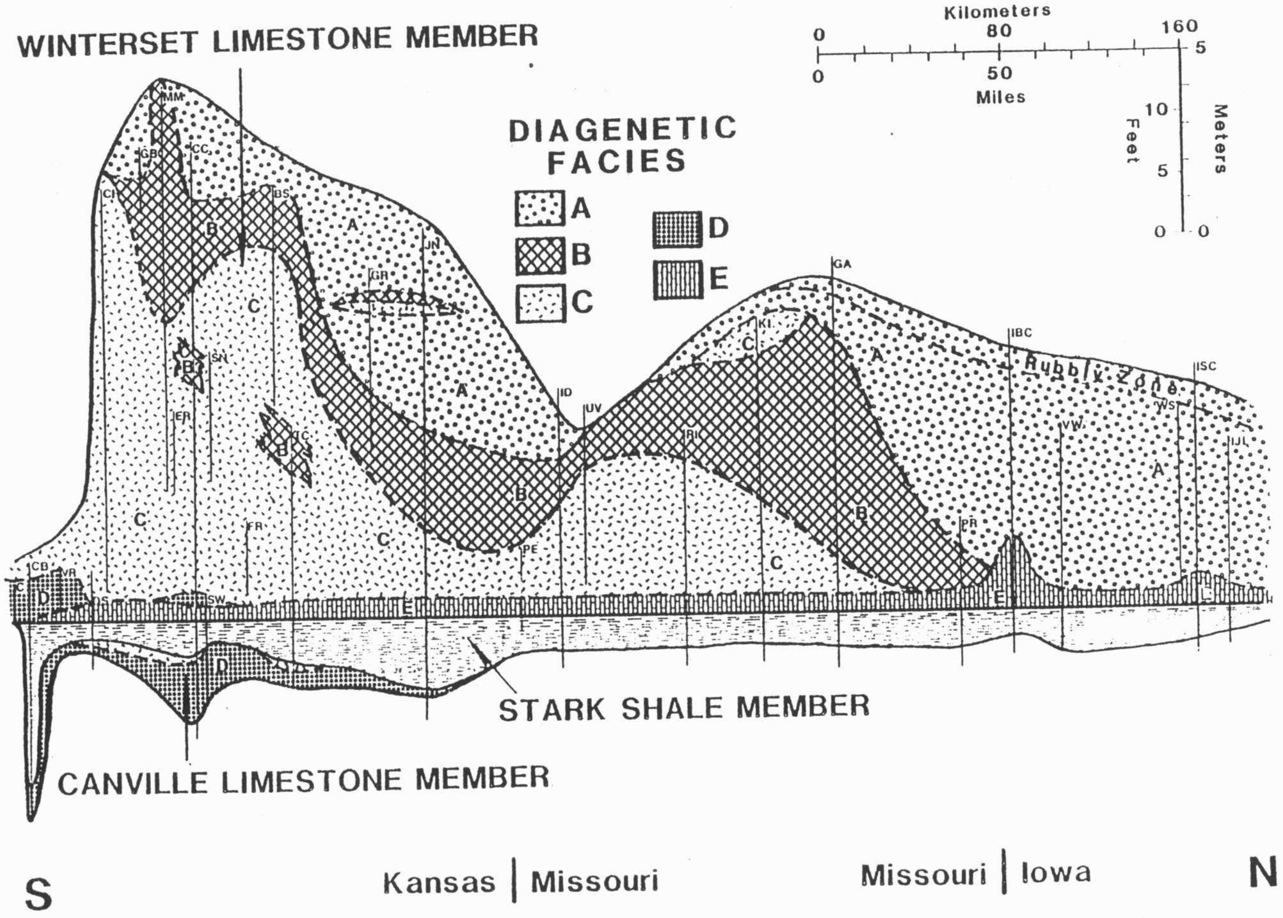

WINTERSET LIMESTONE MEMBER
DIAGENETIC FACIES
A
B
C
D
E
Kilometers
0
80
160
0
50
Miles
5
10
5
0
0
Feet
Meters
Rubbly Zone
STARK SHALE MEMBER
CANVILLE LIMESTONE MEMBER
S
Kansas
Missouri
Missouri
Iowa
N
MM
GB
CC
CI
BS
JN
GR
SA
ER
GC
FR
PE
ID
UV
RI
KI
GA
PR
IBC
ISC
WS
VW
IJL
CB
VR
SW

Figure 7

of Neosho County, Kansas, it is absent. It disappears near Kansas City.

## Preservation of Grains

All phylloid algae, ooids, and molluscs are devoid of relict structure in Facies A. Phylloid algae consist only of clear blocky spar, and the outlines of algal blades are commonly disrupted by brecciation of the surrounding mud, suggesting that the mud collapsed as coherent clasts into the space originally occupied by the algae (Fig. 8a). This fabric is very common in the algal mound facies, and the resulting rock is rich in spar.

Molluscs in Facies A consist of clear blocky spar and, in some calcarenites, can be recognized only by micrite envelopes showing the original external grain shape (Fig. 8b). Clams in Osagia grains in northern calcarenites consist of fine calcite spar in most cases.

Ooids in Facies A consist of clear blocky spar with lumps of micrite generally in their lower halves. Ooids near the top of the Winterset at locality ID (see Appendix B) show no internal structure and consist of clear calcite spar and/or coarse ferroan dolomite.

In summary, originally unstable grains in Facies A show no preserved internal structure within clear blocky calcite. The criteria of Bathurst (1975) suggest that such calcite had a

Figure 8 -- Diagenetic fabrics in Facies A.

a. Brecciated lime mud resulting from dissolution of unstable carbonate grains, probably phylloid algae beneath smooth mud surfaces. Unattached encrusting bryozoan (B) suggests former presence of firm support. (Plane-polarized light; GA8.8; Scale bar is 1 mm.)

b. Clam (lower right) outlined by micrite envelope; other grains are also heavily micritized. Void-filling spar coarsens toward void centers (e.g., to left of clam). (Plane-polarized light; VW4.85; Scale bar is .25 mm.)

c. Fine rhombic dolomite (D) occurring at edges of primary intergranular void and surrounded by calcite (C) that was precipitated later. (Plane-polarized light; ISC86.5; Scale bar is 25 microns.)

d. Coarse ferroan dolomite (D) filling a primary intergranular void in a calcarenite. (Plane-polarized light; IBC497.2; Scale bar is .25 mm.)

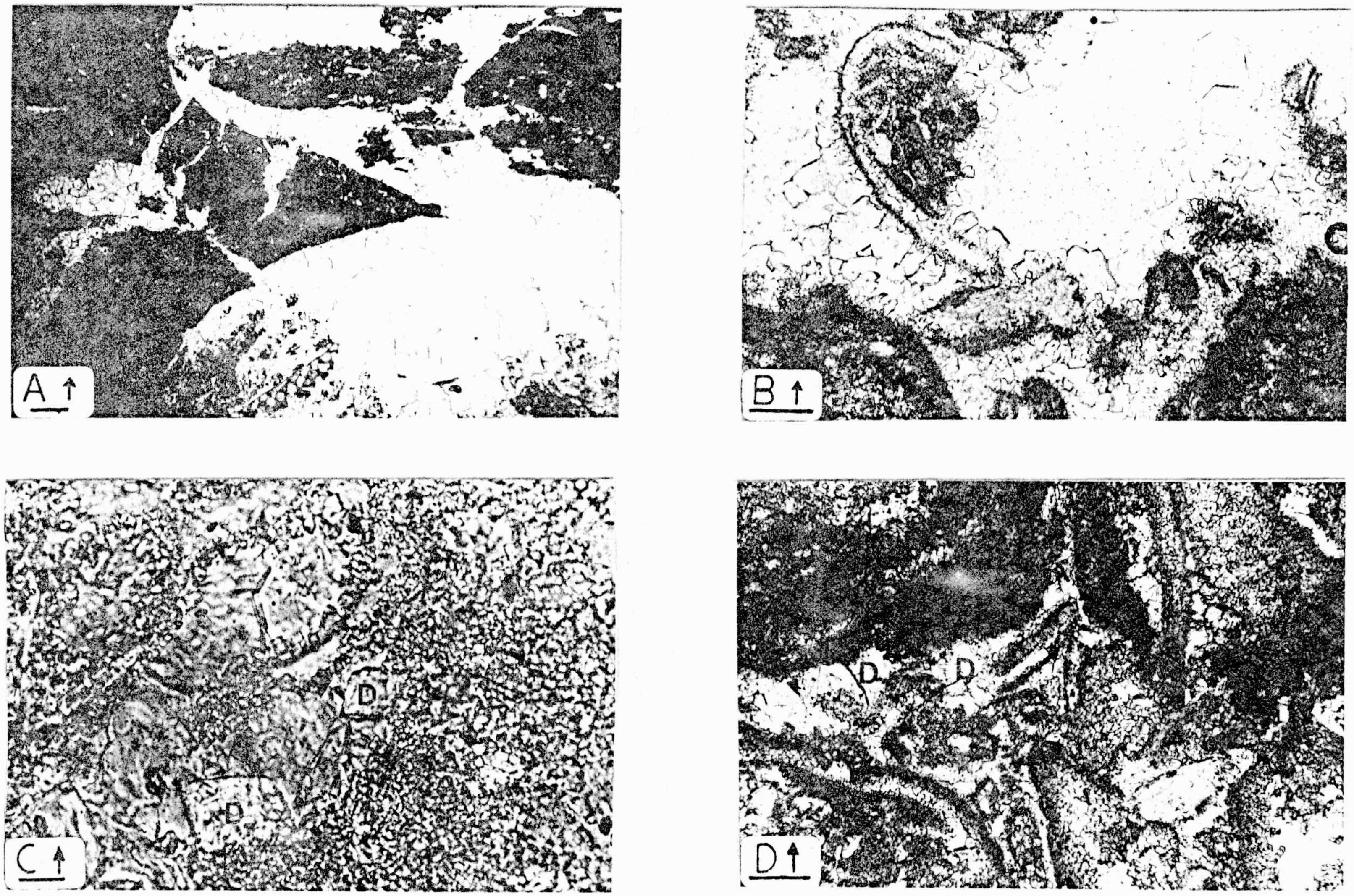


Figure 8

void-filling origin, and the collapse of mud into some grains suggests that extensive dissolution occurred. Other originally calcitic grains in Facies A show few diagenetic effects other than interpenetrating contacts, rare grain breakage, and internal void filling. Some brachiopods display borings that may be attributed to sponges.

## Cements

Cements in Facies A are almost entirely mosaics of clear blocky calcite spar that coarsen toward the centers of voids (Fig. 8b). Cements containing inclusions of microdolomite (Lohmann and Meyers, 1977) are very rare in this facies, in contrast to the facies described below.

Two distinct types of dolomite occur in Facies A, and one is unique to it. The unique type consists of clear small (10-60 microns) rhombs of dolomite that occur in primary voids and are adjacent to grains (Fig. 8c). This spatial relationship suggests formation early in diagenesis. The second type of dolomite occurs in both primary and secondary voids and is coarser, ferroan, and generally clear (Fig. 8d). It is separated from void walls in some cases by crystals of blocky or scalenohedral calcite, suggesting a formation later than that of the first type.

The top of Facies A north of Caldwell County, Missouri, consists of rubbly, nodular calcilutite up to 1 meter thick that contains pockets and fracture fillings of the overlying Cherryvale Shale. Crystal-lined vugs occur in the meter below the rubbly strata at locality TH.

## Facies B

Facies B consists of those strata in which internal structures in originally unstable grains are rarely present or only poorly preserved, but it is distinguished from Facies A by at least minimal preservation. Facies B extends from northern Missouri to Neosho County, Kansas, within the upper, but rarely uppermost, parts of the Winterset Member (Fig. 7). It also occurs in oolite beds lower in the Winterset in southeastern Kansas.

### Preservation of Grains

The preservation of phylloid algae, molluscs, and ooids in Facies B is highly variable and rarely outstanding. In the few cases where preservation is outstanding, original structures within similar grains nearby are completely obliterated (Fig. 9a). Phylloid algae and molluscs show complete internal structure very rarely but instead have remnants of such structures at their outer edges (Fig. 9b). In other cases, the spar composing them shows only cloudy areas parallel to the original structure of the grain.

Ooids show no more preservation of internal structure than

Figure 9 -- Diagenetic fabrics in Facies B.

a. Two snails, one with detailed preservation of structure (lower right) and the other with all original structure destroyed. (Plane-polarized light; MM10.4; Scale bar is 1 mm.)

b. Phylloid algal blade with only minimal preservation of utricles at edges (arrow). (Plane-polarized light; GA3.7 Scale bar is 1 mm.)

c. Oolitic calcarenite with oomoldic porosity (right half) and ooids displaying preserved concentric structure (arrow). (Plane-polarized light; CC12.3; Scale bar is 1 mm.)

d. Skeletal calcarenite cemented by isopachous rims of small sparry calcite crystals followed by poikilotopic cement filling both primary (intergranular) and secondary voids. Areas labelled "P" are all one poikilotopic crystal. (Cross-polarized light; JN5.0; Scale bar is .25 mm.)

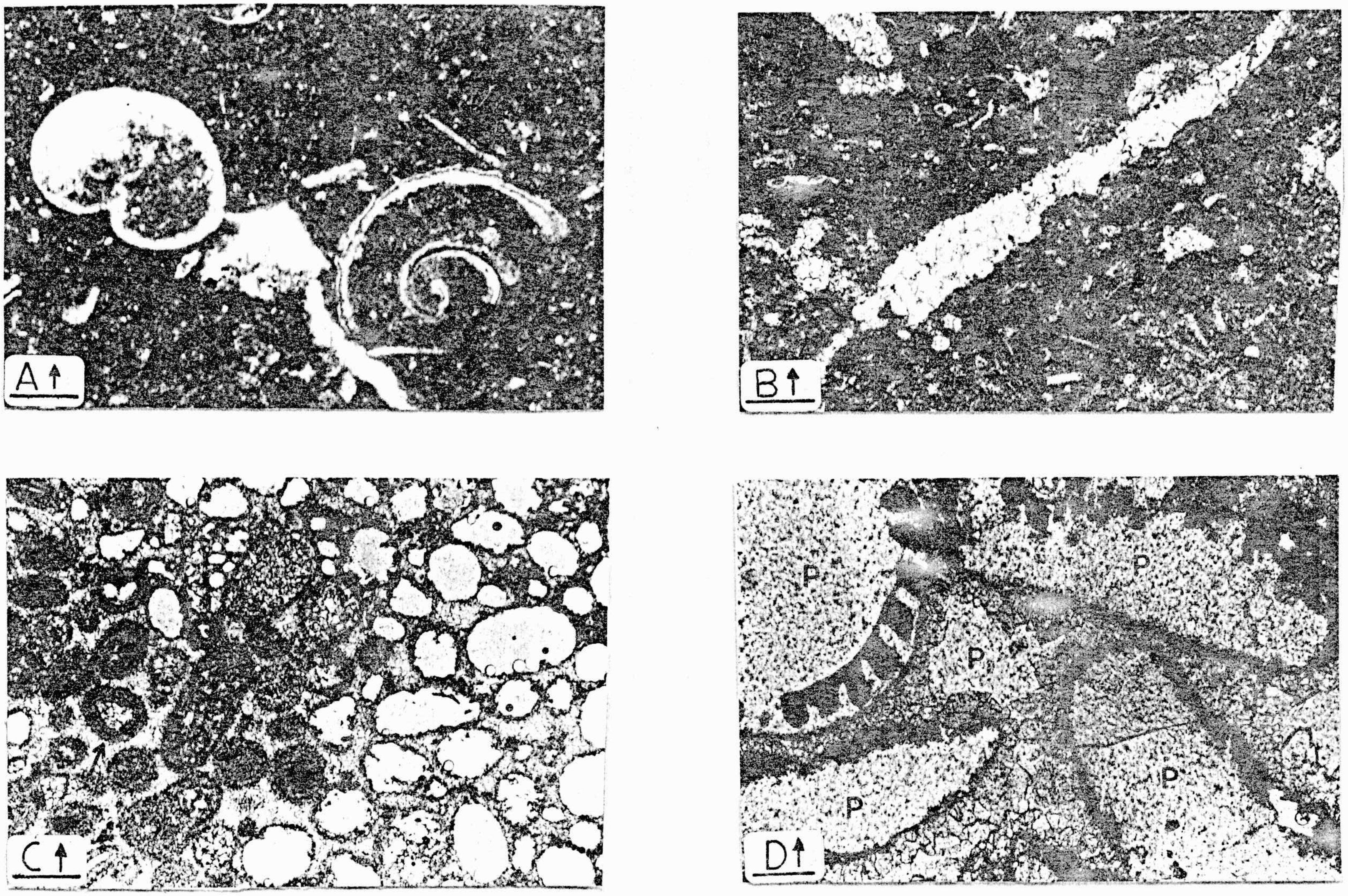


Figure 9

do those in Facies A, except at localities CC and TC. There, ooids in oolite beds are blocky calcite as in Facies A, display concentric structure in a microspar fabric, or are represented only as voids (Fig. 9c) to form "oomoldic porosity" (Choquette and Pray, 1970).

In summary, preservation of unstable grains in Facies B is poor but variable, even within a single thin section. This suggests that diagenesis in Facies B involved both void-filling and neomorphic processes, but that the former predominated.

## Cements

Cements in Facies B consist largely of clear blocky calcite. In some cases grains are surrounded by rims of drusy scalenohedral calcite, with blocky spar in the centers of voids (Fig. 9d). Cements containing rims of microdolomitic inclusions around the edges of voids (similar to Fig. 10d) are more common in Facies B than Facies A.

Some calcarenites in Facies B contain scattered poikilotopic cements that fill apparently leached grains and the centers of intergranular voids (beyond fringing scalenohedral cements) (Fig. 9d). This suggests that the grains were leached after the precipitation of scalenohedral rims but before the precipitation of coarse blocky intergranular cements.

In the algal mound facies, many algal blades are disrupted by brecciated mud, as in Facies A. Most voids in the mud are filled with clear blocky calcite, but some are filled in part with clear ferroan dolomite. In many cases this dolomite is surrounded by euhedral calcite spar, suggesting formation after the calcite, but in some cases both dolomite and calcite crystals are euhedral within a filled void, suggesting virtually synchronous formation. Ferroan dolomite may also extend into micritic areas, where it is not clear, suggesting that it has replaced carbonate mud rather than filled a void. Small stylolites or solution seams (Buxton and Sibley, 1981) cut across some rocks in the algal mound facies. Associated with some of these stylolites are concentrations of fine (5 to 50 microns) rhombic dolomite like that described by Wanless (1979).

## Facies C

Facies C consists of those strata in which originally unstable grains retain considerable internal structure, although some grains show none. This definition requires that the boundary with Facies B be gradational in many cases. Facies C extends from northern Missouri to Oklahoma and consists in general of the lower half of the Winterset Member, although it cannot be extended down to the top of the Stark Shale in many cases because of the lack of originally unstable grains in the basal Winterset (Fig. 7). It also occurs locally in the the top of the Canville Member, commonly where the same facies can be shown to extend in the Winterset down to the Stark. Facies C occurs also high in the Winterset locally, where a bed is isolated by overlying and underlying shale partings (as in oolite beds at localities JN and KI).

## Preservation of Grains

Most ooids, phylloid algae, and molluscs display at least some original structure within unclear spar in Facies C, although some grains are as structureless as those in Facies A or B. Ooids exhibit well preserved concentric structures at locality JN and both radial and concentric fabric at locality KI (Fig. 10a). Within these oolite beds, other grains exist as molds or ferroan dolomite.

Phylloid algae within Facies C show varying preservation. Some Eugonophyllum or similar green algae contain regular utricles at their edges, and red phylloid algae contain scattered cellular structures (Fig. 10b). These structures are not outstanding but are more complete than those in Facies B.

Many molluscs in Facies C display some internal structure, although it is commonly not complete. A few display curved structures in apparently broken voids, suggesting that the original organic microstructure of the grain has been preserved, but not its original position (Fig. 10c).

In summary, preservation of original structures in unstable grains is generally far better in Facies C than in Facies A or

Figure 10 -- Diagenetic fabrics in Facies C.

a. Oolitic calcarenite with ooids containing preserved radial and concentric structure. Contrast with Figure 9c, which shows ooids in Facies B with much less preservation of internal structure. (Plane-polarized light; KI12.4; Scale bar is .25 mm.)

b. Phylloid red algae with partially preserved cellular structure. (Plane-polarized light, TC3.5; Scale bar is 1 mm.)

c. Clam with slumped internal structure. This deformation may have resulted from partial neomorphism followed by dissolution of rest of grain by unsaturated water. This left a void into which preserved feature slumped. Mud to upper right then fractured to slump partly into void. (Plane-polarized light; CH5.3; Scale bar is 1 mm.)

d. Void filling in brachiopod cut by stylolite. A rim of microdolomite inclusions (M) occurs at upper edge of void filling and may represent an early marine high-Mg calcite cement. Stylolite cuts both void-filling calcite (C) and dolomite (D), suggesting that it formed after both. (Plane-polarized light; MM5.4; Scale bar is 1 mm.)

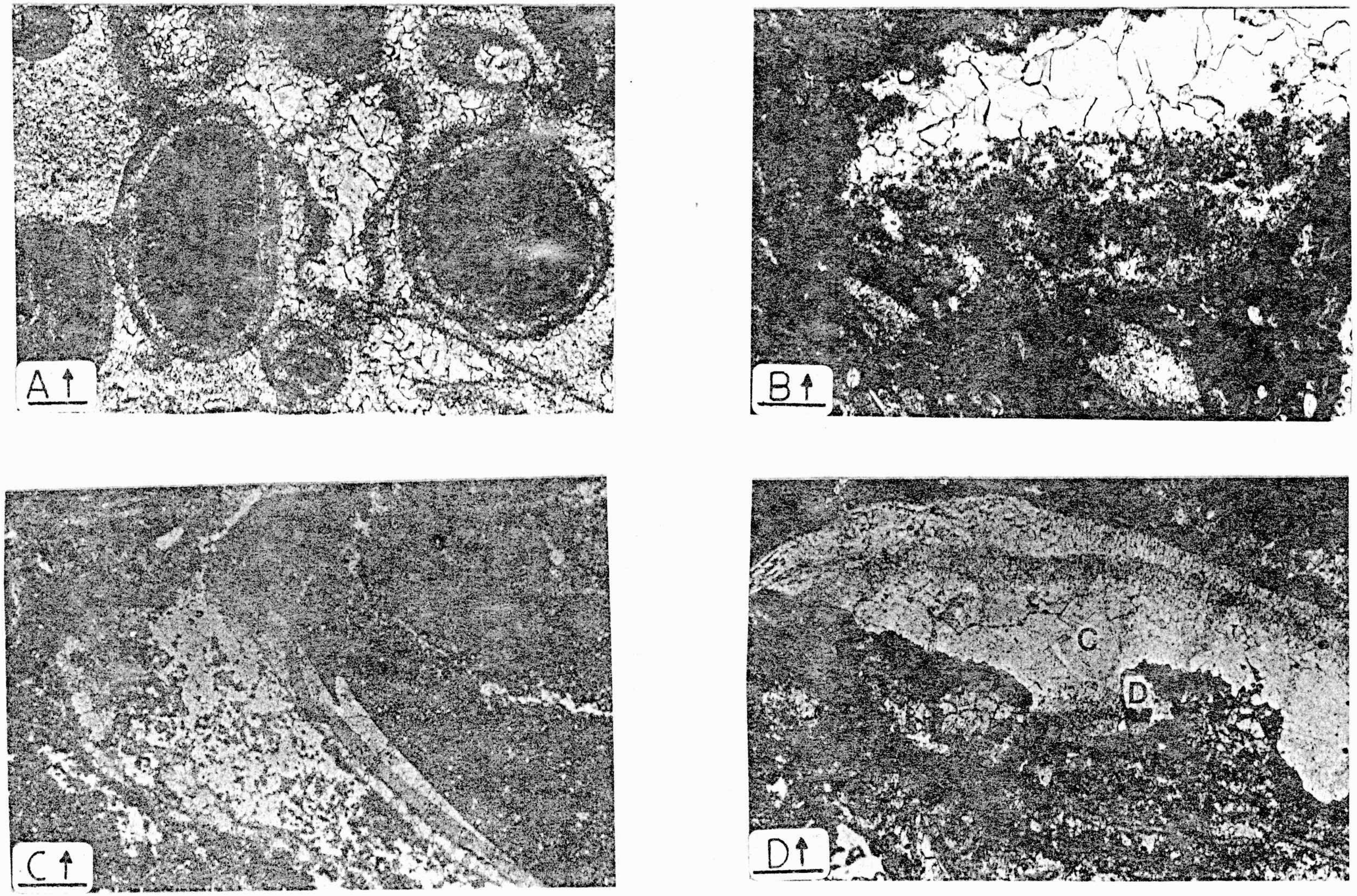


Figure 10

B, but some grains are structureless. This suggests that neomorphism was more important in the diagenesis of this facies than in Facies A or B, but some leaching and void filling did occur.

### Cements

Most cements in Facies C are clear blocky calcite, although some cements at the edges of voids contain microdolomitic inclusions (Fig. 10d). Ferroan dolomite occurs in scattered grains, mostly clams, and in sparry areas in collapsed algal rocks like those described in Facies B.

Small stylolites cut across some rocks in the algal mound facies (Fig 10d). These often cut across and are parallel to spar-filled areas, many of which appear to have resulted from the leaching of phylloid algae. Figure 10d illustrates that such stylolites postdate both calcite and dolomite void filling. Other compaction-related effects are rare in Facies C.

## Facies D

Facies D consists of those rocks in which all unstable grains have retained some form of their original structure. This facies occurs only in southeastern Kansas in the lowermost and southernmost extent of the Winterset Member, and in most of the Canville Member (Fig. 7).

## Grain Preservation and Cements

Molluscs in Facies D contain preserved internal structures (Fig. 11a) that are only rarely disrupted. Spar within molluscs is not clear and generally has complex grain boundaries. Ooids do not occur in the facies, and phylloid algae are rare.

All types of grains in Facies D display features resulting from compaction. Brachiopods are crushed commonly and lack much internal cement (Fig. 11b). Echinoderm fragments are divided into many smaller crystals, suggesting "degrading recrystallization" (Folk, 1965). Grain-to-grain contacts are intergrown commonly and in some cases collectively form "fitted fabric" (Buxton and Sibley, 1981) (Fig. 11c).

Cements in Facies D are rare and generally occur only in intragranular voids. These cements are generally blocky calcite, although a few contain microdolomitic inclusions at the edges of voids. Fine-grained ferroan dolomite also occurs as a cement.

In summary, the spar within discernible grains in Facies D is inclusion-rich jagged spar that, according to the criteria of Bathurst (1975), suggests neomorphic rather than void-filling processes. In contrast, spar that fills primary voids appears to have formed after compaction.

Figure 11 -- Diagenetic fabrics in Facies D and E.

a. Portion of a gastropod shell in Facies D containing relict structure. (Plane-polarized light; VR1.3; Scale bar is 50 microns.)

b. Crushed brachiopod in quartz-rich calcarenite in Facies D. Many carbonate grain-to-grain contacts are stylolitized. (Plane-polarized light; CN0.9; Scale bar is 1 mm.)

c. Calcarenite in Facies D with ubiquitous intergrown grain-to-grain contacts to give "fitted fabric" (Buxton and Sibley, 1981). (Plane-polarized light; CW0.2; Scale bar is 1 mm.)

d. Microspar of inclusion-rich rhombs of ferroan dolomite in Facies E. (Plane-polarized light, TC1.9; Scale bar is 50 microns.)

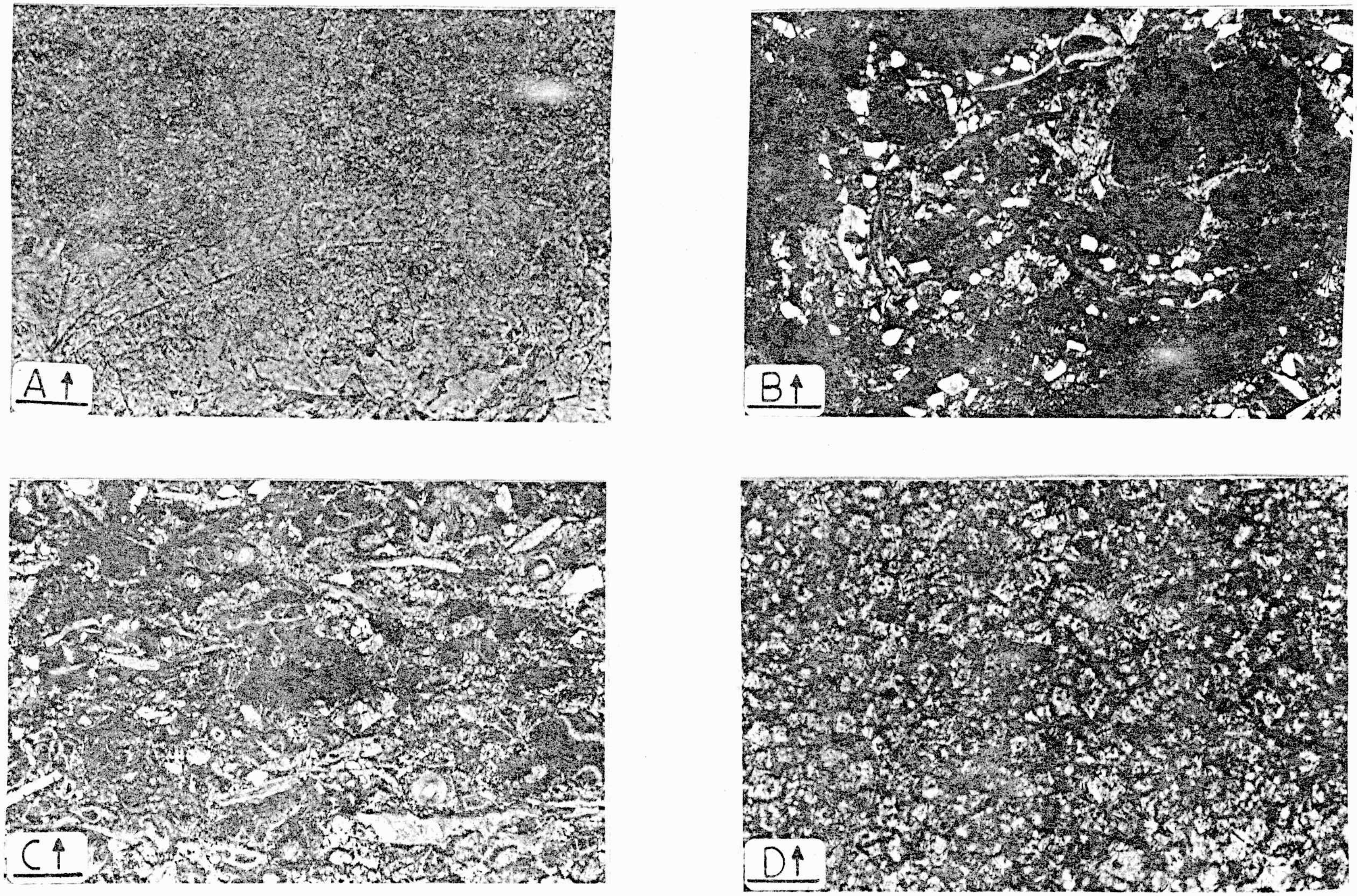


Figure 11

## Facies E

Facies E consists of those rocks containing a matrix of finely crystalline (5 to 50 micron) rhombs of inclusion-rich ferroan dolomite (Fig. 11d). These rocks are generally devoid of grains of originally unstable mineralogies, prohibiting their classification in other facies. Facies E occurs at the base of the Winterset Member throughout the study area (Fig. 7). The same dolomitic texture also occurs locally near shale partings within the Winterset, and in limestone lenses in the thick shale parting between the Winterset Member and the overlying "Inland Drive Bed" at locality ID (See Appendix B). Similar dolomite also occurs in the Canville Member but is poorly developed.

Brachiopod shells and fragments and echinoderm fragments are nearly the only large grains in Facies E, and they are not dolomitized. Brachiopods are generally crushed and contain little internal cement.

## Interfacies Relationships

Diagenetic Facies A, B, C, and D of the Dennis Formation represent a sequence ranging from strata characterized by complete alteration of unstable grains to clear structureless blocky spar, to strata featuring unstable grains altered to inclusion-rich jagged spar containing remnant internal structures. This trend suggests a corresponding sequence from diagenesis dominated by void-filling processes to that dominated by neomorphism. Figure 7 thus shows that leaching and void-filling were the dominant processes in the northern and uppermost parts of the Dennis Formation, whereas neomorphism was dominant in its southern and lowermost extent. Complexities in this regional distribution of facies occur in beds isolated by shale partings or characterized by high primary porosities (Fig. 7).

Within each of these four facies, textures of unstable grains vary considerably, as shown by Saller (1982) in Pleistocene limestones. Clear blocky spar cements occur in Facies A, B, and C; microdolomitic inclusions occur in cements in Facies B, C, and D. Three distinct populations of dolomite occur in the Dennis Formation: fine early dolomite in Facies A, coarse ferroan dolomite in Facies A, B and C, and ferroan dolomitic microspar in Facies E.

Twinned calcite crystals are restricted in general to Bourbon, Neosho, and northeasternmost Montgomery Counties in southeastern Kansas (i.e. in the algal mound facies belt and in the area of the Bourbon Arch).

# CHAPTER 3

# NON-CARBONATE DIAGENETIC MINERALS

## Silica

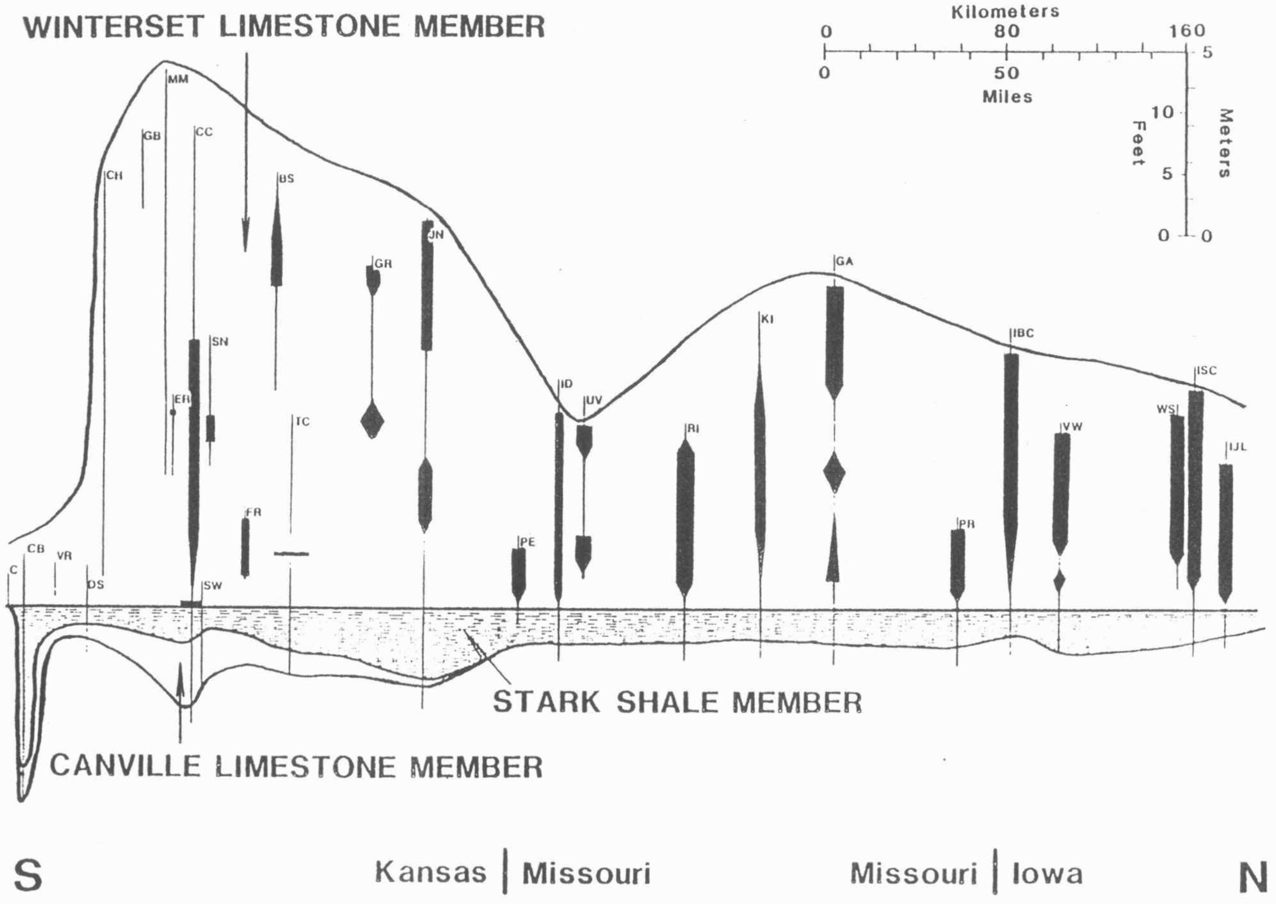
Diagenetic silica occurs in five forms in the Dennis Formation: 1) Well-developed chert nodules; 2) Skeletal grains partially replaced by chalcedony; 3) Void-filling megaquartz; 4) Void-filling chalcedony; 5) A thin bed of entirely silicified rock. Diagenetic silica is limited almost exclusively to the Winterset Member north of central Neosho County, Kansas (Fig. 12).

### Chert Nodules

Well-developed chert nodules with distinct boundaries occur in the upper parts of the Winterset Member north of central Linn County, Kansas. Chert nodules occur in discrete horizons parallel to bedding but are not confined to one host lithology, and they therefore cannot be correlated in conjunction with other lithostratigraphic markers.

Chert nodules in the Winterset Member are gray or tan. They consist of inclusion-rich microcrystalline quartz that has replaced carbonate material. Voids between grains, as in calcarenites, are filled with radial chalcedony, which is

Figure 12 -- Distribution of diagenetic silica in Dennis Formation. Thickness of bars is approximately proportional to abundance of silica observed in thin section and hand specimen.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STARK SHALE MEMBER
CANVILLE LIMESTONE MEMBER
S
Kansas
Missouri
Missouri
Iowa
N

Figure 12

clearer than the microcrystalline quartz but contains bands of darker color.

### Silicified Skeletal Grains

Only brachiopods and, less commonly, echinoderm fragments are silicified in the Winterset Member. Brachiopods are replaced by chalcedony that either cuts across internal shell structures to form subcircular areas (in thin section) or follows the shell structure to form lines of chalcedony (Fig. 13a). In the latter case, delicate interlamination of calcite and chalcedony may occur.

Breakage in brachiopods offsets chalcedonified structures, suggesting that silicification occurred before breakage. Because these brachiopods are also filled with calcite cements, silicification must have occurred before cementation if it occurred before the breaking of the shells.

One 8-cm-thick calcarenite bed at locality TC consists entirely of silicified skeletal grains. Originally unstable skeletal grains, such as pelecypods and phylloid red algae, exhibit delicately preserved internal structures that have been silicified (Fig. 13b). This suggests that silicification occurred while pore fluid compositions were still near those of sea water, because exposure to other fluids, particularly fresh water, would have modified or destroyed the delicate internal structure. The grains in this bed are also strongly compacted,

Figure 13 -- Diagenetic silica.

a. Partially silicified brachiopod fragment consisting of chalcedony preserving internal structure. Silica is light inner area; outer dark portion is calcite. (Plane-polarized light; KI6.0; Scale bar is .25 mm.)

b. Silicified mollusc fragment. Exquisite preservation of internal structure suggests that silicification occurred before grain was exposed to fluids that would have destroyed or intensely modified that structure. (Plane-polarized light; TC3.6; Scale bar is 1 mm.)

c. Brachiopod filled with calcite (darker) and quartz (lighter). Position of calcite around structural elements of shell suggests that calcite precipitated first and quartz then filled remaining void space. (Plane-polarized light; BR3.8; Scale bar is 2 mm.)

d. Zoned void-filling chalcedony with rim of earlier void-filling calcite crystals (C). (Plane-polarized light; SN1.5; Scale bar is 1 mm.)

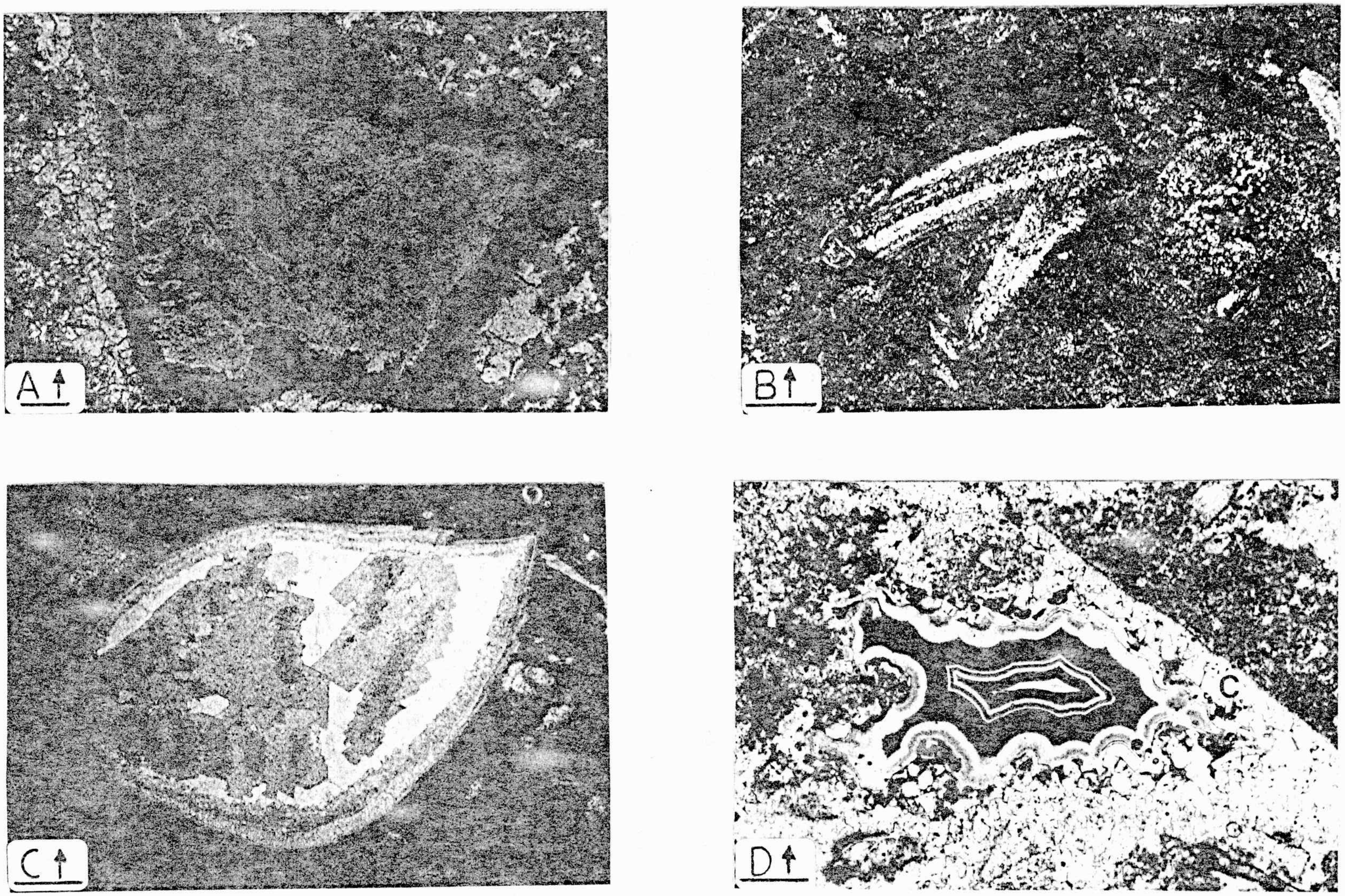


Figure 13

but petrographic evidence is inconclusive as to the relative timing of silicification and compaction.

## Void-Filling Megaquartz

Clear macrocrystalline quartz occurs in primary voids in brachiopods in the Winterset Member. It occurs much less commonly in voids left by dissolution of unstable grains. The clarity of such quartz, its occasionally euhedral form, and its restriction to obvious voids all suggest a void-filling origin.

Most void-filling quartz occurs amidst euhedral void-filling calcite crystals and conforms to the shapes of the calcite (Fig. 13c), suggesting that it formed after the calcite. Some quartz occurs near the edges of voids and is euhedral, with non-euhedral calcite abutting it (See later Fig. 17a), suggesting that quartz formed before calcite. These relationships suggest that quartz was precipitated in voids at nearly the same time as calcite.

## Void-Filling Chalcedony

Radial chalcedony occurs in voids within chert nodules, as discussed above, and less commonly in other voids. In the latter case it is separated from void walls by calcite cement rims, suggesting that precipitation of chalcedony occurred after at least the first stage of calcite precipitation (Fig. 13d).

## Silicified Rock

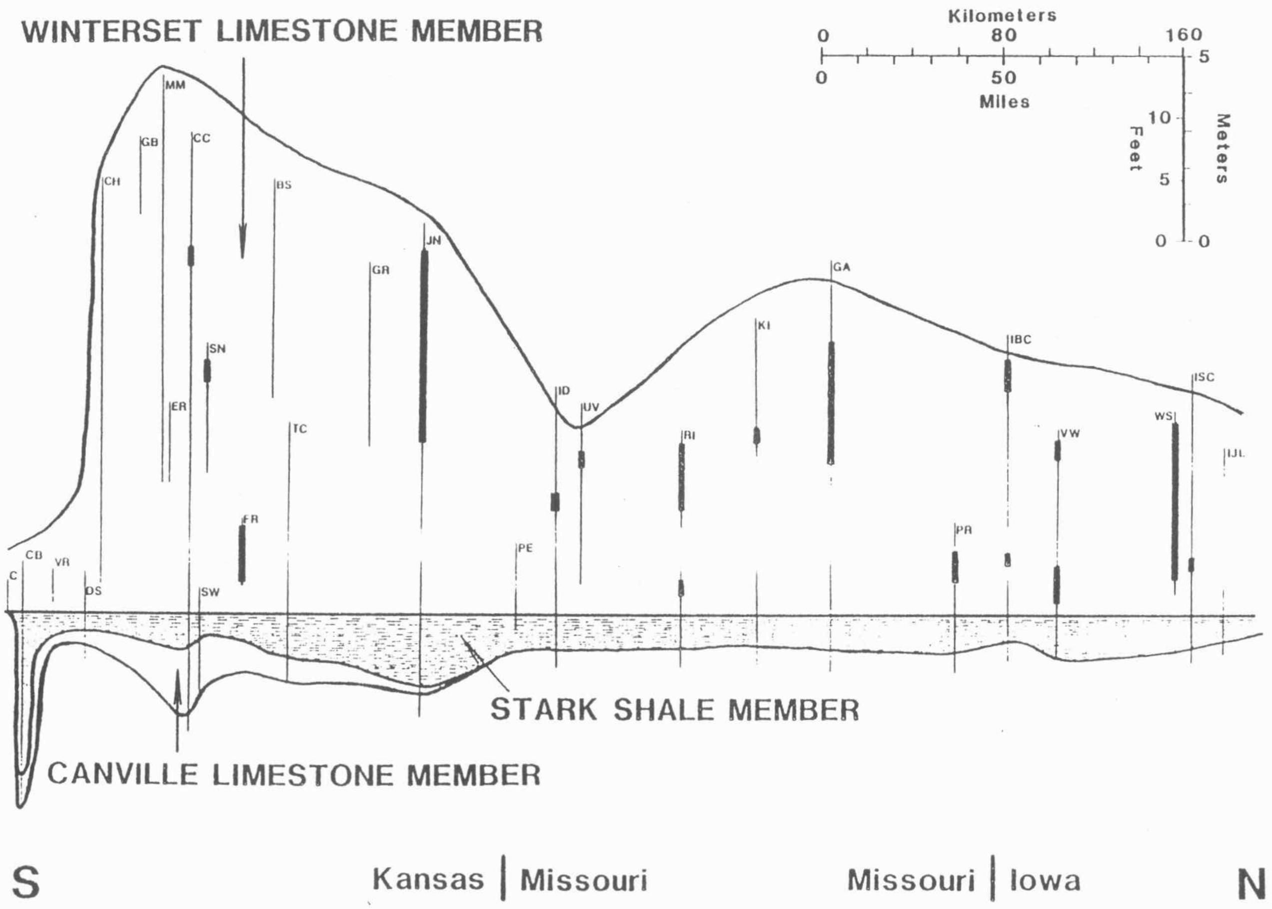
Schutter (1983) noted that the lowermost Winterset at locality CC is completely silicified. He was unable to thin-section the friable rock and found no other occurrence in the Dennis. He reported an abundance of sponge spicules associated with this bed. These sponge spicules consist of microcrystalline quartz, in contrast to calcite-replaced spicules elsewhere (Fig. 14).

## Summary

Petrographic evidence suggests that silicification of carbonate grains occurred early in diagenesis (before calcite cementation), whereas void-filling by silica occurred during or after precipitation of calcite cements.

Diagenetic silica in its various forms occurs in the Winterset Member north of central Neosho County, Kansas (Fig. 12). This distribution coincides closely with that of sponge spicules replaced by clear sparry calcite (Fig. 14). These spicules are most common north of Linn County, Kansas, as are well-developed chert nodules. Sponge spicules of silica occur only in the lowest Winterset Member at locality CC and in scattered chert nodules.

Figure 14 -- Distribution of sponge spicules now consisting of clear blocky calcite in Dennis Formation. Bars represent occurrence only and do not suggest relative abundance.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Miles
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CC
CH
BS
JN
GR
GA
KI
IBC
SN
ER
TC
ID
UV
ISC
WS
VW
RI
IJL
FR
PR
PE
CB
VR
C
DS
SW
STARK SHALE MEMBER
CANVILLE LIMESTONE MEMBER
S
Kansas
Missouri
Missouri
Iowa
N

Figure 14

## Opaque Minerals

Most opaque minerals in the Dennis Formation are pyrite or iron oxides that are commonly pseudomorphs of pyrite. Opaque minerals occur in low concentrations throughout the Dennis Formation, although higher concentrations occur in the Canville Member and the lower parts of the Winterset Member (i.e., near the Stark Shale). Brachiopods and bryozoans are the skeletal grains most commonly replaced by opaques; in brachiopod void fillings, opaque minerals occur at or near the edges of voids (Fig. 15a).

## Fluorite, Barite, and Sphalerite

Barite and fluorite occur in small amounts at locality SN. Fluorite is euhedral and fills obvious voids (Fig. 15b), whereas barite is anhedral. Schutter (1983) reported sphalerite replacing bryozoans in the Winterset Member near the Stark Shale.

Figure 15 -- Other diagenetic minerals.

a. Brachiopod with void-filling calcite. Pyrite occurs at edge of void, on and in brachiopod shell, suggesting that it formed before calcite cement. (Plane-polarized light; DS1.1; Scale bar is 2 mm.)

b. Euhedral fluorite (F) and calcite (C) nearly filling void (V). (Plane-polarized light; SN1.5; Scale bar is 1 mm.)

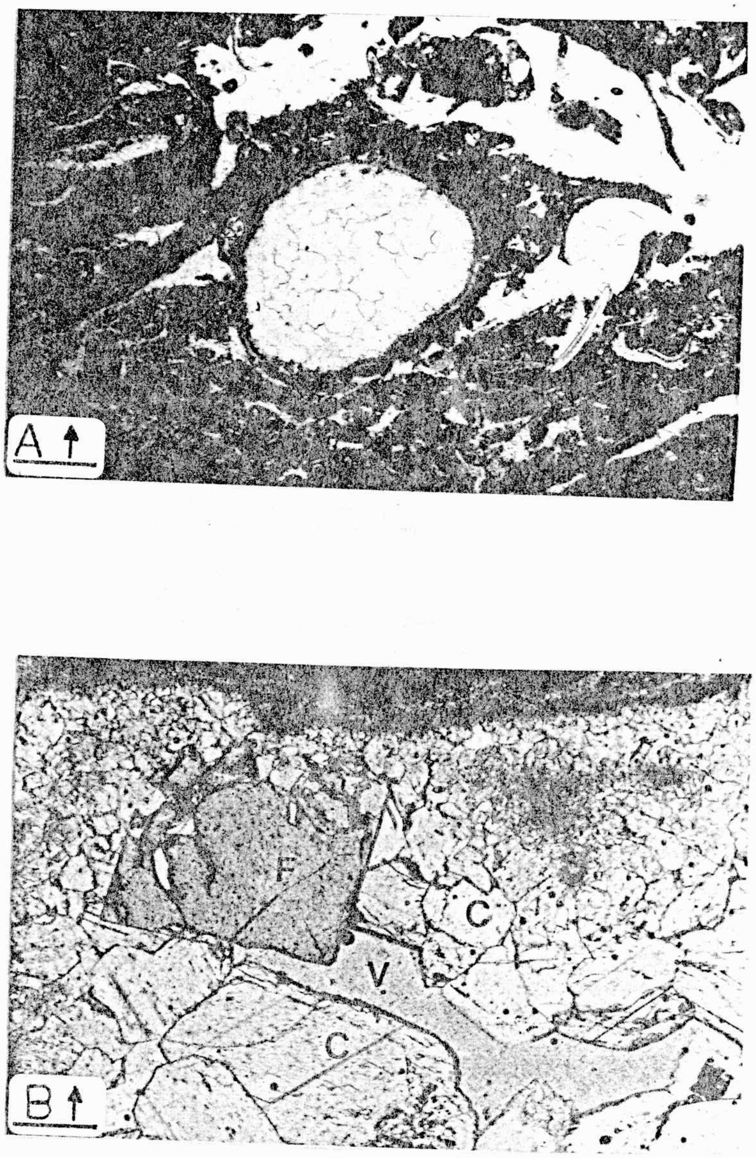

Figure 15

# CHAPTER 4

# CATHODOLUMINESCENCE AND GEOCHEMISTRY

## Trends in Cathodoluminescence

Calcite cements in the Dennis Formation display unzoned weak luminescence in most cases. Small isolated patches of bright luminescence occur in the upper part of the Dennis, and very weak and bright patches are scattered in the lower parts. Dolomite is non-luminescent or very weakly luminescent and is unzoned, and fluorite luminesces bright blue.

Large volumes of void-filling calcite (as in brachiopods) are commonly weakly luminescent without zonation or are zoned in various weak shades. Distinctly zoned calcite fillings show generally (but not in all cases) a zonation from very weak or weak luminescence at edges to brighter luminescence in centers (Fig. 16 and 17). These sequences represent temporal changes in precipitation of cement, with brighter spar forming later.

Where crushed and uncrushed whole brachiopods occur together in thin section, uncrushed brachiopods contain spar darker than that in crushed ones. If resistance to breakage in uncrushed shells was caused by earlier cementation, spar in those shells must be older than that in crushed ones. Thus such spar follows the same temporal trends as that in zoned

Figure 16 -- Cathodoluminescence in Canville Member.

a. Brachiopod with geopetal mud in bottom and calcite filling top. Area in rectangle is shown in Figure 16b. (Plane-polarized light; DSO.1; Scale bar is 1 mm.)

b. Area within rectangle in Figure 16a, shown in cathodoluminescent light. Note weakly luminescent outer (early) rim and bright inner (later) filling. Numbered black dots are targets of microprobe analyses. (Scale bar is .2 mm.)

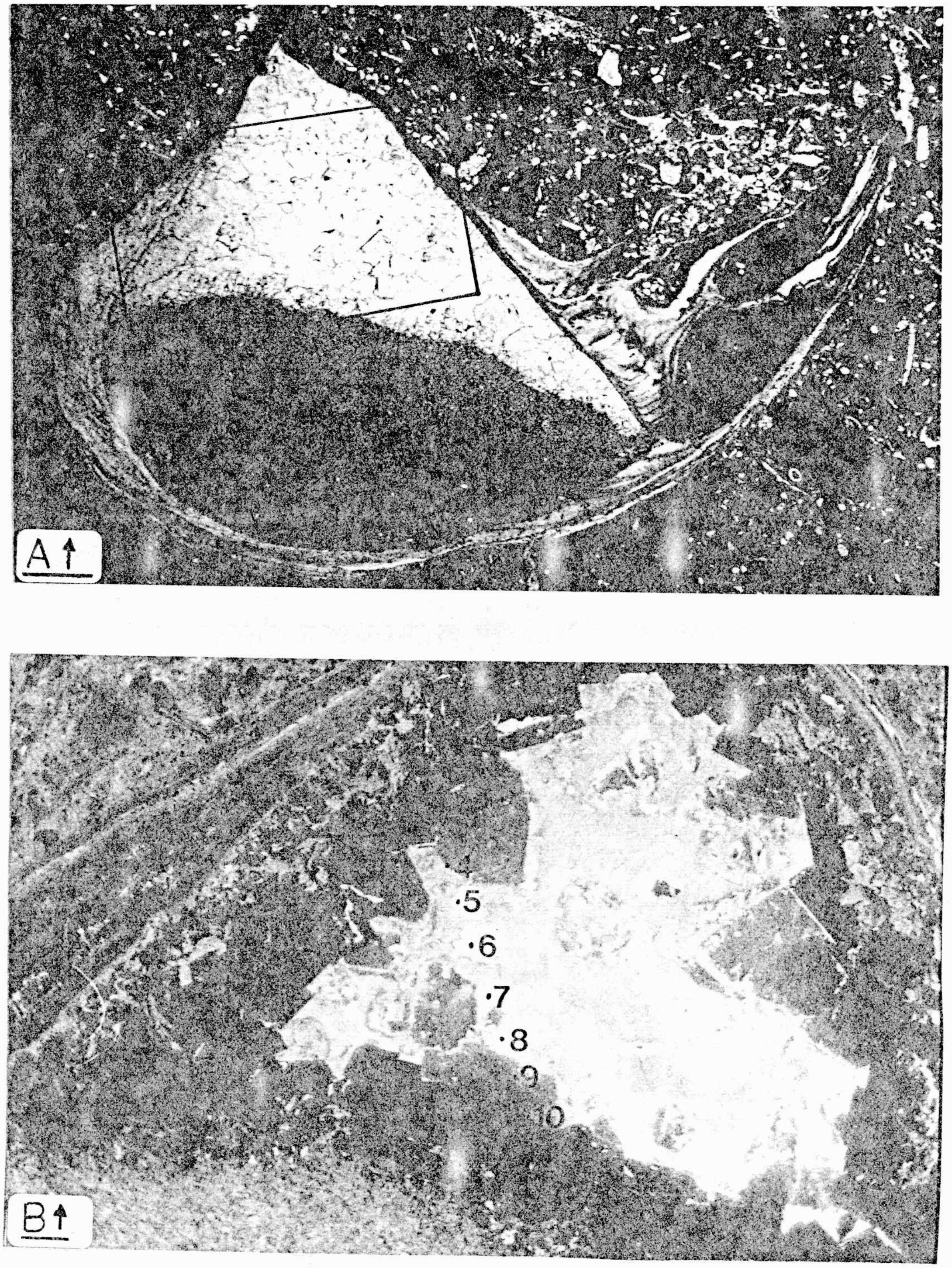

Figure 16

Figure 17 -- Cathodoluminescence in Winterset Member.

a. Brachiopod with geopetal mud filling bottom and crystals of quartz (darker) (Q) and calcite (lighter) (C) filling top. Euhedral shape, clear appearance, and occurrence in primary void all suggest precipitation of quartz in void space before precipitation of surrounding calcite. Area in rectangle is shown in Figure 17b. (Plane-polarized light; GR4.9; Scale bar is 1 mm.)

b. Area within rectangle in Figure 17a, shown in cathodoluminescent light. Note weakly luminescent outer (early) rim and bright inner (later) filling, similar to that in Figure 16b. Numbered black dots are targets of microprobe analyses (7 is missing; Scale bar is .2 mm.)

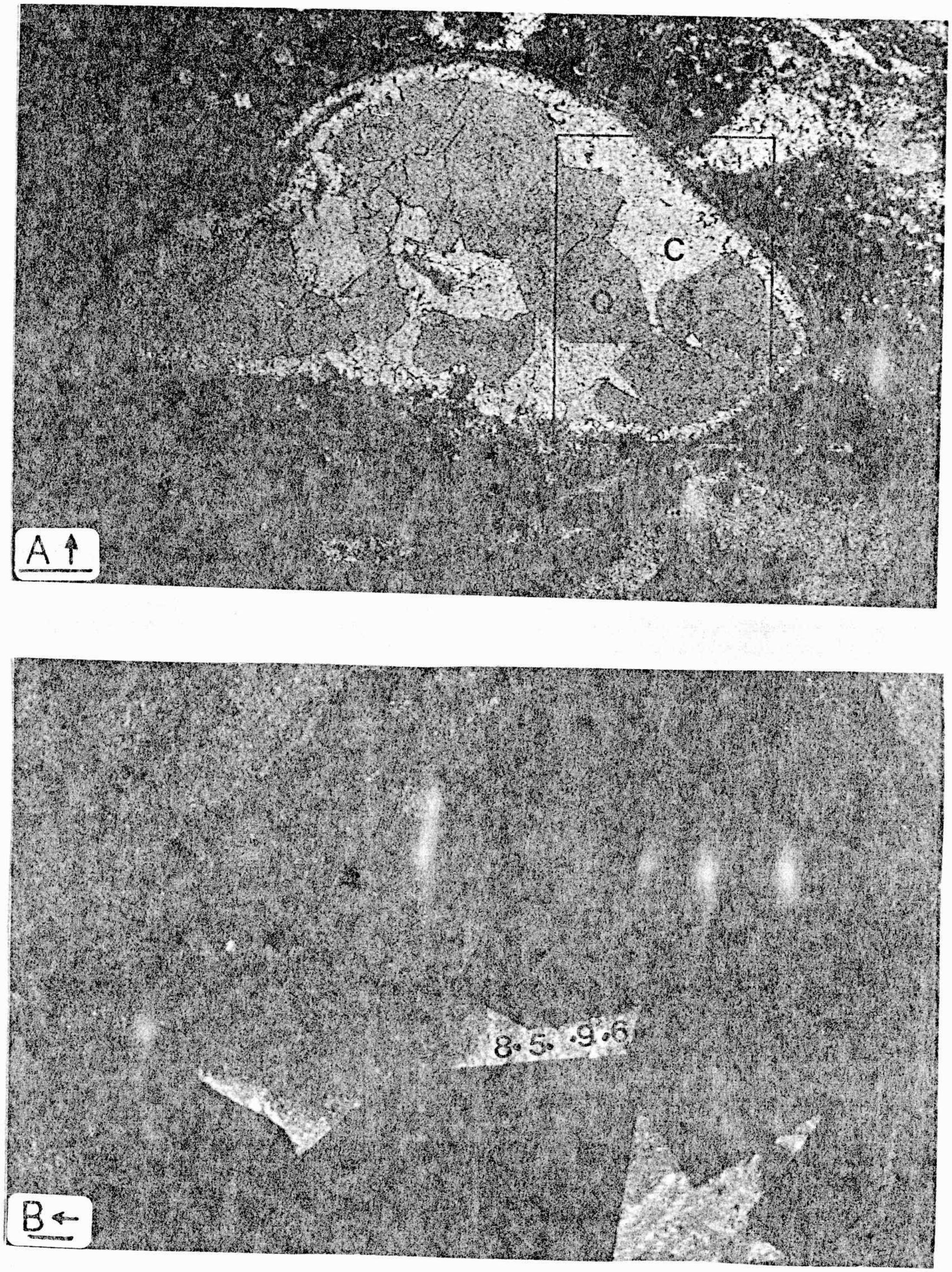

Figure 17

void fillings and suggests that cementation occurred over a long period of time, with changes in the chemistry of the resulting spar with time.

## Geochemistry of Cathodoluminescence in Calcite

Cathodoluminescence in carbonates is attributed commonly to the presence of manganese substituting for calcium in the calcite structure, and ferrous iron substitution is considered to quench cathodoluminescence (Sommer, 1972). Electron microprobe analyses of the void-filling spar in Figures 16 and 17 show that cathodoluminescent zones are not compositionally distinct zones with respect to absolute concentrations of manganese and iron (Fig. 18; data are given in Appendix C). The cathodoluminescent zones are relatively distinct, however, with respect to the ratio of iron to manganese (Fig. 19). This ratio ($FeCO_3/MnCO_3$) decreases with increasing brightness of the luminescence (Fig. 20). Similar relationships have been noted by Frank, Carpenter, and Oglesby (1982).

Trends in the individual concentrations of manganese and iron are more difficult to detect. In both void fillings (Fig. 16 and 17), iron decreases initially (from edge to center), although in one it increases later (in the center) (Fig. 18). Manganese, in contrast, tends to increase in an approximate manner. Concentrations of both iron and manganese are

Figure 18 -- Concentrations of $FeCO_3$ (centered circles) and $MnCO_3$ (dots) in cathodoluminescent calcite. Compositions (in mole percent) are plotted according to distance from void wall in samples DSO.1 (solid lines for two traverses; see Fig. 16) and GR4.9 (dashed lines; see Fig. 17). Numbers by data points refer to points in Figures 16b and 17b. Cathodoluminescence shows little relationship to absolute concentrations in these carbonates. Data are interpreted in Figures 19 and 20. Data were obtained by microprobe and are given in Appendix C.

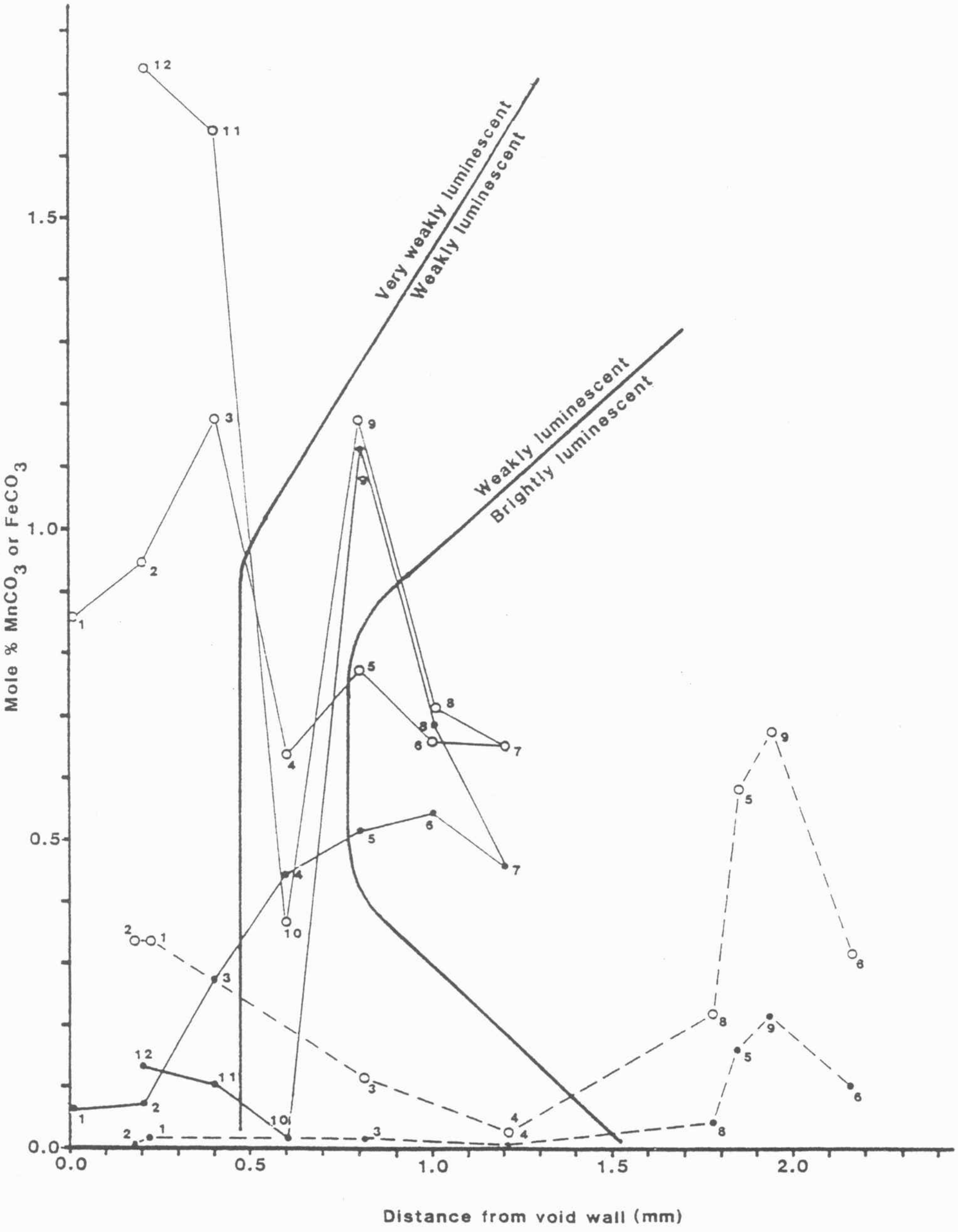
Very weakly luminescent
Weakly luminescent
Weakly luminescent
Brightly luminescent
Mole % MnCO$_3$ or FeCO$_3$
Distance from void wall (mm)
0.0
0.5
1.0
1.5
2.0

Figure 18

Figure 19 -- Ratios of $FeCO_3$ vs. $MnCO_3$ in cathodoluminescent calcite. Ratios are plotted according to distance from void wall in samples DSO.1 (solid lines; see Fig. 16) and GR4.9 (dashed lines; see Fig. 17). Numbers by data points refer to points in Figures 16b and 17b.

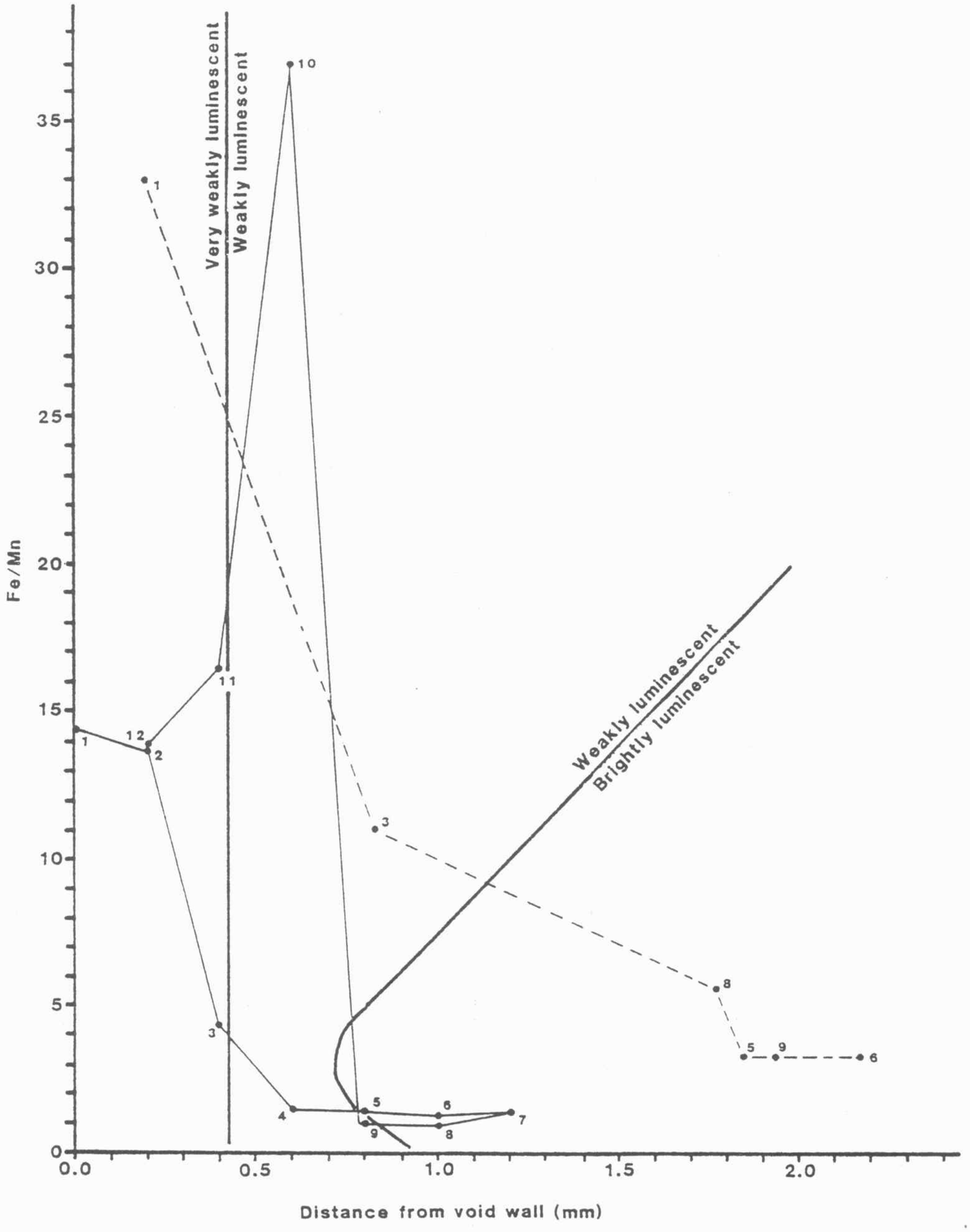
Very weakly luminescent
Weakly luminescent
Weakly luminescent
Brightly luminescent
Fe/Mn
0
5
10
15
20
25
30
35
0.0
0.5
1.0
1.5
2.0
Distance from void wall (mm)
10
1
11
12
2
3
4
5
6
7
8
9
3
8
5
9
6

Figure 19

Figure 20 -- Ratio of iron and manganese in calcite versus luminescence. In general, lower Fe/Mn ratios are associated with brighter luminescence. Vertical lines represent one standard deviation in each direction. "DS" and "GR" refer to samples DS0.1 (Canville Member) and GR4.9 (Winterset Member) respectively (Figs. 16 and 17).

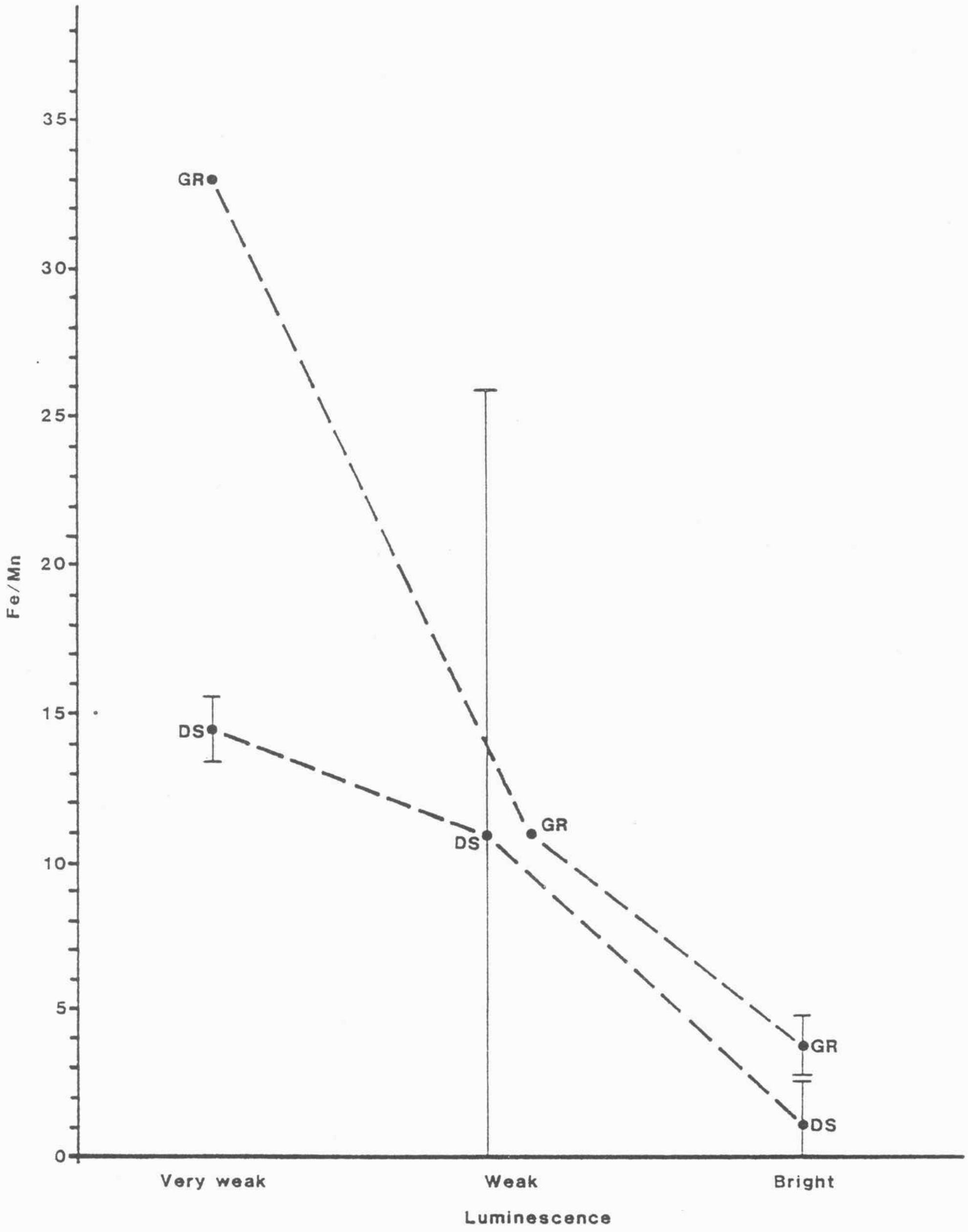
35
30
25
20
15
10
5
0
Fe/Mn
GR
DS
GR
DS
GR
DS
Very weak
Weak
Bright
Luminescence

Figure 20

generally higher in a sample from the Canville Member at locality DS than in a void filling from the Winterset Member at localty GR.

## Geochemistry of Ferroan Dolomite

Electron probe analyses of void-filling ferroan dolomite from the Winterset Member indicate that this dolomite is 54 to 58 mole% $CaCO_3$, 24 to 38% $MgCO_3$, 6 to 20% $FeCO_3$, and less than 2% $MnCO_3$ (Fig. 21). These compositions deviate from stoichiometric dolomite (i.e. 50% $CaCO_3$ and 50% $MgCO_3$) but are apparently not unusual for ferroan dolomite. Data from Goldsmith and Graf (1952) and Radke and Mathis (1980), for example, suggest that $CaCO_3$ contents from 55 to 57 mole % are common.

Dennis dolomite is highly ferroan (i.e. 6 to 20% $FeCO_3$) and Fe/Mn ratios, like those in very weakly luminescent calcite, are high, ranging from 10.4 to 52.1 with a mean 31.1. Although cathodoluminescence of dolomite is not necessarily the same as that of calcite (Fig. 20), high Fe/Mn ratios may explain the minimal luminescence of ferroan dolomite in the Dennis Formation.

Late void-filling ferroan dolomite occurs along the entire Dennis outcrop, but less ferroan compositions (<12% $FeCO_3$) occur in Iowa, whereas more ferroan compositions (up to 20%) occur progressively farther south (Fig. 21).

Figure 21 -- Compositon of ferroan dolomite. Samples are plotted in terms of mole % $CaCO_3$, $MgCO_3$, and the sum of $FeCO_3$ and $MnCO_3$. Lines extending from points represent one standard deviation in each direction. Concentration of iron in dolomite increases southward from Iowa to Kansas. Data were obtained by microprobe and are given in Appendix C.

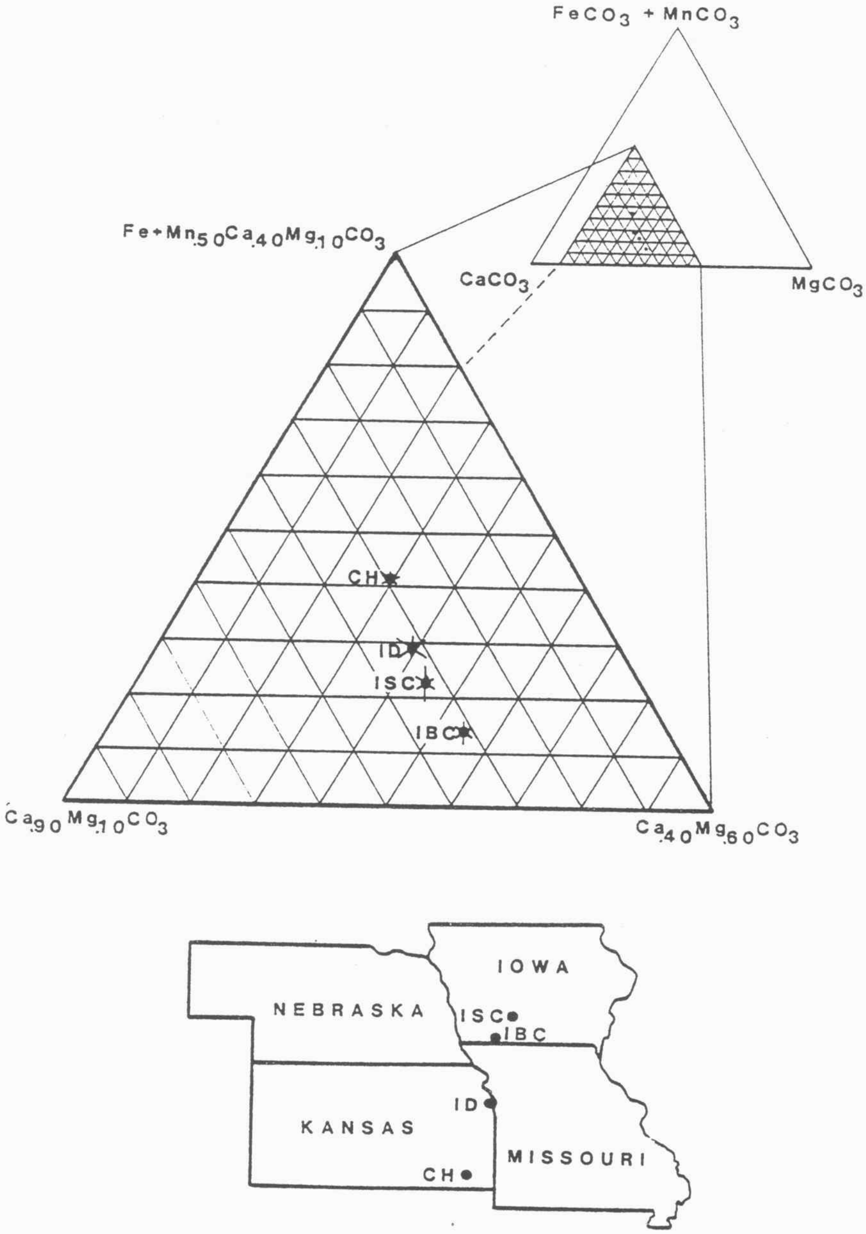
FeCO3 + MnCO3
CaCO3
MgCO3
Fe+Mn.50Ca.40Mg.10CO3
Ca.90Mg.10CO3
Ca.40Mg.60CO3
CH
ID
ISC
IBC
IOWA
NEBRASKA
ISC
IBC
KANSAS
ID
CH
MISSOURI

Figure 21

## Isotopes

Analyses of a limited number of bulk samples of the Winterset Member from Iowa cores reveal a mean $d^{13}C$ value of -0.26 relative to the PDB standard (with a standard deviation of 0.84). $d^{18}O$ has an average of 26.96 relative to the SMOW standard, or -3.78 on the PDB standard (with a standard deviation of 1.91). The mean $d^{13}C$ value falls within Keith and Weber's (1964) average value for selected Carboniferous marine limestones, but the average $d^{18}O$ is heavier (i.e. more positive) than Keith and Weber's corresponding average value.

Carbon and, to a lesser extent, oxygen isotopes display general lightening (i.e. more negative) trends with elevation above the base of the Winterset. Such trends are best illustrated by the Stanzel Core (locality ISC), in which $d^{13}C$ and $d^{18}O$ steadily decrease upward (Fig. 22; data are recorded in Appendix C).

Figure 22 -- Isotopic variation in Winterset Member in Iowa. Vertical axis represents position in Winterset in three cores; complete Winterset thickness is shown for each. In general, isotopic compositions, especially $d^{13}C$, lighten upward. Feet are used in measuring Winterset thickness, as is customary with Iowa cores. Data are given in Appendix C. Analyses were performed by Mr. Ken Schmitz of Northern Illinois University under the direction of Dr. Gene Perry, with funds supplied by NSF grant EAR 7911334 to Dr. Perry.

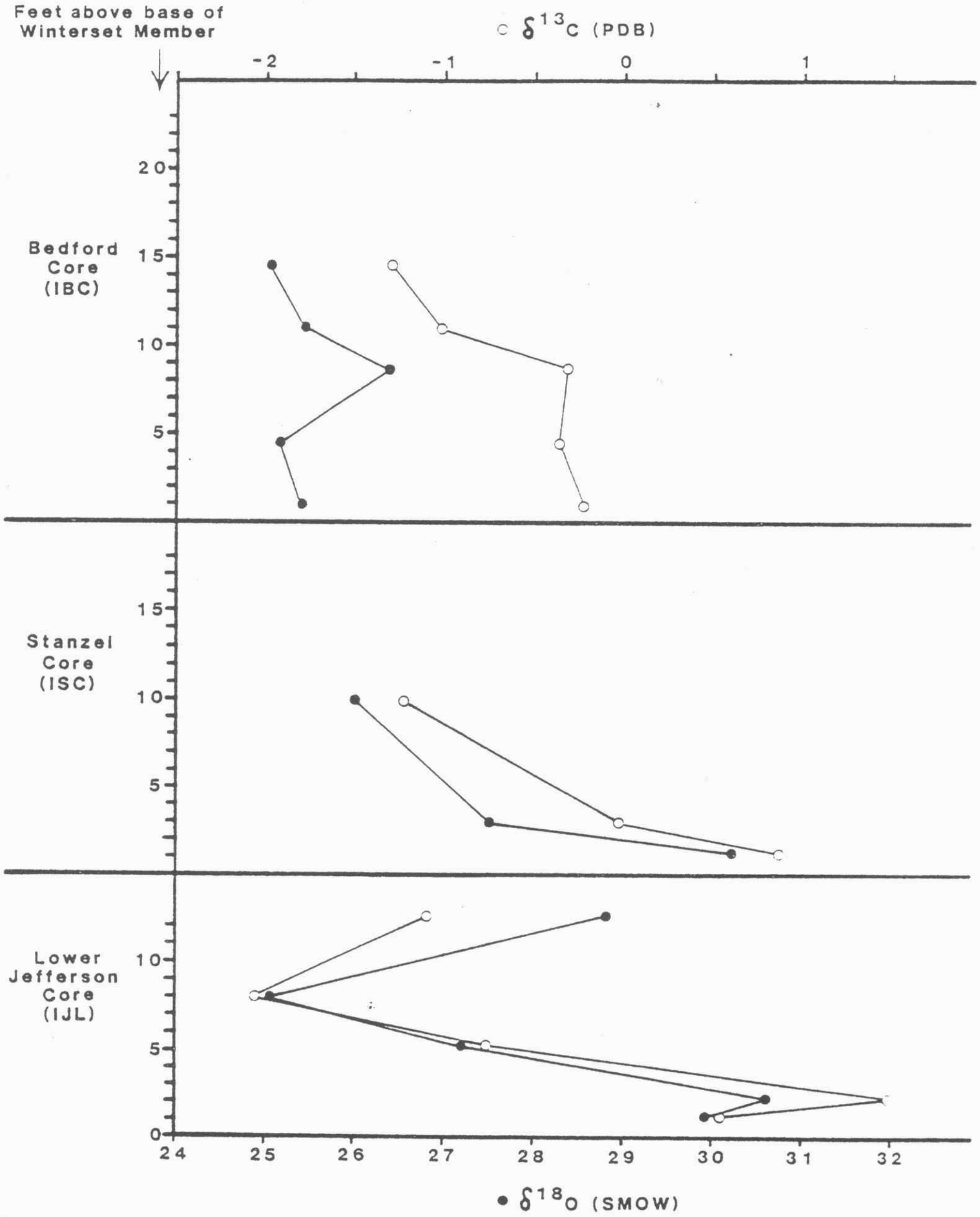
Feet above base of Winterset Member
○ δ13C (PDB)
-2
-1
0
1
20
15
10
5
Bedford Core (IBC)
15
10
5
Stanzel Core (ISC)
10
5
0
Lower Jefferson Core (IJL)
24
25
26
27
28
29
30
31
32
● δ18O (SMOW)

Figure 22

# CHAPTER 5

# DISCUSSION

## Interpretation of Diagenetic Facies

The diagenetic facies described in Chapter 2 suggest that void-filling processes were most important in the northern and upper parts of the Dennis Formation, whereas neomorphic processes were progressively more dominant in the southern and lower extent of the Dennis. This trend in diagenetic fabrics is explained best by introduction of fresh water into the unit, with the earliest introduction of fresh water in the north. Facies A, B, C, and D represent progressive stages in the interaction of meteoric water with the carbonate sediments.

### Facies A

The lack of preserved internal structures in unstable grains in Facies A suggests that the sediments passed from the marine environment to an undersaturated meteoric environment prior to diagenesis in a saturated meteoric environment. A saturated environment would have allowed neomorphism of grains; the absence of neomorphosed grains suggests that saturated conditions did not exist or were not significant in the sequence leading to a meteoric environment undersaturated with respect to $CaCO_3$.

No cements that suggest a vadose environment occur in Facies A, although Heckel (ms. in press) has found possible meniscus cement in the upper Winterset in western Iowa; most cements are compatible with a phreatic origin. However, the rubbly nodular beds at the top of Facies A north of Caldwell County, Missouri, suggest that extensive subaerial exposure occurred, and Siebels (1981) attributed the rubbly limestone to "soil-forming weathering processes." Thus the top of Facies A was obviously in the unsaturated vadose environment for a considerable time, although the lower limit of that environment cannot be determined clearly.

The cements in Facies A suggest that, although the fresh water was originally unsaturated with respect to $CaCO_3$, it eventually became saturated. The compaction features noted in Facies A may have resulted from a lack of cement to stabilize primary intergranular porosity early in diagenesis. The paucity of cements containing microdolomitic inclusions suggests either a lack of early marine cementation or dissolution of early high-Mg calcite cements in the fresh water.

The fine rhombic dolomite in Facies A formed early in diagenesis, before cementation by calcite (Fig. 8c). This suggests that the dolomite formed in an environment between the marine phreatic and meteoric active environments. The most likely dolomite-precipitating environment encountered in passage between these two is the mixing-zone environment, in which the mixing of fresh and marine waters makes precipitation of dolomite chemically reasonable (Hanshaw et al., 1971; Badiozamani, 1973; Land, 1973). The coarse ferroan dolomite in Facies A fills both primary and secondary voids and thus must have formed later than the non-ferroan dolomite. The ferroan nature of this dolomite suggests precipitation in an oxygen-poor burial environment.

Extensive dissolution of phylloid algae in the algal mound facies caused large unsupported voids that collapsed, causing in-situ brecciation of the surrounding mud. Remaining voids were filled by blocky calcite cement.

In summary, the diagenetic fabrics of Facies A are explained most readily by passage from the marine environment through a mixing zone to a meteoric environment originally undersaturated with respect to $CaCO_3$ but later saturated. The meteoric environment extended upward to an unsaturated vadose zone.

## Facies B

The presence of some unstable grains with preserved internal structures in Facies B suggests that the sediment was exposed at least briefly to meteoric waters saturated with respect to $CaCO_3$. Such an environment would have allowed slow replacement of aragonite by calcite to preserve internal structures, and would have allowed precipitation of fringing cements (Fig. 9d). Exposure to unsaturated water then leached remaining unstable grains, and ultimately saturated meteoric water filled voids resulting from the dissolution of grains (areas labelled "P" in Fig. 9d). This suggests passage first to the saturated active meteoric phreatic environment (where minor neomorphism and some void filling occurred) and then to the unsaturated meteoric phreatic environment before final passage to a saturated meteoric environment. In Facies B the first (saturated neomorphosing) environment played a relatively minor role in comparison to the second (undersaturated) environment.

## Facies C

The extensive preservation of structures within unstable grains in Facies C suggests that the sediments were exposed for a considerable time to saturated meteoric water. The presence of leached grains suggests that the sediment was eventually exposed to water unsaturated with respect to $CaCO_3$. Thus the sediments passed from the marine environment to a saturated meteoric phreatic environment and then to an active undersaturated meteoric phreatic environment. This sequence is the same as that for Facies B, but the more extensive neomorphism in Facies C suggests greater importance of (and presumably longer time in) the saturated meteoric environment.

This sequence of diagenetic environments may explain the presence of grains in Facies C that have preserved but slumped internal structures (Fig. 10c). Neomorphism of such grains in the saturated environment may have been only partly complete when they passed into the undersaturated environment, where the rest of the grain quickly dissolved to leave a void into which the neomorphosed or partly neomorphosed portion of the grain slumped.

Ferroan dolomite in both Facies B and C appears to fill voids that remained after most calcite void filling. In the algal mound facies, where dissolution of algae and collapse of mud left large voids, dolomite partly fills many such voids, suggesting formation at least after passage into the unsaturated meteoric environment, if not later. The ferroan nature of such dolomite suggests that it formed in a low-oxygen environment unlike the meteoric unsaturated environment, so dolomite precipitation probably occurred after passage through that environment. The environment of precipitation was probably either a returning stagnant meteoric or later burial environment.

Stylolites in Facies C in the algal mound facies are associated with spar-filled voids left by dissolution of algae. Such stylolites may have resulted from the elimination of remaining void space after precipitation of void-filling calcite and dolomite (Fig. 23).

Figure 23 -- Possible origin of stylolites associated with void filling in algal mound facies. Stippled areas are carbonate mud.

a. Phylloid algal blade with sheltered void.

b. Dissolution of algal blade in coherent mud leaves larger void.

c. Collapse of fractured mud into void causes in situ brecciation.

d. Void is rimmed with cement but interior void space remains.

e. Compaction eliminates remaining void; necessary lateral compaction produces associated stylolites.

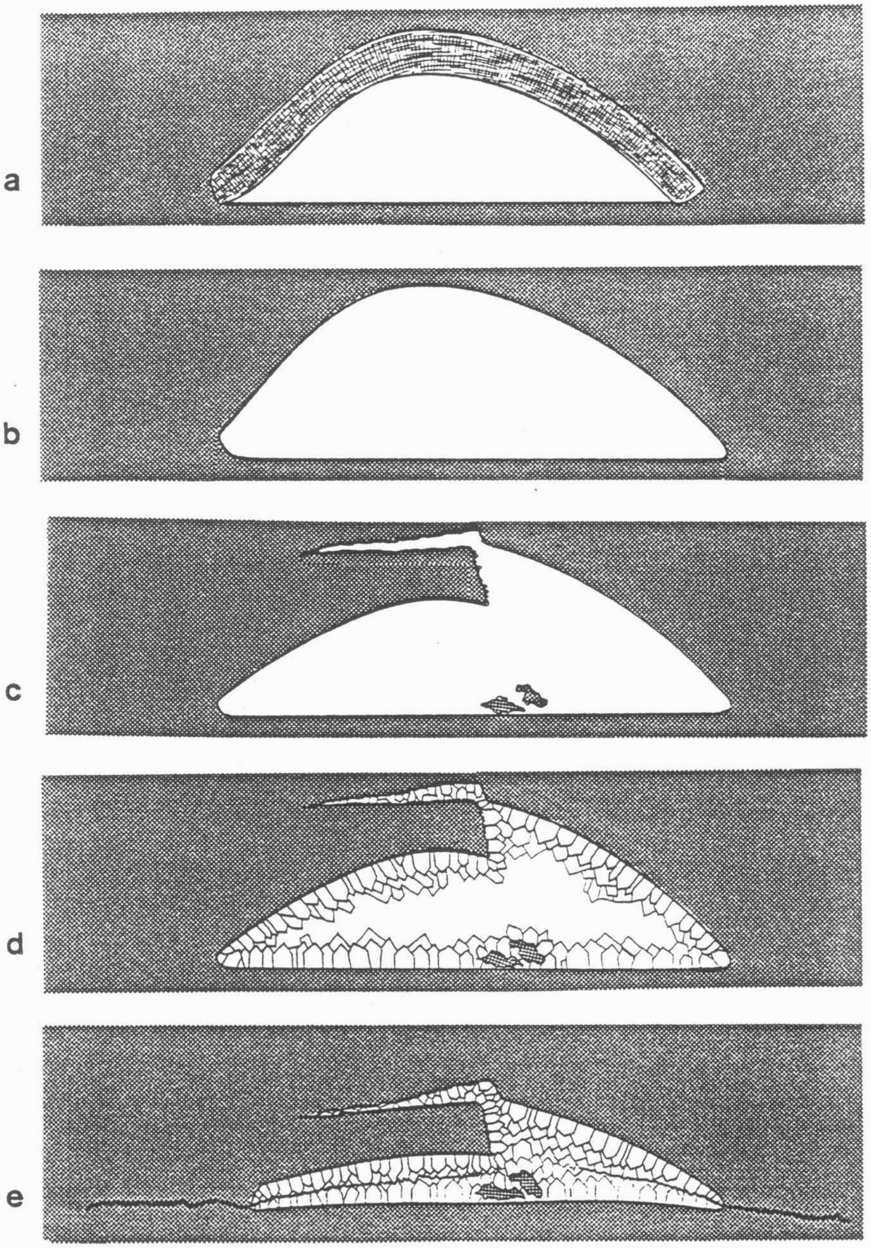

Figure 23

In summary, the diagenetic fabrics of Facies C may be explained by passage through an extensive active saturated meteoric phreatic environment, then an active undersaturated meteoric phreatic environment. The active saturated meteoric environment returned to allow calcite void filling before passage to the burial environment.

## Facies D

The lack of obviously leached unstable grains in Facies D suggests that the sediments either were never exposed to undersaturated meteoric water or were exposed only after neomorphic stabilization of such grains. The extensive compaction in Facies D further suggests that much of the facies never entered the active saturated meteoric phreatic environment, where precipitation of cements would have made later breakage of grains and intergrowth at grain contacts unlikely. Thus Facies D passed from the marine environment either to the stagnant meteoric phreatic or directly to the burial environment.

Tucker (1981, p. 139) stated that degrading neomorphism (recrystallization of large grains to many small ones) occurs only "in limestones which have been subjected to tectonic stress or very low grade metamorphism." Echinoderm fragments recrystallized to small crystals are common in Facies D, but they have been subjected to neither tectonic stress nor metamorphism. The most likely cause for the degrading neomorphism of echinoderms in Facies D is localized differential stress at point contacts between rigid grains during compaction. In other facies such stress did not occur because of earlier cementation, which provided a framework to distribute stress during loading.

### Facies E

The general absence of originally unstable grains in Facies E makes determination of diagenetic environments difficult. The general lack of cement (and resulting crushing of many brachiopods) suggests that the sediment did not pass into the active saturated meteoric environment. Thus Facies E entered only the stagnant meteoric or burial environments with little meteoric effect; the presence of ferroan dolomite suggests diagenesis in the burial environment.

The inclusion-rich ferroan dolomite that pervades Facies E resulted apparently from dolomitization of carbonate mud. The restriction of this fabric to facies adjacent the core shale or shale partings suggests that shales controlled the dolomitization in some way, probably by providing the magnesium for dolomitization. McHargue and Price (1982) have suggested that magnesium was derived from the shales during the diagenesis of clay minerals. Although the processes that they discuss require temperatures that may have been greater than any occurring in the burial history of Mid-Continent Pennsylvanian sediments, they suggest that greater time of burial might allow such processes at lower temperatures. In either case, magnesium would be produced only very late in diagenesis. Schutter (1983) has suggested that magnesium-rich waters in equilibrium with clay minerals would be expelled during compaction, transferring magnesium to the adjacent carbonate sediments. Schutter's hypothesis does not require unlikely high temperatures, and would allow dolomitization early in diagenesis. Unfortunately, the dolomitized rocks are relatively barren calcilutites that give little petrographic evidence as to whether dolomitization was early or late, so it is difficult to evaluate the two alternative models petrographically.

## Diagenetic History

The distribution and nature of Dennis diagenetic facies suggest that fresh water was introduced into the Dennis Formation from its northern and upper extent. This is explained most easily by a regression that subaerially exposed the northern part of the Dennis first. Meteoric water unsaturated with respect to $CaCO_3$ entered the Dennis and dissolved unstable carbonate grains until saturation occurred. This explains the development of Facies A in an initially unsaturated meteoric environment with weathering at the top of the Winterset Member (Fig. 24a).

Dissolution in Facies A allowed the development of saturated water farthest from the influx of fresh water. As regression continued, this saturated water passed farther into the Dennis as more unsaturated water entered at the exposure surface (Fig. 24b). Thus Facies B and C encountered saturated meteoric water first and then unsaturated meteoric water, as petrographic evidence suggests. With time the saturated lens would have grown, allowing more stabilization of grains in strata it encountered later; greater preservation in Facies C supports this hypothesis (Fig. 24c). With maximum regression, unsaturated meteoric water penetrated at least to the bottom of Facies C after extensive stabilization in saturated water (Fig. 24d). No evidence was seen that unsaturated water entered Facies D. Ultimately, transgresson caused a reversal of movement of diagenetic environments until all of the Dennis lay in the burial environment (Fig. 24e). This transgression caused filling of voids as saturated environments returned upward, but its rapidity, if it was like other such transgressions (Heckel, 1977), may have limited this void filling.

This interpretation requires transfer of $CaCO_3$ through the Dennis, largely from Facies A (where leaching occurred in the unsaturated meteoric environment) to Facies B and C (where precipitation of fringing cements and stabilization of grains occurred before leaching of remaining unstable grains).

Figure 24 -- Interpreted progression of waters through Dennis Formation. Datum for stratigraphic sections is top of Stark Shale.

a. Early regression brings unsaturated fresh water to strata in Facies A, and a mixing zone develops between unsaturated fresh water and marine water. Unsaturated fresh water leaches unstable carbonate grains with no neomorphism.

b. Further regression lowers level of marine-fresh water interface. Dissolution in Facies A creates a zone of saturated fresh water, which mixes with marine water. Saturated fresh water allows first neomorphism of unstable grains.

c. Further regression lowers level of fresh water further, and saturated fresh water lens grows. Larger saturated lens allows more extensive neomorphism lower in unit; later intrusion by unsaturated water leaches remaining unneomorphosed unstable grains or parts of grains.

d. Maximum regression allows unsaturated water to reach its lowest level, which includes uppermost Canville Member where intervening Stark Shale is thinnest.

e. Transgression raises mixing zone, and saturated environments return upward into formation. Sediments are progressively isolated in burial environment.

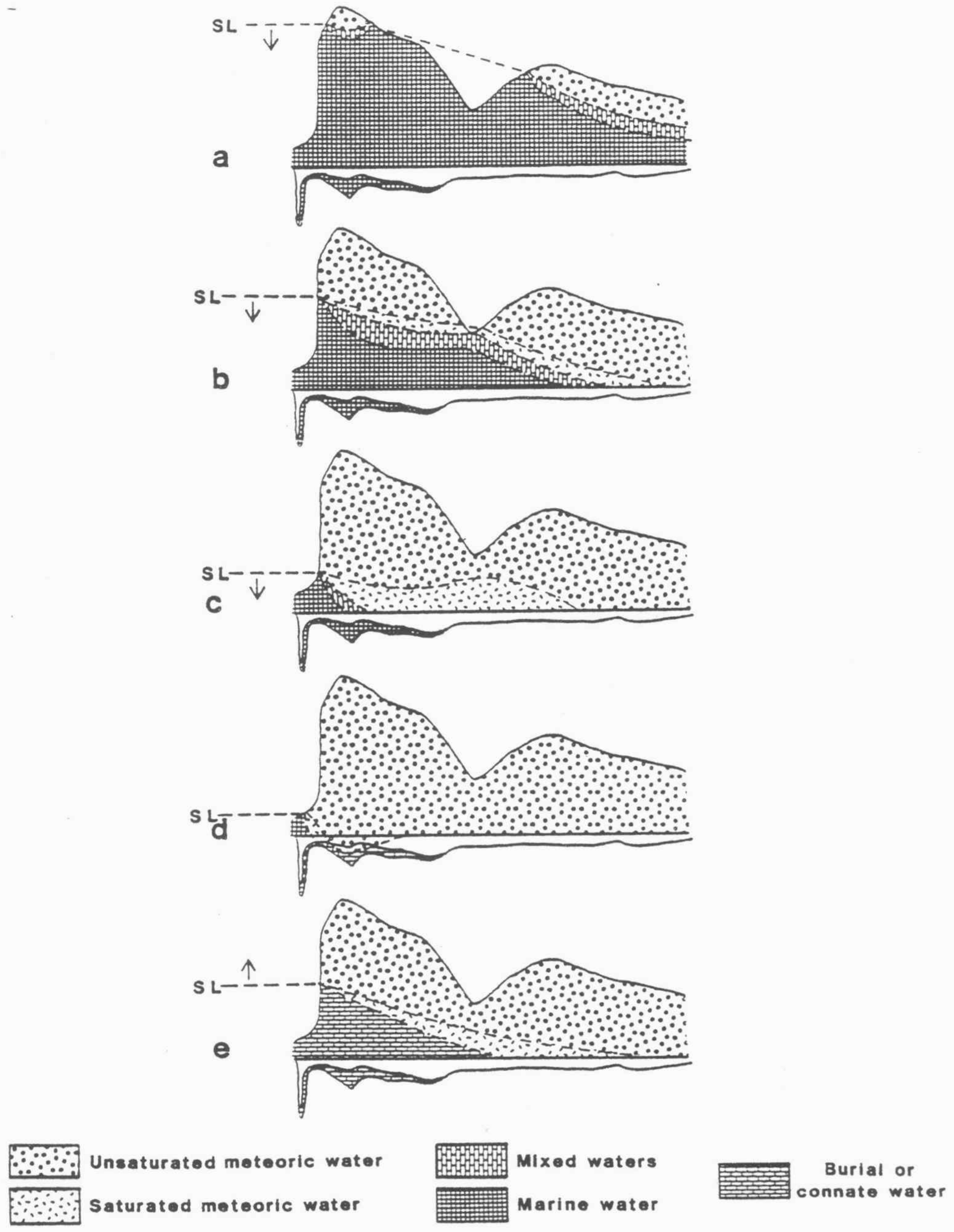
SL
a
SL
b
SL
c
SL
d
SL
e
Unsaturated meteoric water
Saturated meteoric water
Mixed waters
Marine water
Burial or connate water

Figure 24

Bathurst (1975) pointed out that, in such transfer, dissolution of aragonite grains alone cannot provide the volume of cement common in limestones. In the Dennis Formation, $CaCO_3$ was derived most likely from dissolution of both aragonite and calcite in the upper soil zone, allowing transfer of much $CaCO_3$ to the rest of the Dennis while total rock volume in the soil zone decreased.

This transfer of $CaCO_3$ allowed earlier and more extensive cementation in Facies B and C than in Facies A, where carbonate removal was the dominant early process. Thus after early diagenesis, most primary porosity in Facies B and C was filled, whereas it remained open in Facies A. This difference in void filling may explain the distribution of coarse ferroan dolomite, which appears to be a late burial cement in the Dennis because of petrographic evidence and its ferroan nature, which suggests precipitation in an oxygen-poor environment (Choquette, 1971). Ferroan dolomite occurs in secondary voids in Facies B and C but in both primary and secondary voids in Facies A. Because of the transfer of $CaCO_3$, only in Facies A did considerable primary porosity remain to be filled by ferroan dolomite after early meteoric diagenesis. In contrast, only secondary porosity remained unfilled in Facies B and C, resulting in ferroan dolomite void filling and moldic porosity.

Transfer of $CaCO_3$ to Facies B and C also explains the distribution of types of pressure solution effects. Stylolites, which are commonly interpreted as forming in lithified sediments (Buxton and Sibley, 1981) occur in Facies B and C, where cementation occurred first and most extensively. On the other hand, fitted fabric, which is characteristic of uncemented sediments (Buxton and Sibley, 1981) occurs in Facies D, where little cementation occurred because the active saturated meteoric environment did not extend low enough. Less impressive but significant grain-to-grain pressure solution occurred in Facies A, where early cementation was not extensive because saturation was not readily achieved during regression. Thus pressure solution features in the Dennis Formation are predictable from bulk transfer of $CaCO_3$ and resultant cementation.

The diagenetic history discussed above implies that unsaturated fresh water mixed with marine water only in Facies A; in other facies the mixing occurred between marine and saturated meteoric water (Fig. 24). This may explain why dolomite that is interpreted as originating in the mixing zone occurs only in Facies A, although other factors, such as length of time of passage of environments, may also have been a control.

## Anomalies in Regional Trends

Diagenetic Facies A, B, C, and D form roughly subparallel units (Fig. 7), suggesting relatively uniform passage of meteoric water through the Dennis Formation (Fig. 24). Anomalies in these trends occur in beds of oolitic calcarenite at localities CC, TC, JN, and KI. At localities CC and TC, oolite beds in Facies B are surrounded by Facies C, suggesting that greater primary porosity in the oolites may have allowed earlier invasion by unsaturated meteoric water to give more moldic porosity and minimal preservation (Fig. 9c). These beds are not isolated by shale partings.

In contrast, oolitic calcarenites high in the Winterset at localties JN and KI are in Facies C but are surrounded by Facies A and B, respectively (Fig. 7). These beds have thick shale partings both above and below, suggesting that entry into the oolite beds was impeded by relatively impermeable barriers long enough to allow neomorphism of ooids (Fig. 10a). Better preservation of ooids in the lower half of the oolite bed at locality JN may have been caused by density stratification of saturated and unsaturated waters.

These examples suggest that paleohydrologic controls caused local variations in regional diagenetic trends within the Winterset Member. The general absence of meteoric effects in the Canville Member (i.e. below the relatively impermeable Stark Shale) is a more obvious and larger-scale effect of paleohydrologic controls on diagenesis (Heckel, 1982).

## Paleotopography

The stratigraphic cross-sections in Figure 24 contain non-horizontal orientations of interpreted sea level, suggesting that such cross sections do not represent true paleotopographic relations. Figure 25 is a cross section reconstructed to show paleotopography as suggested by diagenetic facies, and to reorient sea level to horizontal. This interpretive cross-section places Facies A (and particularly the northern soil zone) highest so as to allow the most prolonged subaerial exposure. It places the Dennis relatively low in the Kansas City area and in southernmost Kansas, where Facies A is thinnest or does not occur (Fig. 7).

This paleotopographic cross-section (Fig. 25), which is based on diagenetic facies of the Dennis Formation, is in accord with one based on depositional evidence for all Upper Pennsylvanian cyclothems (Heckel, 1977). It supports the claim by Heckel (1977, 1980) that the open marine facies belt (i.e., the Kansas City region) was the "lowest part of the shelf" that extended southwestward from Iowa to the boundary between the algal mound and detrital facies belts. Extensive meteoric influx in southeastern Kansas may have been caused by greater elevation over the Bourbon Arch. (Because calcite twinning results from stress, the concentration of twinned calcite in the area of the Bourbon Arch also may suggest that the arch was still active during and after Dennis deposition and diagenesis.)

Figure 25 -- Inferred paleotopography of Dennis Formation. Arrangement shown has areas of greatest meteoric influence (i.e. Facies A) highest to give earliest and longest subaerial exposure; areas of little meteoric influence are lowest. Scale is same as that in Figure 6. Horizontal datum is parallel to sea level.

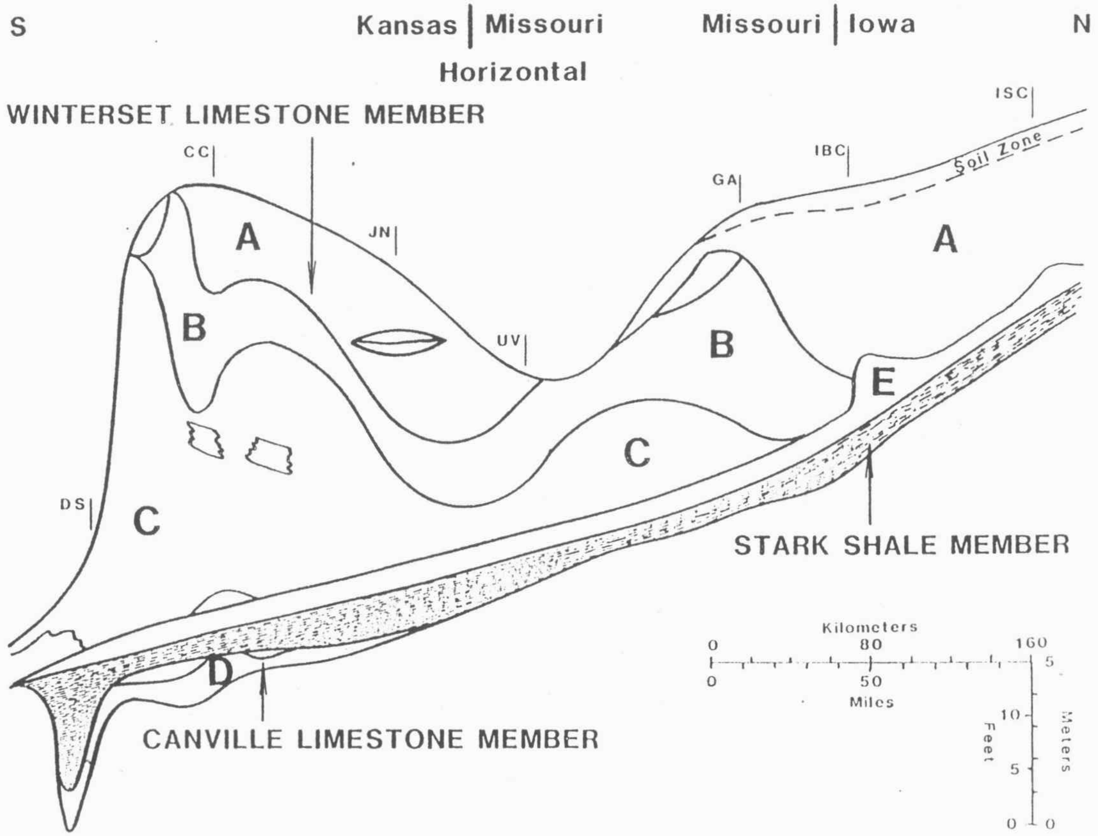
S
Kansas | Missouri
Missouri | Iowa
N
Horizontal
WINTERSET LIMESTONE MEMBER
CC
JN
UV
GA
IBC
ISC
Soil Zone
A
B
C
A
B
C
E
D
DS
C
STARK SHALE MEMBER
CANVILLE LIMESTONE MEMBER
Kilometers
0
80
160
0
50
Miles
5
10
5
0
Feet
10
5
0
Meters

Figure 25

This paleotopography (Fig. 25) and resulting basin configuration may explain the more ferroan nature of late dolomite southward. In the north (i.e., nearshore or at the basin edge) oxygen may have infiltrated the strata more readily than in the more deeply buried southern parts of the basin. Thus more iron would have been oxidized in the north, whereas all such iron in south could enter dolomite lattices.

## Heterogeneity of Diagenetic Textures

Dennis diagenetic fabrics are heterogeneous within the context of one rock or thin section, and also in the preservation of one grain type in one or more facies. The former heterogeneity has been noted in other sediments by Longman (1980) and Saller (1982), and can be explained by diagenesis in successive diagenetic environments. This heterogeneity is caused by diagenesis of different grains at different times, and may result from subtle microstructural differences or short-range porosity differences.

The second type of heterogeneity (variable preservation of one grain type) suggests that diagenesis of carbonate grains involves a spectrum of processes rather than two strongly contrasting processes, such as void filling and thin-film neomorphism. Dennis diagenetic fabrics are compatible with Saller's (1982) claim that processes intermediate between void-filling and thin-film neomorphism occur and result in intermediate textures.

## Cathodoluminescence

The inverse relationship between Fe/Mn ratios in calcite cements and their cathodoluminescence supports the contention of Frank, Carpenter, and Oglesby (1982) that luminescence of cement zones is governed by ratios of ionic concentrations rather than absolute amounts.

The presence of Fe and Mn in calcite may be governed by the degree of oxygenation (pE or Eh) of precipitating waters, because only in oxygen-poor waters will the ions remain in their divalent (soluble) state. Fe is more readily oxidized to the trivalent state, so that progressive oxygenation first removes $Fe^{+2}$ from solution and then $Mn^{+2}$ (Hem, 1972) (Fig. 26). Fe and Mn in calcite cements may be governed also by acidity (pH), presence of sulfur, and simply their availabilty from external sources (Carpenter and Oglesby, 1976).

Early Fe-rich cements associated with pyrite at edges of voids (Fig. 15a) suggest early oxygen-poor conditions. The general decrease in Fe with time in Dennis cement zonations may have been caused by progressively greater oxygenation of waters. Mn, the less common element of the two, may have originally been governed by availability. The later increase in both Fe and Mn (in sample GR4.9; Fig. 18) may have been caused by a

Figure 26 -- pH - pE diagram for iron and manganese. Mn and Fe exist in divalent (soluble) state in lower left stability field, only Mn is divalent in middle field, and neither is divalent in upper right. Increasing pH and pE remove first divalent Fe and then divalent Mn, assuming both are already present. Solid arrow shows possible interpretation of decreasing iron contents in cements (Fig. 17), beginning from anoxic conditions early in burial. Dashed arrow is possible interpretation of reversal of that early trend. Early reducing conditions because of organic-rich black shale, progressive oxygenation with regression, and ultimate return to reducing conditions with burial may explain these trends. Diagram adapted from Hem (1972). Eh is given in parentheses at left.

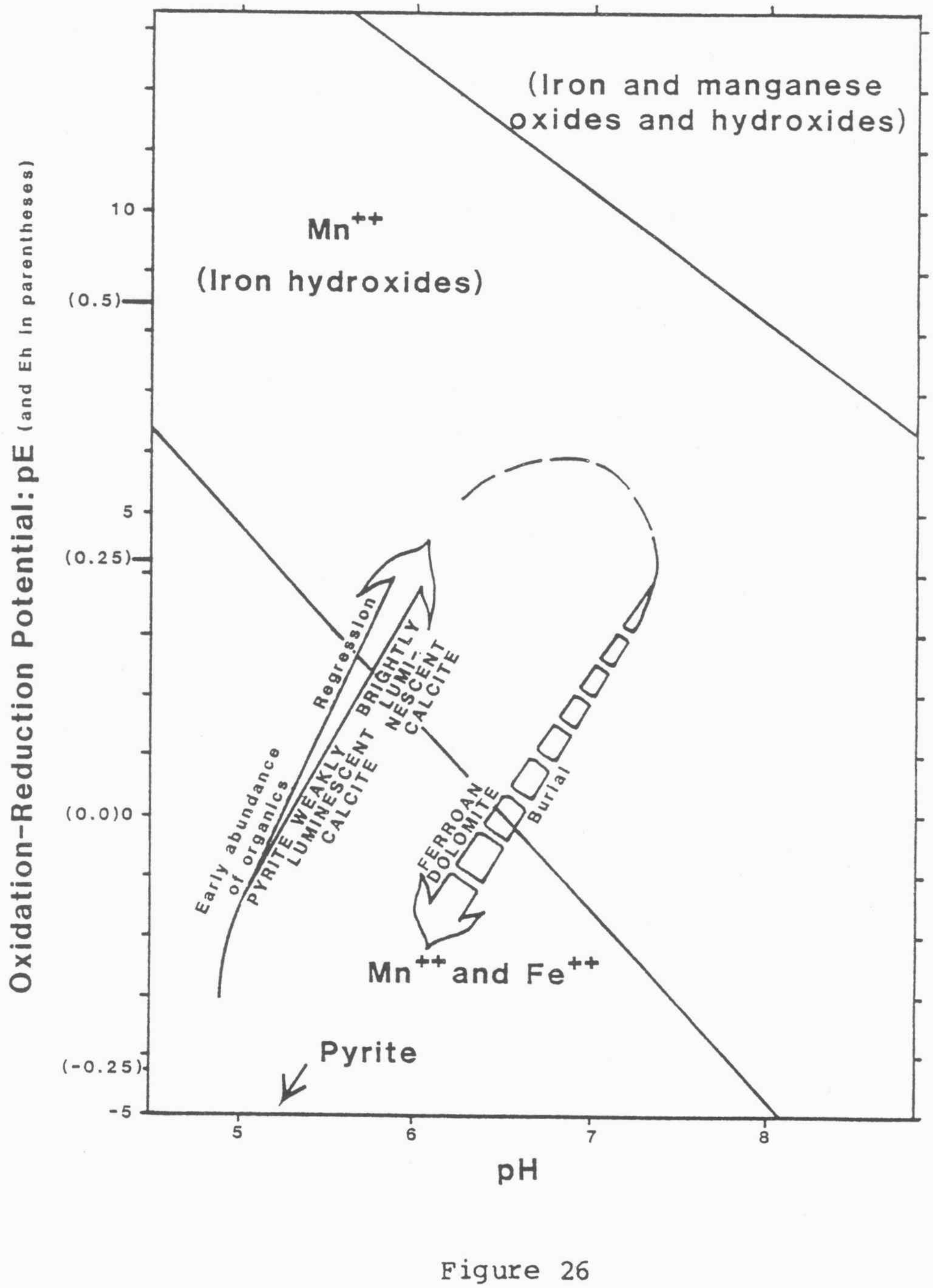
(Iron and manganese oxides and hydroxides)
Mn++
(Iron hydroxides)
Early abundance of organics
PYRITE WEAKLY LUMINESCENT CALCITE
Regression
BRIGHTLY LUMI-NESCENT CALCITE
FERROAN DOLOMITE
Burial
Mn++ and Fe++
Pyrite
Oxidation-Reduction Potential: pE (and Eh in parentheses)
10
(0.5)
5
(0.25)
(0.0)0
(-0.25)
-5
5
6
7
8
pH

Figure 26

late-stage decrease in oxygen abundance following most precipitation of both calcite and quartz cements (Fig. 17).

This sequence of initially low, progressively higher, and final lower oxygenation can be explained by previously interpreted diagenetic trends. Early in diagenesis, little oxygen was available to the buried sediments, and the organic-rich Stark Shale should have created reducing conditions that caused an oxygen gradient in the surrounding limestones. Thus initial cements should have been precipitated in the oxygen-poor conditions interpreted from geochemical data. With further regression and downward movement of meteoric diagenetic environments, oxygen became more available, oxidizing Fe and possibly Mn to give Fe-poor cements, which occluded most remaining porosity. Ultimately, transgression brought stagnant meteoric or burial environments low in oxygen that allowed precipitation of cements richer in Fe and Mn (Fig. 26). Such conditions led to the precipitation of ferroan dolomite.

The higher absolute abundance of Fe and Mn in cements from the Canville sample as compared to the Winterset sample (Fig. 18) may reflect either less oxygenation in the Canville Member (below the sealing black shale) or greater availability of cations from the shale or both. The similarity of cathodoluminescence and geochemistry in the the two samples suggests, however, that they obeyed generally similar chemical controls, implying that the Canville was not completely isolated by the Stark Shale from chemical changes above.

## C and O Isotopes

The lightening-upward trends in C and O isotopes (Fig. 22) may result from meteoric influx into the Dennis Formation. Meteoric waters contain lighter O isotopes because of their differentiation from marine water (Hoefs, 1980); limestones in equilibrium with such waters would also contain lighter isotopes. Thus trends in the Dennis Formation may result from more extensive meteoric interaction in the upper extent of the unit, which would follow logically from the introduction of fresh water at the surface of subaerial exposure. Carbon isotopes may display the lightening-upward trend more clearly because of equilibration with light-carbon soil gas derived from the decomposition of plants at the exposure surface (Allan and Matthews, 1977).

## Diagenetic Silica

Petrographic evidence suggests that silicification (replacement of carbonate grains by silica) occurred early in diagenesis, before cementation by calcite. If extensive cementation occurred in the active saturated meteoric phreatic environment, this suggests that grain silicification occurred in the marine, mixing zone, or stagnant meteoric environment.

Void filling by quartz occurred later, during and after calcite cementation, suggesting that it took place in the active saturated meteoric environment.

The coincidence of most diagenetic silica with sponge spicules replaced by calcite (Fig. 12 and 14) suggests that diagenetic silica was derived from biogenic sources within the Winterset. The occurrence of extensively silicified calcarenites, which presumably had high original porosities (as at localities CC and TC), in strata otherwise not characterized by extensive silicification supports the hypothesis that silica was transported over considerable distances (i.e. at least tens of meters) from such sources.

Thus it appears that Dennis diagenetic silica was removed from local biogenic sources, transferred over some distance, and then replaced carbonate grains early in diagenesis. Knauth (1979) has proposed a model for similar silicification in the meteoric-marine mixing-zone environment. According to Knauth, $CaCO_3$ undersaturation and silica supersaturation coincide when mixed waters of roughly 33 to 78% fresh water occur, assuming the fresh water is already saturated with silica from the leaching of biogenic grains. This chemical combination allows silica to replace $CaCO_3$. The timing of silicification, source of silica, and evidence for lateral transportation all suggest that Knauth's model can be applied successfully to diagenetic silica in the Dennis Formation.

Later void-filling silica is largely megaquartz as opposed to chalcedony, and in a few cases megaquartz follows chalcedony in void-filling sequences. Folk and Weaver (1952) noted similar tendencies and suggested that lower rates of precipitation later during diagenesis may favor precipitation of megaquartz.

## Diagenetic and Depositional Models

The interpretation of diagenesis discussed above suggests that most diagenesis occurred during regression or during the transgression leading to the deposition of the overlying Lower Cherryvale cycle of Heckel and Baesemann (1975). This agrees with Watney's (1980) generalization about cyclothems in northwestern Kansas and southwestern Nebraska that "significant porosity formation ... [resulted from] ... processes of both sedimentation and diagenesis that occurred prior to the deposition of the younger overlying cycle." Porosity in the Dennis Formation was destroyed later in part, however, by ferroan dolomite and pressure solution.

Although this study was not intended or designed as a test of Longman's (1980) model of nearsurface diagenetic environments, the successful and relatively simple application of those environments suggests that his model is a reasonable explanation of regional diagenetic trends in ancient carbonates. This diminishes slightly the suspicions raised by Wilkinson, Janecke, and Brett (1982) that extension of modern diagenetic findings to ancient sediments may involve fallacies based on excessively uniformitarian assumptions.

The results of this study agree in general with conclusions reached by Heckel (1982; ms. in press) in his model for diagenesis of carbonates in Mid-Continent Pennsylvanian cyclothems. He concluded, however, that the middle (transgressive) limestone of a cycle would only rarely be affected by meteoric diagenesis because of burial immediately after deposition under the core shale, which would have formed "an impermeable aquiclude" that would have confined meteoric water to overlying units (Heckel, ms. in press). The extension of Facies C into the Canville Member suggests that Dennis diagenesis was at least one such rare case, and the cathodoluminescent and geochemical trends discussed above corroborate that the black shale did not seal off the middle limestone completely. Although other hypotheses might explain minor meteoric influence in the Canville Member, the extension of Facies C downward in the Winterset Member through the Stark Shale where it is thinnest to the Canville suggests that fresh water did penetrate the Stark.

Interpretations in this study are compatible with Heckel's (1977) model for the deposition of Mid-Continent Pennsylvanian cyclothems. They could also be compatible with that of Merrill (1975), whose claim of nearshore marine deposition of core shales during transgression would not require a different diagenetic history. The results conflict, however, with the model of Zangerl and Richardson (1963) in that non-marine deposition of the core shales would have caused much greater meteoric infiltration of middle limestones.

# CHAPTER 6

## SUMMARY OF CONCLUSIONS

The distribution of diagenetic facies in the Dennis Formation suggests that regression during and after Winterset deposition allowed isotopically light unsaturated meteoric water to enter the formation. This water leached all unstable grains and possibly some stable grains in Facies A (the northernmost and uppermost diagenetic facies) to develop a lens of saturated meteoric water between remaining marine water and the incoming unsaturated water (Fig. 24). These two lenses then migrated southward and downward into the formation. The saturated lens became larger and allowed progressively more neomorphism of unstable grains and cementation in Facies B and C, before entry of unsaturated water caused leaching of remaining unstable grains. Maximum regression allowed unsaturated water to penetrate the top of the transgressive Canville Member. Subsequent transgression brought saturated meteoric water back up through the formation before burial conditions set in. Meteoric water had little or no effect on Facies D and E.

Movement of the unsaturated and saturated lenses through much of the Dennis Formation during regression caused transfer of $CaCO_3$ from Facies A (where leaching was most extensive) to Facies B and C (where more cementation in primary voids and neomorphism occurred). As a result, later ferroan dolomite filled both primary and secondary voids in Facies A but only secondary voids in Facies B and C. Extensive early cementation in Facies B and C allowed little grain-to-grain pressure solution there, whereas grain-to-grain pressure solution occurred in Facies A and D, where there was less early cementation.

Fine clear rhombic dolomite was precipitated in voids in Facies A early in diagenesis, possibly in the mixing zone. Ferroan dolomitization of carbonate mud in Facies E resulted from transfer of magnesium from adjacent thick shales under oxygen-poor conditions.

Heterogeneity of Dennis diagenetic fabrics suggests that alteration of originally unstable grains involved processes intermediate between "thin-film neomorphism" and complete leaching and void filling.

Chemical trends in cathodoluminescent calcite and associated pyrite suggest that reducing conditions existed early in diagenesis, possibly because of the organic-rich Stark Shale. Regression brought greater oxygenation, before burial eventually caused prolonged reducing conditions. The chemistry of late void-filling ferroan dolomite cements may have been controlled by variation in the limited oxygenation of differing parts of the Mid-Continent basin during burial.

Diagenetic silica was derived from biogenic sources within the Dennis Formation. Silicification of carbonate grains occurred early in diagenesis, probably in the mixing-zone environment. Later precipitation of void-filling silica occurred in saturated meteoric environments.

Irregularities in the distribution of diagenetic facies occur in beds that were in anomalous paleohydrologic positions. Examples include less leached beds that were isolated by thick shale partings and more leached calcarenite beds that had higher primary porosities than surrounding strata and were not isolated by shales.

The distribution of diagenetic facies suggests a paleotopography consistent with interpretations by previous workers, and it supports the claim that the Dennis Formation was deposited in a transgressive-regressive cycle. The existence, distribution, and interpretation of diagenetic facies in the Dennis Formation suggests that the concepts of diagenetic facies and interpreted diagenetic environments can be useful in the study of carbonate diagenesis.

# APPENDIX A

## LOCATIONS OF MEASURED SECTIONS

The locality code, political location, and legal location are given for each section measured and subsequently used in the study. Localities are listed in order from south to north (Fig. 6). All cores are now held by the Iowa Geological Survey.

CW (Coffeyville West) - a roadcut 4 miles west of Coffeyville in southern Montgomery County, Kansas. W1/2, SW1/4, NW1/4, Section 6, T35S, R16E.

CN (Coffeyville North) - a roadcut on Cline Street opposite City Park in Coffeyville, Montgomery County, Kansas. E1/2, NE1/4, NW1/4, Section 27, T34S, R16E.

CB (Cedar Bluff) - a roadcut on Cedar Bluff 3 miles north of Coffeyville in southeastern Montgomery County, Kansas. SE1/4, SW1/4, SW1/4, Section 14, T34S, R16E.

VR (Verdigris River) - an outcrop in the Verdigris River roughly 660 feet south of a dead end road, southeast of Independence in Montgomery County, Kansas. SE1/4, NW1/4, Section 28, T33S, R16E.

CH (Cherryvale) - a quarry owned by Midwest Minerals Company southwest of the intersection of U.S. 160 and 169, 5 miles north of Cherryvale in northeastern Montgomery County, Kansas. SW1/4. NW1/4, Section 22, T31S, R17E.

DS (Dennis Southwest) - a roadcut 0.2 miles south of U.S. 160, southwest of Dennis in northwestern Labette County, Kansas. NE1/4, SE1/4, NE1/4, Section 21, T31S, R18E.

GB (Galesburg) - a quarry 1.5 miles east of Galesburg in Neosho County, Kansas. SW1/4, SW1/4, Section 34, T29S, R19E.

MM (Midwest Minerals) - a quarry owned by Midwest Minerals Company 0.3 miles north of Kansas 47 in Neosho County, Kansas. SE1/4, NE1/4, SE1/4, Section 9, T29S, R19E.

ER (Erie) - a quarry 0.6 miles west of U.S. 59 and Kansas 57 southwest of Erie in Neosho County, Kansas. NE1/4, NE1/4, NW1/4, Section 12, T29S, R19E.

CC (Canville Creek) - a roadcut on Kansas 39 and U.S. 59 at Canville Creek, 14 miles east of Chanute in northeastern Neosho County, Kansas. N1/2, NW1/4, NW1/4, Section 23, T27S, R20E.

SW (Stark West) - a roadcut on Kansas 39 and U.S. 59, 15 miles east of Chanute and 1.5 miles west of Stark in northeastern Neosho County, Kansas. SE1/4, SW1/4, Section 13, and NE1/4, NW1/4, Section 24, T27S, R20E.

SN (Stark North) - a quarry on Kansas 39 and U.S. 59 northwest of Stark in northeastern Neosho County, Kansas. SE1/4, SE1/4, Section 12, T27S, R20E.

FR (Flat Rock) - a roadcut at the intersection of Flat Rock Creek, Kansas 39, and a county road, 3 miles east of the Neosho County line in southwestern Bourbon County, Kansas. NE1/4, NE1/4, Section 7, T27S, R22E.

BS (Bronson) - a quarry 2 miles east of Bronson in western Bourbon County, Kansas SE1/4, SE1/4, Section 6, T25S, R22E.

TC (Tippie Creek) - a quarry near Tippie Creek, 5 miles southeast of Xenia in northern Bourbon County, Kansas. NW1/4, SE1/4, SE1/4, Section 17, T24S, R23E.

GR (Goodrich) - a quarry 0.5 miles south of Goodrich in northwestern Linn County, Kansas. NW1/4, SW1/4, Section 28, T20S, R22E.

JN (Jingo North) - a roadcut on U.S. 69, 2 miles north of Jingo in southeastern Miami County, Kansas. SW1/4, SE1/4, Section 31, T18S, R25E.

PE (Peculiar) - a quarry on the I-71 access road 1.5 miles southeast of county road J, southeast of Peculiar in Cass County, Missouri. SE1/4, NW1/4, Section 23, T45N, R32W.

UV (Unity Village) - a roadcut on the west side of U.S. 350, 0.5 miles northwest of Colbern Road in Unity Village (eastern Kansas City) in Jackson County, Missouri. NW1/4, SE1/4, NE1/4, Section 26, T48N, R32W.

ID (Inland Drive) - a quarry on Inland Drive at Inland Dock #2 in Kansas City, Wyandotte County, Kansas. NW1/4, NW1/4, NE1/4, Section 27, T11S, R24E.

RI (Richmond) - a quarry owned by Green Quarries Company on county road EE west of Richmond in Ray County, Missouri. NW1/4, SE1/4, SW1/4, Section 33, T52N, R28W.

KI (Kingston) - a quarry owned by Everett Quarries Company southeast of Kingston in central Caldwell County, Missouri. SW1/4, NE1/4, Section 34, T56N, R26W.

BR (Breckenridge) - a quarry 4 miles west of Breckenridge in northeastern Caldwell County, Missouri. NW1/4, NW1/4, Section 7, T57N, R26W.

GA (Gallatin) - a roadcut north of Gallatin on Missouri 6, 1.4 miles west of Missouri 13 in central Daviess County, Missouri. NE1/4, SW1/4, Section 17, T59N, R27W.

PR (Princeton) - a quarry south of Princeton in central Mercer County, Missouri. SE1/4, NW1/4, Section 11, T64N, R24W.

IBC (Iowa Bedford Core) - a core recovered by the Iowa Department of Transportation from a hole 2 miles southwest of Bedford in southern Taylor County, Iowa. SE1/4, Section 4, T67N, R34W.

VW (Van Wert) - a quarry 4 miles southwest of Van Wert in northern Decatur County, Iowa. SE1/4, SE1/4, SW1/4, Section 21, T70N, R26W.

TH (Thayer) - a quarry owned by Schildberg Construction Company 2 miles south of Thayer in eastern Union County, Iowa. NW1/4, NE1/4, Section 35, T72N, R28W.

WS (Winterset) - a roadcut on U.S. 169 south of the Middle River, southwest of Winterset in central Madison County, Iowa. SE1/4, NW1/4, Section 14, T75N, R28W.

ISC (Iowa Stanzel Core) - a core recovered by the Schildberg Construction company from a hole near Stanzel in western Madison County, Iowa. SW1/4, NE1/4, Section 5, T75N, R29W.

IJL (Iowa Jefferson Lower) - a core recovered by the Schildberg Construction Company from a hole in Jefferson Township in northern Adair County, Iowa. NW1/4, SE1/4, NE1/4, SW1/4, NW1/4, T77N, R31W.

# APPENDIX B

## STRATIGRAPHY OF THE DENNIS FORMATION AT LOCALITY ID

As traditionally recognized (see Heckel and Baesemann, 1975), the Dennis Formation at locality ID (in Wyandotte County, Kansas) consists of approximately 1 meter of Stark Shale and 9 meters of limestone with interbedded shale in the Winterset Member (Fig. 27). The limestone is divided by a 0.8 meter thick shale 3 meters below the top of the Winterset, and the limestone above that shale differs greatly from that below and from typical Winterset strata. The differences include:

1) The black color of the upper unit. Where freshly exposed, the Winterset is always light to medium gray and weathers brown, but at locality ID the upper bed is black or very dark gray. This color may suggest a much higher content of organic material.

2) The cherty nature of the upper unit. The Winterset contains tan and gray chert nodules in its upper extent north of Linn County, Kansas, but the upper bed at locality ID contains much more chert than is usual, and that chert is much blacker.

3) The near lack of conodonts in the upper unit. Heckel and Baesemann (1975) examined the Winterset at locality ID and

Figure 27 -- Stratigraphy of Winterset Member at locality ID. Traditional stratigraphic terminology is shown in columns at right; stratigraphic terminology used in this report is at left. Upper part of the traditional Winterset is removed from Winterset by author because of striking lithologic differences and apparent differences in depositional environments.

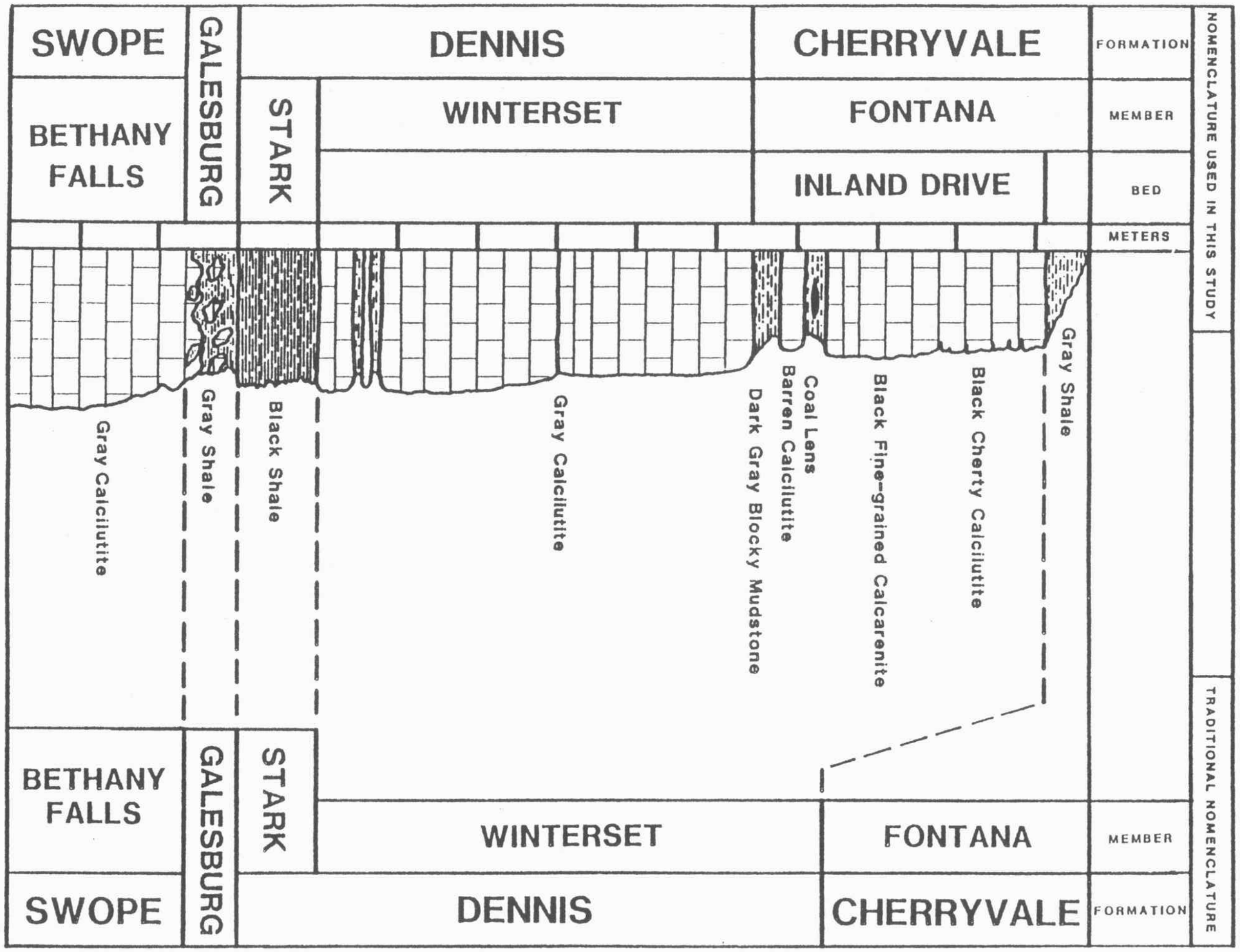
SWOPE
GALESBURG
DENNIS
CHERRYVALE
FORMATION
BETHANY FALLS
STARK
WINTERSET
FONTANA
MEMBER
INLAND DRIVE
BED
METERS
NOMENCLATURE USED IN THIS STUDY
Gray Calcilutite
Gray Shale
Black Shale
Gray Calcilutite
Dark Gray Blocky Mudstone
Barren Calcilutite
Coal Lens
Black Fine-grained Calcarenite
Black Cherty Calcilutite
Gray Shale
BETHANY FALLS
GALESBURG
STARK
WINTERSET
FONTANA
MEMBER
SWOPE
DENNIS
CHERRYVALE
FORMATION
TRADITIONAL NOMENCLATURE

Figure 27

found that, whereas conodonts are moderately abundant and diverse in most regressive limestones in Missourian cyclothems, the upper part of the Winterset contains only a few individuals of one genus.

4) The molluscan fauna of the upper unit. The upper bed at locality ID contains many large clams not found elsewhere in the Winterset.

The intervening shale is also unusual in that it consists of (in ascending order) 0.3 meters of blocky mudstone, 0.3 meters of barren laminated calcilutite in lenses, and 0.2 meters of slightly fissile shale with lenses of vitreous coal. Coal is found nowhere else in the Winterset.

The anomalous nature of the shale and upper limestone unit suggest that they are not part of the Winterset Member depositionally. The coal suggests non-marine deposition and the barren limestone may suggest a nearshore depositional environment. Thus marine Winterset deposition may have ended with deposition of the top of the lower limestone unit, suggesting that the upper part should be considered part of the Fontana Member of the Cherryvale Formation. The change in conodonts and the unusual molluscan fauna also suggest a profound change in depositional environment.

Two stratigraphic features also suggest that the upper bed is not part of the Winterset. Howe (1961) noted that "a thin coal bed is present near the base of the [Fontana] in some places." The coal at locality ID could correspond to this coal. Also, the thickness of the Winterset Member at localty UV (18 miles to the east) is no more than 5 meters, slightly less than the lower limestone unit at locality ID. Thus a truncated Winterset up to the major shale parting at locality ID would agree well in thickness with nearby exposures.

In summary, both depositional and stratigraphic evidence suggest that the true Winterset Member at locality ID extends upward 5.4 meters from the Stark Shale to the major shale bed. The shale bed and upper limestone unit appear to be part of the overlying Fontana Shale. In this study the 2.8 meters of black limestone above the shale will be informally named the "Inland Drive bed" of the Fontana Member of the Cherryvale Formation (Fig. 27), and neither the Inland Drive Bed nor the underlying shale bed will be considered part of the Dennis Formation.

# APPENDIX C

## GEOCHEMICAL DATA

### Table 1

### Chemical Composition of Cathodoluminescent Calcite

| Sample | Point | Unnormalized Oxide Weight Percent Total | Mole Percent $MgCO_3$ | $CaCO_3$ | $MnCO_3$ | $FeCO_3$ |
|---|---|---|---|---|---|---|
| DSO.1 | 1 | | 0.99 | 98.09 | 0.06 | 0.86 |
| DSO.1 | 2 | 96.28 | 1.06 | 97.91 | 0.07 | 0.95 |
| DSO.1 | 3 | 90.41 | 0.62 | 97.94 | 0.27 | 1.17 |
| DSO.1 | 4 | 98.12 | 0.25 | 98.68 | 0.44 | 0.64 |
| DSO.1 | 5 | 97.95 | 0.40 | 98.31 | 0.52 | 0.77 |
| DSO.1 | 6 | | 0.36 | 98.46 | 0.54 | 0.66 |
| DSO.1 | 7 | | 0.33 | 98.56 | 0.46 | 0.65 |
| DSO.1 | 8 | | 0.39 | 98.29 | 0.62 | 0.69 |
| DSO.1 | 9 | 99.75 | 0.32 | 97.37 | 1.13 | 1.17 |
| DSO.1 | 10 | | 0.83 | 98.79 | 0.01 | 0.37 |
| DSO.1 | 11 | | 1.37 | 96.89 | 0.10 | 1.64 |
| DSO.1 | 12 | 95.65 | 1.44 | 96.69 | 0.13 | 1.74 |
| GR4.9 | 1 | 103.05 | 0.82 | 98.84 | 0.01 | 0.33 |
| GR4.9 | 2 | 101.52 | 1.06 | 98.60 | 0.00 | 0.33 |
| GR4.9 | 3 | | 0.17 | 99.70 | 0.01 | 0.11 |
| GR4.9 | 4 | | 0.78 | 99.18 | 0.00 | 0.03 |
| GR4.9 | 5 | 98.37 | 0.32 | 98.92 | 0.18 | 0.58 |
| GR4.9 | 6 | | 0.17 | 99.41 | 0.10 | 0.32 |
| GR4.9 | 8 | | 0.35 | 99.39 | 0.04 | 0.22 |
| GR4.9 | 9 | | 0.27 | 98.85 | 0.21 | 0.67 |

Table 2

Chemical Composition of Ferroan Dolomite

| Sample | Point | Unnormalized Oxide Weight Percent Total | Mole Percent | | | |
|---|---|---|---|---|---|---|
| | | | $MgCo_3$ | $CaCO_3$ | $MnCO_3$ | $FeCO_3$ |
| IBC497.2 | 1 | 94.96 | 37.88 | 56.03 | 0.14 | 5.95 |
| IBC497.2 | 2 | 95.21 | 35.98 | 55.73 | 0.35 | 7.95 |
| IBC497.2 | 3 | 95.06 | 36.79 | 56.19 | 0.22 | 6.80 |
| ID4.1 | 1 | 89.34 | 30.40 | 54.19 | 0.30 | 14.61 |
| ID4.1 | 2 | 90.33 | 31.04 | 55.13 | 0.27 | 13.55 |
| ID4.1 | 3 | 90.85 | 26.97 | 57.62 | 0.29 | 15.12 |
| CH7.0 | 1 | 89.31 | 24.52 | 55.20 | 0.75 | 19.54 |
| CH7.0 | 2 | 90.54 | 24.32 | 54.73 | 0.75 | 20.20 |
| ISC85.8 | 1 | 90.49 | 31.22 | 56.27 | 1.06 | 11.45 |
| ISC85.8 | 2 | 89.23 | 33.97 | 57.40 | 0.40 | 8.23 |
| ISC85.8 | 3 | 90.36 | 30.58 | 56.42 | 1.14 | 11.86 |

## Table 3

## Carbon and Oxygen Isotopes

| Sample | d$^{13}$C(PDB) | d$^{18}$O(SMOW) | d$^{18}$O(PDB) |
|---|---|---|---|
| IBC497.5 | -1.30 | 25.04 | -5.65 |
| IBC501.1 | -1.03 | 25.43 | -5.26 |
| IBC503.2 | -0.318 | 26.35 | -4.37 |
| IBC507.4 | -0.364 | 25.14 | -5.55 |
| IBC511.0 | -0.226 | 25.41 | -5.29 |
| ISC87.7 | -0.726 | 26.00 | -4.71 |
| ISC94.4 | -0.037 | 27.52 | -3.24 |
| ISC96.1 | +0.86 | 30.20 | -0.64 |
| IJL37.75 | -1.10 | 28.80 | -2.00 |
| IJL42 | -2.12 | 25.06 | -5.63 |
| IJL44.7 | -0.79 | 27.18 | -3.57 |
| IJL47.7 | +1.49 | 30.59 | -0.26 |
| IJL48.7 | +0.41 | 29.92 | -0.91 |

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