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A

STUDY OF THE DIAGENESIS OF A PORTION OF THE HOLSTON
LIMESTONE: PARAGENESIS OF CEMENTS AND
EVALUATION OF GEOCHEMISTRY

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ABSTRACT

The Holston Limestone (Middle-Ordovician) of East Tennessee is composed of two dominant lithologies: bryozoan-micrite boundstone and flanking grainstones of ramose bryozoans and echinoderms. The Holston occupied a shelf-edge position. Three [✓]statigraphic sections were studied which ranged from off-shelf to fully on-shelf in their original environmental locations. These were chosen to examine the effect of the relation of each outcrop to the shelf-edge on post-depositional alteration.

Diagenetic studies made use of staining, cathodoluminescence and petrographic examination to determine the paragenetic sequence of cements. Allochems may be cemented initially and then broken by compactional forces, may be broken first and then cemented or, least commonly, aragonitic allochems may develop micrite envelopes followed by cementation and/or fracturing.

Paragenetic sequences indicate the following events within the marine, phreatic diagenetic environment; (1) precipitation of fringe cement (2) breakage by compaction (3) deposition of echinoderm syntaxial overgrowths (4) precipitation of isopachous radial-fibrous cement (probable predecessor to radiaxial cement) (5) stabilization of high-magnesium and aragonitic allochems. Events within the meteoric, phreatic diagenetic environment include (6) transformation of radial-fibrous to radiaxial cement (7) deposition of internal sediment and (8) precipitation of drusy sparite. The products of all of the above events are not always present and some events may have been coeval in part in the sequence. Due to the early occlusion of porosity by

various cements, lithification occurred with little compaction and the resulting displacement of allochems is very minor.

Comparison of the relative abundance of cement types across the three outcrops indicates that syntaxial overgrowths and radiaxial cement are the most prevalent. Echinoderms are the most common substrate for syntaxial overgrowths and radiaxial cement is most commonly observed as isopachous rims around bryozoans. Variations in the amounts of these two cement types depend on the relative abundance of echinoderms and bryozoans. Neither fringe nor drusy sparite are volumetrically important. No trends concerning the relative abundance of cement types were observed across the transect from most basinward to the on-shelf localities.

Facies and allochem mineralogy are important in controlling trace and minor element distribution but atomic absorption data suggest that post-depositional alteration by meteoric waters was also an important factor. Low strontium values indicate few originally aragonitic allochems and/or post-depositional removal of strontium. Sodium values agree with previously published data from other ancient carbonate rock sequences that suggest normal, open marine conditions. Magnesium values vary but are generally quite low. Variations in magnesium may be due to differences in original allochem mineralogy or to unexplained changes within the diagenetic solutions as they passed through the pore spaces. No obvious trends in the concentrations of these elements are present from the most basinward to the on-shelf localities.

Manganese and iron values already present in the depositional environment have been enhanced as equilibration to a meteoric diagenetic

environment has proceeded. These elements are potentially useful as paleobathymetric indicators, with highest values observed at Midway Road (most basinward of the three sections) and lower values at Oglesby Road and Alcoa Highway (on-shelf localities).

Comparison of chemical values across a bryozoan-micrite boundstone reef exposed in the upper part of the Alcoa Highway section show little variation in any of the elements that can be directly attributed to the presence of the reef.

Some allochem and cement components were isolated and run as separate samples from the surrounding matrix. This was done to compare the homogenization or lack thereof, between components and matrix. Enrichment of the bryozoan allochems to matrix was less than two times. Radial spar-rich material showed very similar values to that of the matrix, while a drusy spar sample showed depletion of strontium, sodium and magnesium. The drusy spar sample was enriched in manganese and iron when compared to its matrix.

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I. INTRODUCTION

Purpose

The bulk of the work prior to about 1972 in the Middle and Upper Ordovician of East Tennessee concentrated on correlation of lithostratigraphic units between strike belts and the biostratigraphy of these various rock units.

In recent years, numerous theses, papers and reports have been written concerning the Ordovician. This work has been funded by the National Science Foundation and has been directed by K. R. Walker. Recent developments in carbonate petrology of the past 20 years have been applied to the Middle-Ordovician time-rock units, which have been examined with respect to the environments of deposition, migration through time of the environmental mosaic, and the associated paleoecology.

Since 1973, seven papers have concerned the Holston Formation. Ferrigno (1973), Ferrigno and Walker (1973a, 1973b), Walker and Ferrigno (1973), Moore and Walker (1974), Walker and Benedict (1980) and Walker (1980). Holston-like lithologies exist elsewhere within the Chickamauga group (Keith, 1895); the Meadow Marble within the Chapman Ridge Formation was studied by Sitterly (1976) and the Vestal Marble within the Ottosee Formation was examined by LaFollette (1974).

The present study concentrates on the Holston Formation with a four-fold purpose:

1. to record the relative sequence of diagenetic events, such as compaction, cementation, and deposition of internal sediment, in selected outcrops of the Holston Formation.

2. to describe the petrology of the various stages of cementation and factors that control the cement distribution, such as: substrate, allochem mineralogy, original pore size and pore water chemistry.
3. to study trace element distribution by means of staining techniques, cathodoluminescence petrography and atomic absorption analysis.
4. to integrate the data from 1, 2, and 3 for a better understanding of the history of development of Holston lithologies.

Area of Study

Much of East Tennessee falls within the physiographic province of the Valley and Ridge, a gently rolling terrain composed of a number of parallel northeast-southwest trending ridges and long narrow valleys. These repetitious strike belts are separated by numerous thrusts. The outcrops of Holston Formation studied by this author are located between the Knoxville Fault to the northwest and the Dumplin Valley Fault to the southeast (Figure 1.1). Detailed section localities are listed in Table 1.1. This area includes portions of the Knoxville (GQ115), John Sevier (GQ124) U.S. Geological Survey 7.5 minute geologic quadrangles and Boyds Creek geologic quadrangle (GM156-NW), State of Tennessee, Department of Conservation, Division of Geology.

These outcrops were chosen so as to examine the lateral variability of various diagenetic features such as cement types. All outcrops are well-exposed and are reasonably accessible. The outcrop at Oglesby Road had not been studied prior to this report. The Midway Road outcrop

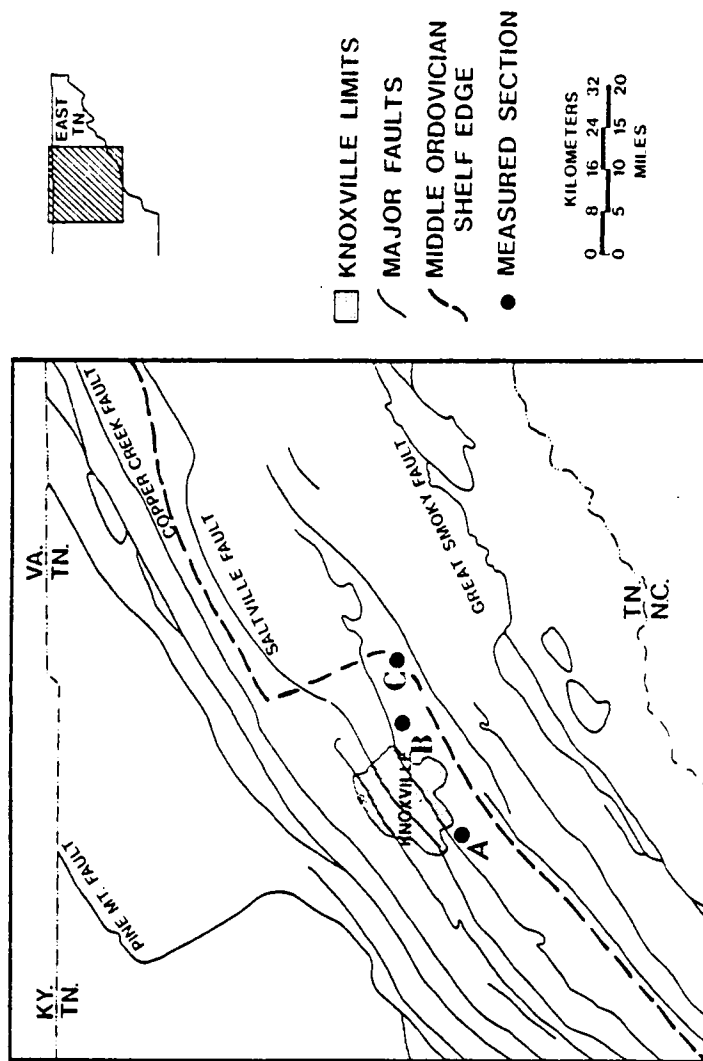


Figure 1.1. Generalized position of the shelf-edge and its relation to major faults in East Tennessee and to measured sections in the study area.

Position of the shelf-edge was determined by previous workers (e.g., Ratcliff, 1974; Ruppel, 1979; Walker and Ferrigno, 1973; and others) and is represented here on a nonpalinspastic base. (Modified after Breland, 1980.)

Table 1.1. List of localities.

Section	Location
A	Northwest part of Boyds Creek Quadrangle. Southern edge of road cut along entrance ramp to I-40 East from Midway Road, about 17 miles east of Knoxville.
B	South central part of John Sevier Quadrangle. The road cut along Hammer Road at the intersection of Oglesby Road. One mile east of Armstrong Island and parallel to and just north of I-40.
C	West central part of Knoxville Quadrangle. On Alcoa Highway 1½ miles south of John E. Karnes Bridge over Fort Loudon Lake in Knoxville.

was studied by Benedict (in prep.) and has been described by Benedict and Walker (1980). The Alcoa Highway section was studied by Ferrigno (1973), Ferrigno and Walker (1973a, 1973b), Walker and Ferrigno (1973) and Walker (1980).

Historical Perspective

The sequence of Middle Ordovician carbonates, sandstones and shales lying above the Knox Dolomite in the Valley and Ridge Province of East Tennessee was originally described by Safford (1869) and named the Trenton and Nashville Series. Within this sequence is the well-known Tennessee Marble, named for its ability to take a high polish and its strength as dimension stone. These marbles consist of white to grey and pink to red limestone. Safford distinguished between a lower red and grey marble and an upper red marble.

Keith (1895) named these units the Holston Marble for their occurrence along the Holston River within the Chickamauga Limestone. He noted that these beds occurred at several different stratigraphic levels in discontinuous fashion.

Ulrich (1911) assigned the Holston Marble to the Chazy Series and to the bottom of the Blount Group. Ulrich considered the Holston of various strike belts to have been deposited contemporaneously within several narrow troughs paralleling the sea.

Stose and Schrader (1923) noted the existence of manganese deposits at the contact of the Holston and Tellico Sandstone. They were probably the first investigators to recognize the two dominant lithologies of the Holston Formation, the "white Bryozoan reef in . . . calcareous mud rock" (plate XXVI, p. 116) and the "sandy beds [that]

fill a channel between white reefs of Bryozoa" (plate XXV, p. 116). Cross-bedding was also noted (p. 119).

Gordon (1924) limited his use of the term "Holston Marble" to those rocks overlying the Stones River group (Lenoir-Mosheim beds) and applied a separate name, the Vestal Limestone, to those lentils of Holston-like lithology occurring near the middle of the Ottosee shale. Gordon also recognized two lithologies, one which "appeared above the surface in the form of reefs, where they were broken up by the waves" (p. 29) and the calcarenites, being composed of bryozoa and crinoids. Gordon attributed the cross-bedding to "sea currents" (p. 29).

Dale (1924) was the first to study the petrologic characteristics of the Holston in thin section, although he concentrated on the stylolites. Cooper (1956) reassigned the Red Knobs Formation (= Holston and Chapman Ridge) to Upper Porterfieldian Stage (= Lower Caradocian Series of Welsh type Ordovician) based on brachiopods. Based on correlation of ectoprocts with assemblages from Minnesota and Alabama, Ferrigno (1973) interpreted the age of the Holston as Middle to Upper Wilderness, a younger age assignment than Chazy (see Ferrigno, 1973, pp. 26-34). Bergstrom (1971) has dated the lower Holston as Lower Porterfieldian age based on conodonts.

II. METHODS

Petrography

Three outcrops were measured and 140 hand samples were collected and their positions noted in stratigraphic sections. Duplicate lithologies were eliminated and about 90 thin sections were chosen for closer examination. Thirty-seven thin sections were point-counted; percentage composition was compiled from an average of 300 points on each thin section (see Appendix A). Fifty samples were dissolved in 25% volume/volume acetic acid; the dried insoluble residue was weighed and subtracted from the total weight of the sample. The insoluble residues were not examined by this writer any further. Previous workers, Ayrs (1933) and Metcalf (1974) have described the composition of the insoluble residue (see Appendix B).

Definition and Recognition of Grain and Cement Categories

Echinoderms are prolific producers of sediment of all shapes and sizes. Each echinoderm piece is a single crystal of calcite exhibiting unit extinction. Occasionally several pieces or ossicles may be found articulated, in which case each ossicle exhibits a separate extinction. Microscopic pores and canals are sometimes filled with mud or are iron stained. This porous network is invisible otherwise, due to later growth of syntaxial cement (or echinoderm syntaxial cement or overgrowth) which fills in the network. In this group, the mud filling or iron stain was tabulated as skeletal material.

Bryozoans, both intact and fragmented, were tabulated as one group. There was no further division into bifoliate, non-bifoliate or

encrusting forms. Cements or micrite occurring within the zooecia were counted separately from the bryozoan whenever possible.

Other fossils (intact and fragments) comprised a small fraction of each thin section (usually less than 10%). This group may be divided into two subgroups. The first includes brachiopods, ostracods and trilobites. The skeletons of these (plus echinoderms) were probably stabilized from high-magnesium calcite (HMC) to low-magnesium calcite (LMC) due to solid-state diffusion (Folk, 1965), which did not change the microarchitecture. These taxa usually do not exhibit solution-reprecipitation, which would involve an open void space and later precipitation of a cement, usually drusy spar, drastically changing texture and destroying microarchitecture.

The second subgroup of fossils, gastropods, pelecypods and cephalopods, often have an original mineralogy of aragonite, a metastable polymorph of calcite. The aragonite is usually dissolved, forming a void (this assumes the surrounding material is lithified) into which drusy spar later precipitates. In the point count process, the in-filling cement was counted, not the original fossil allochem type.

Internal sediment includes micrite and silt-size material. Investigations by Ferrigno (1973) showed that the micrite of the Holston appeared to have had its origins as skeletal debris similar to Honduran lime muds (Matthews, 1966) rather than aragonite needles produced by disintegration of calcareous green algae as proposed for Bahamian muds by Lowenstam (1956) and Purdy (1963). Holston micrite appears as an opaque, iron-stained sediment commonly containing fine fossil hash. These numerous skeletal fragments were generally unidentifiable.

Internal carbonate silt is restricted in size to 10-25 microns (Bathurst, 1975). It is located in "sheltered" areas, such as cavities formed inside of shells of brachiopods, ostracods and stromatactis structures (the latter of problematical origins). According to Bathurst (1975), crystal silts always overlies early cement and underlies a later generation of cement, thus indicating their movement into the void at an intermediate stage of cementation. There are often alternating layers of crystal silt and cement. Dunham's (1969) description of crystal silt also noted that there was frequently cross-lamination and an uneven upper surface. He postulated that these uniform size silts were of external origin and were emplaced by near-surface waters, hence his term vadose silts. This silt may also be observed in a "perched" position on top of various allochems, or infilling allochems in a "geopetal" position.

James et al. (1979) have noted the existence of similar geopetal structures in Holocene-age reefs but offered a different explanation for their location. According to them, much of the fine-grained sediment consisted of chips produced by endolithic sponges and other organisms. It was produced while the sediment was still in the marine environment.

Intraclasts consist of micrite and are of two types, one with well-defined sharp boundaries and the other with slightly curled or ragged edges, as if composed of soft sediment when formed. These intraclasts are most likely derived from penecontemporaneous erosion and redeposition of nearby sediment. Two source areas are possible: the back-reef, lagoonal facies (Lenoir Formation), or nearby bryozoan-micrite reefs.

Cement includes "all passively precipitated, space-filling carbonate crystals which grow attached to a free surface" (Bathurst, 1975). Cement that occurred either in an intergranular or intragranular position (such as bryozoan zooecia or within brachiopod shells) was point counted as to specific type (as discussed below). Note that this is not the standard convention, which is to count as "fossil allochem" all intragranular voids within, for example, a bryozoan. Cement is divided into the following six categories. A list of equivalent terms for the various cements is provided in Appendix E.

First, drusy spar has a length/width ratio averaging less than $1\frac{1}{2}:1$ (Folk, 1965) and characteristics elaborated by Bathurst (1975). It can be recognized by its increasing crystal size away from the substrate surface and plane interfaces between the crystals. A triple junction is the meeting point of three crystals; enfacial junctions occur at a triple junction where one of the angles is 180° . Drusy spar exhibits a high percentage of enfacial junctions among the triple junctions, 30-70% as compared to 2-5% enfacial junctions between the crystals of neomorphic spar (Bathurst, 1975). The presence of two generations of cement and enfacial junctions is good evidence for identifying cement as opposed to neomorphic spar.

The second cement type, syntaxial overgrowths (or syntaxial cements) on the single crystal echinoderm ossicles were abundant, although sometimes difficult to separate from the host echinoderm. Frequently there was a color or inclusion difference between the echinoderm and its overgrowth. This overgrowth is in optical or lattice continuity with the echinoderm fragment--an extension outward of a single crystal as well as penetrating the porous nucleus (Sorby,

1879; Folk, 1965; Bathurst, 1975; Evamy and Shearman, 1969). The extensive development of syntaxial overgrowths on echinoderms has resulted in an impermeable texture and great strength, hence the name Holston "Marble" (Ferrigno and Walker, 1973b). No metamorphic processes have affected this unit.

Syntaxial overgrowths are not limited to echinoderm debris (although they are most extensively developed on those allochems) but are also found on such fossil allochems as trilobites, ostracods and brachiopods. The shells of these organisms are polycrystalline, resulting in a polycrystalline fringing overgrowth. In this thesis, polycrystalline fringing overgrowths will be referred to as fringe or fringing cement.

This fringe or fringing cement is the third type, with a typical morphology of bladed (length:width ratio between $1\frac{1}{2}:1$ and $6:1$, Folk, 1965). The crystal may become extinct along with the host substrate. Fringe cement may also be fibrous--a length:width ratio greater than $6:1$ (Folk, 1965). Fringe cement that does not go to extinction with the host substrate is common on bryozoans and molds of gastropods.

The fourth type, neomorphic spar, is a general term that includes "all transformations between one mineral and itself or a polymorph . . . whether the new crystals are larger or smaller or simply differ in shape from the previous ones. It does not include simple pore-space filling; older crystals must have gradually been consumed and their place simultaneously occupied by new crystals of the same mineral or a polymorph" (Folk, 1965). The use of the term "neomorphism" was intended as a general term, to refer to any "change in form with composition

remaining constant--original polymorphous phase not known" (Folk, 1965). This type of cement is extremely rare within the Holston and is not discussed further, except under the section "Neomorphic Processes" of Chapter III.

The fifth cement type, radiaxial spar or radiaxial fibrous mosaic, refers to elongate crystals (length:width ratio up to 7:1, Bathurst, 1975) that have a preferred orientation normal to the substrate. This crystal is usually composed of several sub-crystals that diverge away from the substrate with the result that the twinning pattern is curved with concave surfaces facing away from the substrate (Bathurst, 1975).

Commonly, radiaxial spar passes into a second generation of cement, usually blocky or equant drusy sparite. The extinction will change from undulose extinction within the radiaxial spar to uniform extinction within the blocky drusy sparite (Bathurst, 1975). When viewed in plane polarized light, there is a corresponding change from honey colored radiaxial spar to clear drusy sparite (Bathurst, 1975). Kendall and Tucker (1973) also noted changes in the inclusion density, which was usually abundant within the radiaxial spar and little to none within the drusy sparite. A secondary characteristic of radiaxial spar is that it commonly forms isopachous rims around the allochems with polygonal boundaries formed by the intersection of the isopachous radiaxial cement (Longman, 1980).

A sixth type of cement, micritic cement, formed in the intra-granular pore spaces of such allochems as echinoderm fragments. Due to its extremely small size, it was impossible to point count this type of cement. It can be recognized as the almost dust-like material that does not share the extinction of the echinoderm and its associated overgrowth.

Microspar is rarely seen within the thin sections. It is greater than 4 microns in crystal size and grades into pseudospar, which is greater than 30 microns. Rhombs of dolomite compose up to approximately 3% of some slides. Baroque dolomite is recognized by its rhombohedral outline and undulose extinction. The smaller rhombs are often iron-stained around the edges. Cryptocrystalline dolomite may be differentiated by staining the slide with Alizarin Red. Dolomite commonly replaces echinoderm fragments.

Staining

A combination stain consisting of Alizarin Red S and potassium ferrocyanide (Lindholm, 1972) was applied to approximately one-fourth of the surface area of each thin section. This was in order to identify dolomite and to examine petrographic relationships between calcite containing little or no iron and calcite containing some concentration of iron.

Classification Schemes

Dunham's classification system (1962) was used in naming rocks. Following the terminology of Nelson et al. (1962), "reefs" refers to a "skeletal deposit formed by an organism possessing the ecological potential to erect a rigid topographic structure." "Bank" is defined as "skeletal deposit formed by organisms which do not have the ecologic potential to erect a rigid wave-resistant structure."

The terms bioherm and biostrome refer to the shape of skeletal deposits. Thus bioherm includes ". . . a reef, bank, mound; . . . of strictly organic origin, embedded in rocks of different lithology." Biostrome refers to "purely bedded structures . . . and not swelling

into mound-like or lens-like forms." Nelson et al. limited the use of these terms to refer to the shape within the stratigraphic sequence and not to the original environment of deposition. According to this terminology, the bryozoan boundstones of the Holston are biohermal reefs.

Cathodoluminescence

The Holston cements examined always exhibit yellow-orange to red-orange luminescence, alternating with dark bands. Other workers (Smith and Stenstrom, 1965; Sippel and Glover, 1965) have shown that bright luminescence is due to the presence of Mn^{+2} "activator" ions and the dark banding is due to the "quenching" effects of Fe^{+2} . This may be true for the Holston as well. Cathodoluminesce photographs are examined within the sequence of photographs and text of Chapter III.

Atomic Absorption Spectrophotometry

Five trace elements were analyzed by this method. These are elements with less than 0.1% concentration (1000 ppm), although in some cases, concentrations exceeded this mark. Trace elements that were run for analysis were iron, sodium, strontium, manganese and magnesium. The geologic information sought from them is discussed in detail under individual element headings in Chapter IV, Trace Element Distribution. Preparation procedures are in Appendix C.

III. PETROGRAPHY

Introduction

The Holston Formation was chosen as an appropriate stratigraphic unit in which to study the diagenetic processes of cementation and compaction. The grainstones of the Holston appear to have been loosely packed and porous at time of deposition. This factor, combined with a well-oxidized, agitated marine environment, allowed the cementation to proceed rapidly within the marine sphere and the cement crystals to precipitate and grow on a scale that is easily visible at a microscopic level. Early cementation also had an inverse relationship to compaction. The ideal or hypothetical relationship is shown in Figure 3.1. The position of the Holston samples is indicated on the diagram. Such early lithification holds the allochems in place and minimizes or prevents breakage. The longer the cementation process is delayed, the more the addition of overburden promotes the breakage of allochems due to compaction. However, the reader should note that breakage may occur in a pre-burial state, that is, at the water-sediment interface. Examples of processes which might cause preburial breakage are storms or agitation by organisms. This case is excluded from breakage or mechanical compaction as recognized in this study. Breakage or mechanical compaction occurs after burial and is observed in thin section as both parts of an allochem exhibiting visible parting or rotation with respect to each other.

The process of cementation within the Holston Formation resulted in two broad generations of spar, marine and meteoric. In

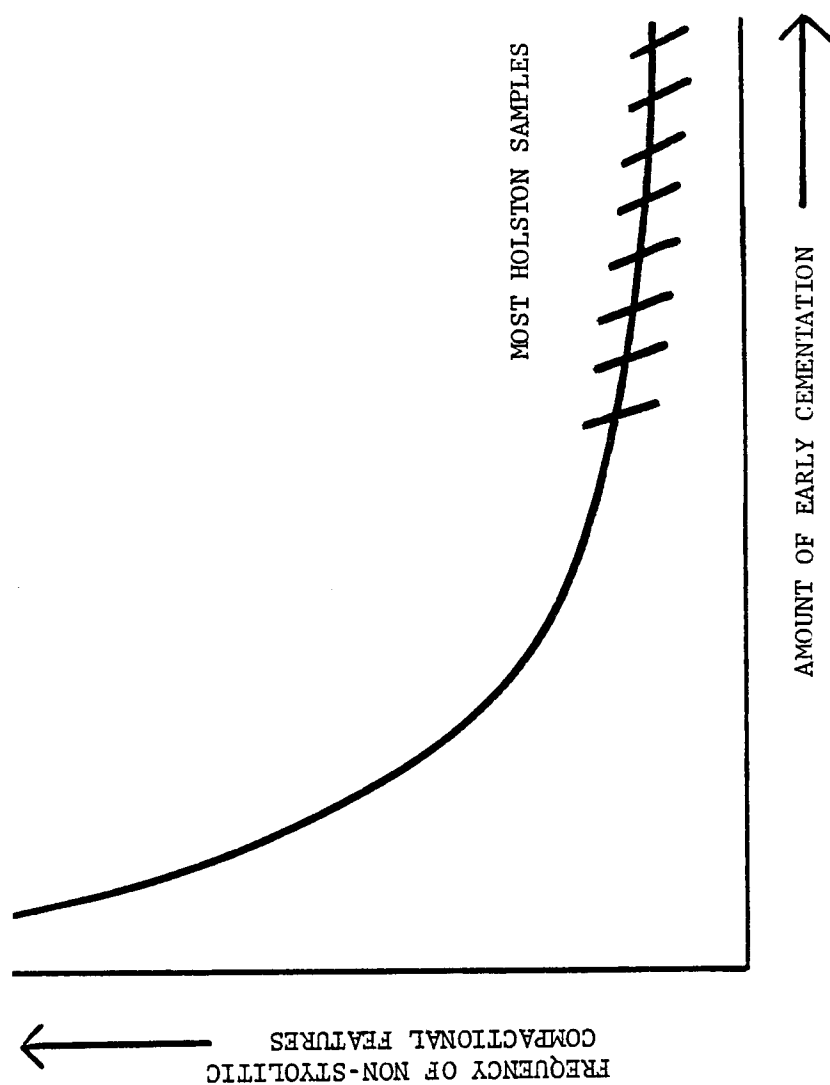


Figure 3.1. Hypothetical relationship between non-stylolitic compactional features and the amount of early cementation. As detailed in the part of this thesis on petrographic relationships, compactional features are uncommon in the Holston, whereas early cements are abundant. Thus, most Holston samples of this study would fall in the cross-hatched area.

general, the marine, non-ferroan phase consists of fringe, radiaxial cement (strictly speaking, its likely radial-fibrous predecessor) and echinoderm syntaxial overgrowths. Meteoric cement consists of drusy sparite.

In the late 1960's and early 1970's, submarine lithification had been observed in Recent sediments and recognized as an active process. These observations have provided an analogy for the interpretation of cementation in ancient carbonate rocks.

Shinn (1969) found that large areas of Recent sediment were lithified by submarine cement in the Persian Gulf. Aragonite cement predominated in sand-sized sediment as two (often gradational) forms: 1) loosely packed acicular needles perpendicular to the grains and 2) tightly packed fibrous cement. High-magnesium cements (no morphology is implied) were commonly observed in lithified muds as well as internal sediment. Shinn further noted that various forms of recrystallization may take place while still in a marine environment. Physical factors that appeared to be necessary for such cementation are relatively normal salinity and temperatures, relatively low rates of sedimentation, sediment stability and high initial permeability of the sediments.

Shinn (1969) found layers of cemented, sand-sized sediments up to 15 centimeters thick that were underlain by soft, uncemented layers. Uncemented layers were probably due to the progressive growth of the cement in the overlying, near-surface horizon. This reduced water circulation and stopped precipitation of cement at depths below 15 centimeters. A high rate of sedimentation also reduced circulation

and, if the rate of sedimentation was high enough, may have prevented water circulation totally. Thus growth of cement was blocked.

Friedman et al. (1974) documented submarine cementation in reefs of the Red Sea. Cement precipitation occurred within a few centimeters below the surface of reef corals, and within 60 centimeters depth, porosity was generally occluded by the cement. The aragonite had a rod or needle-like appearance (up to 50 microns) or grew syntaxially on aragonitic coral, while micritic cement was of high-magnesium calcite.

James et al. (1976) investigated the Belize barrier and atoll reefs and associated sediments. They found sporadic cementation was most common in areas where large volumes of seawater were pumped through the pore network and the sediments were well-oxidized. The carbonate sediments exhibited either intragranular or intergranular cementation. The sediments of the platform interior (behind the barrier reef and atoll reef) were the site of reducing conditions. The sediments there were not cemented.

James et al. (1976) found that cement character was in part controlled by pore size and type of cement. First, silt-sized grains were cemented by high-magnesium calcite micrite. Mixed lime sands and silts were then cemented by "thin rinds of micrite that grade outward into bladed spar." Grainstones with interstices greater than 50 microns were the last to be cemented and exhibit red fringes of high-magnesium calcite bladed spar. There was no evidence that substrate mineralogy controlled cement mineralogy.

James et al. (1976) and James and Ginsburg (1979) described marine cementation in Belize sediments as an episodic event, with silt-sized internal sediment trickling into voids at the same time cementation

was taking place. Internal sediment was produced as a by-product of the boring activity of various organisms, such as sponges, bivalves, endolithic algae and fish, among others.

Ginsburg and James (1976) observed botryoidal aragonite that rims and fills a variety of cavities in Holocene reef-wall limestone of Belize. The aragonite is of marine origin, based on similarity of ages between the host and the cement. Average strontium values, as well as oxygen and carbon isotopes, all indicate marine lithification. Benthic foraminifera and/or internal laminations of silt may be found within the botryoidal aragonite. These botryoids may be found on substrates of aragonite and high-magnesium calcite, again implying no substrate control of the mineralogy of the cement.

Various workers have also recognized marine cements in ancient rocks but their observations differ somewhat, as do the explanations of how the cement has been changed through diagenetic processes.

Purser (1969) described marine cements in Middle Jurassic limestones in the Paris Basin as consisting of short, closely packed fibrous druse with most crystals the same length and adjacent crystals in contact through most of their length. There is also a fibrous druse composed of individual acicular crystals which are not in contact with adjacent crystals, except near their bases.

Kendall and Tucker (1973) consider whether radiaxial cement originates as a primary cement or as a replacement mosaic. Their interpretation requires an earlier predecessor of radial-fibrous cement but they do not speculate further on mineralogy or origin of the predecessor. Replacement occurs through the process of microscale solution and reprecipitation.

Mazzullo and Cys (1979) described aragonite botryoid formation in phylloid algal mounds of Permian age. These structures are presently composed of calcite. The original aragonite is believed to have paramorphically inverted to calcite and then recrystallized to divergent radial mosaics of pseudospar, all upon exposure to freshwater. Thus this fabric has undergone several diagenetic processes, which have altered the original marine cement.

Overview of the Holston Cements

The exact sequence of cements and compactional features within the Holston Formation depends on the initial event during and after burial, cementation, mechanical compaction or boring-micritization. The sequences of events are summarized in three diagrams (Figures 3.2, 3.8 and 3.9). There is no relative sequence among these three initial conditions, since they may all take place concurrently in different areas of the sediment, often just a few centimeters or less from each other. A variety of events may subsequently take place, even within the marine environment.

Case 1: intact allochem with initial cementation. Figure 3.2 illustrates the possible paths an unbroken allochem may follow during diagenesis. The initial cement type is micritic cement filling in the very small pores of such allochems as echinoderm fragments. A modern analogy of high-magnesium micritic cement is provided by James and Ginsburg (1976, 1979) who, upon examination of Belize reefs and associated sediments, found this type of cement to be the earliest of any cement morphology and common only to pores less than 15 microns in size.

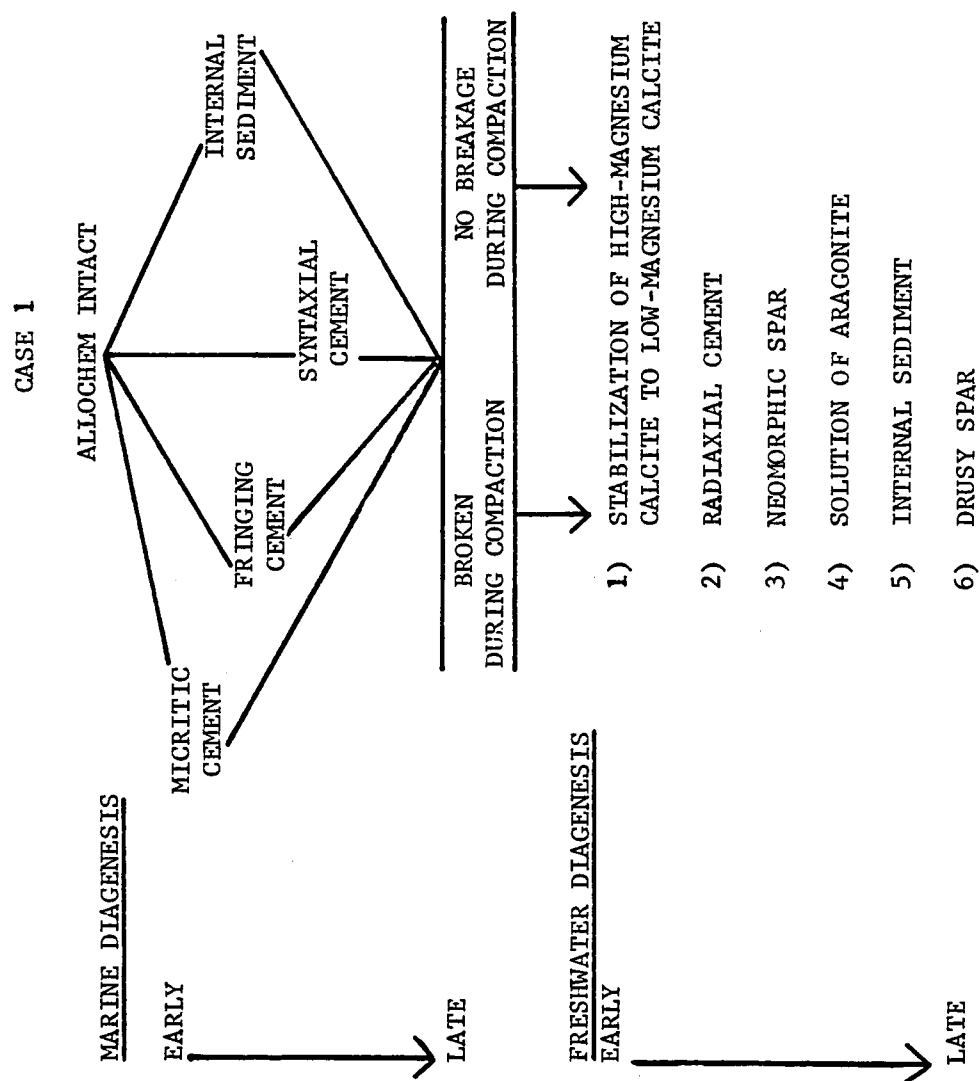


Figure 3.2. Paragenesis of an allochem that is intact.

Small cement crystals (fringe cement) have been observed within the Holston samples to have grown on the echinoderm grains and then to have been later engulfed by the echinoderm syntaxial overgrowth. In Figure 3.3A, an echinoderm grain is at extinction, as is the associated syntaxial overgrowth. The fringe cement that has grown on the echinoderm grain is not at extinction. Fringe cement is also visible on a trilobite fragment.

Fringe cement on the trilobite fragment most likely overlaps in time with the echinoderm syntaxial overgrowth. The fringe cement on the echinoderm is probably very early.

Fringe cement may have either syntaxial (cement goes extinct along with the host substrate) or non-syntaxial extinction (cement extinction is not related to that of the substrate). The former is common on allochems such as brachiopods, ostracods and trilobites. The non-syntaxial fringe cement is common on bryozoans and micrite casts of gastropods. Fringe cements may form either a continuous or discontinuous series of crystals that exhibit an acicular morphology and pointed terminations. Examples of fringe cements with syntaxial extinction appearing on a variety of allochems are illustrated in Figures 3.3A-H.

Fringe cement does not luminesce, thus appearing black. It is occasionally topped by a thin band or zone that brightly luminesces. Figures 3.4A-D illustrate an isopachous rim of fringing cement surrounding bryozoans.

Internal sediment in the form of micrite or silt may have filtered through the pore spaces, blocking the growth of fringing cements as well as other cement types. Internal sediment may be observed in two

Figure 3.3. Features observed in thin sections of the Holston Formation.

A. Trilobite fragment with fringe cement. Both grain and syntaxial overgrowth are at extinction. Note several fringe crystals on echinoderm grain (within box) that are not at extinction. Crossed-nicols. Bar scale is 1 mm. Midway Road section. M-4.

B. Detail of A. Neither the fringe cement nor the trilobite fragment substrate is at extinction. Fringe crystals on the echinoderm grain are visible (center of photograph) and have different extinction than the echinoderm grain and associated overgrowth. Crossed-nicols. Bar scale is 0.1 mm. Midway Road section. M-4.

C. Bryozoan (upper right corner) acting as a substrate for fringing cement (center). Plane light. Bar scale is 1 mm. Oglesby Road section. O-a-16.

D. Fringe cement on trilobite fragment (center). Note perched internal sediment on top of and within the doublure of the trilobite fragment. Plane light. Bar scale is 1 mm. Alcoa Highway section. A-151.

E. Fringe cement on unidentified fossil fragment (center). Note micrite caught in geopetal position in the lower part of the valve. Plane light. Bar scale is 1 mm. Alcoa Highway section. A-151.

F. Fringe cement on unidentified fossil fragment (center). Plane light. Bar scale is 1 mm. Oglesby Road section. C-o-11.

G. Fringe cement at extinction with the host trilobite fragment (upper center to lower right corner). Crossed-nicols. Bar scale is 1 mm. Oglesby Road section. O-a-21.

H. Trilobite fragment with fringe cement (upper center). Echinoderm syntaxial cement at extinction (upper right corner). Crossed-nicols. Bar scale is 1 mm. Midway Road section. M-4.

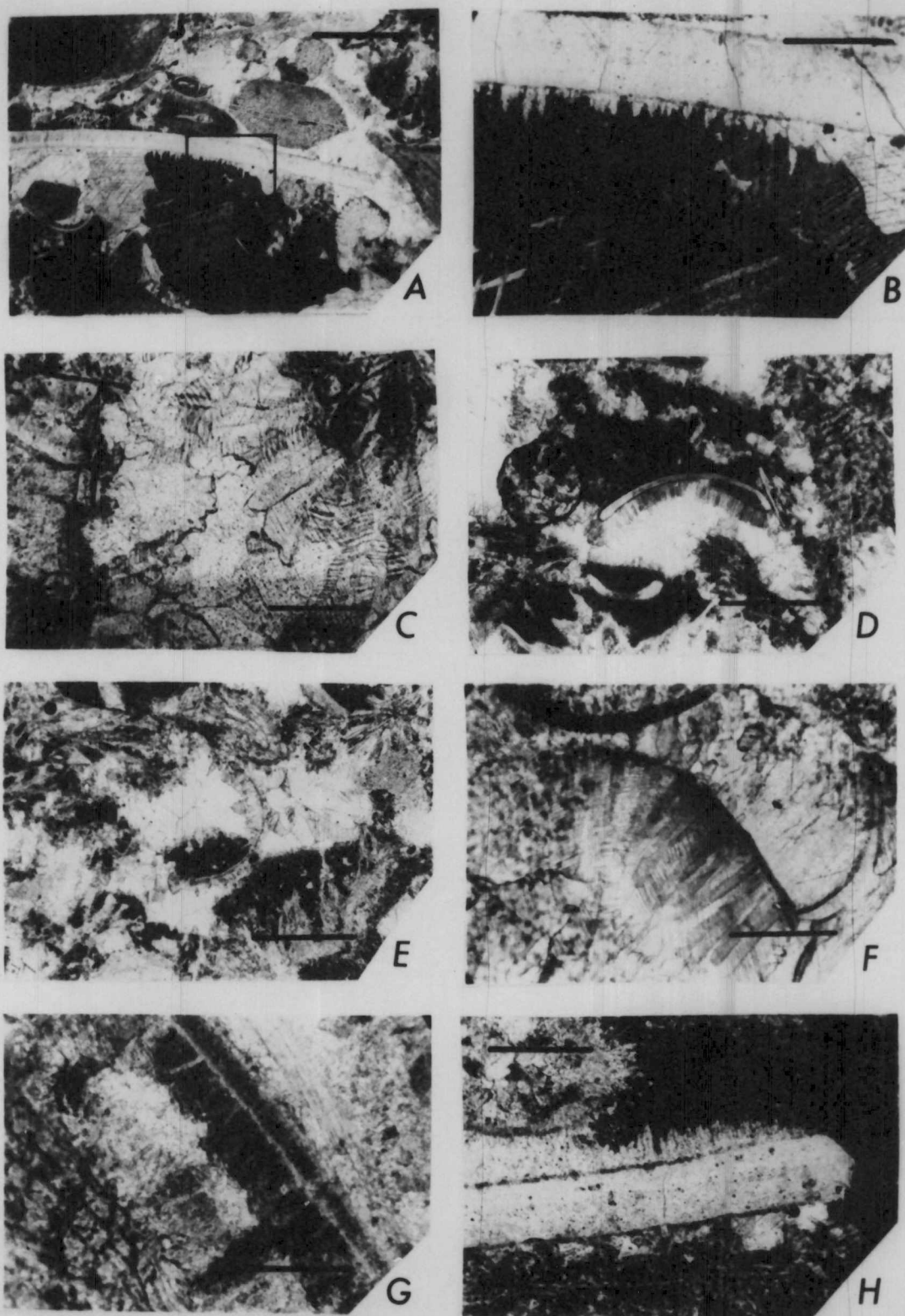


Figure 3.3

Figure 3.4. Features observed in thin sections of the Holston Formation.

A. Bryozoans (center and left side of photograph) surrounded by indistinct fringe cement. Plane light. Bar scale is 1 mm. Alcoa Highway section. A-151.

B. Bryozoans as in A but with cathodoluminescence. Fringe cement forms an isopachous, dark, non-luminescent rim around the bryozoan. Light colored area in upper right is drusy sparite. Bar scale is 1 mm. Alcoa Highway section. A-151.

C. Bryozoan (center) surrounded by indistinct fringe cement. Plane light. Bar scale is 1 mm. Alcoa Highway section. A-151.

D. Same bryozoan as in C but with cathodoluminescence. Another bryozoan is seen distinctly to the left of the bryozoan in the center. Fringe cement forms an isopachous dark, non-luminescent rim around the bryozoans. Light colored area in the lower left is drusy sparite. Bar scale is 1 mm. Alcoa Highway section. A-151.

E. Brachiopod shell partly filled with internal sediment in a geopetal position. Drusy sparite has filled the rest of the pore. Plane light. Bar scale is 1 mm. Alcoa Highway section. A-157.

F. Curved echinoderm grain and its syntaxial overgrowth (arrows). Round micrite cast of gastropod just above echinoderm fragment is nearly surrounded by the syntaxial cement. Plane light. Bar scale is 1 mm. Midway Road section. M-3.

G. Same area as in F but at extinction. Note echinoderm syntaxial cement (arrows) nearly surrounds the micrite cast. Other areas at extinction are coincidental. Cross-nicols. Bar scale is 1 mm. Midway Road section. M-3.

H. Echinoderm grain and syntaxial overgrowth at extinction. Note the pore-filling characteristics of the syntaxial cement. Cross-nicols. Bar scale is 1 mm. Alcoa Highway section. A-154.

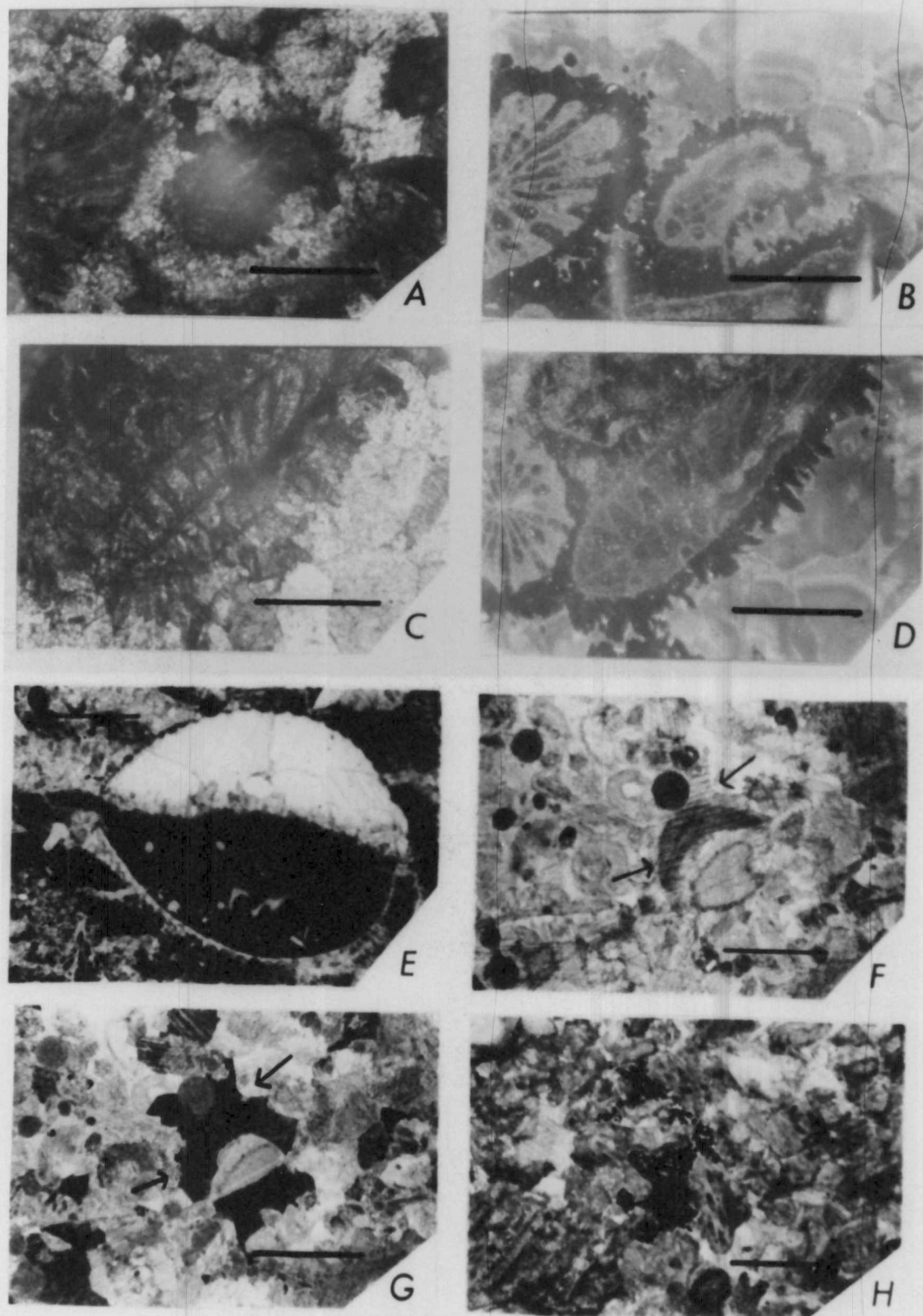


Figure 3.4

positions, either "perched" on top of allochems or in a geopetal position infilling an allochem, such as a brachiopod. Figure 3.3D illustrates micrite caught in the trilobite fragment (center) with fringe cement (exhibiting syntaxial extinction) growing on the "protected" portion of the trilobite fragment. Internal sediment in the form of a geopetal filling is illustrated in Figure 3.4E. Drusy spar has grown later within the cavity.

Echinoderm syntaxial cements or overgrowths probably grew coevally or overlapped in time with fringing cements. Echinoderm syntaxial overgrowths are a very common cementing agent which develops on a monocrystalline substrate (Folk, 1965). Fringe cements that have formed on a polycrystalline substrate as a series of acicular crystals are described and illustrated as "fringe cements". Echinoderm grains are the best known and most common example bearing syntaxial overgrowths which are in optical continuity with the monocrystalline substrate.

Echinoderm ossicles are extremely porous and are often randomly filled with either a finely crystalline micrite that has infiltrated the ossicles from external sources or was a very early high-magnesium calcite micritic cement. Although iron oxide often stains bryozoans, micrite and occasionally other allochems, it very often outlines the network of porous canals within the echinoderm grains. These oxides are probably due to oxidizing conditions in seawater at the time of sediment burial (observed in the Recent by James and Ginsburg, 1979). This infiltration of micrite or alternatively, precipitation of cements, and the precipitation of oxides does not appear to have had

an inhibiting effect on growth of syntaxial cements unless the micrite completely covered the ossicle surface.

Syntaxial overgrowths are generally limited to the area immediately around the ossicle but in Figure 3.4F, the syntaxial overgrowth of the large curved plate in the center of the photograph exhibits a nearly poikilitic distribution, almost enclosing a nearby micrite cast of a gastropod (Figure 3.4G). Figure 3.4H contains an echinoderm fragment in the center of the photograph. The associated overgrowth has spread out to fill empty pore space, traceable for some distance from the echinoderm grain. Both examples must have grown very early in the diagenetic history to fill pore space in this fashion.

In some cases, the echinoderm syntaxial overgrowth appears to have acted as a substrate for radiaxial cement to precipitate, with a sharp boundary generally appearing between the syntaxial overgrowth and the radiaxial cement (as in Figure 3.5A). Occasionally the boundary between the echinoderm syntaxial overgrowth and radiaxial cement appears gradational, as in Figure 3.5B. This occurrence of radiaxial cement may occur between echinoderms, where the radiaxial cement meets in a typical medial line (Figures 3.5C-E). Figure 3.5F illustrates an occurrence between echinoderms and bryozoans.

Other workers have noticed an unusual variation of syntaxial overgrowths surrounding echinoderm grains. Meyers (1974) observed that within Mississippian-age rocks that "cloudy cement coating crinoids often has multiple or wavy extinction, indicating that it is not a simple single crystal syntaxial overgrowth" (p. 840) and "bladed cloudy cements do occur on crinoids in bioherms" (p. 855). Cotter (1966) made similar observations of Mississippian-age rocks

Figure 3.5. Features observed in thin sections of the Holston Formation.

A. Echinoderm grain with syntaxial overgrowth (center). A sharp boundary divides the syntaxial overgrowth from the superadjacent radiaxial-like cement. Crossed-nicols. Bar scale is 1 mm. Midway Road. M-1.

B. Echinoderm grain and syntaxial overgrowth which grades into radiaxial cement (center). Note typical curved medial line formed between radiaxial cements from different substrates (center). Plane light. Bar scale is 1 mm. Alcoa Highway. A-70.

C. Three echinoderm grains and syntaxial overgrowths, all of which have radiaxial cement around the edges (center). A typical curved medial line separates the radiaxial cement that has grown out from individual allochems. Crossed-nicols. Bar scale is 1 mm. Midway Road. M-1.

D. Several echinoderms with syntaxial cement and bryozoan in lower left corner. Radiaxial cement partly rims the edges of echinoderm grains and the bryozoans, resulting in a medial line (center to lower left). Crossed-nicols. Midway Road. M-6-a.

E. Detail of extinction varying across syntaxial overgrowth that grades into radiaxial cement along the edge of the overgrowth. Twinning lines are slightly warped across the radiaxial cement (arrow). Crossed-nicols. Bar scale is 0.1 mm. Midway Road. M-1.

F. Echinoderm grain with syntaxial cement at extinction (center). Radiaxial cement along the edge of the overgrowth forms a medial line with radiaxial cement that has grown out from the bryozoan to left of center. Crossed-nicols. Bar scale is 1 mm. Oglesby Road. O-b-14.

G. Echinoderm grain with syntaxial overgrowth at extinction, lower left of center. The overgrowth has blocked growth of radiaxial cement along the edge of a brachiopod fragment in the center. Crossed-nicols. Bar scale is 1 mm. Oglesby Road. O-a-21.

H. Bryozoan with radiaxial cement (center to right lower corner). Echinoderm grain with syntaxial cement (center) has blocked growth of radiaxial cement along the edge of the bryozoan. Crossed-nicols. Bar scale is 1 mm. Midway Road. M-6-a.

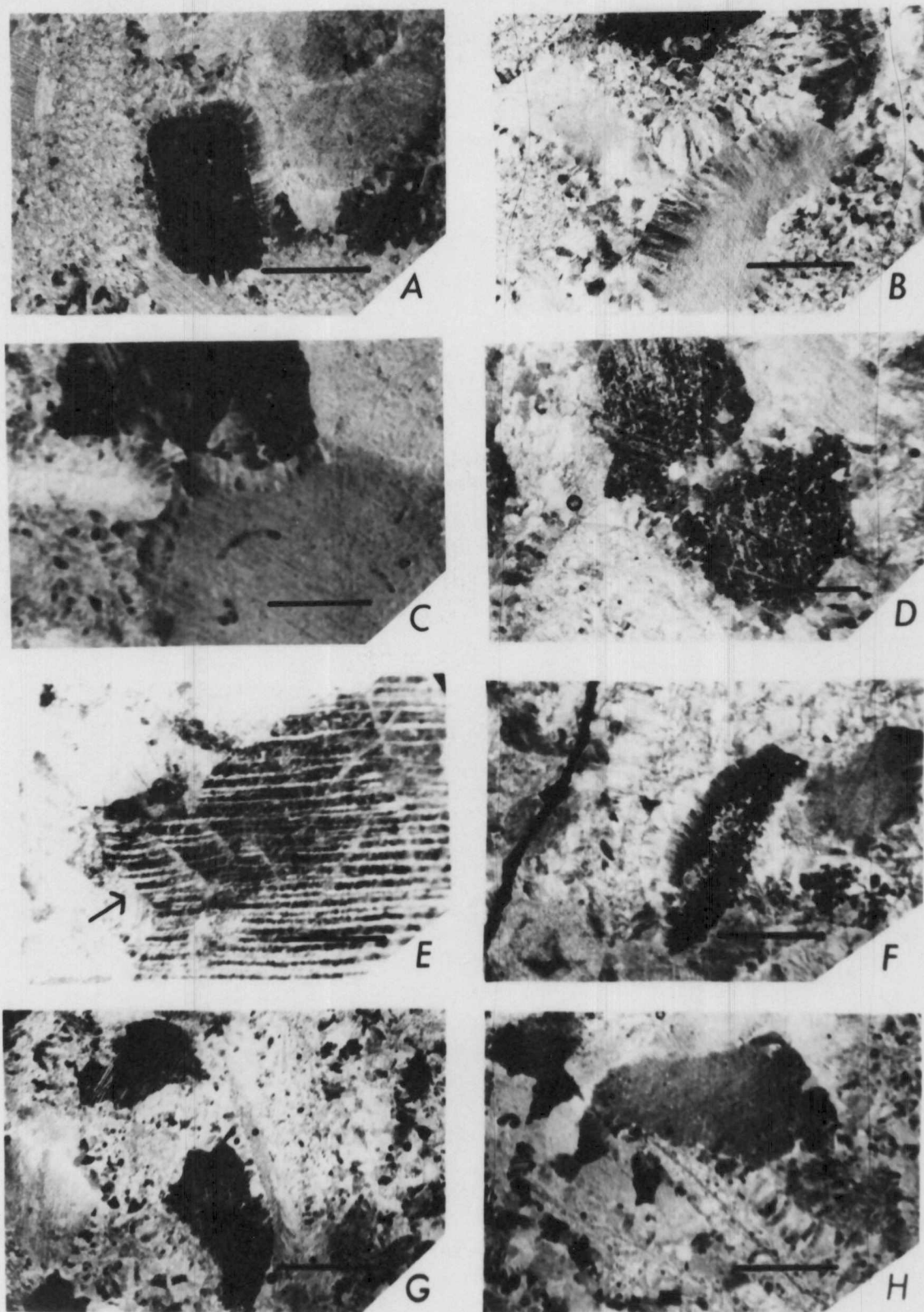


Figure 3.5

where "crinoid surfaces have radiaxial fibrous overgrowths . . . the fibrous mosaic was precipitated as an overgrowth on crinoids that formed part of a primary cavity" (p. 139). All these references are considered "radiaxial cement" in this thesis.

Longman (1980) in his summary of carbonate diagenetic textures, suggested that fibrous cement coating non-micritized echinoderm fragments implied marine cementation. Fibrous cements have been found precipitating only in a marine environment and never in a freshwater environment. Echinoderm syntaxial overgrowths, on the other hand, were believed to be suggestive of freshwater origins, according to Longman (1980). Within the Holston studied by this author, echinoderm syntaxial overgrowths are most likely of marine origin. The present author is not sure how the fibrous cements referred to by Longman (1980) fit into the present categories of cement listed in this thesis.

Purser (1969) assigned a marine origin to echinoderm overgrowths found in Middle Jurassic rocks because the overgrowths had been truncated by later borings, also of marine origin.

Meyers (1974) described echinoderm syntaxial overgrowths with characteristics similar to those found within the Holston. The clarity of the overgrowth varies from clear to cloudy; the overgrowths often engulf nearby allochems and the overgrowths "appear to have outgrown most other cement types, with only prism fringes having been competition for them". The prism fringes of Meyer are considered "fringe cement" in this present work. A marine origin is assigned to the cloudy echinoderm syntaxial overgrowths and the prism fringes in Meyer's work. Meyer (1974) assigned a meteoric origin to the clear echinoderm syntaxial overgrowths.

Holston fringe and syntaxial cements were of marine, early diagenetic origin, since they are the first or earliest cement to be observed on many allochems. It appears improbable that fringe cement could have "displaced" or "intruded" into the echinoderm syntaxial overgrowth, since this would require additional energy for the crystal to expend on growth. In some cases, echinoderm syntaxial cement appears to have limited or inhibited growth of fringe cement on other allochems (see Figure 3.3H).

Echinoderm syntaxial cement and radiaxial cement (more specifically, a probable radial-fibrous predecessor) appear to have grown coevally, although in individual cases, the radiaxial cement may have grown before the syntaxial cement. Figure 3.5H shows a brachiopod valve with radiaxial cement along the left center part of the valve, then the radiaxial cement dies out rather abruptly and echinoderm syntaxial cement grows up to the surface of the brachiopod. Figure 3.5H also illustrates the coeval nature of the two cement types. Radiaxial cement has coated the bryozoan (lower right corner extending to the center) and then becomes shorter just before dying out completely. Echinoderm syntaxial cement from the adjacent echinoderm grain has grown up to the bryozoan surface. While both cements are coeval, there may have been a difference in growth rate due to the surface of nucleation. Folk (1965) suggested a monocrystalline substrate, such as in echinoderm fragments, represents a more favorable crystal lattice for cement to grow on, and therefore grows at a faster rate than fringe cements on a polycrystalline substrate.

Echinoderm syntaxial overgrowths in the Holston are believed to be of marine origin due to their cloudiness and relationships with

radial and fringing cements. Commonly, echinoderm syntaxial cements (usually from adjacent grains) appear to have surrounded the fringe, thus blocking further growth of the fringe, as in Figure 3.3H.

Radial cement or more correctly, a probable radial-fibrous predecessor, is found preferentially upon bryozoans as a substrate. A "medial line" divides radial cement growing out from two bryozoans or forming a triangular junction between several bryozoans (Figure 3.6A). A central cavity rimmed by the radial cement may be filled with second generation drusy spar (Figure 3.6B).

Echinoderm grains that are close to bryozoans may show one of the following alternatives;

1. A syntaxial overgrowth, with a layer of radial cement forming around it (Figure 3.6C, D). A medial line will form as a gently curved line surrounding the substrate, where cement from the echinoderm substrate meets the radial cement from the bryozoan.
2. Echinoderm syntaxial cement may form sharp borders with radial cement radiating from a bryozoan substrate.
3. Echinoderm syntaxial cements may grow right up to the surface of another non-echinoderm allochem, such as a bryozoan (Figure 3.5H).

After initial cementation or internal sedimentation, the allochem may be broken by compaction. The most likely cause of breakage is overburden of additional sediment. Figures 3.6E and F show two valves broken on either side of an intraclast that is bounded on one side by a stylolite. The unidentified shell to the left in Figure 3.6E appears to have been fractured after formation of fringe cement (with syntaxial

Figure 3.6. Features observed in thin sections of the Holston Formation.

A. Bryozoans that have acted as substrates for radiaxial cement. Radiaxial cement from different substrates forms curved medial lines. Crossed-nicols. Bar scale is 1 mm. Alcoa Highway. A-49.

B. Bryozoans in upper right and left corners which have acted as substrates for radiaxial cement, as does the trilobite fragment near the bottom. Echinoderm grain and syntaxial overgrowth in upper center also have radiaxial cement along the edges, facing the pore. Second generation clear drusy spar has filled the pore in the center. Crossed-nicols. Bar scale is 1 mm. Midway Road. M-1.

C. Bryozoan with radiaxial cement (center left). Echinoderm with syntaxial overgrowth (center right) also has radiaxial cement along the edge of the overgrowth (center). Medial line is formed between the radiaxial cement from the different substrates. Plane light. Bar scale is 1 mm. Midway Road.

D. Same as C with crossed-nicols. Note bryozoan has acted as a substrate (center right) for radiaxial cement which has formed medial line with radiaxial cement from echinoderm substrate (left center). Crossed-nicols. Bar scale is 1 mm. Midway Road. M-6-a.

E. Unidentified fossil fragments to right and left of intra-clast in center. These fragments have been broken after cementation processes have started. Plane light. Bar scale is 1 mm. Alcoa Highway. A-154.

F. Detail in previous photograph. Note the lack of fringe cement along the fractured surface of the unidentified fossil fragments (arrows). Plane light. Bar scale is 0.1 mm. Alcoa Highway. A-154.

G. Bryozoan broken prior to cementation. Note fringe crystals line the fractured surface and echinoderm syntaxial cement (at extinction) fills the pore (center, in box). Crossed-nicols. Bar scale is 1 mm. Alcoa Highway. A-123.

H. Detail of fractured surface of bryozoan from previous micro-photograph. Fringe crystals and echinoderm syntaxial cement line the broken surface. Crossed nicols. Bar scale is 0.1 mm. Alcoa Highway. A-123.

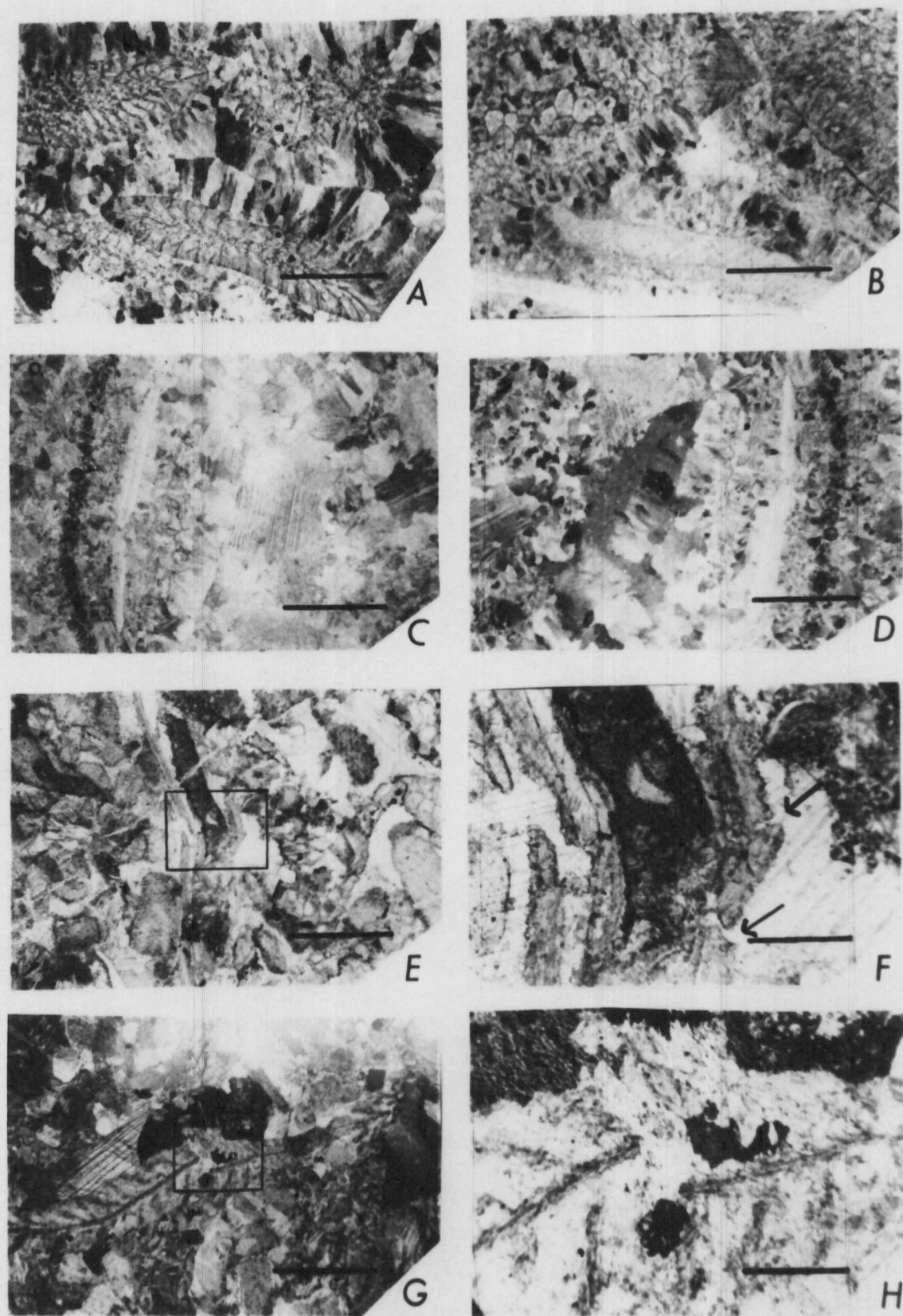


Figure 3.6

extinction) but may have been influenced by the stylolite. The shell fragment to the right of the intraclast shows that the fringe cement exists on the surface but not within the fractures. If the fragment had been broken first, then the fringe cement may have been expected to have formed within the fractures.

A number of processes that may be coeval occur when the lithified sediment is exposed to a freshwater hydrologic system. Neomorphism, defined by Folk (1965) (p. 21) as a process where ". . . older crystals must have gradually been consumed and their place simultaneously occupied by new crystals of the same mineral or a polymorph." It generally results in a fabric in which the original fabric has been obliterated. There is a random distribution of both large and small crystals and cement grains may have a rounded or ragged appearance and non-planar boundaries with surrounding cement crystals.

Radiaxial cement appears to be a replacement cement after an original radial-fibrous marine cement (Kendall and Tucker, 1973). This transformation occurs in the presence of freshwater.

Stabilization of high-magnesium calcite allochems occurs earlier than solution of aragonite, according to studies by Gavish and Friedman (1969). This would include stabilization of the high-magnesium calcite echinoderms and perhaps some of the bryozoans. The slightly later solution of aragonite would provide a local source of cement.

Figure 3.7A illustrates a fracture filled with clear drusy spar and sediment lining the bottom of the fracture. Figure 3.7B is a close up of the sediment and overlying drusy spar. The drusy spar has precipitated in these fractures as well as other voids of organic and

Figure 3.7. Features observed in thin sections of the Holston Formation.

A. Fracture lined with internal sediment and filled with clear drusy spar. Both sediment and drusy spar are of probable freshwater origins. Plane light. Bar scale is 1 mm. Midway Road. M-6-a.

B. Detail from A. Internal sediment has lined the bottom of the fracture and clear drusy spar has filled it. Both are of probable freshwater origin. Plane light. Bar scale is 0.1 mm. Midway Road. M-6-a.

C. Unidentified fossil fragment broken and then cemented (box). Plane light. Bar scale is 1 mm. Oglesby Road. c-o-16.

D. Detail of fractured surface in C. Internal sediment has been deposited on displaced surface of fossil fragment (left arrow) and fringe cement has formed over the fractured surface (right arrow). Plane light. Bar scale is 0.1 mm. Oglesby Road. c-o-16.

E. Echinoderm grain broken before cementation has started. Outer fragments of echinoderm grain have split away (box). Plane light. Bar scale is 1 mm. Oglesby Road. b-0-13.

F. Detail of fractured area from echinoderm grain. Box has been rotated 90° counterclockwise from echinoderm grain. Note how the sides of the echinoderm grain have split away. Plane light. Bar scale is 0.1 mm. Oglesby Road. b-0-13.

G. Broken echinoderm grain. Fragment has been rotated away from the rest of the grain, then syntaxial overgrowth has formed. Plane light. Bar scale is 1 mm. Oglesby Road. c-0-16.

H. Echinoderm grain with a fractured part that has rotated away from the rest of the grain. Plane light. Bar scale is 1 mm. Oglesby Road. c-0-16.

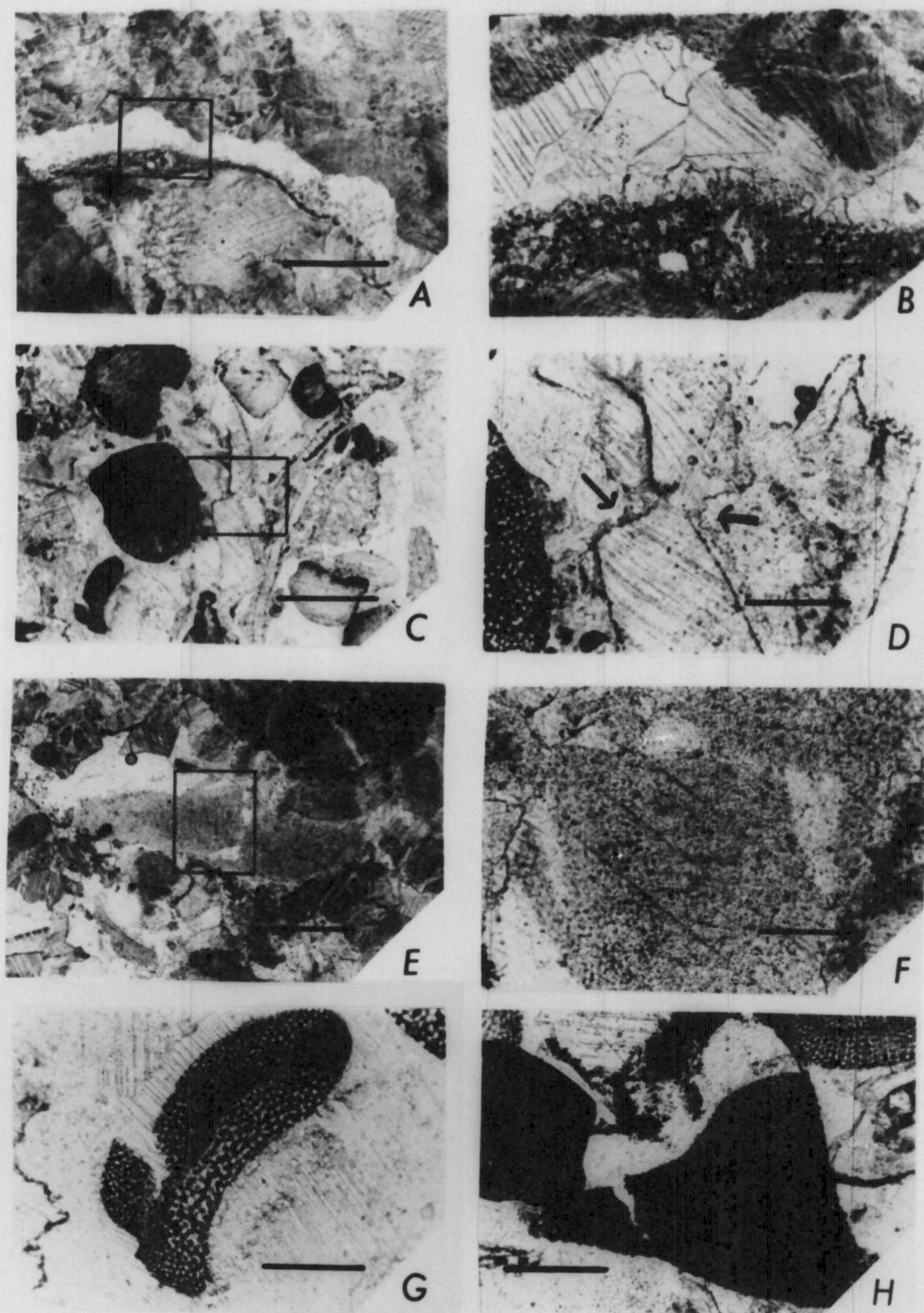


Figure 3.7

inorganic origin. Internal sediment has infiltrated and lined the bottom of the fractures before the precipitation of spar.

Case 2: allochem broken during compaction. Figure 3.8 illustrates what may happen to an allochem that has been broken before the cementation processes have started. There are four alternatives that may take place after breakage. All of these alternatives take place, with considerable overlap in time, in middle marine diagenesis. Early cementation has the effect of minimizing breakage due to compaction (see Figure 3.1).

As discussed before under Case 1, micritic high-magnesium cement may form in very small pores and later stabilize to low-magnesium cement. Micritic cement in Recent sediments (James and Ginsburg, 1979) is an analog for the result of such a process.

Figure 3.7C is an overview of a broken valve where a fringe cement with syntaxial extinction forms a continuous crust across the break. Internal sediment is perched on one side of the displaced shell (best visible in Figure 3.7D). It appears to have been deposited before the formation of the fringe cement and thus blocked the fringe cement from growing on the displaced edge. The sequence of events is thus 1) breaking of shell (marine early diagenesis) 2) deposition of internal sediment onto displaced edge 3) formation of fringe cement.

A broken allochem may have internal sediment filter in and upon its surfaces, although this is difficult to recognize in thin section and distinguish from an allochem which had internal sediment in a perched position and then was fractured. Most likely, the internal sediment will have filtered through the broken surface and continued

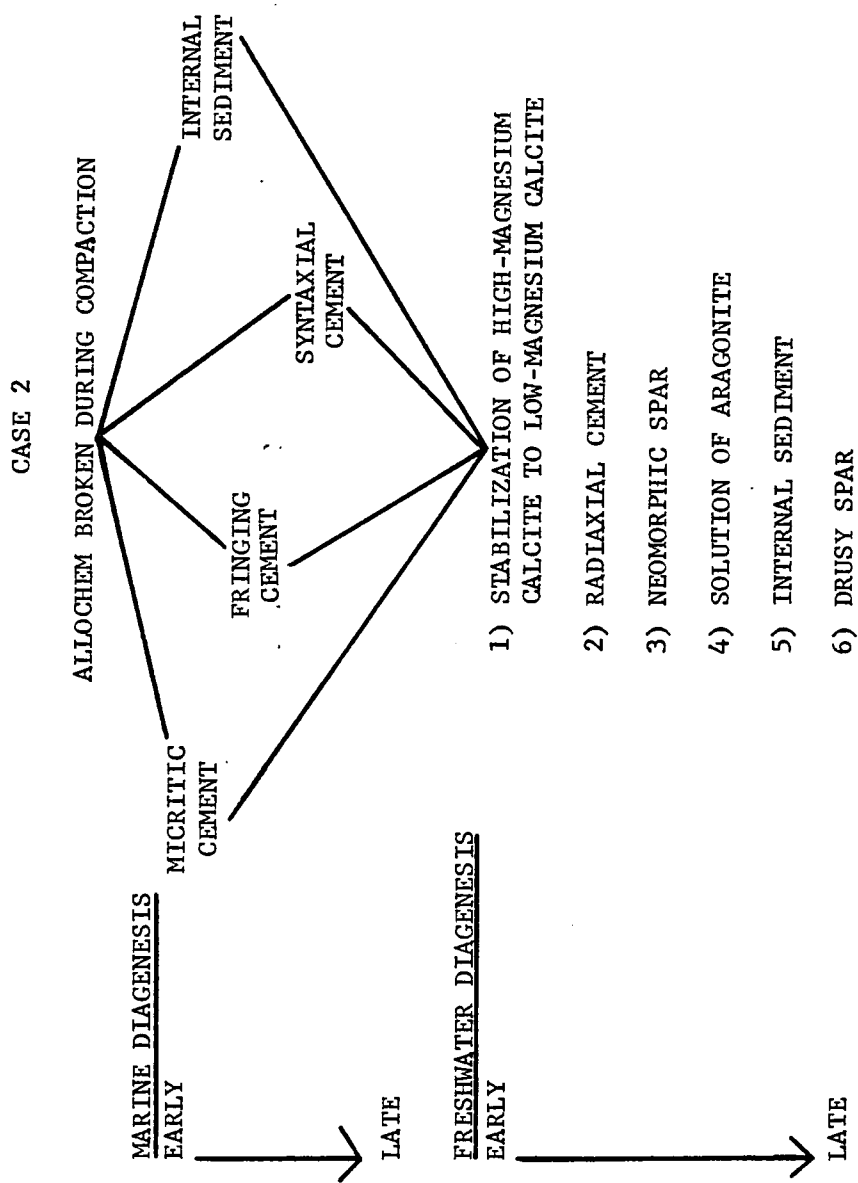


Figure 3.8. Paragenesis of an allochem that is broken during compaction.

movement downward. Only rarely may this sediment be "frozen" or lithified as it moves through the break.

Figure 3.6G shows a bryozoan that has been broken early in the diagenetic history and fringe cements that have formed on the fractured surface. This was followed later by syntaxial cement from an adjacent grain. Figure 3.6H shows the fractured area in detail.

Figure 3.7E shows an echinoderm grain that is stained with iron oxide. The grain has been fractured and several of the fragments have spalled away from the original position. Syntaxial cement then grew over the fragments.

Figure 3.7G shows another iron-stained echinoderm grain that evidently was broken early and one fragment rotated away from the rest of the grain. The later syntaxial overgrowth is oriented with respect to each fragment and twinning lines are observed to make a slight angle (17°) with each other (visible along the bottom of the grain).

Figure 3.7H is another example of an echinoderm broken first, then cemented.

The fourth alternative, where radial fibrous cement grows on a grain after breakage, is difficult to distinguish from that in which an allochem is broken after radial-fibrous cement has precipitated. This is because of the masking effects of the transformation from radial-fibrous to radiaxial cement. The replacement of radial-fibrous by radiaxial cement most likely has an "annealing effect" on the fracture of the cement.

After growth of cement or deposition of internal sediment, there could conceivably be another episode of breakage, although there are no

unequivocal examples of this second event of mechanical compaction occurring within the Holston Formation.

Upon exposure to a freshwater diagenetic environment, the sequence of events is the same as earlier recorded. The processes of neomorphism, transformation of early cement to radiaxial cement, as well as stabilization of high-magnesium components occur at this time. Solution of aragonitic allochems may occur at this time, although it may also happen earlier. Internal sediment may filter in, with precipitation of drusy spar occurring later.

Case 3: aragonitic allochem undergoes boring and micritization.

The third of the initial events that may happen to an allochem is the formation of a micrite envelope (Figure 3.9). The process of boring an aragonitic grain by endolithic algae and fungi, then filling of the bore by aragonite or high-magnesium calcite carbonate in micritic habit occurs while the grain is still in a marine environment (Bathurst, 1975). The resulting micrite envelope preserves within it a rough mold of the grain; the aragonite center is dissolved and later filled with drusy spar (Bathurst, 1975).

Micrite envelopes found within the Holston Formation are filled either with radiaxial spar and a later, second generation of drusy spar or just drusy spar with no radiaxial spar present. However, micrite envelopes are not common within the Holston Formation, which may be due to several reasons;

1. Endolithic algae are photosynthetic and therefore need to be within the photic zone (less than 40 meters and probably less than 15-18 meters. Bathurst, 1975). Some of the

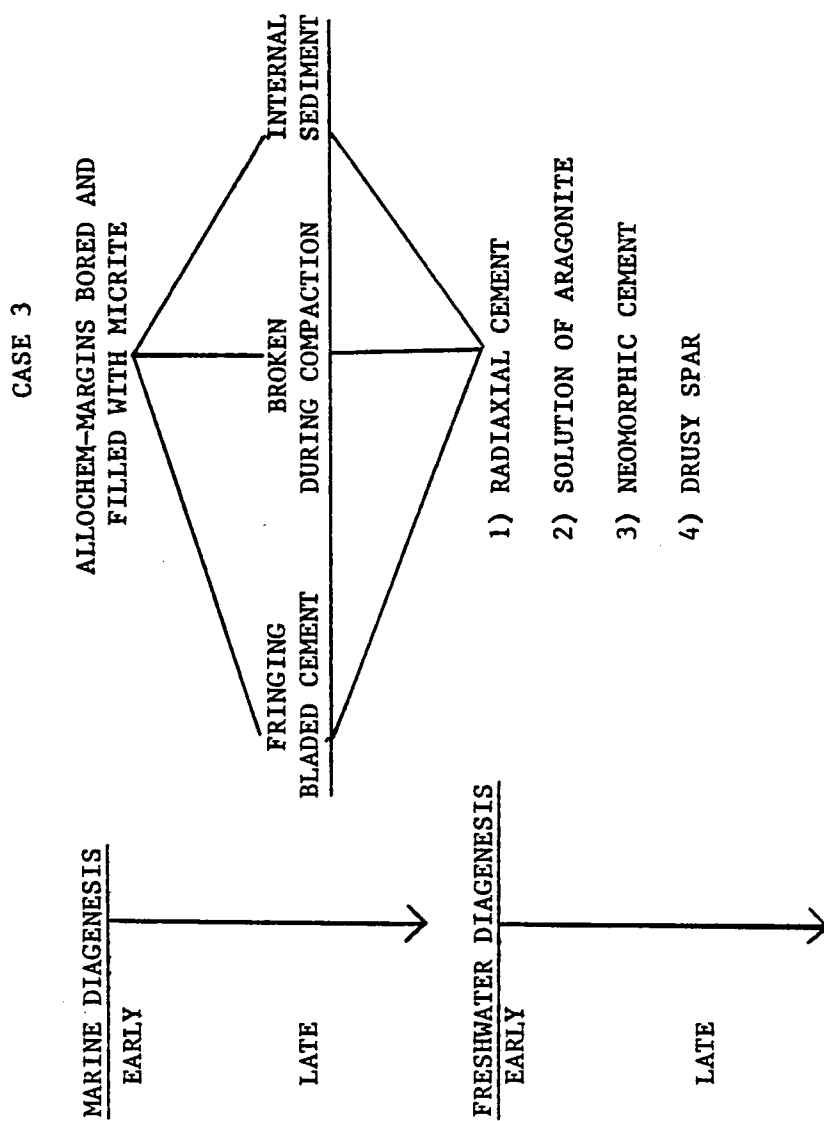


Figure 3.9. Paragenesis of an aragonitic allochem with margins bored and filled with micrite.

Holston lithologies were probably deposited below the photic zone (Walker, 1980), but boring may still occur at some depth by fungi (Perkins and Halsey, 1971).

2. Rarity of originally aragonitic organisms in the Holston.

This may suggest deeper-water deposition (Bencini and Turi, 1974)

Several events may happen during the middle to late stage of marine diagenesis. Radial-fibrous cement can be precipitated both around the inner and outer edges of the micrite envelope. Internal sediment may also filter through the sediment and surround, at least partly, the allochem. Breaking of the micrite envelope may also occur.

Freshwater processes occur as described previously. Stabilization of high-magnesium components, replacement of radial-fibrous by radiaxial cement, solution of aragonite and precipitation of drusy spar all continue with exposure to a meteoric diagenetic environment.

Neomorphic Processes

Some processes operating throughout the post-cementation diagenetic history of the Holston can be included under the term "neomorphism", proposed by Folk (1965). His definition was intended to be a "general term of ignorance" that included "all transformations between one mineral and itself or polymorph . . . older crystals must have been consumed and their places occupied by new crystals of the same mineral or polymorph."

Bathurst (1971) expanded upon the three types of transformations proposed by Folk (1965); examples have been given by Ferrigno (1973). The three types are discussed below.

1. Polymorphic transformations- alteration of aragonite of molluscan valves and the (probable) aragonite walls of the bryozoan Nicholsonella sp. to calcite via a wet, in situ process; not common within the Holston Formation.
2. Wet recrystallization- large calcite crystals grow at the expense of fine calcite crystals by crystal boundary migration; Bathurst (1971) stated that this process operates only in the later stages of aggrading neomorphism. It is difficult to distinguish between this term and the following term.
3. Aggrading neomorphism- finely crystalline carbonate (such as micrite) is replaced by a coarser sparry mosaic. Bathurst stated that this process combines some of the in situ processes listed above. However, Folk (1965) excluded the process of recrystallization from his definition of neomorphism.

Despite Bathurst's interweaving of wet recrystallization and aggrading neomorphism, Ferrigno (1973) attributed wet recrystallization with the transformation of original echinoderm grains to larger crystals involving the echinoderm and its syntaxial overgrowth. Ferrigno may have used the term "wet recrystallization" to emphasize that the ossicle is composed of tiny crystalites that are in similar, if not the same, orientation and these grow to form a large crystal, including overgrowths (Bathurst, 1971). This process can be just as easily included under "aggrading neomorphism", where the small crystalites that composed the ossicle are transformed (recrystallized) to a larger calcite crystal, including overgrowth.

"Aggrading neomorphism" probably was used by Ferrigno (1973) to distinguish the process where randomly oriented micrite particles as opposed to the similarly oriented crystalites, are altered to coarse spar.

The term favored by this author is aggrading neomorphism, rather than recrystallization, since the latter has traditionally implied grain growth during metamorphism, which is not the case with the Holston. However, recrystallization has been used with the same meaning as aggrading neomorphism, so this present author recognizes that either term can be used in reference to the Holston. Within the Holston, aggrading neomorphism appears to have selectively attacked certain types of grains, the echinoderms being the most common group. However, trilobites and ostracods, with their sweeping extinction and fairly similar orientation of smaller crystal units may have undergone the same process.

Cement-Type Abundance at Each Outcrop

Figures 3.10, 3.11 and 3.12 illustrate distribution by percentage volume abundance of cement types at each of the three outcrops. There is a predominance of marine cements or their transformed equivalents (fringe, syntaxial and radiaxial) at each outcrop, with the second generation drusy spar occupying very little volume. Porosity was nearly occluded early in diagenesis by the first generation marine cements. No trends in cementation are evident from the most basinward (Midway Road section) towards the on-shelf localities (Oglesby Road and Alcoa Highway sections).

There is an inverse relationship between echinoderm syntaxial cement and radiaxial cement, the latter usually on bryozoan grains. This reflects the different substrates used by these cements, and thus, the relative abundance of these faunal elements.

There appears to be a positive relationship between fringing cement (first generation) and drusy spar (second generation) and a weaker relationship of these two cement types with echinoderm syntaxial cement. It is not known why fringing cement is observed on some allochems, such as bryozoans, while at other times radiaxial cement appears to be the dominant cement type upon bryozoans. However, it appears that when fringing cement is observed, and conversely there is a decrease in radiaxial cement, more porosity is left open within the rock. A much later, second generation of drusy spar cement then precipitates in the pores.

The weaker relationship between fringing/drusy cements and echinoderm syntaxial cement indicates that fringe cement must have grown very early in the marine diagenetic environment. Most likely, echinoderm syntaxial cement grew at close to, if not the same, rate as fringe cement. For unknown reasons, during the transformation of a predecessor to radiaxial cement, much of the fringe cement is usually destroyed or altered.

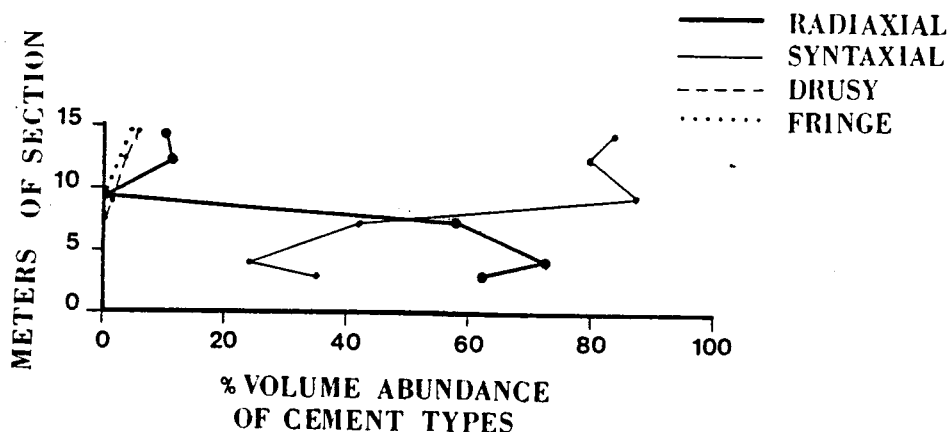


Figure 3.10. Percent volume abundance of cement types at Oglesby Road section.

* micritic cement and neomorphic cement were not point counted because of extremely small size (in case of micritic) and/or very rare (neomorphic).

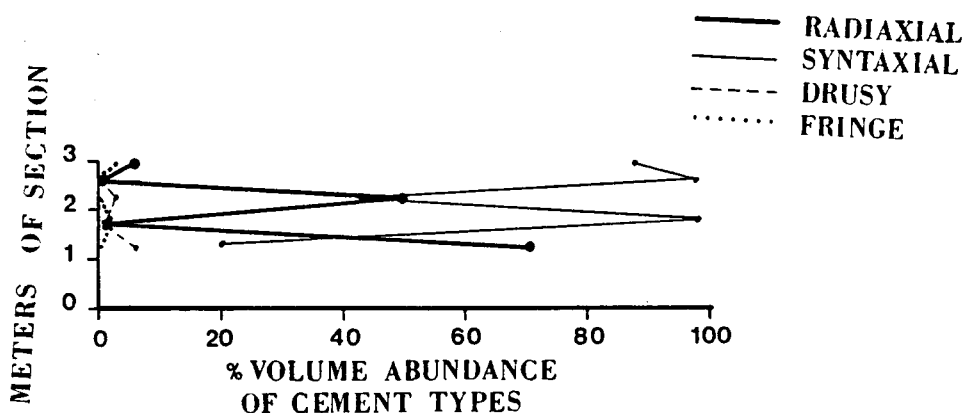


Figure 3.11. Percent volume abundance of cement types at Midway Road section.

* micritic cement and neomorphic cement were not point counted because of extremely small size (in case of micritic) and/or very rare (neomorphic).

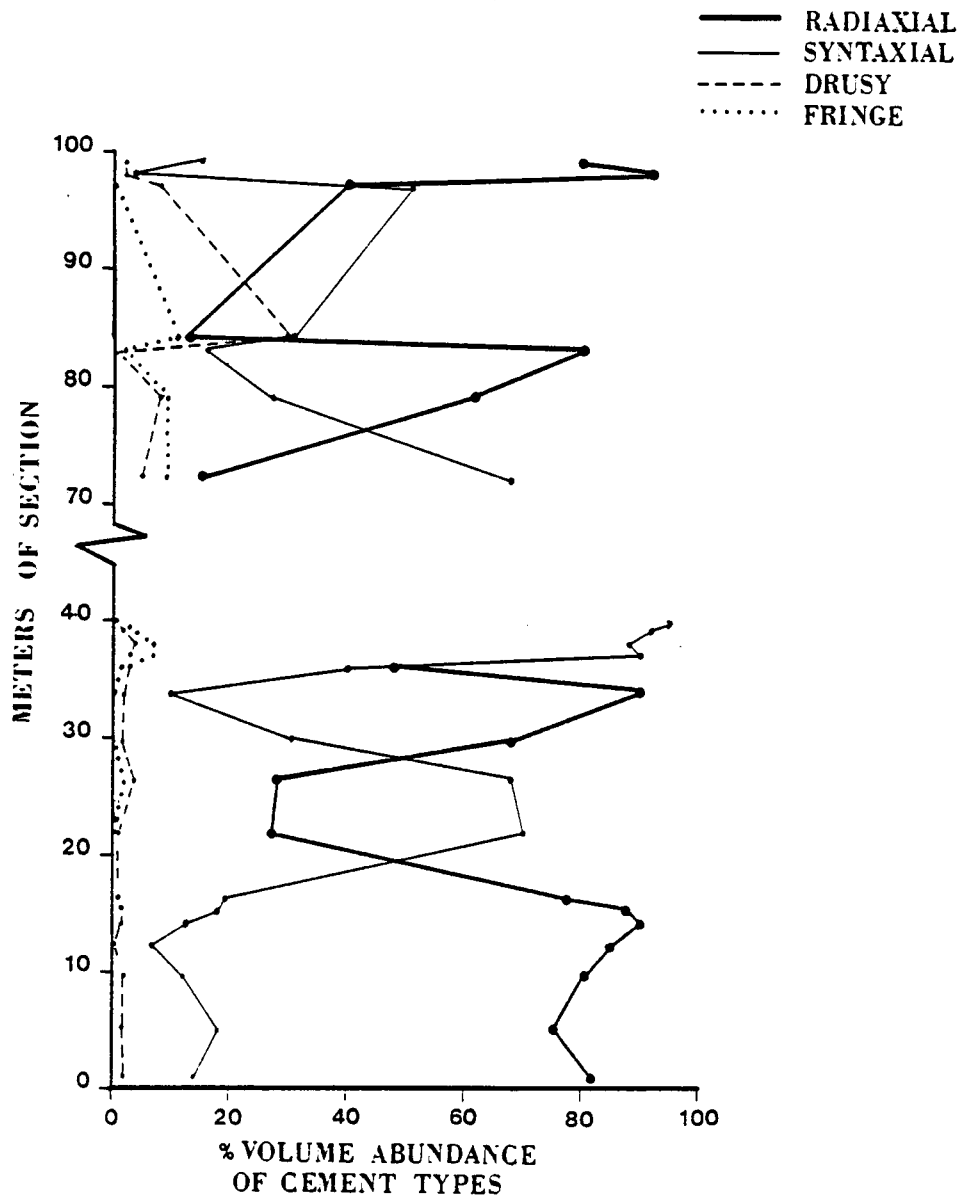


Figure 3.12. Percent volume abundance of cement types at Alcoa Highway section.

* micritic cement and neomorphic cement were not point counted because of extremely small size (in case of micritic) and/or very rare (neomorphic).

IV. TRACE ELEMENT DISTRIBUTION

Purpose

Geochemical analysis of the Holston Formation of the study area was undertaken with a two-fold purpose:

1. Record the amount and distribution of five trace or minor elements (magnesium, strontium, manganese, iron and sodium) within the three studied outcrops of the Holston Formation (see Figure 1.1 for locations of outcrops).
2. Investigate differences or similarities observed within the Holston Formation. The three outcrops were chosen to represent a transect from basinward to on-shelf positions. (The outcrops were all within the same strike belt to avoid complications in correlations across strike belts.) This transect may reveal chemical differences due to changes in mineralogy, rate of sedimentation or position along the transect.

Introduction

The two dominant minerals of carbonate sediments are orthorhombic aragonite and rhombohedral calcite. Specific cations may substitute for the Ca^{+2} cation within the carbonate lattice, depending on similarity of ionic radius and charge. Because of size requirements within the lattice, strontium substitutes for Ca^{+2} in preferential amounts in the aragonite lattice. Other elements that are of interest in this study, such as manganese, iron, sodium and magnesium, prefer the calcite lattice.

The distribution of these minerals, calcite and aragonite, is in turn governed by the original depositional environment. Examination of

Recent sediments shows that aragonite and high-magnesium calcites are found primarily in shallow waters, while low-magnesium calcites are generally associated with deeper water depositional settings (Veizer and Demovic, 1974).

Other factors that may control distribution of trace elements in Recent sediments include partition coefficients (Kinsman, 1969) and biological fractionation (Lowenstam, 1961; Milliman, 1974).

If these sediments that were precipitated in equilibrium with seawater, were subjected to meteoric water diagenesis, a redistribution of trace elements results. In ideal conditions, this redistribution of trace elements will eventually reach equilibrium with the meteoric water diagenetic environment. Factors that control such redistribution include not only the aforementioned mineralogy and depositional environment, but such factors as the degree to which a system is open or closed (which includes such related factors as flow rate of the diagenetic fluid, residence time, number of pore-volumes of diagenetic fluids and variations in groundwater acidity) and recrystallization (Veizer, 1977; Veizer et al., 1978; Morrow and Mayers, 1979; Pingitore, 1978; Brand and Veizer, 1980).

Taking depositional, mineralogical and diagenetic factors into consideration, Brand and Veizer (1980) summarized the general trends of selected trace elements under ideal conditions (Figure 4.1). Figure 4.1 has been redrawn after Brand and Veizer (1980) to show general trends within the part of the Holston discussed herein. Trace element distributions are given in Table 4.1.

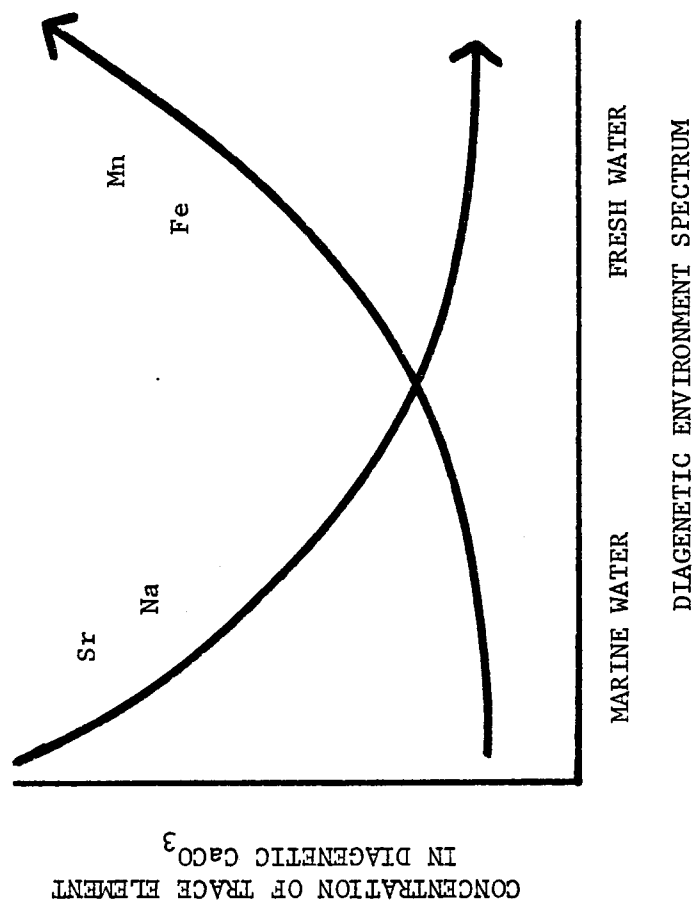


Figure 4.1. Trends in trace element distribution within a portion of the Holston Formation as the diagenetic environment has moved from marine to freshwater. Modified after Brand and Veizer, 1980).

Table 4.1. Trace element distribution within a portion of the Holston Formation. All values stated in parts per million (ppm).

Sample Number	Sr	Mn	Fe	Na	Mg
<u>Midway Road Section</u>					
M-1	271	103	680	138	1485
M-5-a	408	2079	6806	107	1951
M-4-a	437	2322	6840	80	2051
	$\bar{X}=372$	1468	4775	105	1820
<u>Oglesby Road Section</u>					
O-b-14-2	309	274	694	149	2888
O-a-19-2	237	469	845	117	3383
O-a-21	195	175	466	124	2093
O-b-24	188	210	803	111	2387
O-b-28	272	387	4143	109	3946
	$\bar{x}=240$	303	1330	122	2939
<u>Aloca Highway Section</u>					
A-30	200	154	313	102	2262
A-40	232	181	227	128	2006
A-53	293	146	200	113	2159
A-62	417	363	1196	126	1962
A-67	319	177	225	125	2366
A-70	319	222	287	136	3149
A-72-1	264	175	215	69	2364
A-84-1	190	244	558	86	1696
A-86	199	215	364	90	1558
A-93	163	180	413	94	1604
A-99	284	147	167	115	2066
A-105	184	167	317	113	1765
A-112	201	377	1336	73	2536
A-115	184	248	834	76	2482
A-116	177	258	727	88	2189
A-123-2	235	407	1081	100	2348
A-124	193	372	923	69	2072
A-132-2	168	145	173	125	1710
A-142-1	167	162	431	85	1491
A-150	223	244	327	140	2035
A-151	200	331	1182	87	2149
A-156	312	228	405	127	2926
A-157	297	290	592	139	3765
A-165	319	634	887	131	3777
	$\bar{X}=196$	257	553	105	2308
All Sections	$\bar{X}=269$	674	2218	110	2355

Trace Element Data

Strontium. Kinsman (1969) suggested that strontium repartitioning in ancient carbonates depended on whether recrystallization took place in an open or closed chemical system. Carbonate diagenetic studies since Kinsman's evaluation suggest that there are other factors at work. Strontium content will vary according to the original mineralogy, depositional facies and salinity. In general, strontium will decrease with increasing degree of freshwater diagenetic alteration (Veizer and Demovic, 1974; Veizer, 1977; Davies, 1972; Morrow and Mayers, 1978; Pingitore, 1978; Brand and Veizer, 1980).

In Recent carbonate sediments, aragonite contains the most strontium (8000 to 10000 ppm), high-magnesium calcite contains strontium ranging from 1000 to 3000 ppm and low-magnesium calcite contains from 1000 to 2000 ppm (Pilkey et al., 1969; Land and Goreau, 1970; Land and Hoops, 1973; James et al., 1976; Morrow and Mayers, 1978). Decreases in strontium values within Pleistocene samples are recorded by Land and Hoops (1973).

Several authors (Bencini and Turi, 1974; Veizer and Demovic, 1974; Veizer, 1977) have used this information to infer original mineralogy and paleobathymetric position of facies. The bathymetric relationship is a result of a shallow to deep progression from dominant aragonite to dominant calcite in modern carbonate regimes. One problem involved in application of these modern distributions to ancient rocks is the expulsion of strontium from the lattice during aragonite-calcite transformations. Nonetheless, the above-mentioned studies have suggested that ancient facies may be distinguished on the basis of trace elements.

Bausch (1968) conducted a literature survey of strontium content in ancient carbonates. Results indicated that reef and associated back-reef limestones may be separated from basinal and fore-reef limestones by their strontium content. The former contain from less than 100 ppm to 400 ppm and the latter range from 500 to 3000 ppm.

Distribution of strontium within the Holston Formation of this study is summarized in Table 4.1 and Figure 4.2 illustrates stratigraphic distribution of strontium according to outcrop. All values fall within the range from 163 to 437 ppm. The mean for all values combined from the three sections is 269 ppm.

Manganese. Manganese concentrations have been used as a paleo-environmental indicator; a higher manganese content implies an original calcite mineralogy common to deeper waters and reducing conditions at depths that favor the incorporation of manganese into the calcite lattice. Low manganese concentrations imply an original aragonite mineralogy more typical of shallower water (Bencini and Turi, 1974).

Brand and Veizer (1980) hypothesize that sediments lithified in the marine environment will undergo extensive chemical changes during later diagenetic equilibrium with meteoric water. Post-depositional meteoric alteration can theoretically lead to an increase in manganese values, compared to values in the marine diagenetic environment.

Distribution of manganese within the Holston Formation is summarized in Table 4.1. Figure 4.3 illustrates the stratigraphic distribution of manganese according to outcrop. Note that manganese values increase at the top of each section. Most values fall within 100-500 ppm, plus several anomalously high values. One of the anomalous

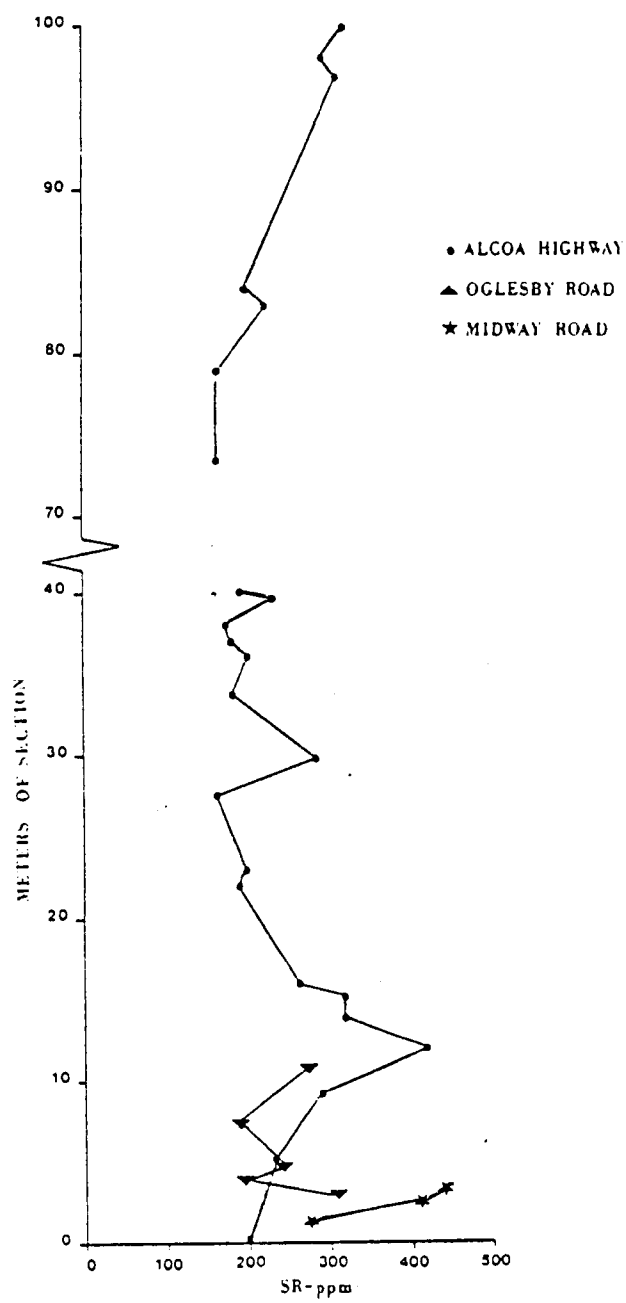


Figure 4.2. Strontium concentrations at three localities of study area.

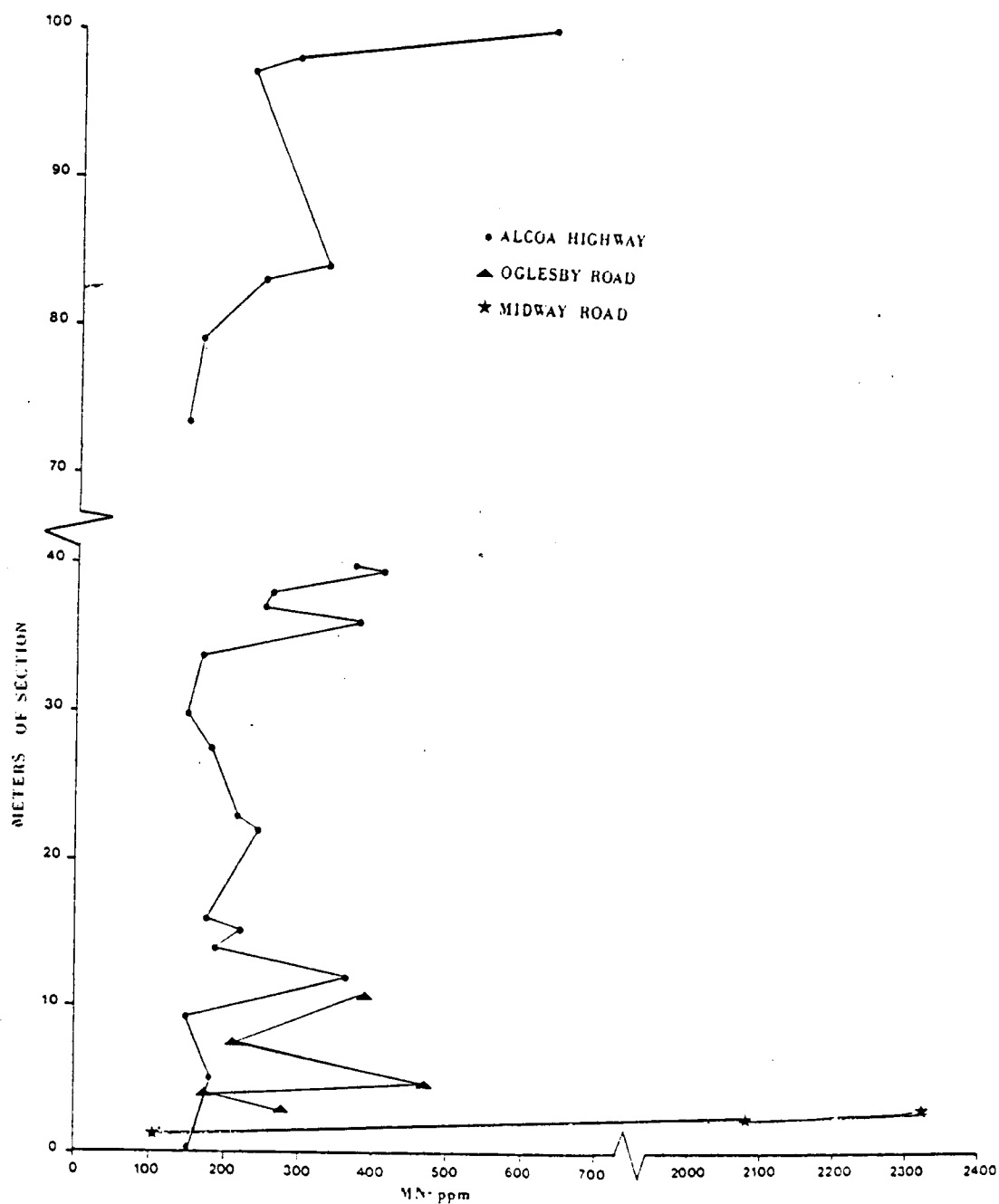


Figure 4.3. Manganese concentrations at three localities of study area.

values (634 ppm) is present at the top of the Alcoa Highway section. The other two anomalous values are near and at the top of the Midway Road section (2079 ppm and 2322 ppm, respectively). Values from all sections combined have a mean of 674 ppm. Due to the skewness of the mean, the median of 244 ppm is more meaningful. Manganese values reported for Midway Road in this study follow the trend reported by Walker and Benedict (1980) for this section.

Iron. This element is highly reactive with two oxidation states, making iron difficult to trace through the diagenetic process (Gavish and Friedman, 1969). For this reason, few researchers have reported concentrations of iron and related iron to carbonate depositional or diagenetic factors.

Lindholm (1974) listed seven examples of Silurian to Recent age rocks in which there were two generations of spar, as determined from stained thin section. In six of the seven cases, the first generation was an early diagenetic, non-ferroan cement, followed by a second generation, ferroan sparry mosaic. In the seventh case, the first generation was ferroan, followed by a second generation, non-ferroan cement. Stained thin sections of the Holston Formation of the study area agree with the majority of cases as listed by Lindholm (1974). The first generation of cement is composed of radiaxial, non-ferroan cement, followed by a second generation of pore-filling, ferroan sparry mosaic. Echinoderm overgrowths may occasionally exhibit alternation of non-ferroan and ferroan stages.

Iron values are listed in Table 4.1. The stratigraphic distribution of this element is shown in Figure 4.4. Iron ranges from 167

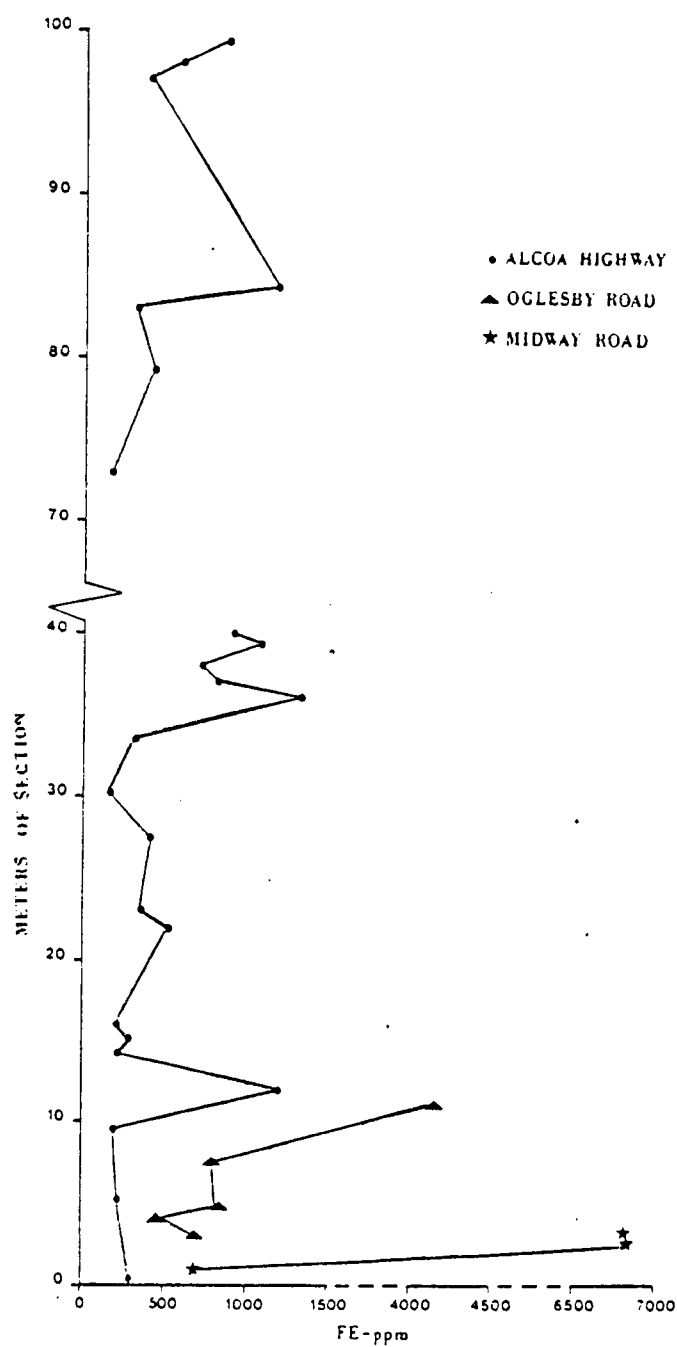


Figure 4.4. Iron concentrations at three localities of study area.

ppm to 6840 ppm, with a mean of 2218 ppm. The mean appears skewed because of several anomalously high values present at the top of two of the sections, Midway Road and Oglesby Road. The median value of 592 ppm is probably more representative of values.

Iron and manganese have a high positive correlation ($r=0.84$) (see Appendix D). This is in part due to similar chemistries of manganese and iron. Both are mobile under reducing conditions and insoluble under an oxidizing environment; they also behave similarly with respect to pH-Eh conditions (Mason, 1966).

Sodium. Land and Hoops (1973) analyzed a number of Recent and Pleistocene carbonate samples and found that sodium was incorporated into marine skeletal material in significant but variable quantities--probably due to differing biological fractionation of sodium among different groups of organisms.

Data gathered by Land and Hoops (1973) and Land (1973) indicate a decrease in sodium content of Pleistocene age rocks with increasing diagenesis. Older rocks exhibit further decreases in sodium values. Increasing equilibration with a meteoric diagenetic environment may be responsible for low sodium values (Brand and Veizer, 1980). Veizer et al. (1978), in their study of early Paleozoic formations, stated that the sodium values reflected the paleosalinities of depositional and early diagenetic environments, despite the decreases as a whole.

Figure 4.5 illustrates the variation of sodium concentrations with stratigraphic position within the Holston Formation outcrops. Values range from 69 to 149 ppm, with a mean of 110 ppm. All values and means are listed in Table 4.1.

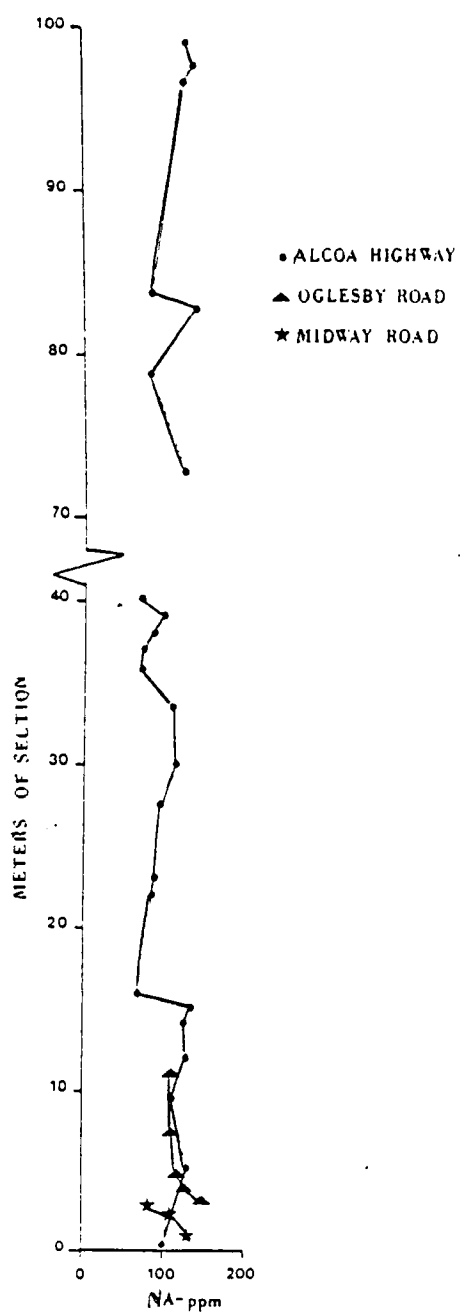


Figure 4.5. Sodium concentrations at three localities of study area.

Magnesium. Magnesium content varies among various groups of Recent organisms, probably due to biological fractionation (Brand and Veizer, 1980). In general, calcite can be divided into high magnesium calcite (greater than 4 mole % MgCo) and low-magnesium calcite (less than 4 mole % MgCo). It has been established that high-magnesium calcite is the most unstable, compared to aragonite or low-magnesium calcite, and will stabilize most quickly in time by elimination of magnesium (Gavish and Friedman, 1969). This is followed by stabilization of aragonite to low-magnesium calcite. According to Brand and Veizer (1980), magnesium may also be lost from low-magnesium calcite during stabilization within a meteoric environment.

Table 4.1 lists all values and means for the Holston Formation in this study. Figure 4.6 illustrates how magnesium values vary with stratigraphic position. Magnesium values range from 1485 to 3946 ppm, with a mean of 2355 ppm. These values appear to be very low, assuming that the Holston limestone was composed of originally high-magnesium components, such as echinoderm grains.

Reef Cross-Section

Trace element values across a bryozoan-micrite boundstone near the top of the Alcoa Highway section show the following trends. The grainstone (A-156) immediately below the boundstone has values for each element that are relatively low. At the boundstone (A-157), strontium and sodium remain at similar values. Iron, manganese and magnesium values increase. The grainstone (A-165) collected from the contact of the Holston and Chapman Ridge Formations (and above the reef) shows that

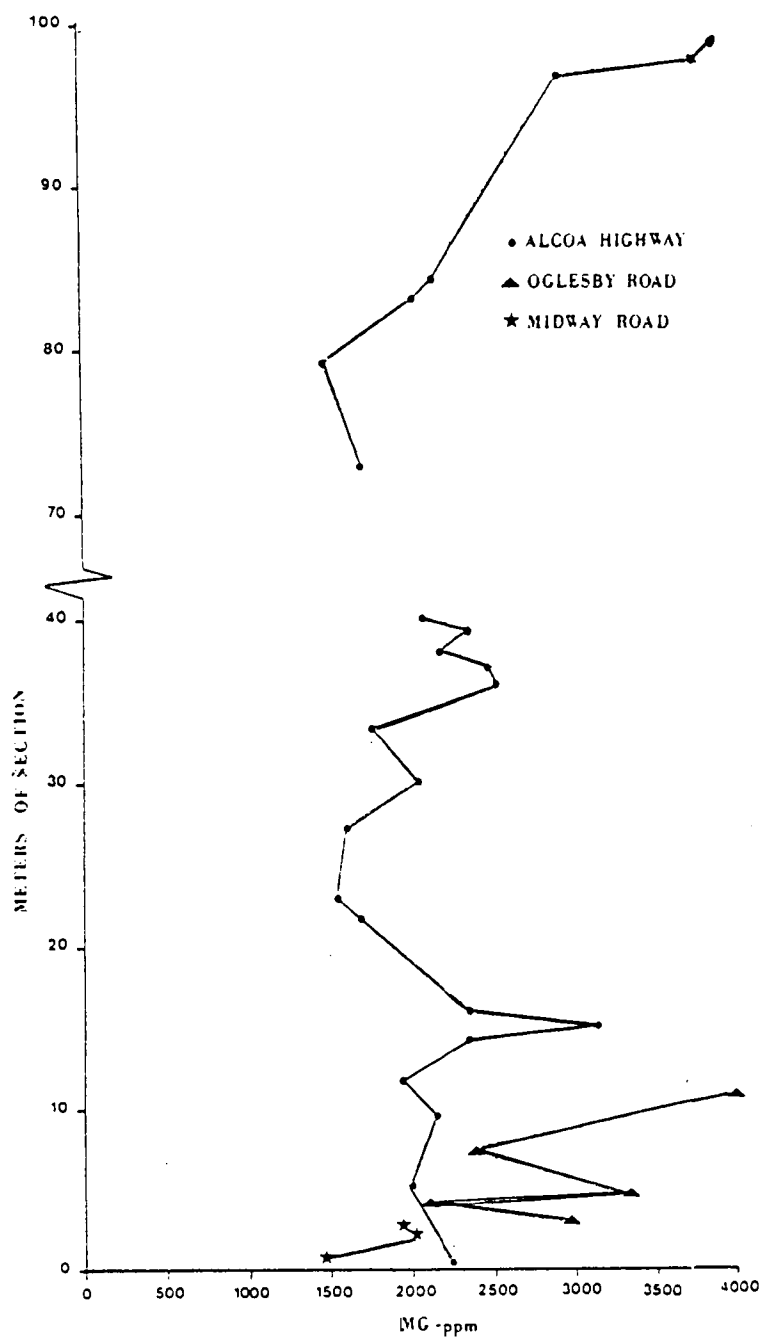


Figure 4.6. Magnesium concentrations at three localities of study areas.

values for iron, manganese and magnesium continue to increase. Sodium and strontium values remain about the same as the previous two samples.

Analysis of Components and Enclosing Rock

This section of the study was inspired by Brand and Veizer's 1980 study of the degree of homogenization between allochems of variable original mineralogy and the enclosing matrix. Components and matrix from two formations, the Mississippian Burlington Limestone of Iowa and Missouri and the Silurian Read Bay Formation of Arctic Canada, were compared in Brand and Veizer's study.

In the present thesis study, a total of seven components were analyzed: five bryozoans, one sample of drusy spar and one sample of radiaxial spar-rich rock. These components were separated from the enclosing matrix by use of the Felker rock saw. Samples were then dissolved and analyzed in identical fashion to the carbonate-soluble fraction of the whole rock sample. Results are recorded in Table 4.2. The chemical values of the rock enclosing or surrounding the bryozoans have been corrected by the following formula. The correction factor was in order to determine the relative enrichment or depletion of the bryozoan, compared to the enclosing rock (minus the trace element value contributed by bryozoans in the enclosing rock).

Step 1	percent volume bryozoans in the enclosing rock (determined by point count analysis)	x	chemical value of the separate bryozoan component sample
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= average amount of trace element contributed by the bryozoan to the enclosing rock.

Step 2	trace element value for the enclosing rock	-	average amount of trace element contributed by the bryozoan to the enclosing rock
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Table 4.2. Trace element concentrations of selected components and surrounding rock matrix.

Sample	SR(ppm)	MN(ppm)	FE(ppm)	NA(ppm)	MG(ppm)
O-b-14-1 radiaxial spar	300	257	585	154	2159
O-b-14-2 matrix	309	274	694	149	2888
O-a-19-1 drusy spar	108	521	2122	77	2959
O-a-19-2 matrix	237	469	845	177	3383
A-72-1 bryozoan	384	287	69	88	3122
A-72-2 matrix	264	175	215	69	2364
corrected value of matrix	201	133	164	53	1803
A-84-2 bryozoan	172	227	510	92	1559
A-84-1 matrix	190	244	558	86	1696
corrected value of matrix	114	147	336	52	1020
A-123-1 bryozoan	225	418	1317	75	2447
A-123-2 matrix	235	407	1081	99	2348
corrected value of matrix	172	297	789	72	1714
A-132-1 bryozoan	190	160	355	20	1795
A-132-2 matrix	168	145	173	25	1710
corrected value of matrix	116	100	64	86	1183
A-142-2 bryozoan	188	175	354	99	1670
A-142-1 matrix	167	162	431	85	1491
corrected value of matrix	117	113	302	60	1046

= corrected value for the rock minus the bryozoan contribution

The conclusions of this component analysis are incorporated into the overall discussion below.

Discussion

A major interest in this study is the possibility of using trace elements to determine the general facies or to determine the relative position of the facies with respect to a variable, such as water depth. If the original depositional differences are significant and are not completely "masked" or altered by subsequent meteoric diagenesis, then these trace elements may be suitable to interpret the facies with respect to its original depositional environment.

Manganese and iron appear to be potential bathymetric indicators. There is a high correlation between the two elements ($r=0.84$) (see Appendix D) between the two elements, probably due to similar chemistry.

At the most basinward or closest to the Middle-Ordovician shelf-edge (see Figure 1.1) of the three sections, Midway Road, there are very high concentrations of these elements. The values are 2979 ppm and 2322 ppm for manganese and 6806 ppm and 6840 ppm for iron. Iron and manganese form a discontinuous crust of iron and manganese oxides at the contact of the Holston and overlying Ottosee Formation. The iron and manganese values are presumed to have been incorporated within the calcite lattice, since care was taken to dissolve only the carbonate fraction and not the iron-manganese oxide crust. There are smaller increases in magnesium and strontium at this contact as well. The "spike" in concentrations at the upper contact may be best explained

by a surface of non-deposition or extremely low sedimentation between the Holston Formation and the overlying shaly Ottosee Formation.

Also present at these stratigraphic levels is collophane (identified as carbonate fluorapatite by Benedict, 1980) which has formed discontinuous laminae around detrital carbonate and in botryoidal habit encrusting small cavities. This suggests either a very shallow water estuarine environment or oceanic upwelling onto a warm water shelf (Bromley, 1967). Since there is no evidence for an estuarine environment, oceanic upwelling is suggested, implying water depths greater than 30 meters (Bromley, 1967). This interpretation supports the previous interpretation by Walker and Benedict, 1980).

At the Oglesby Road section, which occupies an intermediate position on the shelf (about 4 miles from the Middle-Ordovician shelf-edge), there is again a correlation between iron and manganese. There is an increase in both elements at the contact of the Holston with the overlying shaly Ottosee Formation. However, the increases in values are not as sharp as at the Midway Road section. Means for iron and manganese found for this section, 303 ppm manganese and 1330 ppm for iron, fall in between means reported for iron and manganese at the Midway Road and Alcoa Highway sections.

The Alcoa Highway section occupies a position furthest on-shelf, about 5 miles from the Middle-Ordovician shelf margin. It also has a positive correlation between iron and manganese. Again, the highest manganese value (634 ppm) is found at the top of the formation. A relatively high iron value (887 ppm) is found at the top of the Alcoa Highway section, but it is not the highest value for that section. The

mean for manganese values is 252 ppm and the mean for iron values is 196 ppm. The three outcrops can be distinguished, paleobathymetrically, on the basis of iron and manganese means. The highest averages occur at the most basinward (and deepest water) of the three sections. Moderate averages of iron and manganese are found at the Oglesby road section, which occupies a position about 4 miles from the Middle-Ordovician shelf-edge. Alcoa Highway has the lowest average and occupies an on-shelf position about 5 miles from the Middle-Ordovician shelf-edge.

The low strontium values for this study area (269 ppm) are most likely caused by two general factors. One is the influence of the original depositional environment. The biota of the depositional environment was composed of two dominant faunal groups, echinoderms and bryozoa. Both were composed probably of high-magnesium calcite (Chave, 1964), similar to Recent echinoderms and bryozoa (Land and Hoops, 1973). Generally, organisms composed of high-magnesium calcite contain moderate values of strontium, from 1000-3000 ppm (Land and Hoops, 1973). The second factor is diagenesis. As meteoric diagenesis proceeds (including repeated recrystallization), strontium is removed from the system. Veizer and Demovic (1974) divided carbonate rocks (composed originally of aragonite, high-magnesium calcite and low-magnesium calcite) into two groups: 1) low-strontium group that was "formed by original magnesium calcite and low-strontium aragonite" and 2) high-strontium group that was formed by original calcite and high-strontium aragonite". Veizer and Demovic (1974) noted that the low-strontium group (100-250 ppm) consisted of "light-colored biosparites, biomicrites and micrites associated predominantly with reefal and

reef-detrital sequences and shallow neritic and pelagic limestones". Veizer (1977) qualified this low strontium group by adding a later statement that "the low-strontium group also comprises facies characterized by a high degree of open-system diagenetic stabilization, high percentage of late diagenetic sparry calcites (e.g. biohermal and detrital sequences, limestones subjected to multiple recrystallization processes and possibly other causes". The high strontium group (600-700 ppm) discussed by Veizer and Demovic (1974) is composed of "biomicrites of variable skeletal composition, micrites, pelagic (deep-sea) limestones, and micrites associated with partly "hypersaline" sequences".

The strontium values of the Holston generally fall into the low-strontium group of Veizer and Demovic (1974) and Veizer (1977). The strontium values within the Holston appear to indicate re-equilibration with a meteoric environment. What is not clear is how such low values of strontium, sodium and possibly magnesium can be attained when this facies had little porosity left for meteoric fluids to circulate after early marine cementation.

Comparison of the three outcrops shows that the means (373 ppm at Midway, 240 ppm at Oglesby and 196 ppm at Alcoa Highway) decrease slightly from basinward to on-shelf, the opposite of trends that are predicted. At the contact of the Holston and the overlying formation (Ottosee Formation at Midway Road and Oglesby Road; Chapman Ridge at Alcoa Highway) there is a tendency for strontium to have slightly higher values compared to the rest of the section values. At the Midway Road section, this may be possibly accounted for by the

substitution of strontium for calcium in collophane (Dana, 1977). Strontium does not correlate with any other element in this study (see Appendix D). It is probable that manganese and strontium will have a negative correlation (as predicted by Brand and Veizer, 1980) after facies representing a full span of paleoenvironments within the Middle-Ordovician of East Tennessee have been examined.

Sodium values for the Holston of this study are very low but fall within the low sodium end of the range given by Veizer (1977) and Veizer et al. (1978). These researchers suggested an approximate division at 230 ppm; with a higher value suggesting hypersaline conditions. An intermediate class from 150 to 300 ppm suggested restricted marine conditions. The Holston averages about 110 ppm, suggesting open marine conditions, as does the associated fauna. Sodium values do not correlate with other trace elements in this study (see Appendix D). There are no apparent trends from basinward towards on-shelf localities. Meteoric diagenesis and/or recrystallization has depleted the sodium present within the Holston study area but values seem to have environmental significance as well.

Magnesium values for the Holston are very low, from 1491 ppm to 3946 ppm. There are no trends present from basinward towards the on-shelf localities. However, magnesium values increase slightly towards the top of each section. As discussed before, the Holston fauna is composed of echinoderms and bryozoa, both probably originally composed of high-magnesium calcite (Chave, 1964; Lohmann and Meyers, 1977), so original magnesium values were probably much higher. Magnesium may be lost from low-magnesium calcite as well as high-magnesium calcite during

stabilization within a meteoric environment (Brand and Veizer, 1980). Variations in the concentration of magnesium do not appear to be directly related to the faunal content, as seen in thin section.

Bryozoan reef masses have been described by previous workers within the Holston Formation (see Historical section). Walker and Ferrigno (1973) characterized and described the ecology of the bryozoan-micrite boundstones at the Alcoa Highway section.

This author analyzed samples of the boundstone (BD) (A-157) and compared the trace element content with samples of echinoderm-bryozoan grainstone (GN) about 15 feet away (on the outcrop face) from the reef mass; the second grainstone was located about 400 feet (on the outcrop face) in an up-dip direction from the reef mass. As shown in Figure 4.7, there do not appear to be any systematic changes in the trace element content that are directly related to the presence of this small reef mass.

While only very limited conclusions can be drawn from the component-matrix study, the bryozoans generally contain higher values for each of the trace elements by an amount up to two times that of the matrix. The drusy spar sample has higher manganese values and even higher iron values, when compared to the matrix. The same spar sample has lower magnesium, sodium and strontium values than the matrix. Matrix and radial spar-rich material have similar values.

It is interesting to speculate that at least some of the original depositional differences between bryozoans and matrix may have been preserved. The samples may have been altered somewhat by post-depositional alteration by meteoric waters. The drusy spar sample

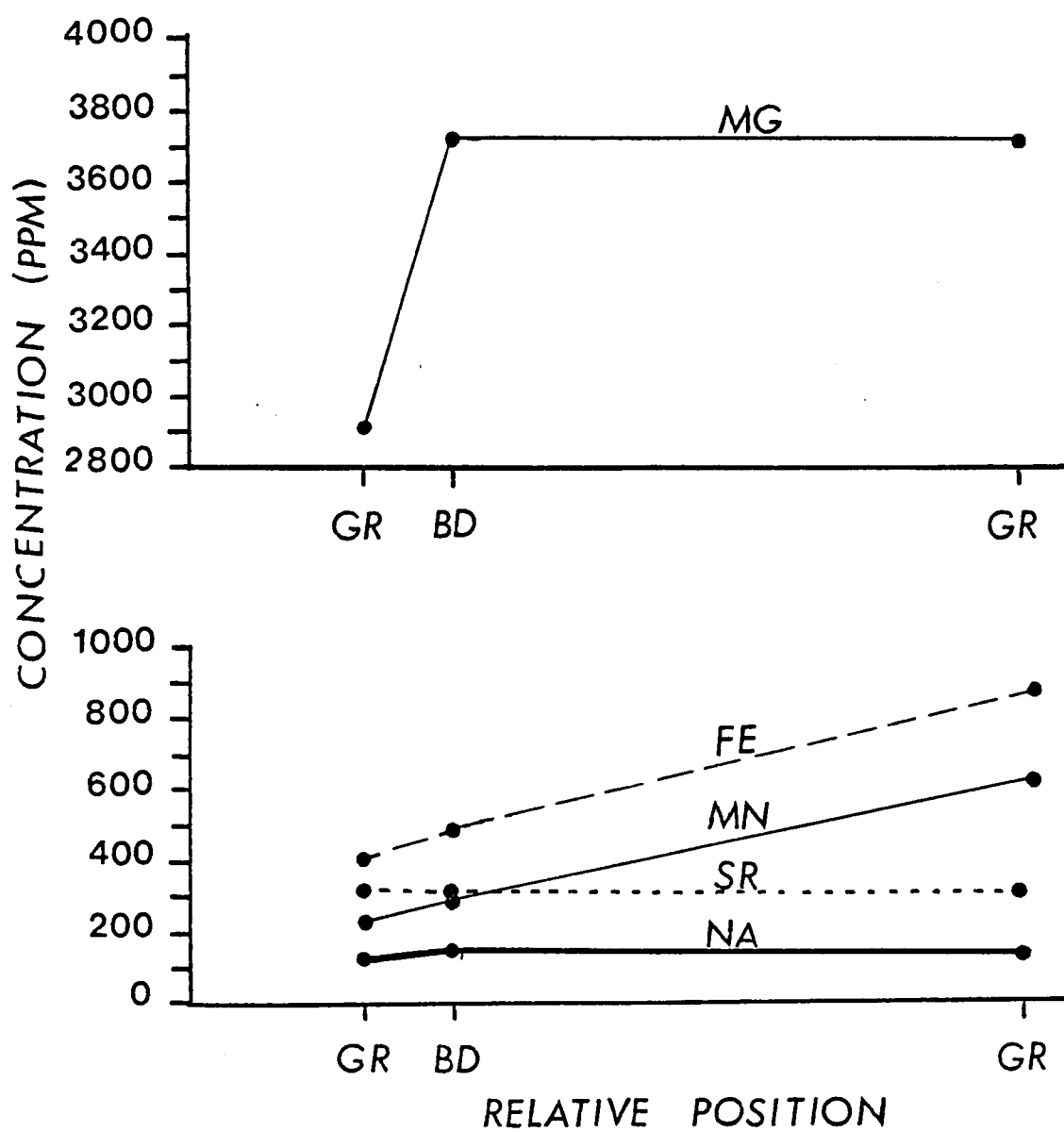


Figure 4.7. Illustration of values across grainstone (GR) flanking sands, boundstone (BD) and grainstone at the contact of the Holston and Chapman Ridge Formation.

values indicate that meteoric (or perhaps deep-burial waters) were enriched somewhat in manganese and iron compared to the matrix or to the bryozoans.

V. SUMMARY AND CONCLUSIONS

1. Investigation into the diagenetic history of the Holston Formation has indicated a definite paragenetic sequence of cementation and internal sedimentation. The first or earliest generation of cements precipitated while the sediment was still in a marine environment. Formation of micrite envelopes on aragonitic allochems also occurred early in time. The various cements are coeval or overlap in time. Micritic cement is probably the earliest, followed by development of fringe cement. The deposition of internal marine sediment shows considerable overlap in time with development of fringe cement. Echinoderm syntaxial cement also overlaps with fringe cement and internal sediment. These observations are evidence that echinoderm syntaxial cements or overgrowths occur in the marine diagenetic environment, instead of the freshwater environment.

Meteoric diagenesis is probably responsible for the transformation of a probable radial-fibrous predecessor to radiaxial cement. Stabilization of high-magnesium calcite to low-magnesium calcite, solution of aragonite, formation of neomorphic spar and the transformation of radiaxial cement are difficult to place in relative order.

Internal sediment may be emplaced in fractures and cavities during meteoric diagenesis. The precipitation of drusy spar may or may not overlap in time with the emplacement of the internal meteoric sediment. The second generation includes the internal meteoric sediment and the clear drusy spar that is in a central pore-filling position. At least some of the spar may be of a deep-burial origin.

Breakage due to compaction may take place before or during cementation and internal sedimentation processes of the marine diagenetic environment. However, breakage usually occurs early in diagenesis and decreases in importance with time. Figure 5.1 is a summary of the relative diagenetic history.

2. Strontium, sodium and magnesium means for all three outcrops are similar, implying similarity of depositional environments and/or of diagenetic events. Because the samples varied in petrography and other features indicating a span in paleoenvironments, the more or less invariant concentrations of these elements suggest that they are not particularly sensitive to environment of deposition. The strontium and sodium averages agree with values in the literature for other facies that imply a normal open marine environment.

3. Manganese and iron concentrations (with a positive correlation) appear to be potential indicators of paleobathymetric conditions. Higher concentrations are found at the probable deep water locality (Midway Road) and lower concentrations at the on-shelf localities (Oglesby and Aloca Highway sections). Iron may not be suitable as an indicator in other geologic situations due to its extremely reactive chemistry.

4. Comparison of individual components (radial-rich material, drusy spar and bryozoans) with the surrounding matrix indicates that these components may be somewhat enriched in trace elements. While speculative, that may suggest that some original depositional differences may still exist between component and matrix.

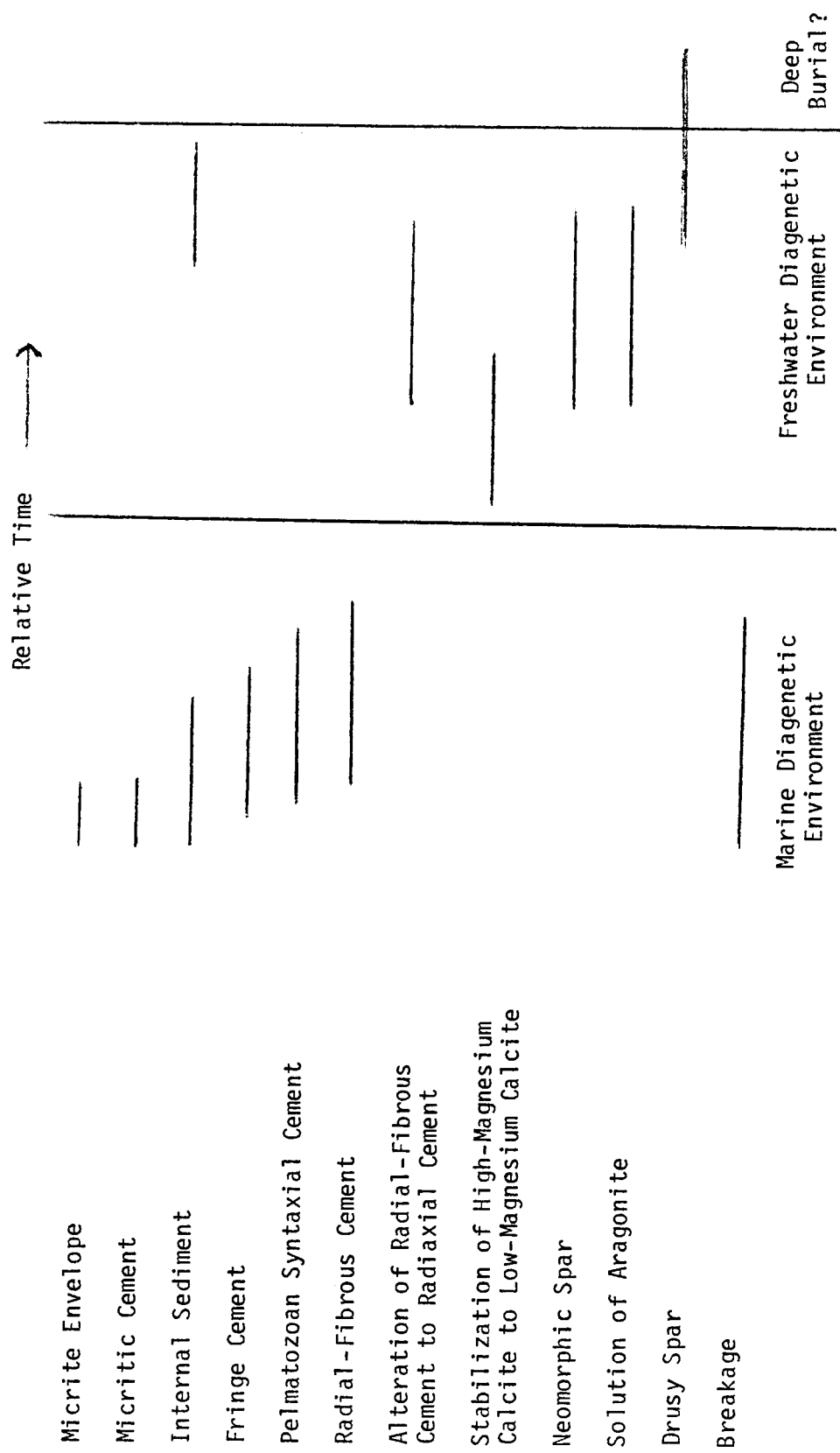


Figure 5.1. Summary of Paragenetic Sequence of Cements and Sediments

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APPENDICES

APPENDIX A
POINT-COUNT DATA

Table A-1. Percent volume abundance of components within the Holston Formation thin sections

Sample Number	Bryozoans	Pelmatozoans	Other Fossil Groups	Intracrysts	Micrite	Fringe Cement	Drusy/Bladed Cement	Syntaxial Overgrowths	Radiaxial Cement	Microspar/Pseudospar/ Neomorphic Spar	Dolomite
M-1	13.5	19.0	5.0	0.0	1.0	0.0	4.0	12.5	40.5	0.0	0.0
M-4	3.5	40.5	8.5	0.0	22.0	0.5	0.0	20.0	0.0	0.0	0.0
M-6-a	6.5	11.0	2.0	0.0	0.5	0.0	2.0	33.0	38.0	0.0	0.5
M-5-a	5.0	35.5	11.0	0.5	4.5	0.0	0.0	38.5	0.0	0.0	0.0
M-4-a	2.5	49.0	9.5	0.0	9.0	1.0	1.0	23.5	1.5	0.0	0.0
b-0-13	19.5	36.5	2.5	0.0	0.0	0.5	0.5	40.6	0.0	0.0	0.0
0-b-14	17.0	31.0	0.5	0.0	0.0	0.5	0.0	18.0	30.5	0.0	0.0
0-a-21	16.5	15.5	7.5	0.5	4.5	0.5	0.0	11.0	35.5	0.0	0.5
0-b-24	25.5	9.5	4.0	0.0	0.0	0.0	0.0	25.5	40.0	0.0	0.0
0-b-26	15.5	25.0	5.5	0.0	6.5	2.5	0.0	39.0	3.5	0.0	1.0
0-b-28	17.0	17.5	8.5	0.0	9.5	2.5	0.0	38.0	4.5	0.0	3.0
A-30	24.0	7.5	1.0	1.0	1.5	0.0	2.5	10.0	53.0	0.0	0.0
A-40	16.5	11.0	1.0	0.0	0.5	0.0	1.0	13.5	53.5	3.5	0.0
A-53	23.5	7.0	1.5	0.5	0.5	0.0	3.5	7.5	52.0	0.0	0.0
A-57	10.0	7.5	3.0	0.5	0.5	1.5	1.5	5.5	66.0	0.0	3.5
A-62	13.5	12.5	1.5	0.0	0.0	0.0	0.0	4.5	58.5	1.5	5.0
A-67	21.0	5.5	3.0	0.0	0.0	0.0	1.0	10.0	53.5	2.0	0.0
A-70	18.5	10.0	3.5	0.5	0.0	0.0	1.5	1.5	50.0	0.0	0.0

Table A-1 (continued)

Sample Number	Bryozoans	Pelmatozoans	Other Fossil Groups	Intraclasts	Micrite	Fringe Cement	Drusy/Bladed Cement	Syntaxial Overgrowths	Radiaxial Cement	Microspar/Pseudospar/ Neomorphic Spar	Dolomite
A-72	23.5	7.0	3.5	0.5	0.0	0.0	0.5	13.0	51.0	0.0	0.0
A-84	40.0	25.0	3.5	0.0	0.0	0.0	0.0	22.0	8.5	0.0	0.0
A-93	24.5	14.0	1.5	0.0	0.0	1.0	2.0	37.5	16.0	0.0	0.0
A-99	33.5	10.0	1.0	0.0	0.0	0.0	0.5	17.0	37.0	0.0	0.5
A-105	27.5	9.0	1.5	0.5	0.0	0.0	0.5	6.0	55.5	0.0	0.0
A-112	31.5	18.0	4.5	0.0	0.0	0.5	1.5	19.0	22.5	0.5	2.5
A-115	27.0	13.0	2.5	0.0	20.0	0.0	0.0	37.5	0.0	0.0	0.0
A-116	25.0	21.5	5.0	0.0	22.0	2.0	1.0	24.0	0.0	0.0	0.0
A-123	27.0	18.0	3.0	0.0	10.5	1.0	11.0	19.5	0.0	0.0	1.0
A-124	31.5	24.5	4.0	0.5	11.5	0.0	7.0	16.5	0.0	0.0	0.5
A-132	31.0	34.0	4.0	0.0	0.5	2.5	1.5	18.5	4.5	0.0	0.0
A-142	30.0	16.0	3.0	0.0	1.5	0.0	4.5	14.0	31.0	0.5	0.0
A-150	27.0	16.0	7.0	0.0	0.0	1.0	0.0	7.5	37.0	0.0	0.5
A-151	37.0	7.0	2.5	0.0	31.5	2.5	8.0	6.5	2.5	0.0	0.0
A-156	36.5	12.5	2.5	1.0	6.0	0.0	2.5	18.5	14.5	0.0	0.0
A-157	29.0	4.0	3.0	0.0	25.5	0.0	1.0	2.0	35.0	0.0	0.0
A-165	29.0	7.5	0.5	0.0	11.0	0.0	1.5	8.5	41.5	0.0	0.0

APPENDIX B
INSOLUBLE RESIDUES

INSOLUBLE RESIDUES

In this study, the insoluble residue was weighed but no more detailed identification was carried out. Previous workers have examined and identified components of the insoluble residue of the Holston, among them, Dale (1924), Ayrs (1933) and Metcalf (1974). A summary of minerals positively identified by these authors from the Holston Formation insoluble residue are as follows:

- collophanite
- dolomite
- feldspar (plagioclase)
- hematite
- pyrite
- rhodochrosite
- quartz
- limonite
- magnetite
- chloritic clay
- kaolinite
- garnet
- muscovite
- biotite
- hornblende
- carbonaceous matter
- clays

APPENDIX C

ATOMIC ABSORPTION SAMPLE PREPARATION

ATOMIC ABSORPTION SAMPLE PREPARATION

Sample Choice

Recognizing that the rock chips that have been sawn off the thin sections as the closest similar or representative sample of that thin section, the author aimed for a uniform representation of the "whole rock" (actually the soluble carbonate fraction) by using the four corners or strips of the rock chip to prepare a sample. Various components were also isolated if there seemed to be enough to constitute a sample. These various components were; bryozoan, radiaxial cement and drusy spar. Thin sections match all samples with one exception.

Methods

The Felker saw was used to trim several small "chips" of the rock. The chips were polished with grit to remove saw contamination. These chips were rinsed in tap water, air-dried and rinsed again in deionized water. The author wore disposable-type plastic gloves to prevent contamination. Storage was in small glass bottles with tight caps.

Each sample was then ground to a fine powder with a ceramic mortar and pestle. After each grinding the mortar and pestle was washed with a cleaning solution of $\text{HCL}:\text{HNO}_3:\text{H}_2\text{O}$ in a ratio of 12:4:9, respectively. This was followed by a 25% volume/volume (1 part glacial acetic acid to 3 parts water) acetic acid rinse. By alternating two mortars and pestles, each was given at least 15 minutes to air-dry between usage.

The total sample weight for each rock before dissolution was 1.25 grams. This sample was randomly chosen from the total ground

sample by inserting a spatula to the bottom of the vial. It was weighed to the nearest .0001 gram using the Mettler balance. This sample was then put into solution with 50 milliliters acetic acid (25% volume/volume) and allowed to digest for 12 hours. After filtering, additional dilute acetic acid was used to wash insoluble residue from the beaker into the filter.

After the solution had completely filtered through, a quick "spray" of acetic acid was used to wash through any final soluble ions. At this point, if the solution appeared free from insoluble residue, it was then brought up to a volume of 100 milliliters by adding acetic acid (25% volume/volume). If a very fine insoluble residue still remained after the initial filtering then the solution was filtered again.

The oven-dried filters were then weighed in the Mettler balance to the nearest .0001 gram and weight of the filters subtracted, leaving the balance of insoluble residue and amount in solution. Four samples were prepared in triplicate as well as two blanks (composed of 25% volume/volume acetic acid) plus 2000 ppm KNO_3 (if this was added to the sample solution) to act as checks on the consistency of data generated. The total of 50 samples is divided as follows; 41 "whole rock" samples (includes triplicates), 7 samples of various components and 2 blanks.

Control Data

While running the atomic absorption analysis, several types of controls were used to define the precision of the data. The first type of control was to run a standard or blank after every third sample.

This was done to insure accurate calibration of the instrument. The standards were tested periodically for accuracy.

A second type of control was to re-analyze the original solution at a later time. Samples were picked from throughout the range of standards in order to insure precision at all parts of the range. This procedure tested the precision or repeatability of the instrument. These reruns are so labeled.

Sets consisting of three samples that were made up from one powdered sample were put into solution using identical techniques. These are labeled by -1, -2 or -3 at the end of the sample label. Such samples allowed the determination of precision of the solution preparation procedures and this author's ability in running the analysis.

Results are summarized in Table C-1.

Table C-1. Samples that were analyzed more than once

SAMPLE	ORIGINAL	RERUN
<u>Fe</u>		
M-1	680	653
M-4-a	6840	6371
M-5-a	6806	6192
O-a-19-1	2122	2267
A-40-1	227	
A-40-2	227	
A-40-3	252	
A-99-1	167	
A-99-2	170	
A-99-3	203	
A-116	727	734
A-156-1	405	422
A-156-2	409	411
A-156-3	398	388
A-157-1	592	578
A-157-2	478	478
A-157-3	493	475
<u>Sr</u>		
M-1	271	258
M-4-a	437	423
M-5-a	408	425
O-b-14-1	300	280
A-62	417	413
A-99-1	284	275
A-99-2	280	266
A-99-3	284	266
A-150	223	222
A-156-1	312	305
A-156-2	296	286
A-156-3	290	279
A-157-1	297	
A-157-2	253	
A-157-3	260	

Table C-1 (continued)

SAMPLE	ORIGINAL	RERUN
<u>Na</u>		
M-1	128	126
M-4-a	80	77
A-40-1	128	
A-40-2	127	
A-40-3	129	
A-62	126	127
A-99-1	115	113
A-99-2	116	113
A-99-3	117	115
A-112	73	68
A-116	88	83
A-132-1	120	119
A-150	140	139
A-156-1	127	122
A-156-2	110	109
A-156-3	110	109
A-157-1	139	
A-157-2	109	
A-157-3	116	
<u>Mg</u>		
M-1	1485	1520
O-a-19-2	3383	3587
A-30	2262	2249
A-40-1	2007	2099
A-40-2	2069	2146
A-40-3	2118	2223
A-99-1	2066	
A-99-2	2090	
A-99-3	2070	
A-124	2072	2165
A-156-1	2925	2986
A-156-2	2907	2763
A-156-3	2832	2748

Table C-1 (continued)

SAMPLE	ORIGINAL	RERUN
A-157-1	3765	2400
A-157-2	3722	2140
A-157-3	3651	
Mn		
M-4-a	2322	
M-5-a	2079	
A-40-1	181	
A-40-2	188	
A-40-3	188	
A-62	363	392
A-72-1	175	169
A-84-1	244	249
A-99-1	147	
A-99-2	146	
A-99-3	145	
A-112	377	409
A-156-1	228	
A-156-2	214	
A-156-3	217	
A-157-1	290	282
A-157-2	264	258
A-157-3	263	262
A-165	634	632

APPENDIX D
SPEARMAN CORRELATION CO-EFFICIENTS

SPEARMAN CORRELATION CO-EFFICIENTS

	Mg	Mn	Fe	Na	Sr
Mg	1.00	0.41	0.19	0.16	0.35
Mn		1.00	0.84	-0.14	0.34
Fe			1.00	-0.27	0.14
Na				1.00	0.40
Sr					1.00

APPENDIX E

LIST OF EQUIVALENT TERMS USED
IN DESCRIPTION OF CEMENT

LIST OF EQUIVALENT TERMS USED
IN DESCRIPTION OF CEMENT

Two Generations of Cement

(Cement = Spar = Sparite)

I. Marine

- A. syntaxial cement: syntaxial overgrowths, echinoderm syntaxial overgrowth, echinoderm syntaxial cement, syntaxial rim cement.
- B. micritic cement: has a likely predecessor of "high-magnesium calcite micrite" or "micrite high-magnesium cement".
- C. fringe cement: fringing cement, fringing bladed cement, bladed fringe cement, fibrous fringe cement, fringe cement with syntaxial extinction, fringe cement with non-syntaxial extinction, polycrystalline fringing cement, prism fringes, fibrous cement.

II. Meteoric or Freshwater

- A. drusy sparite - drusy spar, drusy calcite spar, blocky drusy sparite, equant drusy sparite, clear drusy sparite, blocky sparite.
- B. neomorphic cement - neomorphic spar, neomorphic sparite, neomorphic mosaic, neomorphic spar mosaic.
- C. radiaxial cement - radiaxial sparite, radiaxial spar, radiaxial-fibrous mosaic, radial-fibrous spar (the last two terms refer to the likely marine predecessor of "radiaxial cement"; the term "radial-fibrous predecessor" is included in the term

"fringe cement" in Figures 3.2, 3.3 and 3.8, for the sake of brevity. In Figure 5.1, the term radial-fibrous predecessor is listed separately).

VITA

Mary Margaret McGill was born in Fort Dodge, Iowa. She attended elementary school in Fort Dodge, Iowa and was graduated from St. Edmond High School in 1974. The following August she entered University of Iowa. In December, 1978, she received a Bachelor of Science degree in Geology.

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