Thomas V. Danahy. Petrology, depositional environment, and diagenesis of the Hillsdale Limestone (Mississippian, Meramecian) in Washington County, Virginia. (Under the direction of Dr. Donald W. Neal) Department of Geology, December 3, 1986.

The Mississippian (Meramecian) Hillsdale Limestone consists of gray, medium-bedded to massive, cherty skeletal wackestone with minor interbedded lime mudstones, packstones, grainstones, and terrigenous siltones and shales. It was deposited during a transgressive onlapping of the underlying Little Valley Limestone, allowing for the development of a homoclinal carbonate ramp with a discontinuous offshore shoal sequence. The Hillsdale Limestone is approximately 90 meters thick in the study area, which is located in the Greendale Syncline in Washington County, Virginia. Petrographic point count data, measured outcrop sections, stable isotopic data, and trace element data were used for depositional and diagenetic interpretations.

Four lithofacies are recognized: (1) shallow-subtidal siliciclastics, (2) lagoonal pelloidal wackestones and lime mudstones, (3) shoal ooid and echinoid grainstones, and (4) outer ramp skeletal packstones and wackestones. The outer ramp facies is the most abundant facies, accounting for 73.9% (204.5m) of the total combined stratigraphic thickness (276.9m). Skeletal wackestones are the most abundant lithology. A total of four shallowing-upward sequences can be recognized in the Hillsdale Limestone.

Petrographic evidence indicates a complex diagenetic history.

Early diagenetic events include: micritization and pyritization in stagnant marine environments in stagnant marine environments, and isopachous rim cementation and hematite formation in active marine environments. Localized meteoric-vadose environments resulted in limited formation of a meniscus cement. With encroachment of meteoric groundwater, the presence of a mixing zone resulted in dolomitization. With establishment of freshwater conditions, the meteoric-phreatic environment resulted in aragonite leaching, magnesium calcite stabilization, microspar formation, sytaxial cementation, blocky and drusy pore-filling cementation, and calcification. Compaction, sutured grains, stylolitization, and fracturing occurred throughout the burial of the Hillsdale Limestone. Textural relationships of pore-filling silica cements (within a rugose horn coral) indicate silicification occurred after dolomitization and before calcification. This indicates that this silicification occurred in the meteoric-phreatic environment. The diagenetic origin of chert nodules in the Hillsdale Limestone is indicated by the partial replacement of fossils within the chert nodules. Trace element and stable isotopic data of selected fossils indicate that brachiopods underwent only minor alteration in a partially closed system. Since brachiopods secret their shell in isotopic equilibrium with seawater, the good chemical preservation of the brachiopods allows for an estimate of the stable isotopic composition of Meramecian seawater. Comparison of the oxygen isotopic ratios of the brachiopod and silica cement indicates that silicification may have occurred in isotopically light (-6.5 SMOW) meteoric-phreatic waters.

PETROLOGY, DEPOSITIONAL ENVIRONMENT, AND DIAGENESIS OF THE HILLSDALE LIMESTONE (MISSISSIPPIAN, MERAMECIAN) IN WASHINGTON COUNTY, VIRGINIA

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Thomas V. Danahy

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AND DIAGENESIS OF THE HILLSDALE LIMESTONE
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INTRODUCTION

The Hillsdale Limestone of the Greenbrier Group is a siliceous limestone of Late Mississippian (Meramecian) age. Northeast striking outcrop belts of the formation are located in West Virginia and southwestern Virginia (Figure 1). The Hillsdale has been correlated with the St. Louis Limestone and possibly the lower Ste. Genevieve of the Mississippi Embayment (Slagle, 1978). The Hillsdale Limestone has thin to massive beds consisting of a medium to dark gray, cherty skeletal wackestone with interbedded skeletal packstones and minor grainstones, ooid grainstones, lime mudstones, and terrigenous siltstones and shales. A previous study of the depositional environment of the Greenbrier Group (Blancher, 1974) discussed the possible origins of the dark gray nodular chert present in the Hillsdale Limestone. No adequate explanation was given and, thus, the origin of the silica remains problematic. No detailed geochemical study has been conducted on the Hillsdale Limestone. The purpose of this petrographic and geochemical study of the Hillsdale Limestone is to better understand the diagenesis of this formation and the formation of the chert.

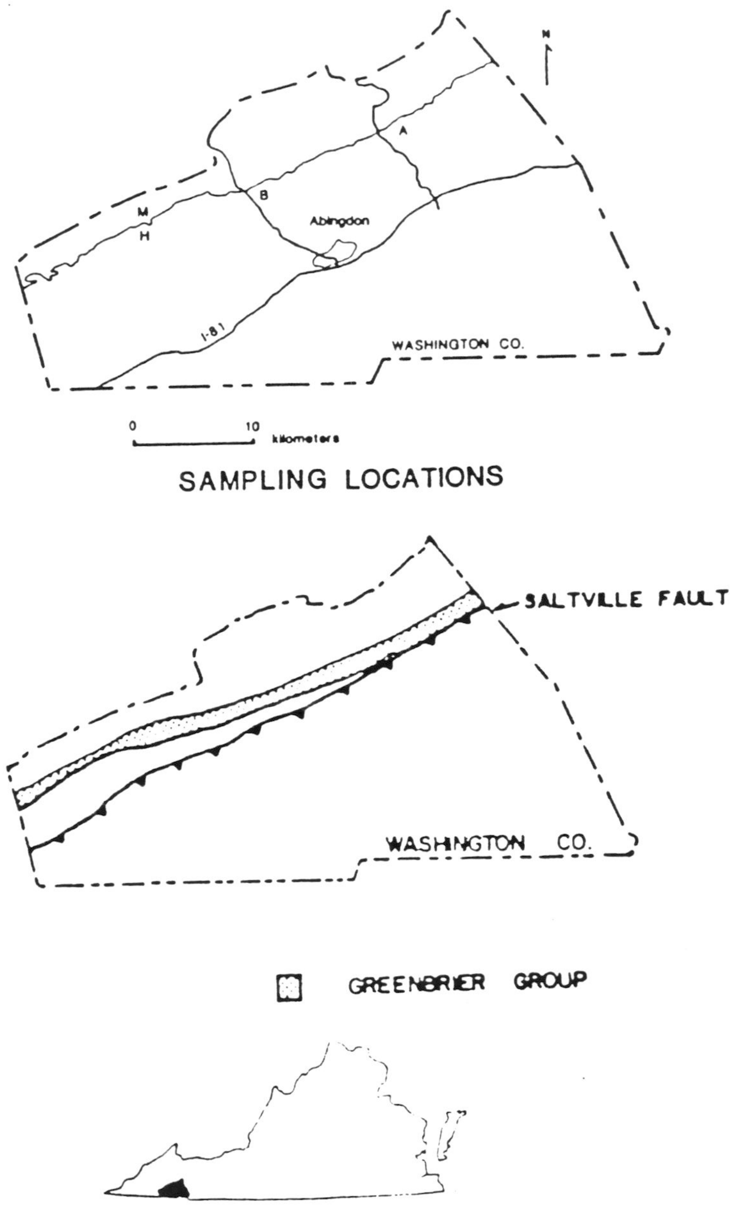


Figure 1. Sampling locations and outcrop belt.
A - Hayter's Gap Section.
B - Holston Section.
M - Horseshoe Bend Section.
H - Muddy Hollow Section.

PREVIOUS WORKS

Type Locality and Correlation

Reger (1926) named the Hillsdale Limestone for 15.2 meters of black, chert-bearing, fossiliferous limestone on the west limb of the Hillsdale anticline, east of Hillsdale, Monroe County, West Virginia. Butts (1940) correlated similar strata in the Appalachian basin with the St. Louis Limestone of the type Mississippian section of the mid-continent region. Cooper (1944) preferred the use of Hillsdale, rather than St. Louis as used by Butts (1940), for this strata in the Appalachian basin because the rock units are not contiguous with the St. Louis Limestone of the mid-continent region. Bartlett and Webb (1971) used the Hillsdale Limestone to designate strata in the Greendale Syncline, which is the location of this study (Figure 1). Slagle (1978) studied the paleontology and the paleoecology of two of the four stratigraphic sections located just north of Abingdon ("A" and "B" in Figure 1). He concluded that the Hillsdale Limestone is equivalent to the St. Louis Limestone and possibly the lower Ste. Genevieve Limestone of the type Mississippian section of the mid-continent region. Due to local variations in lithologic characteristics, the St. Louis Limestone in eastern Tennessee has recently been renamed and subdivided by Brent (1982). The St. Louis is correlated with the lower Clifton Creek Limestone, the Snow Flake Formation, and the upper Laurel Branch Limestone of Tennessee (Brent, 1982).

Several studies have focused on the Hurricane Ridge Syncline along the border of Virginia and West Virginia. Blancher (1974) did a regional study of the depositional environments of the Greenbrier Group in the Hurricane Ridge Syncline. Mississippian conodont biostratigraphy of the Hurricane Ridge Syncline was done by Chaplin (1984). Numerous studies of the regional geology near the study area have been performed by various workers (Bartlett and Webb, 1971; Butts, 1917, Cooper, 1966; Craig and Connor, 1979; Craig and Varnes, 1979; Ettensohn et al., 1984; Wipolt and Marden, 1949).

Economic Potential

Butts (1927) reported on the potential for oil and gas production near Early Grove in Scott County, Virginia. In 1938, commercial volumes of natural gas were produced from Carboniferous rocks in Virginia. Initial production was from sandy zones in the Little Valley Limestone of the Early Grove gas field of Scott and Washington Counties, Virginia (Averitt, 1941). Regionally, gas production also has been obtained from the Price Formation (Figure 2). Le Van (1962, 1981) reported on oil and gas wells drilled in Virginia. In southern West Virginia, localized evaporitic and oolitic units within the lower Greenbrier Group have produced gas and oil (Youse, 1964, p. 465-486). Although freshly broken samples have a distinct petroliferous odor, the Hillsdale Limestone is not a hydrocarbon producer due to lack of significant porosity.

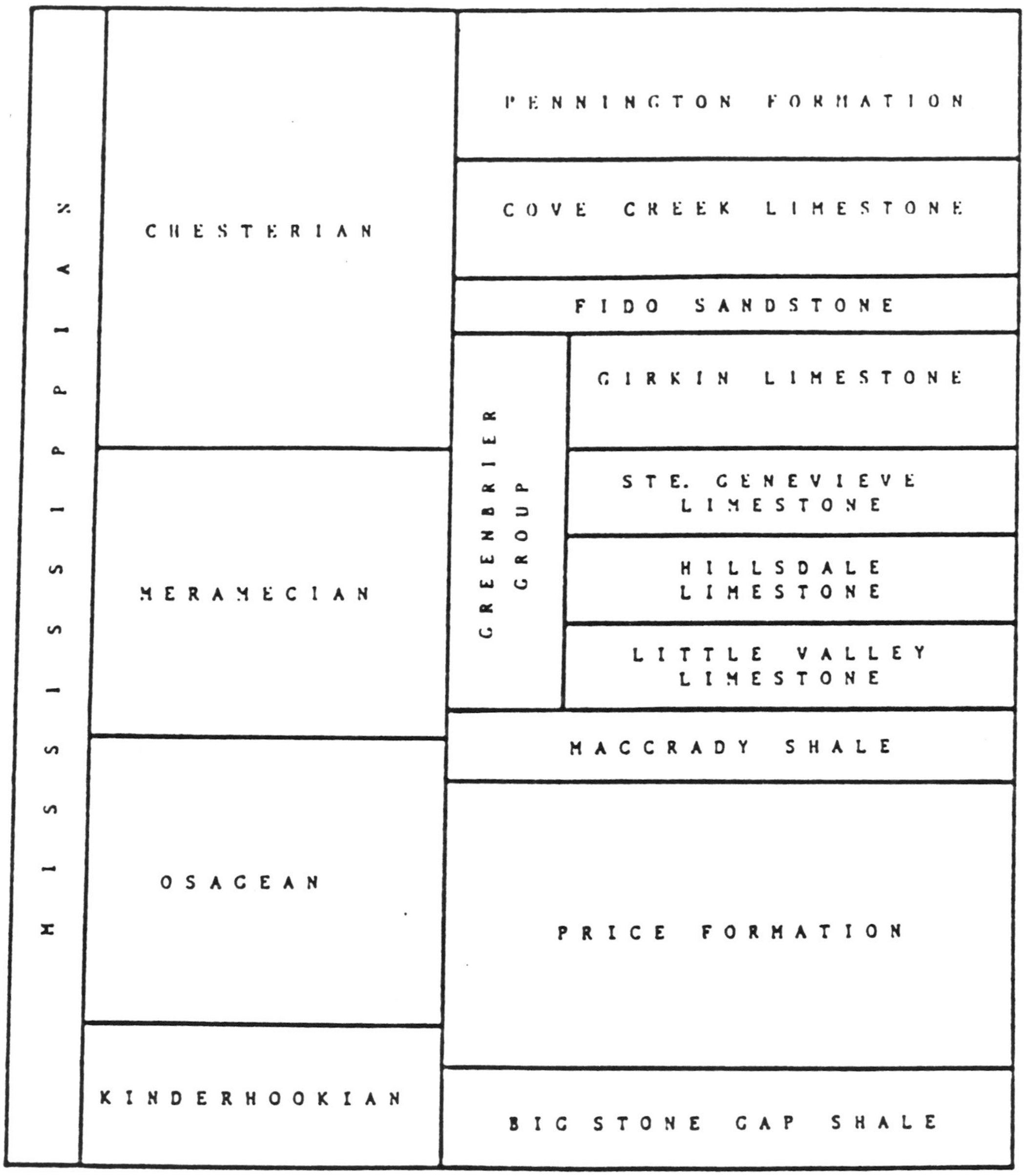


Figure 2. Mississippian stratigraphy of the Greendale Syncline.

The Greenbrier Group has been a principal source of crushed stone. It has been quarried at several localities for roadstone and concrete aggregate (Englund, 1979).

OBJECTIVES

The four main objectives of this study are: 1) to identify the lithofacies present and to interpret depositional environments for these lithofacies; 2) to characterize the major and trace element content for selected macrofossils; 3) to characterize the carbon and oxygen isotope content for selected macrofossils, and; 4) to derive the possible diagenetic sequences that are supported by these data.

METHODS

Four outcrop sections were measured and sampled. This study involved the description of 75 hand samples and 80 thin sections. Point counting (300 points per slide) of 55 representative thin sections was performed. Thin sections from each sample were stained with a solution of alizarin red S and potassium ferricyanide. Using this method, calcite stains red, ferroan calcite stains muave to purple, ferroan dolomite and ankerite stain turquoise to blue, and dolomite does not stain (Evamy, 1969).

For the purpose of point counting, materials less than approximately 0.005mm were classified as matrix. Terrigenous clays and microcrystalline calcite are the dominant matrix materials. The staining technique described above allowed this distinction to be made in thin-section (micrite stains red, clays do not stain). Due to the small size and occassional coexistance of these two matrix constituents, insoluble residue analysis proved useful.

Sampling

The study area is located in Washington County of southwestern Virginia (Fig. 1) within the Valley and Ridge Physiographic Province. All sections sampled are less than 1 km from the North Fork of the Holston River which flows to the southwest through the study area. The sections are located on the northwest limb of the southwest plunging Greendale Syncline. Each section is designated by a letter and samples are labeled with the letter of the section followed by a number. Sample numbers increase numerically up-section. The first section (A in Fig. 1) is located northeast of Abingdon, the county seat. Virginia Route 80 exposes a section 89.6m in stratigraphic thickness. It is located in the Hayters Gap 7.5 minute Quadrangle, and it will be referred to as the Hayters Gap section. The lower part of the overlying Ste. Genevieve was also sampled at this section. The second section, the Holston section, is located approximately 10 km northwest of Abingdon (B in Fig. 1). The roadcut of U.S. Highway 19 (Alternate 58) results in an exposure of the Hillsdale Limestone that has a stratigraphic thickness of 96.8m. The third section, the Horseshoe Bend section (M in Fig. 1), is located in the Wallace 7.5 minute Quadrangle. The section is exposed along the North Fork of the Holston River in the middle of Horseshoe Bend, a horseshoe-shaped meander. An incomplete fourth section, the East Muddy Hollow section (H in Fig. 1), exposes the upper part of the Hillsdale along hillslopes approximately 300 meters west of Horseshoe Bend. These sections were sampled at approximately 9m intervals. The sampling interval was altered depending on lithologic variation and accessibility.

Insoluble Residue Analysis

The insoluble residue content of twenty-six (26) samples was determined by placing a crushed sample of known weight (approximately 25 grams) in a beaker with concentrated hydrochloric acid until digestion was complete. The remaining acid insoluble residue was collected by filtering, oven dried and weighed. The insoluble residue weight divided by the original weight multiplied by one hundred (100) gives the insoluble percent of the sample (Appendix A).

Chemical Analysis

Major and trace element analyses were performed on selected fossils. Stable isotope analysis of fossils and chert cement was also conducted. For further description of chemical analyses, the reader is referred to the section on chemical diagenesis.

STRATIGRAPHY AND DISTRIBUTION

Local Distribution

The stratigraphic section of the Greendale Syncline is one of the most complete Mississippian sections in North America (Fig. 2). Within the Greendale Syncline, the Hillsdale is present from the Tennessee line north to Cedar Branch, about one mile northeast of Saltville. Slightly west of Cedar Branch, the outcrop is found along the axis of the syncline, which plunges to the southwest, and continues southwest along the southeast limb of the syncline until it is terminated by the Saltville Thrust Fault near Blackwell in Washington County (Fig. 1; Butts 1940). Blancher (1974) indicates that the Greenbrier Group in the Greendale Syncline consists of, in ascending order: the Little Valley Limestone, the Hillsdale Limestone, the Ste. Genevieve Limestone, and the Gasper Limestone (Figure 2). In order to simplify regional terminology, the Gasper Limestone has since been renamed the Girkin Limestone (de Witt and McGrew, 1979).

Hillsdale Contacts

The lower contact of the Hillsdale with the Little Valley

Limestone is conformable and it is easily recognized by a distinct lithologic change. The fine-grained black shale beds of the upper Little Valley Limestone interfinger, within a short interval, with the massive- to thick-bedded, light gray cherty limestone of the Hillsdale. The contact was placed at the top of the uppermost shale bed of the Little Valley Limestone. The upper contact of the Hillsdale with the Ste. Genevieve is a conformable biostratigraphic contact that is not always lithologically distinctive. The lowermost abundant occurrence of the Ste. Genevieve guide fossil *Platycrinities huntsvillae* Troost (= *Platycrinus penicillius* Meek and Worthen) defines the location of the upper contact of the Hillsdale Limestone. Transverse sections of the columnals of this crinoid have an elliptical football-like shape with radiating spines projecting outward along the perimeter. The use of any guide fossil to locate a formational contact is of limited value due to possible reworking or inconsistent distribution of the fossil due to environmental restrictions. Fortunately, in the study area, the upper contact of the Hillsdale usually coincides with the top of a siltstone unit that has shaly weathering.

Timing of Maximum Transgression

For the Appalachian Basin in general, the maximum of the Meramecian transgression occurred during St. Louis time when northeast Kentucky and central Ohio were inundated (de Witt and McGrew, 1979).

In the study area, the Hillsdale lithologies suggest depositional environments that in general represent deeper water conditions than both the underlying Little Valley Limestone and the overlying Ste. Genevieve Limestone. The Hillsdale Limestone has a greater distribution than the underlying Little Valley Limestone. Thus, the deeper water depositional environment and the greater areal extent of the Hillsdale Limestone suggests a transgressive overstepping of the argillaceous Little Valley Limestone. The subsequent offlap is represented by the silty units of the upper Hillsdale and Ste. Genevieve Limestone. Echinoderm grainstones within the upper Hillsdale, and more commomly within the Ste. Genevieve, represent an offshore barrier bar facies deposited above normal wave base (Bedell, 1986).

Insoluble Residue Content

The stratigraphic column for the Holston section illustrates the relationship between major lithologies and the percent insolubles (Fig. 3). Low insoluble content suggests that the majority of the Hillsdale Limestone represents accumulation of relatively pure carbonate sediment. Diagenesis can alter the insoluble content of rocks and invalidate such interpretations. However, this interpretation of the insoluble residue content is valid because the same trend of low insolubles in the middle of the Holston section exists even when considering the percentage of insolubles due to

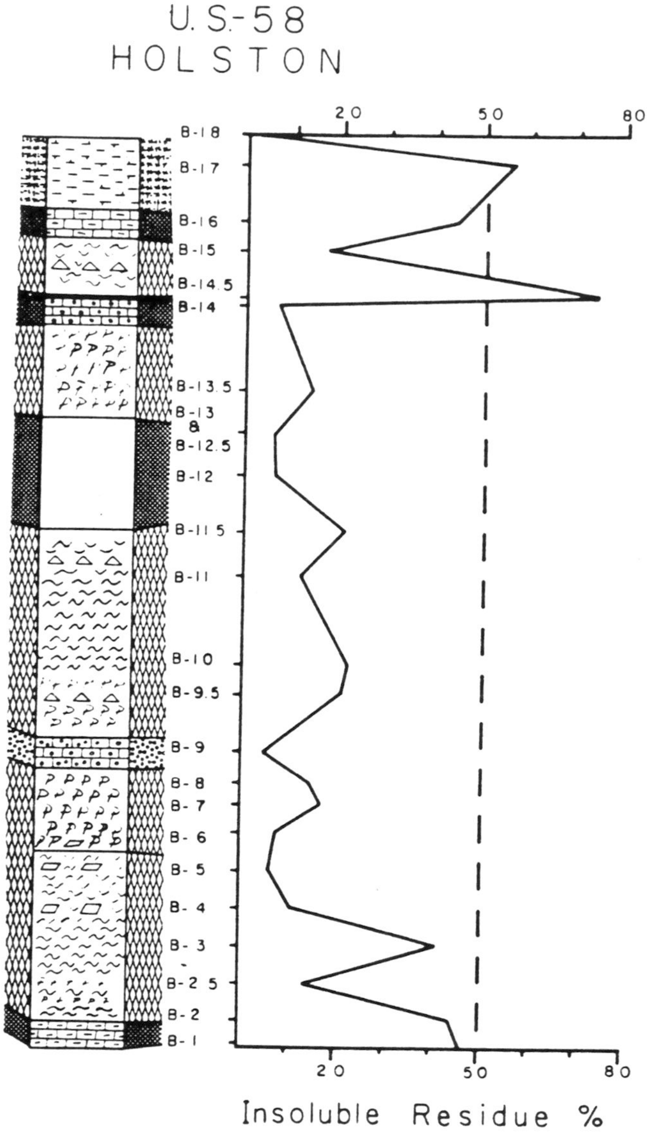


Figure 3. Percent insolubles for the Holston section. (less than 50% insolubles = carbonate rock)

silicification (ie. 0-5% silcification by volume). This apparent trend may also be due to a lateral change in environment (ie. inlet or channel shift), or it may be due to a change in sedimentation rates. However, considering the timing of transgression discussed above, this trend could indicate a greater degree of isolation from terrigenous input during the deposition of the middle Hillsdale representing a more offshore depositional environment due to transgression. Thus, the stratigraphic variation of insoluble residue percentages for the Holston section appears to corroborate that the peak of the basin-wide transgression occurred in middle Hillsdale time. The vertical distribution of lithofacies in the Hillsdale Limestone can be viewed as a series of shallowing-upward sequences. These sequences will be discussed later in the section dealing with the evolution of the depositional environment.

Regional Distribution

The biostratigraphic upper contact of the Hillsdale cannot be adequetely placed on subsurface well-logs. In the study area, relatively shaly intervals at the top of the Little Valley and at the top of the Hillsdale Limestone allow for an approximate location of the Hillsdale contacts on well-logs. In the subsurface, strata equivalent to the Hillsdale Limestone and Ste. Genevieve are included within the well drillers' Big Lime of eastern Kentucky, southwestern Virginia, and most of West Virginia (de Witt and McGrew, 1979).

Regionally, the thickness of the Hillsdale Limestone is only known from measured outcrop sections that allow for good paleontologic control. The maximum thickness of the Hillsdale (96.8m) occurs in the study area on U.S. 19/ Alt 58. From this location, the Hillsdale thins in all directions. Presumably, the thining is greatest on the paleoshelf margin towards the east and southeast. However, no estimate of the rate of thining can be made due to insufficent data. To the west, Butts (1940) reported thicknesses of 1.5 to 6.1 meters of St. Louis along the Cumberland escarpment from Cumberland Gap to Big Stone Gap. The Hillsdale (St. Louis) thins more gradually to the north of the study area, 35m of St. Louis (Butts, 1940) is found at Richlands in Tazewell County, Virginia. Further to the north in West Virginia, the Hillsdale terminates near the town of Marlington, in northern Pocahontas County (Wells, 1950). The Hillsdale also pinches out just south of the 38th Parallel Lineament in Randolph County, West Virginia. Yielding (1984) suggested that this was an erosional pinchout, possibly due to a basement fault with roughly an E-W trend.

GEOLOGIC SETTING

Appalachian Basin

The southeastward-thickening wedge of Mississippian rocks in the Appalachian basin (Fig. 4) obtain a maximum thickness of over 7,000 feet (Englund, 1979). The tectonic framework of the basin

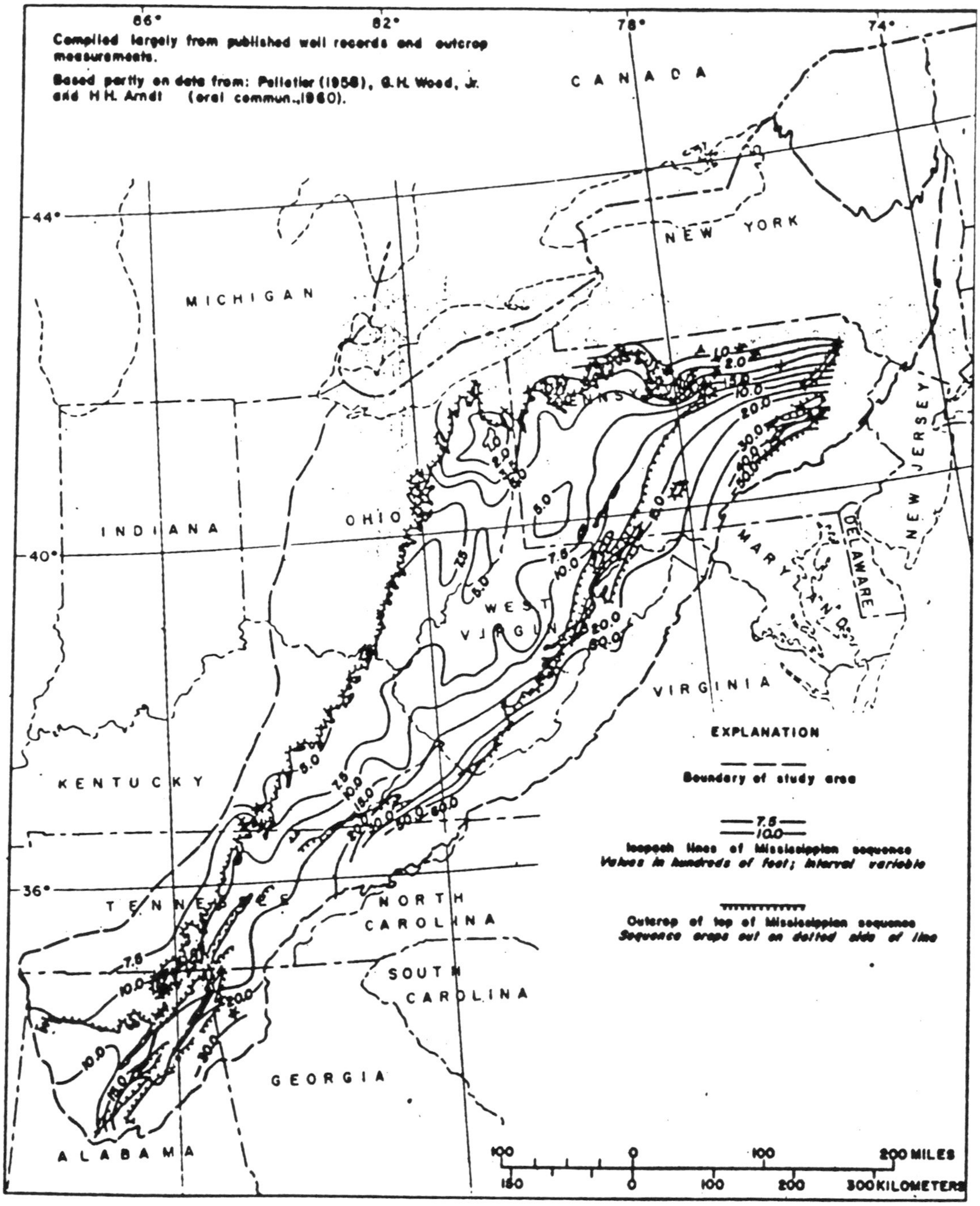


Figure 4. Isopach Map of the Mississippian sequence in the Appalachian Basin (after Colton, 1970).

during Mississippian time was inherited with little change from the Devonian. The eastern part of the Appalachian basin was composed of an arcuately elongate geosynclinal segment extending from eastern Pennsylvania to northern Mississippi (Fig. 4). Maximum subsidence occurred in the southeastern part of the basin where the thickest accumulation of sediments are found. The slightly smaller western part consisted of a subparallel unstable shelf segment (de Witt, and McGrew, 1979). The paleogeography for Late Meramecian time, which includes the time of Hillsdale deposition, is shown in Figure 5.

Structure

The strata of the northwest limb of the Greendale Syncline dip 25-30 degrees to the southeast. The southeast limb of the syncline is overturned and mostly covered by the Saltville Thrust Sheet which is composed of Cambro-Ordovician carbonates. In order to reconstruct the original position of the units before faulting and folding (ie. palinspastic reconstruction), thrust sheets must be moved to the southeast 25-65 miles (Dennison and Woodard, 1963). Palinspastic reconstruction also suggests that current Southwest-Northeast striking trends , such as the Greendale Syncline (Fig. 1), were originally more North-South. This pivoting of strike trends implies that the sections sampled in this study represent a cross-section which nearly parallels the paleoshoreline (Fig. 5).

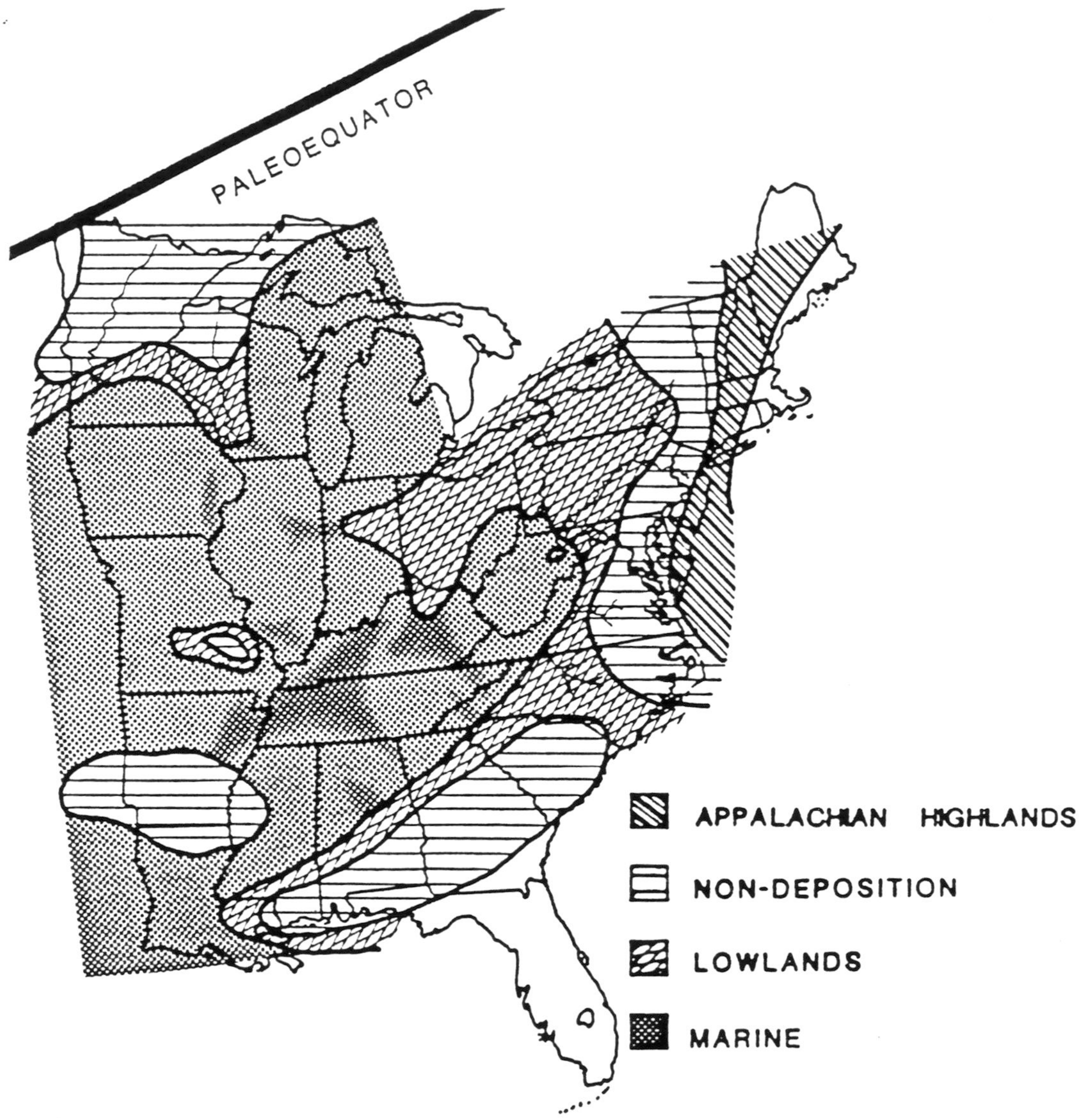


Figure 5. Meramecian Paleogeography
(modified after de Witt & McGrew, 1979).

Timing of Tectonic Events

During Mississipian time, slight warping occurred in areas of West Virginia (Cooper, 1961; Thomas, 1966), along the Waverly arch in Kentucky (Englund, 1972), and along the Greendale Syncline in Virginia (Cooper, 1964). However, evidence for folding in Virginia during Hillsdale time is inconclusive. Localized downwarping is suggested by thicker sediment accumulations in the Greendale Syncline than in adjacent areas.

The Cincinnati arch was emergent during the early Meramecian (Youse, 1964). With the middle Meramecian (St. Louis) trangression, limited onlapping and marine deposition occurred across the Cincinnati arch. The western margin of the basin, which overlapped the eastern flank of the Cincinnati arch, was uplifted during Early Pennsylvanian time with subsequent erosion truncating Early Pennsylvanian and Late Mississippian strata. During the Appalachian orogeny, from Late Pennsylvanian to Early Permian time, northwest directed compressional forces produced broad folding and thrust faulting in the Valley and Ridge Province.

PETROLOGY

Classification

Carbonate rock samples were classified according to Dunham

(1962). Non-carbonate rocks were classified according to Picard (1971). Some Hillsdale lithologies have a matrix composed of a mixture of carbonate and non-carbonate material. The non-matrix constituents can be categorized into carbonate and non-carbonate constituents. Carbonate constituents are further subdivided into the various allochems. The lithologies and constituents of the Hillsdale Limestone are given in Appendix B - Measured Outcrop Descriptions.

CARBONATE CONSTITUENTS

Interstitial Matrix

The four main constituents of interstitial matrix material in the Hillsdale Limestone are: 1) micrite, 2) sparite, 3) terrigenous clay minerals, and 4) dolomite. Terrigenous clay minerals are discussed under Non-Carbonate Constituents. Dolomite and sparite cements will be discussed under Diagenesis.

Micrite is a term for microcrystalline calcite. Micrite is translucent, appearing brown-gray in thin section, with essentially equant crystals in the 1-4 um range (Folk, 1959). Micrite can be formed by chemical and biological precipitation, abrasion of invertebrate skeletal material, boring activities and decomposition of biogenic hardparts.

Fossils

Algae

Algal laminated limestone nodules and microborings of bioclastics indicate the presence of algae in the Hillsdale Limestone. Oncoids (ie. algal laminated limestone nodules) are easily mistaken for chert nodules in outcrop because chert nodules contain carbonate impurities and both types of nodules will effervesce in a 10% HCl solution. The distinction is only confidently made with stained thin-sections. Occassionaly, chert nodules in the upper part of the Holston section (B in Appendix B) appear to have laminations similar to algal laminations.

Arthropods

Arthropods in the Hillsdale Limestone are represented by rare occurrences of trilobites and ostracodes. Trilobite fragments have characteristic fine prismatic microstructure with "sweeping" extinction, and tangential sections exhibit the characteristic "shepard's crook" shape. Ostracodes, also present in trace amounts, were recognized by their small size, morphology, and thin, homogeneous prismatic wall structure.

Brachiopods

Brachiopods account for a minor pecentage of fossils locally in the Hillsdale Limestone, usually in association with an abundance of echinoderms or bryozoans. Productid and spirifierid brachiopods are present. Productid brachiopods become dominant in slightly fossiliferous (10% allochems) lime mudstones (Sample # B-1 in Appendix B) of the lower Holston section. Whole brachiopods are present, along with fragments of brachiopods. The brachiopod spines of the productids are identified by the presence of a hollow central canal, concentric parallel-laminated inner walls, and radial-laminated outer walls.

Bryozoans

Bryozoans are present in great abundance in the Hillsdale Limestone, and are second in abundance only to echinoderms. They consist primarily of fenetstrate forms, however, branching and encrusting forms are also present. The zoeccia of the fenestrate forms are commonly filled with sparry calcite.

Echinoderms

Echinoderms, recognized by their characteristic unit extinction, are represented by blastoids, echinoids, and crinoids.

All three echinoderms are difficult to distinguish from one another in thin-section; therefore they were all classified as echinoderms. Echinoderms are the most abundant allochem in the Hillsdale Limestone. Occassionally, the echinoderms form encrinites (ie. pure clean echinoderm grainstones with a sparry calcite cement).

Foraminifers

The foraminifers usually occur in minor amounts in the Hillsdale Limestone, becoming dominant in only one sample (M-8 in Appendix B). The chambered tests are commonly filled with spar and the outer walls are usually micritized. Miliolid-type foraminifers are most common, although Globigerinid-type foraminifers are rarely present. *Eostofella sp.* was identified in sample B-7 (Appendix B).

Mollusks

Mollusks are present in minor amounts in skeletal wackestones of the Hillsdale Limestone. The only mollusks identified were bivalves and a few rare gastropods.

Intraclasts

Intraclasts are penecontemporaneously reworked fragments of sedimentary accumulations formed within or on the fringes of the basin of deposition. Present in only minor amounts, intraclasts in the Hillsdale Limestone are rounded to subangular and range in size from 0.6 to 7 mm in diameter.

Ooids

Ooids are spherical to ellipsoidal particles, less than 2mm in diameter, with concentric laminae or radial structure or both. Ooids are usually calcareous and commonly have a distinguishable nucleus. Modern marine ooids are composed of aragonite, however, ancient ooids may have been composed of aragonite, calcite or Mg-calcite (Sandberg, 1975).

Ooids in the Hillsdale range from 0.2 to 2.0 mm in diameter. The ooids are usually well developed with cortex thickness equal to or greater than the nucleus diameter. Occassionally, poorly developed (superficial) ooids are present. Oolitic units in the Hillsdale Limestone usually have a grain-supported framework infilled with sparry calcite cement; thus, these units are classified as ooid grainstones. However, occassionally oolitic units have a micrite or microspar matrix.

Pellets

Pellets are locally abundant in the Hillsdale Limestone. They are spherical micritic aggregates lacking obvious structure and are less than 0.5mm in diameter. Pellets may originate from the fecal matter of burrowing organisms or they may represent small intraclasts formed from the abrasion of lithified micrite. Large spar-filled vertical cavities (ave. diameter 18mm) are interpreted as burrow tubes and are found in association with a pelletal unit of the Hillsdale Limestone, supporting a biogenic origin.

NON-CARBONATE CONSTITUENTS

Quartz

Detrital quartz occurs as angular to subrounded grains ranging in size from fine silt to medium sand. Most quartz grains exhibit straight to moderately undulose extinction and are free of inclusions. Polycrystalline quartz grains are present in the uppermost units of the Hayters Gap Section of the Hillsdale Limestone.

Mica

Muscovite is present in trace amounts in many argillaceous samples. The mica flakes are usually nearly parallel to bedding planes.

Feldspars

Of all the Hillsdale samples studied only one grain of feldspar was identified. This medium sand-sized grain, within a sandy ooid-intraclast packstone (A-12 in Appendix B), was identified by the presence of characteristic plagioclase twinning.

Clay Minerals

Terrigenous clays in the Hillsdale Limestone are dark gray to dark brown; some weather to a green color. These argillaceous units are calcareous to slightly calcareous and fissile. Disseminated pyrite is common. Silt size, angular quartz grains are usually present in abundance forming siltstones.

Terrigenous clays in thin section are distinguished from micrite by staining techiniques. Insoluble residue analysis is also useful in making this distinction. Thin shale units dominantly composed of terrigenous clays are present, but more commonly terrigenous clays form the matrix of siltstone units. Occassionally, both micrite and terrigenous clays are present forming a mixed-composition matrix.

FACIES

INTRODUCTION

The concept of lithofacies implies a lateral change of rock type within a time-stratigraphic unit in response to a change in depositional environment. Such a change may involve depth of water, paleogeographic situation, climatic variations, fluctuations of ocean currents, seasonal tides, and the effects of crustal disturbance and gravitational slumping on sediment masses (Conybeare, 1979). On the basis of point count data, lithologic characteristics and stratigraphic relationships, four facies are recognized within the Hillsdale Limestone (Table 1). They are 1) shallow subtidal facies, 2) lagoonal facies, 3) shoal facies , and 4) outer ramp facies (B in Figure 6). The four measured outcrop sections of the Hillsdale studied were summed yielding 276.9 meters of total stratigraphic section. The thicknesses of each facies present in all four stratigraphic sections were totaled and divided by the total stratigraphic thickness (ie. 276.9 meters) and multiplied by 100 percent to get a percentage of the total stratigraphic section represented by each facies (Table 1).

SHALLOW SUBTIDAL FACIES

The shallow subtidal facies is represented by terrigenous

Stratigraphic thickness(meters)	23.0m	34.2m	15.2m	204.5m	81.9m	122.6m	TOTAL 276.9m
Percent of total	8.3 %	12.4 %	15.5 %	73.9 %	29.6 %	44.3 %	100 %
FACIES	SHALLOW SUBTIDAL	LAGOONAL	SHOAL	OUTER RAMP	(Subdivisions of outer ramp facies)		
Lithology	Siliciclastics	Lime Mudstones	Grainstones	Packstone/ Wackestone	PACKSTONE SUBFACIES	WACKESTONE SUBFACIES	
# in data set	n=9	n=9	n=4	n=33	n=19	n=14	
Constituent	Avg. %	Avg. %	Avg. %	Avg. %	Avg. %	Avg. %	
Micrite	0.0	50.5	0.0	42.1	34.1	53.0	
Sparite	0.0	7.2	16.9	1.4	1.7	1.0	
Microspar	0.0	1.1	0.0	0.0	0.0	0.0	
Matrix	51.2	0.0	0.0	0.0	0.0	0.0	
Dolomite	0.0	0.0	0.0	5.1	2.9	8.2	
Ooids	0.0	8.7	57.8	0.4	0.6	0.0	
Pelloids	0.0	19.1	0.0	0.5	0.1	1.0	
Intraclasts	0.0	0.0	6.75	0.4	0.6	0.1	
Echinoderms	2.3	0.7	16.25	19.4	24.2	12.9	
Brachiopods	1.2	1.4	1.0	4.0	6.3	1.0	
Bryozoans	2.0	0.3	1.0	17.0	19.4	13.7	
Ostracodes	0.0	0.03	0.0	0.04	0.1	0.02	
Calcispheres	0.0	0.0	0.0	0.01	0.0	0.02	
Forams	0.0	0.1	0.0	1.8	2.8	0.42	
Oncolites	0.0	0.0	0.25	4.3	4.9	3.5	
Bivalves-Und.	0.0	0.0	0.0	0.1	0.1	0.0	
Gastropods	0.0	0.0	0.0	0.2	0.0	0.4	
Pelecypods	0.0	0.0	0.0	0.2	0.3	0.02	
Trilobites	0.0	0.0	0.0	trace	trace	0.0	
Coral	trace	0.0	0.0	trace	0.0	trace	
Quartz	43.2	10.7	0.0	2.1	1.9	2.4	
Feldspars	0.0	0.0	0.0	trace	trace	0.0	
Micas	trace	0.0	0.0	trace	trace	trace	
Clays	0.0	0.0	0.0	0.4	0.0	0.8	
Pyrite	trace	0.08	0.0	0.1	trace	0.1	
Hematite	0.0	0.0	0.0	0.2	0.03	0.3	
Glauconite	0.0	0.0	0.0	trace	0.0	trace	
Gypsum	0.0	0.0	0.0	0.02	0.0	0.04	
Unknown	0.0	0.03	0.0	0.1	0.0	0.2	
TOTALS	99.9	99.94	99.95	99.87	100.03	99.12	

Table 1 - Facies Constituents
trace = constituent observed, but not during point count survey

siliciclastics consisting of calcareous quartz siltstones with a micrite and/or terrigenous clay matrix. This facies accounts for 23.0 meters (8.3%) of the total 276.9 meters of stratigraphic thickness. The North Fork of the Holston River has eroded the lower part of the Muddy Hollow section. Measurements on the remaining section, which partly consists of the shallow subtidal facies, yields a calculated percentage higher than the actual percentage of terrigenous siliciclastics. These siltstones display a wide range of bedding forms, from thin laminations (0.5mm-3mm) to thick-bedding; some units have shaly weathering characteristics. The variability of bedding is attributed to the degree of bioturbation. Extensive bioturbation may have caused the obliteration of bedding planes at some locations. Colors vary from dark gray to light brown and greenish-gray. Detrital quartz silt grains range from 9.9 to 85.0 percent of the constituents (ave. 43.2%). The insoluble content of two siliciclastic units analyzed averages at 65.4% insoluble material. Allochems are represented by bioclastic fragments of echinoderms (2.3%), bryozoans (2.0%), and brachiopods (1.2%). One specimen of a rugose horn coral, <u>Heterophrentis sp.</u> , represents only a trace amount of the allochems. Pyrite and hematite are commonly present in trace amounts in most siltstones in the form of framboids, as small opaque grains distributed throughout the matrix, and in wall linings of skeletal fragments. Non-fossiliferous calcareous terrigenous shales are recognized within this facies.

LAGOONAL FACIES

Pelloidal and lime mudstones are the dominant lithologies of the lagoonal facies which accounts for 12.4% of the total stratigraphic section. These mudstones are composed of micrite (50.5%), pelloids (19.1%) and silt-sized quartz grains (10.7%) with minor constituents of ooids (8.7%), brachiopods (1.4%), and trace amounts of other allochems. Bedding is usually well preserved, but bedding thickness varies from thin laminations to medium- and massive-bedding. The thin laminations and the sparse amounts of biota are characteristic of a protected, restricted, low energy environment. Extensive bioturbation resulted in the formation of massive bedding and sparite filled burrows in pelloidal units (B-12, B-12.5, B-13 in Appendix B). This facies is interpreted as having been deposited in a low energy lagoonal environment located on the carbonate ramp and isolated from wave energy by a shoal environment.

SHOAL FACIES

The shoal facies in the Hillsdale Limestone is represented by ooid and echinoderm grainstones. These grainstones account for 15.5% of the total stratigraphic section. Grainstones which lack micritic mud indicate deposition in a high energy environment that effectively winnowed away any mud. The depositional environment of this facies is interpreted as a series of discontinuous offshore shoals above the normal wavebase. Significant wave energy exerted on this bar sequence would have resulted in reworking and migration of this facies.

OUTER RAMP FACIES

The outer ramp facies is the most abundant lithofacies (73.9% of the total stratigrahic thickness). The outer ramp facies is represented by skeletal packestones and wackestones composed of micrite (42.1%), echinoderms (19.4%), bryozoans (17.0%), brachiopods (4.0%), and quartz (2.1%). This facies can be further divided into subfacies of packstones (29.6%) and wackestones (44.3%). Although a greater number of packstones were sampled, skeletal wackestones are the most abundant facies because this subfacies accounts for the greatest stratigraphic thickness (122.6m) in the Hillsdale Limestone. Since the sampling interval was varied with lithologic variability, a sampling bias is responsible for the greater number of packstones samples. Wackestones are usually fairly uniform in outcrop, whereas packstones commonly are interbedded with adjacent facies. The increased lithologic variability near packstones required a smaller sampling interval.

Bryozoans are the most abundant allochem in wackestones (13.7%) and echinoderms are the most abundant allochem in packestones (24.2%). These observations are due to both 1) the original ecological populations, and more importantly, 2) post-mortem transport (ie. sorting and durability) of these fossils. Echinoderms are larger in size and more resistant to abrasion and they accumulate in higher energy environments (ie. packstones and grainstones). An oncolitic wackestone (B-11.5 in Appendix B) in the Holston section has (40%) algal laminated nodules (0.5 to 4.5cm) within micritic matrix (40%). Interruption and deformation of bedding planes by these oncoids indicates detrital reworking of these algal nodules with final deposition in a relatively low energy facies.

DEPOSITIONAL ENVIRONMENT

Stratigraphic and lithologic data were analyzed to derive a depositional environment for the Hillsdale Limestone. The lithofacies identified in the Hillsdale Limestone are interpreted as having been deposited on a homoclinal carbonate ramp with minor ooid-echinoderm shoals (depths up to approximately 5 meters), with most depositon below normal wavebase (ie. greater than 5-20 meters water depth). Homoclinal ramps have uniform, gentle slope (generally less than one degree) into the basin (Read, 1985).

Starting from the nearshore environment, the depositional environments and the associated lithofacies are summarized below and illustrated in Figure 6B. The shallow subtidal facies reflects nearshore terrigenous input of siliciclastics. The siliciclastics are commonly interbedded with pelloidal and silty lime mudstones of the lagoonal environment. The lagoonal facies were probally deposited in areas protected from wave energy by shoal sequences which formed

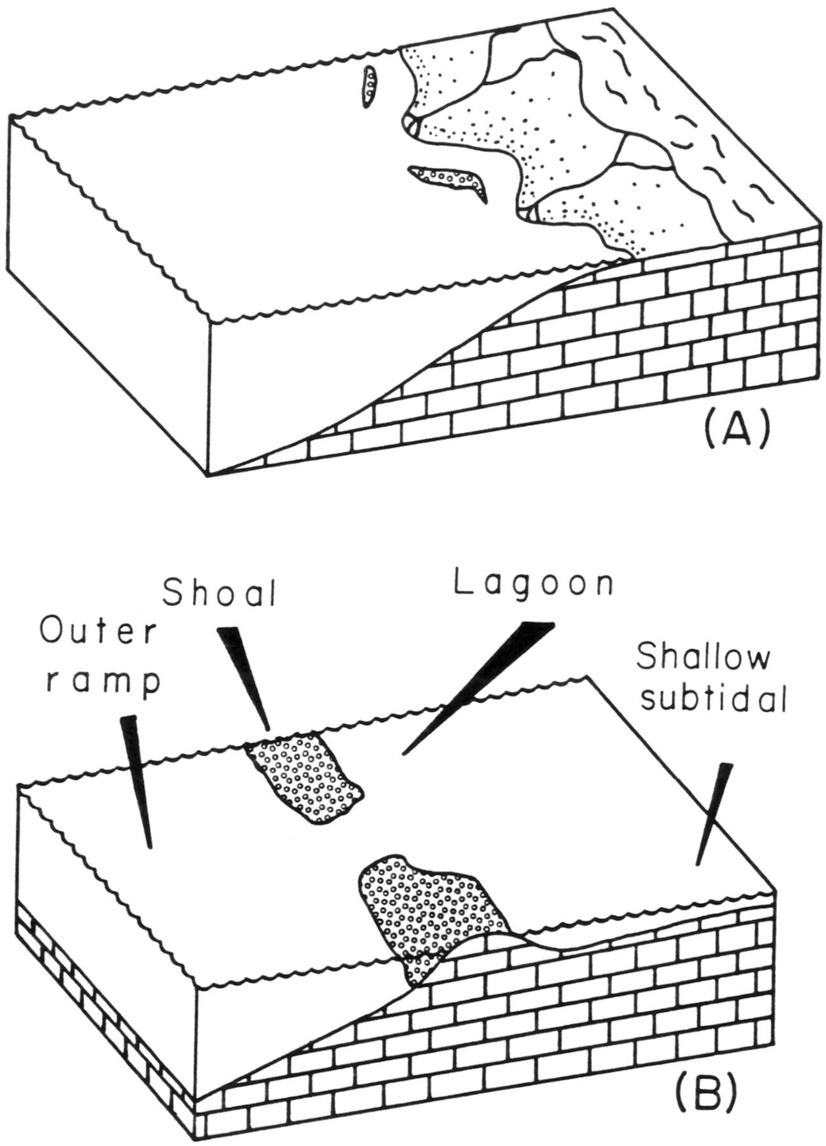


Figure 6. Evolution of Depositional Environments.
A) Little Valley Depositional Environment.
Mixed carbonate-siliciclastic ramp with minor fringing ooid shoals.
B) Hillsdale Depositional Environment.
Carbonate ramp with discontinuous offshore shoals.

grainstones. The grainstones of the discontinuous shoals are composed of either ooids or echinoderms. Seaward of the shoals, depostion of skeletal packstones and wackestones represents the largest depositional environment of the outer carbonate ramp. Packstones are interpreted as generally being more common near the high energy shoal facies. In general, these packstones grade seaward into wackestones, but local variations in energy, sedimentation rate, and other depositional factors cause intimate deposition of both packstones and wackestones.

Lateral Distribution of Facies

The stratigraphic cross-section and facies correlation are shown in Figure 7 which is a composite of Appendix B. The lateral variations in facies distributions are best illustrated by the Muddy Hollow (H in Appendix B) and Horseshoe Bend (M in Appendix B) sections which are only 300 meters apart (Figure 7). An echinoderm grainstone (H-5) is correlated with an echinoderm wackestone (M-10) and ooid grainstone (M-9). This correlation is supported by the equivalent stratigraphic position of these units and the presence of quartz siltstone units directly above and below the correlated units. This stratigraphic correlation illustrates the lateral variations of facies over a short interval (300 meters). This is especially true of the discontinuous shoal facies represented by the grainstones. Thus, correlation between other stratigraphic sections is difficult,

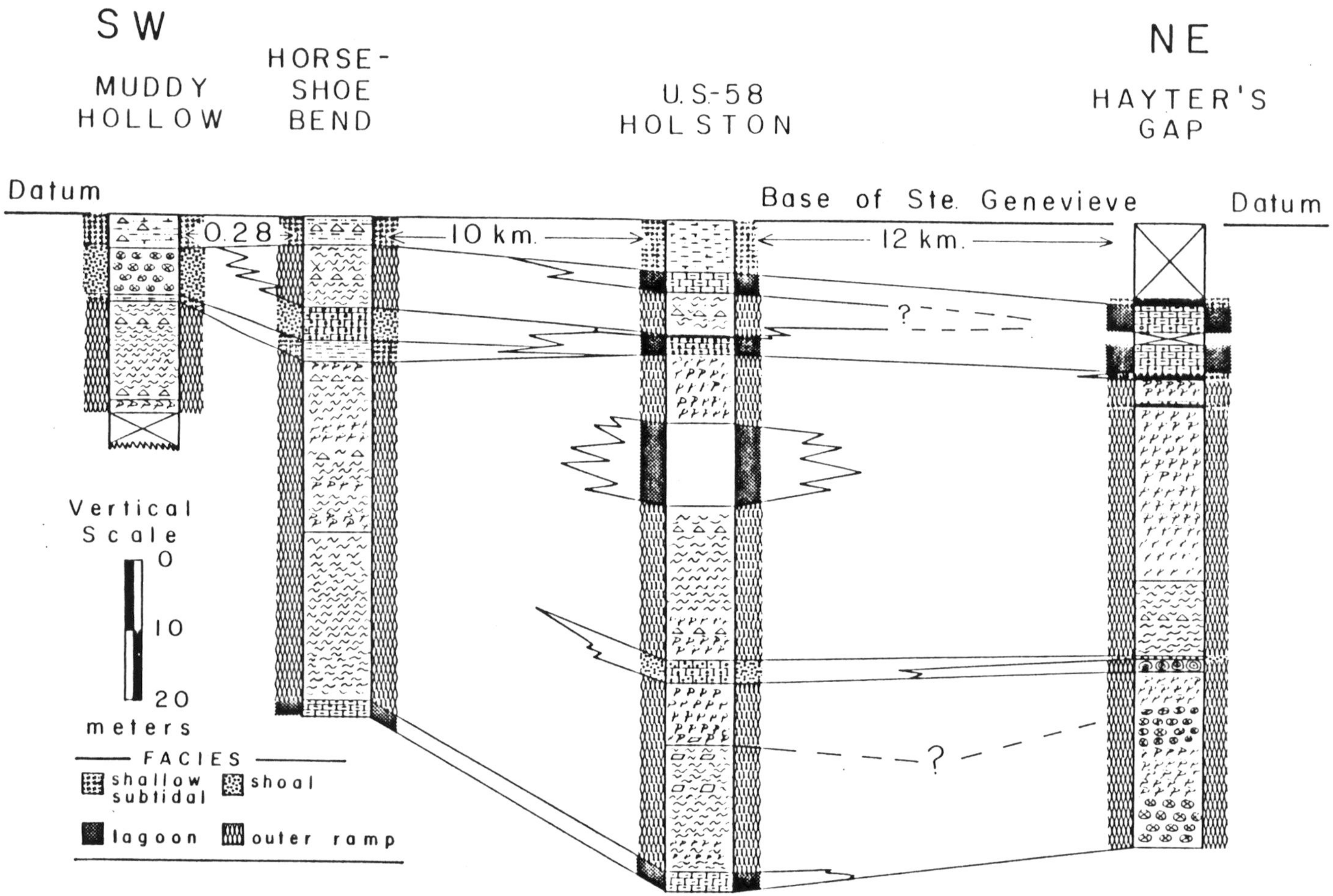


Figure 7. Stratigraphic cross-section with facies correlation.

considering the larger lateral distance between sections. However, similar vertical variations of facies for different stratigraphic sections may indicate basin-wide base-level fluctuations (ie. subsidence/relative sea level rise).

Vertical Distribution of Facies

According to Read (1985) oncolites may occur near ooid or echinoderm shoals. In the lower part of the Hayter's Gap Section, an echinoderm wackestone (A-2) grades up into an echinoderm packstone (A-3) overlain by an oncolitic packestone (A-4) directly overlain by an ooid grainstone (A-5; all in Appendix B). This is an excellent shallowing-upward sequence showing the transition of environments from outer ramp to shoal facies. The oncolitic unit is in an intermediate position in this section.

Four shallowing-upward sequences can be identified in both the Hayter's Gap (A) and Holston (B) sections. The first (lowermost) sequence in each of these two well-exposed sections is culminated with an ooid grainstone shoal facies overlaying outer ramp skeletal wackestone and packestones. In the Holston section, the second shallowing-upward sequence is capped by a lagoonal pelloidal grainstone (B-12.5 and B-13), whereas in the Hayter's Gap section the second cycle is culminated by a thin (0.3m) terrigenous shale (A-11 in Appendix B). The most obvious shallowing-upward sequence of each stratigraphic section is found at the top. The top of all four sections has two cycles of carbonates overlain by quartz siltstone or terrigenous shale. For the Muddy Hollow (H) and Horseshoe Bend (M) sections only two cycles are identified due to limited exposure. The shallowing-upward sequences represent basin infilling occurring at a rate greater than basin subsidence or relative sea level rise. Alternatively, episodic influx of terrigenous detritus due to tectonism could explain the occurrence of siliciclastic units. These cycles are useful to discuss the vertical distribution and cyclicity of lithofacies, however the lack of significant stratigraphic boundaries (ie. unconformities) in the Hillsdale Limestone requires a subjective placement of sequence boundaries. Another placement of the sequence boundaries can outline deepening-upward sequences. However, considering that carbonate sedimentation generally greatly exceeds subsidence or sea level rise (Schlager, 1981), shallowing-upward sequences due to upbuilding to sea level are expected in carbonate environments with small-scale (few meter) sea level/subsidence oscillations. According to Read (1985), small-scale (few meter) sea level fluctuations (periods of 20,000 to over 100,000 yr) will result in discrete shallowing-upward sequences on aggraded shelves.

In contrast, modern carbonate platforms represent the result of large-scale (over 300 meters) sea level oscillations due to glacio-eustatic sea level flutuations. These incipiently drowned platforms have disconformable shallowing-upward sequences with well-developed karst features, regolith, and soils or caliches. Because of the magnitude of sea level fluctuations, these shelves rarely build to sea level and thus, modern platforms are poor analogs of ancient aggraded platforms.

Evolution of the Depositional Environments

Regional stratigraphic relationships and insoluble residue content in the Hillsdale (see section on Timing of Maximum Transgression) indicate that the transgession during St. Louis (Hillsdale) time was of wide extent, occurring throurghout the Appalachian Basin. The onlapping of the Hillsdale on the Little Valley Limestone represents a relative rise in sea level (or change in shoreline position), extending the basin landward (to the east), which allowed for the development of an ooid-shoal complex (Figure 6A; DiRenzo, 1986). The majority of the Hillsdale in the study area was deposited downslope of the small ooid-shoal complex, on a relatively low energy deep ramp (greater than 10 meters water depth) as a skeletal packstone and wackestone facies. Ephemeral input of upward-fining storm deposition is illustrated by an ooid grainstone (A-5 in Appendix B) that has graded bedding of the ooids. With the peak of the transgression, the ooid-shoal ramp probably coalesced and evolved into a homoclinal ramp with an offshore ooid-skeletal bar by late Hillsdale/early Ste. Genevieve time (Figure 6B). Increase in siliciclastics in the upper Hillsdale is additional evidence of termination of the transgression. The subsequent regression represented by the Ste. Genevieve contains lithofacies suggestive of of this ooid-barrier complex such as megarippled and rippled, cross-bedded ooid/skeletal sands (Bedell, 1986). This interpretation of the Hillsdale depositional environment is, in general, in agreement with the conclusions of Slagle (1978). Slagle (1978) concluded that the Hillsdale Limestone was deposited in a "moderately warm, agitated, littoral or shallow sublittoral, open (or in some places slightly restricted) marine environment".

DIAGENESIS

INTRODUCTION

Diagenesis refers to all the textural and mineralogical changes a sediment undergoes from the time of deposition until the time of final lithification, exclusive of metamorphism. The Hillsdale Limestone has had a complex diagenetic history.

MICRITIZATION

Micritization is the replacement of original carbonate grains by microcrystalline carbonate at the sediment-water interface (Kobluk and Risk, 1977) from the intertidal zone to depths of at least 780m (Perkins and Halsey, 1971). Because it precedes other diagenetic products, micritization is an early diagenetic process.

Micritization is produced by two different processes. Borings of carbonate grains by algal, fungal, or bacterial organisms are later filled by micrite producing degrading micritization (Bathurst, 1966; Klement and Toomey, 1967). Aggrading micrite rims form from the growth of micro-organisms on the surface of carbonate grains which subsequently protect the grains from destruction (Kobluk and Risk, 1977).

In the Hillsdale Limestone, a wide range of micritization is present. Commonly foraminifers are completely micritized. Micritic envelopes of echinoderms and bryozoans are very common. Micitized ooids have partial to complete obliteration of the internal structure.

CEMENTATION

Sparite refers to crystalline, chemically precipitated, sparry calcite cement. In the Hillsdale Limestone various forms of sparite are present in the ooid and echinoderm grainstones.

Isopachous Rim Cement

Isopachous rim cement is a finely crystalline, isopachous, sparry calcite crust on grains. It is formed in the marine phreatic environment (Longman, 1980). Fibrous to bladed crystals grow normal to the surfaces of grains into the available pore space. Non-ferroan isopachous rim cement fills pore spaces of allochems in packestones and wackestones of the Hillsdale Limestone.

Meniscus Cement

One oolitic unit (B-14) in the Hillsdale Limestone contains a meniscus cement that forms calcite crystals between ooid contacts. This discontinuous meniscus cement around grains suggests that the pore spaces contained air and that precipitation of this cement occurred only where capillary fluids were present near grain contacts. This indicates precipitation in the vadose environment, which probally occurred during exposure of an ooid bar.

Syntaxial Cement

Syntaxial rim cement is sparry calcite cement which has precipitated in optical continuity with the host grain. Ferroan syntaxial overgrowths of echinoderm fragments are common in the Hillsdale Limestone. These overgrowths formed after development of thin micritic envelopes. Most workers interpret syntaxial cements as diagnostic of an early diagenetic event which occurs in the meteoric phreatic zone (Land, 1970; Longman, 1980).

Pore Filling Cement

Sparry calcite cement fills the pore spaces of grainstones and some packstones of the Hillsdale Limestone. The cement is blocky or granular. The non-ferroan blocky granular cement in the Hillsdale Limestone is interpreted as forming in the marine phreatic environment.

Drusy cement is an early diagenetic texture characterized by anhedral to subhedral calcite crystals increasing in grain size outward from pore walls. Longman (1980) interpreted drusy cement as developing in the freshwater environment. The ferroan drusy sparite in the Hillsdale developed in the meteoric phreatic zone and thus, it may be contemporaneous with the ferroan syntaxial rim cementation.

DOLOMITIZATION

Replacement of allochems and matrix material by dolomite illustrates the secondary origin of dolomite. Minor dolomite is present as euhedral crystals replacing allochems. The matrix of skeletal wackestones in the lower part of the Holston Section (B-4, B-5, and B-6) has undergone extensive neomorphic recrystallization of the original micrite matrix to form a crystalline dolomite matrix.

The insoluble residue content of skeletal wackestones may be a controlling factor in the process of dolomitization (Appendix A). Non-dolomitized skeletal wackestones average 27.27 % insolubles (range 11.86 % to 44.24 %). Dolomitized skeletal wackestones average 8.27 % insolubles (range 6.47 % to 10.83 %). Primary marine dolomite develops in restricted, highly evaporative, lagoon waters. The relatively abundant and diverse biota present in the dolomitic wackestones are indicative of non-restricted, open marine conditions, which precludes a primary origin for dolomite formation. Since secondary dolomite cannot replace insoluble phases, the lower percent insolubles of dolomitized skeletal wackestones indicates these skeletal wackestones had insoluble residue contents that were originally lower than the non-dolomitized skeletal wackestones. Because dolomitized and non-dolomitized skeletal wackestones are found in close proximity (ie. similar diagenetic history), the original insoluble content appears to be an indicator of secondary dolomitization. Lower insoluble contents are expected in units with greater porosity and permeability allowing magnesium-rich waters to percolate through, thus, these rocks are more susceptible to dolomitization. The stratigraphic relationships of relatively impermeable insoluble-rich units (B-1, B-2, and B-3 in Appendix B) directly below the zone of dolomitization is perhaps the greatest factor influencing the location of dolomite formation. The Holston Section is the thickest accumulation of the Hillsdale indicating these units were deposited in an area of high subsidence that developed into the Greendale Syncline. Magnesium-charged brines could have migrated downward into the subsiding basin. These diagenetic fluids, charged with magnesium due to recrystallization of high magnesium calcite (HMC) to low magnesium calcite (LMC), would then pool above the insoluble-rich units resulting in dolomitization of the matrix.

MICROSPAR FORMATION

Microspar was described by Folk (1959, 1965, 1974) as equant, euhedral to subhedral calcite crystals generally 5-10um in diameter. Bosselini (1964) used the size range of 4-30um to characterize his similar micrite II. This wider range is used for the size range of microspar. Microspar in the Hillsdale Limestone occurs in various sizes in ooid and skeletal wackestones.

Two possible origins of microspar have been proposed. Folk (1974) proposed that crystals of microcrystalline calcite (micrite crystals) were restricted in size by the presence of Mg++ cations. In the mixing zone or in the meteoric zone, Mg++ cations are removed and aggrading neomorphism of micrite to microspar can occur. Another possible origin of microspar, proposed by Lasemi and Sandberg (1984), suggests a one step formation of microspar directly from aragonitic mud, bypassing the calcitization of the aragonitic mud to micrite.

SILICIFICATION

The terminology presented by Folk and Pittman (1971) for microfabrics of quartz is summarized in Figure 8. Megaquartz and microquartz are distinguished by crystal widths greater or less than 20um, respectively. Microquartz is further subdivided into: 1) microcrystalline quartz, composed of equant grains typically less than 10um, usually 1-4um, with "pinpoint" extinction and, 2) chalcedonic

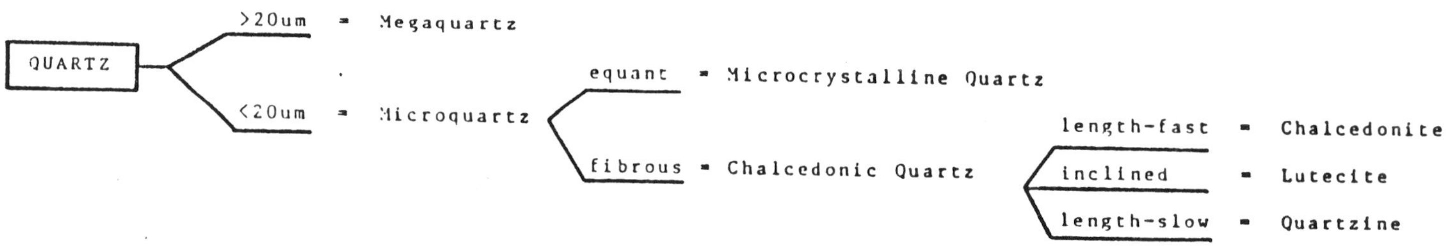


Figure 8. Microfabrics of Quartz (after Folk & Pittman, 1971).

quartz in the form of fibrous crusts and spherulites.

Chalcedonic quartz displays three morphologies differentiated by variations in optical properties. Chalcedonite is the common length-fast variety, with the epsilon vibration direction perpendicular to the long dimension of the quartz fibers. Quartzine is the length-slow variety. Lutecite has the epsilon vibration direction inclined at an angle of about 30 degrees to the quartz fibers. Chalcedonite, microcrystalline quartz, and megaquartz are recognized in the Hillsdale Limestone.

Silicification in the Hillsdale Limestone forms dark gray to black chert nodules, silicified fossils, and pore infillings. Microcrystalline quartz replaces allochems, pseudomorphs dolomite, and forms chert nodules that replace matrix and partially to totally replace fossils. This indicates the non-fabric selective diagenetic origin of the chert nodules. Replacement of allochems is fabric selective with silica replacement usually not present outside of the allochem. A hierarchy of susceptibility to silica replacement is recognized with bryozoans being most easily replaced, brachiopods intermediate, and echinoderms least easily replaced. This hierarchy is probably due to characterisics of original skeletal morphologies and textures. Silicified bryozoans are commonly found in units containing chert nodules. The thin, extensive areal morphology of easily replaced bryozoans may act as a pathway assisting silica migration. Dolomitized allochems are probably most easily silicified. In some fossils, silica replacement of dolomite results in pseudomorphs of microquartz after dolomite. In matrix replacements, small crystals (ave. 0.2mm) of dolomite within a microcrystalline quartz are interpreted as remnants of incomplete replacement of dolomite by microcrystalline quartz. Silicification after dolomitization is also indicated by the textural relationships of pore-filling cements of chalcedonite and megaquartz within a rugose horn coral from sample B-17. Dolomite crystals anchored on the coral project outward into pore spaces and are overlain by chalcedonite followed by megaquartz (Plate 1). The diagenesis revealed by the pore-infillings of this horn coral will be discussed further.

Formation of Chert

Studies of siliceous sediments encountered by the Deep Sea Drilling Project (DSDP) have increased the understanding of chert diagenesis (Lancelot, 1973; Wise and Weaver, 1974; Heath and Morberly, 1971). Extensive work on the Monterey Formation of California has outlined a diagenetic sequence for chert (Murata et al. 1977). The same sequence has been observed in other studies of silica mineral diagenesis (Aoyagi and Asakawa, 1984; Aoyagi and Kazama, 1980; Mitsui and Taguchi, 1977; Robertson, 1977). All of these studies indicate a two-stage formation of chert (Fig. 9B), which begins with the dissolution of amporphous opal of biogenic or abiogenic origin. The dissolved silica first crystallizes as disordered opal-CT, which then dissolves and reprecipitates as microquartz (ie. either

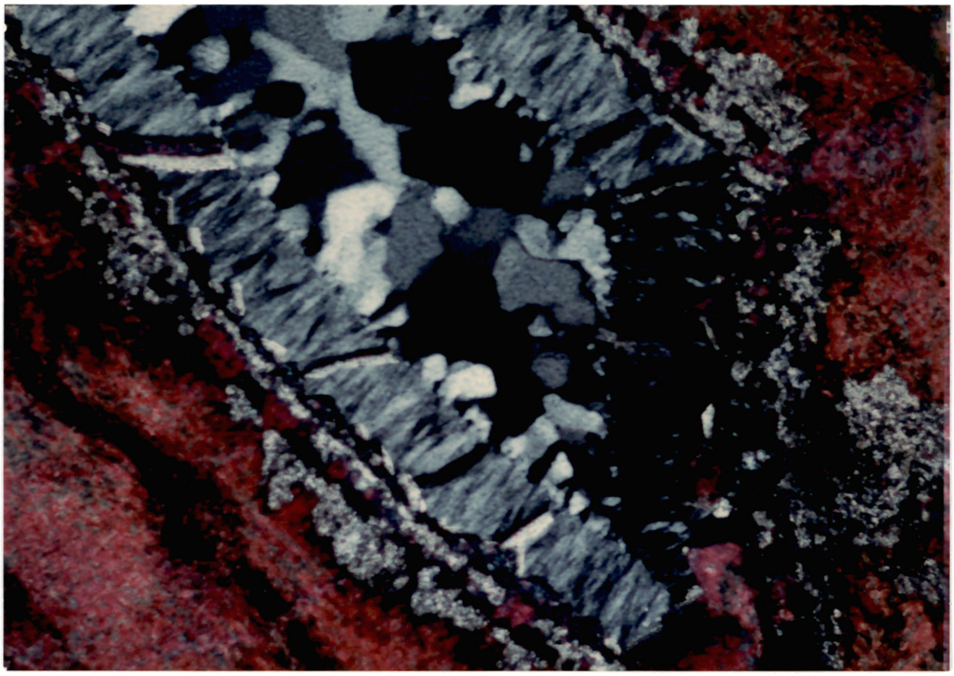
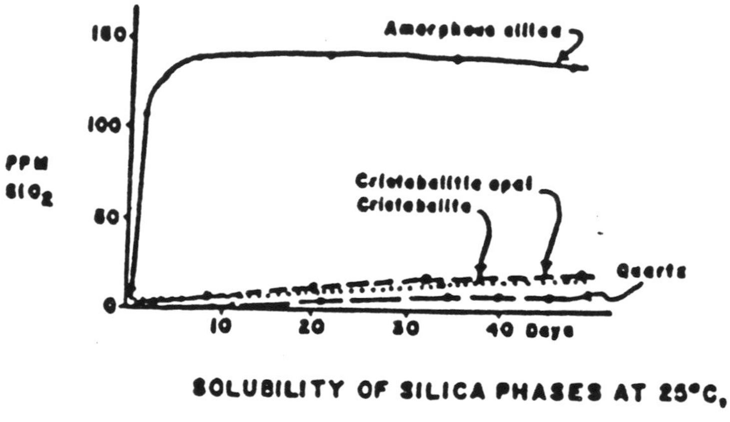
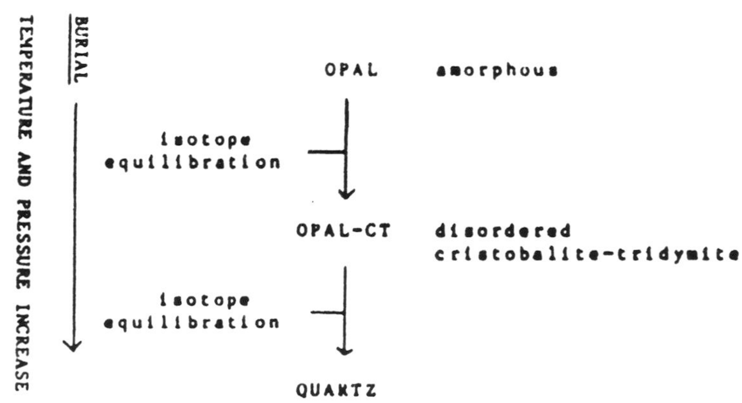


Plate 1. - Photomicrograph of *Heterophrentis sp.* rugose horn coral showing textural relationships of cements (crossed nichols).Non-Ferroan calcite (red), overlain by dolomite (unstained, birefringent), followed by chalcedonite and post-chalcedonite megaquartz.



(A)



(B)

Figure 9. - Solubility and Diagenesis of Silica Minerals.
A - Solubility (after Millot, 1970).
B - Diagenesis (after Murata et al., 1977).

microcyrystalline quartz or chalcedonic quartz). Each dissolution-reprecipitation step allows for isotopic re-equilibration. The precursor opal-CT occurs as spheres in cavities in deep-sea and terrestrial porcelanites. These spherical aggregates, 10-15um in diameter, composed of finely bladed crystals 30-50nm thick, were termed "lepispheres" by Wise and Kelts (1972). Kastner and Keene (1975), Meyers (1973) and Meyers and James (1978) suggest that megaquartz precipitates directly from solution when the concentration of silica in solution is less than the equilibrium solubility values for opal-CT. Thus, megaquartz is the only microfabric of quartz that will have an isotopic composition representative of the environment of formation.

Meyers (1973, 1977, 1978) and Meyers and James (1978) concluded that chertification of the Little Valley Formation (Mississippian, Osagean), in New Mexico, occurred in the meteoric phreatic environment. Supportive evidence includes isotopic data, regional petrographic data, and regional sedimentological data. Their interpretations included calcite cementation and opal-CT (precusor of microcrystalline quartz and chalcedonite) formation in the more seaward portions of a meteoric-phreatic environment. Megaquartz was interpreted as precipitating in the more landward portions of the groundwater system (Meyers and James, 1978).

Silicified Horn Coral

In the Hillsdale Limestone, petrographic evidence indicates at least two stages of silicification (ie. chalcedonite and megaquartz formation). The textural relationships of various mineral phases within a rugose horn coral from sample B-17, illustrates the following diagenetic sequence: 1) non-ferroan calcite cementation in the marine phreatic environment producing isopachous rim cement and drusy cement; 2) ferroan dolomite pore-filling in the mixing zone; 3) meteoric phreatic silicification resulting in pore-infillings of a chalcedonite-precursor and post-chalcedonite megaquartz, and; 4) meteoric-phreatic calcitization of chalcedonite resulting in non-ferroan calcite after spherulitic chalcedonite (Plate 1). During chalcedonite formation dolomite was incompletely replaced. No dolomite is preserved within megaquartz. Megaquartz precipitates only after dissolved silica concentrations have been depleted below a threshold necessary for the precipitation of chalcedonite.

Dolomitization is interpreted as occurring in the mixing zone between marine and meteoric waters. Silicification is interpreted as occurring in the meteoric-phreatic environment, after further encroachment of meteoric groundwaters (Fig. 10). These interpretations are in agreement with the silicification model of Meyers and James (1978). Isotopic evidence will be presented that suggests silicification occurred in the meteoric-phreatic environment.

A thin layer of non-ferroan dolomite is occassionally present

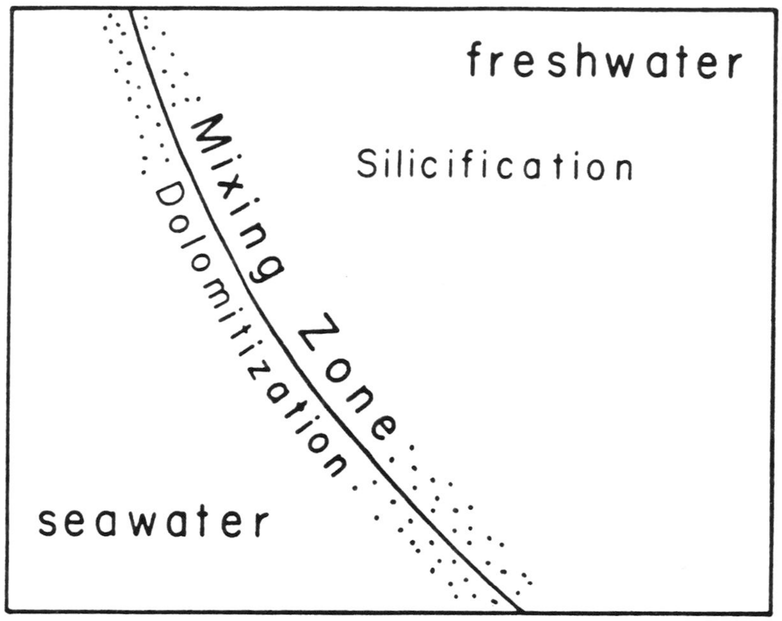


Figure 10. Cross-section of Diagenetic Environments. Showing environments of Dolomitization (Mixing Zone) and Silicification (Meteoric-Phreatic) (after Meyers and James, 1978).

at the boundary between silica and the original calcite. This thin layer may have been formed due to the 8 percent volume reduction occurring during the transformation of calcite to dolomite, yielding to the crystallization pressure of growing silica crystals. Magnesium ions would be supplied by the dissolution of the calcite being replaced.

Source of Silica

The five possible origins of silica for the nodular chert are: 1) siliceous volcanic material; 2) alteration of clay minerals; 3) dissolution of feldspars; 4) dissolution of siliceous organisms; and 5) dissolution of quartz. The silica may have been derived from within the basin, from outside of the basin, or both. Intrabasinal sources will be considered in detail and extrabasinal sources will be considered in general.

The sources of silica within the basin can be evaluated using the physical evidence preserved in the rock units. For example, the absence of any interbedding of volcanic units makes the first alternative, volcanic material, an unlikely mechanism. Craig and Varnes (1979) concluded that the Southern Appalachian borderlands to the east and south were quiescent during the Mississippian. These borderlands were probably reduced to areas of low relief in which chemical erosion was dominant. At the same time, the Northern Apppalachians were characterized by elevated borderlands that were being eroded at a decreased rate during Meramecian time. These interpretations of subdued tectonism also detract from vulcanism as a possible source of silica. Alteration of clays, the second alternative, is not believed to be significant within the basin because the chert nodules are not resricted to lithologic units that contain abundant clays. Inconsistent spatial relationships between pelitic units and chert nodules in the Hillsdale suggests that the alteration of intrabasinal clays appears to be an unlikely, but possible, mechanism for the source of silica. In addition, alteration of clays on the fringes or outside the basin remains as a possible source of silica. Petrographic analysis during this study and in previous studies found no evidence of siliceous organisms or significant feldspar accumulations (Blancher, 1974; Slagle, 1978). Because amorphous biogenic silica (opal) is the most soluble silica phase (Fig. 9A), the siliceous organisms may have been present and subsequently totally dissolved. However, no molds of these organisms are recognized. Similarly, no molds of feldspar grains have been recognized. An insignificant amount of authigenic quartz overgrowths in the silty units indicates that pressure solution of detrital quartz within the Hillsdale is negligible.

Another possible mechanism involves upwelling of deep waters enriched in silica. This is a seemingly viable mechanism due to the paleogeography of the Appalachian basin during deposition of the Hillsdale. With the study area located at approximately 15 degrees South latitude (Fig. 5), the predicted prevailing wind direction would have been southeastly. This wind pattern would cause surface currents to move toward the northwest with upwelling occurring along the eastern margin of the basin. Upwelling of deep ocean waters typically increases the dissolved silica in the water column (Aston, 1985). However, because the Hillsdale sea is interpreted as a broad shallow platform, it is believed deep ocean silica-rich waters were not in close proximity.

Having considered the possible sources of silica, the most plausible explanations remaining are 1) extrabasinal and/or intrabasinal alteration of clays, or 2) dissolution of quartz . Terrigenous siliciclastics are present and presumably these siliceous units were abundant near point sources of terrigenous input (ie. in nearshore channels) and on land beyond carbonate deposition. However, the solubility of crystalline silica, particularly quartz, is very low (6 mg/l SiO_2 at 25 degrees celsisus; Matthess, 1982). The solubility of amorphous silica is hardly affected by pH changes from 0 to 9 and thus, the dissolution of silica is not likely in the pH range of natural waters (5.0 to 8.0; Matthess, 1982).

Clay minerals may undergo various diagenetic transformations that release silica. The smectite to illite transformation in shales (Fuchtbauer, 1979) and the alteration of illite to muscovite (Towe, 1962) can produce silica. Deep burial, such as that suggested by the thick accumulation of sediments above the Hillsdale Limestone, is required for these clay mineral alterations. Thus, intrabasinal alteration of clays is a possible origin of silica.

Weathering of clay minerals may release silica (Aston, 1985). Extrabasinal siliciclastics containing clay minerals could have supplied silica by these weathering reactions. Matthess (1982) states that the bulk of silica in groundwater comes from the weathering of silicate minerals. This mechanism is interpreted as the most influential because the depositional environment has been interpreted as nearshore, littoral or shallow sublittoral (Slagle, 1978). The adjacent meteoric environment would allow for weathering of adjacent terrigenous clay units.

In summary, silicification in the meteoric-phreatic environment is indicated by petrographic evidence. Initial precipitation of an opal-CT precursor of chalcedonite and microcrystalline quartz occurred in the seaward edge of the meteoric-phreatic environment, followed by direct precipitation of megaquartz in the landward portions of the meteroic-phreatic environment. Oxygen isotopic data indicate that silicification may have occurred in isotopically light meteoric-phreatic waters. This interpretation is in general agreement with the model of meteoric-phreatic silicification of carbonates by Meyers and James (1978). The source of silica is believed to be the intrabasinal and/or extrabasinal alteration of clay minerals.

COMPACTION

Compaction refers to any process that reduces the bulk volume of sediments. Compaction is generally considered to be an early diagenetic event because later significant cementation can support the sediment and retard compaction. However, with deep burial some carbonate sediments yield to compactional processes (Flugel, 1982). Compaction in the Hillsdale Limestone is illustrated by ooid deformation and pressure solution.

Pressure solution is the preferential dissolution of mineral matter at points of stress. Two types of pressure solution, sutured and non-sutured seam solution, are present in the Hillsdale Limestone. Stylolites and grain-to-grain contact sutures form irregular interpenetrating surfaces with shortening parallel to the direction of maximum stress. Bathurst (1975) indicated the timing of grain-to-grain sutures as prior to the emplacement of a second generation cement.

Non-sutured seam solution occurs in pelitic units. Abundant clay or platy minerals produce a diffuse seam of insoluble remnants following solution. These diffuse seams are on the order of 0.5 to 2.5cm thick.

PYRITE AND HEMATITE FORMATION

Pyrite in the Hillsdale Limestone is a widely distributed, isometric, opaque mineral. Pyrite commonly oxidizes to hematite and iron hydroxides which often form psuedomorphs. A study of nearshore marine muds by Reaves (1986) demonstrated a seasonal climatic variation of reducing (summer) vs. oxidizing (winter) environments in nearshore marine muds of Connecticut. Ferrous sulfide minerals that formed during summer anoxic-sulfidic conditions are oxidized during winter when microbial activity is low and oxygenated water is present. However, pyrite can form under a wide range of geologic conditions.

In the Hillsdale Limestone, pyrite is found replacing allochems or, more commonly, it is distributed throughout the matrix. Pyrite framboids are commonly found within the zoeecia of byrozoans in wackestone units. The pyrite is interpreted as having formed during early diagenesis, under reducing conditions in a stagnant marine environment. Sulfur reducing microorganisms may have assisted this pyritization. Pyrite between deformed grain boundaries of the Hillsdale indicates pyritization was an early diagenetic process.

CALCITIZATION

The replacement of an inner layer of spherulitic chalcedony by non-ferroan calcite indicates calcitization after silicification (Plate 2). This is the only example of calcitization observed. This calcitization is interpreted as occurring in the meteoric phreatic environment.

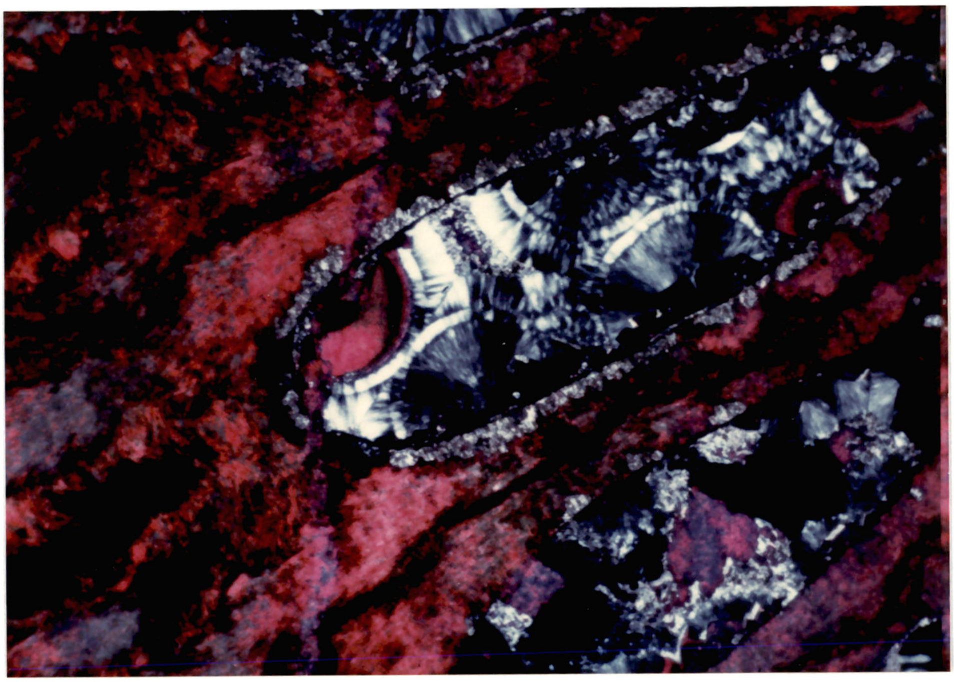


Plate 2. - Photomicrograph of calcification of spherulitc chalcedonite (crossed nichols). Non-ferroan calcite (red) has replaced inner band of chalcedonite.

SUMMARY OF DIAGENESIS

The petrographic data described above are summarized in Figure 11. Early diagenetic events include: micritization and pyritization in stagnant marine environments, and isopachous rim cementation and hematite formation in active marine environments. Localized exposure of an ooid bar to the meteoric-vadose environment resulted in the formation of a meniscus cement. With the encroachment of meteoric groundwater, the presence of a mixing zone of sea water and freshwater resulted in dolomitization. The stratigraphic distribution of insoluble minerals appears to have been a controlling factor of the location of dolomitization. With further encroachment of freshwater, establishment of a meteoric-phreatic environment resulted in: 1) aragonite leaching in the solution zone; 2) the formation of microspar, syntaxial cement, blocky and drusy pore-filling cements, and calcification in the active zone. The active zone is defined as an area of the meteoric phreatic environment where groundwater flow allows for removal of dissolution products. Magnesium calcites are interpreted as stabilizing in the stagnant zone of the meteoric-phreatic environment, where low groundwater flow resulted in the accumulation of Mg^{++} ions in solution and precipitation of these magnesium calcites. Compaction, sutured grains, stylolitization, and fracturing occurred throughout the continued burial of Hillsdale sediments.

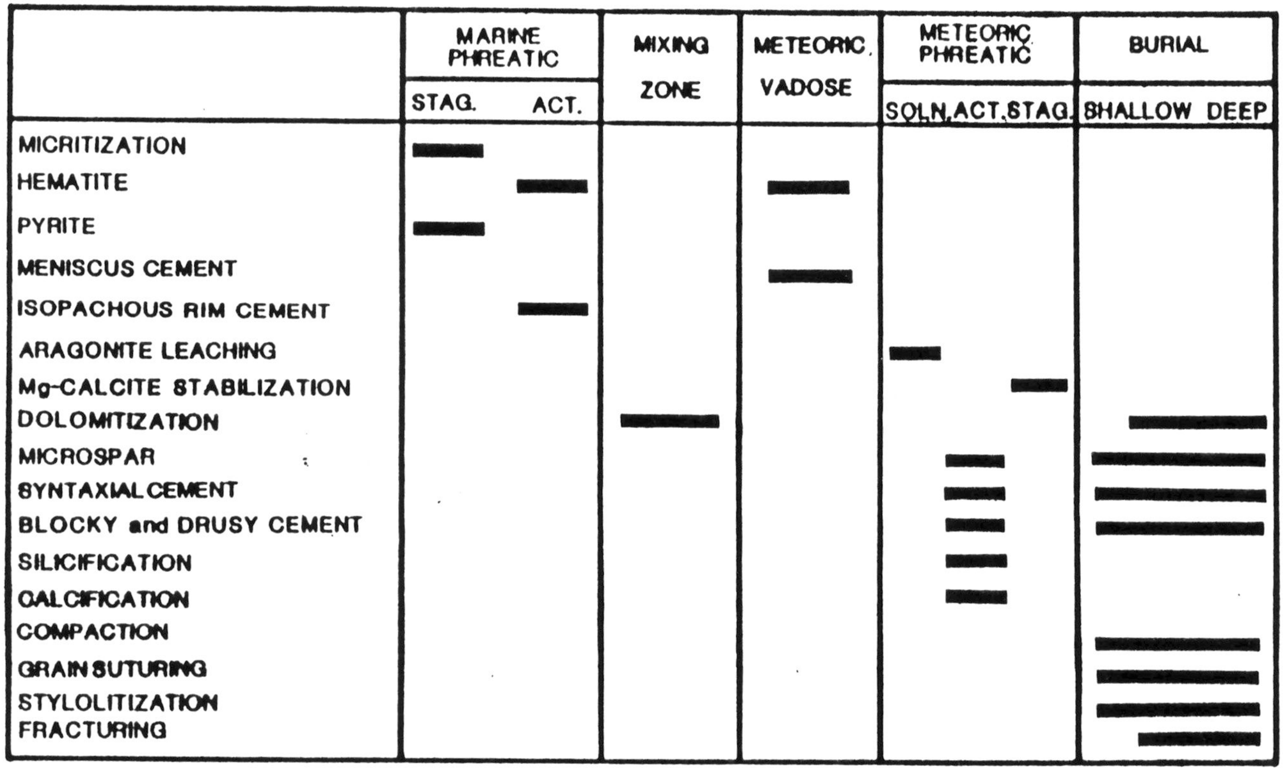


Figure 11. Summary of Diagenesis

CHEMICAL DIAGENESIS

Sample Preparation

Carbonate sediment or rock is a heterogeneous composite of constituents which differ structurally, texturally, and chemically. In order to eliminate the problem of inhomogeneity, fossil specimens were physically separated from rock matrix for analysis. Fresh unweathered surfaces were examined with a binocular microscope and the fossils were removed by chipping and extraction with a hypodermic needle attached to a vacuum pump. All samples for elemental analysis were ground into a powder using an agate mortar and pestal. Samples for isotopic analysis were not ground before shipping to commercial laboratories. All equipment was washed with 10% HCl solution, rinsed with distilled water, and air dried between samples to avoid intersample contamination.

Theoretical Considerations

Recent studies of chemical diagenesis have resulted in theoretical models for carbonate diagenesis (Kinsman, 1969; Pingitore, 1978, 1982; Brand and Veizer, 1980). These workers considered the diagenetic reaction zone to be a "thin film" water reaction zone where an unstable mineral phase undergoes dissolution and a stable mineral phase is precipatated (Fig. 12). Brand and Veizer (1980) revised this

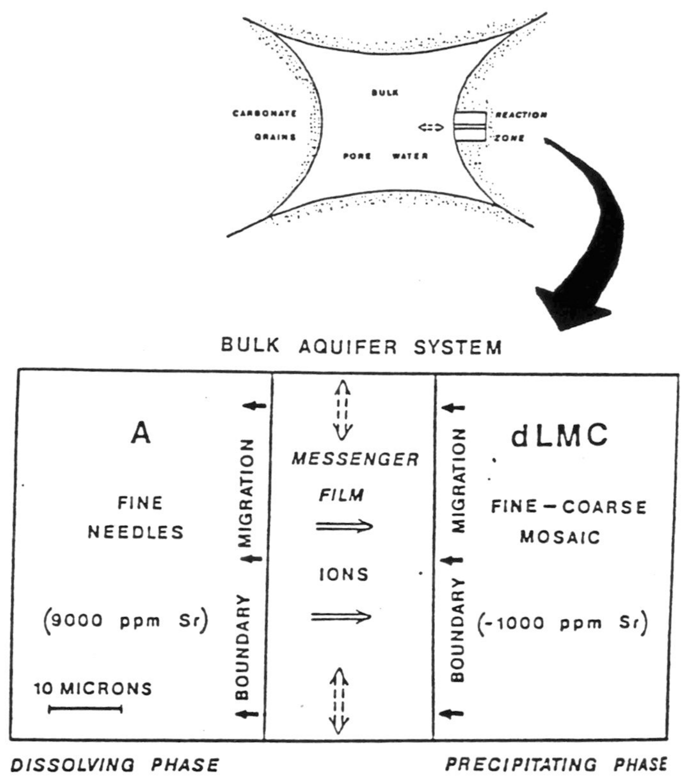


Figure 12. Partly Closed Reaction Zones showing Messenger Film. Functional and spatial relationship between the reaction zone, carbonate grains, and bulk pore water (top). Transfer of chemical and textural information takes place via the "Messenger Film". The reaction zone water (messenger film) is in disequilibrium with that of the bulk aquifer (pore water). Metastable phases (in this example aragonite = A) dissolve; due to partial chemical isolation (ie. disequilibrium) the precipitating phase will retain some chemical characteristics of the dissolving phase (bottom diagram). This process will proceed until all of the metastable phases are transformed into stable diagenetic Low-Magnesium Calcite (dLMC) (after Brand and Veizer, 1980).

term to "Messenger Film", indicating that this term is dimensionless and it illustrates that the main function of the water film of the reaction zone is the transfer of textural and chemical information from the dissolving carbonate phase to the precipatating carbonate phase. The reaction zone is usually physically isolated from the bulk aquifer pore water. The degree of isolation between these two water systems is variable. The degree of chemical isolation between the reaction site and the bulk aquifer pore water has been a matter of discussion. Most workers (Pingitore, 1982; Brand and Veizer, 1980; Veizer, 1978) prefer the "bulk solution disequilibrium model" which invokes at least partial chemical isolation (ie. disequilibrium) of the reaction zone. This model is more realistic than the proposed model of Morrow and Mayers (1978a, 1978b) called the "bulk solution equilibrium model" by Veizer (1978).

The proportions of trace elements and the isotopic compositions of phases derived from the dissolving solid phase versus those derived from the bulk solutions are important considerations. Brand and Veizer (1980) summarized the diagenetic trends of carbonate mineral stabilization with respect to meteoric water (Fig. 13; A = Aragonite, HMC = High-Magnesium Calcite, and LMC = Low-Magnesium Calcite). Diagenetic alteration leads to increasing textural maturity, increases in Mn++ and Fe++ contents, and decreases in Sr++, Oxygen-18 and possibly Carbon-13 contents in carbonate components (Brand and Veizer, 1980). Figure 13 was developed from the accumulation of chemical data from approximately 2100 samples of

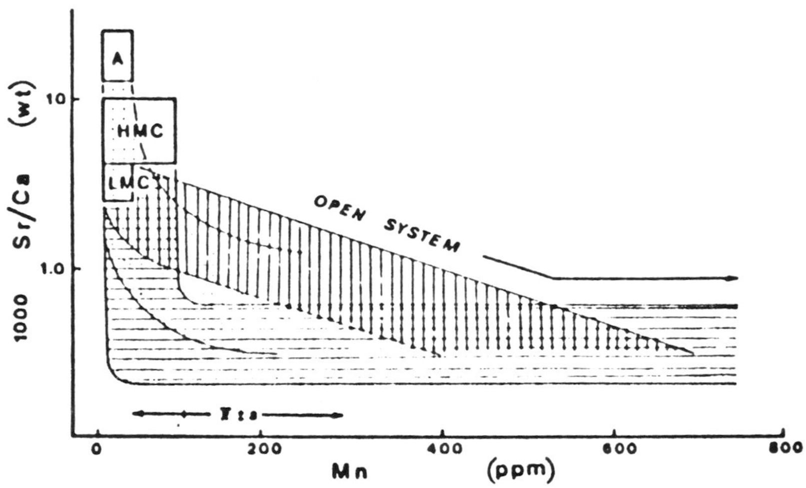


Figure 13. Summary of diagenetic trends for A, HMC and LMC with stabilization by meteoric water. The $\bar{X} \pm S$ (geometric mean and standard deviation) represents the data review of approx. 2100 samples from various carbonate facies, localities, and ages. "Open sustem" designates the field where no chemical differences between the fossil and the matrix/cement are evident (after Brand and Veizer, 1980).

various carbonate facies, localities, and ages. The boxes in Fig. 13 outline the fields of the theoretical possible range of A, HMC, and LMC in inorganic and organic equilibrium with present-day seawater (Brand and Veizer, 1980). A high water/rock ratio creates an open diagenetic system and vice versa (Veizer, 1983). An 'open system' is characterized by a high water/rock ratio that results in total chemical equilibration such that there are no chemical differences between fossils and surrounding matrix/cement.

The rate-limiting step of the dissolution-reprecipitation process is the precipitation of diagenetic Low-Magnesium Calcite (=dLMC; Bathurst, 1975). As a result of this dissolution-reprecipitation process, the chemistry of the reaction zone will be "buffered" (ie. controlled) by the dissolving metastable phase. The dissolved ions in the reaction zone are derived from both the dissolving metastable phase and the surronding bulk aquifer (pore) water. The relative input of ions from each source is dependant on the dissolution-reprecipitation rate versus the rate of diffusion of ions and on the flow transport between the water in the reaction zone and the surrounding (bulk) pore water. The rate of diffusion and flow transport depends on local permeability and hydrostatic head. For specimens analyzed from the same sample, these variables (bulk aquifer chemistry, rate of diffussion, and flow transport) can be assumed to be constant; the only remaining variable is the chemistry of the dissolving phase.

Brachiopods

Most recent and fossil articulate brachiopods secrete low-magnesium calcite (LMC) shells which usually contain less than 4 mole% $MgCO_3$ (Chave, 1954; Brand, 1981). However, Jaanusson (1966) suggested that Trimerellidae secreted originally aragonitic shells. Recent and ancient brachiopods are known to have secreted their shells in isotopic equilibrium with ambient seawater (Lowenstam, 1961; Veizer, 1977). Interpretations of ancient seawater isotopic composition are often based on the isotopic composition of unaltered brachiopods.

Crinoids

Recent crinoids secrete a high-Mg calcite (HMC; 8-16 mole % $MgCO_3$) endoskeleton (Brand, 1981). Ancient crinoids are also believed to have secreted originally HMC endoskeletons (Brand and Veizer, 1980). However, ancient crinoids commonly are altered to diagenetic low-Mg calcite (dLMC; Brand and Veizer, 1980). The variability in magnesium content of crinoids has been attributed to several factors. Milliman (1974) demonstrated that temperature of the ambient seawater is directly related to the Mg content of crinoid endoskeletons. However, Weber (1973) and Kolesar (1978) suggest that Mg content may be a consequence of growth rate, which may be influenced not only by temperature but also by food supply, dissolved oxygen, and other physiological factors.

Rugose Corals

Sandberg (1975) illustated that Paleozoic rugose corals secrete a calcitic skeleton. Veizer (1983) considers rugose corals to be LMC or possibly intermediate High Magnesium Calcite (iHMC; 4-8 mole % $MgCO_3$).

Sampling

An echinoid grainstone (Sample # A-110) from the lower Ste. Genevieve Limestone was selected for stable isotope (3 samples) and trace element (5 samples) analysis of unaltered fossils. This highly fossiliferous (70% allochems) sample contains a clean sparry calcite cement that facilitated removal of closely packed macrofossils. The corallum of a rugose horn coral (Sample B-17), identified as Heterophrentis sp., was analysed for trace elements. This rugose coral contained a siliceous infilling of megaquartz and chalcedony that was analysed for oxygen isotopic content. Comparison of the oxygen isotope content of this siliceous cement with the oxygen isotope content of an unalterted brachiopod enables an interpretation of the environment of silicification.

MAJOR AND TRACE ELEMENT ANALYSIS

The major and trace element content of fossils may indicate the degree of alteration and can aid in the interpretation of stable isotope ratios and the diagenetic history (Brand and Veizer, 1980). The results of major (Ca) and trace element (Sr, Mn, Fe and Zn) analyses of selected fossils are shown in Table 2. Strontium and manganese are especially useful diagenetic indicators due to their widely divergent partition coeffients and their large compositional differences in marine versus meteoric water (Brand and Veizer, 1980).

Analysis

Major (Ca) and trace element (Sr, Mn, Fe, and Zn) analyses were performed using a Kevex Energy Dispersive X-ray Fluorescence Spectrometer (EDXRF) at the Shared Research Resources Laboratories of the East Carolina University School of Medicine. EDXRF uses semiconductor detectors to directly measure the x-ray energy emitted from a sample excited by high energy x-rays. The smaller sample size (approx. 1 mg) needed for the thin film EDXRF technique, utilized by this particular instrumentation, is more advantageous to the trace element analysis of microfossils. The molecular percent $MgCO3$ of powdered microfossils was determined by an x-ray diffraction (XRD) technique modified after Goldsmith et al. (1955) by Hutchinson (1974). This technique is based on the relationship of displacement of the carbonate 104 peak relative to the silicon 111 peak, which varies according to the mol% $MgCO3$ in the carbonate.

Results and Interpretations

The x-ray diffraction indicated that all of the fossils analyzed are currently in the LMC range (ie. $<$ 4 mole % $MgCO3$). The preservation of the original chemical content (via the 'Messenger Film') provides a tool for the evaluation of the degree of diagenetic alteration. With increased diagenetic alteration of fossils in the meteoric environment, Mn^{++} and Fe^{++} will be increased, whereas Sr^{++} will be decreased (Brand and Veizer, 1980). Figures 14 and 15 are respective plots of the LMC and HMC samples within the envelopes of the diagenetic trends presented by Brand and Veizer (1980).

In Figure 14, the three brachiopod samples from the same rock sample (A-110) are clustered near the LMC field, indicating that the brachiopods underwent equilibration in a partially closed system. The lack of elemental alteration of the single sample of Heterophrentis sp. from sample B-17 is demonstrated by the plot of the horn coral very near the LMC field. The low iron content of the horn coral also implies pristine chemical composition (Table 2). Less alteration of the horn coral, relative to the brachiopods, is attributed to greater chemical isolation of the coral. The horn coral was contained in a calcareous quartz siltstone (56.3 % insolubles) with a fine-grained matrix of quartz silt and mud. The brachiopods were contained in an

Sample	Ca	Sr	Sr/Ca X 1000	Mn	Fe	Zn (ug/g)
A-110-1 Crinoid	337,000	1396	4.14	95	1225	21
A-110-5 Crinoid	319,000	516.8	1.62	89	1230	25
A-110-2 Brachiopod	408,000	1303	3.19	44	222	25
A-110-3 Brachiopod	277,000	719.2	2.60	56	499	25
A-110-4 Brachiopod	253,000	651.1	2.57	52	273	24
B-17-1 Horn Coral	257,000	1632.3	6.35	51	242	34
PRECISION	± 8.84%	± 9.12%	± 8.98%	± 7.63%	± 6.04%	± 18.31%
ACCURACY	7.78%	5.44%	6.61%	24.36%	9.77%	8.09%

Table 2. Major and trace element content of fossils (in ug/g). Precision is the standard deviation (1 sigma; n=4 for B-17-1; n=3 for all other samples) of replicate analyses of selected samples divided by the mean and multiplied by 100 percent. Accuracy is the average percent difference between accepted literature certified concentrations of the standards and the average calculated concentration divided by the literature concentration. Calcium and strontium precision and accuracy averaged for Sr/Ca values.

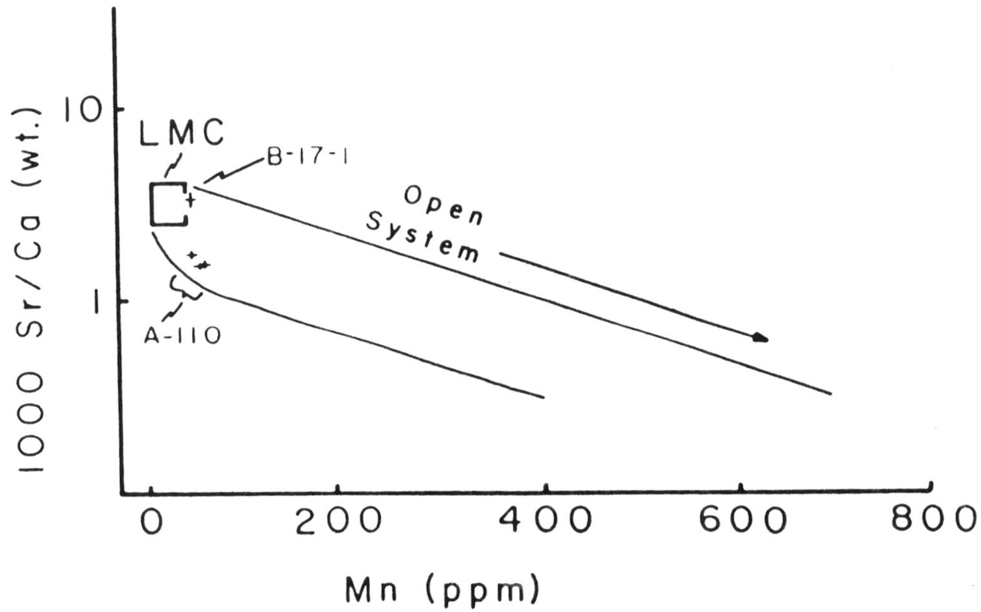
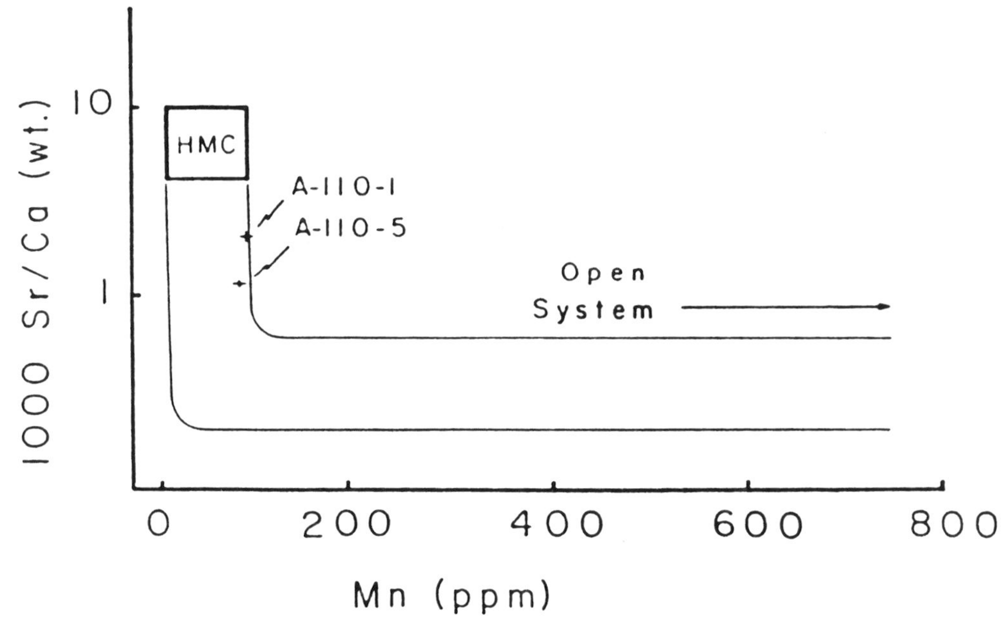


Figure 14. Diagenetic equilibration of LMC (and iHMC?) fossils. LMC field delineates the theoretical range of LMC in inorganic and organic equilibrium with present-day seawater (Brand and Veizer, 1980).

B-17-1 = Heterophrentis sp. - Horn coral.

A-110 = Three speriferid brachiopod plots.



<u>Figure 15.</u> Diagnetic stabilization of High-Mg Calcite crinoids. The HMC delineates the theoretical possible range of HMC in inorganic and organic equilibrium with present day seawater (Brand and Veizer, 1980).

echinoderm grainstone (7.9 % insolubles) which had a sparry calcite cement. The echinoderm grainstone (A-110) originally had a higher permeability than the siltstone (B-17) which would have allowed for greater alteration due to a larger rates of diffussion and flow transport. Thus, the grainstone containing the brachiopods was a more open system than the calcareous siltstone which contained the horn coral.

In Figure 15, the plots of the calcitic crinoids (originally HMC) are located within the diagenetic envelope. Both samples are close enough to the HMC field to indicate a partially closed system. The more altered crinoid (A-110 #5) is dark gray in color and it was purposely selected to test for the visual identification of altered samples.

Higher iron content in originally HMC crinoids, relative to LMC braciopods and the LMC (or iHMC?) horn coral, is attributed to the Fe^{++} substitution for Mg^{++} in HMC and/or diagenetic alteration of the crinoids. All samples have low zinc concentrations, which approach the detection limit of the analytical technique. These values are within the range of zinc equilibrium concentrations for marine calcites (10-39ppm; Veizer, 1983). The trace element results indicate that brachiopods and crinoids from sample A-110 equilibrated in a partially closed system. Therefore, brachiopods may be useful as indicators of Meramecian sea water isotopic composition. The elemental content of the crinoid samples probally indicate meteoric alteration resulting in syntaxial overgrowths.

STABLE ISOTOPE ANALYSIS

Oxygen isotopic ratios may indicate the influence of freshwater or saltwater during the formation of secondary silica and carbonate (Degens and Epstein, 1962; Choquette, 1968; Knauth and Epstein, 1976; Meyers and James, 1978). Carbon isotope analysis augments the interpretation of the oxygen isotope content of the carbonate samples. Samples of silicified and unaltered (non-silicified) macrofossils were sent to commercial laboratories for carbon and oxygen isotope analysis. Three specimens (two brachiopods and one crinoid), each weighing approximately 5 mg, were prepared and sent to Coastal Science Laboratories, Austin, Texas, for carbon and oxygen isotope analysis. One of the brachiopod samples was insufficient in size for accurate results. The siliceous infilling cement of a rugose horn coral, <u>Heterophrentis sp.</u> from sample B-17, was analyzed for oxygen isotopic composition by Geochron Laboratories in Cambridge, Massachusetts. The coral contained extensive pore-infillings of length-fast chalcedony (ie. chalcedonite) and post-chalcedonite megaquartz. The carbonate was selectively dissolved and the remaining silica was analyzed for oxygen isotope content.

Discussion

The stable isotope values for the samples, shown in Table 3,

Sample	δ Carbon-13 PDB	δ Oxygen-18 PDB	δ Oxygen-18 SMOW
Crinoid A-110	+2.9	-1.3	+29.5
Brachiopod A-110	+2.6	-0.4	+30.4
Chalcedony and Megaquartz B-17	----	----	+30.2

Table 3 Isotopic Composition of Samples
Accuracy and precision are $\pm$ 0.2 for carbonate samples and $\pm$ 0.02 for silica sample.

are expressed using delta notation. Carbonate samples are reported relative to the Pee Dee Belemnite (PDB) standard. The delta O-18 values were converted to the Standard Mean Ocean Water (SMOW) standard using

$$\text{delta X SMOW} = 1.03037\ (\text{delta X PDB}) + 30.37$$

(after Faure, 1977)

for comparison with the silica sample which was reported relative to the SMOW standard. Positive delta values indicate enrichment of the heavy isotope relative to the standard. Negative delta values indicate depletion of the heavy isotope relative to the standard. Delta O-18 and delta C-13 ratios of the carbonate samples are plotted in Figure 16. The experimental error of $\pm$ 0.2/mil is represented by the width of the black boxes. The large boxes, labeled "R" and "C" in the center, represent the field of isotopic values for calcium carbonate secreted in isotopic equilibrium with Recent and Carboniferous seawater, respectively (after Brand, 1982).

Recent and ancient brachiopods are known to have secreted their shells in isotopic equilibrium with the ambient seawater (Lowenstam, 1961; Veizer, 1977; Brand and Veizer, 1981; Brand, 1982; Popp et al., 1986). Thus, the stable isotope content of isotopically unaltered brachiopods may represent the stable isotope content of seawater during the secretion of the shell. Weber (1968) demonstated that Recent crinoids secrete endoskeletons that are not in equilibrium

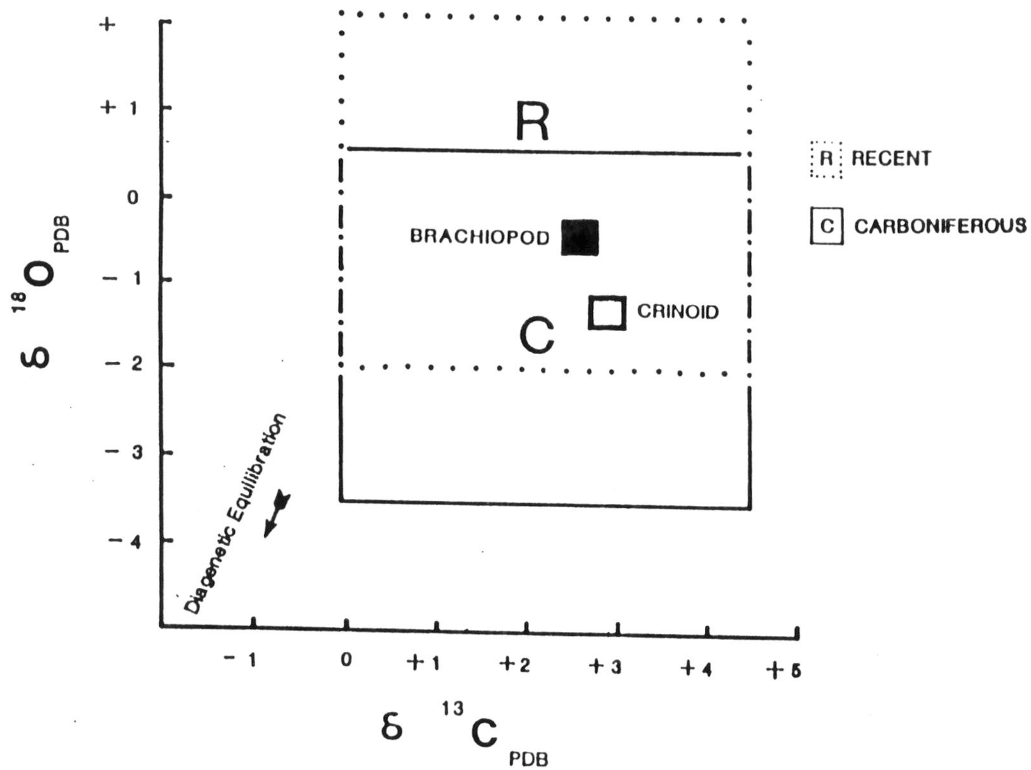


Figure 16. Plot of stable isotope data.
Brachiopod and crinoid from A-110.

with the ambient seawater. This biological fractionation of isotopes by organisms is commonly referred to as a "vital effect". Echinoderms, especially crinoids, exhibit this vital effect because of their primative respiratory system (Weber, 1968). Because crinoids lack a sophisticated respiratory system, metabolic carbon dioxide (enriched in C-12 and O-16 with respect to seawater bicarbonate) is incorporated into the endoskeleton (Weber, 1968). Thus, the skeletal calcite of unaltered crinoids typically has negative delta values.

Results and Interpretations

Both the brachiopod and the crinoid data plot within both the Recent and Carboniferous equilibrium field (Fig. 16). With meteoric diagenetic alteration, metastable aragonite and HMC undergo dissolution and reprecipitation to the more stable dLMC. Isotopic exchange occurs during this reaction. Because meteoric water is characterized by depleted oxygen isotopic values (delta O-18 = -30 to -40 PDB), meteoric diagenetic alteration and isotope exchange results in a negative shift in the stable isotope composition of the altered material such that the values would plot well off Figure 16 (arrow).

The trace element and isotopic data for Hillsdale crinoids is similar to the data of Meyers and Lohmann (1985). The Hillsdale crinoid data compare well with oxygen isotopic contents of modern crinoids, but the values are noticeably enriched in carbon-13. Mississippian crinoids from other localities are also enriched in carbon-13. For example, Mississippian crinoids from England and New Mexico range from +2.1 to 2.6 permil PDB, and Mississippian echinoids (+1.0 to 3.4 permil PDB) and crinoids (+1.8 to 4.0 permil PDB) from the Burlington Formation of Missouri and Iowa (Meyers and Lohmann, 1985) illustrate the enrichmnent of carbon-13. The large relative enrichment of carbon-13 in the Mississippian crinoids with respect to modern crinoids (-3 to -6 permil PDB; Weber and Raup, 1968) is probally not due to similar diagenetic processes. The carbon-13 enrichmnent is not attributed to diagenesis because strikingly similar diagenetic events would have to operate over the large geographical extent of the Mississippian examples. Meyers and Lohmann (1985) concluded that Mississippian crinoids precipitated HMC with a carbon isotopic content similar to the ambient seawater, followed by variable depletions of carbon-13 with diagenesis.

Modern and ancient brachiopods secrete shells in isotopic equilibrium with seawater (Lowenstam, 1961; Popp et al., 1986). Trace element analysis has demonstrated the pristine nature of brachiopods from the Hillsdale Limestone. Thus, the brachiopod delta O-18 value of +0.4 PDB represents calcite precipitated in isotopic equilibrium with Meramecian seawater in the study area. Using the brachiopod delta O-18 value of 0.4 PDB, assuming a delta O-18 value of 0.0 for seawater and using the paleotemperatue equation of Craig (1965), yields a temperature of precipitation of 18.6 $\pm$ 0.9 degrees celsius. Silica precipitated from the same water (at the same temperature) would have an expected delta O-18 value of +37 SMOW (Meyers and James, 1978; Labeyrie, 1974). The silica delta O-18 value of +30.2 SMOW indicates isotopic equilibration occurred with 1) higher burial temperatures and/or 2) waters isotopically lighter than the brachiopod seawater value (ie. meteoric waters).

Using the silica delta O-18 value of 30.2 SMOW, assuming meteoric water was appoximately the same temperatue as seawater (18.6 degrees celsius), and using the equation of Labeyrie (1974), yields a delta O-18 value of -6.5 SMOW for the water of silica precipitation. A present day carbonate environment located at the same latitude (Central America, 15 degrees) as the Hillsdale during deposition (Fig. 5) has meteoric waters with delta O-18 values of approximately -5.0 SMOW (Taylor, 1974). Mississippian seawater is considered to have been about 1.5 permil lighter (ie. -1.5 SMOW) than present day ocean water (Brand and Veizer, 1980; Meyers and Lohmann, 1985). Adding this correction factor (-1.5 SMOW) to the modern day meteoric water value (-5.0 SMOW) yields an estimated delta O-18 value of -6.5 SMOW for meteoric water in the study area during Meramecian time. This suggests that <u>one stage of silica equilibration</u> may have occurred in isotopic equilibrium with isotopically light meteoric-phreatic waters, which is in agreement with the model of Meyers and James (1978). Petrographic evidence in the Hillsdale Limestone indicates silica cementation of the horn coral occurred in the meteoric-phreatic environment. Meyers and James (1978) used petrographic and geochemical evidence to demonstrate that silcification in the Lake Valley Limestone (Mississippian) of New Mexico occurred in the meteoric environment.

Alternatively, the isotopic composition of the Hillsdale silica may represent the recrystalization of opal-CT to chalceodonite, which allows for isotopic re-equilibration (Fig. 9B). This conversion may take place significantly after the initial precipitation of disordered opal-CT (up to 100 million years; Robertson, 1977). Thus, the conversion could have occurred at a higher temperature due to deep burial. It should be noted that the two silica phases (ie. chalcedonite and megaquartz) represent two different stages of silicification. Because these two silica phases were not separated before isotopic analysis, interpretation of the silicification event(s) is limited. Since no intermediate phases occur in the precipitation of megaquartz, the isotopic composition of unaltered megaquartz reflects the isotopic composition of water of original precipitation. Meyers and James (1978) had similar isotopic data. On the basis of regional stratigraphic relationships and extensive oxygen isotopic data for the individual microfabrics of quartz, they concluded that silicification occurred in isotopically light (-7 permil) meteoric waters. The critical data for Meyers and James' (1978) conclusions was their petrographic evidence that demonstated that megaquartz is a silica cement (ie. authigenic) and the isotopic composition of megaquartz which is best interpretated as the result of precipitation in the meteoric environment.

In summary, the stable isotope data suggest that the siliceous infilling of a horn coral equilibrated in the meteoric-phreatic environment. The oxygen isotope composition of the silica is compatible with petrographic and trace element diagenetic interpretations. The meteoric-phreatic silicification model of Meyers and James (1978) is supported by petrographic evidence and this model of silicification can be resolved with the stable isotope data of the Hillsdale Limestone. The oxygen isotopic composition of the siliceous infilling of the horn coral (B-17) may not be representative of other silicified fossils and/or the chert nodules in the Hillsdale Limestone.

CONCLUSIONS

A summary of the evidence presented in this study of the Hillsdale Limestone indicates the following conclusions:

1) Four major lithofacies are recognized including 1) terrigenous siliciclastics (8.3%), 2) pelloidal wackestones and lime mudstones (12.4%), 3) ooid and echinoderm grainstones (15.5%), and 4) skeletal packstones/wackestones (73.9%). Skeletal packstones/wackestones is the most abundant facies and can be further divided into subfacies of packstones and wackestones. Skeletal wackestone is the most common lithology accounting for 122.6 meters (44.3%) of the combined total 276.9 meters studied.

2) The depositional environment of these four facies is

interpreted as a homoclinal carbonate ramp with a small discontinuous offshore shoal sequence. From nearshore to offshore the facies are interpreted as: 1) shallow subtidal siliciclastics, grading into; 2) a lagoonal lime mudstone facies, protected from wave energy by; 3) a discontinuous offshore shoal sequence, usually composed of ooid grainstones with minor occurrences of echinoderm grainstones, followed by; 4) outer ramp skeletal packstones which generally grade outward into bryozoan wackestones. Facies 1 through 3 are interpreted as deposited above normal wave base, with facies 4 interpreted as deposited below normal wave base.

3) The stratigraphic distribution of the facies suggests four sequences of shallowing-upward sequences. The most distinctive shallowing-upward sequence occurs at the top of each stratigraphic section with limestones overlain by calcareous quartz siltstones or terrigenous shales.

4) Stratigraphic distribution of Hillsdale lithologies and insoluble residue percentages support the interpretation of other workers that a transgression occurred during Hillsdale (St. Louis) time for the Appalachian Basin in general. In the study area, the peak of the transgession appears to occur in middle Hillsdale time.

5) The diagenetic history of the Hillsdale Limestone is complex. Early diagenetic events include: micritization and pyritization in

stagnant marine environments, and isopachous rim cementation and hematite formation in active marine environments. Localized exposure of an ooid bar to the meteoric-vadose environment resulted in the formation of a meniscus cement. With the encroachment of meteoric fresh water, the presence of a mixing zone of sea water and fresh water resulted in dolomitization. The stratigraphic distribution of insolubles appears to have been a controlling factor of the location of dolomitization. With further encroachment of groundwaters, establishment of a meteoric-phreatic environment resulted in: 1) silicification; 2) aragonite leaching in the solution zone, and; 3) the formation of microspar, syntaxial cement, blocky and drusy pore-filling cements, and calcification in the active zone. Magnesium calcites may have stabilized in the stagnant zone of the meteoric-phreatic environment. Compaction, sutured grains, stylolitization, and fracturing occurred throughout the continued burial of Hillsdale sediments.

6) Trace element analysis of microfossils indicates that brachiopods (low magnesium calcite), and a rugose coral (originally low to intermediate high magnesium calcite) have undergone slight alteration in a partially closed system. Crinoids (originally High Magnesium Calcite) have undergone more significant alteration. The pristine chemical composition of brachiopods facilitates use of stable isotopic ratios as indicators of the stable isotopic content of Meramecian seawater in the study area.

7) Silicification in the meteoric-phreatic environment is indicated by petrographic evidence. This interpretation is in general agreement with the model of meteoric-phreatic silicification of carbonates by Meyers and James (1978). The model invokes initial precipitation of an opal-CT precursor of chalcedonite and of microcrystalline quartz occurred in the more seaward portions of the meteoric-phreatic environment, followed by direct precipitation of megaquartz in the more landward portions of the meteoric-phreatic environment.

Oxygen isotopic data for the Hillsdale indicate that silicification may have occurred in the meteoric-phreatic environment. The tentative interpretations of the isotopic data reflect the limited number of stable isotope analyses (only one composite silica sample and comparison with one brachiopod value). The source of silica is believed to be the intrabasinal and/or extrabasinal alteration of clay minerals.

8) Oxygen isotope composition of the brachiopod allows for the calculation of a Meramecian seawater paleotemperature of 18.6 ± 0.9 degrees celsius. No latitude or salinity corrections were applied to this temperature calculation.

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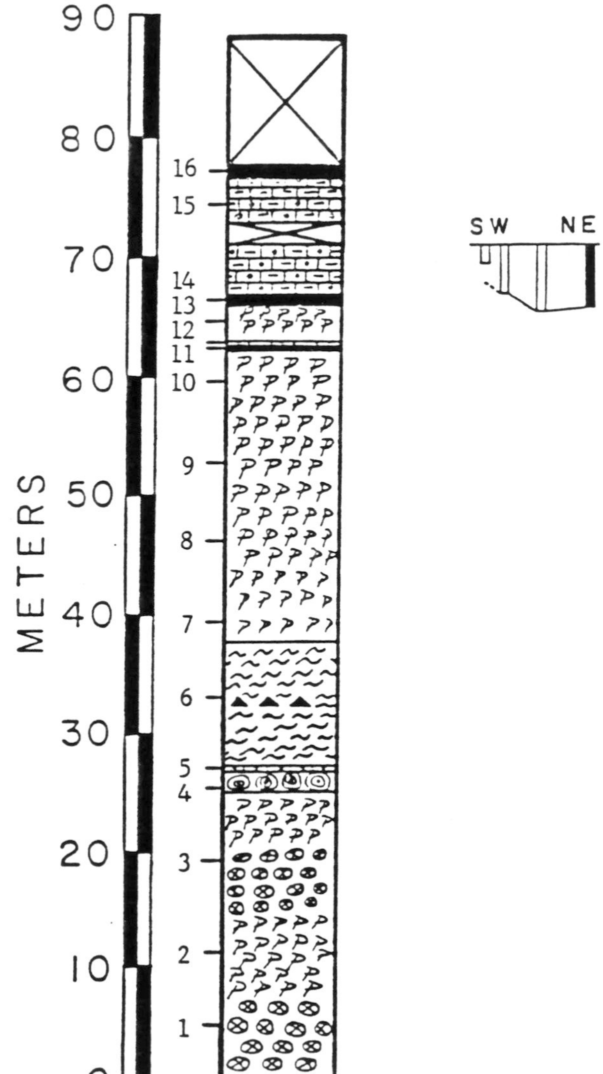
APPENDIX A - INSOLUBLE RESIDUE PERCENTAGES

INSOLUBLE RESIDUE PERCENTAGES

Sample #	Description	Insoluble Percent
A-110	Echinoderm Grainstone (Isotope Sample)	7.9
B-19	Cherty Skeletal Wackestone	14.6
B-18	Ooid Grainstone	3.1
B-17	Calcareous Qtz Siltsone (Isotope Sample)	56.3
B-16	Calcareous Qtz Siltstone	44.1
B-15	Skeletal Wackestone	17.0
B-14.5	Terrigenous Shale, Fissile	74.5
B-14	Ooid Wackestone	6.8
B-13.5	Skeletal Packestone	14.1
B-13	Pelloidal Grainstone	2.3
B-12.5	Pelloidal Grainstone	4.8
B-12.5	" " Duplicate	11.5
B-12	Pelloidal Wackestone	6.3
B-11.5	Oncolitic Boundstone	20.9
B-11	Skeletal Wackestone	11.9
B-10	Skeletal Wackestone	21.9
B-9.5	Cherty Skeletal Packstone	20.6
B-9	Ooid Grainstone	4.4
B-8	Skeletal Packstone	14.2
B-7	Skeletal Packstone	16.7
B-6	Dolomitized Skeletal Packstone	7.5
B-5	Dolomitized Skeletal Wackestone	6.5
B-4	Dolomitized Skeletal Wackestone	10.8
B-3	Skeletal Wackestone	41.3
B-2.5	Skeletal Packstone	13.7
B-2	Skeletal Wackestone	44.2
B-1	Lime Mudstone	46.1

APPENDIX B - MEASURED OUTCROP DESCRIPTIONS



HAYTER'S GAP (A) SECTION

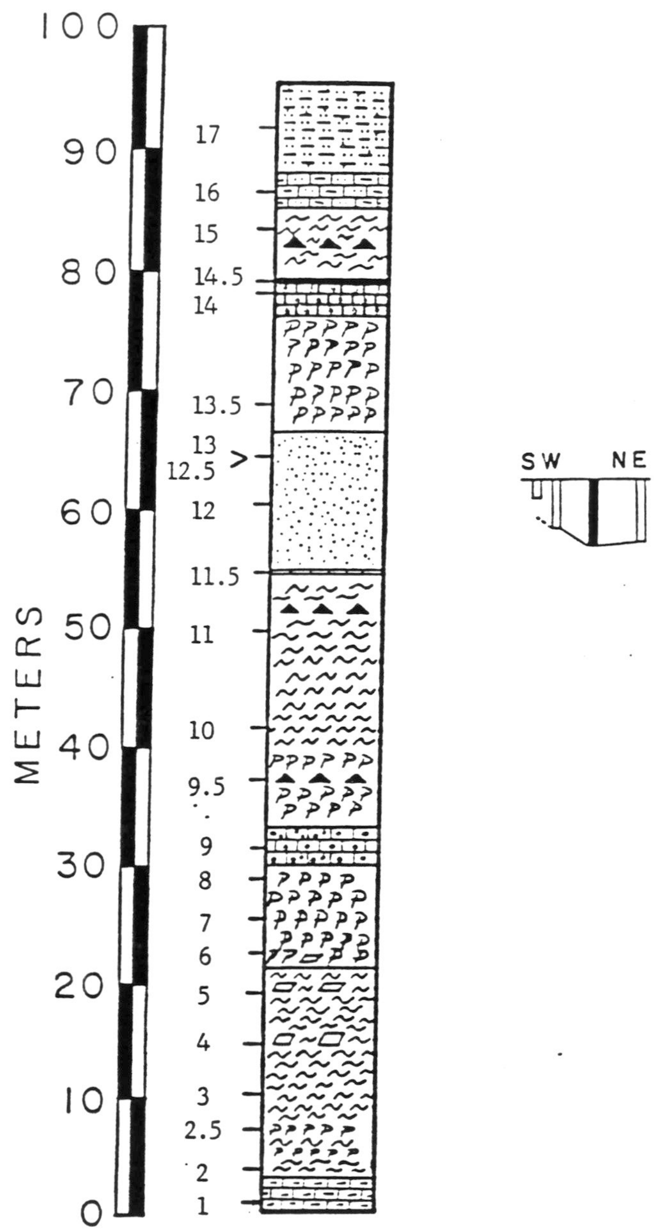
Locality- Hayter's Gap (A) Section Route 80
Approximately 11km northeast of Abingdon

Sample Description	Thickness (meters) Total	Unit
Ste. Genevieve Limestone.	Unmeasured.	
--- Formational Contact ---		
Hillsdale Limestone. Covered Section - presumed to be uppermost shaly unit of Hillsdale Limestone	90.0	10.2
A-16 Terrigenous Shale. Dark gray, nonfossiliferous.	78.8	1.0
A-15 Ooid-bearing Lime Mudstone. Light gray, coarse-sand size ooids, petroliferous, thick-bedded, partly covered, weathers to a brown-gray.	77.8	10.8
A-14 Terrigenous Shale. Dark gray, nonfossiliferous.	67.0	0.2
A-13 Bryozoan Packstone. Light gray, very fossiliferous, brachiopods and crinoids.	66.8	2.9
A-12 Sandy Ooid Intraclast Packstone. Brown-gray, coarse- to medium-grained polycrystalline 'strained' medium-grained quartz sand, brachiopods, sedimentary rock fragments, trace trilobites, coral, with lime mud matrix.	63.9	0.6
A-11 Terrigenous Shale. Dark gray, nonfossiliferous.	63.3	0.3
Skeletal Packstone. A-7, A-8 Bryozoan Packstone, in bottom half. Medium-gray, micrite matrix, minor silicification, massive bedding. Grades up into A-9, A-10 Echinoid-Bryozoan Packstone, top half. Medium-gray, micrite matrix, brachiopods, trace forams, massive bedding.	63.0	25.0
A-6 Echinoid-Bryozoan Wackestone. Dark gray, chert nodules in middle part, brachiopods, horn coral, thick-bedded.	38.0	10.9
A-5 Ooid Grainstone. Dark gray, fining-upward graded bedding, pooly sorted, trace dolomite.	27.1	0.3

A-4 Oncolitic Packstone. Medium-gray, sparite cement, micritized oncolites, thick-bedded.	26.8	2.0
A-1, A-3 Echinoid Grainstone, in lower and upper part. Dark gray, micrite cement, brachiopods, trace bryozoans, massive-bedded, interbedded with A-2 Echinoid Packstone, in middle part.	24.8	24.8

--- Formational Contact ---

Little Vallley Limestone. Shaly weathering. Unmeasured.

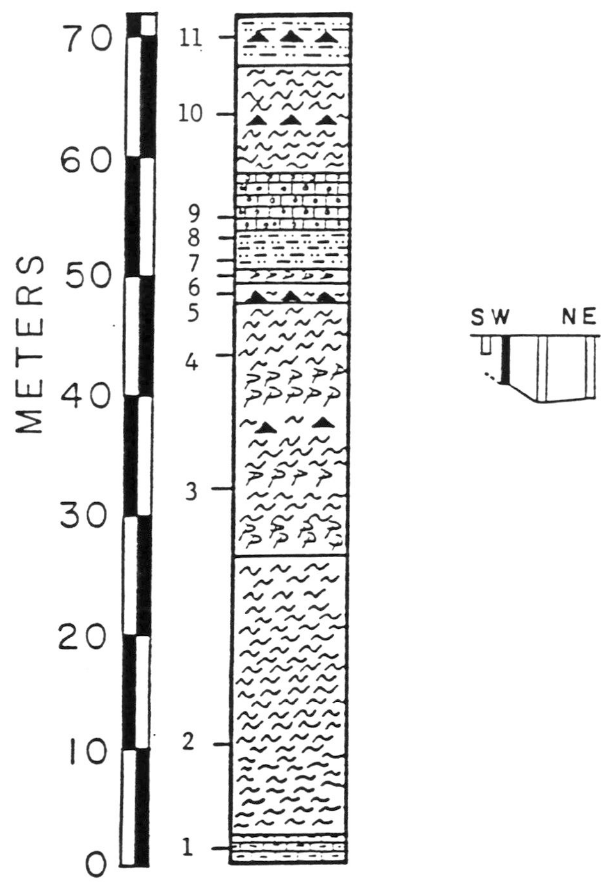


HOLSTON (B) SECTION

Locality- Holston (B) Section. Route 19/Alt 58
Approximately 10km northwest of Abingdon

Sample Description	Thickness (meters) Total	Unit
Ste. Genevieve Limestone. B-18 Oolitic Grainstone, dark gray. Bottom of this unit is the lower contact of the Ste. Genevieve Limestone. Overlying this unit are cherty skeletal wackestones of the Ste. Genevieve.	Unmeasured	1.0
--- Formational Contact ---		
Hillsdale Limestone. B-17 Calcareous Quartz Siltstone. Green-gray, medium- to fine-grained detrital quartz silt, fossiliferous in upper part with silicification, Heterophrentis sp. (rugose horn coral). Pyrite. B-16 in lower part, silty lime mudstone, dark gray, non-fossiliferous. Shaly weathering with 3-5mm thick shaly partings.	96.8	10.8
B-15 Brachiopod-Bryozoan Wackestone. Light gray, thick-bedded, chert nodules in middle part. Calcite veins up to 2mm thick. Styolites.	86.0	6.0
B-14.5 Slightly calcareous shale. Dark gray, fissile. Pyrite and Hematite.	80.0	0.3
B-14 Oolitic Wackestone. Dark gray, thinly laminated, micritic cement and microspar, intraclasts, echinoids, with thin interlaminae of micrite separated by styolites.	79.7	3.0
B-13 Bryozoan-Echinoid Packstone. Dark gray, very fossiliferous, silicified brachiopods, minor shaly interbeds.	76.7	9.7
B-12.5 Pelloidal Wackestone grades up into B-12 Pelloidal Grainstone. Intraclasts, burrows filled with sparry calcite.	67.0	12.0
B-11.5 Oncolitic Wackestone. Gray brown fissile shaly beds deformed around light- to dark-gray oncolites. Average diameter 10mm, max. 36mm. Micrite and angular quartz silt matrix.	55.0	0.3

B-9.5 Cherty Echinoid-Bryozoan Packstone with burrows and brachiopods, grades up quickly into B-10 and B-11 Echinoid-Bryozoan Wackestone. Massive bedding with chert in upper part.	54.7	21.3
B-9 Oolitic Wackestone. Light brown, medium- to coarse-grained sand-sized well-rounded ooids, thick bedded. Sparry calcite cement, oncolites.	33.3	3.5
Skeletal Packstone. Thick bedded, light- to dark-gray. B-6 Bryozoan-Echinoid Packstone with minor dolomitization and silicification grades up into B-7 Brachiopod-Echinoid Packstone which grades up into B-8 Echinoid Packstone with minor productid brachiopods.	29.8	8.8
B-3 , B-4 , B-5 Dolomitic Bryozoan Wackestone. Dark gray, thick bedded. Echinoids in lower part, *Syringopora virginica* (colonial coral) in upper part. Minor silicification.	21.0	14.0
B-2 Bryozoan-Brachiopod Wackestone, light gray with minor interbeds of B-2.5 Echinoid-Bryozoan Packstone, dark gray. Shaly weathering.	7.0	4.0
B-1 Lime Mudstone. Fissile, slightly fossiliferous with productid brachiopods up to 25mm in diameter.	0.0	3.0
--- Formational Contact ---		
Little Valley Limestone.	Unmeasured.	



HORSESHOE BEND (M) SECTION

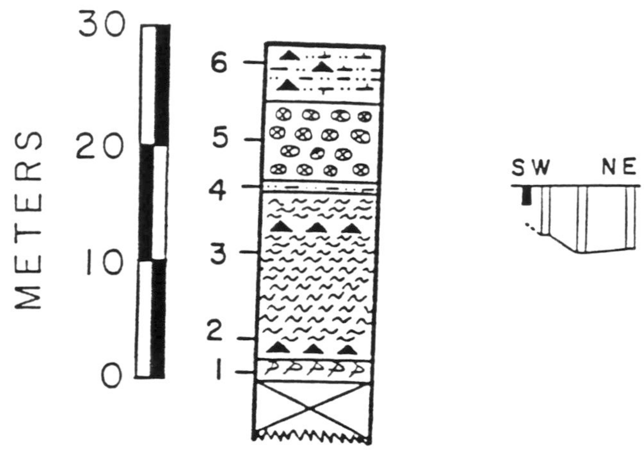
Locality - Horseshoe Bend (M) Section.
Exposures within interior of meander on
the North Fork of the Holston River,
Wallace 7.5 min. Quadrangle.

Sample Description	Thickness (meters) Total	Unit
Ste. Genevieve Limestone	Unmeasured.	
--- Formational Contact ---		
Hillsdale Limestone.		
M-11 Quartz Siltstone. Weathers green, slightly fossiliferous, byozoans, crinoids, medium to thick-bedded, nodular and ragged chert.	72.3	4.3
M-10 Echinoid Wackestone. Dark gray, gastropods, brachiopods, oncolites, nodular chert, minor silicification of crinoids, oblique styolites.	68.0	9.2
M-9 Ooid Grainstone. Light-gray, micritized ooids, medium- to coarse-grained, brachiopods, bryozoans, echinoids, horizontal and vertical styolites, massive bedding.	58.8	4.8
M-7, M-8 Quartz siltstone. Brown-gray, laminated, 0.1mm thick horizontal and vertical veins of calcite, trace pyrite, weathers to light green.	54.0	3.3
M-6 Foraminferal Packstone. Dark gray, brachiopods, echinoderms, 12% micrite, 30% sparite, minor silicification.	50.7	1.5
M-5 Bryozoan Wackestone. Dark gray, abundant black chert nodules, *Syringopora virginica* , echinoderms,algal nodule, and minor silicification of trace brachiopods.	49.2	1.5
M-4 Bryozoan-Echinoid Wackestone. Dark gray, micritization, and minor silicification of allochems, with minor interbeds of M-3 Echinoid-Bryozoan Packstone. Dark gray, echinoids 40%, bryozoans 40%, and micrite 20%.	47.7	21.3
M-2 Bryozoan-Echinoid Wackestone. Dark gray, thick-bedded, partly covered.	26.4	24.0
M-1 Lime Mudstone. Dark gray, slightly fossiliferous, byozoans 2%, pyrite 5%,	2.4	2.4

quart silt 3%, echinoids 1%, trace mica.

--- Formational Contact ---

Little Valley Limestone. Shaly weathering. Unmeasured.



MUDDY HOLLOW (H) SECTION

Locality - Muddy Hollow (H) Section.
280 meters west of Horseshoe Bend Section,
Wallace 7.5 min. Quadrangle.

Sample description	Thickness (meters) Total	Unit
Ste. Genevieve Limestone	Unmeasured.	
--- Formational Contact ---		
Hillsdale Limestone. Incomplete section, lower part covered.		
H-6 Calcareous Quartz Siltsone. Cherty, slightly fossiliferous, weathers green.	29.0	5.0
H-5 Echinoderm Grainstone. Light gray, micritization, isopachous rim cement, blocky spar, oncolites, trace polycrystalline quartz.	24.0	6.6
H-4 Calcareous Quartz Siltstone. Mud matrix, thin-bedded.	17.4	0.8
H-2, H-3 Bryozoan Wackestone. Chert nodules regularly spaced 0.3m to 0.4m apart in lower part; more irregularly spaced in upper part, laminated.	16.6	14.6
H-1 Echinoid-Bryozoan Packstone. Medium gray, minor silicification of echinoids.	2.0	2.0
Lower Hillsdale Limestone is covered.	?	?