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entitled THE PETROLOGY, STRATIGRAPHY, AND ORIGIN OF
PHOSPHATIC NODULES IN UPPER DEVONIAN AND LOWER
MISSISSIPPIAN ROCKS OF THE EASTERN INTERIOR

be accepted as fulfilling this part of the requirements for the degree of MASTER OF SCIENCE

Approved by:

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The Petrology, Stratigraphy, and Origin of
Phosphatic Nodules in Upper Devonian and Lower
Mississippian Rocks of the Eastern Interior

A Thesis submitted to the
Division of Graduate Education and Research
of the University of Cincinnati
in partial fulfillment of the
requirements for the degree of

MASTER OF SCIENCE

in the Department of Geological Sciences of the
College of Arts and Sciences

1979

by

Barry W. Acomb

B.S., University of Cincinnati, 1976

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Abstract

Phosphate nodules in Upper Devonian and Lower Mississippian rocks of the Eastern Interior represent lag deposits. The phosphatic lag deposits were formed by current erosion, bioerosion, and dissolution of phosphatic and limestone hardgrounds.

Evidence suggests that phosphate nodules form through four different combinations of complex syngenetic and diagenetic processes acting in situ during times of nondeposition or low terrigenous influx. These processes were acting on shallow seafloors prior to the Early Mississippian clastic deposition represented by the Borden Formation in Kentucky, and also at the end of clastic deposition on the Borden delta front in Early Mississippian time throughout southern Kentucky, Tennessee, northern Alabama, and northwestern Georgia.

The texture of the original carbonate sediment is important in controlling the degree of phosphate replacement. The texture of the sediment at the time of phosphate replacement was controlled by the amount of bioturbation, including both pre-lithification burrowing and post-lithification boring.

Phosphate nodules are common in Upper Devonian black shales of Kentucky and Indiana, as well as in Lower Mississippian glauconitic shales of southern Kentucky, Tennessee, northern Alabama, and northwestern Georgia. Because of their wide distribution, phosphate nodules are useful as stratigraphic markers in both the Devonian black shales and the overlying Lower Mississippian glauconitic shales.

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Purpose

The objectives of this study have been:

1. To determine whether phosphatic nodules were formed in place (direct precipitation of phosphate), or represent replacement of a pre-existing sediment.
2. To determine the nature of the original rock if the phosphate represents a replacement of some previous sediment.
3. To determine what controls the phosphate replacement. (What is the role of grain size, porosity, bioturbation or reworking ?)
4. To determine the lateral continuity of the phosphate nodule horizon, and decide whether or not it represents a consistent stratigraphic marker in the Upper Devonian-Lower Mississippian system.
5. To contribute to an understanding of the overall sedimentologic regime of the Upper Devonian and Lower Mississippian system in Kentucky and Tennessee.

Location of Study

Sample locations are shown generally on Figure 1, and are listed as to specific location in the Appendix. The samples studied came from surface outcrops located on the flanks of the Cincinnati arch in Ohio, the Lexington Dome in central Kentucky, and the Nashville Dome in central Tennessee. Exposures are controlled structurally and are only present where the slightly dipping Devonian strata intersect the surface around the domes. With the exception of a single outcrop at Menlo, Georgia, located in the Appalachian Fold Belt, all study locations are tectonically undisturbed.

Method of Investigation

Field observations were made at 25 localities and samples were collected at 11 localities in Ohio, Indiana, Kentucky, Tennessee, and Georgia (Fig. 1), an area of approximately 51,000 square miles. Photographs were taken of the various shapes, sizes, and arrangements of nodules in the enclosing shale. Initially, nodules from each outcrop were analyzed by X-ray diffraction (Appendix B) to determine if the nodule was truly phosphatic and to determine the identities of the phosphate and associated minerals. Selected nodules were also cut into slabs and analyzed with a Faxitron X-ray radiograph to resolve bedding and bioturbation structures. Thirty-five petrographic thin sections were studied with a Zeiss polarizing microscope to determine rock texture, mineral associations, replacement fabric, and grain-size. Photomicrographs were taken with the Zeiss polarizing research microscope.

Regional Stratigraphy

Stratigraphy used in this reports involves the Upper Devonian and Lower Mississippian series in Ohio, Kentucky, Indiana, and Tennessee in which phosphate nodules are found. Stratigraphic nomenclature changes across physiographic provinces (ie. Cincinnati arch), most often reflecting lithologic variations in stratigraphically equivalent units, particularly in the Lower Mississippian series. The Devonian black shale is known as the Ohio Shale east of the Cincinnati arch, New Albany Shale west of the arch, and Chattanooga Shale south of the Lexington dome.

In Ohio, the Ohio Shale is divided into three members: the Huron, the Chagrin, and the Cleveland Members. The Cleveland Member is overlain by

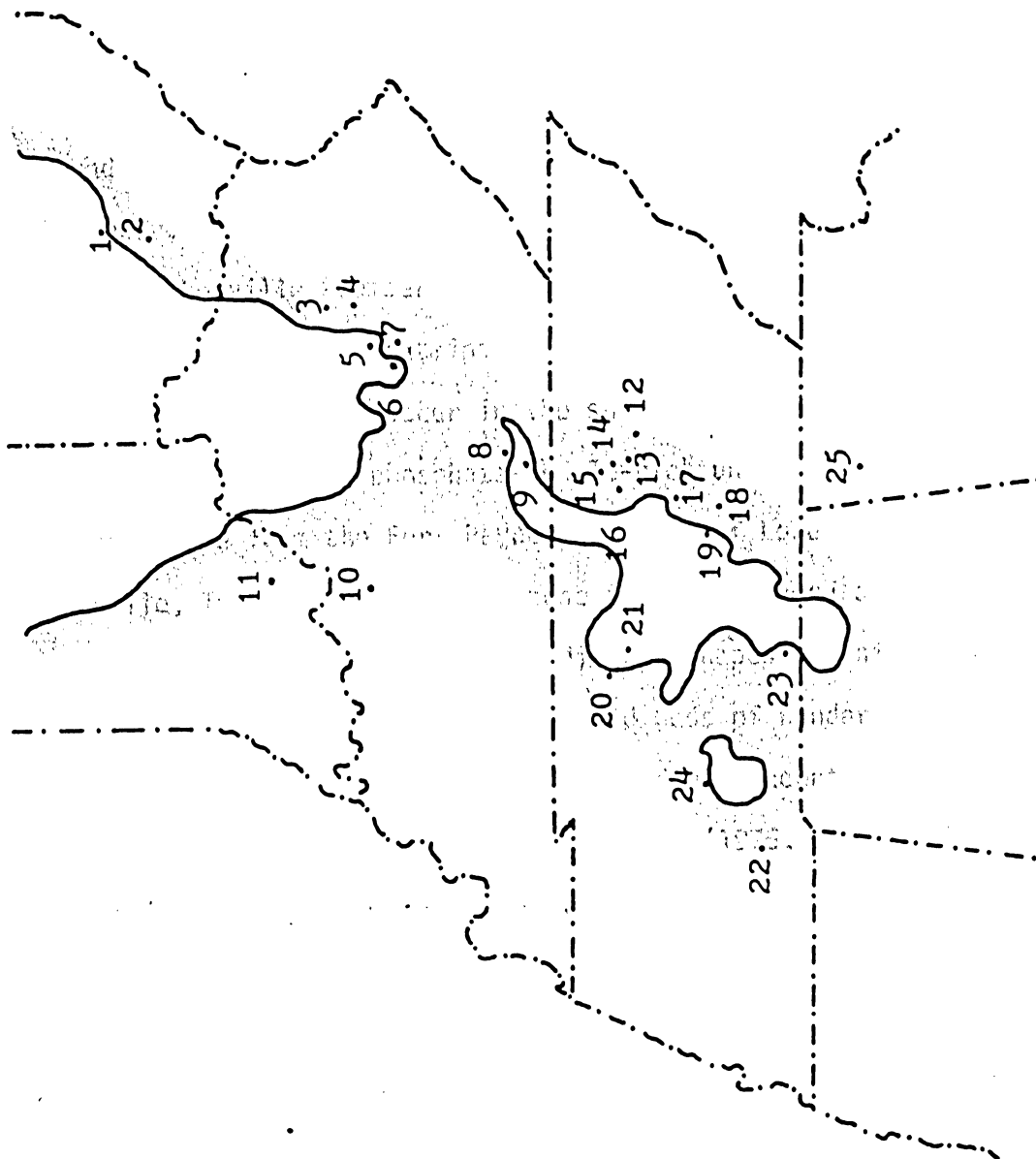


Fig. 1 Study locations and generalized outcrop pattern of black shale on the flanks of the Cincinnati arch.

coarser clastics, the Bedford Shale, and the Berea Sandstone. The Berea Sandstone is overlain by the Sunbury Shale, which closely resembles the Ohio Shale in appearance. Prove et al (1977) report the occurrence of phosphate nodules in the upper few feet of the Cleveland Member of the Ohio Shale at Tener Mountain, Adams County, Ohio. I did not find phosphate nodules at this locality.

In northern Kentucky phosphate nodules are located in both the New Albany Shale and the overlying New Providence Shale, member of the Borden Formation in the vicinity of Clay City, Kentucky. Nodules are also found in the upper few feet of the Ohio Shale east of Irvine, Estill County, and at Berea, Madison County, Kentucky. Further southwest, near Burkesville, Cumberland County, the black shale (here known as the Chattanooga Shale) contains abundant phosphate nodules in its uppermost part. They also occur in the shale of the overlying Maury Formation, a glauconitic, phosphate-nodule-rich unit which separates the Chattanooga Shale from the Fort Payne Formation of Lower Mississippian age. At Smithville, Tennessee the nodule zone is concentrated as a conglomerate in lensoid beds containing nodules of diverse shapes and sizes, apparently without preferred orientation. The lensoid beds of Kinderhookian age lie directly upon the Chattanooga Shale and forms a paracontinuity (Conkin, 1975) with the underlying Chattanooga. Conkin (1975, p. 2) defines the paracontinuity as a geographically widespread diastem which is manifested by both a physical break and a faunal gap. Nodules are rarely found within the Chattanooga, but rather occur on top of the formation. In the southern and western parts of Tennessee, as well as northern Alabama and Georgia, nodules are again concentrated on top of the Chattanooga, in Kinderhookian rocks.

W. KENTUCKY
(KEPFERLE, 1971)

OHIO & E. KY.
(PROVO, ET AL, 1977)

INDIANA
(LITZBACH, 1968)

TENNESSEE
(COVANT, ET AL, 1961)

SYSTEM	SERIES	FORMATION & MEMBER	SERIES	GROUP	FORMATION & MEMBER	SERIES	GROUP	FORMATION & MEMBER	SERIES	GROUP	FORMATION & MEMBER
MISSISSIPPIAN	LOWER	BORDEN FORMATION	OSAGE	BORDEN	MULDRAUGH	KINDERHOOK	BORDEN	NEW ALBANY	UPPER	OHIO SHALE	NEWMAN LS. (KY.)
					FLOYDS KNOB MEMBER			CLEGG CR. MEMBER			BORDEN FORMATION (KY.)
					HOLTSCLOW SILTSTONE MEMBER			CAMP RUN MEMBER			CUYAHOGA GRP. (OHIO)
					NANCY MEMBER			MORGAN TR. MEMBER			SURBURY SHALE
DEVONIAN	MIDDLE & UPPER	NEW ALBANY SHALE			KENWOOD SILTSTONE MEMBER			ROCKFORD LS.		CHATTANOOGA SHALE	MAURY
					NEW PROVIDENCE SHALE MEMBER			CLEGG CR. MEMBER			SALEM & WARSAW
								CAMP RUN MEMBER			FORT PAYNE
								MORGAN TR. MEMBER			
		BEECHWOOD LS. MEMBER OF SELLERSBURG LS.						SELWIER MEMBER			
								BLOCHER MEMBER			
								N. VERNON LS.			
											DOWELLTOWN MEMBER

Fig. 2 Stratigraphic nomenclature used in this report.

In Indiana, phosphate nodules are located in Lineback's (1968, p. 1297) Falling Run Bed of the Clegg Creek Member of the New Albany Formation (equivalent to the Chattanooga and Ohio Shale). The Falling Run Bed is overlain by greenish glauconitic shale of Jacob's Chapel Bed of the Clegg Creek Member. The Jacob's Chapel Bed in turn is overlain by the Rockford Limestone.

It is a notable feature in the regional stratigraphy that the nodulose zone vertically separates the Devonian black shale from the Borden "delta front" (Peterson and Kepferle, 1970) in most of Kentucky, and separates the Fort Payne Formation from the Chattanooga Shale in Tennessee, Alabama, and Georgia. It is particularly important that in the latter case the phosphate nodules are associated with glauconite lying on the starved Borden delta front as well as on Devonian pro-delta sediments which were later covered by the Borden delta progradation (Fig. 3).

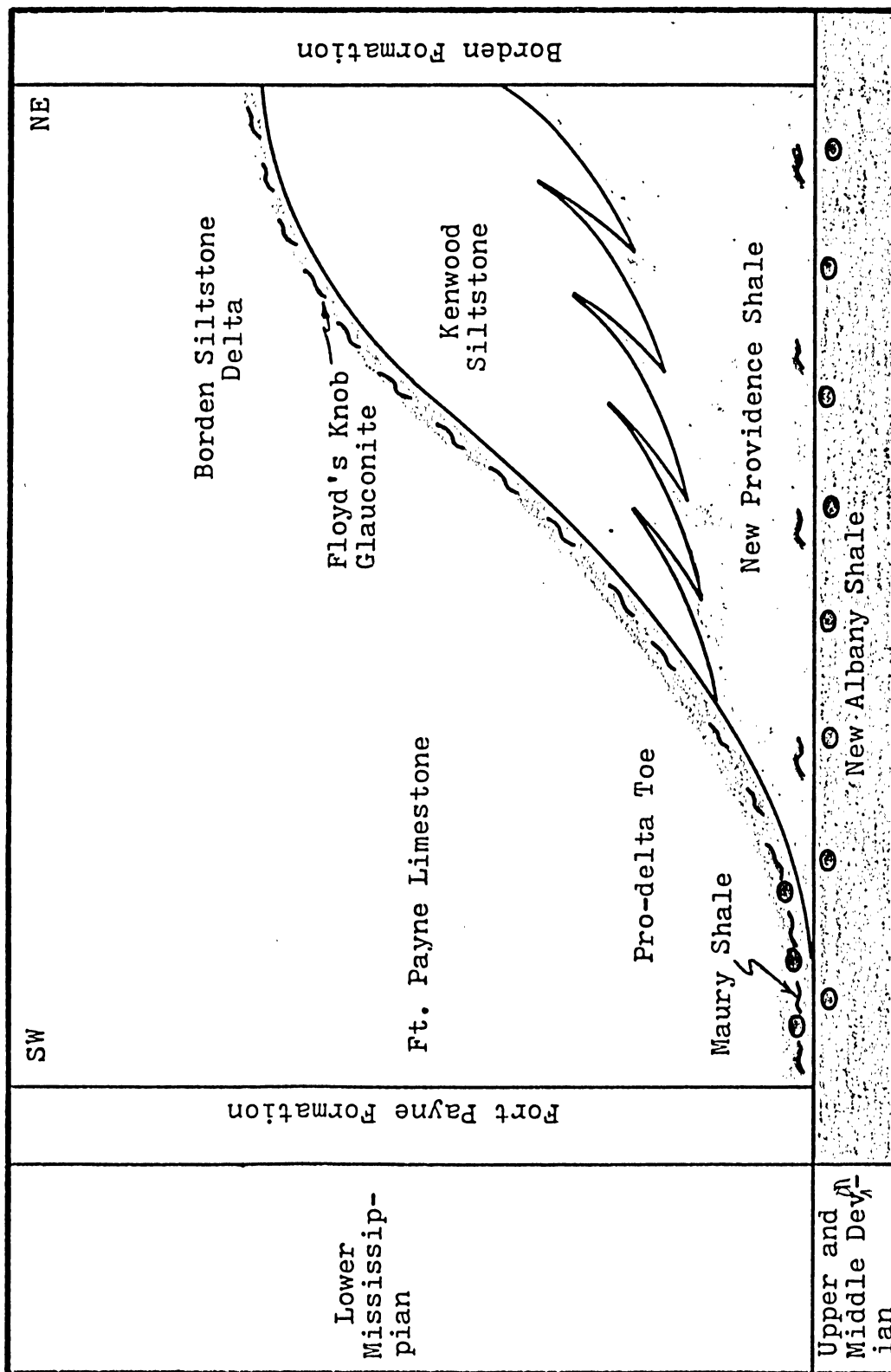


Fig. 3 Schematic cross-section showing paleotopography of the Borden delta (modified from Kepferle, 1977) and regional stratigraphy from central Kentucky through Tennessee.

Previous Work with Nodules from Devonian Black Shales

Previous studies of Devonian-Mississippian black shales have been predominately stratigraphic, paleontologic, or economic in nature. Mention of phosphate nodules is given by Safford and Killibrew (1900, p. 141-142), Campbell (1946, p. 848-849), Glover (1959, p. 140), Conant and Swanson (1961, p. 65-67), Lineback (1968, p. 1250), and Provo, et. al. (1977, p. 15). The above authors regarded the nodules simply as possible local or regional stratigraphic markers. Each of these authors has studied the nodulose zone in a limited area but has not considered its total areal extent; the nodulose zone was used in the field merely to aid in locating particular stratigraphic horizons in black shales. Thus very little petrographic work has been done on the phosphate nodules which might be of help in determining their nature and origin.

Conant and Swanson (1961) and Campbell (1948) give a simple description of the appearance and content of the nodules in Tennessee. They noted (Conant and Swanson, 1961, p. 65) that the nodules occur in a single layer 2 to 3 inches thick, are very numerous and occupy all available space. They also found that (Conant and Swanson, 1961, p. 65) nodules varied in size from half an inch in diameter to elongate flattened forms several inches long, but their thickness seldom exceeded 2 inches. The nodules were found to vary in texture, internal appearance, and faunal content, and more importantly, seem not to have all formed at the same time.

Conant and Swanson (1961, p. 65) note that zones of tightly packed nodules, where present, are in the lower part of the Maury Formation, and where the

concentration is greatest have their greatest variation in shape and size. Earlier workers noted that the beds of tightly packed nodules are commonly about 6 inches to one foot thick, but thickness differs greatly in short lateral distances.

Conant and Swanson (1961) discovered that a large proportion of the nodules contain one or more fossils which they believed served as nuclei around which the calcium phosphate accumulated. Among the fossils they recognized were linguloid brachiopods, conodonts, cephalopods, crustaceans, bone fragments, and plant remains. Although the fossil content of the nodules was studied, no detailed study was made of the matrix material and phosphate minerals contained in the nodules. Earlier workers (Conant and Swanson, 1961, and Campbell, 1948) inferred that the phosphatic material consisted of collophane, an informal term frequently applied to amorphous, phosphate - rich solids.

Previous Work on Phosphate Deposits Worldwide

Mode of Phosphatization

The origin of phosphate deposits, both in ancient seas (as recorded on the continents) and on the modern sea floor, has been a much debated issue during the past half century. D'Anglajen (1967) notes that marine phosphorites are the end-product of imperfectly known processes that are largely inferred from studies of ancient deposits. Little information has been gathered regarding phosphate deposition in the modern seas. Degens (1965) provided a very useful review of the problem. He summarized the ideas about the origin of marine sedimentary phosphates under three categories based on mode of phosphatization: (1) Direct chemical precipitation of phosphatic deposits from super-saturated natural waters (e.g., Kazakov, 1937, 1950; McKelvey, et al., 1953; McKelvey, 1967; Dietz, et al., 1942; Emery, 1960). (2) biochemical concentration of phosphate through the precipitation and the accumulation of organic residues (e.g., Cayeux, 1936; Yousseff, 1965; Baturin, 1971), and (3) the replacement of pre-existing calcareous materials by phosphates (e.g., Bushinsky, 1935, 1964; Ames, 1959; D'Anglejan, 1968).

Direct Chemical Precipitation

Kazakov (1953) suggested that phosphate precipitation will occur in areas of cold upwelling currents. As these currents ascend, the temperature increases, the partial pressure of CO₂ decreases, and the pH rises accordingly. Phosphate solubility varies inversely with pH,

and the increase in pH and decrease in CO_2 results first in the precipitation of calcite and then apatite. Kazakov maintained that the precipitation occurs at depths of 50 to 200m and that it would not take place within the photosynthetic zone, where any available phosphate would be taken up by phytoplankton. This hypothesis is accepted by many workers and has been used successfully to explain the sedimentary association of many phosphate deposits. McKelvey, et al. (1953) used a modified version of Kazakov's hypothesis to explain the juxtaposition of various sedimentary units in the Phosphoria Formation. These authors suggested however, that calcite is precipitated after, not before apatite, as was proposed by Kazakov. Dietz, et al. (1942) believed that both the internal structure of phosphatic nodules and their occurrence at the sediment-water interface suggested a formation in situ by precipitation from seawater. However, in recent years, increasing doubts have been expressed as to the relevance of these essentially inorganic reactions to a natural system in which there is a prolific biota. The details of the inorganic process remain obscure and several questions have yet to be answered: Except at and near the surface, the oceans should be nearly saturated with respect to hydroxiapatite (Silllean, 1960); thus; unknown factors must explain why marine apatite deposition is restricted in space and time. Smirnov (1962) also concluded that diffusion of CO_2 from upwelling seawater is too slow to produce a significant amount of apatite as an inorganic precipitate. In addition, Bushinski (1966) points out that any phosphate precipitate would be so fine-grained that there would be little possibility of it settling onto the sea floor in areas in which there is any current activity. This view

is echoed by Senin (1970) who also notes that if the phosphate were a fine inorganic precipitate it would be associated with the fine pelitic sediments of the shelf. In fact, he finds the highest phosphate concentrations in the sandy sediments.

Biochemical Precipitation

The second category is the concentration of phosphate through the biochemical precipitation and accumulation of organic residues. McConnell, et al. (1961) demonstrated that biochemical precipitation of francolite, a carbonate-fluorapatite, is induced by a common enzyme, carbonic anhydrase. In 1965, McConnell pointed out that special inhibitors or catalysts may well control the formation of phosphorites. Early workers such as Murry^e and Renard (1891, 1918) concluded from the abundance of organic remains in many phosphorites that they were biogenic precipitates. Senin (1970) concludes that, "the recent phosphorites off southwest Africa are of biochemical origin because of the high biological productivity of this region, the extraordinary high concentrations of organic carbon for bottom sediments... the significant coprolite content, the high concentration of P in certain biogene sediments." In upwelling areas, phytoplankton are likely to be an important biochemical agent and there is no doubt that phytoplankton can concentrate phosphate to a very high degree, but incorporation of phytoplankton in sediments would produce nothing more than a slightly phosphatic organic-rich sediment, and therefore decay and other forms of post-depositional modification (ie. concentration) are required before a phosphorite can result.

Replacement of Pre-Existing Sediments

The third category is the replacement of pre-existing calcareous materials by phosphates. Ames (1959) suggested that phosphatization was the end product of diagenetic replacement in which dissolved phosphate ions substitute for carbonate in calcareous material. In modern sediments the replacement of calcium carbonate has been reported in tests of living foraminifera (Murray and Renard, 1891). An occurrence of phosphorite over a calcareous substrate was recently observed on the Blake Plateau by Pratt and McFarlan (1966). D'Anglejan (1968) found that francolite (carbonate-fluorapatite), the mineral of marine phosphorite, forms contemporaneously within the sediments by the replacement of skeletal carbonate in a core sample of foraminiferal ooze from the eastern tropical Pacific. He notes a systematic increase in apatite with depth, suggesting that replacement is proceeding at a decreasing rate in present-day sediments. The reaction of CaCO_3 with soluble phosphate in conditions within the sediments favoring the slow dissolution of the carbonate mineral may result in an increase of the carbonate ion concentration. To D'Anglejan (1968), this appeared to control the rate of replacement.

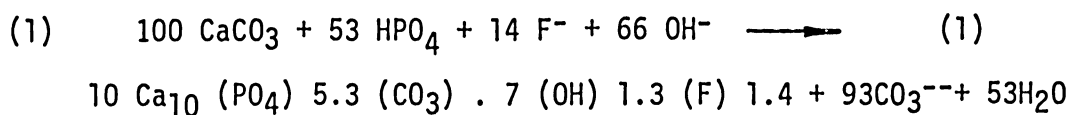
In controlled experiments Ames (1959) has succeeded in synthesizing carbonate apatites with various carbonate compositions by substituting PO_4 for CO_3 in calcite. He studied the formation of carbonate apatite by replacement of calcite in the system $\text{Na}_3\text{PO}_4\text{-H}_2\text{O}$ at low temperatures, and found that alkaline phosphate solutions replace calcite with a carbonate: apatite ratio of variable composition. The relative replacement rates are a function of (1) solution pH, (2) PO_4 concentration, and (3)

calcite grainsize. Ames concluded replacement of calcite with apatite occurs under conditions that are consistent with field occurrences and laboratory investigations of phosphorites:

- 1) A non-depositional environment
- 2) Limey sediments or limestone available for replacement
- 3) Seawater saturated, or nearly so, with respect to CaCO_3 in order that the limestone present be in near equilibrium with seawater
- 4) $\text{pH} = 7.0$ or greater
- 5) PO_4 concentrations of 0.1 ppm or greater

Ames' (1959) Mechanism for CaCO_3 Replacement by Phosphate

Equation 1 expresses schematically the formation of carbonate-fluorapatite by reaction of calcite with dissolved phosphate on the sea floor (Ames, 1959). For convenience, the molar proportion of phosphate and carbonate in the phosphate mineral was adjusted to reflect average Ca/P and Ca/C ratios, 2.43 and 46.75 respectively, observed for 60 samples of the Phosphoria Formation of Permian age (Gulbrandsen, 1966). These ratios are not significantly different from those in modern phosphorites.



Carbonate ions are a secondary product of the reaction; these could serve to increase the ambient alkalinity. Any resistance imposed by chemical or physical barriers in the sediments to the various concentrations or pressure gradients will decrease these rates (Ames 1959). Because the rates of calcium carbonate replacement are inversely related to the

relative concentration of carbonate and phosphate ions in the system, the increase of carbonate alkalinity could slow or even suppress the conversion of calcium carbonate to apatite (Ames, 1959). If, on the other hand, reaction (1) takes place in a situation that favors a free ionic circulation in the sediments, a favorable equilibrium may be attained between the carbonate ion concentrations, and the concentrations of the phosphate ion, which result from (or depend mainly upon) phosphate regeneration in the bottom deposits.

A critical factor in Ames' laboratory simulation of the natural system was the flow rate of the influent phosphate-rich solutions. Phosphate precipitation is therefore dependent partially on the amount of permeability, which is in turn related directly to the textural nature of the carbonate sediment.

Garrison and Kennedy (1975a) discussed phosphatization of chalks which were fully lithified and exposed at the sediment-water interface for long periods of time. They listed this succession of events in the diagenetic process:

- (1) Lithification of the chalk ooze on the sea floor, either by precipitation of an aragonite or a magnesium calcite cement. Modern instances of lithification of deep water carbonate sediments suggest that the cement was probably calcite.
- (2) Exposure of the lithified sediment to a continuously renewable supply of seawater containing the requisite phosphate ions. This led to the replacement of calcite by apatite, in the manner suggested by Ames (1959). The metastable aragonite or high Mg-calcite cement probably was replaced first, followed by replacement of more stable low magnesium calcite skeletal material.
- (3) Prolonged exposure facilitated diffusion of bicarbonate ions (produced when apatite replaced calcite) out of the sediment before they could inhibit the phosphatization process.

Another study by Kennedy and Garrison (1975b) of a glauconitic marl, provided similar results. Kennedy and Garrison (1975b) surmised that the glauconitic marl and the phosphates contained in it formed in a normal marine environment. Associated faunas suggested that water depths were of the order of 50 meters. The sequence was believed to be condensed, since signs of repeated current and biogenic reworking appeared on the sea floor.

Mineralogically, the phosphates of the glauconitic marl are carbonate apatite. In every case examined by Kennedy and Garrison (1975b), they found the phosphate to be replacing the lithified carbonate fraction of the sediment in the form of pre-fossilized infillings of organisms, or of reworked calcareous concretions. In addition, evidence suggested that phosphatization affected lithified carbonate sediments which were exposed on the sea floor for extended periods of time. J. Milliman (1973, 1974) has noted that pelagic carbonate sediments on the modern deep sea floor which vary from unlithified ooze to lithified sediment become phosphatized upon prolonged exposure at the sediment-water interface. Heezen, et al. (1973) likewise emphasized this tendency for phosphates preferentially to replace lithified carbonate sediments on western Pacific guyots.

The lithification and phosphatization of a protophosphorite accumulate on the seafloor off southern Africa is considered by Parker (1975) to have resulted from phosphate replacement brought about by the reaction of phosphate-rich interstitial waters with finely divided calcite/lime mud.

The work of Parker and Siesser (1972) on certain phosphatized limestones from the Argullus Bank further supports this idea. In the phosphorites from the Argullus Bank the enclosed skeletal calcite has not been phosphatized. This is considered to be due to the effect of surface area. The extremely fine grained lime mud with a high solid surface area would be more susceptible to penetration by phosphate-rich liquids than would large, massive skeletal calcite fragments.

In summary, petrographic evidence does not support large-scale inorganic precipitation of marine apatite. Despite such direct observations and experiments on the relationship between dissolved phosphate and solid carbonates, many geologists give replacement processes subordinate roles in the genesis of phosphorites. They seem to favor direct precipitation of carbonate-fluorapatite from seawater. Direct precipitation is also supported by recent studies which establish the probable state of saturation of seawater with respect to various forms of apatite (Kramer, 1964). The relative importance of direct precipitation versus replacement in the formation of phosphorite has to be reassessed in the light of the experimental evidence, and new field observations which support replacement (D'Anglejan, 1968). Workers have demonstrated that phosphatization of calcium carbonate occurs in sediments of all ages, but it is difficult to establish when it occurs in the evolution of ancient phosphorites. Perhaps, as noted by Cook (1970), this is due in part to the length, regularity, and complexity of the diagenetic events that have altered the primary minerals and textures of many deposits to such an extent that reconstruction of the original depositional conditions is no longer possible.

Earlier studies which supported the direct precipitation mechanism involved relatively little petrographic examination of the phosphatic material. More recent studies of both ancient (Kennedy and Garrison, 1975a and b) and recent phosphorites (D'Anglejan, 1968) have demonstrated unequivocally the importance of petrography in understanding the formation of phosphorite.

Source of Phosphate

Wolfe (1975) notes that above-average concentrations of phosphate can occur in the marine environment in association with (a) volcanic exhalations (b) estuarine waters (c) cold surface currents, and (d) upwelling currents. Although biological production might be regarded as an additional source of phosphate it is not considered as such by Wolfe. He maintains that high biological production is merely a result of the pre-existing abundance of phosphate (and other nutrients) and as such is the result rather than the cause of high phosphorous concentrations in seawater.

A volcanogenic origin has been suggested for a number of deposits. Mansfield (1940) considered that fluorine played a vital role in the precipitation of phosphate and suggested that there is a correlation between times of volcanism (when fluorine-rich gases are common) and phosphate deposition. Bidant (1953) also attributes the Dinantian phosphorites of the Pyrenees to the action of submarine fumeroles rich in fluorine. However, as pointed out by Kazakov (1950), there is in fact sufficient fluorine in seawater to bring about the precipitation of carbonate fluorapatite. Rooney and Kerr (1967) found that the zeolite clinoptilolite is ubiquitous in the phosphorites of North Carolina. They conclude from this that volcanism played a major role in the formation of these deposits and suggest that:

"ash falls of long duration killed large numbers of marine organisms whose subsequent death contributed phosphate." However, as pointed out by Cathcart (1968) clinoptilolite is a comparatively minor constituent of sediment, forming only 0-5 percent of the total. Consequently, there is no compelling evidence to associate large-scale volcanism with any of the major sedimentary phosphate deposits.

Rivers are known to carry abundant phosphate in solution and are capable of supplying directly much of the phosphate present in phosphorites. Pevear (1966) has suggested that Cenozoic phosphorites of the eastern U.S. are of estuarine origin. Recent investigations by Cook and Mayo (1974) into the distribution of phosphorous in the water and sediments of a tropical estuary have shown that the phosphate concentration in estuarine waters is not necessarily the most critical determining factor in producing phosphorites. Phosphatization of sediments occurs more frequently in areas of low phosphate concentration in the surface water and low SEDIMENTATION rate than in areas of very high phosphate concentration and high sedimentation rate. This points out the major difficulty in postulating an estuarine source for the phosphate in phosphorites: there is generally a high rate of sedimentation in estuaries. High phosphate concentration and high sedimentation rates will in most cases produce nothing more than a very slightly phosphatic mud or sand. Powell, et al. (1974) found little evidence to support an estuarine origin for most of the phosphorites they examined. An estuarine source is conceivable only when the great bulk of the river sediment is prevented from reaching the estuary or being distributed throughout the estuary.

Cold oceanic currents, on the other hand, affect the phosphate abundance of oceanic zones over considerable distances at the present time. Presumably, cold ocean currents also occurred in the past, although to a greater or lesser degree, depending on the size of the polar ice caps and the configuration of the oceans and continents. In many areas, the presence and productivity of cold surface currents is associated with oceanic upwelling. Sheldon (1964) has shown that virtually all important phosphorites were deposited within 40 degrees north or south of the paleoequator and that within this range of latitudes most cold currents are associated with coastal upwelling. Coastal upwelling may occur in response to seaward-moving surface water (divergent upwelling) or the movement of a current over a topographic high (dynamic upwelling).

Phosphates as Indicators of Depositional Environment

It is known that phosphorites are formed predominately under marine conditions, but their areal location on the sea floor, and the water depth, and physico-chemical conditions of their depositional environment are somewhat uncertain. Kazakov (1937) considered that phosphorites form at water depths of 50-200 meters. McKelvey, et al. (1953) subsequently suggested that phosphorites form at water depths of 200-1000 meters.

Krumbein and Garrels (1952) considered the pH of the environment to be ^{of} major importance. Precipitation of apatite occurs within the pH range of 7.1-7.8. Eh, on the ^{other} hand, is regarded as being of little or no significance in the precipitation of phosphates. The abundance of organic material in

most pelletal phosphorite suggests a reducing environment of deposition, but this may only indicate that the Eh is negative below or just at the sediment-water interface. The overlying waters could conceivably still have been quite strongly oxidizing.

In general, phosphorites are believed to have been deposited in marine waters of normal salinity. Areas flanking the regions of phosphate deposition were commonly hypersaline however. This association is illustrated by phosphorites of the Phosphoria Formation, which grade laterally into carbonates of the Park City Formation, and then into the red beds and evaporites of the Chugwater Formation.

The modern phosphorites off southwest Africa are being deposited within the euphotic zone on the inner shelf in water depths of 50-150 meters. Senin (1970) found that this depth corresponds closely to ^{the} change within the water column (and the bottom sediments) from oxidizing to reducing conditions. Romankevich and Baturin (1972) record extreme redox conditions in the shelf sediments of -233 mv. where anaerobic conditions obviously predominate. Flanking these phosphorites is the arid hinterland of the Namib coastal desert, where saline coastal lagoons are common. This situation is apparently analogous to the landward equivalents of the Phosphoria Formation. Similarly, the phosphorites of the Peruvian shelf are bordered by an arid hinterland. Baturin (1971) notes that several changes of sea level occurred during the Quaternary and that considerable reworking of shelf sediments took place. Veeh, et al. (1973) note that the phosphorites occur at water depths varying from 100 to 400 meters. They also point out that the phosphorites are confined to two narrow bands corresponding to the upper and lower boundaries of an oxygen minimum layer in the seawater.

Sediments of this portion of the shelf are strongly anoxic.

In summary, many of the features of the depositional environment⁰ evident in modern phosphorites may be found in ancient deposits. Most phosphorites probably formed in shelf environments at water depths considerably less than 500 meters. Conditions within the water column were conducive to the development of a prolific biota, but were strongly reducing at or just below the sediment-water interface. Also, mechanical reworking of sediments was a most important feature in producing and upgrading phosphatic sediments. Such reworking may have occurred in response to the influx of bottom currents or to relative changes in sea level.

Nodule Description

Two distinct generations and sizes of phosphate nodules are found in the Upper Devonian and Lower Mississippian shales studied during the course of this project. Each generation of nodule has distinct physical characteristics (size) and will be discussed separately, although the processes involved in forming each type are similar. The smaller nodules are referred to simply as phosphatic nodules, or sometimes "hiatus" nodules, while the larger forms are here called phosphatic clasts.

The external appearance of phosphate nodules found in Upper Devonian and Lower Mississippian shales varies widely. As shown in Figure 4 (locality 6), the nodules typically take on a variety of shapes and sizes. Nodules at locality 6 ranged in size from 3 cm to 10 cm (pebble to large cobble range) in their greatest dimension. The flatter, polygonal or amoebiform types were largest, while the smaller nodules were usually well-rounded forms the size of golf balls. These well-rounded nodules appear to have been mechanically reworked. The flatter, amoeboid variety was frequently found in the bottom of the nodulose zone, while the rounded forms were found in the top of the zone. In short, roundness increased upward. This same upward increase in roundness occurs at locality 8 where flatter nodules are found in the upper most few inches of the Chattanooga Shale, and much smaller, rounded nodules were found in the overlying Maury Shale. This "pseudo-grading" is also present at localities 13, 14, 15, and 16, but is there condensed into a one-meter-thick bed of phosphate nodules and clasts. The overlying Maury Shale and underlying Chattanooga Shale enclose the nodulose zone, rather than interbedding with the nodules. The

greatest variability in nodule size is found at locality 20. Here the nodules are as large as 30 cm in their greatest dimension, which in every case lies parallel to the horizontal bedding planes. The smaller nodules are approximately 3 cm in their greatest dimension. The thickness of the nodules rarely exceeds 8 cm, and is most often about 3 cm thick.

The lateral spacing of the nodules is as variable as the size and shape. At many localities a regular lateral spacing is present, as illustrated by Figure 5. Where a consistent nodule size and shape are found, a consistent lateral pattern is also present. This phenomenon indicates that a genetic relationship exists among the individual nodules in the same bedding plane.

At some localities (13, 14, 15 and 16) a conglomeratic bed of phosphatic clasts as well as phosphatic nodules directly overlies the Chattanooga Shale. Typically the unit appears at the surface as a zone of rubble (Figure 6). It has a maximum thickness of 55 cm, and thins to 5 cm in short lateral distances (30 meters or less). The maximum lateral extent of the lens is 50 meters, but most lenses are less than 10 meters wide.

The conglomeratic unit is considered part of the Maury Formation, but is only locally present in the study area. The basal contact between the conglomerate zone and the underlying Chattanooga Shale represents a paracontinuity surface (Conkin, 1975) (Figure 7). It should be noted that the absence of truncated bedding suggests the lenses do not cut bedding surfaces of the Chattanooga Shale. Rather, they seem to fill topographic lows on the black shale surface. I believe that the wavy surface in the upper-most shale (Figure 7) is produced by differential compaction beneath the conglomeratic unit.

The conglomeratic bed is made up mostly of phosphatic clasts of various shapes and sizes. The boulders or clasts found in these lenses are as much as 25 cm in length and 10 cm thick, but most are about 15 cm in length (cobble to boulder size). Their shape is elongate parallel to the direction of bedding, with slightly rounded to distinctly rounded corners. The clasts differ from the nodules in that the clasts are usually several times larger than nodules, much less rounded than nodules, and occur laterally in a much more regularly spaced manner than do the nodules. These conglomeratic beds of clasts also show a very close genetic relationship to continuous thinly-bedded sediments which have been differentially eroded.

The large phosphatic clasts consist of a bioturbated mixture of phosphatized micrite, quartz, and a few fossils. Only one large clast was observed to have bedding. In one 10 cm thick, discontinuous bed of closely-spaced clasts (Figure 9) small scale slump structures can be seen cutting and deforming normal planar laminations. Slumping is rare because most bedding structures have been eliminated by gross bioturbation. The bioturbation includes pre-lithification burrowing and post-lithification boring. Some clasts contain small phosphate nodules which range in size from 1 to 5 cm in diameter. ^(Fig 33) These nodules were probably derived from a pre-existing nodulose layer and were incorporated in the phosphatic mudstone beds during or shortly after the mud was deposited and before it was lithified.

Clasts, nodules, and discontinuous phosphate beds have numerous prominent vertical joints (Figure 8 and 9). The determination of the relative age of formation of such joints is essential to the interpretation of the origin

of the lensoid conglomerate beds, and their verification as possible hardgrounds (Bromely, 1968). In order to establish the presence of a hardground at localities 13, 14, 15, and 16, it must be shown that sub-aqueous lithification of the phosphate beds occurred before the reworking of the same beds, and before deposition of the overlying shale of the Maury. In Figure 9 all of the clasts are vertically jointed, but they are sometimes found turned on end (Figure 10) possibly as the result of bioturbation or current action. Such a clast exhibits "pseudo-horizontal" joints because of its rotation. This phenomenon suggests that vertical joints formed in a lithified sea floor, and preceeded mechanical reworking by borers and/or currents which altered the original geometry of the bed.

Fig. 4 Various shapes and sizes of phosphate nodules found imbedded in the uppermost zone of the New Albany Shale, Berea, Kentucky, locality 6. Pen is 14 cm in length.

Fig. 5 Phosphate nodules imbedded in black shale at locality 11. Note the curvature of the black shale around the nodules both on top and bottom. This indicates that formation of the nodule occurred before compaction of the enclosing shale. Note also the lateral spacing of the nodules in the bedding plane.

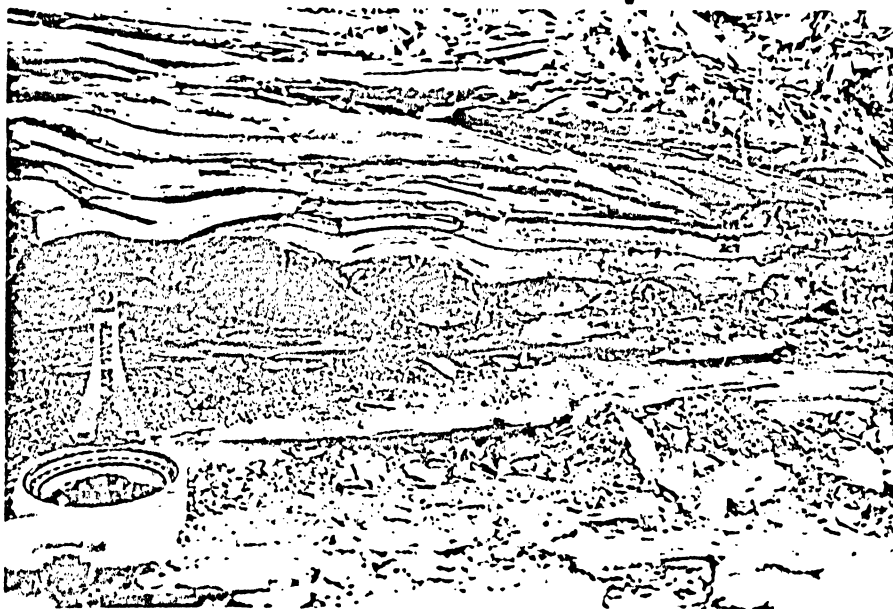
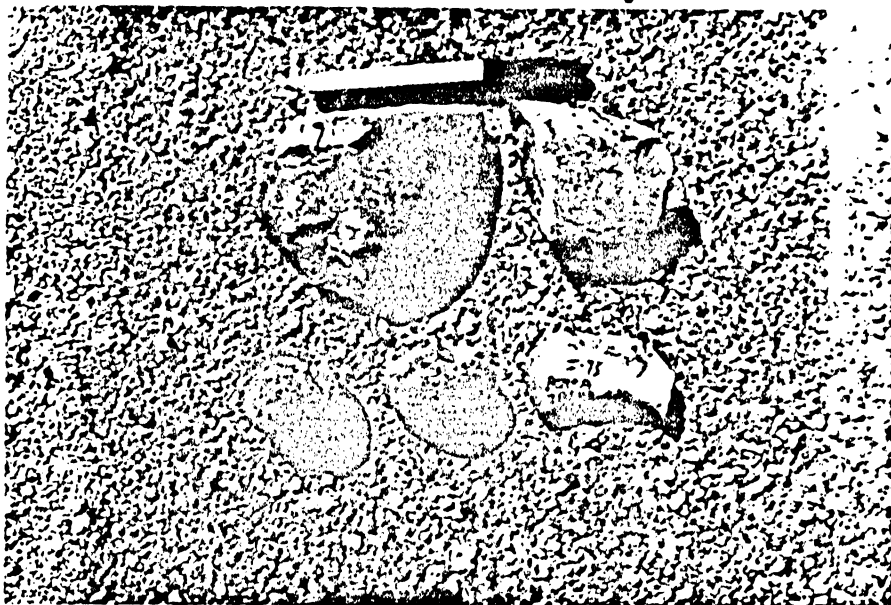


Fig. 6 Conglomeratic facies at the base of the Maury Formation at locality 15. Meter stick represents scale; colored segments are ten centimeters.

Fig. 7 Contact of the Chattanooga Shale with the overlying conglomeratic bed of the Maury Formation. Note the wavy surface of the contact which is defined by Conkin (1975) as a "paracontinuity". Locality 15, hammer serves as scale.

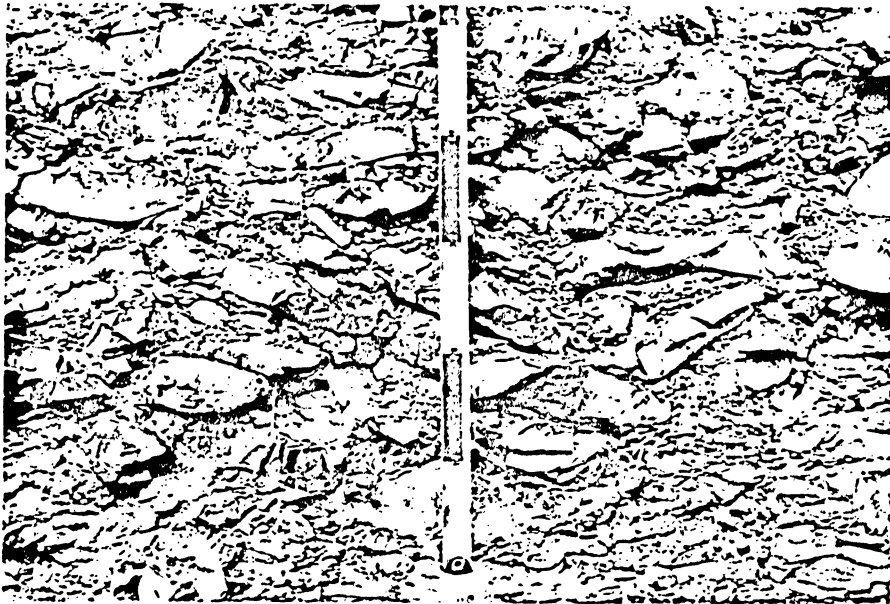


Fig. 8 Large, flattened phosphatic clasts and smaller, rounded nodules of the conglomeratic facies of the Maury Formation. Note vertical jointing in clasts. Meter stick serves as scale; colored segments are ten centimeters in length. Locality 15.

Fig. 9 Discontinuous bed of phosphatic rock overlying "rubble" of the conglomeratic bed in the lower Maury. Locality 13. Scale - bed is 16 cm thick.

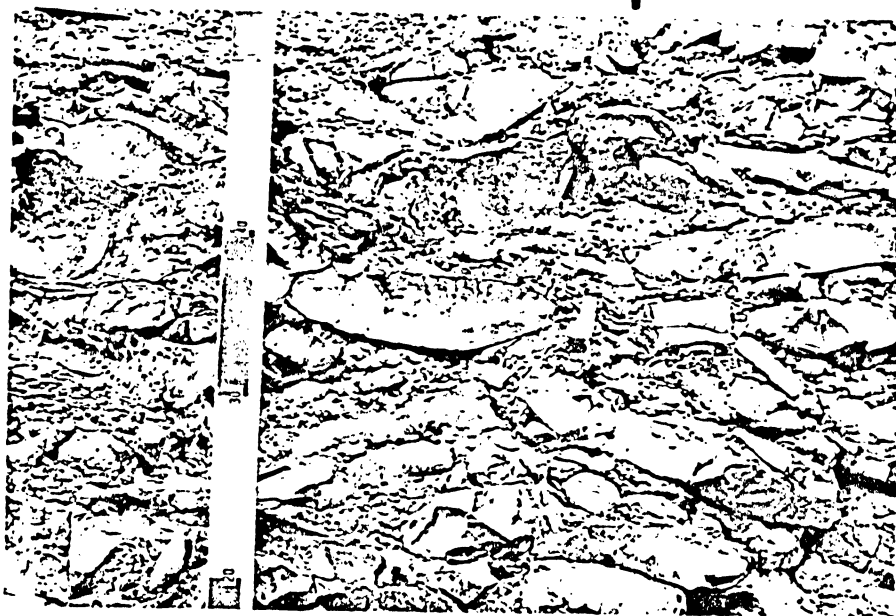


Fig./0 Conglomeratic facies of the Maury Formation. The large clasts are predominately horizontal or nearly horizontal, except the clast between the 15 and 30 cm marks on the meter stick, left of center. Notice the joint pattern which appears to be horizontal because the clast has been reworked and rotated on end. This phenomenon dates the joint system in the clasts. The joints must have been formed before reworking and before the overlying Maury shale was deposited. Locality 15.



Petrology

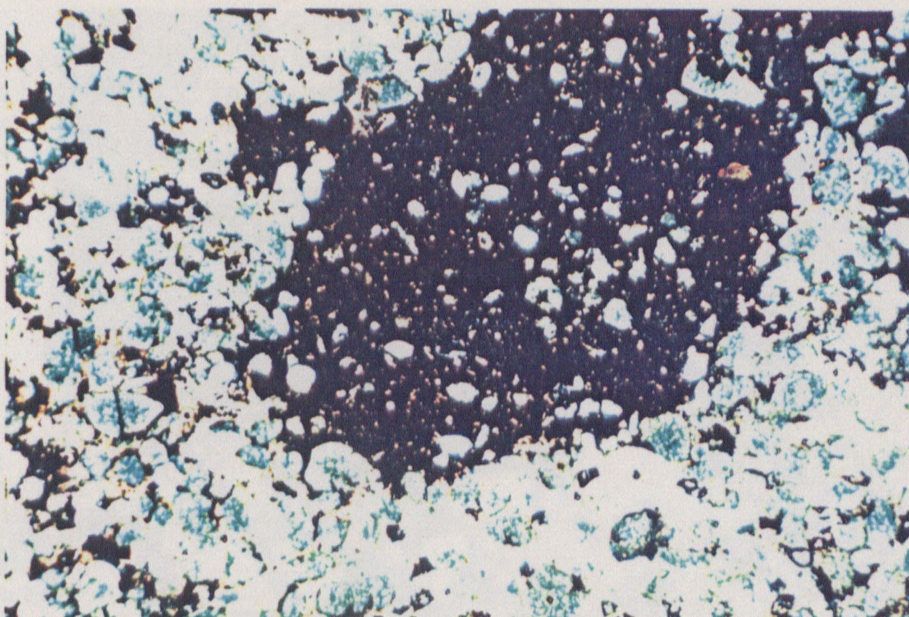
Kinderhookian nodules range from mudstone to packstone textures, while Devonian nodules range from mudstone to wackestone textures. Both Kinderhookian and Devonian nodules predominately have wackestone textures (see Appendix E). Nodule composition is primarily phosphatic micrite (ave. 66 percent of rock), with varying amounts of intraclasts (ave. 1 percent), fossils (ave. 3 percent), glauconite pellets (ave. 3 percent), phosphatic pellets (ave. 14 percent), phosphatic druse (ave. 2 percent), sparry calcite (ave. 8 percent), quartz (ave. 2 percent), and minute amounts of mica, and pyrite.

1. Pellets and Intraclasts

Pellets and intraclasts are ubiquitous in nodules from localities 3, 6, 13, 15, 16, and 22, and are occasionally found in samples from other localities studied. Most pellets are structureless forms which lack concentric (oolitic) layers. For the most part pellets are medium to light olive brown in color and contain micritic or clay-sized material. This material is most often phosphatized, although the samples from locality 22 contain pellets that are predominately glauconitic. At locality 15, much of the pellet material is found in borings within nodules. The pellets apparently were torn loose from boring walls as the organism dug into the hard substrate (proto-nodule). The pellets are fecal in origin, but appear not to have been deposited by the boring organism. Instead, the pellets were probably deposited by burrowing organisms which inhabited the sediment prior to lithification. Intraclasts are also found in borings at locality

Fig. 11 A boring which trends obliquely to the plane of the photograph, occurs in a glauconitic siltstone cemented by sparry calcite. Note the roughly circular pattern of boring and the arrangement of grains within the boring. Note also the contrast between sparry calcite cement in the undisturbed area and the fine-grained phosphatic nature of boring fill.
Crossed-nicols, locality 22.

Fig. 12 Bioturbation in glauconitic siltstone. The siltstone has a packstone texture in unbioturbated portions and a mudstone to wackestone texture in bored areas. A glauconite-filled, longitudinal section of a sponge spicule is in the lower right corner.
Crossed-nicols, locality 22.



1 mm

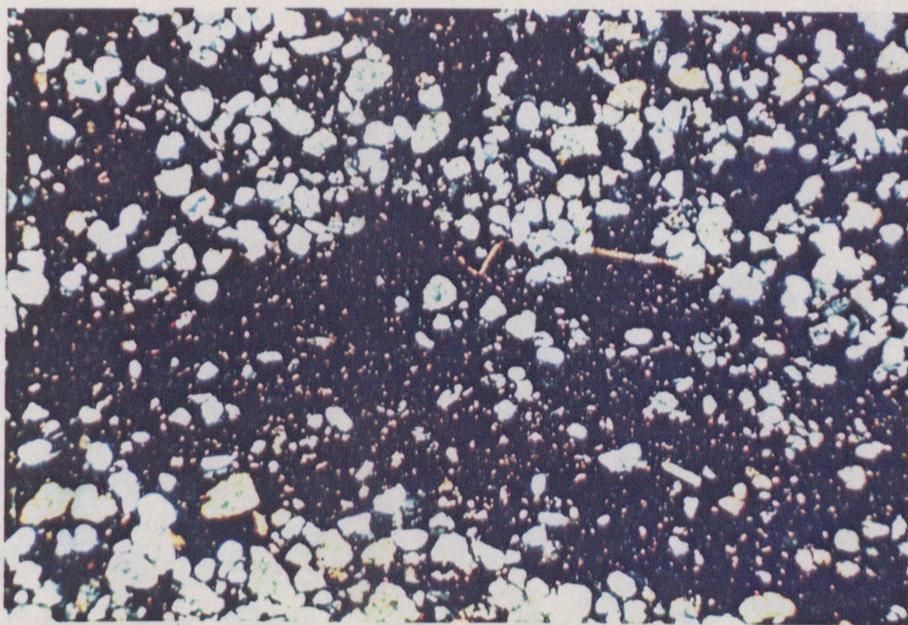
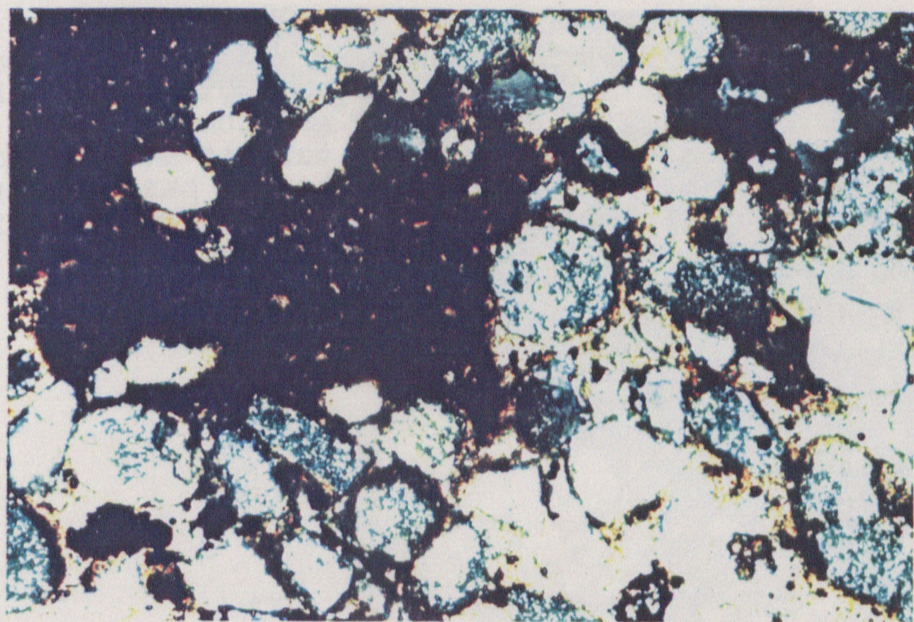


Fig. 13 A glauco-phosphatic quartz pelsparite with a bioturbative "channel". Phosphatic micrite occupies the "channel", and is starting to replace sparry calcite matrix around the grains. Fecal pellets have apparently been recycled by boring organisms.
Crossed-nicols, locality 22.

Fig. 14 Almost complete replacement of sparry calcite matrix by fine-grained phosphate. Note the various shapes and sizes of fecal (?) pellets.
Crossed-nicols, locality 22.



100 μ

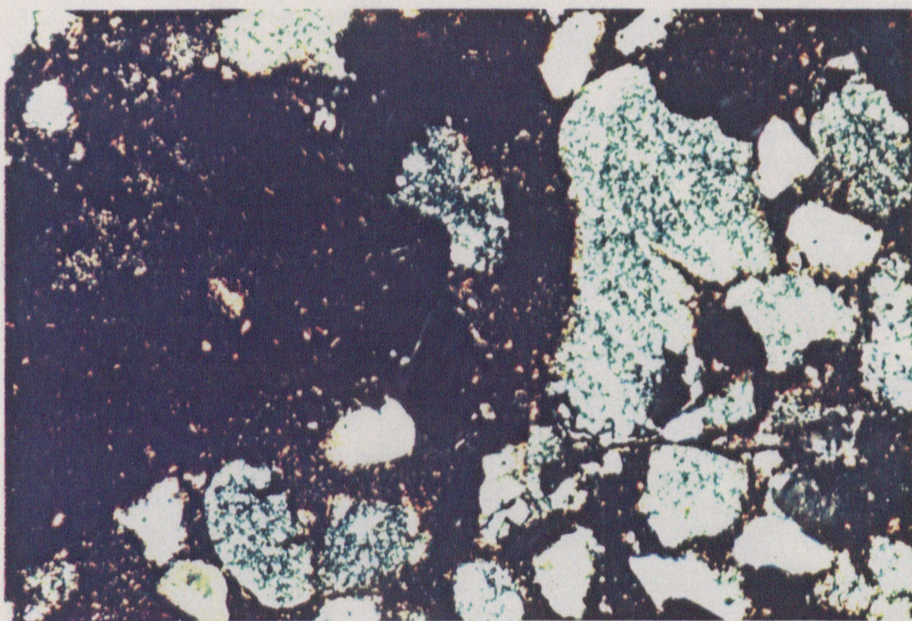
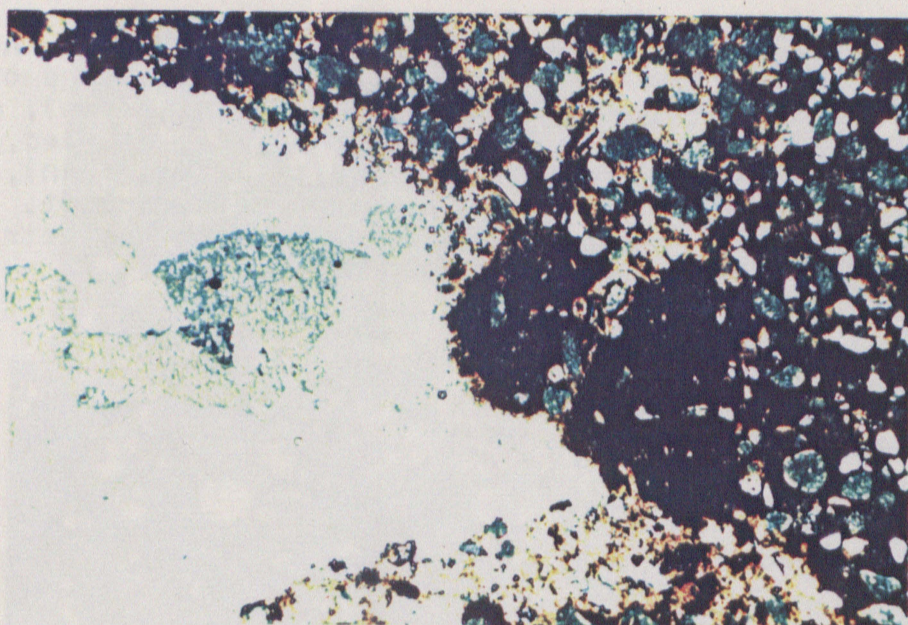
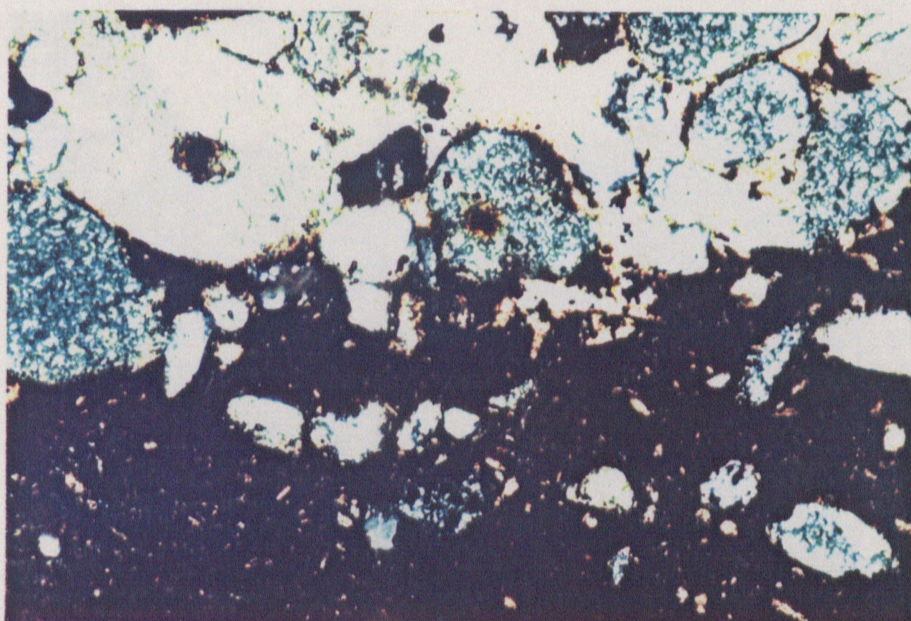


Fig. 15 This glauconitic siltstone contains a spar-filled boring and sparry matrix, quartz grains, and glauconite pellets of various shapes and sizes. Note the black phosphatic boring with quartz and glauconite absent. Phosphate seems to replace sparry calcite matrix generally, but especially where burrowing or boring has taken place. Phosphate has not replaced several large sparite crystals of the infilled boring, however. Crossed-nicols, locality 22.

Fig. 16 Glauconitic siltstone. Note the phosphate has replaced the sparry matrix, especially at and around grain boundaries (eg. quartz, glauconite pellets, and echinoid plate). The single large grain of sparry calcite (echinoid plate) is not phosphatized, but the sparry cement around it shows evidence of replacement. The large dark area at the bottom is a boring. Crossed-nicols, locality 22.



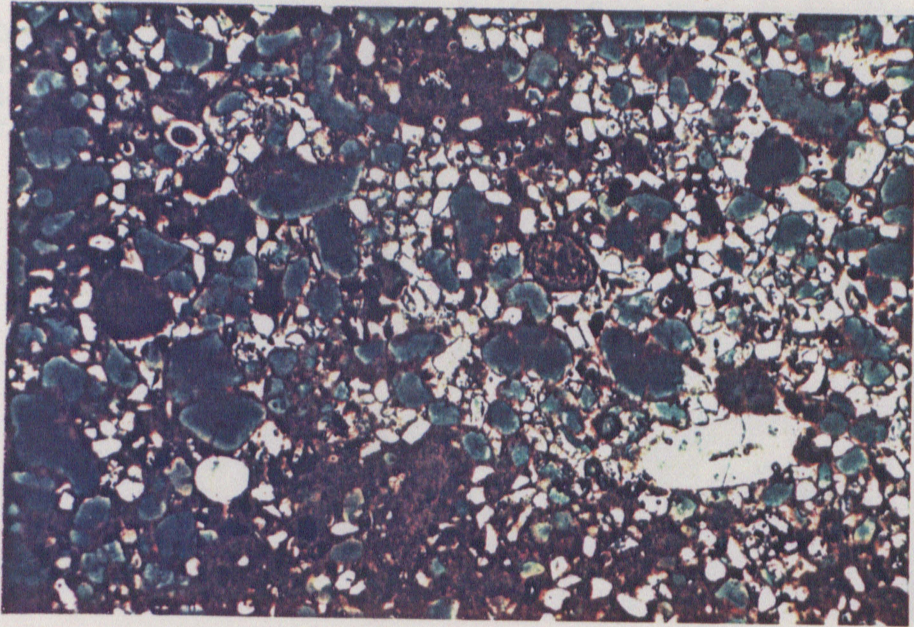
1 mm



100 μ

Fig. 17 A glauco-phosphatic quartz pelsparite. The material present includes an ovoid echinoid spine of spar (white), two phosphatic fecal (?) pellets (brown), quartz, which varies in shape from angular to well-rounded, various shapes and sizes of glauconite pellets (green), and sparry calcite cement and collophane replacing it. Phosphate replaces calcite at grain-cement contacts and in areas which have been disturbed biologically. Plane light, locality 22.

Fig. 18 A glauco-phosphatic quartz pelsparite with a large boring filled with spar (top). Note pyrite (opaque) occurs around the edge of the spar-filling. Brown phosphate pellets are scarce, but glauconite pellets are common and these are rimmed with phosphate. Plane light, locality 22.



1mm

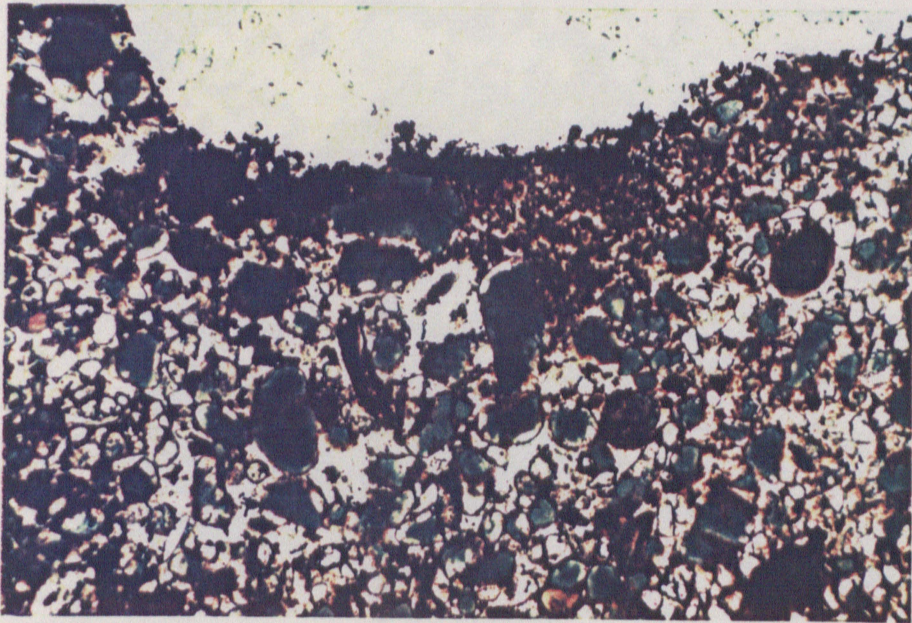
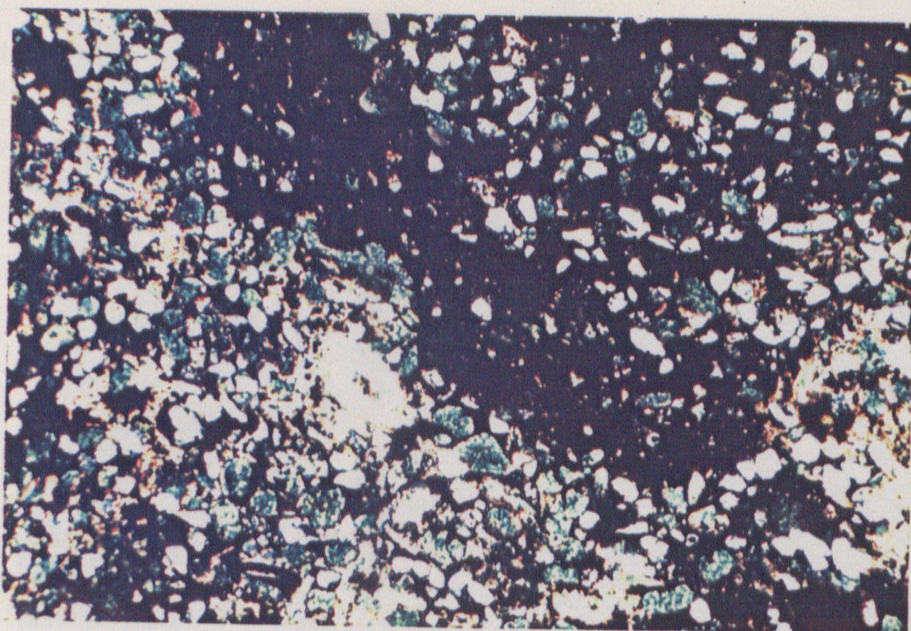


Fig. 19 A glauco-phosphatic quartz pelsparite with a boring in the plane of the photograph. Phosphatized micritic material is concentrated in the boring, but coarse grains of quartz and glauconite are rare in the bioturbative structure. Note also the sparry calcite in the echinoid plate cross-section. Crossed-nicols, locality 22.

Fig. 20 A glauco-phosphatic quartz pelsparite with a boring approximately at right angles to the plane of the picture. Note the circular trend of quartz and glauconite grains in a phosphatized micritic matrix. Crossed-nicols, locality 22.



1 mm

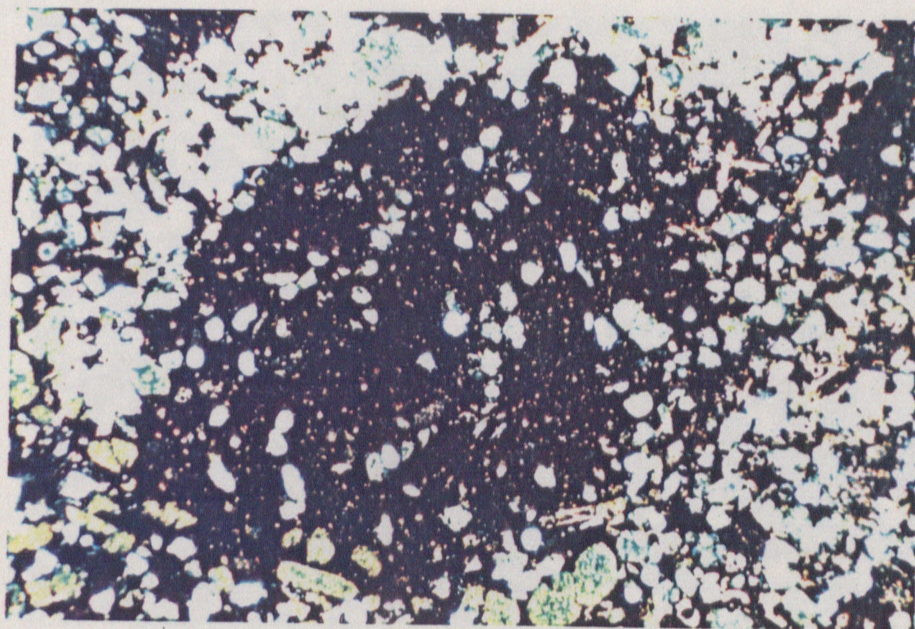
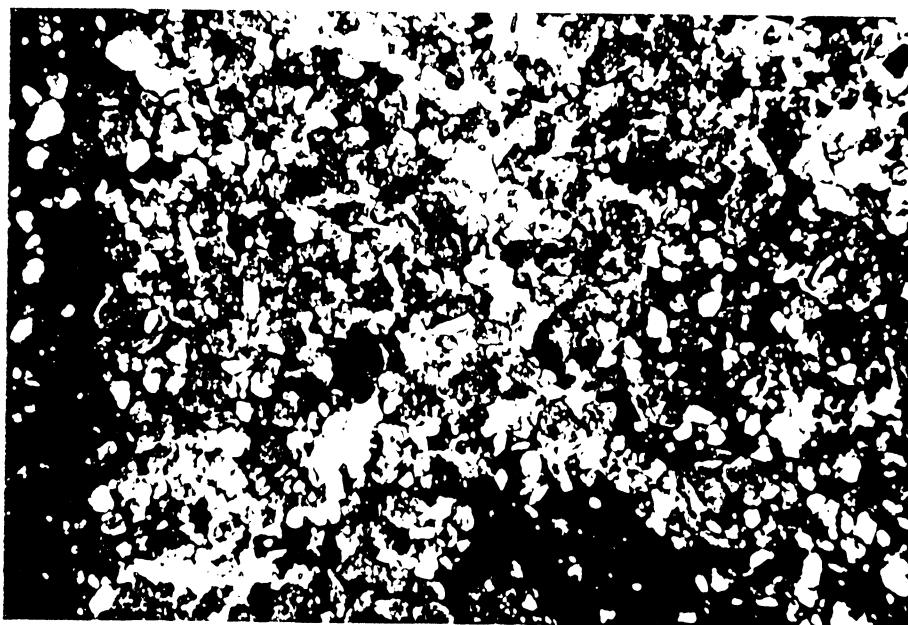
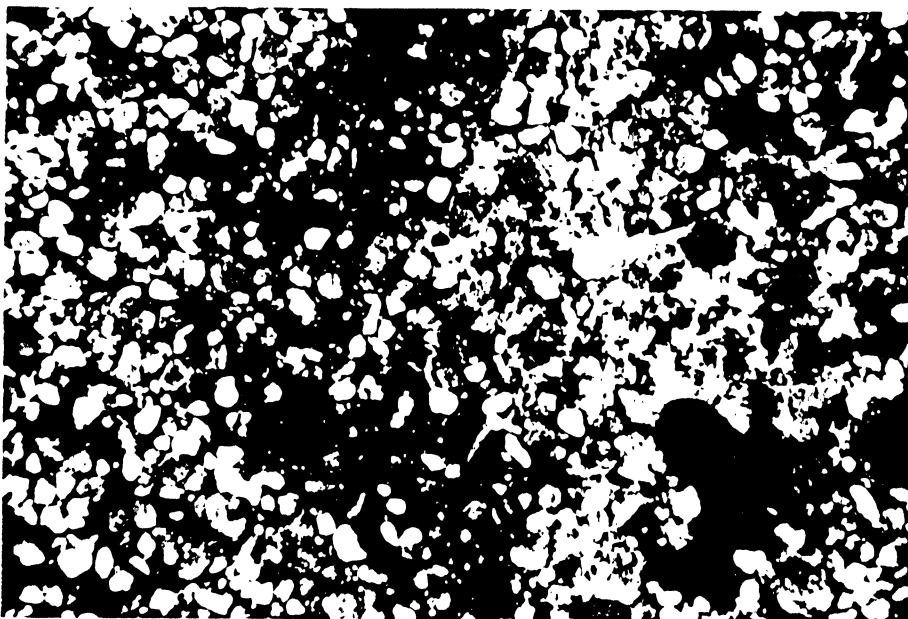


Fig. 21 A glauco-phosphatic quartz pelsparite with re-worked portions of the bottom and left of the photo. The texture in the center of the photo is relatively undisturbed. Note the degree of phosphatization in bioturbated versus undisturbed parts. Matrix spar in the center is only partially replaced, this occurring at quartz and glauconite grain boundaries. Crossed-nicols, locality 22.

Fig. 22 Bioturbation in a glauco-phosphatic quartz pelsparite. Note the rounded nose of the boring and also the absence of glauconite pellets in the boring. Crossed-nicols, locality 22.



1 mm



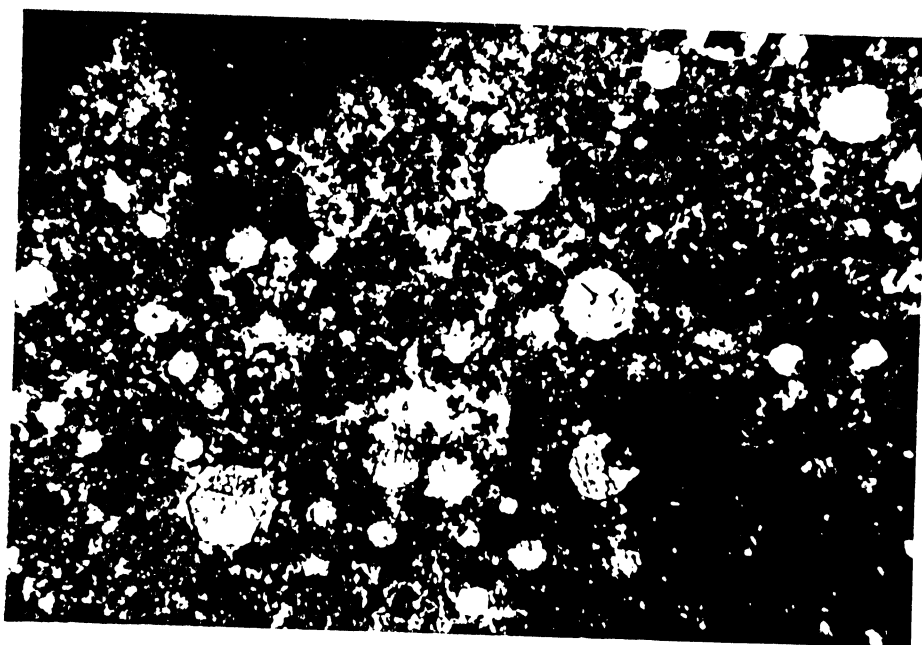
15, but their origin differs from that of the fecal pellets. Intraclasts are structureless, subspherical masses of variable size which are also torn from the walls of borings. Intraclasts are found in borings which cut through zones of fine-grained phosphatic matrix (mudstone), whereas pellets are found in borings which cut through pelletal zones (wackestone to packstone texture). The intraclasts are, therefore, a direct result of boring, versus the pellets, which are indirectly related to the boring episode, but were actually formed during an earlier episode of burrowing. Fecal pellets and intraclasts can be distinguished from one another because the fine-grained material in fecal pellets gives rise to a "pseudo-circular" texture (Figure 11). Intraclasts, on the other hand, are structureless internally, irregularly shaped, and are variable in size. Fecal pellets are smaller than intraclasts and are rather uniform in shape and size.

At locality 22, abundant glauconite pellets of probable fecal origin occur in Kinderhookian age nodules (Figures 11-22). The rock, a glauco-pelsparite, is poorly sorted, with grains of silt to sand-size. Glauconite pellets occur in a variety of shapes, ranging from angular to rounded. Van Wie (1971) has described the shapes of these pellets variously as: elongate ellipsoidal, conical spherical, blade-like or discoidal, and irregular. Most glauconite pellets have a micaceous appearance with phosphatized outer rims in many cases. In a few instances, the glauconite pellets contain pyrite.

At localities 3 and 6, nodules contain two distinct types of pellets: (1) a reddish-brown phosphatic type with well-defined outer margins and of probable fecal origin, and (2) a structureless, olive-colored, micritic type, enclosed along sutured boundaries by acicular (fibrous) rinds of drusy phosphate (Figures 24 and 25). These rinds could be formed by a selective

Fig. 23 Patchy nature in a nodule caused by large crystals of sparry calcite. Note the syntaxiality of the spar with sphaeromorphs. Collophane (brownish-tan) is replacing spar to varying degrees.
Crossed-nicols, locality 3.

Fig. 24 A phosphate nodule composed mainly of fecal pellets, intraclasts, and sphaeromorphs. The fecal pellets and intraclasts are various shades of brown, while sphaeromorphs are white.
Plane light, locality 3.



1mm

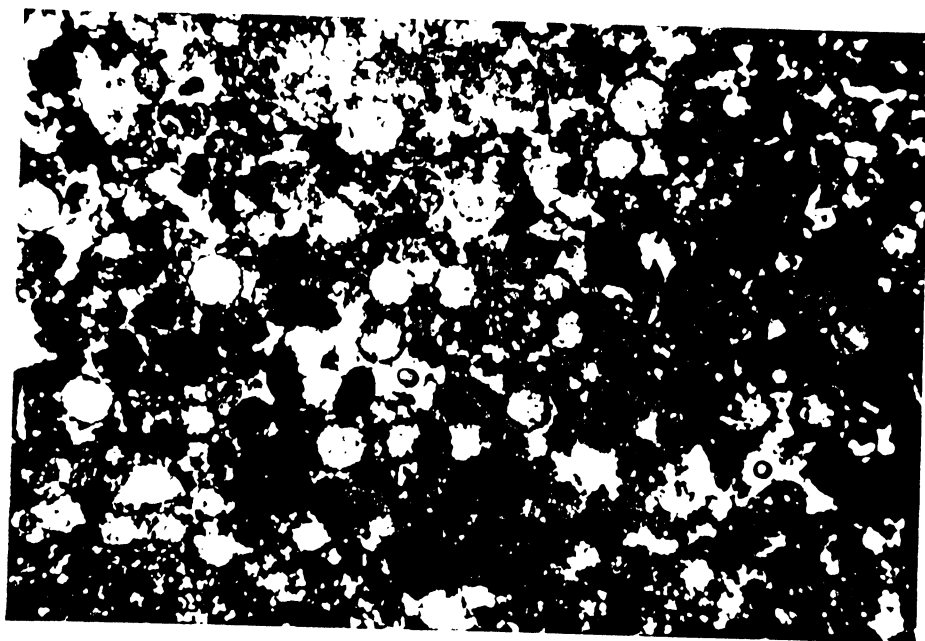
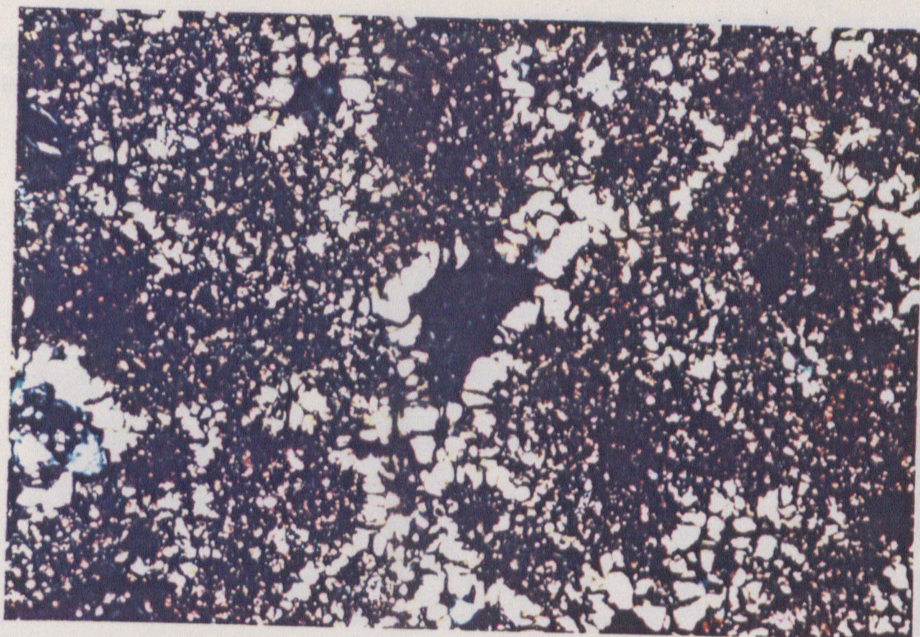
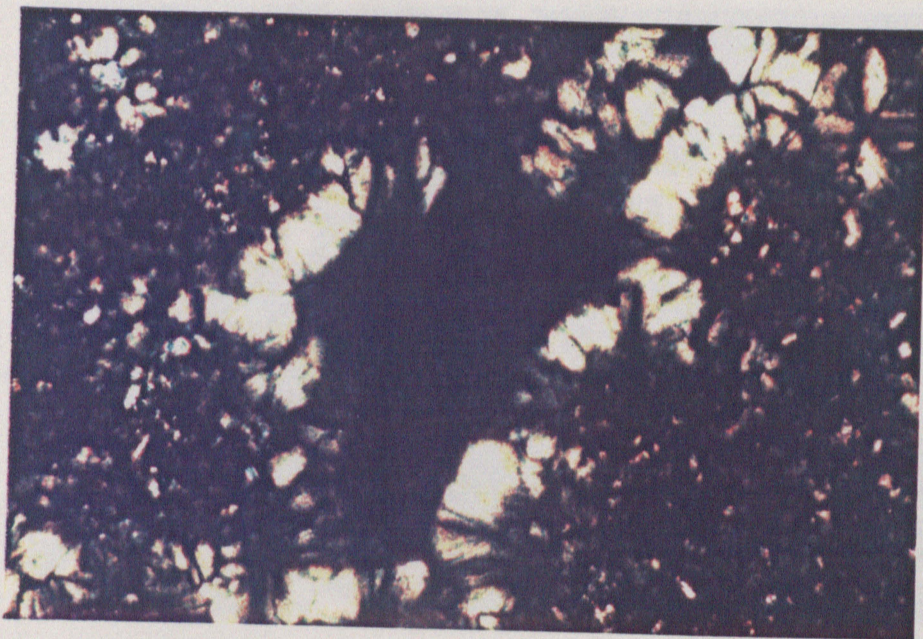


Fig. 25 A phosphate nodule with porous nature. Intraclastic pellets have fibrous (drusy) dahlite (?) rinds growing around the grain borders into void spaces. Note the fine-grained (micritic) phosphate in intraclastic pellets. Note also the lack of structure in the pellets. Crossed-nicols, locality 3.

Fig. 26 A close-up of dahlite (?) rinds on the grain boundaries of pellets. Crossed-nicols, locality 3.



100 μ



100 μ

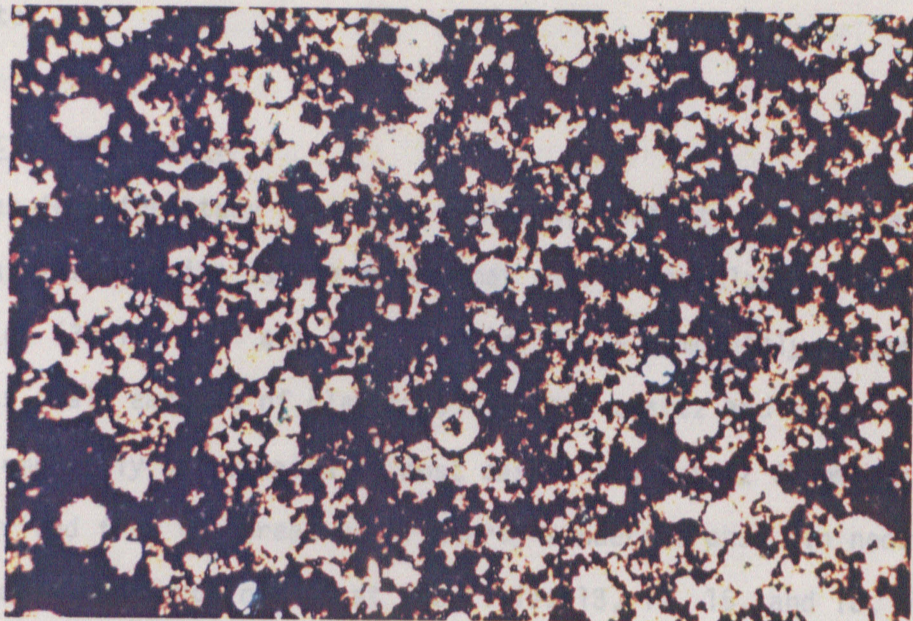
Fig. 27 Phosphate nodule with a dark, splotchy appearance caused by the replacement of sparry calcite by phosphate. Note the "inflated", spar-filled sphaeromorphs. Crossed-nicols, locality 3.

Fig. 28 Same slide as above, but X4. An inflated sphaeromorph is filled with syntactic sparite, but has not been phosphatized.

dissolution of calcite matrix, with ensuing precipitation of fibrous calcite on relict pellets (?) and later, replacement of fibrous calcite by phosphate.

3) Cementation

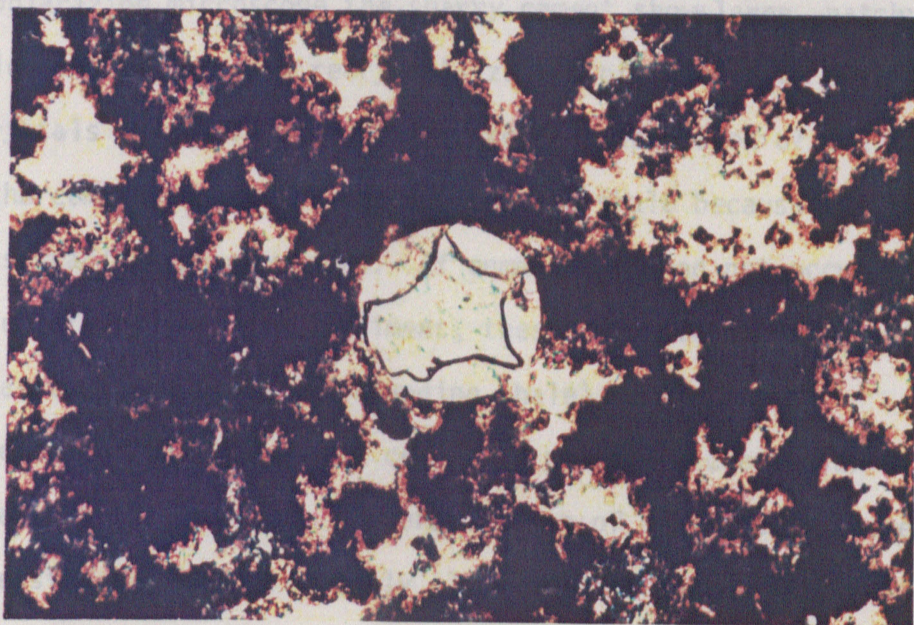
Nodule types and matrix at locality 3 consist of micrite, and contain matrix is probably de incorporated as well as drusy microcrystalline cement serves as matrix. At locality 20, nodules with mud-supported texture more than ninety percent micrite.



1mm

Cementation (matrix) in nodules at locality 3 consists of large crystals of sparry calcite which are syntactic with framework grains (Figure 23).

Under the microscope, the nodules show areas of extinction. The spar crystals are visible in the shale and the and support to compaction flattened. Replaced patchy appear occur most grain cement contacts.



100u

dissolution of calcite matrix, with ensuing precipitation of fibrous calcite on relict pellets (?) and later, replacement of fibrous calcite by phosphate.

3) Cementation and Matrix

Nodules from the study area show a wide variability in cementation type and matrix. Micrite is the predominant matrix for clasts and nodules at localities 13, 14, 15, and 16. The micrite is completely phosphatized, and contains small amounts of clay to silt-sized quartz and mica. The matrix is completely bioturbated in most cases, and quartz fragments are probably derived from the break-up of cherty sphaeromorphs. In nodules incorporated in the large clasts at localities 13, 14, 15, and 16, micrite as well as drusy microcrystalline cement serves as matrix. At locality 20, nodules with mud-supported textures contain more than ninety percent micrite.

Cementation (matrix) in nodules at locality 3 consists of large crystals of sparry calcite which are syntactic with framework grains (Figure 23). Under the polarizing microscope the sparry cement shows large, patchy areas of extinction indicating slow recrystallization of micrite to sparry cement. The spar crystals must have formed prior to the deposition of the overlying shale and the compaction of all the surrounding shale because the spar fills and supports fragile sphaeromorphs. If cementation had not occurred prior to compaction of the enclosing sediment, these delicate spores would be flattened (as they are in the surrounding shale).

Replacement of sparry calcite cement by phosphate creates an extremely patchy appearance (Figure 27). Phosphatization of sparry cement seems to occur most easily and most frequently along crystal boundaries, and around grain cement contacts.

At locality 22, two grain-sizes of matrix exists: (1) fine-grained phosphate, and (2) coarse-grained sparry calcite. The sparry calcite is much finer-grained than that at localities 3 and 4, and this smaller grain-size could be the reason why phosphate matrix is replacing the sparry cement more extensively at locality 22 than at localities 3 and 4. The replacement begins at framework grain-to-framework grain (quartz and glauconite pellets) contacts, or at framework grain-to-cement contacts, and does not usually occur at contacts between large spar crystals.

4) Quartz

The matrix fraction of nodules at localities 13, 14, 15, and 16 contain silt-sized and smaller quartz grains. The silt-sized grains of quartz are derived presumably from the abrasion of chert-filled sphaeromorphs through boring and burrowing.

Unit quartz in the glauconitic pelsparites at locality 22 is silt-sized to fine-sand sized, moderately sorted, and angular to sub-rounded in shape. Most of the larger quartz grains are contained in the grain-supported (framework) fraction (Figure 20). The smaller-sized fraction is located predominately in borings, where abrasion by boring organisms has decreased the grain-size (Figure 12).

5) Fossils

Fossil hardparts are not abundant in the nodulose zones. Fossils contained in nodules include phosphatic brachiopod fragments (probably *Lingula*), brachiopod spines, echinoid spines (Figure 29 and 30), and conodonts of unknown affinity. Sphaeromorphs are the most common fossil and they occur

as calcified, silicified, pyritized, and phosphatized grains. The variety of infill compositions found at a single locality suggests they may have been transported from varied sources. Vegetable matter and plant fragments are sometimes present in nodules; these fragments seem to be most abundant at the more northeasterly locations.

6) Bioturbation (Boring and Burrowing)

Nodules and clasts at localities 13, 14, 15, and 16, and nodules at locality 22 show signs of extensive bioturbation. Two distinct episodes of bioturbation occurred at these locations. Prelithification burrowing occurred first. Burrowers concentrated quartz and mica relative to phosphatic micrite in burrows. Burrowed areas were also cleaned of organic matter. The burrowing assemblage must have been a sediment feeding type which had to ingest large amounts of micrite in order to separate the organic debris.

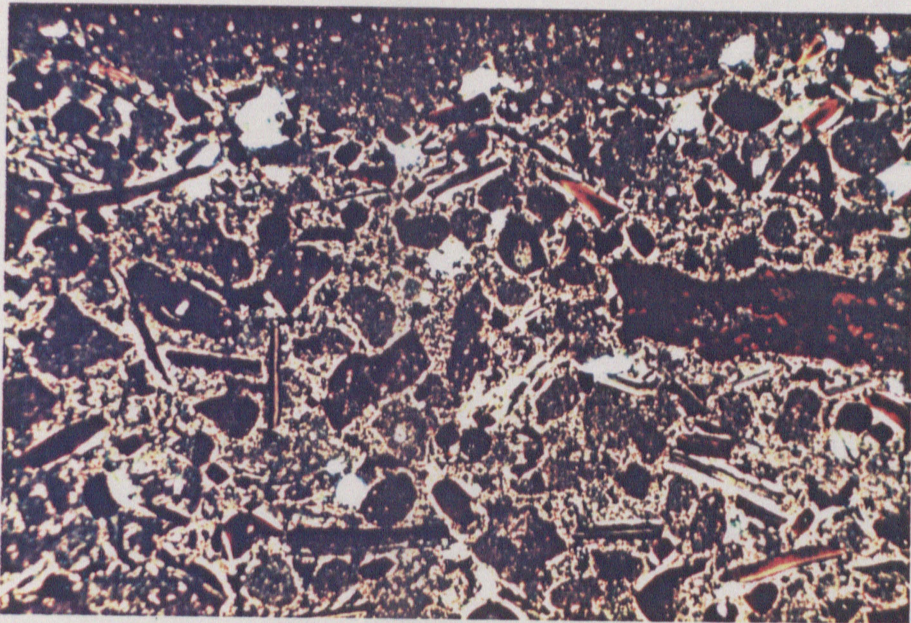
Burrowing was followed by lithification and probable phosphatization of the calcareous sediment. Next, a boring ichnocoenose disrupted the lithified floor with borings of variable size and shape. The boring ichnocoenose entered the sediment after lithification, and cut across pre-existing burrows (Figure 31). Borers appear to have no orderly mechanism to disperse sediment as compared to burrowers, which shift soft sediment back-and-forth into U-shaped structures (Figures 31 and 32). Borers dig into the hard sediment, tearing off intraclasts from boring walls and concentrate both intraclasts and fecal pellets in boring cavities (as at locality 15, 34, and 35). In some cases, a fossil "hash" of brachiopod fragments is aligned parallel to the boring wall.

Fig. 29 A large phosphatic clast with a phosphatized, micritic matrix and containing intraclasts, fecal pellets, and fossil debris. The fossil debris consists mainly of brachiopod (*Lingula*) fragments. A few quartz grains are also present.
Crossed-nicols, locality 15.

Fig 30 A large phosphatic clast with "hash" of fossil, fecal, and intraclastic debris alligned predominately with a boring (horizontal in picture-lower three quarters).
Crossed-nicols, locality 15.



1 mm



Borers have homogenized the grain components in rocks (nodules) at locality 22, and have also reduced the over-all component grain-size; the reverse of the effect of borers at locality 15 which have increased the grain-size in Borings. Borers tend to reduce the grain-size by abrading both the glauconite pellets and coarse, sparry cement. The process of abrading the softer grains (relative to quartz) creates concentrations of quartz grains and phosphatic micrite in the borings (Figures 11, 12, 19-22).

The occurrence of glauconite, phosphate, and bioturbation has been noted by Bromely (1975a) as an indication of a period of non-deposition. Therefore, the sediment (hardground) at locality 22 could have undergone repeated episodes of burrowing and boring, but certainly occurring prior to the deposition of the overlying shale.

7) Order of Diagenesis

Deciphering the order of diagenesis is difficult. At northern localities (3, 4, 5, and 6) carbonate mud has recrystallized first to form micrite, then micro-spar, and finally spar. The large crystals of spar indicate slow, undisturbed growth. Phosphatization followed carbonate recrystallization, and involved chemical breakdown and replacement of cement-grain contacts, fecal pellets, and intraclasts. At localities 6 and 7 intraclasts of carbonate mud are replaced by phosphate and are also rimmed with acicular crystals of what presumably was fibrous: *CALCITE OR ARAGONITE AND IS NOW REPLACED BY PHOSPHATE (Fig 35)*. THE FIBROUS nature of the drusy rim cement indicates the presence of void space during crystal growth. This void space could have influenced the phosphatization process. The probable order of diagenesis here was: carbonate mud going to

micrite; a break-up of micrite to form intraclasts; the formation of drusy calcite cement on intraclasts adjacent to pore spaces; and , finally, replacement of both drusy calcite cement and micrite in intraclasts by phosphate.

At localities 13, 14, 15, and 16, carbonate mud seems to have been disrupted by bioturbation from the time of its deposition to the time of its phosphatization; disruption continued long after the phosphatization. Carbonate mud seems to have been replaced early-on by phosphite, with lithification occurring simultaneously with phosphatization, or shortly after phosphatization.

At locality 22, nodules of Kinderhookian age consist of a glauconitic quartz pelsparite which was originally cemented by carbonate mud, and was later recrystallized to spar. Borings can be observed (Figures 11-16, 19-22) cutting through the rock. The process of boring mechanically reduced the sparry cement to a clay-silt fraction. Phosphate replacement ensued following the mechanical break-down of spar and is^{by} far most common in bioturbated zones.

Controls on Phosphatization

Regional variations in the degree phosphate replacement are caused by concordant variations in carbonate grain-size (including both primary, detrital grains and secondary matrix cementation). Nodules composed of micrite or microspar have been replaced more often and more completely than the coarser, sparry-cemented specimens. This is especially evident at Smithville, Tennessee, where nodules and clasts with a fine-grained, micrite texture show complete replacement of carbonate by phosphate. Another example of preferential phosphate replacement in finer-grained textures is at locality 22 where micrite and fine-grains of spar are replaced, but a large echinoid spine filled with coarse spar is not replaced (Figure 16, and 19). Nodules with sparry cement are partially replaced in some cases, but usually this occurs at detrital grain-to-cement contacts, or at cement grain-to-cement grain contacts. Replacement never occurs where sparry cement fills large void space (Figure 15 and 18); if replacement is initiated at all in this case, it occurs at the rims of the void where spar grains are smallest. It appears then that there is a relationship between carbonate grain-size and the degree of phosphate replacement. This is reasonable because smaller grains provide greater surface area, and thereby allow greater contact with the phosphatic pore fluids that initiate replacement.

The feature most strikingly related to the degree of phosphatization is bioturbation (burrowing and boring). Garrison and Kennedy, 1975, and Ames, 1959, noted that grain-size is an extremely important factor in controlling the degree to which phosphate will replace calcite. I

believe bioturbation played an essential role in controlling the overall grain-size in Upper Devonian and Lower Mississippian carbonate sediments which subsequently became phosphate nodules. In particular, boring of limey hardgrounds decreased the overall grain-size of coarse grained, sparry cement. Boring brings about grain disintegration, resulting in an increase in surface area. This in turn facilitates phosphate replacement of carbonate material. Boring was especially important in the phosphatization of Kinderhookian nodules at locality 22 (Figure 11--2). In some cases, (locality 13, 14, 15, and 16) boring might be responsible for an apparent phosphate enrichment of previously phosphatized carbonate mud.

Prior to lithification (submarine cementation), most hardgrounds appear to have been intensely burrowed. In the process of burrowing, the grain-size of the sediment is homogenized and exposed anew to bottom water or perhaps to a new supply of interstitial^{it} water. The combination of fine-grained, homogenized limey mud, and the continual influx of new bottom or ^opre water produces the most completely phosphatized sediment (e.g. localities 13, 14, 15, and 16).

Other important factors controlling phosphatization are the porosity and permeability of the sediment (Ames, 1959). Porosity and permeability appear to be influenced strongly by bioturbation. Boring could possibly have increased porosity and permeability in "tightly" cemented hardgrounds of Early Mississippian age at locality 22. The exposed, open borings would have allowed renewed supplies of phosphate-rich bottom waters to flow freely through large volumes of lithified substrate.

Lastly, the presence of organic matter has been proposed by McConnell (1961) as a prerequisite for phosphate formation. Phosphate nodules from

the black shale are undoubtedly associated with large amounts of organic debris, but nodules are also found in all horizons of the overlying Maury Formation. This unit apparently has a much lower organic content than the black shales. However, the organisms responsible for the bioturbation could possibly contribute ^eadquate amounts of organic debris (primarily fecal) to influence phosphatization.

Processes of Phosphate Nodule Formation

I have recognized four distinct kinds of processes which have produced similar phosphatic nodules.

Case 1 - Localities 13, 14, 15, 16, Kinderhookian Age.

Local and sporadic deposition of fine-grained carbonate mud in topographic lows at times of calm water produced small carbonate bodies with a limited areal extent and thickness of less than a meter. The fine-grained texture of the material is evidence for little or no current activity during deposition because even very low-velocity currents would winnow out the fines. Micritization of carbonate mud is followed by phosphatization and probable lithification at this stage. Lithification is followed by the formation of shrinkage cracks, similar to those described by Wilson (1975) which are easily formed in thinly bedded sediments (Figure 36). The cracks could also be joints produced by minor sagging of the carbonate beds due to loading or the dewatering and compaction of underlying clays. The joint system could be polygonal (Shinn, 1969). Submarine erosion at the joints would produce the rounded edges which are found in the flattened, polygonal phosphatic slabs (Figure 37). Then the slabs could be reworked repeatedly until ovoid nodules in the pebble-to-cobble size ranges were produced (Figure 38). Once this process is finished, more carbonate mud is deposited (Figure 39) presumably in a topographic low. The origin of the carbonate mud is uncertain, but at this location the nodules are of Kinderhookian age and are paleotopographically low relative to the Borden delta front. The carbonates could therefore be the result

of current reworking of carbonates topographically higher on the delta slope, transported sporadically by scouring currents to areas at the delta toe. Although the carbonate beds are channel shaped, they do not represent channels which have cut into the underlying black shale. These "channel-like" bodies are local, fine-grained carbonate bodies less than a meter thick, which include the already-present nodules. A burrowing fauna began to homogenize the carbonate sediment, avoiding the lithified nodules. This is seen, for example, in Figure 33. I feel that burrowing played an important but indirect role in the phosphatization of the carbonate mud. As I noted earlier, homogenization of the sediment increases surface area and also brings about renewed circulating of phosphate-rich pore and bottom water. Again, lithification occurred and the burrowing fauna was replaced by a boring ichneocoenose. Borers randomly riddled the phosphatic bed (Figure 33), and may actually have increased the overall grain-size of the sediment in some instances (Figure 33). Large intra-clasts and fecal pellets^{WERE} produced, and both were concentrated in open borings. Intraclasts and pellets located in these porous ducts seem to be slightly enriched in phosphate, and are sometimes weakly cemented in the borings by an unidentified yellow mineral (Figure 35). It is evident that boring also enhances mineralization. The lithified sediment is so thoroughly bored that it is difficult to determine whether boring or jointing occurred first. As is evident in Figure 10, jointing occurred before the reworking of the phosphatic clasts and the deposition of the overlying glauconitic shale of the Maury Formation. The vertical joints are prominent in all clasts except one which has "pseudo-horizontal" joints (Figure 10). In actuality this clast contains vertical joints and has been reworked and

turned on end after the lithification and jointing stages. The boring and jointing are the most important processes in the submarine erosion of this hardground, and account for the brecciated or conglomeratic appearance of the unit. From the onset of lithification of the carbonate sediment, to the formation of the conglomeratic facies, all processes acting on this unit were in situ. The evidence found at localities 13-16 parallels that of hardgrounds studied by Bromely (1975a and b) (Figure 40).

Case 2 - Locality 22, Early Mississippian Age

Sedimentary processes acting during a period of nondeposition (or at least slow deposition) initially produced a glauconitic-quartz siltstone which was held together by a carbonate mud matrix. Such a rock formed in a paleotopographically low position at the delta toe after cessation of clastic sedimentation on the Borden delta front. Silt-sized quartz probably came from the reworking of siltstones and fine-grained sandstones further up the delta front to the northeast. Glauconite was produced by organic reworking and fecal deposition in carbonate muds all along the delta front. This is discussed in detail by Van Wie (1971). Lithification of the thin glauconitic siltstone was produced by subaqueous micritization of ^{the} carbonate mud matrix. This stage was followed by recrystallization first to microspar and subsequently to a coarser-grained spar (Figure 11). This series of transformations yielded the glauconitic quartz pelsparite discussed in the petrology section. Once lithification was completed, a boring assemblage mechanically began to break-up the hardground. Borers reworked the sparry cement until it was mud-sized (Figures 11-16 and 19-22). Phosphate replaced the fine-grained carbonate in the borings and, to a lesser extent, in nearby areas at grain contacts where the spar was of the finest grain size.

Much of the spar has not been replaced, presumably because of its coarse texture (Figures 15, 16 and 18). Such coarse, massive spar has been replaced only where borings cut it (Figure 15). Continued biologic reworking and submarine erosion produced cobble-sized phosphatic clasts.

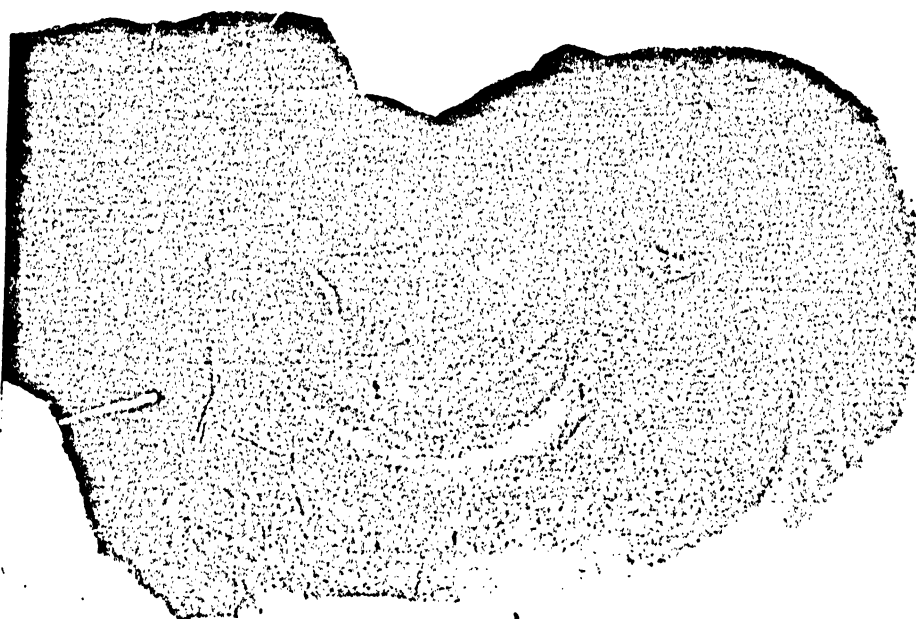
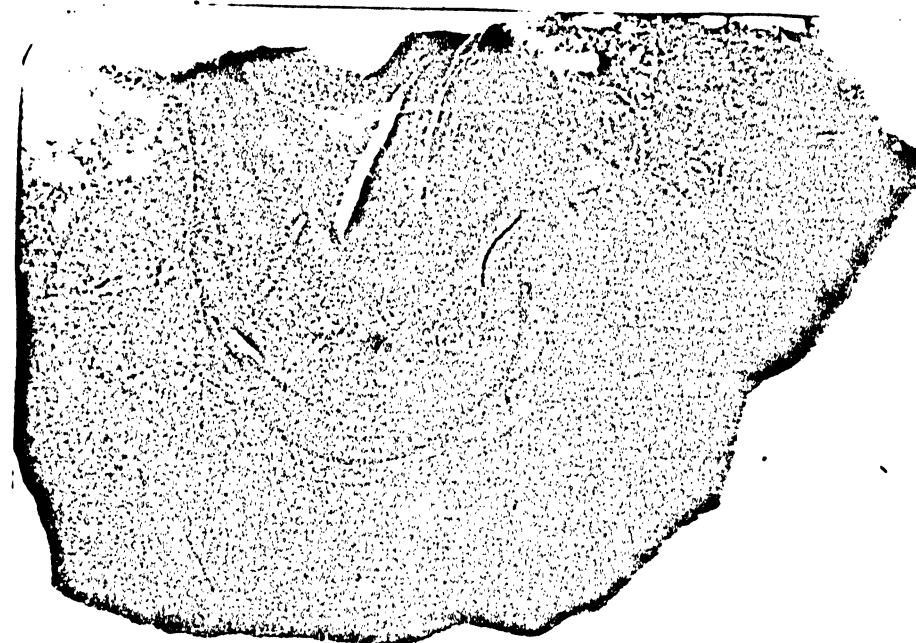
Cases 3 and 4, Locality 3: Late Devonian and Early Mississippian

Near the close of the Devonian period and early part of the Mississippian the rate of black shale deposition slowed. The deposition of shale was interrupted intermittently by minor amounts of carbonate sedimentation. These thin beds of limestone, which covered a considerable area (the entire study area, with the exception of south central Tennessee), were also exposed to phosphatization and, subsequently, nodule production. At localities 22b, 11, 12, 4, 5, 6, 7, 8, 9, 20, and 21, fine-grained carbonate appears to have been phosphatized and lithified penecontemporaneously. Little to no bioturbation has disturbed the sediment at these localities. Upon lithification, jointing and cracking occurred by means of the processes described for Case #1. Submarine erosion working around the joint sets over time produced the oriented, polygonal phosphatic nodules.

At locality 3, phosphatization did not occur until the carbonate had recrystallized to coarse spar (Figure 23) and lithified. Phosphate rarely replaced the coarse spar; when replacement occurs it is most commonly at cement-grain contacts. Pellets of probable fecal origin, (Figure 24) which make up an average of six percent of the nodules' volume, are always phosphatized. I feel that these were selectively phosphatized before lithification, and could represent the source of phosphate for the subsequent replacement of the sparry cement. The replacement reactions undoubtedly continued at a slow rate because of the large grain-size and lack of porosity

of (or in) sparry cemented nodules. Bioturbation did not disturb this sediment after lithification occurred. Post-lithification nodule formation is identical to that described for Case 3.

Fig. 31 U-shaped burrow with a post-lithification boring cutting through the burrow. Also note the numerous other borings and burrows at various angles to bedding planes. Scale- actual size. Locality 15.



Figs. 32 (top) and 33 (bottom). Top-locality 22, bottom- locality 15. Top- Glauco-phosphatic quartz pel-sparite with bioturbation. Bottom- phosphatic clast from an intraformational conglomerate. Note the two phosphatic lag nodules (hiatus nodules) at the right. Also note the boring which glances off the hiatus nodule. Scale- actual size.

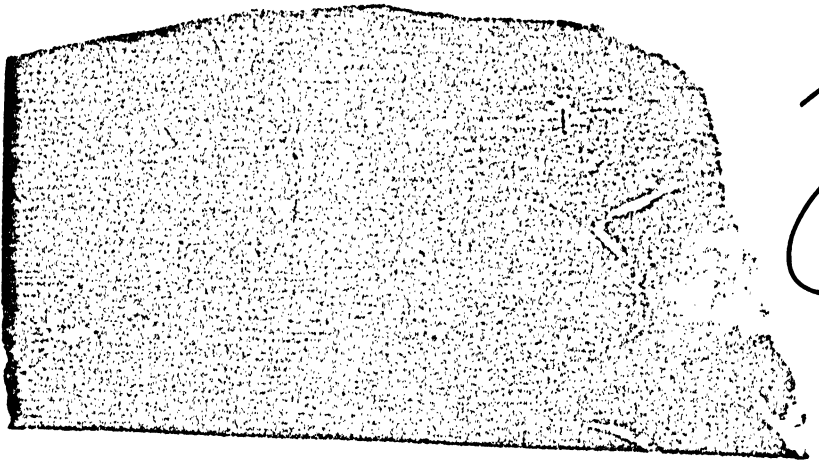
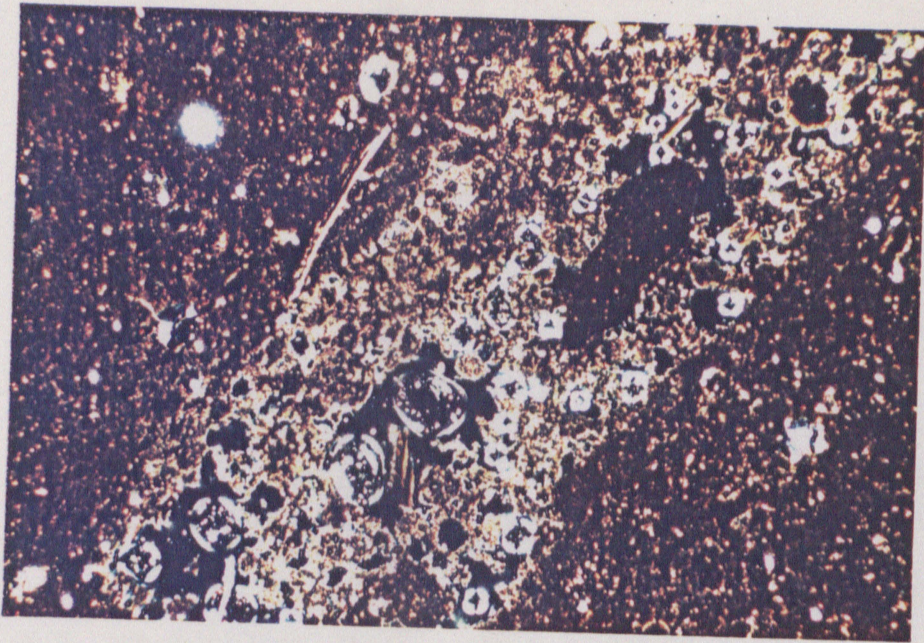
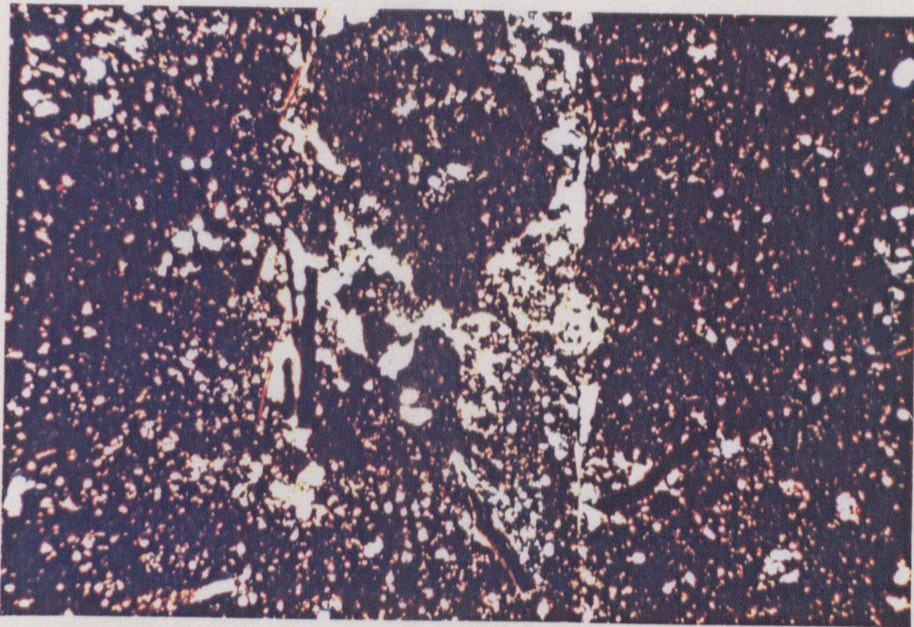


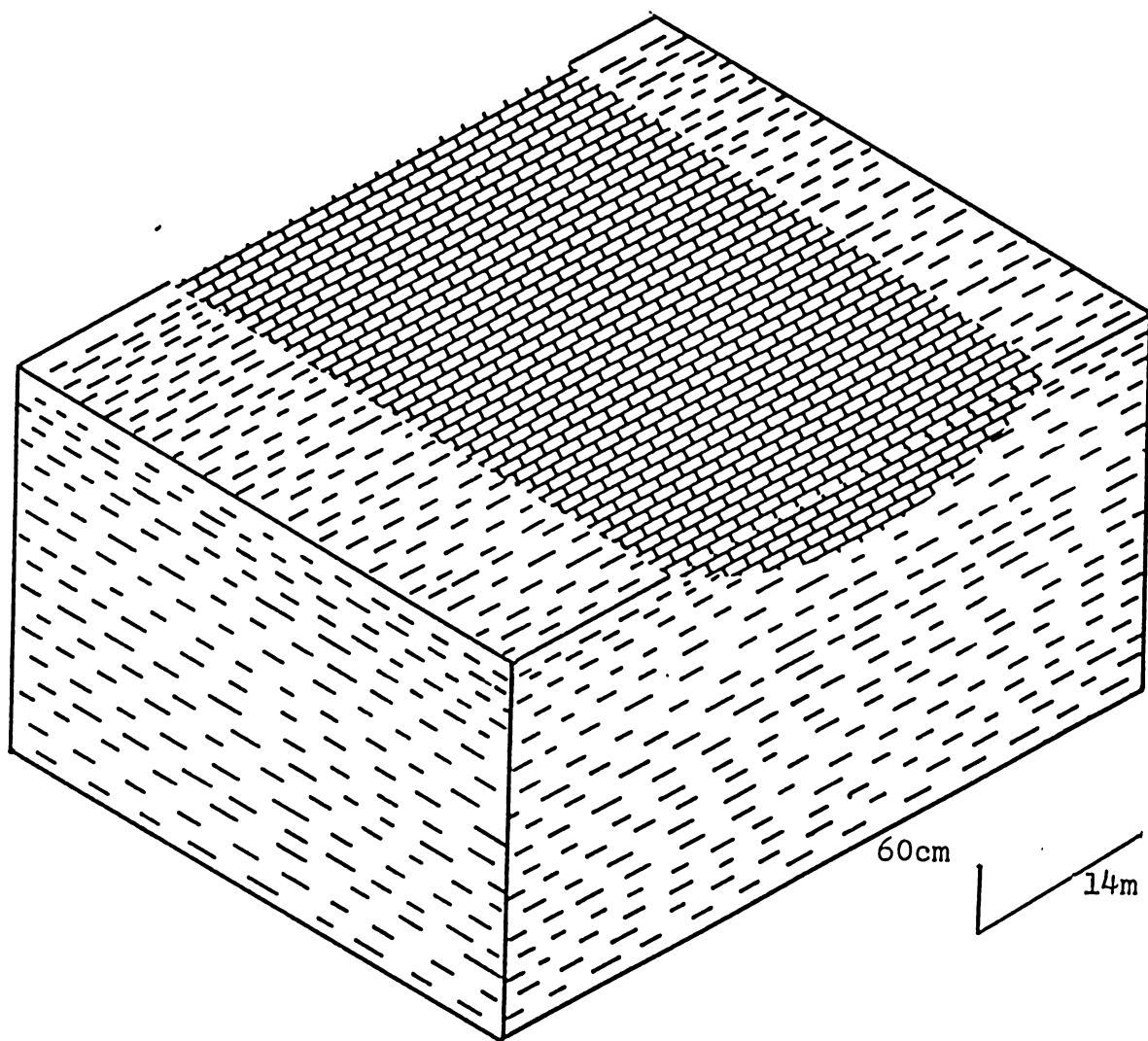
Fig. 34 A large phosphatic clast with a distinct diagonal boring. The large structureless intraclast in the boring indicates that the surrounding phosphatic mudstone was lithified or semi-lithified before boring occurred. Boring produces a grain-supported texture in this mudstone and the resulting increase in porosity facilitates mineralization (bright yellow) after the episode of boring. Fossil debris is alligned parallel to the direction of boring.
Crossed-nicols, locality 15.

Fig. 35 The same type of boring as shown in Fig. 34, with a structureless intraclast torn from the boring wall during bioturbation.
Crossed-nicols, locality 15.

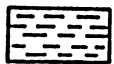


1mm





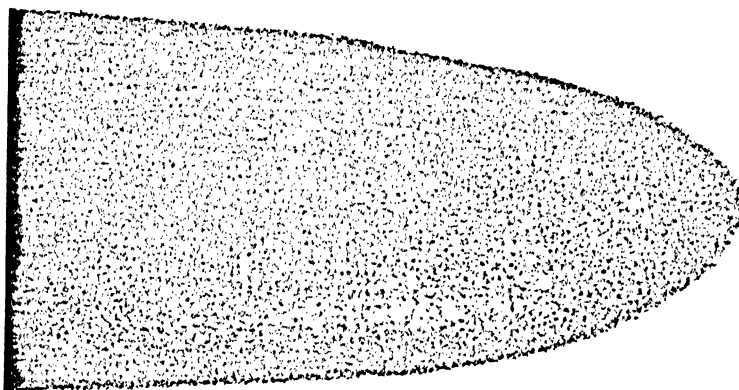
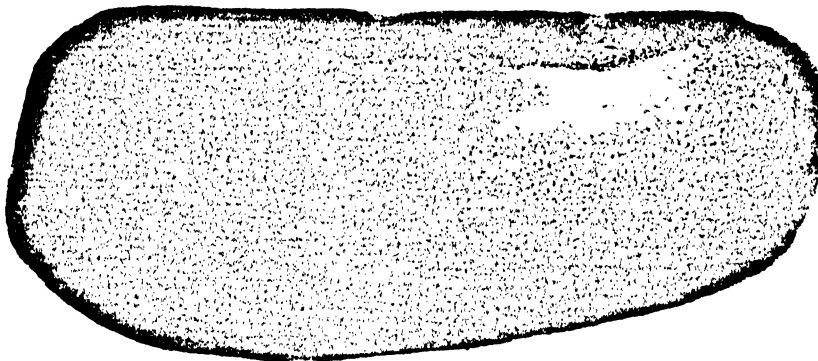
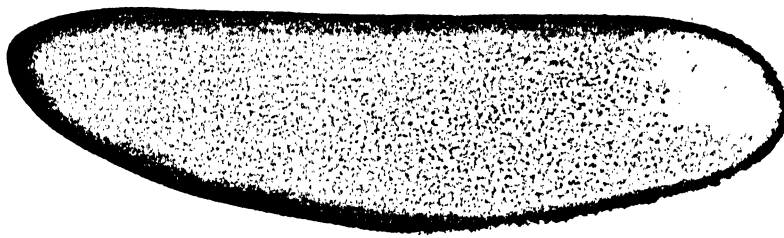
Lime mud of Kinderhookian age (Maury Formation)

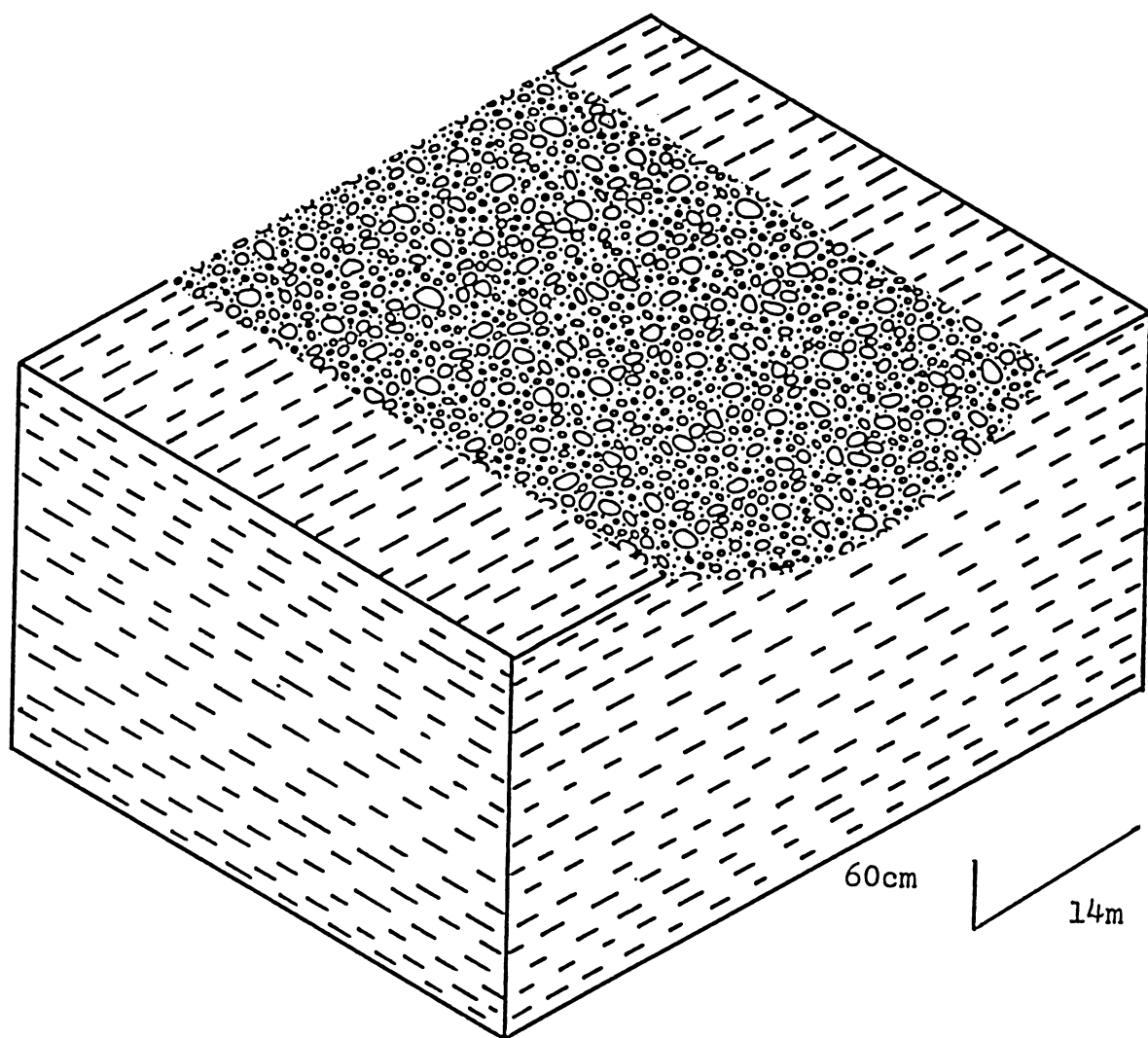


Black shale-Upper Devonian in age (Chattanooga Shale)

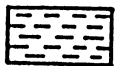
Fig.36 The deposition of fine-grained carbonate sediment in seafloor lows is followed by intense burrowing, phosphatization, lithification, jointing and cracking.

Fig.37 Top and middle- Locality 20. Bottom- Locality 6
X-ray radiographs of nodules showing planar bedding and
abruptness with which it terminates at the nodule's edge.
Note the difference in the degree of rounding of nodules.
Scale- actual size.



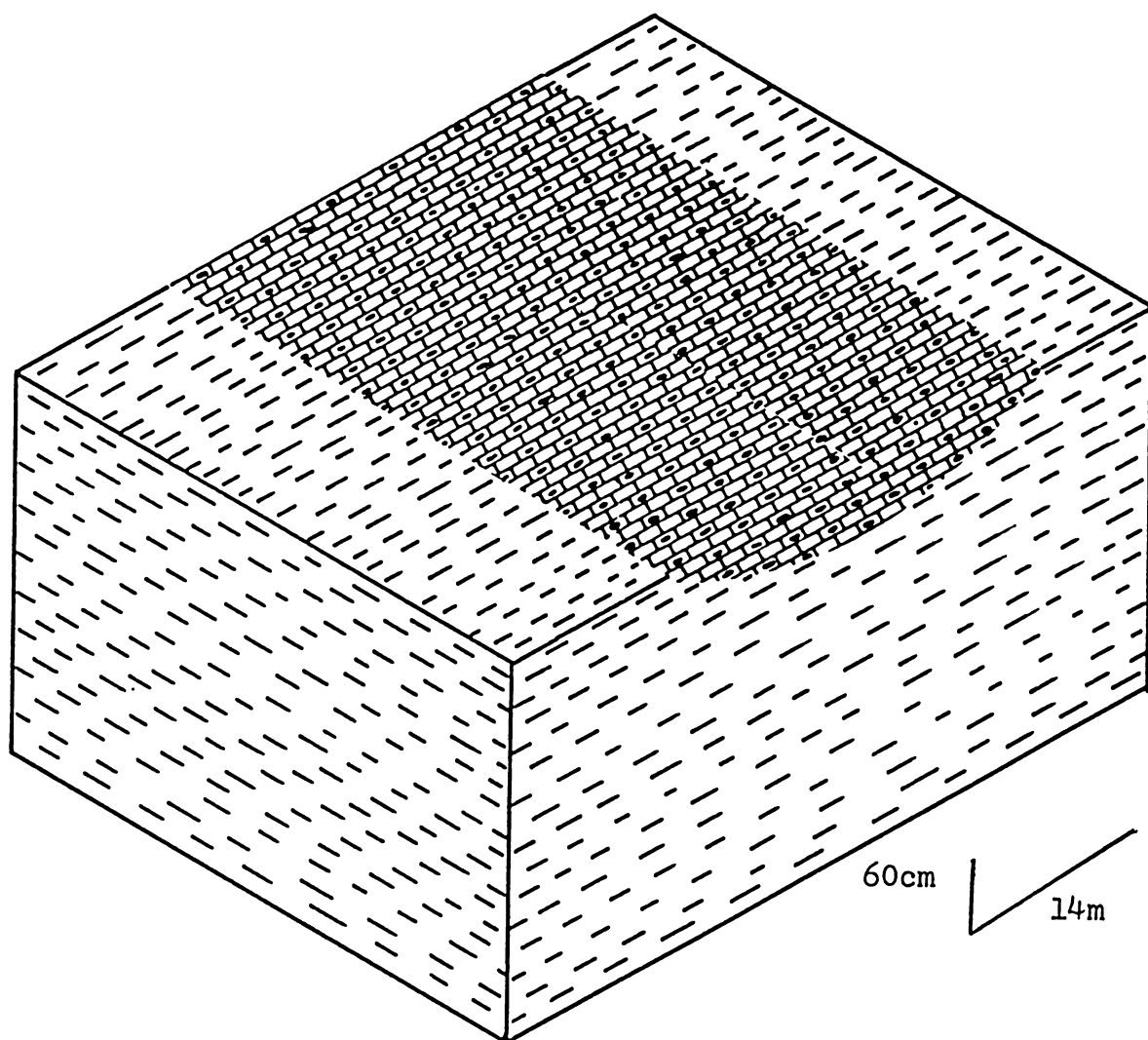


Phosphatic nodules

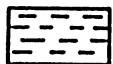


Black shale

Fig. 38 The sub-aqueous erosion of jointed phosphate beds forms lag deposits of phosphatic nodules.



Phosphatic intraformational conglomerate



Black shale

Fig. 39 Renewed sedimentation deposits fine-grained carbonate mud, which is followed by burrowing, phosphatization, lithification, jointing and cracking, and boring. The bed is worked into another lag deposit, or intraformational conglomerate with the older and smaller phosphatic nodules included in the newer and larger phosphatic "clasts".

- A. Fine-grained lime mud is deposited in lows on top of a slightly rolling surface of Chattanooga shale. B. Lithification occurs, either by subaqueous phosphatization or micritization, producing a hardground. C. Shrinkage cracks are initiated. D. Erosion undermines the hardground by washing out at joints or by subsolution of the joints. E. Renewed sedimentation of more fine-grained carbonate mud, and burrowing organisms homogenize the new sediment. The homogenization includes working-in the phosphate nodules which represent a lag deposit, and are here called hiatus nodules. F. Cementation occurs by phosphatization. G. Jointing by shrinkage processes occurs. H. Undermining at joints, extensive boring, and overturning of hardground clasts.

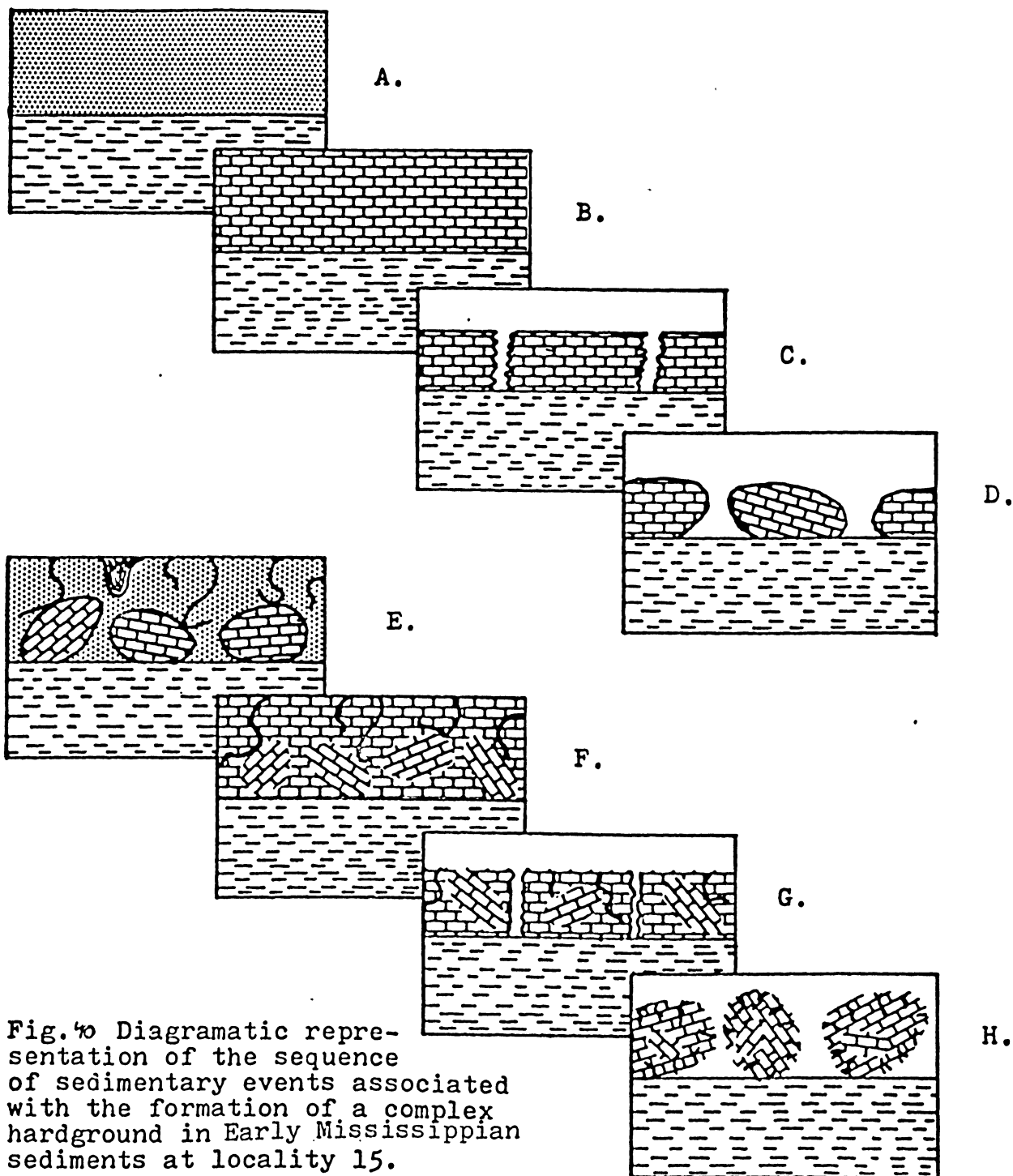


Fig. 40 Diagrammatic representation of the sequence of sedimentary events associated with the formation of a complex hardground in Early Mississippian sediments at locality 15.

Depositional Environments

Phosphate nodules occur in two stratigraphic positions in Kentucky and Tennessee. One position is in Upper Devonian black shales; the other is in glauconitic shales and hardgrounds of the Maury Formation, which are Kinderhookian age. Kepferle (written communication) reports phosphate nodules in a third stratigraphic horizon; the Floyd's Knob Bed (Osagean) of the Borden Formation in central Kentucky (Figure 3).

The Floyd's Knob glauconite lies over Lower Mississippian sediments on the southwestward-dipping paleoslope of the Borden delta front and merges with the Maury Shale at the base of the delta front. Phosphate nodules and glauconite occur in a paleotopographically low position on the delta in the Maury Formation and Floyd's Knob Bed in central and southwest Tennessee and southern Kentucky and occur also paleotopographically high on the delta in the Floyd's Knob Bed in central Kentucky (Kepferle, written communication). The glauconite is believed to have been deposited in a starved basin after Borden clastic sedimentation had ceased (Lineback, 1966). The association of glauconite, phosphate nodules, hardgrounds, and bioturbation has been noted by numerous workers^{elsewhere}, and is thought to indicate slow or non-depositional periods and stratigraphic breaks. It has been noted that phosphate nodules form only (1) during periods in which the influx of terrigenous sediments is low, or (2) during extended periods of sediment-water contact. The abundance of bioturbation in the phosphatic sediments and phosphatic hardgrounds attests to the great length of time that sediments were exposed to non-depositional processes. The relatively fine-grained nature of sediments associated with

the phosphate nodules indicates relatively calm waters, and the paleogeographic position of the nodules at the prodelta toe, and beyond, denotes shelf conditions.

Commonly, hardgrounds are associated with stratigraphic breaks and unconformities. Hardgrounds produced by the subaqueous cementation of carbonate sediment appear to require more time of sediment-water exposure to form than is normally available in areas of continuous sedimentation. Therefore hardgrounds are believed always to be associated with a hiatus. The simplest process for creating a hiatus or non-depositional period (in areas of primarily clastic sedimentation) would be to shut-off the sediment supply. This could occur with a lateral shifting of the source (and transport mechanism), or cessation of continental erosion. The absence of terrigenous sedimentation would allow increased time for existing sediment-seawater exposure, and could lead to lithification and phosphatization.

The abundance of burrowing and boring organisms suggests the presence of overall oxidizing conditions while the phosphate hardgrounds were formed. The presence of glauconite indicates micro-reducing conditions in the sediment, predominately in association with fecal pellets and mucous-lined burrows.

Overall, the lag deposits of phosphate nodules and phosphatic intraformational conglomerates, glauconite, bioturbation, and hardgrounds are representative of widespread non-depositional shelf conditions during Kinderhookian and Osagean time. Water depth varied, probably between tens and hundreds of meters, but at its shallowest was still below wave base.

Upper Devonian phosphate nodules also represent periods of low terrigenous influx, but indicate only minor time breaks in sedimentation. Non-deposition during Late Devonian time in Kentucky and Tennessee indicates

the remote influence of the terrigenous source. This suggests why phosphate nodules are not found in more northerly locations (northern Ohio); in the north, terrigenous influx at the close of the Devonian period was characterized by widespread, thinly-bedded siltstones (the Bedford and Berea) rather than fine-grained carbonates and clays. The deposition of siltstones was cyclic, but occurred with enough regularity to keep terrigenous influx too high for phosphate nodule formation. This more northerly portion of the basin is controlled by turbidite sedimentation in front of the Catskill delta system in New York.

Lateral Continuity

The recognition of key marker beds within the Upper Devonian black shale sequence is a useful step in understanding the internal stratigraphy of black shales in this region (Provo et al. 1977).

Thin-bedded nodulose zones are easily recognized, and extend over wide areas in Kentucky, Tennessee, Georgia, and Indiana. They provide a useful marker bed in most instances, but fail in others.

Phosphate nodule beds are concentrated in two stratigraphic horizons: (1) in upper Devonian black shales, and (2) in lower Mississippian glauconitic shale (the Maury Formation of Kinderhookian age). Each stratigraphic horizon was considered separately in terms of lateral continuity.

Upper Devonian

Beds containing phosphate nodules are consistent in their stratigraphic position and lateral continuity in Kentucky^K east of the Cincinnati arch, but lack lateral continuity west of the arch. The nodules are located in thin, two-inch beds, usually within two or three feet of the top of the New Albany and Ohio black shales. Nodule beds at the eastern localities are more continuous, while western localities have only scattered occurrences of nodule beds. (eg. locality 11 in southern Indiana has nodule beds,) while 35 miles south at locality 10 nodules are absent). All eastern localities in Kentucky (3, 4, 5, 6, 7, 8, and 9) contain nodule beds in a similar stratigraphic position, approximately 0-2 feet from the top of the black shale unit. Phosphate nodule beds were not found at the more northerly locations in Ohio (localities 1 and 2). In Tennessee the persistent nodule

bed in the uppermost few feet of the Chattanooga Shale dies out and is found only at a single outcrop (locality 22b) in southwestern Tennessee. This outcrop of Chattanooga Shale is characterized by much coarser sediments, sandstones and siltstones which are absent in other parts of the study area. These coarse sediments are probably derived from local highs such as the Hohenwald Platform, which is located on the west flank of the Nashville dome. The coarser nature of the Upper Devonian black shales in this region leads me to conclude that higher rates of sedimentation were characteristic of this area. With locality 22b being an exception, phosphate nodule formation, was apparently not compatible with higher sedimentation rates in this area during Upper Devonian time.

Lower Mississippian (Kinderhookian)

Phosphate nodule beds are continuous over wide areas of Tennessee, Georgia, and southern Kentucky in the Maury Formation (Kinderhookian age). The nodule beds were present at all the outcrops studied in this area with the exception of two. No nodules were found at outcrops 18 and 19; there was no obvious difference in the appearance of the Maury or Chattanooga shales there, but nodules were simply absent.

Nodulose beds are effective stratigraphic markers for the Upper Devonian black shales of Kentucky, particularly east of the Cincinnati Arch. Upper Devonian nodule beds lack good lateral continuity west of the arch and die out in northern Tennessee, and cannot therefore, be used to delineate the stratigraphy of black shales across western Kentucky and Tennessee. Conversely, nodule beds of Kinderhookian age are continuous across Tennessee, southern Kentucky, and northwestern Georgia. Kepferle (1977) reports nodules at Big Stone Gap, Virginia (a more easterly location than any in this study) in a position that is difficult to assign. This unit could represent the base of the Sunbury Shale (Early Mississippian).

Conclusions

Phosphate nodules of Upper Devonian and Lower Mississippian ages form in four distinct ways, involving generally these steps:

- 1) Deposition of fine-grained carbonate mud in topographic lows;
- 2) burrowing of soft sediment in some cases;
- 3) subaqueous lithification, possibly by phosphatization in some cases, but more commonly by micritization of carbonate mud;
- 4) "polygonal cracking and shrinkage, causing brecciation of hardened or semi-lithified bed rock owing to temperature changes and force of crystal growth within sediment" (Wilson, 1975);
- 5) boring in some cases, followed by phosphatization if not previously phosphatized by step #3. (In some instances where phosphatization has already occurred enrichment occurs.);
- 6) in-situ subaqueous reworking, erosion, and subsolution of polygonal slabs into nodules-either elongate, amoeboid, or spherical in shape, depending on the amount of reworking;
- 7) nodules are left as a lag; sometimes with oriented nodules because of in-situ erosion along preferred joints sets;
- 8) In some instances there is a repetition of the cycle producing intraformational conglomerates with the earlier-formed nodules incorporated as lag intraclasts or "hiatus nodules".

Initiation of these episodes is dependent on the following:

- 1) Long periods of non-deposition or low terrigenous influx, possibly caused by lateral change in the sediment source, or cessation of continental erosion.
- 2) Long periods of sediment-water contact.
- 3) pH of 7.0 or more (Ames, 1959).
- 4) PO_4 concentrations of 0.1 ppm or more (Ames, 1959).

Rock texture is the most important factor controlling the degree of phosphate replacement. This, in turn, is controlled directly by the extent of bioturbation (burrowing and boring) in producing finer-grain size, greater porosity, and greater permeability.

Nodulose zones are adequate as marker beds for delineating the inter~~an~~ stratigraphy of Upper Devonian black shales in eastern, central, and southern Kentucky; they are also effective in marking stratigraphy in Lower Mississippian sediments in southern Kentucky, Tennessee, and northwestern Georgia.

X-ray data indicate that the phosphate phase in nodules of both Upper Devonian and Lower Mississippian age is fluorapatite.

APPENDIX

Appendix A

Outcrop Localities

Ohio

1. Ross County - Copperas Mountain, 3.9 airline miles east, of Bainbridge by way of U.S. 50, Jones Levee Road, and Storm Station Road.
2. Adams County - Tener Mountain on S.R. 32, east of Peebles, numerous cuts along both sides of the highway.

Kentucky

3. Powell County - Near Clay City, where S.R. 1057 crosses over Mountain Parkway.
4. Powell County - East of Vaughn's church in creek bed which cuts under S.R. 1057, approximately 7 miles south of Clay City.
5. Estill County - Cuts on both sides of S.R. 52, 5 miles west of Irvine.
6. Madison County - On northbound side of I-75, $\frac{1}{4}$ mile south of junction with S.R. 21.
7. Madison County - On south side of S.R. 21, 1 mile of Berea, at church parking lot which borders creek.
8. Cumberland County - 2 miles east of Burkesville on S.R. 90, deep highway cut with benches.
9. Cumberland County - 2 miles south of Burkesville on S.R. 61 in bluff on east side of highway.
10. Bullitt County - 10 miles south of Louisville in clay pit by way of I-65 S., then S.R. 1020 to the end of old Barricks Road.

Indiana

11. Clark County - 5 miles south of Sellersburg on east side of I-65 in small cut.

Tennessee

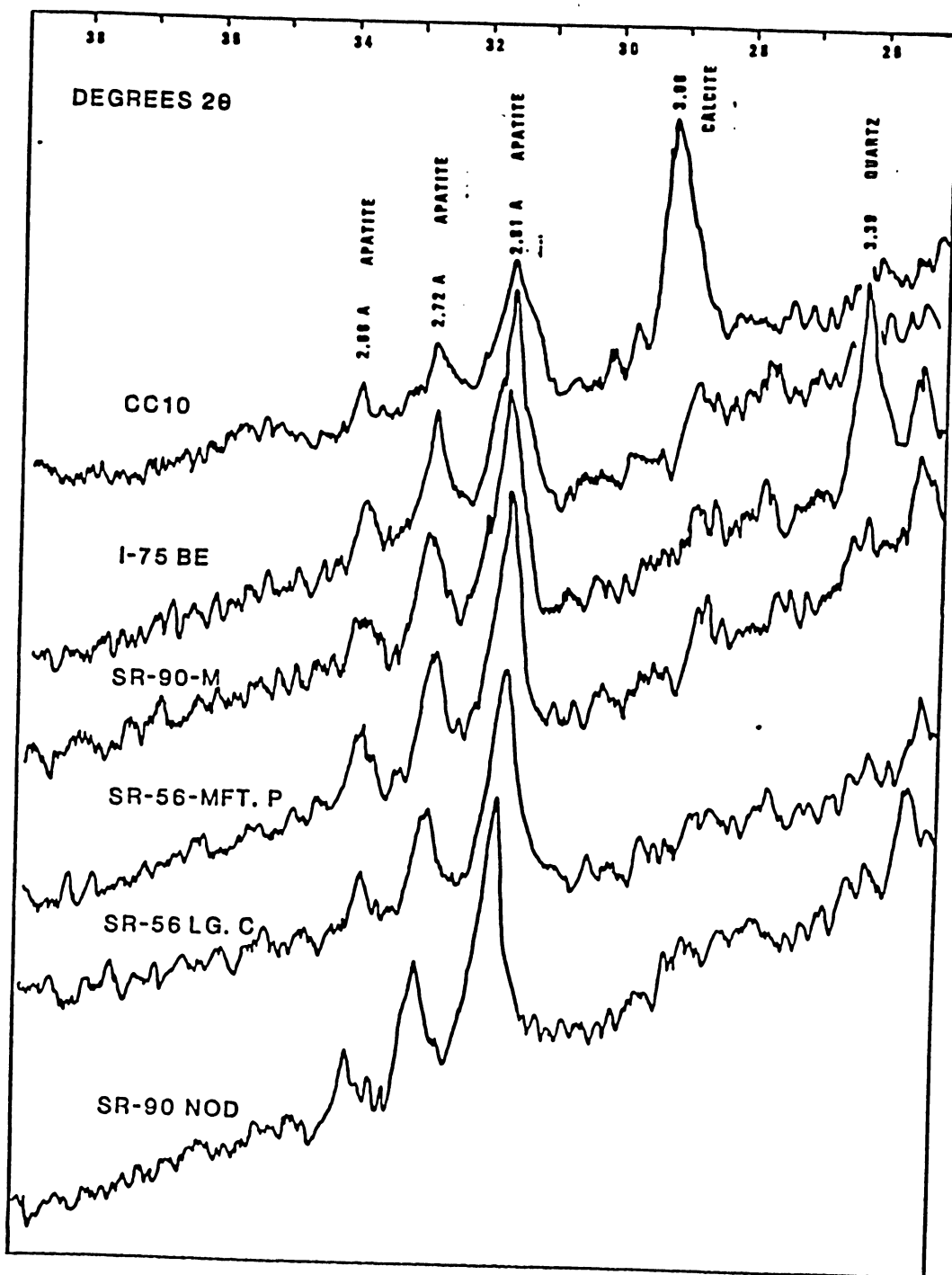
12. Dekalb County - 7 miles east of Smithville on S.R. 26 on east and west approaches to Sligo Bridge.
13. Dekalb County - 7 miles north of Smithville on S.R. 56 on east side of road near bend in highway and descent to Hurrican Bridge.
14. Dekalb County - 10 miles north of Smithville on S.R. 56 on north-east side of highway.
15. Dekalb County - 11 miles north of Smithville on S.R. 56 at slight bend in road on east and west sides of road.
16. Dekalb County - 1 mile southwest of junction of Floating Mill Road and S.R. 56, on Floating Mill Road in bank cut into hill along north side of road.
17. Cannon County - 2 miles south of Woodbury on S.R. 56 on west side of road at crest of hill.
18. Coffee County - 7 miles north of Manchester on U.S. 41 on west side of road on bluff.
19. Coffee County - 11 miles north of Manchester on U.S. 41 on both sides of highway at crest of hill.
20. Cheatham County - 2.2 miles west of Pegram on U.S. 70 in vertical bluff on north side of highway.
21. Davidson County - 5.8 miles southwest of Richland, a

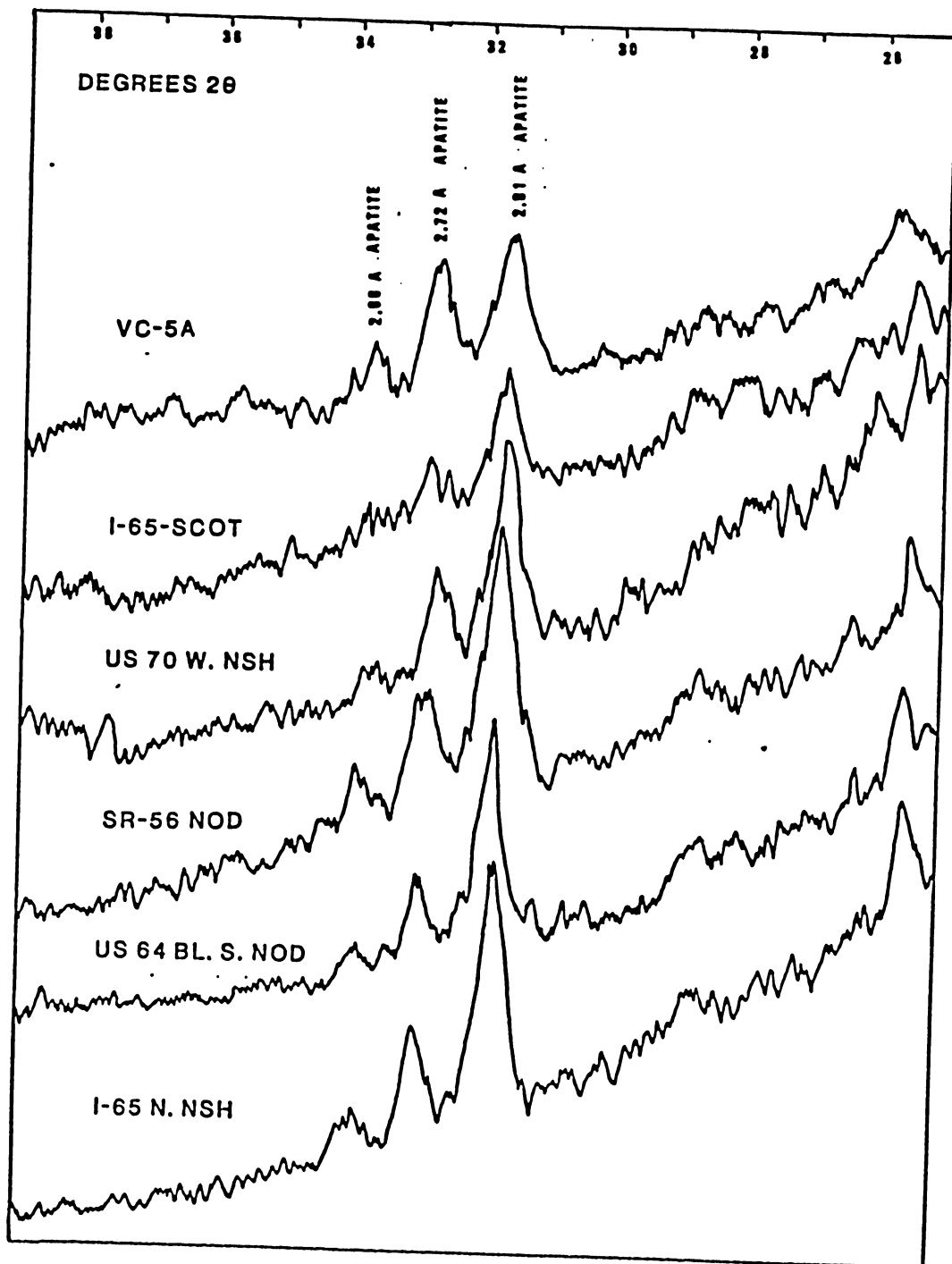
western suburb of Nashville, on U.S. 70 N., 2.3 miles northeast of junction with U.S. 70 at bluff on north side of road.

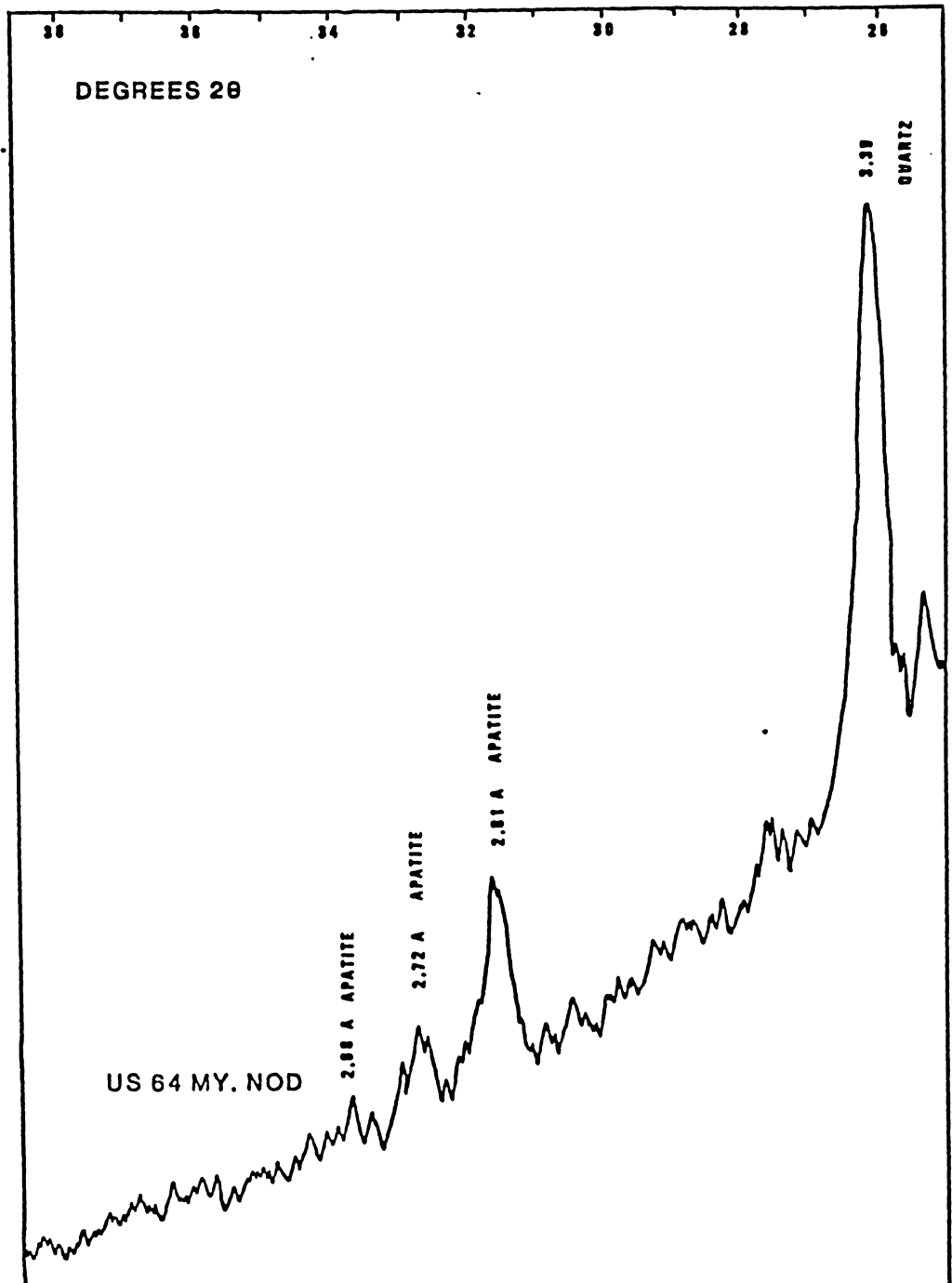
- 22. Hardin County - 15 miles west of Waynesboro on U.S. 64, excellent outcrops on both sides of highway, outcrop is approximately one-eighth mile long.
- 23. Giles County - 3 miles south of junction with U.S. 64 on I-65; east side of highway.
- 24. Perry County - 1 mile south of Linden, on west side of S.R. 13 at top of bluff.

Georgia

- 25. Chattcoğa County - .5 miles west of Menlo on S.R. 48 and 4.4 miles east of Alabama state line; outcrop is on north side of highway.







Appendix C

Key for X-ray Samples

<u>Sample</u>	<u>Locality</u>	<u>Description</u>
CC-10	3	Phosphate nodule from Devonian Black shale
I-75-BE-1	6	"
SR-90-M	8	Small rounded phosphate nodule from Maury Formation-Kinderhookian
SR-56-MFT.P	15	Phosphate nodule from Maury Formation at contact with overlying Ft. Payne Formation
SR-56-Lg.C.	15	Large phosphatic clast from intraformational conglomerate of Maury Formation
SR-90-Nod	8	Phosphate nodule-Dev. black sh.
VC-5a	4	"
I-65-Scot	11	"
US-70-W.NSH	21	Phosphate nodule-Maury Formation
SR-56-NOD	15	Phosphate nodule from Maury at locality of intraformational conglomerate, but possibly a "hiatus concretion"
US-64-B1.S.Nod	22b	Phosphate nodule-Chattanooga Shale
I-65-N.NSH		Phosphate nodule from talus north of Nashville, Tenn. (not an official outcrop)
US-64-My. Nod.	22a	Phosphate nodule from Maury (Glaucinitic-phosphatic pelsparite)

Appendix D

Thin Section Index

<u>Locality</u>	<u>Sample No.</u>	<u>Type of Section</u>	<u>Magnification</u>
15	SR56-1	Large Phosphatic Clast with Nod- ules Included	x 2.5
15	SR56-2	"	x 2.5
15	SR56-3	"	x 2.5
15	SR56-4	"	x 2.5
15	SR56-5	"	x 2.5
15	SR56-6	"	x 2.5
16	SR56-8	"	x 10
16	SR56-9	"	x 10
13	SR56-12	"	x 10
13	SR56-16	"	x 10
20	SR70-N-1	Large Phosphate Nodule	x 10
20	SR70-N-2	"	x 10
8	SR90-1	Phosphate Nodule	x 10
11	BA-1-65-1	"	x 10
11	BA-I-65-2	"	x 10
3	CC-M-2	"	x 10
3	CC-4	"	x 10
3	CC-5	"	x 10
3	CC-7	"	x 10
3	CC-8	"	x 10
3	CC-9	"	x 10

3	CC-10	"	x 10
3	CC-11	"	x 10
4	VC-3	"	x 10
4	VC-5a	"	x 10
4	VC-5b	"	x 10
22	US-64-W-1	Early Miss. Phos- phate Nodule	x 10
22	US-64-W-2	"	x 10
22	US-64-W-4	"	x 10
22	US-64-W-5	Devonian Phos- phate Nodule	x 10
2	I-64-1	"	x 10
2	I-64-2	"	x 10
6	I-75-BE-1	"	x 10
6	I-75-BE-2	"	x 10

Appendix E

PERCENTAGES OF CONSTITUENTS

	ALLOCHEMS				ORTHOCHEMS				MISCELLANEOUS			
Sample Number	Intraclast	Fossils	Glauconite Pellets	Phosphatic Pellets	Phosphatic Micrite	Phosphatic Microspar	Phosphatic Druse	Sparry Calcite	Quartz	Feldspar* Mica	Pyrite	
SR56-1	2	5		33	56				2			
SR56-2		2		45	50				1			
SR56-3		8		15	75							
SR56-4		2		24	51		16		4			
SR56-5		2		50	48							
SR56-6	4	3		27	63		2		1			
SR56-8		4		15	81				1			
SR56-9	2	2		7	84				5			
SR56-12		1		3	95				2			
SR56-16		4		5	85				6			
SR70-N-1		7			93							
SR70-N-2		9			91							
SR90-1		5		6	88						1	
BA-I-65-1		1		56	36				5			
BA-I-65-2		6		30	64							
CC-MP-2		3			60	3		32	3			
CC-4		3		6	53		2	29	2		5	
CC-5	5			5	52		37					
CC-7	18	2		7	27		44		2			
CC-8	21	3		9	21		45					
CC-9		10		22	47			12			8	

Sample Number

CC-10		2			95					3	
CC-11	4	3		3	51	38		1			
VC-3		2		20	77						
VC-5a		1		8	66		18			6	
VC-5b					72		27			1	
US-64-W-1		2	23		32		24	15		3	
US-64-W-2			30		45			20	2*	3	
US-64-W-4		1	22		40		22	12		2	
US-64-W-5				35	65						
I-64-1		1			45		49			5	
I-64-2					57		42			1	
I-75-BE-1		2		18	78					2	
I-75-BE-2				19	80					1	

Appendix F

Samples Grouped by General Geographic
Location and Location in Section (Age)

<u>Group #</u>	<u>Locality</u>	<u>Samples</u>	<u>Age</u>
1	13, 15, 16	SR-1 thru SR56-6, SR56-8, 9, 12, 16	Early Miss.
2	20	SR70-N-1,2	"
3	8	SR90-1	Upper Devonian
4	11	BA-I-65-1,2	"
5	3	CC-MP-2, CC-4, 5, 7, 8, 9, 10, 11	"
6	4	VC-3, VC-5a, 5b	"
7	22	US64-W-1, 2, 4	Early Miss.
8	22	US64-W-5	Upper Dev.
9	2	I-64-1, 2	"
10	6	I-75-BE-1, 2	"

Appendix G

PERCENTAGE OF CONSTITUENTS AVERAGED FOR * GROUPS
(Rounded to nearest whole integer)

AVERAGES FOR GROUPS (Rounded to nearest whole integer)															
Group Number	ALLOCHEMS					ORTHOCHEMS					Folk(1962) Classification	Dunham (1962) Classification			
	Intraclasts	Fossils	Glauconite Pellets	Phosphatic Pellets	Phosphatic Micrite	Phosphatic Microspar	Phosphatic Druse	Sparry Calcite	Quartz	Mica *Feldspar			Pyrite		
#1 ^k	1	3		22	69		2		2			Sparse Biomicrite	Wackestone		
#2 ^k		8			92							Fossiliferous Micrite	Mudstone		
#3		5		6	88						1	Sparse Biomicrite	Wackestone		
#4		4		43	51				2			Sparse Biomicrite	Wackestone		
#5	6	3		7	51		21	9	1		2	Poorly Washed Biosparite	Wackestone		
#6		1		9	72			15			2	Fossiliferous Micrite	Wackestone		
#7 ^k		1	25		39			15	16	1*	3	Poorly Washed Biosparite	Wackestone-Packstone		
#8				35	65								Wackestone		
#9		1			51			46			3	Poorly Washed Biosparite	Mudstone		
#10		1		19	79						1	Sparse Biomicrite	Wackestone		
Average of all Groups	1	3	3	14	66		2	8	2		1	Sparse Biomicrite	Wackestone		
Average of all Kinderhookian grps.		4	8	7	67			5	6		1	Sparse Biomicrite	Wackestone		
Average of all Devonian Groups	1	2		17	65		3	10			1	Sparse Biomicrite	Wackestone		

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