BURIAL ENVIRONMENT, DIAGENESIS, MINERALOGY, AND MG & SR CONTENTS OF SKELETAL CARBONATES IN THE BUCKHORN ASPHALT OF MIDDLE PENNSYLVANIAN AGE, ARBUCKLE MOUNTAINS, OKLAHOMA

Thesis by

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DEDICATION

To my late father,
CARL STANDEFER SQUIRES,
no other man will I hold in
such high regard, nor owe
so much.

ACKNOWLEDGMENTS

To my thesis advisor, Dr. Heinz A. Lowenstam, I owe much gratitude for his suggestion of the specific thesis problem and for his patient guidance and encouragement throughout the course of the research. I shall also always be grateful to the late Dr. William E. Ham, of the Oklahoma Geological Survey, for his invaluable guidance in the field work. Dr. Robert Fay, also of the Oklahoma Geological Survey, gave me important insights into the regional geology of the area.

Special thanks is owed to Mr. Albert DeFratus, who so kindly allowed me to excavate and to work on his property. In addition, I thank Mr. Paul Thompson, who also allowed me to conduct field studies on his property.

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ABSTRACT

The Buckhorn asphalt quarry in the northern part of the Arbuckle Mountains, Oklahoma, contains chemically well preserved marine invertebrate fossils of Middle Pennsylvanian age. The main purpose of this investigation was to study the chemistry of these fossils, and at the same time analyze the geologic setting of the deposits containing the fossils.

Due to early sealing by oil, many of the shells still have the original aragonite and nacreous luster. The oil prevented the grainstones from becoming well cemented and allowed them to become compacted during the Arbuckle orogeny. Deformation related to this orogeny probably caused the devolatization of the oil and, hence, conversion into asphalt.

Most of the fossils occur as fragments in several skeletal debris grainstones which are shallow, turbulent water inferred channel deposits. The ancient shoreline was only six miles to the northeast. Underlying calcareous sponge spicule-echinoderm-brachiopod-fusulinid mudstones and wackestones were deposited in less turbulent water environments.

Mineralogical data were obtained by means of x-ray diffraction, infrared spectroscopy, and chemical staining. Quantitative analyses of the elemental constituents for various shell layers were obtained with an electron microprobe.

The original mineralogy of skeletal carbonates was established

for the first time in the following. Aragonite occurs in the inner layers of the gastropods Naticopsis wortheni and Trachydomia whitei, whereas their outer layers consist of calcite. Aragonite also occurs in the shell walls of the scaphopod Plagioglypta ? sp., the coiled nautiloids Metacoceras cornutum and Domatoceras sp., and the ammonoids Pseudoparalegoceras sp. and Wellerites mohri ?. The orthocone nautiloid "Orthoceras" unicamera has aragonitic shell walls, septa, and cameral deposits. Skeletons of the foraminifera Globivalulina sp. and Wedekinellina ? sp., the presumed tabulate Chaetetes cf. favosus, the cryptostome bryozoans Penniretepora ? sp. and Streblotrypa ? sp., the brachiopod Anthracospirifer opimus, four ostracodes, and the spines of the echinoid Archaeocidaris megastyla ? consist of calcite.

As reported by others, calcitic outer layers and inner aragonitic layers were also found in Bellerophon (Bellerophon) sp., Straparollus (Euomphalus) sp., and Chaenocardia ovata. The shell walls and cameral deposits of Pseudorthoceras knoxense also are aragonitic.

Previously unreported moderately high Mg contents occur in the calcite of Chaetetes cf. favosus. The spines of Archaeocidaris megastyla ? are inferred to have been originally Mg-calcite.

Diagenetic effects were detected in the skeletal carbonates. The amount of replacement calcite and degree of obliteration of shell microarchitecture in the skeletal aragonites increase with decreasing asphalt content. Asphalt-impregnated skeletal calcites contain more Mg and usually less Sr than corresponding nonasphalt-impregnated specimens.

Data obtained on the Mg and Sr concentrations of the best preserved specimens indicate the following. The Sr/Ca ratio for the coiled nautiloid Metacoceras cornutum is similar to that for the modern-day Nautilus sp. The Mg contents in the calcites of the foraminifera, bivalve, and ostracodes are similar to those in related Recent forms. The shell walls of the extinct orthocone nautiloids have lower Sr contents relative to the cameral deposits. These large differences are apparently due to the "vital effect" of the organism.

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I. INTRODUCTION

The Problem

The Buckhorn asphalt quarry south of Sulphur, Oklahoma (Fig. 1) in the northern part of the Arbuckle Mountains (Fig. 2) contains one of the world's oldest well preserved marine invertebrate fossil assemblages. The fossils are mineralogically and geochemically comparatively well preserved due to early sealing by oil which later converted to asphalt.

The main effort of this investigation was to study the mineralogy of these fossils, and at the same time analyze the geologic setting of the deposits containing the fossils. Comparative studies were also made on the nearby Stock Pond, Thompson Ranch, and DB-III and DB-IV sections (Fig. 3), which are asphaltic, partly asphaltic, and mostly nonasphaltic, respectively. Such studies were made on these other deposits in order to understand the significance of the localized unusual fossil preservations which occur in the quarry.

The initial phase of the overall study consisted of determining the litho- and biofacies sequences in the asphalt quarry and Stock Pond section and correlating these with the partly asphaltic to nonasphaltic sections nearby. Channel section collecting of fossils and fabric studies of the rocks containing these fossils were necessary. Based on data from depositional environment studies, post-depositional events, and tectonic history, it was possible to develop an interpretation to account for the facies differences in and outside of the studied asphaltic sections.

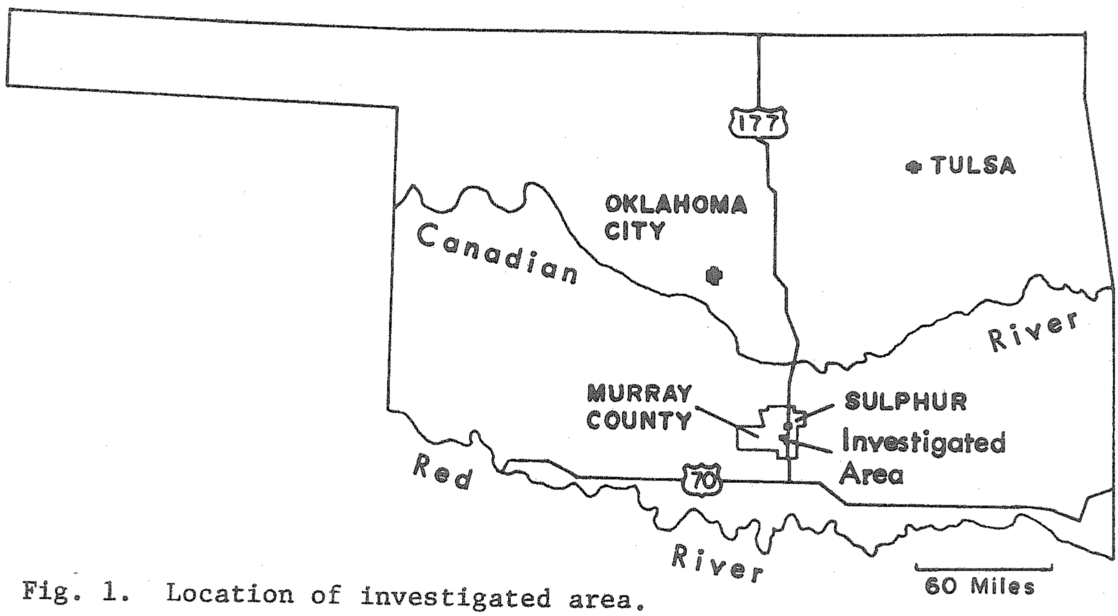


Fig. 1. Location of investigated area.

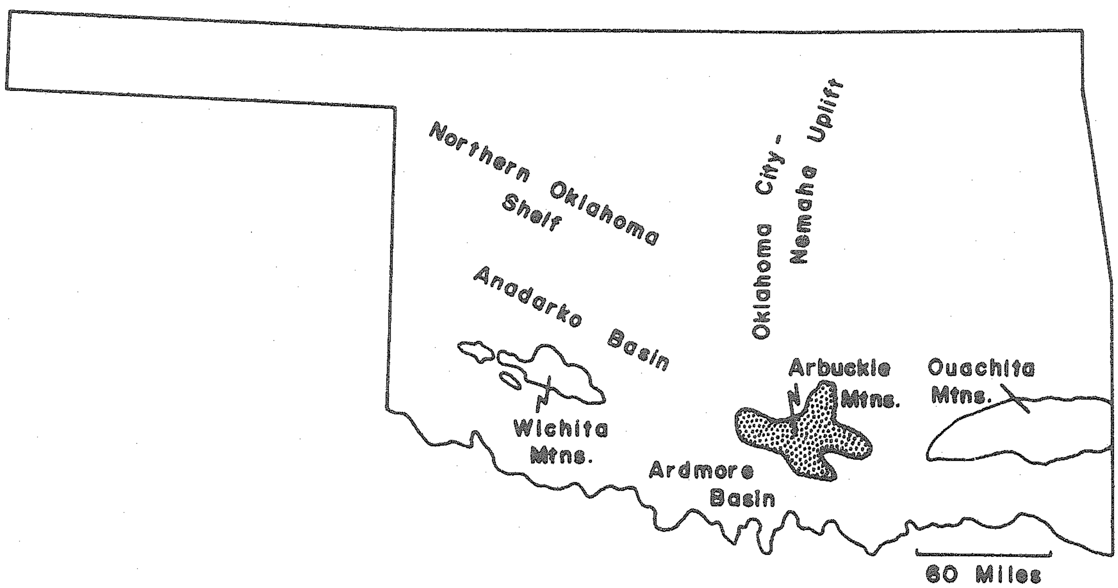


Fig. 2. Structural provinces of Oklahoma.

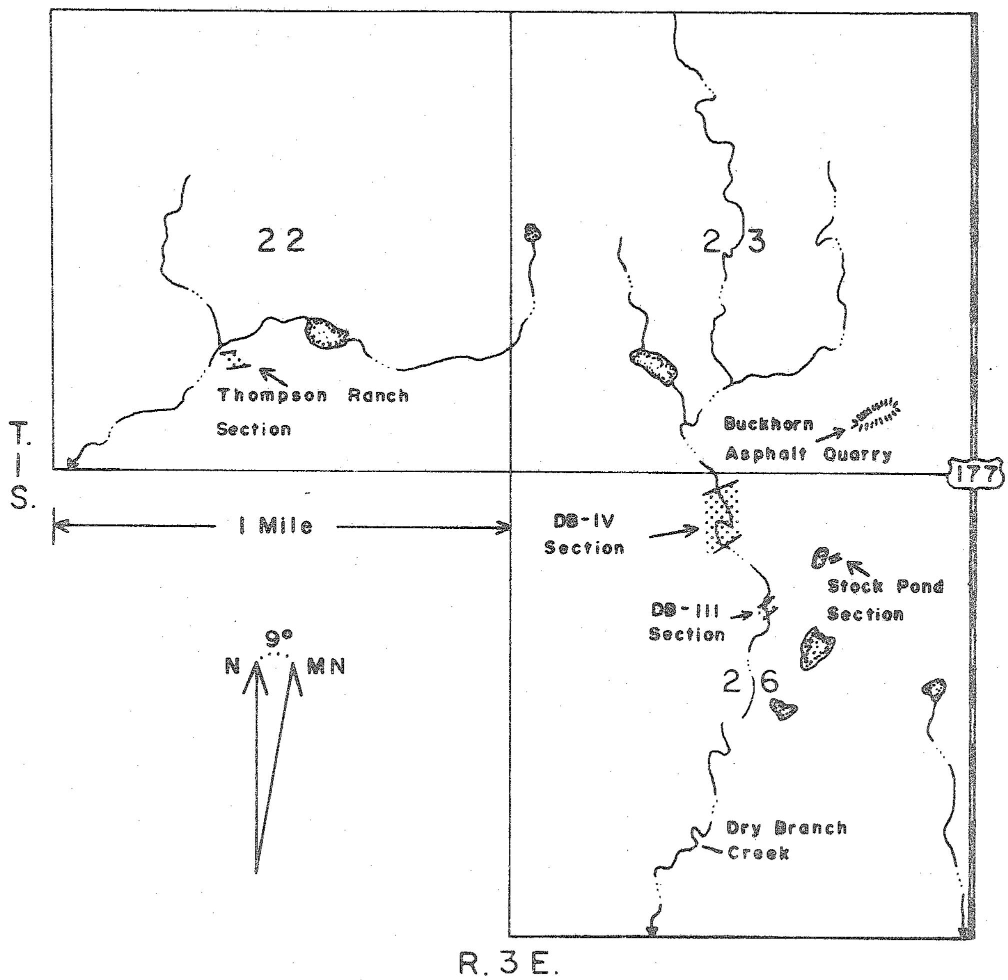


Fig. 3. Index map of the Buckhorn asphalt quarry region.

Comparisons were also made of facies cementation and diagenesis within the sedimentary rocks and fossils. The determinations of the mineralogy of the fossils and cements and their Mg and Sr contents were carried out by means of infrared spectroscopy, x-ray diffraction, chemical staining, and electron microprobe techniques.

The main emphasis in the asphaltic occurrences was placed on the study of the Buckhorn asphalt quarry because of the abundant preservation of iridescent aragonite fossils, the variety of marine invertebrates, and the accessibility of the deposits.

Geologic Setting and General Stratigraphy

The Pennsylvanian age rocks, which comprise the field area, are along the northern flank of the Arbuckle Mountains - Tishomingo Segment, as defined by Ham (1969, p. 16) (Fig. 4). The strata are preserved within the south flank of the Mill Creek syncline and are locally overturned to the south in the vicinity of the Buckhorn asphalt quarry. The northern boundary of the field area is delineated by a normal fault, which truncates the Pennsylvanian age rocks (Fig. 5).

Desmoinesian age strata which have been assigned to the Deese group are the principal deposits in the area. The top of the Deese is eroded and unconformably overlain by blanketing conglomerates of Virgilian age.

The Deese group conglomerates contain detritus shed periodically during uplift of the Hunton anticline in the Arbuckle Mountains, approximately 6 miles to the northeast. The overturning and faulting of the Deese beds was the result of the later Arbuckle orogeny, which

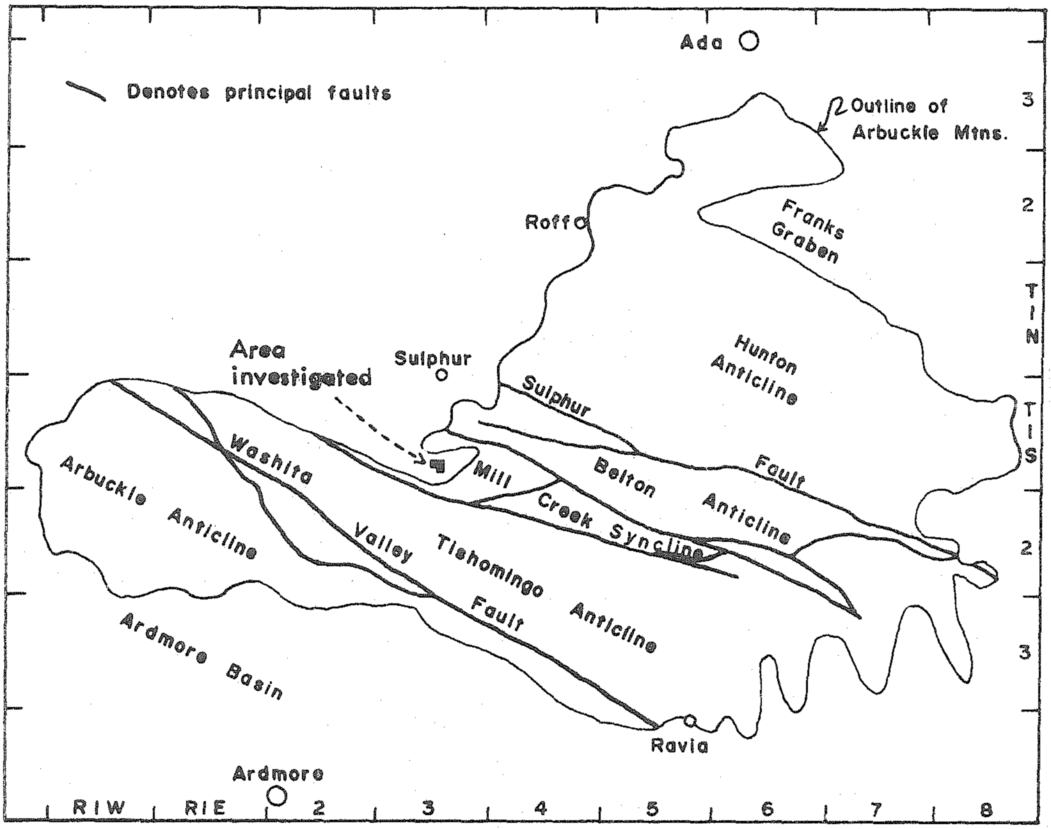


Fig. 4. Index map of the Arbuckle Mountains showing principal structural features (modified from Ham, 1954, p. 2040).

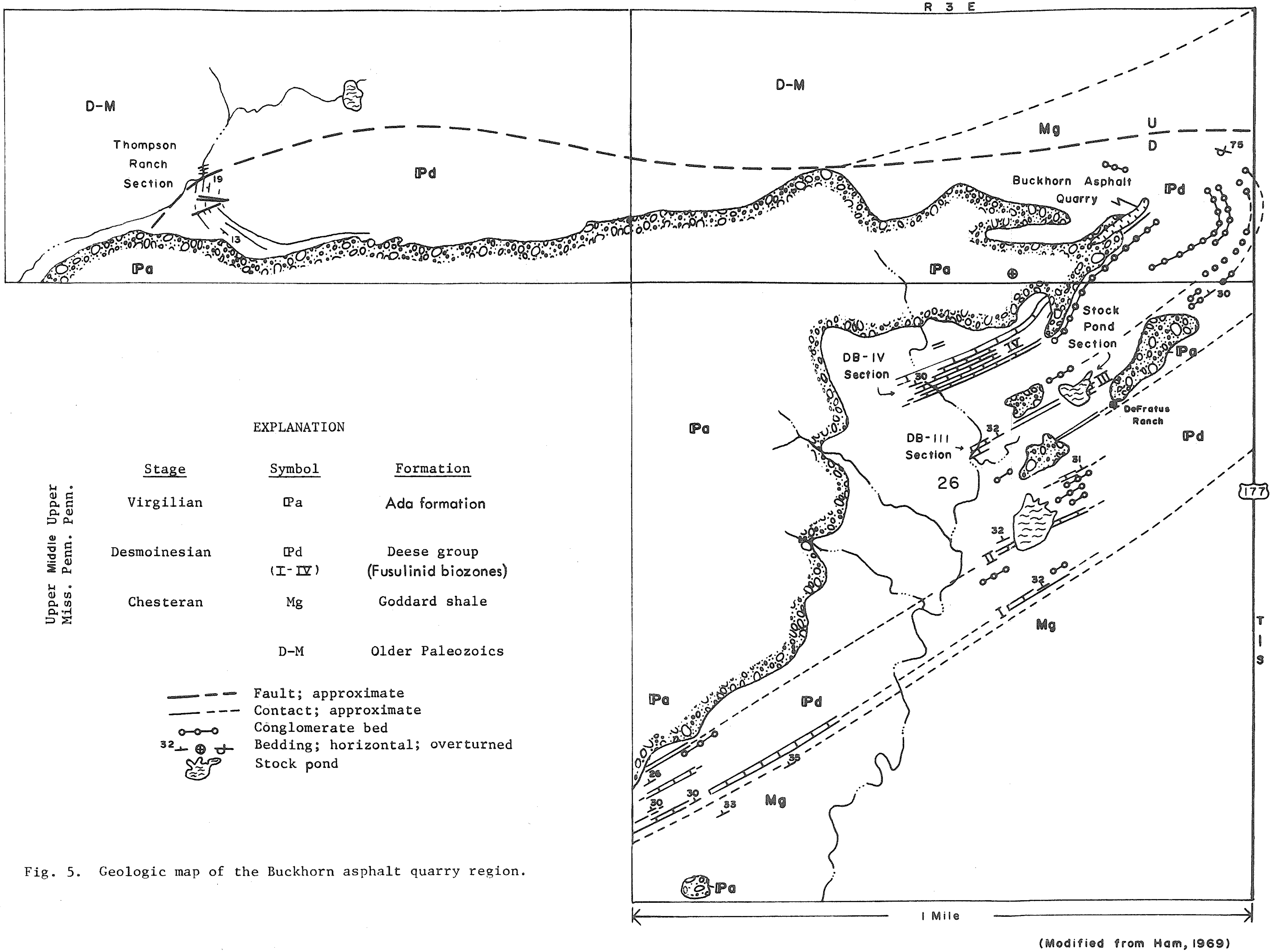


Fig. 5. Geologic map of the Buckhorn asphalt quarry region.

produced the Arbuckle Mountains region. This orogeny can be correlated with the unconformity at the base of the Vanoss formation (Ham, 1969, p. 17-18).

The Deese group, which contains the deposits investigated, is at least 1300 feet thick and consists of marine shales and limestones with interbedded conglomerates. The principal fusulinid-bearing limestones, exposed in the Buckhorn quarry area were studied by D. W. Waddell, and reported by Ham (1969, p. 49) who compared them to Waddell's (1966a, 1966b) fusulinid biozones in the Ardmore Basin, about 20 miles to the southwest. Beds which correlate with "Waddell's Zone IV of the Ardmore Basin, of early middle Desmoinesian age and including the lower-middle part of the Deese Group as well as the Boggy-Sonora of the Oklahoma coal basin" were studied in the present investigation (Ham, 1969, p. 49).

D. W. Waddell and G. A. Sanderson are in the process of attempting to correlate, on the basis of fusulinids, the Buckhorn asphalt beds with those near the Dry Branch Creek exposures to the west, but this study has not yet been published. The outcrop distribution of these beds, as well as other principal fusulinid limestones in the area, was figured by Ham (1969, p. 48). A modified version based on personal studies of this map is presented in Figure 5. The beds marked as I, II, III, and IV all contain species of *Fusulina* and *Wedekinellina*. They refer to four distinct fusulinid biozones of the Pennsylvanian System in southern Oklahoma, as reported by Waddell (1966a, 1966b). These unit designations are used in this present paper. The DB-III and DB-IV sections will be terms used throughout this present report to refer to specific strata along and near the Dry Branch Creek (see Figs. 3 and 5).

Previous Investigations of the Area Studied

The field locality occurs within the historic Buckhorn asphaltic region, which was heavily mined about the beginning of the century and again during the forties. Eldridge (1901, p. 273-306) reported on this district in his comprehensive report on the asphalt and bituminous rock deposits of the United States. He commented on the geology of many of the quarries in the Buckhorn area. In particular, he described the general stratigraphy (p. 283) of the Buckhorn asphalt quarry, which was then called the No. 2 quarry.

Taff (1904, p. 7) briefly mentioned the Buckhorn asphalt quarry in his discussion on the types of asphalt deposits to be found in the Chickasaw Nation, Indian Territory.

Smith (1931, 1935, 1938) described some of the mega-faunal constituents of the quarry. Most of his M.S. and Ph.D. studies dealt with the cephalopod fauna and only the part dealing with them was published in 1938. Unklesbay (1962) updated the taxonomy of the cephalopods from the quarry.

In 1969, Ham (p. 48-49), made specific mention of the field locality in "The Geology of the Arbuckle Mountains", a guidebook published by the Oklahoma Geological Survey. In this guidebook there is a map of the quarry area and some mentioning of the age of the sediments. Much of an earlier work of Ham (1954, p. 2041-2044) regarding the age of the Deese group in the Buckhorn area is reviewed in this guidebook article.

In the past fifteen years there have been several publications

(Odum, 1951, 1957; Stehli, 1956; Goldsmith, 1960; Lowenstam, 1961, 1964; Grandjean et al., 1964; and Hallam and Price, 1966) concerning chemical data obtained from studies of specific megafossils from the quarry. Grégoire and Teichert (1965) published some electron microscope photographs of exceptionally well-preserved nautiloid conchiolin. Recently, Voss-Foucart and Grégoire (1971) included specimens of quarry nautiloids in their work on the biochemistry and submicroscopic structure of fossil conchiolin. Grégoire (1966) also included quarry shell material in his study of the experimental diagenesis of cephalopod shells. Fischer and Finley (1949) briefly reported on the general geologic aspects of the quarry and upon the excellent morphologic and chemical preservation of the cephalopod fauna. Fischer and Teichert (1969) reported on the cameral deposits of many of the orthocone nautiloids from the Buckhorn asphalt quarry.

Field and Laboratory Procedure of Investigation

Offset sampling of hand specimens was necessary in places outside the quarry to fill gaps between the creek-bank exposures. Additional exposures were sought after and also sampled in the course of the mapping. Initially, the exposed and badly weathered quarry rocks were also mapped by means of tape and with the Brunton compass. Some samples were taken at that time. After re-excavation of the quarry, by means of bulldozers, a back-hoe tractor, and dynamiting, fresh bedrock exposures were mapped and channel samples were taken across the middle of the quarry. The richest fossil-bearing bed in the quarry was fully exposed for a distance of 125 feet. Nearly 1½ tons of dynamited dislodged samples from this bed, as well as in situ samples, were collected.

Columnar sections of each sampled section were prepared by combining field data with information obtained from hand specimen- and thin section-determined lithologies and faunal contents.

Insoluble residue determinations were made of representative samples of each major lithologic zone collected from the different sections. One gram pieces of some of these samples were treated with 50% HCl until the calcareous material was dissolved, and the remaining material was weighed.

By means of a Soxyhlet extraction apparatus with dichloromethane (B.P. 40°C) as a solvent, representative samples from the quarry channel section were cleaned of asphalt (see Appendix I). This allowed for a determination of the asphalt content of the rocks and for ease of breaking up the remaining weakly cemented limestone. Many microfossils, as well as megafossils, were thereby also easily removed intact. The microfossils were sieved and hand-picked and logged onto the columnar section.

After deasphaltization, thin-sections were prepared of the lithologic samples from the quarry. Thin sections were made also of each hand specimen of limestone collected outside of the quarry. The lithologies as revealed by thin section examination were classified according to Dunham's (1962) classification (Table I). Leighton and Pendexter's (1967, p. 35) definition of cement was used to supplement Dunham's terms. Point counting was done on some of the coquina beds in order to determine the ratios of skeletal grains to matrix. The

TABLE I

CLASSIFICATION OF CARBONATE ROCKS ACCORDING TO DEPOSITIONAL TEXTURE

Depositional Texture Recognizable					Depositional Texture Not Recognizable
Original Components Not Bound Together During Deposition				Original components were bound together during deposition	
Contains Mud (particles of clay and fine silt size)			Lacks mud and is grain-supported		
Mud-Supported		Grain-supported			
Less than 10 percent grains	More than 10 percent grains				
Mudstone	Wackestone	Packstone	Grainstone	Boundstone	Crystalline Carbonate

(after Dunham, 1962, p. 117)

Wentworth (1922) grade scale was used in the analysis of size distributions in thin sections, as well as in the study of the particle size of the various conglomerate beds. Some fossils, as well as the textures of typical asphaltic grainstones, were examined by means of a scanning electron microscope. Quantitative elemental analyses of various fossil skeletal carbonates, primarily from the asphalt quarry, were performed with a MAC-5-SA3 electron microprobe (see Appendix I). Spatial distributions of Mg and Sr were determined in some fossils by means of the electron beam scanning capability of the microprobe. The samples were analyzed for their Mg, Al, Si, P, Ca, Mn, Fe, and Sr contents. The probe sections were next treated with appropriate chemical stains to determine the mineralogies. Aliquots of many of the same fossils were analyzed by means of infrared spectroscopy in order to determine their carbonate mineralogy. X-ray diffractometer determinations of the carbonate minerals were also carried out for some of the samples (see Appendix I).

II. LITHO- AND BIOSTRATIGRAPHY OF KEY SECTIONS

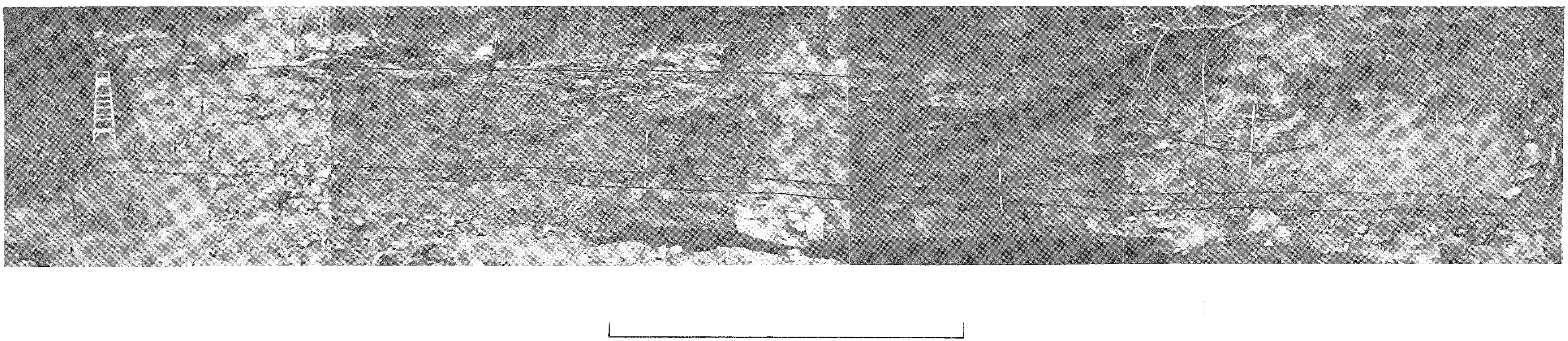
Introduction

The lithologies and burial assemblage constituents of the various units in both the Buckhorn asphalt quarry and in the locally asphaltic Stock Pond section are described below. For purposes of comparison with the locally asphaltic deposits, and to establish possible correlation criteria between the various asphaltic and nonasphaltic units, descriptions are also given for partly asphaltic strata in the Thompson Ranch section, and to nearby mostly nonasphaltic strata in the DB-III and DB-IV sections in Dry Branch Creek (Fig. 3).

Buckhorn Asphalt Quarry Section

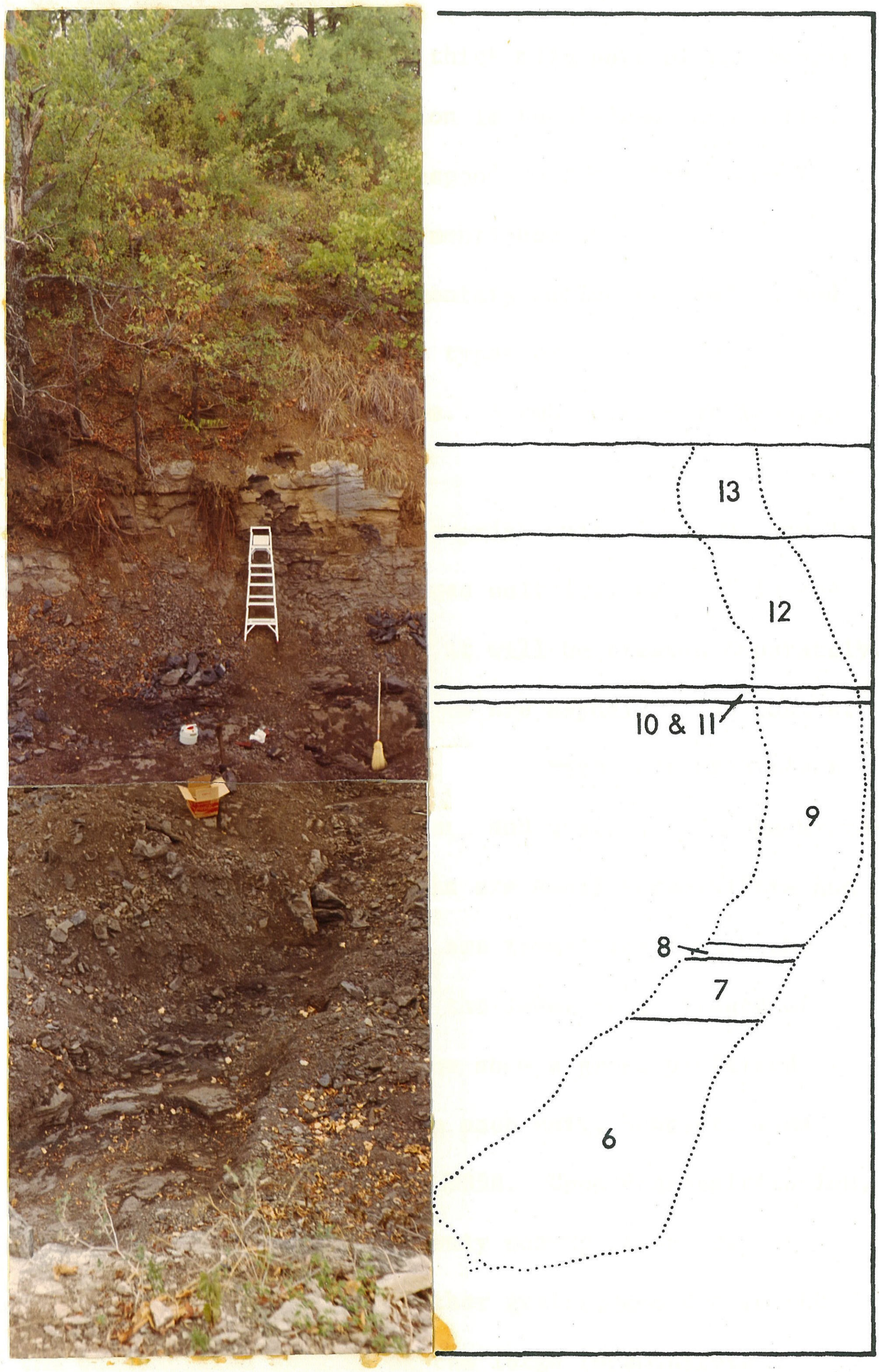
The Buckhorn asphalt quarry section occurs along the crest of the hill in the SE ¼, sec. 23, T. 1 S., R. 3 E. (Fig. 3). The quarry, which trends along the northeastwardly striking beds, is about 600 feet long, 70 feet wide, and, on the average, about 20 feet deep (Pl. 1, in pocket). Extensive re-excavation was carried out, exposing a continuous section of the 35° dipping bedrock in the center of the quarry. The north wall of the quarry is shown in Plate 2, and the channel sample trench is shown in Plate 3.

One of the most salient stratigraphic marker beds in the vicinity of the quarry is a traceable ridge which underlies the quarry. This ridge, which shows only dislodged cobbles of dark gray limestone and some chert at the surface, also extends southeastward and underlies the



30 Feet

Pl. 2. North wall of the Buckhorn asphalt quarry. Rock units in ascending order are: 9) asphaltic foraminifera-cephalopod coquina in the upper part of unit 9; 10 & 11) coal? bed with emanating gilsonite dikes and overlying mollusk-ostracode mudstones; 12) partly asphaltic to nonasphaltic bivalve mudstones with interbedded channel in upper part; and 13) asphaltic foraminifera-cephalopod grainstones. The geologic contacts are dashed where covered by talus. The upper half of the channel section is to the right of the ladder. The staff is 5 feet long and is subdivided into 5-one foot long intervals. The ladder is 6 feet in length.



Pl. 3. Channel sample trench of the Buckhorn asphalt quarry. The various exposed units of the section are so-marked. The outline of the trench is denoted by the dotted line. The ladder is 6 feet in length.

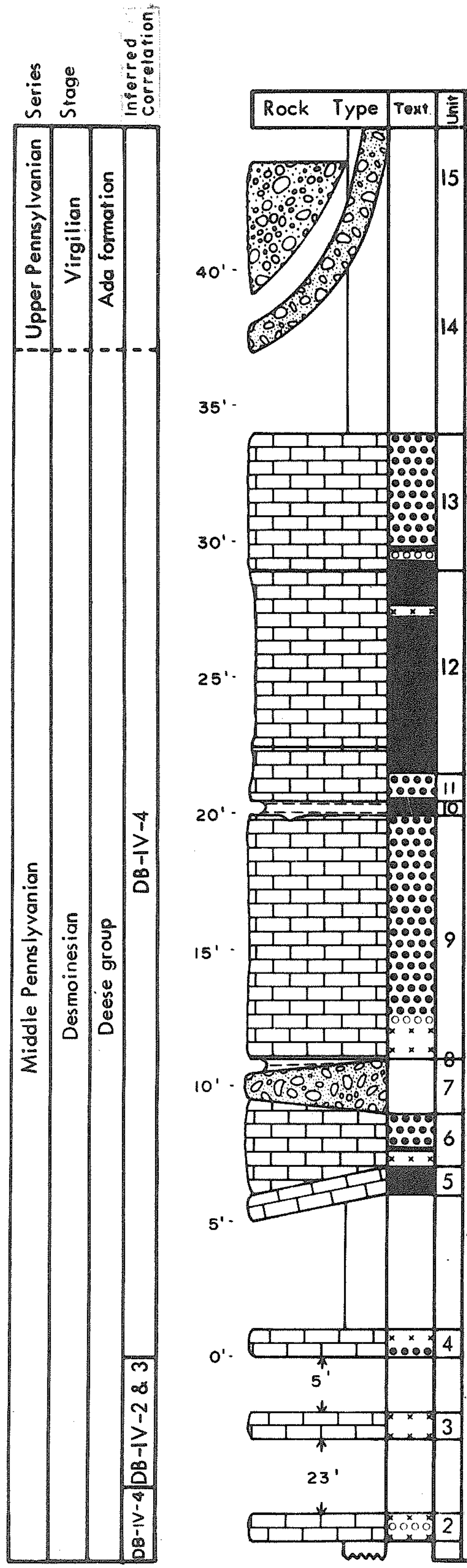
eastern part of the DB-IV section.

A columnar section of the 33-foot thick main part of the quarry section is shown in Figure 6. The section is subdivided into units, and units 2 through 15 in Figure 6 correspond to the units shown in Plate 1. Unit 1 is the traceable ridge mentioned above.

There are four main types of sedimentary facies exposed in and near the Buckhorn asphalt quarry. These types are grainstones, wackestones, mudstones, and conglomerates. A subordinate facies type is represented by an apparent coal bed.

Foraminifera-mollusk grainstones comprise units 4, 6, 9, and 13. An ostracode-gastropod grainstone comprises unit 11. Unit 11 is the only example of this biofacies type, and it will be treated separately. All of the foraminifera-mollusk grainstones are asphaltic and consist primarily of broken and abraded skeletal debris with scattered plant remains, scattered silt-size detrital chert and quartz, and some micro-scour channels. The most abundant fossils are small foraminifera and cephalopod fragments. These grainstones are transitional with the underlying wackestones and packstones in the lower foot of each of these units. Gilsonitized plant fragments show a gross preferred orientation in a northerly direction. In each unit, however, some show a definite preferred orientation of N35E. Upon deasphaltization, the grainstones are friable as they are only weakly cemented.

Unit 4 differs slightly from the other grainstones due to the presence of the unidentified species of the large foraminifera *Trochammina*, *Climmacammina*, and *Fusulina*. Most of these forms are slightly abraded.



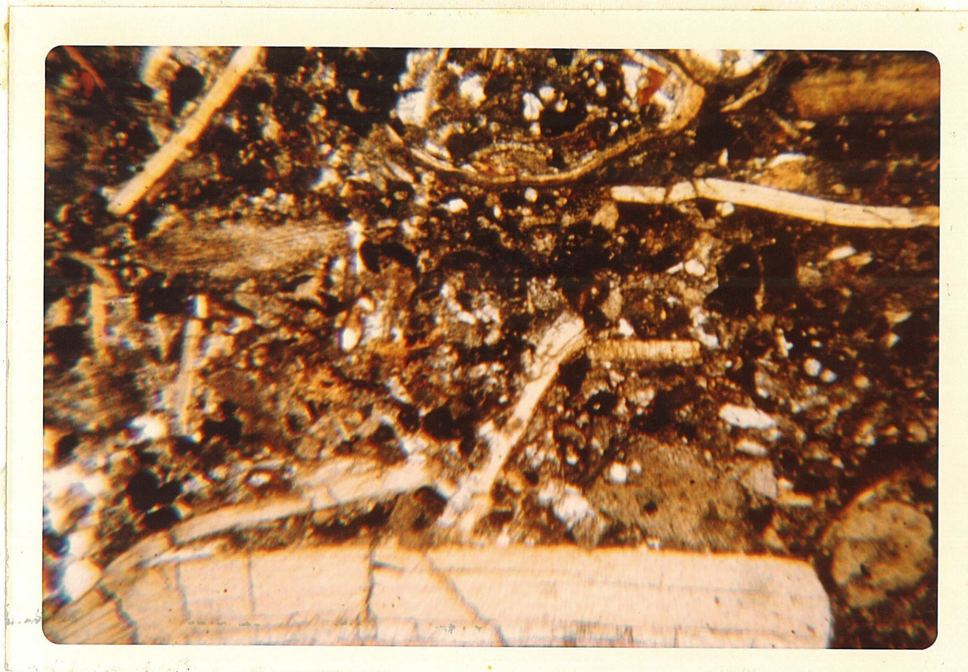
Unit	Lithologic Description	Floral & Faunal Constituents
15	LS cobble conglomerate: nonasphaltic, poorly sorted & moderately well rounded medium size pebbles to small size cobbles.	See text.
	Local unconformity	
	Covered section: clayey shale	
14	Chert & LS pebble conglomerate: nonasphaltic, poorly sorted & well rounded, small size pebbles to small size cobbles.	See text.
	Unconformity	
	Covered section: clayey shale?	
13	Foraminifera-cephalopod grainstones: mudstones & packstones in lower foot, asphaltic (avg. 20% by wt.), insoluble residue = 13% in lower part, minor amount fine silt to medium sand size detrital chert and qtz, with 2-3% granule to medium pebble size chert and non-asphaltic LS clasts in upper 2 feet; micro-channels and cross-bedding in lower foot.	Plant fragments, small foraminifera, Wedekinellina ? sp., Chaetetes cf. favosus fragments, Penniretepora ? sp., Streblotryra ? sp., Anthracospirifer opimus, brachiopod spines, gastropods, Plagioglypta ? sp. nautiloids, bivalves, Bairdia sp. A., Cavellina sp., & echinoderm frags.
12	Bivalve mudstones: partly asphaltic to nonasphaltic, insoluble residue = 7% in lower foot, small amount of medium to coarse silt size detrital chert and qtz; minor amount of replacement dolomite in lower part. Channel in upper part. Microchannels, crossbedding and laminated bedding in lower and upper foot.	Plant fragments, small foraminifera (includ. Globivalulina sp.), Anthracospirifer opimus, Prothyris sp., Acanthopecten ? sp. & echinoderm fragments. Coiled nautiloid fragments & Proparaparchites sp. in channel.
11	Mollusk-ostracode mudstones: gastropod-ostracode coquina in lower part, slightly asphaltic, insoluble residue = 40%, trace amount well rounded qtz; some silification & replacement dolomite.	Wedekinellina ? sp, Chaetetes aff. favosus, Anthracospirifer opimus, gastropods, Pseudorthoceras knoxense, Prothyris ?sp, Hypotetragona sp., Proparaparchites sp., & echinoderm frags.
10	Coal? bed: gilsonitized zone with emanating dikes.	Plant fragments & Proparaparchites sp.
9	Foraminifera-mollusk grainstones: wackestones & packstones in lower foot, foraminifera-cephalopod coquina in upper aprt, asphaltic (avg. 12% by wt.), local zones of gilsonite, insoluble residue = 33% in lower part, 13% in upper part; minor coarse silt to medium sand size clasts; microchannels in lower foot and middle of unit, crossbedding? in lower foot.	Plant fragments, small foraminifera, Wedekinellina ? sp., Chaetetes sp. fragments, bryozoans, brachiopod spines, Naticopsis spp, Trachydomia whitei, Pseudorthoceras knoxense, "Orthoceras" unicamera, Metacoceras cornutum, Domatoceras sp., Pseudoparalegoceras sp., Wellerites mohri ?, unidentified cephalopod fragments, Chaenocardia ovata, Bairdia sp., Proparaparchites sp., & Archaeocidaris megastyla ? spines.
8	Calcareous SH: 5% small to large size pebbles.	Bivalves
7	Chert peb. congl: asphaltic, poor sort., mod well rnd, 40-50% granules to v.lge pebs; intbd. lamin. grainstones; microchannels.	Silicified logs, Chaetetes sp. frags, & nautiloids. Small forams & echinoderm fragments in interbedded grainstones.
6	Foram packstones & grainstones: wackestones & packstones at base, asphaltic, clasts & plants incr. in content upwds; microchannels.	Calamites ?, sm. forams, Wedekinellina ? sp., Straparollus (Euomphalus) sp., nautiloids, Bairdia sp., Proparaparchites sp., & echinoderm frags.
5	Chaetitid mudstone: asphaltic, minor amount coarse silt size qtz; some large in situ Chaetetes cf. favosus colonies.	Chaetetes cf. favosus & Straparollus (Euomphalus) sp.
	Covered section	
4	Foram wackstone & grainstone: asphaltic, insol. res.=30% tr. silt size clasts, 2% med silt to v.f. sand size clasts in up.pt.	Small foraminifera, Trochammina sp., Climmacammina sp., Fusulina sp., gastropods, Glyptopleura sp., Bairdia sp., & echinoderm fragments.
	Covered section	
3	Wackestone: some asphalt	Small forams, bryozoans, spiriferid brachiopods, gastropods, bivalves, & Bairdia sp.
	Covered section.	
2	Fusulinid wackestone with interbedded packstone: nonasphaltic, trace medium to very fine silt size detrital chert & qtz.	Trochammina sp., Fusulina sp., calcareous sponge spicules, productid brachiopods, ostracodes, & echinoderm fragments.

Grainstone — Packstone — Wackestone — Mudstone

Fig. 6. Columnar section of the main part of the Buckhorn asphalt quarry section.

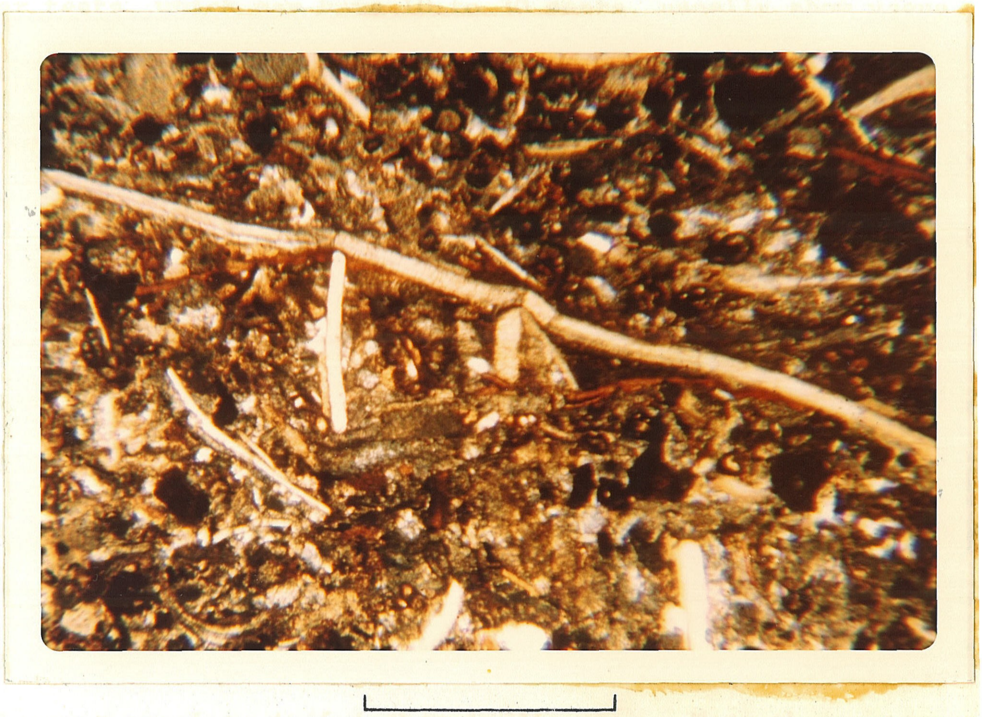
Plant remains, possibly represented by Calamites ? sp., are abundant in the upper part of unit 6. This unit is 3½ feet thick in the center of the quarry, but it is only 2 feet thick in the northeastern part. Foraminifera are the most abundant fossils, and, unlike the other quarry grainstones, cephalopods are only a minor constituent. Trace amounts of heavy minerals and glauconite were detected throughout the unit, and the wackestones and packstones in the lower foot are laminated.

The main asphalt unit in the quarry is unit 9. The lowermost foot has patchy asphalt distribution, whereas the rest of the 9-foot thick unit is rich in asphalt. Numerous fragments of orthocone nautiloids, especially "Orthoceras" unicamera, and Pseudorthoceras knoxense, fragments of coiled nautiloids and ammonoids, and fragments of the bivalve Chaenocardia ovata occur in the middle and upper parts of the unit. The upper part of the unit is a foraminifera-molluscan coquina (Pl. 4). The size distribution of the various components is bimodal. Cephalopod fragments account for about 40 to 50% of the total volume of the rock. Most of these fragments are in the sand or pebble size range. The remaining skeletal debris consists mostly of small whole to broken foraminifera tests and very fine sand to fine sand-size molluscan fragments. Many of the foraminifera, nautiloid, and bivalve fragments are angular to subrounded. Some of the shell fragments were further broken by post-depositional compression, as evidenced by embayed contacts of adjacent shell fragments. In one instance, a shell fragment has been actually impressed into a larger shell fragment, as shown in Plate 5. A small percentage of the



1 mm

Pl. 4. Photomicrograph of foraminifera-cephalopod coquina from the upper part of unit 9 in the Buckhorn asphalt quarry. A bivalve shell, scattered echinoderm fragments, and chert and quartz clasts are also present. The rock was richly asphaltic (12% by weight), and the asphalt was extracted prior to the making of the thin section.

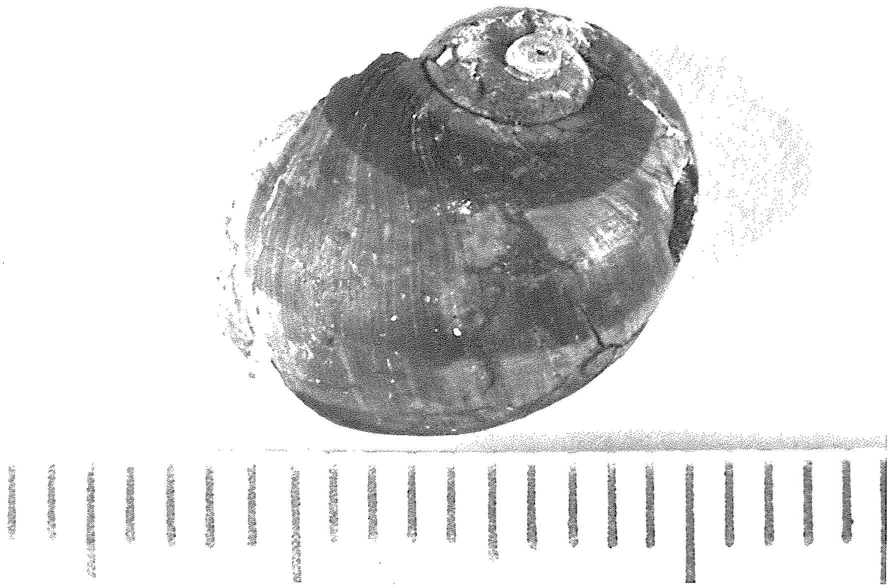


Pl. 5. Photomicrograph of grain impression due to compaction. The material is from the foraminifera-cephalopod coquina in the upper part of unit 9 in the Buckhorn asphalt quarry. The grains involved in the compaction effects are cephalopod shell fragments.

orthocone nautiloids are several inches long. The single largest orthocone is a specimen of P. knoxense that measures $1^3/_4$" in diameter and 3" in length. No complete shells, however, were found. These longer tests, which may have 10 to 30 septa, usually show vague preferred orientations in either the north or N35E direction, as do plant remains, possibly fragments of Calamites ? sp. in the lower part of the bed.

The fusulinid tests, as all fusulinid tests in the other quarry units, are so badly abraded that identifications are unattainable or tenuous at best. In most forms, only the first volution is all that remains, and the chomata and tunnels are readily visible on the outer surfaces. Several single valves of Chaeonocardia ovata and one articulated specimen were found in the upper 2 feet of unit 9. Several complete Pseudoparalegoceras sp. were found in the basal part of the unit. The largest specimen is 6 inches in diameter. Near the eastern margin of the quarry, the cross sections of three large coiled cephalopods were found in the isolated outcrop of the basal part of unit 9. Other complete unabraded fossils are represented by a few specimens of Naticopsis shumardi, N. virgata, and N. wortheni, and Trachydoma whitei, as well as by a few ostracodes and foraminifera. All of the Naticopsis spp. forms have well preserved color patterns. Those of N. wortheni are shown in Plate 6. This photographed specimen is an ephebic form and represents a previously undescribed color pattern for the mature shell. A detailed description is given in Appendix II.

Throughout the quarry, poorly sorted scattered chert and quartz clasts are present in minor amounts. These clasts range in size from



Pl. 6. Color pattern of an ephebic specimen of Naticopsis wortheni. The specimen is from a talus slope boulder along the southern margin of the Buckhorn asphalt quarry (see Appendix II). The color pattern of a mature specimen has been previously unknown. The scale is in millimeters.

coarse silt to medium sand. A few small and large pebbles of reworked nonasphaltic brown limestone were located in the upper few inches of unit 9. About 2½ feet above the base of unit 9, one of the very coarse sand-size clasts is partially encrusted by a small Chaetetes sp. colony. The coquinas contain localized concentrations of silt to sand-size clasts. These concentrations appear to be feeding trails of burrowing organisms. Such structures, however, are uncommon. There is possible crossbedding in the basal part, and there are commonly both concave-up and concave-down shell fragments in any hand specimen of coquina in unit 9. Some local zones of gilsonite, which may be cross-sections of dikes, occur in the lower middle part of unit 9.

The cephalopod remains in unit 13 are mostly orthocone nautiloids with a few scattered coiled cephalopod fragments. Only one whole specimen of Pteronites ? sp. was found in the lower middle part, and mostly disarticulated small nuculoid-type bivalve shells were found in the upper middle part. Only one possibly adult specimen of Naticopsis sp. was found. Anematina minutissmus is common in the middle part. Suggestions of feeding trails are indicated in the middle of the unit in the form of concentrated chert and quartz clasts. Most of the clasts are moderately well rounded and black and gray in color. The uppermost foot of the unit is rich in asphalt near the channel sample trench area, but it is nonasphaltic 200 feet to the northeast. This same horizon contains scattered algal-like structures in both areas. Traces to minor amounts of replacement dolomite rhombs occur in various parts of the unit.

This one foot-thick unit 11 is a distinctive biofacies indicated by the presence of abundant ostracodes and gastropods. The ostracodes are represented mostly by disarticulated valves of Proparaparchites sp. A few complete Hypotetragona sp. are also present. In addition to Trachydomia whitei and T. sayrei, there is a variety of unidentified species of Naticopsis, and some Taosia ?, Worthenia, Murchisonia ?, Paleostylus ?, Straparollus (Euomphalus), Anematina, and Bellerophon. Both juvenile and adult specimens of Naticopsis and Trachydomia are present. Shells of these particular gastropods are commonly better preserved than those of the other gastropods which have been slightly compressed. Small Chaetetes aff. favosus colonies, and a few Globivalulina-type foraminifera are also present in the lower part of the unit. A few well-rounded quartz grains and scattered chert pebbles occur in the lower part. Replacement type small dolomite rhombs occur throughout the unit, except for the lowermost few inches. The upper part of the unit is gradational with the overlying mudstones.

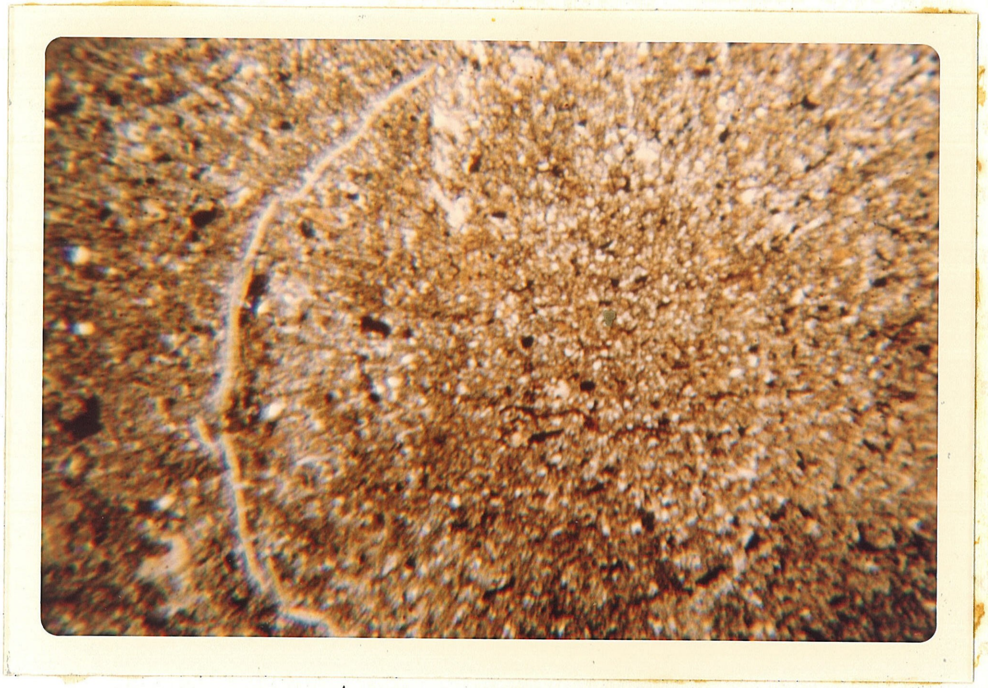
Wackestones are of minor importance in the quarry section. They include units 2 and 3 and an interbed in the mudstone unit 12. The interbed will be treated separately in the description of unit 12. The other wackestones are nonasphaltic, well-cemented, fossiliferous, free of clasts. Unit 2 is separated from the traceable ridge of unit 1 by 40 feet of covered section. Unit 2 is a one-foot thick exposure of a fusulinid-productid brachiopod wackestone. It crops out along the eastern part of the quarry (see Plate 1). Unit 3 is a one-foot thick exposure of a mollusk-bearing wackestone.

Mudstones are represented by units 5, 8, and 12 in the quarry. These mudstones are nonasphaltic, well-cemented, silty, and relatively unfossiliferous, except for a few scattered bivalve shells.

Unit 5 differs somewhat with the general description of the quarry mudstones in that it is asphaltic. The fossils are sparse and mainly include several large in situ Chaetetes cf. favosus colonies with associated whole Straparollus (Euomphalus) sp. gastropods.

Unit 8 is a 6-inch thick limonite-stained calcareous shale with a chert pebble layer. The only fossil remains are an external mold of a pectinid-type bivalve. This shale unit wedges out near the eastern margin of the quarry.

Scattered ostracodes and a few small foraminifera occur throughout the 7½-foot thick unit 12. The greatest concentration of foraminifera occurs in the interbedded wackestone near the top of the unit. These foraminifera tests, including a few minute fusulinids, are fragmentary. Bivalves occur in the middle and upper parts (see Pl. 7). Near the east central part of the quarry, there is a 15-foot wide and 2-foot deep section of channel fill. The channel occurs in the upper 2 feet of the unit. The lower part of the channel fill consists of much broken shell material with a few recognizable coiled nautiloid fragments and disarticulated Proparaparchites sp. valves. The channel deposits contain minor amounts of black chert clasts ranging in size from small to medium sized pebbles. They further contain abundant plant remains and some clay balls. The plant remains have a preferred orientation in a N35E direction. Microchannels and some laminated sediments occur in the lower and upper parts of the unit. Microcrossbedding was found in the lower part. Replacement type dolomite rhombs are a common constituent in the lower part and a minor



1 mm

Pl. 7. Photomicrograph of bivalve mudstone from the middle part of unit 12 in the Buckhorn asphalt quarry. Scattered dolomite crystals and silt-size chert and quartz clasts are present. The rock was only partly asphaltic, and the asphalt was extracted prior to the making of the thin section.

constituent in the middle part. No dolomite rhombs occur in the uppermost part of unit 12. This unit is also transitional with the under- and overlying units.

Conglomerates present in the quarry consist of two distinct types. One is an asphalt-impregnated, poorly cemented type with interbedded grainstones and the other a nonasphaltic, well-cemented type.

Unit 7 is a poorly sorted asphalt-impregnated conglomerate with interbedded laminated asphaltic grainstones. The conglomerate consists of 40 to 50% by volume of clasts from granule size to small cobble size (i.e., 2 mm to about 75 mm in diameter). Most of the clasts are in the medium to large pebble size range, and only 1% by volume are small cobbles. The largest clasts are from the bed in the eastern part of the quarry. Most clasts consist of black, white, or blue-colored cherts in the granule to small pebble size range. There a few medium size pebbles of echinoderm-bearing limestone. The matrix consists of silt to sand-size detritus. Most of the clasts are moderately well rounded. The lower contact of the bed locally consists of an undulating erosional surface. Unit 7 is interpreted as a channel-filling conglomerate. The grainstone interbeds contain scattered small pebbles and straight orthocone nautiloids. Small silicified logs, small to large orthocone nautiloids, large coiled cephalopods and *Chaetetes* sp. fragments were found in unit 7 near the eastern margin of the quarry. The coiled cephalopods are in the lower part of the unit, whereas the large orthocone nautiloids and logs are in the middle part. The unit is 2 feet thick in the eastern part of the quarry and only 1 foot thick in the western part.

There is a covered interval between the main part of the quarry section and the overlying unconformable conglomerate unit 14. This covered interval is about 2 feet near the western margin of the quarry and 10 feet thick near the eastern margin. Most likely, the covered interval consists of clayey shale.

Unit 14 is a 1-foot thick limestone pebble conglomerate and is nonasphaltic. It was not possible to determine the dip of this conglomerate because of lack of suitable exposures. Due to the channel nature of the conglomerate, the underlying covered interval has a variable thickness, as mentioned above. Near the western margin of the quarry, there is an exposure of a small channel truncating another one within the conglomerate unit. The channels are about 5 feet wide. The unit 14 conglomerate consists of poorly sorted and moderately well-rounded small pebble to small cobble-size chert and limestone clasts. Most of the clasts are in the small to large pebble-size range, and only 1% by volume are cobbles. The clasts comprise roughly 50% by volume of the total rock mass, and the calcareous matrix is very fine grained. The amount of chert clasts, most of which are white, brown, and yellow in color, is approximately the same as the amount of limestone clasts. The limestone clasts consist of nonasphaltic echinoderm-bearing wackestones, some of which have abundant sparry clacite. These wackestones are unlike the underlying quarry wackestones.

Another covered interval separates unit 14 from the overlying locally unconformable unit 15. According to Eldridge (1901, p. 283), there is a pink and yellow to gray clayey shale bed between units 14 and 15. During the re-excavation of the quarry, no exposures of the clayey unit were found, but pink and yellow clayey shale float was abundant on the quarry floor.

Unit 15 is a limestone cobble conglomerate and is nonasphaltic. There is a 5-foot thick exposure of this unit near the western margin of the quarry. A few isolated patches of outcrop also occur near the center of the quarry. The horizontal conglomerate consists of poorly sorted and moderately well-rounded medium pebble to small cobble size limestone clasts with some granule size light-colored chert clasts. Most of the limestone clasts are in the very large pebble size fraction. None of these limestone clasts are similar in lithology to those in the underlying quarry limestones. The matrix of the conglomerate is calcareous and contains a few scattered coarse sand size well-rounded clear quartz grains and limestone clasts.

Unit 10 is an apparent coal horizon. In places along the strike, there is an unconformable relationship between unit 9 and the overlying 6-inch thick limonite-stained unit 10. The middle 4 inches have been gilsonitized. Throughout all the quarry beds, plant remains can be shown to be selectively gilsonitized, and it is likely that the gilsonite in this particular bed has also replaced plant material. The gilsonite content is so high in unit 10, that it is quite possible that this bed was essentially a coal bed. Shearing is evident in the gilsonitic parts of unit 10, and it appears that the shearing action obliterated the plant remains and most other fossils. The only recognizable fossil forms are a few Proparaparchites ostracodes which are associated with some well-rounded quartz grains in the middle of the bed. Near the middle of the quarry, there are three gilsonite dikes which emanate from the unit. The dikes, which essentially trend perpendicularly to the strike of the quarry units, cut units 11, 12, and 13. The basal and upper parts of unit 10 are gradational with the adjacent rock types.

Stock Pond Section

The asphalt exposure is of rather small areal extent in the SE ¼ NW ¼ NW ¼, sec. 26, T. 1 S., R. 3 E. (Fig. 3). The vertical extent of the outcrop is 4 feet and the lateral extent about 15 feet (Pl. 8). The outcrop is on the east side of a small stock pond. Above the asphalt beds, there is a 19-foot thick covered interval and then 4 feet of broken outcrop (Fig. 7). The only exposed possible laterally equivalent strata are to the southwest, and they crop out along a prominent ridge which extends from the west side of the pond to Dry Branch Creek about 500 feet to the southwest. Ham (1969, p. 48) designated these strata as belonging to the DB-III unit. This asphalt-bearing rock is about 250 feet stratigraphically lower than the Buckhorn asphalt quarry.

The surfaces of the basal asphalt-bearing beds are badly weathered. Their asphalt content extends only a few inches into the unit and is as high as 30 percent by weight. Upon deasphaltization, the rock is friable as it is only weakly cemented. Foraminifera and gastropod packstones and grainstones constitute the asphalt unit (Fig. 7). Unlike most of the Buckhorn asphalt quarry grainstones, no cephalopods occur in this exposure. These grainstones are fine-grained and poorly sorted.

Pl. 8. Surface exposure of the asphaltic part of the Stock Pond section. The staff is 5 feet long.

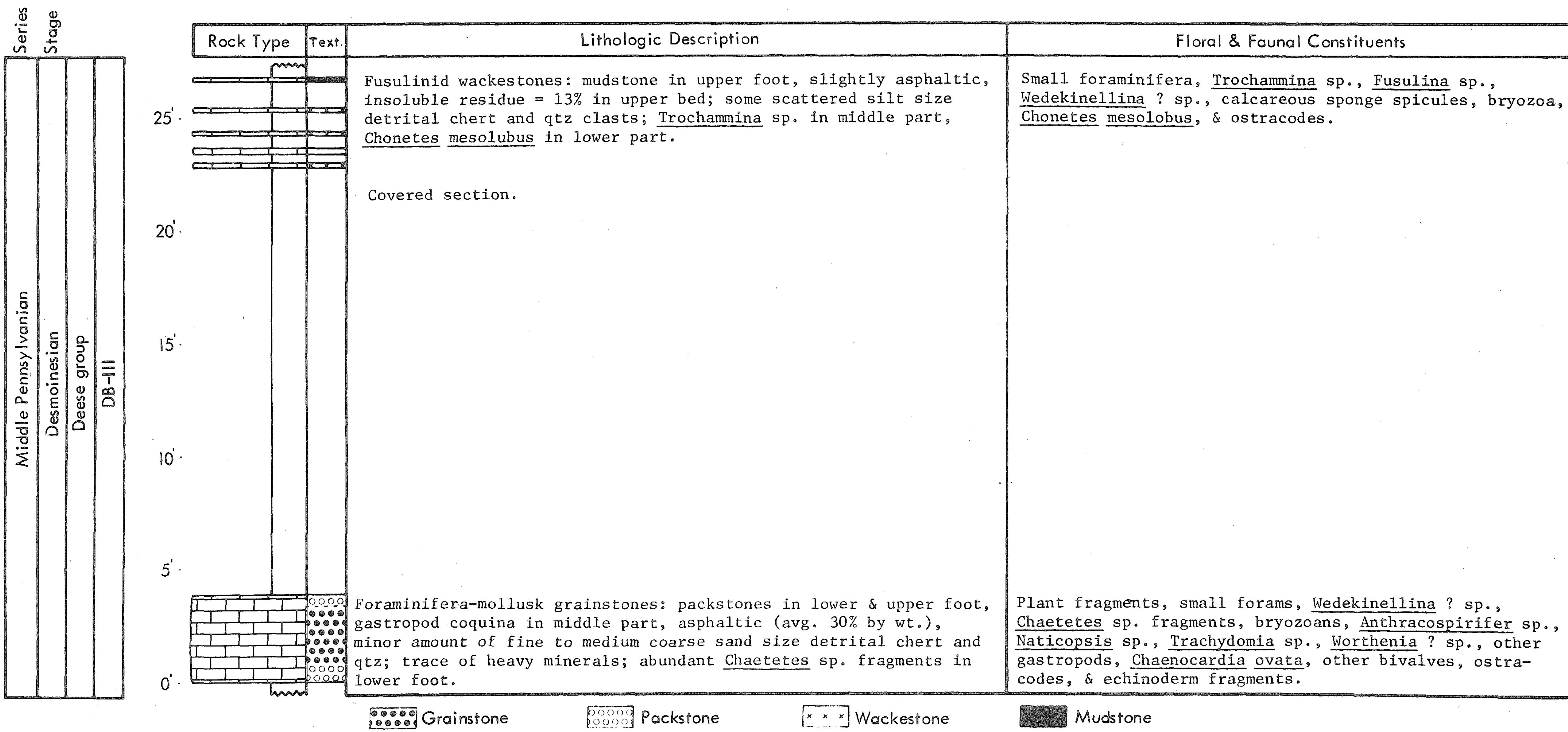


Fig. 7. Columnar secton of the Stock Pond section.

The lower foot contains abundant fragments of Chaetetes sp. Complete Naticopsis sp. and Trachydomia sp. gastropods are common. A few badly worn specimens of Wedekinellina ? sp., Anthracospirifer sp., as well as some plant remains, heavy minerals, and a minor amount of sand size detrital chert and quartz are also present.

The upper part of the section consists of slightly asphaltic mudstones and wackestones with some skeletal remains of Chonetes mesolobus, Fusulina sp., Wedekinellina ? sp., and calcareous sponge spicules. The fusulinids are robust and most are complete or only slightly worn. However, a few are broken but not abraded.

Thompson Ranch Section

A partly asphaltic section was sampled on the Thompson Ranch along the east bank of an unnamed creek in the E ½, SW corner of sec. 22, T. 1 S., R. 3 E. (Fig. 3). Some of the more resistant beds also crop out as far as 450 feet to the southeast in a hillside exposure. A total of 85 feet of section, which exposes only 20 percent of the litholotig sequence, was examined. The lower 44 feet are poorly exposed in the upthrown block of the major fault which cuts this area. The lowest exposed bed is a 3-foot thick chert and limestone pebble conglomerate. Above this conglomerate is a 35-foot thick covered interval. The main part, or upper 37 feet, of the section is shown in Figure 8.

The sedimentary facies in the main part of the Thompson Ranch section (Fig. 8) include foraminifera grainstones and foraminifera-

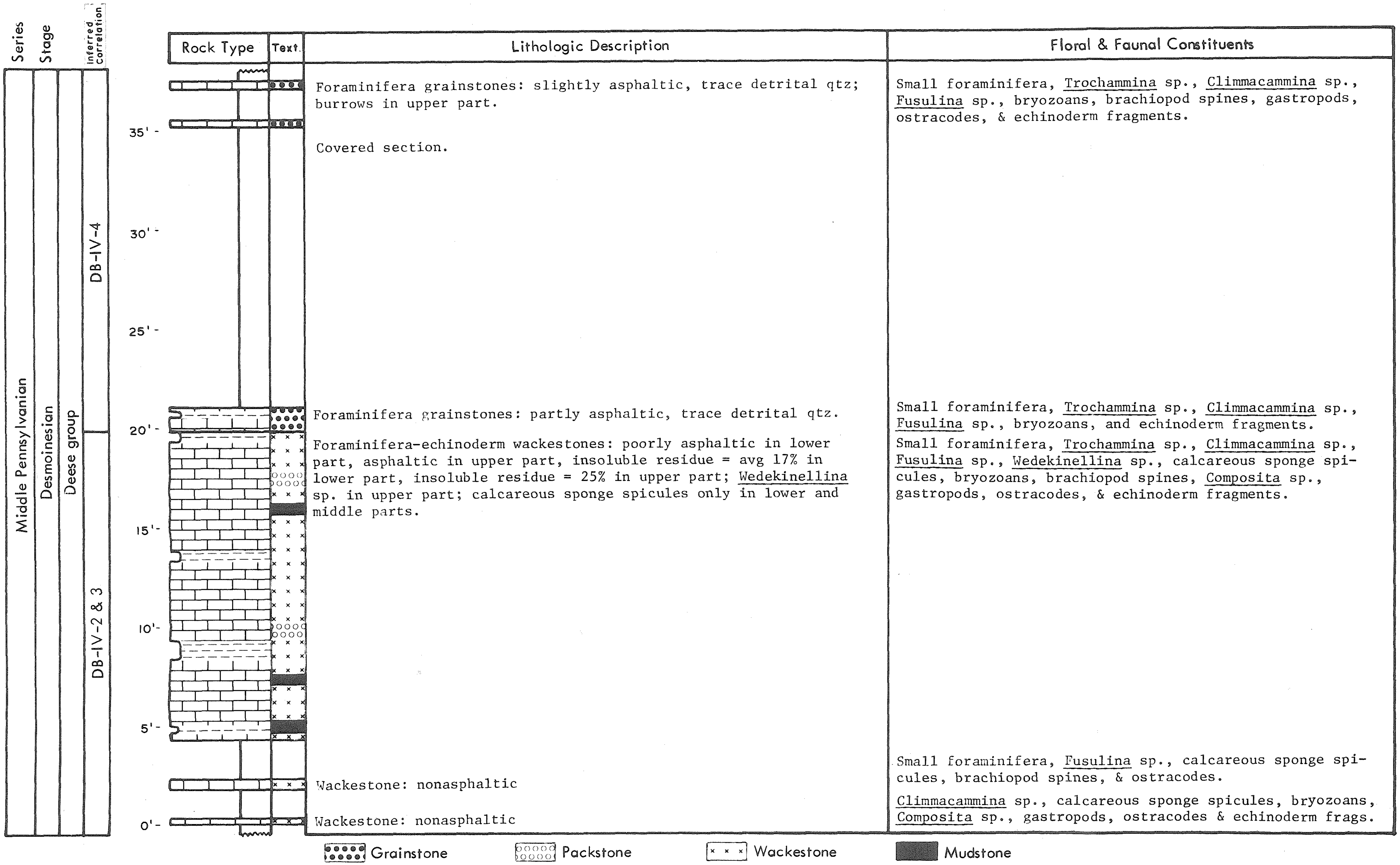


Fig. 8. Columnar section of the main part of the Thompson Ranch section.

echinoderm wackestones.

The foraminifera grainstones occur in the poorly exposed upper 17 feet of the main part of the section. They are partly asphaltic, moderately well-cemented, and contain a trace of detrital quartz. The uppermost horizon, however, is only slightly asphaltic and contains recognizable feeding trails. The abundant small foraminifera are mostly broken. The large foraminifera include unidentified species of Trochammina, Climmacammina, and Fusulina.

In the middle of the main part of the section, the foraminifera-echinoderm wackestones are partly asphaltic. They are poorly asphaltic to non-asphaltic in the lower main part of the section and more cemented. Smaller foraminifera, most of which are complete and unabraded, are abundant in the middle part. The larger foraminifera include unidentified species of Trochammina, Climmacammina, Fusulina, and Wedekinellina, and most of these are slightly worn.

DB-III Section

Near the middle of section 26 along the east bank of Dry Branch Creek, there is a 149-foot thick section which consists of about 25 percent outcrop. Ham (1969, p. 48) designated these strata as belonging to the DB-III unit (Fig. 3). The resistant parts of this unit crop out along a prominent ridge which is traceable for 500 feet in a northeastwardly direction up to the west side of the stock pond, which is adjacent to the Stock Pond section.

The sedimentary facies exposed in the DB-III section include foraminifera-mollusk packstones and grainstones, fusulinid-bearing wackestones, a mudstone, and a chert pebble conglomerate (Fig. 9).

The six-foot sequence of packstones and grainstones is asphaltic. The packstones occur in the lower three feet. The common fossils are small broken foraminifera, complete gastropods, and rounded echinoderm fragments. Minor constituents include plant fragments, spiriferid brachiopods, feeding trails, a minor amount of medium to coarse silt-size detrital quartz, and a trace amount of heavy minerals.

The fusulinid-bearing wackestones are asphaltic to nonasphaltic and occur in the poorly exposed part of the bluff above the grainstones. The *Fusulina* sp. specimens are slightly worn. The mudstone units are very slightly asphaltic and badly recrystallized. The chert pebble conglomerate contains some plant fragments.

DB-IV Section

This section is near the head of Dry Branch Creek and consists of beds of unit IV. The outcrops are along the west bank in the north-central part of sec. 26, T. 1 S., R. 3 E. (Fig. 3). The more resistant beds extend as far as 1300 feet northeast of the creek and crop out very close to the asphalt quarry, which is 1900 feet northeast of the creek. The traceable ridge which underlies the quarry extends southeastward and underlies the easternmost part of the DB-IV section. This traceable ridge overlaps the easternmost exposures of DB-IV for only about 160 feet due to removal by erosion.

As can be seen in Figure 5, the DB-IV beds strike N65E in the

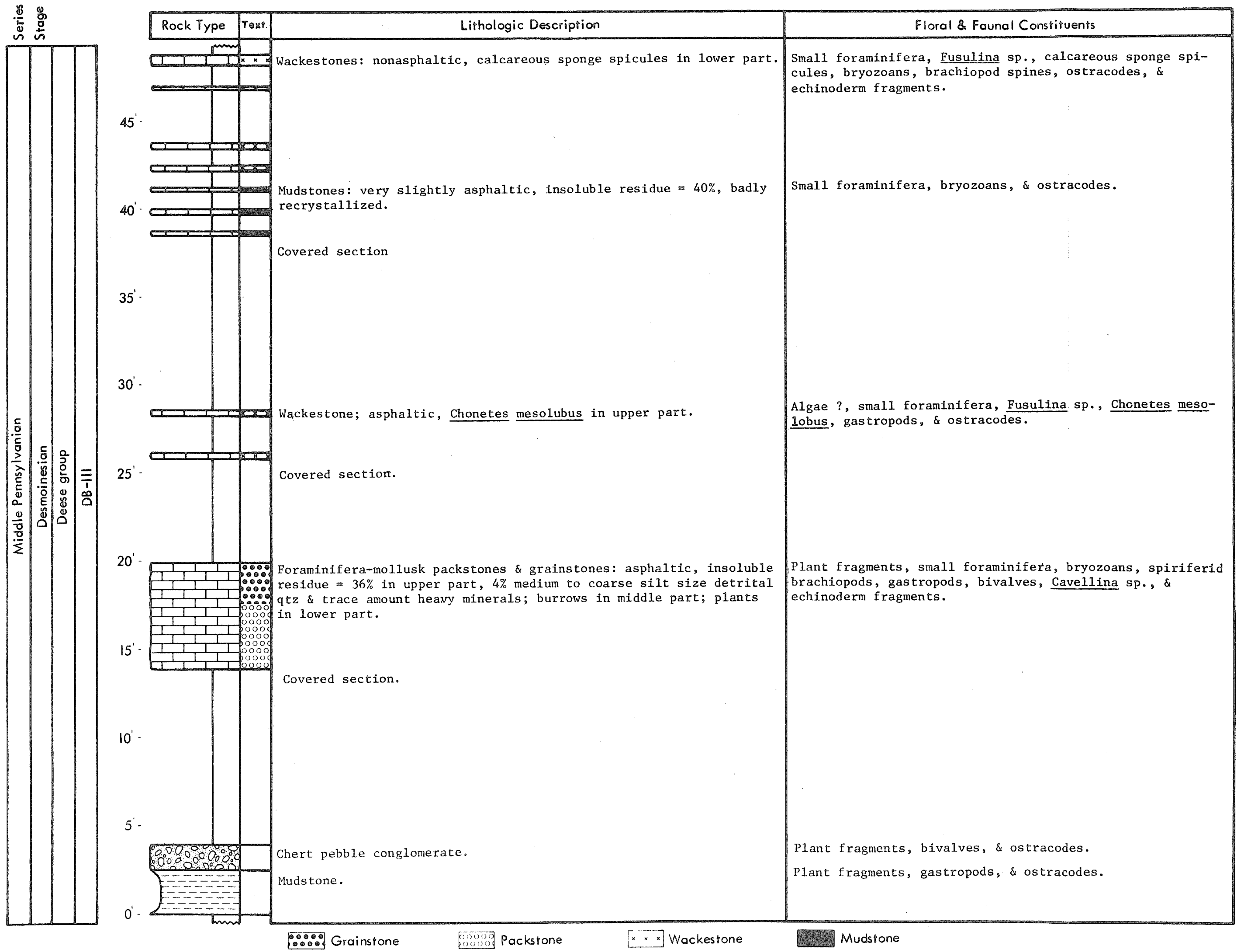


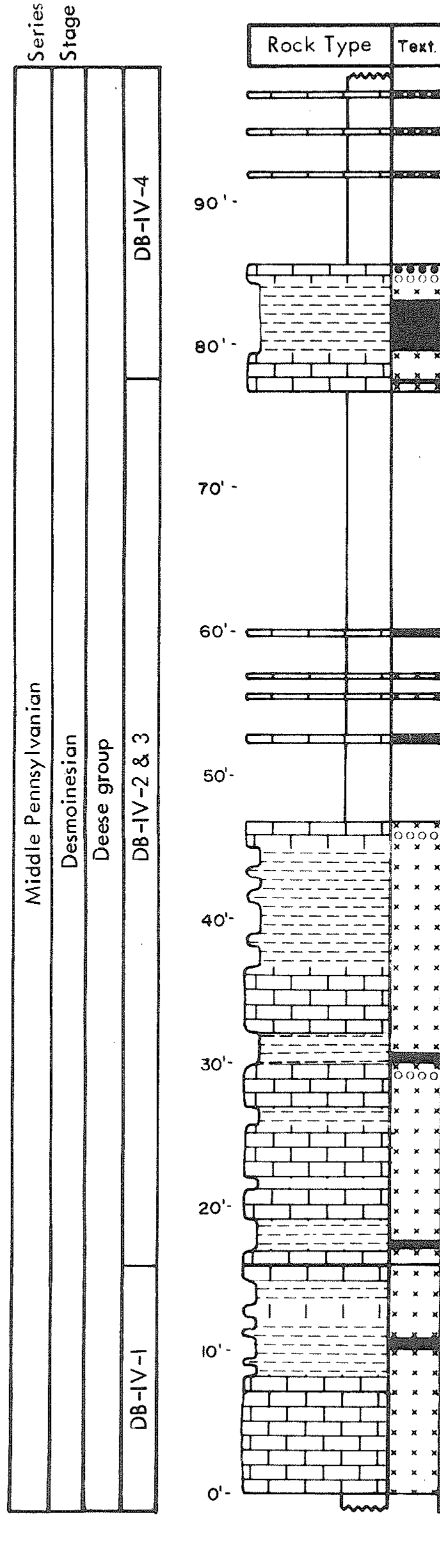
Fig. 9. Columnar section of the DB-III section.

creek area. As these beds are mapped to the northeast, the attitudes remain the same as far as about 1000 feet northeast of the creek. These beds strike increasingly more northerly in the vicinity of the quarry beds. The easternmost DB-IV beds strike N40E. The strike of the underlying traceable ridge continues to become more northerly as it approaches the quarry. Then in the quarry area, the strike of the traceable ridge becomes more eastwardly again. It is apparent, therefore, that a minor flexure has affected the beds in the area between the creek and the quarry, and a bed common to both sections has also been affected.

In the description of the Dry Branch section, which is 250 feet thick, it will be useful to further subdivide the exposed 98 feet of fusulinid biozone IV into limestone subunits of DB-IV-1, DB-IV-2, DB-IV-3, and DB-IV-4. The designations of these subdivisions are based on Ham's (1969, personal communication) recommendation and are embodied in his unpublished field work descriptions of this area. The strata which comprise the above mentioned "traceable ridge" are considered as part of DB-IV-1.

The lower 50 feet of the exposed DB-IV section consists of 90 percent exposure, whereas the next 50 feet consists of only 30 percent exposure. Lithologic types and faunal distributions of the main part, or exposed bed, of the section are shown in Figure 10. The DB-IV-4 beds are described from the hillside exposures northeast of the Dry Branch Creek.

Foraminifera grainstones occur in the stratigraphically highest exposed Deese group beds in this section (i.e., the DB-IV-4 beds).



Lithologic Description	Floral & Faunal Constituents
Foraminifera grainstones: slightly asphaltic (avg. 10% by wt.), insoluble residue = 17%, in the upper half there is 1% coarse to very coarse sand size white & dark gray chert clasts which coarsen upwards to small pebble size. Percent and size of chert clasts increase in the direction of the quarry; Trochammina sp., Climmacammina sp., & Wedekinellina sp. in upper part.	Small foraminifera, Trochammina sp., Climmacammina sp., Fusulina sp., Wedekinellina sp., bryozoans, ostracodes, & echinoderm fragments.
Foraminifera grainstones: slightly asphaltic, insoluble residue = 16%, trace fine silt size detrital chert & qtz. Percent and size of clasts increase in the direction of the quarry; calcareous sponge spicules in lower part, gastropods in middle part.	Small foraminifera, Trochammina sp., Climmacammina sp., Fusulina sp., calcareous sponge spicules, bryozoans, gastropods, ostracodes, & echinoderm fragments.
Covered section.	
Mostly covered section-mudstones and wackestones: extensive diagenetic alteration in the form of presence of large patches of replacement calcite.	Small foraminifera, Fusulina sp., calcareous sponge spicules, gastropods, ostracodes, & echinoderm fragments.
Calcareous sponge spicule wackestones & packstones: patchy asphalt, wackestone near middle, insoluble residue = 3%, packstone near top, insoluble residue = 37%; Climmacammina sp. in upper part, Fusulina sp. at middle and in upper half; Lophophyllidium sp., colonial coral, & bivalves in lower part; Pseudorthoceras knoxense, and bivalves in upper foot.	Small foraminifera, Trochammina sp., Climmacammina sp., Fusulina sp., calcareous sponge spicules, Lophophyllidium sp., colonial coral, bryozoans, Composita spp., gastropods, Pseudorthoceras knoxense, bivalves, ostracodes, & echinoderm fragments.
Calcareous sponge spicule-bryozoan, brachiopod-echinodern wackestones: patchy asphalt, insoluble residue = 64-70%, minor amount detrital qtz at 25 feet horizon, foraminifera in middle of unit; Anthracospirifer sp. in middle & upper parts; orthocone nautiloid in middle of unit; Angyomphalus sp. in lower part, Anomphalous sp. & associated bellerophonid gastropods in middle part; crinoid columnals, bryozoans, and echinoid spines in lower & middle parts.	Small foraminifera, calcareous sponge spicules, Lophophyllidium sp., bryozoans, Composita spp., Anthracospirifer sp., brachiopod spines, Angyomphalus sp., Anomphalous sp., bellerophonid gastropods, orthocone nautiloid, ostracodes, crinoid columnals, and echinoid fragments.
Fusulinid wackestones with fusulinid-brachiopod mudstones in upper part: slightly asphaltic, wackestones insoluble residue = 63-75%, mudstone insoluble residue = 20%; few Wedekinellina sp. in lower part; Antiquatonia sp. in lower foot and near middle of bed; Composita sp. in upper part; Lophophyllidium sp. near top.	Small foraminifera, Trochammina sp., Climmacammina sp., Fusulina sp., Wedekinellina sp., calcareous sponge spicules, Lophophyllidium sp., bryozoans, Antiquatonia sp., Composita sp., gastropods, Bairdia sp. B, crinoid columnals, and echinoid fragments.

Fig. 10. Columnar section of the main part of the DB-IV section.

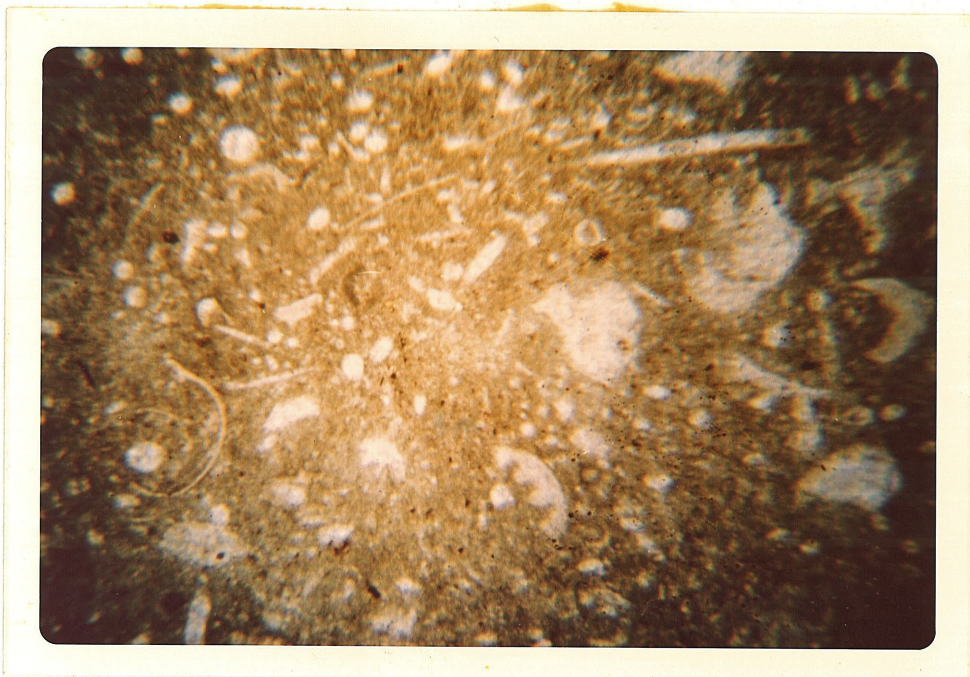
The DB-IV-4 subunit is 21 feet thick with the upper part represented by discontinuous outcrop. The low part of the section consists of fossiliferous wackestones with interbedded mudstones and packstones.

The foraminifera grainstones are slightly asphaltic. The small foraminifera are commonly slightly worn. Complete large foraminifera are represented by unidentified species of Trochammina, Climmacammina, Fusulina, and Wedekinellina. There are trace to minor amounts of fine silt to very coarse sand size white and dark gray chert clasts. The size and amount of these clasts increase upwards and also in the direction of the quarry. The lower group, which occurs in the lower half of the DB-IV-4, contains only a trace of fine silt-size clasts. This lithologic unit can be traced eastward another 990 feet to the northeast, where it contains 1 percent very coarse sand-size white and dark gray chert clasts. The upper group contains 1 percent coarse to very coarse sand-size white and dark gray chert clasts which coarsen upwards to small pebble size. The asphalt content of the group of beds averages about 10 percent by weight. This lithologic unit can be traced northeastward another 800 feet, to within 600 feet of the asphalt quarry. At its easternmost exposure, this unit contains 2 percent asphalt and 8 percent of coarse pebble-size white to dark gray chert clasts and fossiliferous limestone clasts. The amount of clasts increases, as well as the clast size, to the east. A large fragmentary orthocone nautiloid was found at its easternmost exposure.

A 24-foot thick covered section separates these slightly asphaltic grainstones from a 10-foot thick low topographic ridge. This ridge occurs along the south bank of a small creek in the southwestern part of the hillside exposure. The ridge, which strikes in the same direction as the underlying DB-IV units and appears to be conformable with them, is traceable for about 200 feet in the direction of the asphalt quarry. *In situ* rocks which form this ridge are not exposed. To the northeast, the low topographic ridge and the overlying covered interval are truncated by the same horizontal conglomerates which cap the Buckhorn asphalt quarry section.

Fusulinid wackestones and fusulinid-productid brachiopod mudstones characterize the upper part of DB-IV-1 (Fig. 10). Mature specimens of *Fusulina* sp. occur throughout the subunit. Most are complete, but a few are broken. *Antiquatonia* sp. is the only readily identifiable productid brachiopod genus. Isolated, hollow, pearly productid spines occur in nearly every bed in the entire section.

Calcareous sponge spicule wackestones comprise the DB-IV-2 and 3 subunit. The lower half is well exposed, whereas the upper half is poorly exposed. The lowermost 15 feet of the lower part contains abundant crinoid columnals and echinoid spines (Pl. 9). Several articulated crinoid stems, each about one foot in length, complete *Composita* spp., and spiriferoid brachiopods, a single compressed orthocone nautiloid, and a few *Fusulina* sp., were also found. The upper 15 feet of the lower part consists of some packstone interbedded with the wackestones. Small and large foraminifera are common. The large foraminifera are represented by unidentified species of *Trochammina*, *Climmacammina*, and *Fusulina*. The echinoderm remains are less abundant as compared to the underlying 15 feet. One incomplete specimen of *Pseudorthoceras knoxense* was found in the packstones at the top of the lower part.



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Pl. 9. Photomicrograph of a calcareous sponge spicule-bryozoan-brachiopod-echinoderm wackestone near the base of DB-IV-2 & 3.

The upper half of DB-IV-2 and 3 is poorly exposed, and there are only a few sparse outcrops, all of which have undergone extensive diagenetic alteration. In places, the original texture and fossil contents have been obliterated by zones of large crystals of replacement blocky calcite.

III. STRATIGRAPHIC RELATIONSHIPS

Introduction

Based on the foregoing presentation of the litho- and biostratigraphy, as well as the field relations, of the various key sections, possible correlations of the different sections can be offered.

Buckhorn Asphalt Quarry Section vs. Stock Pond Section

From the data presented above, it would appear that the Buckhorn asphalt quarry and the Stock Pond sections might be correlative, as both are richly asphaltic. The Stock Pond section is, however, 250 feet stratigraphically below the Buckhorn asphalt quarry. Three possibilities which could account for this stratigraphic separation are: 1) displacement by a fault, 2) both are part of a continuous broad 250-foot thick channel-fill deposit of similar lithology, and 3) there is no correlation. These various possibilities will be considered below.

There is no field evidence of a fault between the two sections. Unit 1 underlying the Buckhorn asphalt quarry can be traced 660 feet to the southwest where it overlaps the easternmost exposures of the DB-IV beds. There is only one very small area where a fault could conceivably bend around between these overlapping beds, and this area is only 100 feet wide where blanketing conglomerates and slope wash obscure the outcrop. Whether the fault exists or not is a moot consideration in light of the lack of duplication of lithologies between the two sections

Considering possibility 2, there is no evidence for a continuous type of lithology between the two sections. Although the two sections have asphaltic grainstones, the fossil contents of these grainstones are quite distinct. The quarry grainstones have abundant cephalopod remains, whereas the Stock Pond grainstone has none. Also, the units in the upper part of the Stock Pond section and units 2 and 3 in the basal part of the quarry section are not asphaltic grainstones. Hence, it is more reasonable to conclude that possibility 3 is the most likely case, and that the two sections are not correlative.

Stock Pond Section vs. DB-III Section

To the southwest, the Stock Pond section units can be seen to crop out for about 50 feet along the bottom of the adjacent stock pond. The more resistant parts of the DB-III section crop out along the west side of this stock pond. There is, therefore, only about a distance of 70 feet where the outcrops are covered by the stock pond. It seems conceivable that the two sections are correlative, particularly when the lithologies and faunal contents are considered (Fig. 11). The lower parts of both sections consist of an asphaltic packstone and grainstone unit. The main fossils are small foraminifera, gastropods, and spiriferid brachiopods in the DB-III section. The upper parts of both sections consist of poorly exposed fusulinid wackestones.

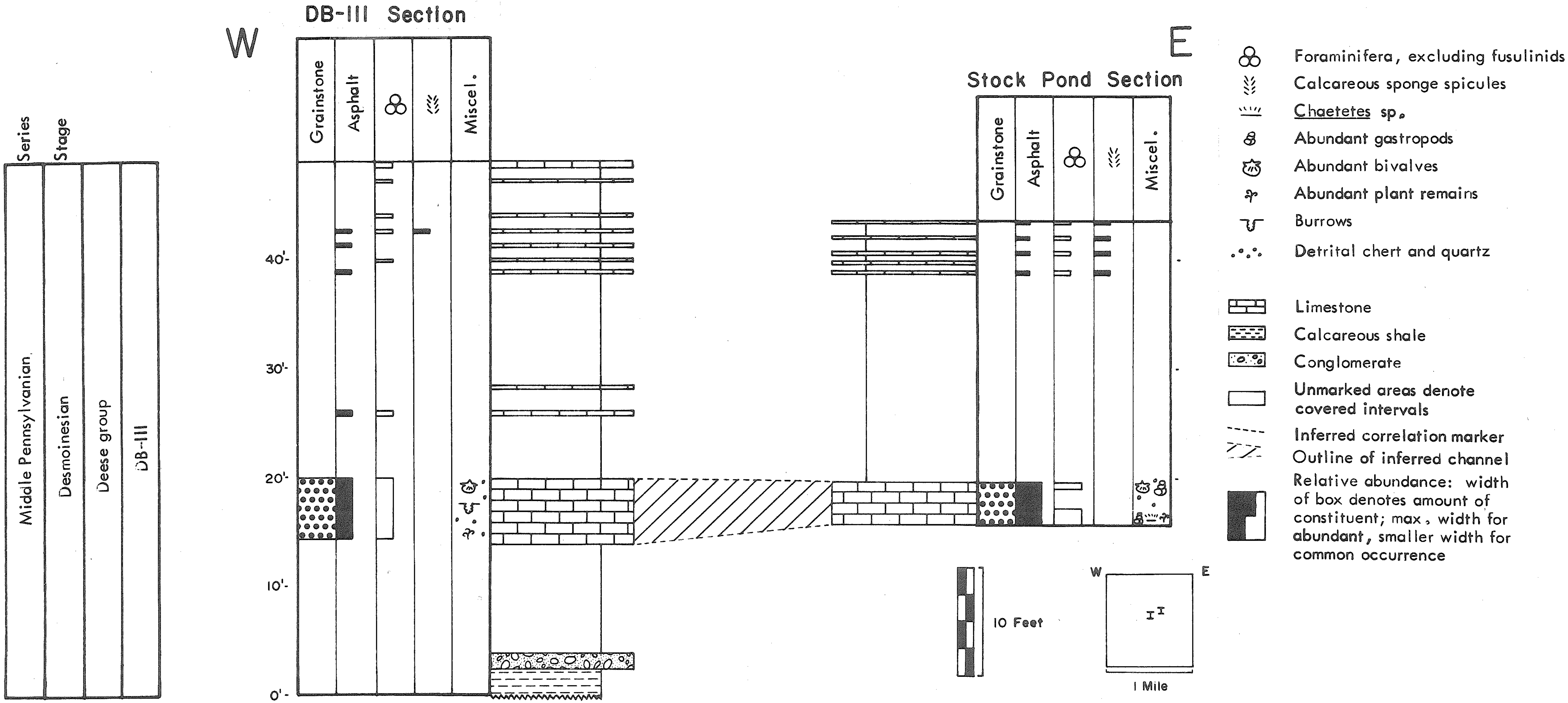


Fig. 11. Geologic cross section of the Stock Pond section and correlative strata.

Buckhorn Asphalt Quarry Section vs. DB-IV Section

Based on aerial photographs and field mapping, the Buckhorn asphalt quarry section seems to be correlative with the DB-IV section. One of the main arguments for this interpretation is the fact that the traceable ridge underlying the quarry also overlaps the easternmost part of the DB-IV beds. (See Fig. 5).

The possibility that the two sections are juxtaposed by a fault is remote for the same reasons discussed before in the consideration of possible faulting between the asphalt quarry and the Stock Pond sections.

When the Buckhorn asphalt quarry section is contrasted in terms of lithologies and faunal contents with the DB-IV section, the principal similarities occur between the asphaltic grainstones in the upper part of the quarry section and the slightly asphaltic grainstones in DB-IV-4. (See Pl. 10, in pocket). The grainstones in DB-IV-4 consist of foraminifera microcoquinas and are very similar to those in the quarry units 4 and 6. Small unidentified foraminifera occur in all of these foraminifera grainstones. Unidentified species of the larger foraminifera *Trochammina*, *Climmacammina*, and *Fusulina* occur in the DB-IV-4 beds, as well as in unit 4 of the quarry. The stratigraphically lowermost grainstones in each section are not separated by similar thicknesses from the basal traceable ridge common to the quarry section and to the eastern part of the DB-IV section. (See Pl. 10, in pocket).

The nonasphaltic wackestones underlying the grainstones in each section are similar. Unit 2 in the lower part of the quarry section is especially similar to beds in the lower part of DB-IV-2 and 3 by the

the presence of productid brachiopods. These are the only horizons in any studied section which contain such brachiopods. The lack of any marked contrasts in lithology and fossils in the lower parts of both sections argues against a facies change between the two.

The only clasts in DB-IV are in DB-IV-4, except for one minor occurrence downsection in DB-IV-2 and 3. Clasts occur in all of the quarry units, except for units 2 and 3. The uppermost foot of exposed DB-IV-4 can be traced to within 600 feet of the western margin of the quarry, and the unit is very similar in fossil composition and lithology to conglomerate unit 7 of the quarry. Unit 7 consists of 40 to 50 percent by volume of detrital clasts from granule size to very large pebble size. The largest clasts in this unit are from the eastern part of the quarry. The clasts are mostly black, white, or blue-colored cherts and some limestone clasts. Some fragments of large orthocone nautiloids also occur in this unit. Unit 7 thins to the southwest, and one foot above the unit there are highly abraded tests of Wedekinellina ? sp. At its easternmost exposure, the uppermost foot of DB-IV-4 consists of 8 percent by volume of coarse sand to large pebble-size white and dark gray chert and a few limestone clasts. A fragment of a large recrystallized orthocone nautiloid was also found. At 1400 feet from the quarry towards the Dry Branch Creek, this same unit contains 1 percent coarse to very coarse sand-size white and dark gray clasts with a few small chert pebbles and a few Wedekinellina ? sp. in the matrix.

Based on these data, it is inferred that quarry unit 7 correlates with the uppermost part of DB-IV-4. It is further inferred that the foraminifera grainstones in the DB-IV-4 beds correlate with the lowermost grainstones (i.e., units 4 and 6) in the quarry. As the comparable units do not have the same thickness above a common datum (i.e., unit 1), it seems more likely that the DB-IV-4 and quarry grainstones are part of the same sedimentary unit which was deposited in a channel. The boundaries of this inferred channel are shown in Plate 10 (in pocket). The base of the inferred channel would be located just below unit 4 in the quarry and just below the 126-foot horizon in DB-IV. Due to extensive cover in the upper part of the DB-IV-4 beds, it cannot be determined if the rocks in the covered interval (DB-IV-4 ? in Pl. 10, in pocket) above the uppermost exposure of DB-IV-4 beds are also channel-deposited or deposited under a different environment. The discussion of the western boundary of this inferred channel involves consideration of the Thompson Ranch section, which consists of the westernmost outcrops of the Deese group in the area.

DB-IV Section vs. Thompson Ranch Section

From aerial photographs and field mapping, it is readily apparent that the strata in the partly asphaltic Thompson Ranch section crop out along the north limb of the overturned syncline in which the quarry and DB-IV are structurally situated. The Thompson Ranch section is slightly over one mile west of the Dry Branch Creek.

The foraminifera grainstones in the upper part of the Thompson Ranch section are very similar to those in the DB-IV-4 beds of the DB-IV section. Unidentified species of the foraminifera *Trochammina*, *Climmacammina*, and *Fusulina* are present in both groups of grainstones. The presence of similar genera is, of course, not as convincing as similar species would be for correlation purposes.

The basal part of the Thompson Ranch section is like the basal part of the DB-IV section in that it consists of a chert pebble conglomerate overlain by a 35 to 40-foot thick covered interval. (See Pl. 10, in pocket). Overlying the covered interval, there is a 6-foot thick fusulinid and echinoderm-bearing limestone sequence. It appears that this stratigraphically lowermost limestone sequence in the Thompson Ranch section is stratigraphically equivalent to some part of the DB-IV-1 unit.

The limestone sequence in the Thompson Ranch section is truncated by faulting and occurs in the upthrown northwestern side of the fault. The grainstone units in the downthrown southeastern side of the fault are similar to those in DB-IV-4. It is likely, therefore, that most of the DB-IV-2 and 3 subunits are not exposed in the Thompson Ranch section due to omission by faulting.

It is conceivable that the Thompson Ranch grainstones are part of the same inferred channel deposit that is exposed in the DB-IV and quarry sections. The fact that the non-grainstone units in the lower part of the Thompson Ranch section are similar to the non-grainstone units in the lower part of the DB-IV section makes the inferred correlation even stronger.

IV. DEPOSITIONAL ENVIRONMENTS

Introduction

Heretofore, field mapping data, gross lithologies, and faunal compositions have been utilized to determine various inferred correlations. In particular, such types of data combined with the spatial relationships between similar deposits in the Buckhorn asphalt quarry, DB-IV, and Thompson Ranch sections have been the basis for inferring a channel environment for the strata in the upper parts of these sections. It will now be useful and instructive to consider the more detailed lithologic and paleontologic, as well as regional paleogeographic, data to see if they lend support to the channel hypothesis. The depositional environments of the strata underlying these inferred channel deposits in each section will also be included.

The depositional environments of the strata in the Stock Pond and DB-III sections will also be discussed, as will those for the conglomerates overlying the Deese group beds in the investigated area.

Buckhorn Asphalt Quarry, DB-IV, and Thompson Ranch Sections

One of the most important factors to consider is that during the deposition of the Deese group beds in this area, the shoreline was only 6 to 7 miles to the northeast along the margin of the Hunton anticline. (Ham, 1969, p. 17). The presence of abundant rafted plant remains and logs in the quarry units are best explained by nearness to land.

The quarry conglomerate unit 7 contains material which was mostly land derived, and this unit thins seaward. Unit 10 in the quarry contains identifiable plant remains, but extensive gilsonite formation within the unit has obscured much of the plant remains. The unit, in fact, has the appearance of a coal bed when examined in outcrop. Based on the scour features at the base of the unit, it is concluded that the unit is probably an allochthonous coal bed deposited in a channel environment.

The trend of the inferred channel under consideration is approximately N30E, which would have been roughly perpendicular to the ancient shoreline. The gross preferred orientations of plant remains and orthocone nautiloids in the quarry units are mostly about N35E, which is in agreement with the inferred channel trend.

The only main concentrations of clasts occur in the upper parts of each section. As discussed earlier, it is inferred that the quarry conglomerate unit 7 correlates with the uppermost part of DB-IV-4. The amount and size of the detrital chert and quartz in this unit decrease in the direction of the DB-IV section. This supports the interpretation, therefore, that there existed a gradient of water turbulence during the deposition of this unit between the quarry area and the DB-IV-4 beds, with the more turbulent water and increased capacity to carry clasts in the landward direction toward the quarry.

The source for the clasts was probably a deposit of clasts from the Woodford chert of Devonian-Mississippian age. Such a conclusion is based on the marked lithologic similarity of the unit 7 pebbles to Woodford chert, which has been described in the literature (Fay, 1969).

Based on regional studies, Ham (1969, p. 17) commented on the fact that the pebbles and cobbles in the lower Deese in the vicinity of Mill Creek, which is about 10 miles southeast of the Buckhorn area, were probably derived from the erosion of the Woodford formation in the Hunton anticline. He further commented on the younger Deese clasts being derived from limestones of the Arbuckle group, of Upper Cambrian age. There is, therefore, "stratigraphic inversion" in derived clastic material represented in the Deese group.

The fragmental nature of the skeletal debris and the much abraded Wedekinellina ? sp. tests are also indicative of the presence of water agitation. However, some of the more angular fragments in the quarry units are due to post-depositional compression. There are great concentrations of shells throughout the inferred channel deposits, especially coquinas in the quarry portion, relative to the non-grainstone deposits in the lower parts of the various sections. The abundance of nektonic cephalopod forms in units 9 and 13 in the quarry is certainly unusual. In the wackestones and packstones below the DB-IV-4 beds, for example, there are only a few scattered orthocone nautiloids. This is what would be expected, as the cephalopods have been interpreted to have been predators and, if so, their numbers should be low. One explanation for the great concentrations of cephalopod shells in the quarry may be that the floatable shell remains of these nektonic animals were concentrated by waves into a relatively quiet-water bay marginal to the Hunton anticline. Subsequently, heavy runoff or earthquake-triggered slumping along seacliffs could have caused turbulent waters charged with these shells and land-derived detritus and plants to scour semi-quiet water marine sediments. Such channel-fill deposits would contain admixed marine and nonmarine fossils, which is what is seen in the quarry grainstones.

The principal differences, other than asphalt content, between the quarry grainstones and the DB-IV-4 and Thompson Ranch grainstones are: 1) the seemingly virtual absence of cephalopod remains outside of the quarry, and 2) the occurrence of unidentified species of the large foraminifera Trochammina, Climmacammina, and Fusulina in only the lowermost quarry grainstones.

These differences can best be explained by considering the problem of lack of exposures of the upper parts of the DB-IV-4 and Thompson Ranch sections. The only grainstones common to each section are the basal ones with the Trochammina sp., Climmacammina sp., and Fusulina sp. specimens.

As with the other quarry coquinas or near-coquina deposits, most of the faunal constituents in the unit 11 coquina are derived. The ostracodes may have been transported, but not for long distances. Most of the ostracodes are disarticulated, but most of the single valves are unbroken. Small Chaetetes aff. favosus colonies are present, but they appear to have been rounded during water transport. The gastropods are unabraded, and there are nearly complete growth series in some of the more abundant genera. The gastropods, therefore, are most likely indigenous benthonic forms or they floated in attached to some objects. Foraminifera are not common.

Abundant micro-scour channels occur throughout the quarry units. One large channel also occurs in the upper part of unit 12. This channel is 15 feet across and 2 feet deep and contains bivalve and cephalopod fragments. These scour-channels, possible crossbedding in the basal parts of units 9 and 13, and definite crossbedding in the basal part of unit 12, all indicate that the water conditions were agitated and possibly above effective wave base, which is usually taken to be near 40 feet (Newell and Rigby, 1957, p. 26).

The $7\frac{1}{2}$-foot thick silty mudstone deposit of unit 12 is anomalous when compared to the grainstones in the quarry. Unit 12 is most certainly a quieter water deposit than the grainstones, but it is nevertheless a shallow water deposit as evidenced by the crossbedding in the lower part of the unit. The lower part of the unit is transitional with the underlying unit. Disarticulated ostracodes and single valves of *Anthracospirifer opimus* occur in the lower part of unit 12, but there are no gastropods, plants, or echinoderm remains. Whole *in situ* burrowing bivalves occur in the middle and upper parts. Evidently, unit 12 represents a relatively quiescent period in the channel environment. The water depth probably fluctuated between just above and below effective wave base, as evidenced by the presence of both crossbedding and well-laminated beds.

Most of the molluscan shells are concave-down in the quarry units. This particular orientation is typical of turbulent water (Emery, 1968, p. 1264-1269). The fact that there are some concave-up molluscan shells in these same beds probably indicates that there was some scavenger disturbance of the shell material.

From the above discussions, it is evident that the interpretation of a channel deposit environment for the upper parts of the Buckhorn asphalt quarry, DB-IV, and Thompson Ranch sections is fully supported by the detailed lithologic, paleontologic, and paleogeographic data.

Wackestones and mudstones characterize the strata below the inferred channel environment strata in the quarry, DB-IV, and Thompson Ranch sections. Such wackestones (with minor interbedded packstones) and mudstones contain whole to slightly abraded fossils and disarticulated sponge remains. The sponge spicules are characteristic of the wackestones and mudstones, and they are not present in grainstones. The calcareous sponge spicules became disarticulated upon death due to natural disintegration of the organisms.

In DB-IV-2 and 3, there are several articulated crinoid stems which are nearly a foot long, and there is also a criquina composed of shorter articulated crinoid stems. These skeletal remains most certainly were not subjected to strong water agitation. Nearly all of the large foraminifera, brachiopods, tetracorals, and ostracodes in the wackestones and mudstones throughout the area show little or no evidence of abrasion or rounding due to water turbulence or water transport. These wackestones and mudstones below the inferred channel deposits, therefore, are clearly quieter water deposits than those within the inferred channel.

Stock Pond and DB-III Sections

The field relations of the Stock Pond and DB-III grainstones have shown that they are very likely lateral equivalents of one another. The paleogeographic conditions of a nearby shoreline were the same as for the Buckhorn asphalt quarry, DB-IV, and Thompson Ranch grainstones 250 feet stratigraphically higher in the Deese group. Also, the Stock Pond and DB-III sections are aligned in a N30E trend, which is about perpendicular to the ancient shoreline. The Stock Pond and DB-III gross lithologic and paleontologic data are similar to those for the Buckhorn asphalt quarry, DB-IV, and Thompson Ranch strata involved in the channel interpretation. The lithologic and paleontologic data from the Stock Pond and DB-III sections will be considered below in order to see if they lend support to a channel hypothesis.

The only concentrations of clasts occur in the grainstones of the two sections. Plant remains are also restricted to the grainstones. The fossils are derived and occur mostly as fragmental skeletal debris, as evidenced by the abundant broken small foraminifera and abundant rounded Chaetetes sp. fragments. The gastropods are mostly whole, and they are either in situ forms or nearby derived. The burial assemblages in these grainstones are totally unlike the calmer water sponge spicule-bearing wackestones elsewhere in these sections. It seems, therefore, that the grainstones in these sections are most likely part of the same channel deposit. The similarity to the Buckhorn asphalt quarry, DB-IV, and Thompson Ranch sections' inferred channel is a point in favor of considering such grainstone deposits as cyclically-occurring phenomena, which would not be at all out of place with the interpretation of an adjacent tectonically unstable area nearby.

Conglomerate Overlying Deese Group Beds

The horizontal unit trancating the Deese group beds in the area under investigation is a limestone cobble conglomerate which, heretofore, in the discussion parts of this report, has not been given a formation name. Clearly, it is not part of the Deese group, as shown by its regional unconformable relationship with the Deese group beds.

Fay (1968, p. 12) referred this conglomerate to the Ada formation, which is of middle Virgilian age. Ham (1969, p. 17-18, 49) correlated the conglomerate with the Vanoss formation of late Virgilian age. His age assignment of the conglomerate was based on the presence of Precambrian age granite clasts. During the course of the present investigation, no granite clasts were found in the formation and, hence, the name Ada formation will be used. Based on regional studies, the date of the Arbuckle orogeny, which was the most intense deformation to affect the Arbuckle Mountains region, can be correlated with the unconformity at the base of the Ada formation, according to Ham (1969, p. 17).

The Ada formation is a channel deposit in the vicinity of the Buckhorn asphalt quarry. The conglomerate is probably the result of fluvial environments, since marine fossils are lacking. This channel cuts out more section along the eastern margin of the hillside exposures of the DB-IV beds than along the Dry Branch Creek exposures of these beds. The truncation also cuts out considerable section in the quarry area. The Ada formation is thin over the western margin of the quarry and does not crop out along the eastern part. Nevertheless, there are only a few feet of covered interval separating the Ada formation from the top of unit 13. It seems likely that the chert-limestone pebble conglomerate (i.e., unit 14) is part of the Ada formation. This two-foot thick channel conglomerate is in composition like that of the Ada formation in that it is nonasphaltic, unfossiliferous, and contains lithologies totally unlike the asphaltic Deese group chert pebble conglomerate (unit 7) in the underlying quarry section.

V. POST-DEPOSITIONAL CHANGES IN DEPOSITS

Introduction

The post-depositional changes which occurred in the strata in the studied sections are considered below. The alterations in the Buckhorn asphalt quarry strata are emphasized. The diagenetic alterations include cementation, compaction, oil impregnation, asphalt and gilsonite formation, replacement calcite formation, silicification, and dolomitization. The other major post-depositional process which has affected some of the deposits is weathering. Changes in the mineralogy of shells will be discussed only in a general way. Changes in the carbonate mineralogy and Mg and Sr contents of individual shell layers will be treated in full detail in later sections of this report.

Diagenesis

Cementation, Compaction, and Hydrocarbon Effects

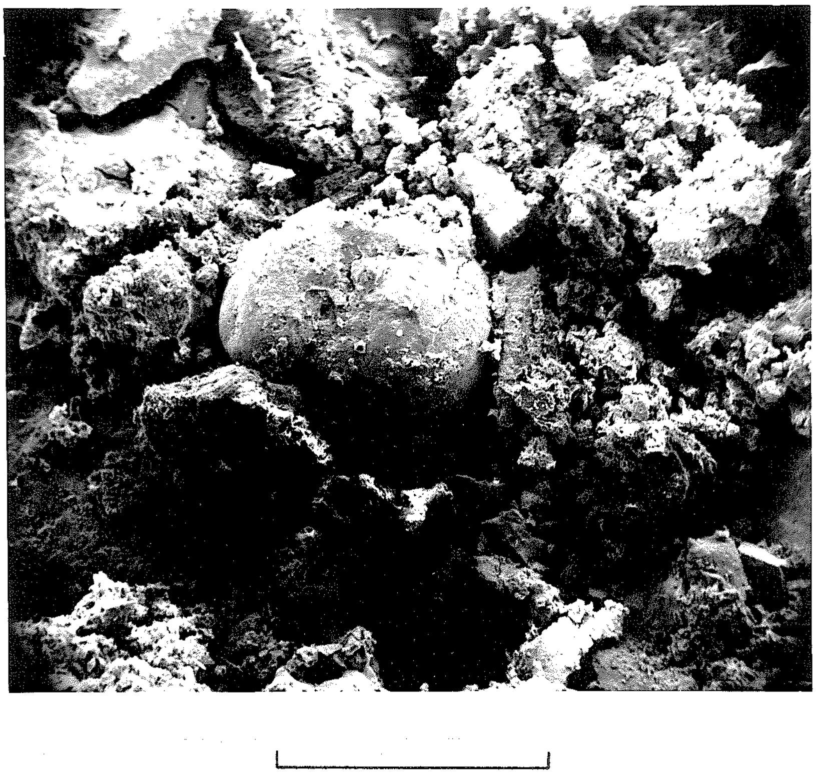
Most of the asphaltic quarry and Stock Pond units have only incipient cementation and show compactional features. The limited cementation, except in the partly asphaltic to nonasphaltic units in the quarry (i.e., units 11 and 12) is apparent after the removal of the asphalt, as the limestone is usually friable. A typical sample of the friable grainstone was examined by means of a combination of petrographic microscope and scanning electron microscope investigation. This sample is from the middle of unit 9 of the Buckhorn asphalt quarry, and it contained about 12% by weight of asphalt. The SEM examination of a part from which the asphalt had been extracted revealed a highly porous, grain-supported fabric. The cementing agents which can be seen optically include the following: blocky calcite within gastropod chambers, mega-quartz partial replacement of shell walls, euhedral dolomite partial replacement of shell walls and finer grain groundmass, and blocky calcite areas within the matrix. All occur in trace amounts except the last-mentioned type which occurs in minor amounts. Impressed contacts were also found.

Another grainstone sample from near the top of unit 13 contained about 30% by weight of asphalt. It crumbled almost entirely in the Soxyhlet extractor upon removal of the asphalt. A SEM photograph of a part of this sample is shown in Plate 11. The material is highly porous and shows grain support. On the surface of the foraminifera grain, which is shown in a close-up in Plate 12, there is a scattered surface carbonate coating, which may be cement. Optically, several types of cement are observable and include: blocky calcite within gastropod chambers, euhedral dolomite partial replacement of matrix and partial filling of pores, and partial replacement of shell walls by blocky calcite. The blocky calcite in the shell chambers is a trace constituent, but the other types of cementation are of minor importance. The amount of cement in this unit 13 sample is less than in the previously mentioned sample, and this is in accord with the fact that the unit 13 material mostly disaggregated upon removal of the asphalt.

These observations indicate that cementation was terminated following invasion of oil into the pore spaces of the grainstones.

500μ

Pl. 11. Scanning electron microscope picture of deasphaltized foraminifera-cephalopod grainstone from the middle of unit 13 in the Buckhorn asphalt quarry.



Pl. 12. Scanning electron microscope picture of a closeup of part of the grainstone illustrated in Plate 11. The large grain in the center is a foraminifera test. The surface carbonate coating may be cement.

The time for the oil impregnation had to occur between post-deposition of the quarry and Stock Pond strata, which are of early middle Desmoinesian age, and the deposition of the overlying nonasphaltic Ada formation conglomerate sequence, which is of middle Virgilian age. This entrapment of oil in the quarry and Stock Pond rocks was undoubtedly due to the highly porous and permeable nature of the channel grainstones. The overlying shale beds in each area could have served as the impervious covers for the channel stratigraphic traps.

The early stages of the Arbuckle orogeny, which can be correlated with the uplift of the Hunton anticline, probably provided the tilting or fracturing of the underlying rocks required to introduce the oil into the channel deposits. Fischer and Finley (1949) stated that the quarry asphalt was derived from oil originally entrapped in Ordovician strata.

According to Eldridge (1901, p. 227, 273), the Buckhorn asphalt district has an area of about 30 square miles. Asphalt occurs throughout the area in rocks of Ordovician age, as well as in rocks of Pennsylvanian age. The asphalt occurrence, therefore, is not restricted to only the Buckhorn asphalt quarry and immediate vicinity.

The weak cementation of the grainstones allowed them to become compressed during later deformation and/or by sediment loading. Evidences of grain impressions due to compaction are common throughout the asphaltic grainstones, as shown in Plate 4. Pray (1960) commented that limestones normally show scant evidence for compaction. This is not the case for the asphaltic strata in the various studied sections, but is for the nonasphaltic strata. These nonasphaltic deposits show no compaction effects and, hence, were already well-cemented when the compaction occurred which affected the uncemented channel rocks. The channel beds could only have escaped cementation if the pore spaces had already been impregnated with oil.

The most likely cause of the compaction of the asphaltic deposits was the deformation related to the Arbuckle orogeny, dated at the base of the Ada formation. In addition, there may have been some compaction due to the sediment load caused by deposition of late Desmoinesian and Missourian age sediments, which were later removed prior to the deposition of the Ada formation strata.

Such deformation undoubtedly caused the more volatile constituents to be driven off from the oil, thereby causing the oil to be converted into asphalt. The surrounding temperature was never great, as the asphalt would have been converted to kerogen or other pyrobitumens, which is clearly not the case.

The formation of gilsonite areas, dikes, and dikelets which are common throughout the quarry strata is best related to deformation during the Arbuckle orogeny. This deformation was probably post-asphalt formation. The deformation continued throughout Virgilian time, so there would be ample opportunity to form the gilsonite and later shear it.

The presumed allochthonous coal bed, unit 10 in the quarry, is heavily impregnated with gilsonite which selectively replaced plant remains. Evidence of shearing is shown in this bed. Hence, it seems likely that ground waters entered along this zone of weakness and subsequently locally altered the asphalt quarry units.

Replacement Calcite, Silicification, and Dolomitization

In places in the presumed allochtonous coal bed in the quarry, large gilsonite areas are cut by an extensive network of fractures. These fractures, which do not extend beyond the edges of the gilsonite areas, are filled with blocky calcite crystals. The calcite crystals in these fractures contain inclusions and are identifical in texture to calcite crystals within gastropod chambers and calcite crystals replacing shell material only a few inches away from the gilsonite areas. It is conceivable that the fracture- and gastropod chamber-filling calcite was originally pore-filling and later recrystallized.

Many of the edges of the gilsonite areas have been replaced by megaquartz crystals. Such a conclusion is based on the occurrence of boundaries between former edges of gilsonite areas and fractures filled with calcite preserved in the form of gilsonite inclusions in the megaquartz crystals.

At the top of unit 9 and near the base of unit 11, many gastropod shells have been broken by shearing and/or compaction. Most of the shells show partial replacement by both calcite and megaquartz crystals.

Tiny rhombs (20-30μ) of dolomite occur in units 9, 11, 12, and 13 of the quarry. The clear rhombs replace matrix, as well as fossil shell material. The time of the dolomitization relative to stages of replacement by calcite and quartz could not be ascertained since the dolomite occurrences are not associated with other diagenetically introduced minerals.

Weathering

Weathering of the asphalt occurs fairly rapidly upon exposure to the elements. Freshly excavated dark black asphalt weathered to a bluish gray and has a leached appearance on the outer surfaces after having been exposed to about 1 inch of rainfall. The deposits which are rich in asphalt contain aragonitic skeletal remains. These aragonitic skeletons have partly or completely altered to calcite where the asphalt content has been reduced by weathering or where the original asphalt content was low.

Upon re-excavation of the quarry, the original floor was locally encountered. The floor surface had a slight weathered appearance, but the asphalt appears to be extremely fresh only fractions of a millimeter into the bedrock from the weathered surfaces.

VI. REVIEW OF PREVIOUS RESEARCH ON MINERALOGY AND MG & SR CONTENTS OF CALCAREOUS FOSSIL REMAINS

Introduction

As mentioned by Dodd (1967, p. 1313), much research has been conducted in the past 25 years on the carbonate mineralogy and chemistry of invertebrate skeletons. Some of the most important data are shown in Figures 12 through 19. Investigations into the mineralogy and Mg & Sr contents of calcareous fossil invertebrate skeletons, however, have been limited. The relative scarcity of such papers dealing with fossils is not due to a lack of interest, but rather is due to a lack of available and suitable unaltered material. The problem becomes more acute with increasing geologic age of the sediments.

In the following discussions, most of the important papers dealing with the carbonate mineralogy and chemistry of fossil invertebrates will be mentioned. Those dealing specifically with specimens from the Buckhorn asphalt quarry will be listed separately.

Previous Research (Excluding Buckhorn Asphalt Quarry)

Odum (1951, 1957) reported on the Sr/Ca values of various fossils ranging in age from Cambrian to Pleistocene. Included in this list were a few unidentified nautiloids from the Buckhorn asphalt quarry. Kulp, Turekian, and Boyd (1952) analyzed various recrystallized and nonrecrystallized invertebrate fossils from Cambrian to mid-Pliocene age rocks. Stehli (1956, p. 1031-1032) reported on the occurrence of aragonite in fossils from the Buckhorn asphalt deposits and the Kendrick shale (Lower Pennsylvanian) of Kentucky. In 1960, Siegel analyzed Pleistocene corals and Krinsley (1960) analyzed Pleistocene gastropods. Turekian and Armstrong (1961) reported on the chemistry of Cretaceous mollusks, and Lowenstam (1961) investigated the oxygen isotopes and Sr/Ca and Mg/Ca values of brachiopods from late Mississippian to late Pliocene age rocks. Prokofyev (1964) followed with a report on the amounts of certain trace elements in several Paleozoic brachiopod genera. Lowenstam (1964) later analyzed archaeogastropods from early Pennsylvanian to late Cretaceous age rocks. The chemistry of Miocene to Pleistocene mollusks was studied by Pilkey and Goodell (1964), and late Cretaceous age mollusks were studied by Lerman (1964).

Grandjean et al. (1964) listed the mineral components in shells of fossil mollusks of Ordovician to Tertiary age. Cephalopod shell fragments of Ordovician age were reported as the oldest occurrences containing traces of aragonite.

The oldest recorded occurrence of in situ aragonite shell material is from cephalopods found in the Lower Carboniferous of Scotland (Hallam and O'Hara, 1962, p. 273-274). The nacreous shells of a goniatite ammonoid and an orthocone nautiloid were found to be aragonite. Other specimens of the same cephalopods, as well as of a zygoplenid gastropod, appeared chalky and were found to consist of mixtures of aragonite and calcite.

Hallam and Price (1966) reported on the strontium contents of unidentified orthocones, a goniatite ammonoid, and an unidentified goniatite of early Carboniferous age from central Scotland. Hallam and

Price (1968) later reported on the strontium contents of cephalopods of Jurassic to Miocene age. Yochelson *et al*. (1967) reported on the mineralogy of mollusk shells from the Pennsylvanian Kendrick shale in Kentucky.

Weber and Raup (1968) determined the magnesium concentrations in fossil echinoid skeletons, ranging in age from Devonian to Pleistocene.

Previous Research Regarding Buckhorn Asphalt Quarry

The iridescence of the nacreous layers of shells from the Buckhorn asphalt quarry was first noted by Eldridge (1901). Stehli (1956) investigated the mineralogy of the shells. He analyzed representatives of six major phyla but did not note the "Buckhorn" localities from which they were recovered.

Goldsmith (1960, p. 108) made mention of analyses of a Pennsylvanian echinoid spine which, according to Lowenstam (Personal communication, 1972) came from the asphalt quarry. Lowenstam (1963a, p. 189) reported Hare's analyses on the amino acid contents of organic matrix material of a *Pseudorthoceras knoxense* specimen from the quarry.

Lowenstam (1963b, p. 127) determined the Sr/Ca ratio of an *Euphemites* sp. from the Buckhorn asphalt quarry. Grandjean (1964), in his summary of the mineral components in fossil mollusk shells, mentioned the occurrence of aragonite in *Pseudorthoceras knoxense* and various unidentified nautiloids and ammonoids from the quarry. Hallam and Price (1966, p. 26) reported on the strontium contents of unidentified orthocone nautiloids from the Buckhorn asphalt quarry.

VII. MICROARCHITECTURE, MINERALOGY, AND MG & SR CONTENTS OF SKELETAL CARBONATES FROM THE BUCKHORN ASPHALT QUARRY

Introduction

One of the primary goals of this investigation was to determine the original mineralogy of late Paleozoic age carbonate skeletons. Attention was also focused on determining whether the Mg and Sr contents of these skeletal carbonates are original or altered. The Mg and Sr contents were specifically studied because they are (1) commonly major elements which substitute for Ca in skeletal carbonates, and (2) can be utilized, in some cases, for evaluation of paleoenvironmental conditions. Other elements were analyzed for, but they were found only as trace constituents. Treatment of these data was beyond the scope of this report because there were no apparent correlations in the trace element concentrations which could be related to the elucidation of the objectives in this present study. The data are listed in Appendix II.

In the evaluation of the original versus altered Mg and Sr contents in the skeletal carbonates, certain problems exist. The evaluation was hampered by not knowing the paleo-temperature, paleo-water chemistry, or biochemical evolutionary trends which may have affected the skeletal carbonate Mg and Sr contents. Indeed, the admixed burial assemblages which occur in the quarry may contain carbonate skeletons which could have been derived from drastically different paleoenvironmental conditions.

Attempts were made to evaluate what is original or near-original versus diagenetically altered skeletal carbonates. The question was also considered whether possible alterations of the mineralogy and the Mg and Sr contents may have occurred prior to the sealing by oil. As will be shown, some alterations have occurred in the mineralogy and Mg and Sr contents. Considering the limited number of suitable samples available for investigation, it seemed that with little confidence one would gain pertinent information in further exploration of the trace constituents or stable isotope contents of these skeletons.

Presentation of Data

Table II lists the preservational, microarchitecture, mineralogy, and Mg and Sr data for each skeletal carbonate.

Bøggild's (1930) terminology and Majewske's (1969) photomicrographs of microarchitectures of invertebrate skeletons were used in describing the fabric types encountered in the thin-section studies of the fossils.

The mineralogical studies were carried out by means of x-ray diffraction, infrared spectroscopy, and chemical staining techniques. The Mg and Sr contents were determined by means of electron microprobe analyses. Some of the Mg contents were also determined by means of x-ray diffraction techniques. Prior to the chemical analyses, the fossils were deasphaltized by means of a Soxyhlet extraction process using dichloromethane. Details of the extraction procedures and of the

TABLE II

MICROARCHITECTURE, MINERALOGY, AND MG & SR CONTENTS IN SKELETAL CARBONATES FROM THE BUCKHORN ASPHALT QUARRY AND VICINITY

EXPLANATION

Q	Buckhorn asphalt quarry	CS	Chemical staining
Asp	Asphalt	EM	Electron microprobe
mAsp	Mostly asphalt	*	Electron microprobe technique used, except where otherwise noted
sAsp	Some asphalt		
C	Calcite	†	Average Mg & Sr concentrations in those cases where there was more than one determination in each shell layer per specimen
C_{II}	Replacement calcite		
A	Aragonite		
XR	X-ray diffraction		
IR	Infrared spectrophotometer		

Specimen	Appendix Code Number	Strati-graphic Unit	Sealing Agent	Morphological Unit of Carbonate Skele-ton Investigated	Carbonate Polymorph (Technique Used)	No. of Analyses for Mg & Sr	mol %* $MgCO_3$ †	$(Sr/Ca) \times 10^{-3}$* (atom) †
Foraminifera								
Globivalulina sp.		Q:13	Asp	Wall	C (IR)	1	3.02±0.09	<1.0
Wedekinellina sp.	1	Q:13	Asp	Wall	C (CS)	2	3.07±0.09	<1.0
	2	Q:11	mAsp	Wall	C (CS)	2	3.49±0.10	1.10±0.17
	3	Q:9	Asp	Wall	C (CS)	1	2.91±0.09	1.14±0.17
Coelenterata ?								
Chaetetes aff. *favosus*		Q:11	Asp	Bulk colony	C+D (XR)	1	C:2.50±0.5(XR)	
				Corallite walls & tabulae	C (IR)	2	5.28±0.11	<1.0
				Secondary rim	D (IR)	2	29.92±0.30	<1.0

Continued on next page

TABLE II

Specimen	Appendix Code Number	Strati-graphic Unit	Sealing Agent	Morphological Unit of Carbonate Skeleton Investigated	Carbonate Polymorph (Technique Used)	No. of Analyses for Mg & Sr	mol %* $MgCO_3$ †	(Sr/Ca)×10^{-3}* (atom) †
Coelenterata ?								
Chaetetes aff. favosus		Q:13	Asp	Wall	C (CS)	2	4.90±0.10	1.74±0.23
Bryozoa								
Penniretepora ? sp.		Q:13	Asp	Wall	C (CS)	1	2.75±0.08	0.95±0.14
Streblotrypa ? sp.		Q:13	Asp	Wall	C (CS)	3	3.30±0.10	<1.0
Brachiopoda								
Anthracospirifer opimus		Q:7	C	Wall	C (IR,CS)	2	0.83±0.06	1.14±0.17
Gastropoda								
Bellerophon (Bellerophon) sp.		Q:Float	Asp	Outer foliated?	SiO_2 (CS)			
				Inner crossed-lamellar?.	$A>C_{II}$ (IR,CS)			
Straparollus (Euomphalus) sp.	1	Q:11	sAsp	Outer prismatic	C (CS)	1	3.58±0.11	1.98±0.26
				Inner crossed-lamellar	$A+C_{II}$ (CS)			
	2	Q:7	C	Outer prismatic	C (CS)	1	3.45±0.10	1.30±0.20
				Inner crossed-lamellar	$C_{II}>A$ (IR,CS)	1	2.25±0.07	<1.0
Naticopsis wortheni	1	Q:9	Asp	Outer prismatic	C (CS)			
				Inner crossed-lamellar	$C_{II}\simeq A$ (IR,CS)	2	2.31±0.07	0.97±0.15
	2	Q:Float	Asp	Outer prismatic	C (CS)		0.43±0.07	1.41±0.20
				Inner crossed-lamellar	$C_{II}+A$ (CS)			
Trachydomia whitei	1	Q:11	mAsp	Outer prismatic	C (CS)	1	1.68±0.07	<1.0
				Inner crossed-lamellar	$A+C_{II}$ (CS)			
	2	Q:9	Asp	Outer prismatic	C (CS)			
				Inner crossed-lamellar	$A>C_{II}$ (IR,CS)		1.85±0.07	1.39±0.20
	3	Q:9	mAsp	Inner crossed-lamellar	$A+C_{II}$ (CS)			

TABLE II

Specimen	Appendix Code Number	Strati-graphic Unit	Sealing Agent	Morphological Unit of Carbonate Skeleton Investigated	Carbonate Polymorph (Technique Used)	No. of Analyses for Mg & Sr	mol %* $MgCO_3$ †	$(Sr/Ca)\times10^{-3}$* (atom) †
Scaphopoda								
Plagioglypta ? sp.		Q:13	Asp	Wall	A (CS)			
Cephalopoda								
"*Orthoceras*" *unicamera*		Q:9	Asp	Nacreous wall	A (IR,CS)	3	<0.40	1.09±0.16
				Nacreous septum	A (IR,CS)	2	<0.40	1.65±0.23
				Cameral deposits	A (IR,CS)	1	<0.40	5.82±0.47
				Endosiphuncular deposits	A (IR)	1	<0.40	6.50±0.56
Pseudorthoceras knoxense	1	Q:9	Asp	Nacreous wall	A (CS)	1	<0.40	1.33±0.20
				Nacreous septa	A (CS)			
				Cameral deposits	A (CS)	2	<0.40	7.15±0.57
				Endosiphuncular deposits	A (CS)	1	<0.40	7.01±0.56
	2	Q:11	sAsp	Cameral deposits	C_{II}>A (IR,CS)	2	0.97±0.06	2.64±0.31
				Endosiphuncular deposits	C_{II}+A? (CS)	1		
	3	DB-IV-2&3	C	Cameral deposits	C_{II} (CS)	1	1.95±0.08	1.26±0.19
Metacoceras cornutum		Q:9	Asp	Nacreous wall	A (IR,CS)	2	<0.40	2.52±0.33
Domatoceras sp.		Q:9	Asp	Nacreous wall	A≈C (IR,CS)	2	<0.40	1.64±0.23
Pseudoparalegoceras sp.	1	Q:9	Asp	Nacreous wall	C_{II}≈A (IR,CS)	2	<0.40	2.36±0.31
	2	Q:9	Asp	Nacreous wall	C_{II}>A (XR)	1	C:0.00±0.50-(XR)	
Wellerites mohri ?		Q:9	Asp	Nacreous wall	C_{II}+A (CS)	2	<0.40	1.88±0.24
Bivalvia								
Chaenocardia ovata	1	Q:9	Asp	Outer prismatic	C (CS)	1	3.24±0.10	1.03±0.16
				Inner crossed-lamellar	A+C_{II} (CS)	2	<0.40	1.33±0.20
	2	Q:9		Outer prismatic	C (XR,CS)	1	2.61±0.08	<1.0
				Inner crossed-lamellar	A>C_{II} (XR,CS)	1	<0.40	1.63±0.23

TABLE II

Specimen	Appendix Code Number	Strati-graphic Unit	Sealing Agent	Morphological Unit of Carbonate Skeleton Investigated	Carbonate Polymorph (Technique Used)	No. of Analyses for Mg & Sr	mol %* $MgCO_3$ †	$(Sr/Ca)\times10^{-3}$* (atom) †
Ostracoda								
Hypotetragona sp.	1	Q:11	Asp	Wall	C (CS)	2	3.35±0.10	<1.0
	2	DB-IV-2&3	C	Wall	C (CS)	2	1.22±0.07	0.98±0.15
Proparaparchites sp.		Q:11	Asp	Wall	C (CS)	1	3.04±0.09	1.26±0.19
Bairdia spp.	sp. A	Q:13	Asp	Wall	C (CS)	1	2.25±0.07	1.03±0.16
	sp. B	DB-IV-1	C	Wall	C (CS)	2	1.41±0.07	1.36±0.20
Cavellina sp.	1	Q:13	Asp	Wall	C (CS)	2	2.03±0.08	2.78±0.34
	2	DB-III	C	Wall	C (CS)	1	2.10±0.08	1.82±0.24
Echinoidea								
Archaeocidaris megastyla ?	1	Q:9	Asp	Spine, stereom	C + tr. D &	1	C:3.0 ±0.5 (XR)	
					SiO_2 (XR,IR)	8	6.57±0.13	1.42±0.20
	2	Q:9	Asp	Spine, stereom	C + D & tr.			
					SiO_2 (XR,IR)	3	12.00±0.12	1.60±0.22
				, medulla		1	1.90±0.08	<1.0
	3	Q:Float	sAsp	Spine, stereom	C + D? (IR)	2	2.24±0.09	2.33±0.31
	4	DB-IV-2&3	C	Spine, stereom	C + D & SiO_2	3	C:0.0 ±0.5 (XR)	
					(XR,IR)		2.37±0.10	2.50±0.32
	5	DB-IV-2&3	C	Spine, stereom	C+D & SiO_2(IR)	3	3.47±0.10	2.13±0.28
				, medulla	C (CS)	1	<0.40	<1.0
	6	DB-IV-2&3	C	Spine, stereom	C+D & SiO_2(IR)	1	3.54±0.11	2.50±0.32
	7	DB-IV-2&3	C	Spine, stereom	C+D & SiO_2(IR)		2.86±0.09	2.68±0.35
Calcite cement	1	Q:9			C (IR)	2	1.61±0.07	<1.0
	2	Q:13			C (IR)	1	1.19±0.06	<1.0

methods used to determine the Mg and Sr contents of the skeletal carbonates are given in Appendix I.

Discussion of Data

Introduction

In this section, original skeletal carbonates are distinguished from replacement mineral phases. Various chemical and morphological criteria for distinguishing between these primary and replacement minerals will be presented. In addition, the Mg and Sr contents of these primary and variously diagenetically altered skeletal carbonates will be included in the discussions. Comparisons with the mineralogy and Mg and Sr contents of taxonomically similar forms of similar geologic age and Recent age are also useful in the alteration evaluations.

Skeletal Aragonites

The determinations that the original mineralogy of a skeletal carbonate from the quarry was aragonite and that the Mg and Sr contents are more likely to be preserved are valid if any or all of the following occur: 1) the microarchitecture or the aragonitic skeleton is preserved, 2) nearby calcitic areas (or corresponding calcitic areas in other specimens of the aragonite species) show total or near-total obliteration of the microarchitecture, as maintained by Bøgglid (1930), and 3) the organic matrices are physically preserved.

There are areas of crossed-lamellar microstructure preserved in the inner layers of some of the quarry gastropods. These areas consist of aragonite with the organic matrices still intact. The other areas consist of calcite with some intermixed aragonite, and in such cases there is partly to near-total obliteration of the crossed-lamellar microstructure. It can be concluded that crossed-lamellar inner layers occur in the gastropods *Straparollus* (*Euomphalus*) sp., *Naticopsis wortheni*, and *Trachydomia whitei*. A specimen of the gastropod *Bellerophon* (*Bellerophon*) sp. also appears to have a crossed-lamellar inner layer.

The shell microarchitecture and mineralogy data for some of these gastropods are in agreement with similar genera studied by other workers. Stehli (1956) reported that *Straparolus* (*Amphiscapha*) sp. has an inner aragonite layer. Yochelson *et al.* (1967) reported that *Bellerophon* (*Pharkidonotus*) sp. and *Straparollus* (*Amphiscapha*) sp. indet. have inner aragonite layers.

Furthermore, that *Straparollus* (*Euomphalus*) sp. has a non-nacreous aragonitic inner layer is in keeping with the general characteristics of the suborder Macluritina to which it belongs (Knight *et al.*, 1960, p. I 184). The lamellar, non-nacreous, aragonitic inner layers in *Naticopsis wortheni* and *Trachydomia whitei* are in keeping with the characteristics of their suborder Neritopsina (Knight et al., 1960, p. I 275).

Due to surface damage under the microprobe beam of the aragonite parts of these gastropod inner layers, the summations of the elemental oxides in these layers total far below 100 percent (see Appendix II). The Mg and Sr contents, therefore, could not be adequately determined. The surface damage was probably similar to the vaporization problems described by Moberly (1968, p. 67) in his microprobe analyses of biogenic carbonates.

Microprobe analyses, however, were made on the replacement calcite (with some intermixed original aragonite) parts of the inner layers in a single specimen of Straparollus (Euomphalus) sp., and asphalt-impregnated single specimens of Naticopsis wortheni, and Trachydomia whitei. The Mg and Sr contents are tabulated in Table III. The Sr contents are also plotted in Figure 12, and the Mg contents are plotted in Figure 13. The amount of aragonite is greater in the specimens which were asphalt-impregnated. The amount of Mg decreases and the amount of Sr increases with increasing aragonite content.

As shown in Figure 12, Lowenstam (1963b, p. 127) reported a Sr/Ca = 5.9 for the aragonite layer in Euphemites sp. from the Buckhorn asphalt quarry. This value is close to his values for other studied archaeogastropods of middle Pennsylvanian age from the Kendrick shale in Kentucky.

Aragonite occurs in the shell walls of the scaphopod Plagioglypta ? sp. No alteration to calcite could be detected, and the shell consists of a single lamellar layer which has parallel extinction under crossed nicols. As with the gastropods, no adequate determinations of the Mg and Sr contents could be made due to the surface damage under the microprobe beam of the scaphopod aragonite.

TABLE III

MG AND SR CONTENTS IN GASTROPOD SKELETAL ARAGONITES FROM THE BUCKHORN ASPHALT QUARRY

Specimen	Sealing Agent	Carbonate Polymorph	No. of Analyses	mol % $MgCO_3$	$(Sr/Ca)\times10^{-3}$ (atom)
S. (Euomphalus) sp.	C	$C_{II}>A$	1	2.25±0.07	<1.0
N. wortheni	Asp	$C_{II}\approx A$	2	2.31±0.07	0.97±0.15
T. whitei	Asp	$A>C_{II}$	1	1.85±0.07	1.39±0.20

Explanation

Asp - Asphalt
C - Calcite
C_{II} - Replacement calcite
A - Aragonite

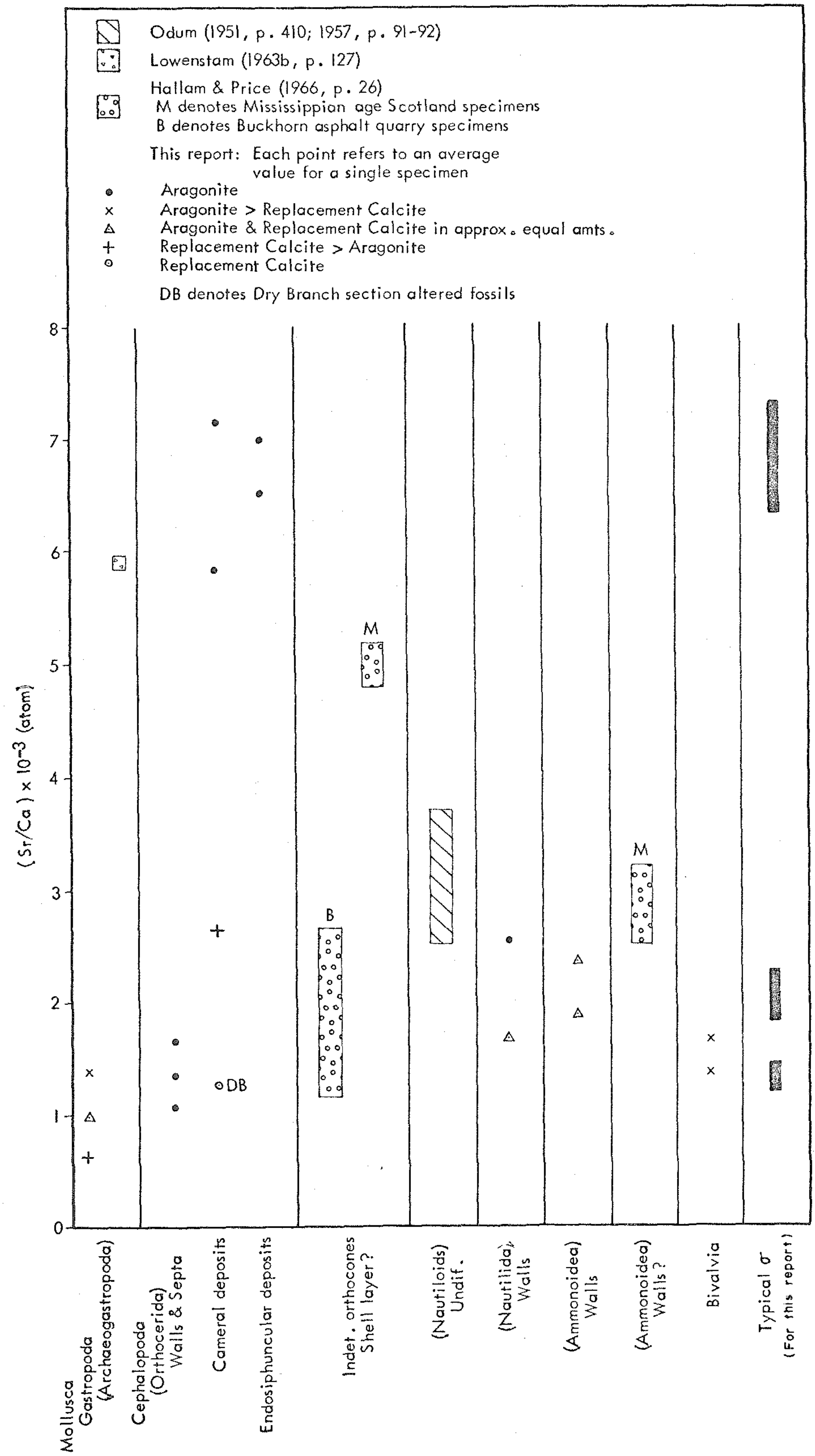


Fig. 12. (Sr/Ca × 10^{-3} atom ratio in middle Pennsylvanian age aragonitic skeletons.

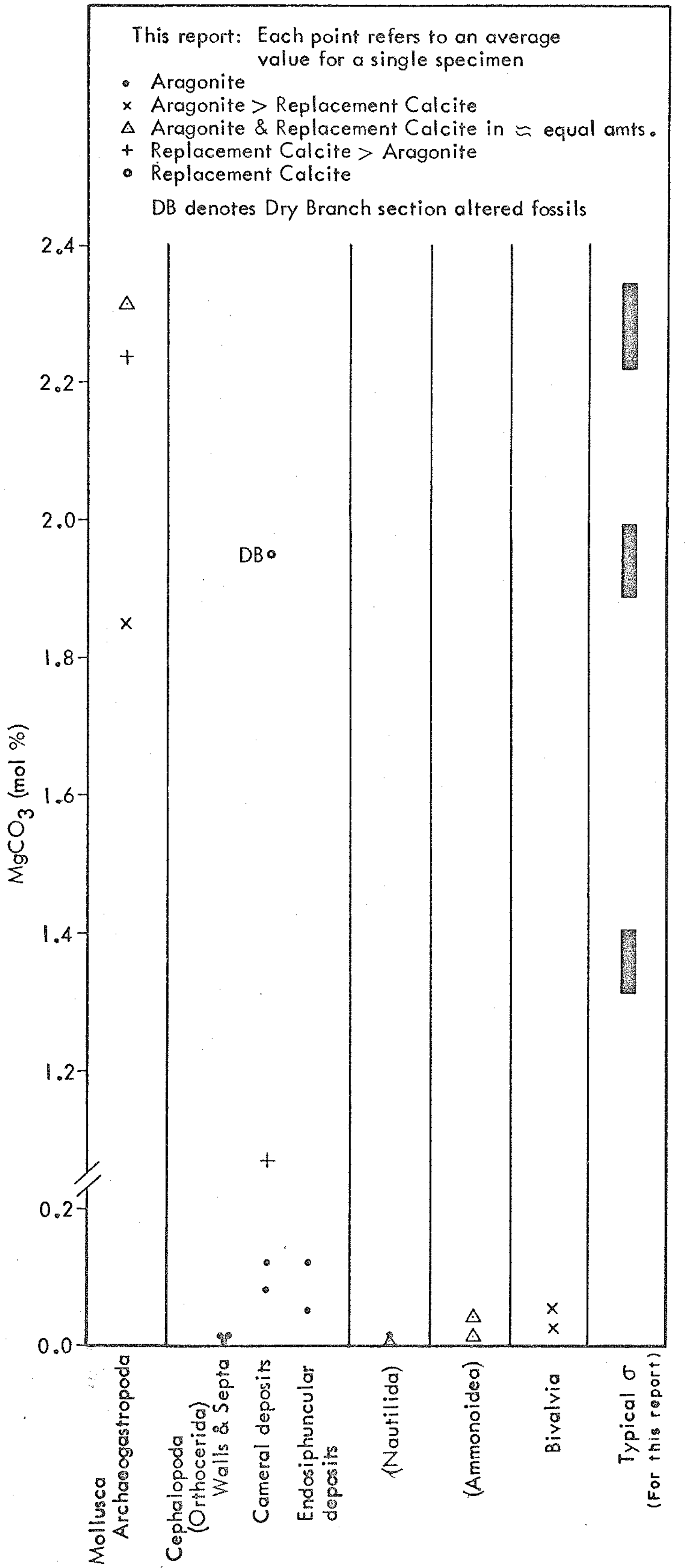


Fig. 13. $MgCO_3$ (mol percent) in middle Pennsylvanian age aragonitic skeletons.

The aragonitic orthocone nautiloid shell walls, septa, and cameral and endosiphuncular deposits are exceptionally well preserved in terms of presence of microarchitecture and organic matrices.

My study of the microarchitecture of the orthocone nautiloids from the quarry is in agreement with that of Fisher and Teichert (1969). The outer walls of "Orthoceras" unicamera and Pseudorthoceras knoxense consist of three thin nacreous aragonite layers. The septa are also nacreous. The cameral deposits, however, have a radial-fibrous microarchitecture and contain organic material. This organic material is not as rich in the aragonite of the endosiphuncular deposits, which appear to be extensions of the aragonite of the cameral deposits. In some quarry specimens, especially those from only slightly asphaltic units, the shells and cameral deposits have been partly replaced by calcite, with resulting partial obliteration of microarchitecture. To complete the spectrum of varying degrees of alteration, a specimen of Pseudorthoceras knoxense from outside of the quarry was found to consist entirely of calcite with total obliteration of the former shell microarchitecture.

Stehli (1956) also reported that the external shell of Pseudorthoceras knoxense was found to consist entirely of aragonite but that the cameral deposits always have variable amounts of replacement calcite.

Lowenstam (1963a, p. 189) reported that Hare studied the amino acid composition of the decalcified organic matrices from original aragonites in the walls and cameral deposits of quarry specimens of Pseudorthoceras knoxense. The ratios of these amino acids are similar to those in organic matrices in Recent molluscan skeletal carbonates.

Much work has also been done on the ultrastructure of such organic matrices from quarry specimens of Pseudorthoceras knoxense. Micrographs of these conchiolin sheets are figured in Grégoire and Teichert (1965) and in Teichert (1964, K16-K19).

The fact that organic matrices occur in the cameral deposits of nautiloids from the Buckhorn asphalt quarry clearly proves these deposits to be original organic precipitates, as pointed out by Lowenstam (1963a, p. 189). Two modes of formation of these cameral deposits have been discussed, based on specimens from the Buckhorn asphalt quarry, by Fisher and Teichert (1969, p. 21-28). Both involve formation after the development of the rest of the shell. These processes are deposition from tissues within the chambers and deposition from cameral fluids. The results of this present investigation strengthen the thesis that the cameral and endosiphuncular deposits formed by a vital process different from that involved in the formation of the walls and septa.

The shell wall and septal aragonites of "Orthoceras" unicamera and Pseudorthoceras knoxense have lower Sr contents relative to the associated cameral and endosiphuncular deposits (see Table IV and Fig. 12). These large Sr differences are apparently due to the "vital effect" of the organism. An alternative explanation for the Sr differences is that there has been diffusion of the Sr out of the shell walls and septa. This seems unlikely since 1) Lowenstam (1963b, p. 127) also found high Sr contents in the skeletal aragonites of Euphemites sp. from the Buckhorn asphalt quarry, and 2) such a diffusion process undoubtedly would have been related to temperatures in excess of those

TABLE IV

MG AND SR CONTENTS IN ORTHOCONE NAUTILOID ARAGONITES

FROM THE BUCKHORN ASPHALT QUARRY

Asphalt-Impregnated Specimen	Shell Layer	No. of Analyses	$(Sr/Ca)\times10^{-3}$ (atom)
"O". unicamera	Wall	3	1.09 ± 0.16
	Septum	2	1.65 ± 0.23
	Cameral deposits	1	5.82 ± 0.47
	Endo-siphuncular deposits	1	6.50 ± 0.52
P. knoxense	Wall	1	1.33 ± 0.20
	Cameral deposits	2	7.15 ± 0.57
	Endo-siphuncular deposits	1	7.01 ± 0.56

to which the quarry rocks were ever subjected. If such higher temperatures (i.e., about 400° to 500°C) had affected the quarry strata after the time of oil impregnation, which would have been early in the post-depositional history of the rocks, there would be no asphalt in the quarry today. According to Abraham (1929, p. 44), when asphalt is heated at 450° to 700°C depolymerization occurs and only a residue of coke is left. Furthermore, if these high temperatures had existed in the quarry before the oil impregnation, the skeletal aragonites would have undoubtedly inverted to calcite. According to Johnston and Williamson (1916), a temperature of 400°C will rapidly invert aragonite to calcite by a dry solid state (isochemical) process. The Mg contents in the aragonite orthocone nautiloid shell walls and cameral and endo-siphuncular deposits are below the detection limit of the electron microprobe (Fig. 13).

The slightly asphalt-impregnated specimen of Pseudorthoceras knoxense, which has more replacement calcite than aragonite in the cameral and endosiphuncular deposits, contains lower Sr and higher Mg contents in the cameral deposits compared to unaltered forms. A completely calcitic specimen from DB-IV-2 and 3 contains even lower Sr and higher Mg in these inner shell deposits (Figs. 12 and 13).

Odum (1951, 1957) reported Sr/Ca ratios for undifferentiated types of nautiloids from the quarry. The values plot in Figure 12 in the same area where partly altered cameral deposits plot. Hence, it would appear that he analyzed partly altered cameral deposits of orthocone nautiloids.

Hallam and Price (1966, p. 26) analyzed the strontium contents of unidentified orthocone nautiloids from the asphalt quarry. These values were all significantly lower than the Sr/Ca values they obtained for shells of Mississippian age from Scotland (Fig. 12). According to these investigators, their quarry forms were partly altered to calcite, whereas the Scotland specimens were unaltered aragonite. It is difficult to compare their data with those in the present report as they made no mention of whether the shell walls, cameral deposits, or bulk samples of the nautiloids were analyzed. The data for their quarry shells plot in Figure 12 in the area of altered cameral deposits, and their Scotland data plot below the range of well-preserved cameral deposits as presently determined.

The inner part of the shell wall of an asphalt-impregnated specimen of the coiled nautiloid Metacoceras cornutum from the quarry consists of nacreous aragonite with the organic matrices still intact. A specimen of the coiled nautiloid Domatoceras sp. has a chalky inner shell wall which does not have the nacreous microstructure preserved as well as that in the Metacoceras cornutum specimen. This chalky wall consists of about an equal mixture of replacement calcite and aragonite.

Yochelson et al. (1967) reported that a specimen of Metacoceras sp. from the Pennsylvanian Kendrick shale in Kentucky consists of all aragonite.

The Sr/Ca ratio in the shell wall of Metacoceras cornutum is, on the average, 2.52 ± 0.33, which is roughly twice those ratios for the orthocone nautiloid shell walls. The Mg content for the coiled nautiloid shell wall is below the detection limit of the electron microprobe.

In the partly altered Domatoceras sp., the Sr/Ca ratio is

1.64 ± 0.23 and lower than that for Metacoceras cornutum. Mg was analyzed for in the conch wall of Domatoceras sp. but was again below the detection limit.

The asphalt-impregnated shell walls and septa of the ammonoids Pseudoparalegoceras sp. and Wellerites mohri ? were found to consist of a chalky mixture of approximately equal amounts of nacreous aragonite and intermixed replacement calcite, based on single specimens of each. The Sr/Ca ratios are 2.36 ± 0.31 and 1.88 ± 0.24, respectively (Fig. 12).

The Sr/Ca values for two Mississippian age goniatite ammonoids, analyzed by Hallam and Price (1966) plot in Figure 12 just above those values for the analyzed goniatites from the quarry.

As with the other molluscan aragonites from the quarry, the Mg contents for the ammonoids are below the detection limit of the electron microprobe (Fig. 13).

The inner layers of two asphalt-impregnated specimens of the bivalve Chaenocardia ovata have most of the crossed-lamellar micro-architecture preserved. The layers consist of mostly aragonite with the organic matrices presumably still intact and with intermixed replacement calcite.

Stehli (1956) also reported that the inner layer of Chaenocardia ovata consists of crossed-lamellar aragonite.

The Sr/Ca ratios of 1.33 ± 0.20 and 1.63 ± 0.23 for the two specimens are slightly lower than for other partly altered mollusks from the quarry (see Fig. 12). The Mg contents are below the detection limit of the microprobe (Fig. 13).

Nature of Diagenetic Alterations of Skeletal Aragonites

The foregoing data show that the amount of replacement calcite in the aragonitic shell layers of the quarry specimens increases with decreasing asphalt content of the stratigraphic unit in which they were deposited. It is especially apparent in the case of the specimens of *Pseudorthoceras knoxense*. In the asphalt units, the shells and internal deposits are all aragonite with well-preserved microarchitecture. In the specimen from the slightly asphaltic unit 11, the aragonite has been mostly replaced by calcite, with resulting partial obliteration of the microarchitecture. Furthermore, the specimen from a nonasphaltic unit outside of the quarry consists entirely of replacement calcite with total obliteration of the microarchitecture. The Sr contents in the cameral deposits are higher in the aragonitic skeletons and lower in the calcitic specimens. The corresponding Mg contents vary in the opposite way.

The inner aragonitic layer of *Straparollus* (*Euomphalus*) sp. from unit 11 has more intermixed replacement calcite, lower Sr content, and also higher Mg content relative to other aragonitic gastropod layers from asphalt-impregnated units.

In those fossiliferous units in the quarry where there is only slight to no asphalt impregnation (i.e., units 11 and 12), there is more cementation and dolomitization, and even some silification and calcite veinlet formation, relative to the more asphaltic quarry units. Thus, these units have been affected by solutions (probably ground waters) which have caused significant diagenetic changes.

This correlation of increasing diagenetic alteration with decreasing asphalt content, therefore, lends support to the interpretation that the replacement calcite in these shells formed by a process of dissolution of the aragonite and precipitation of the calcite.

Skeletal Calcites

Determining whether a calcitic skeletal element was originally calcite or was altered diagenetically to calcite is one of the more difficult tasks encountered in mineralogical work on fossil skeletons. Perhaps even more difficult is the differentiation between original calcites with low Mg contents from replacement calcites also with low Mg contents without stable isotope determinations.

Criteria most likely to infer original skeletal calcites are 1) if the original microarchitecture of the skeletal carbonates is preserved, 2) if color patterns are preserved, and 3) if the Mg content of the skeletal calcite is in excess of the amounts normally found in diagenetically altered skeletal calcites. According to Goldsmith (1960) "...diagenetically altered fossils have usually only traces of Mg in the carbonates and contain, even in exceptional cases, no more than 3 mol percent of $MgCO_3$".

For the present study, wherever possible, the Mg contents of asphalt-impregnated skeletal calcites from the quarry will be compared with those in the same species outside of the quarry. If the altered specimens from outside the quarry have Mg contents significantly lower than those in the quarry, it seems reasonable to suspect that the quarry specimens are, at least, closer to the original Mg contents.

The tests of Globivalulina sp. and the fusulinid Wedekinellina ? sp. were determined to be composed of calcite. No patches of replacement calcite were detected in the polished sections of the single-layer walls of the specimen of Globivalulina. In each of three minute specimens of Wedekinellina ? sp. from various quarry units, only the first one or two test volutions are preserved while the others were abraded during water transport. The tunnel and chomata are clearly visible in each of these badly abraded specimens.

The Globivalulina sp. test contains 3.02 ± 0.09 mol % $MgCO_3$ (Fig. 14), and the Sr content is below the detection limit of the electron microprobe (Fig. 15). Based on the lack of obvious replacement calcite, the apparently well-preserved microstructure, and the > 3 mol % $MgCO_3$ contents, it is concluded that the test of Globivalulina sp. was originally calcite.

In Wedekinellina ? sp. the Mg contents of the tests range from 2.91 ± 0.09 to 3.49 ± 0.10 (Fig. 14), and the Sr/Ca ratios range from below the electron microprobe detection limit to 1.14 ± 0.17 (Fig. 15). For reasons stated above, the tests of Wedekinellina ? sp. are concluded to be originally calcite. The Mg contents of Wedekinellina ? sp. are similar to those reported by Lowenstam (1963a, p. 186) for middle Pennsylvanian age fusulinids; namely, 3 mol % $MgCO_3$ (Fig. 14). Odum (1957, p. 92) reported a Sr/Ca ratio of 2.26 for Pennsylvanian age Fusulina sp. with "fair" preservation (Fig. 15).

A small asphalt-impregnated colony of Chaetetes aff. favosus from the middle of the slightly asphaltic unit 11 (Pl. 13) consists of

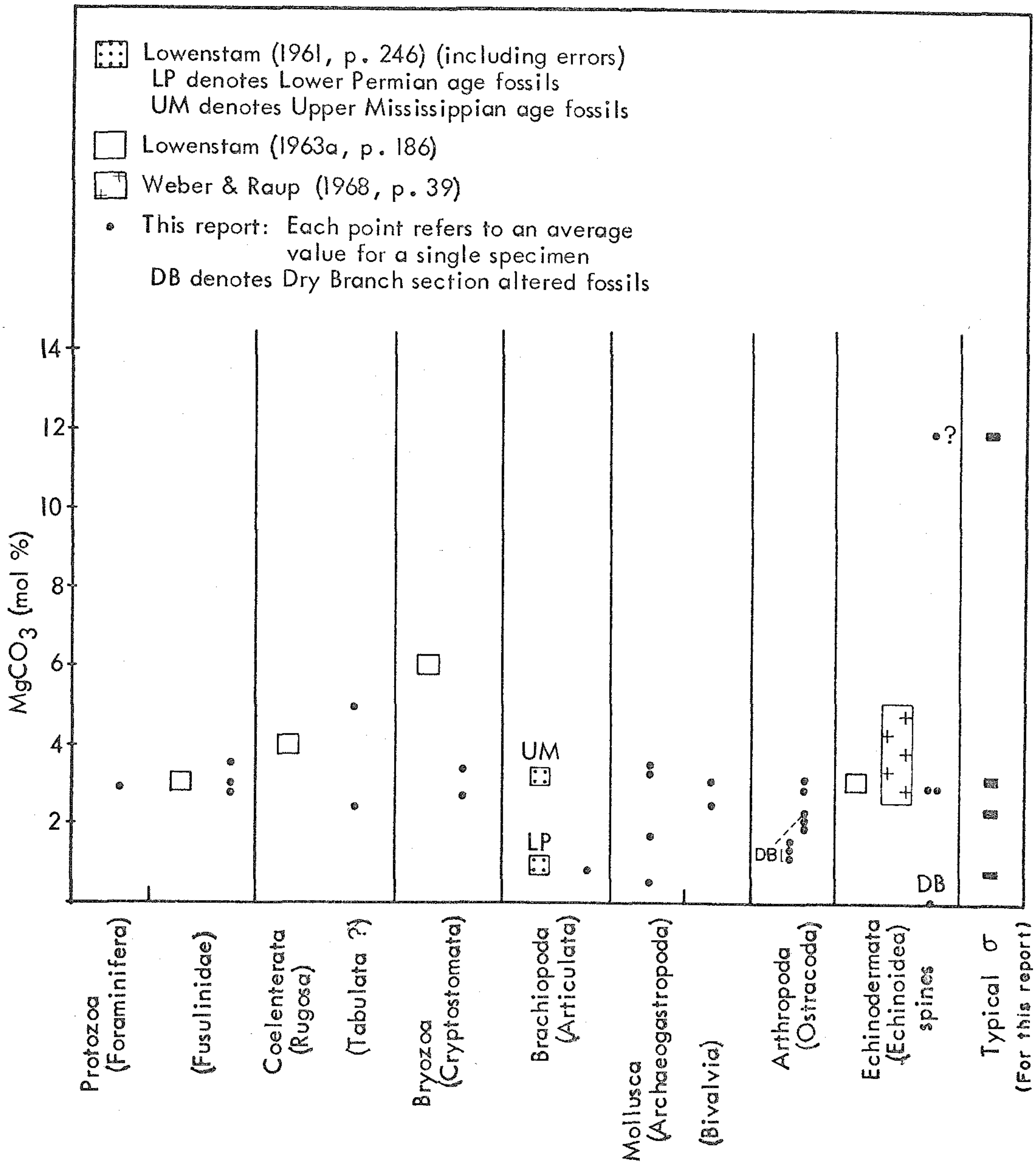


Fig. 14. $MgCO_3$ (mol percent) in middle Pennsylvanian age calcitic skeletons.

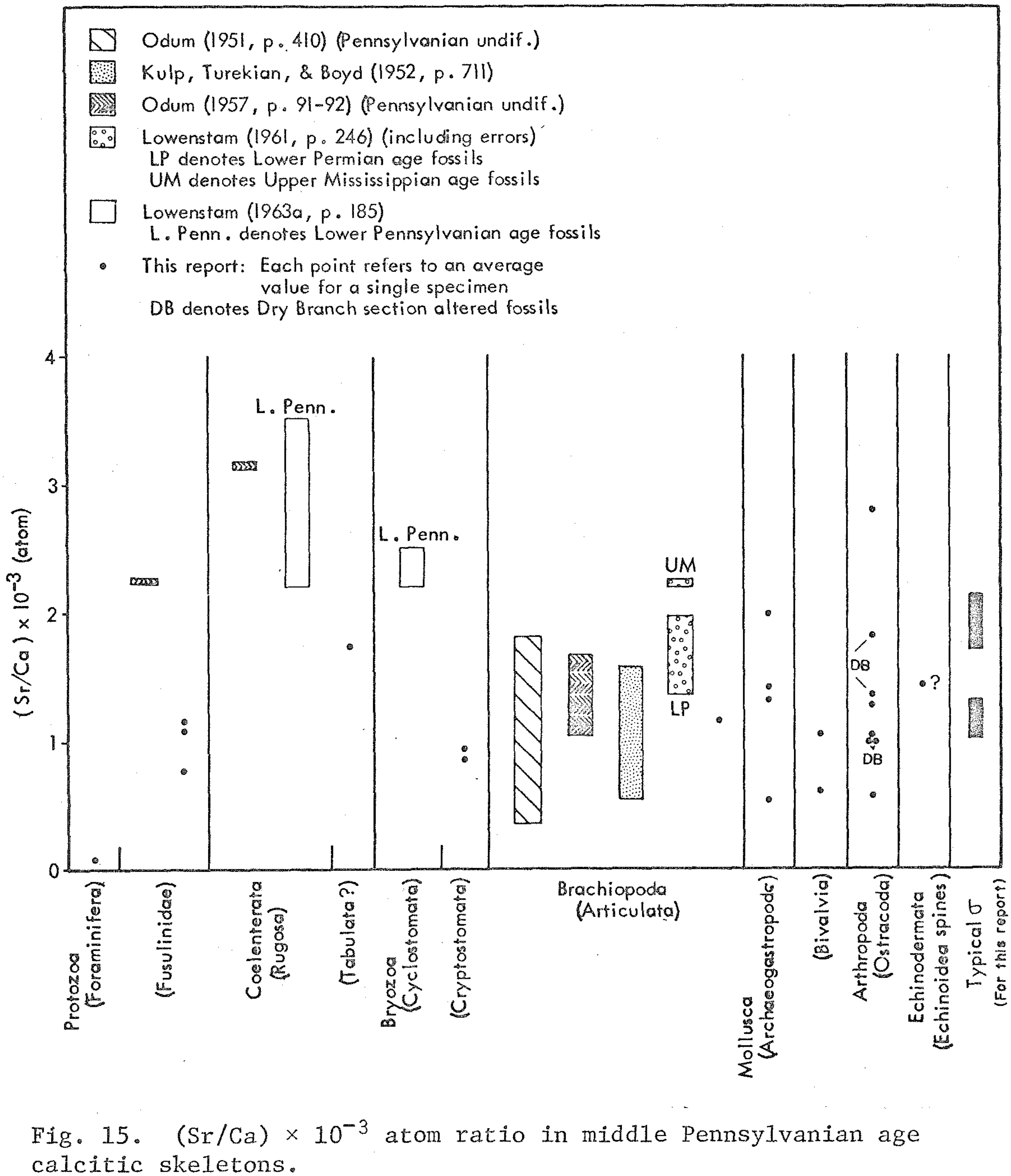
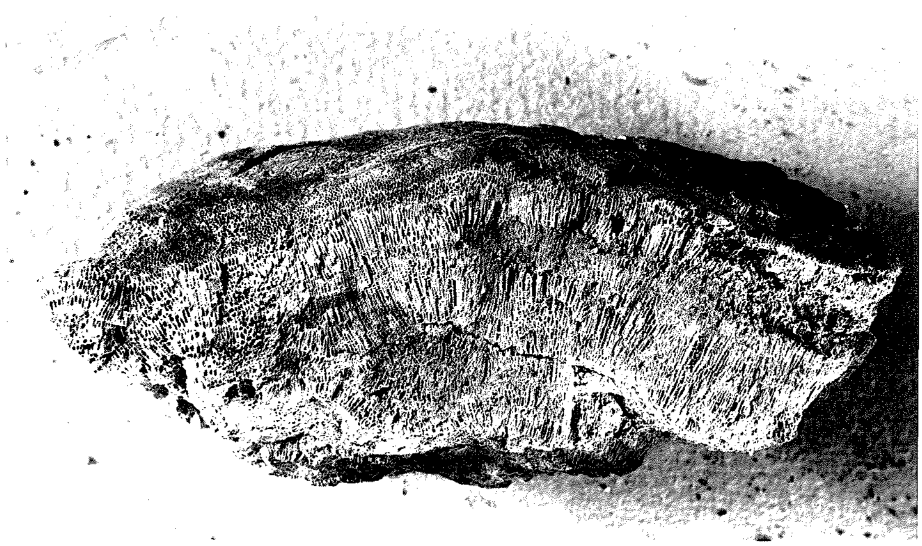


Fig. 15. $(Sr/Ca) \times 10^{-3}$ atom ratio in middle Pennsylvanian age calcitic skeletons.

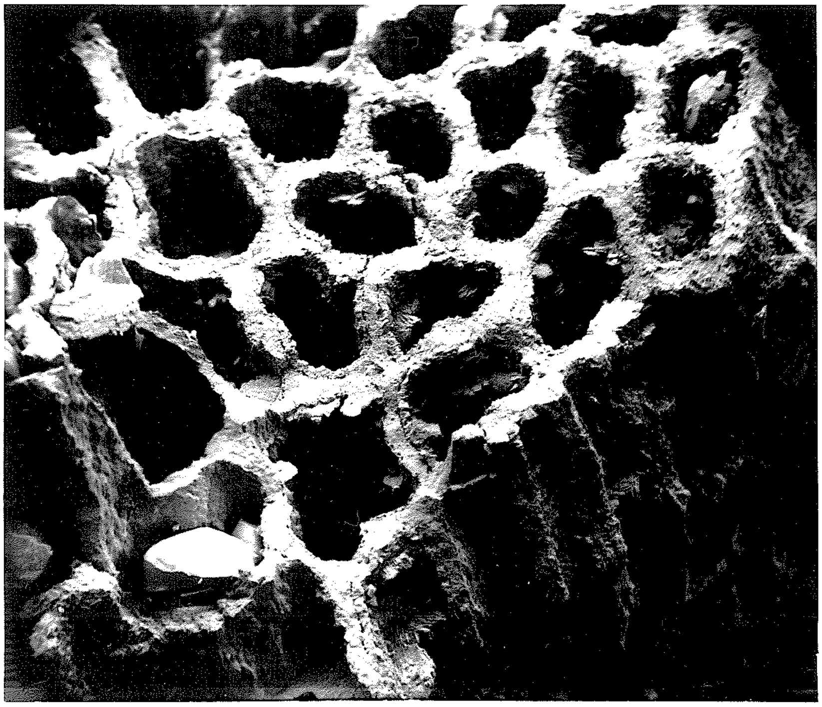


Pl. 13. Front view of a small colony of Chaetetes aff. favosus. The specimen is from the lower part of unit 11 (see Appendix II). The corallum was originally shiny black due to asphalt impregnation.

microarchitecturally well preserved brown dense calcitic corallites and tabulae rimmed by a thin transparent dolomite layer, which is on the average 0.02 mm thick (Pls. 14 and 15). Some of the corallites are also partly filled with transparent areas of blocky sparry calcite. A small asphalt-impregnated fragment of Chaetetes cf. favosus from unit 13 has "beaded" nature of the corallite walls and very well preserved microarchitecture. This fragment consists also of calcite, but there is neither dolomite coating on the walls nor secondary sparry calcite areas in the corallites. It is concluded that the dolomite coating in the previously mentioned colonial specimen is secondary in origin.

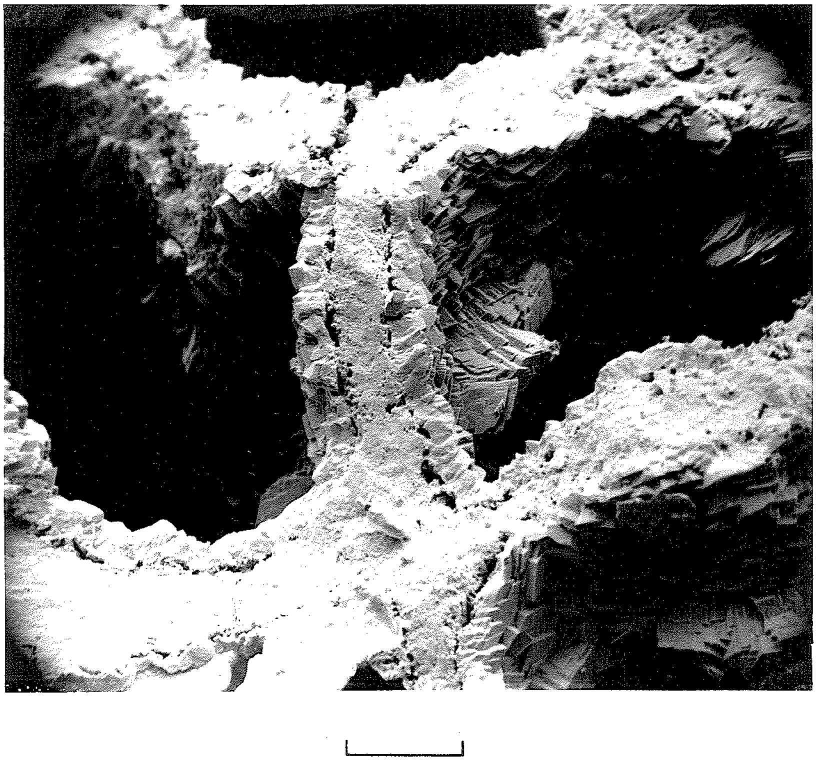
Quantitative x-ray diffraction determinations of the colonial specimen from unit 11 indicate 2.5 ± 0.5 mol % $MgCO_3$ in the bulk analysis of the calcitic corallite walls. There is, however, 5.28 ± 0.11 mol % $MgCO_3$ based on electron microprobe data. Hence, during the electron microprobe analysis of the walls, the beam must have analyzed a mixture of calcite and dolomite. The non-dolomitic fragmentary specimen of Chaetetes cf. favosus contains, on the average, 4.90 ± 0.10 mol % $MgCO_3$, based on electron microprobe data. This amount of Mg represents the highest for any fossil studied from the quarry.

The Sr contents are lower in the colonial specimen than in the fragmentary specimen. This may be the result of dolomite interferences integrated during the electron microprobe analyses. The corallite walls in the colonial specimen have Sr contents below the detection limit of the electron microprobe, whereas the corallite walls in the fragmentary specimen have, on the average, a Sr/Ca ratio of 1.74 ± 0.23.



0.5 mm

Pl. 14. Scanning electron microscope picture of top view of part of the same colony of Chaetetes aff. favosus depicted in Plate 13. Note the thin dolomite coating surrounding most of the calcitic corallite walls. In some cases, the dolomite coating occurs in the form of small protuberances. The large single crystals in the lower left and upper right corners are calcite.



Pl. 15. Scanning electron microscope picture of a close-up of part of the specimen of Chaetetes aff. favosus depicted in Plate 14. The platy dolomite coating is distinctively different than the dense corallite walls which consist of calcite.

These data indicate that 1) the skeletons of Chaetetes sp. in the quarry were originally composed of calcite, 2) the Mg contents of the walls were at least about 5 mol % $MgCO_3$, but could have been considerably higher, and 3) the Sr/Ca ratios of the walls were at least 1.7, but possibly also higher.

The approximately 5 mol % $MgCO_3$ content in the calcitic walls of the quarry specimen of Chaetetes cf. favosus is slightly higher than the 4 mol % $MgCO_3$ reported by Lowenstam (1963a, p. 186) for rugose corals of lower Pennsylvanian age (Fig. 14).

Odum (1957, p. 91) reported a Sr/Ca ratio of 3.16 on a "poorly" preserved tetracoral of Pennsylvanian age (Fig. 15). Lowenstam (1963a, p. 185) reported a range in Sr/Ca ratios from about 2.2 to 3.6 for rugose corals of lower Pennsylvanian age (Fig. 15).

The quarry Chaetetes sp. specimens were compared to coelenterates of similar geologic age because this genus has been referred to as belonging to tabulate corals by Moore, Lalicker, and Fischer (1952, p. 113) and Hill and Stumm (1956). Based on studies of Recent specimens of six species of sponges with skeletons composed of siliceous spicules, organic matrices, and aragonite, Hartman and Goreau (1970, p. 228) suggested that Chaetetes sp. may be a coralline sponge. Comments on the comparison between the skeletal mineralogy of the quarry Chaetetes sp. and these Recent coralline sponges are included in Part VIII of this report.

The microarchitecture of the asphalt-impregnated single specimens of the cryptostome bryozoans, Penniretepora ? sp. and Streblotrypa ? sp. could not be readily determined due to the fact that the minute specimens were used for microprobe studies rather than thin-sectioned. As seen in polished sections for microprobe study, the coenosteum in each appears to consist of dense-looking calcite, and the zooecia are free of secondary calcite or dolomite in fillings.

The colonial walls of the Penniretepora ? sp. specimen contain 2.75 ± 0.08 mol % $MgCO_3$ and have a Sr/Ca ratio of 0.95 ± 0.14. The walls of the Streblotrypa ? sp. specimen contain on the average 3.30 ± 0.10 mol % $MgCO_3$ and have Sr contents below the detection limit of the electron microprobe.

These data indicate that the bryozoan skeletons probably consisted originally of calcite. The Mg and Sr contents are most likely diagenetically altered because they are much lower than other similar geologic age bryozoan calcites. Lowenstam (1963a, p. 185-186) reported a value of 6 mol % $MgCO_3$ for calcitic cryptostome bryozoa of lower Pennsylvanian age, and he reported a range in Sr/Ca ratios from about 2.2 to 2.5 for cyclostomata bryozoa of Lower Pennsylvanian age.

Most of the brachiopods were recovered as steinkerns in asphalt-poor units of the quarry. One specimen, however, was recovered from the asphaltic unit 7. The specimen occurred on a weathered surface of this otherwise asphaltic unit. This shell with pearly luster and prismatic shell microstructure was determined to be composed of calcite. On the average, this specimen contains 0.83 ± 0.06 mol % $MgCO_3$ and a Sr/Ca ratio of 1.14 ± 0.17 (Figs. 14 and 15).

The data indicate that the shell of this brachiopod was originally calcite, but the fact that the specimen occurred on an asphalt-depleted rock surface most likely means that the Mg and Sr contents are altered.

Lowenstam (1961 and 1963c) reported the Mg and Sr contents of late Mississippian and early Permian age brachiopods (Figs. 14 and 15). Anthracospirifer opimus has significantly lower Mg and Sr contents compared with the late Mississippian age brachiopods. In comparison with the early Permian age brachiopods, Anthracospirifer opimus has similar Mg and slightly lower Sr contents. A proper evaluation of these comparisons is dependent upon a knowledge of the paleoenvironmental temperatures which Anthracospirifer opimus experienced. Without such temperature data, it is not possible to distinguish whether there have been diagenetic effects leading to reduction in Mg and Sr in Anthracospirifer opimus, and/or whether the various similarities and differences are due to temperature effects.

The Anthracospirifer opimus Sr/Ca value plots within the ranges of the Sr/Ca values for other Pennsylvanian age articulate brachiopods reported by Odum (1951, 1957) (Fig. 15). The quarry brachiopod, furthermore, has a Sr/Ca value which would plot within the middle of the range of values, reported by Kulp, Turekian, and Boyd (1952, p. 711), for Desmoinesian age articulate brachiopods from the boggy shale (lower-Middle Deese group equivalent) about 20 miles northeast of the investigated area. In addition, this particular range of Sr/Ca values is similar to the range reported by the same investigators for another, slightly older age brachiopod and for a younger brachiopod assemblage of Missourian age (Pennsylvanian) from the Lower Francis formation from the same region.

The outer shell layers of the gastropods Straparollus (Euomphalus) sp., Naticopsis wortheni, and Trachydomia whitei all have well preserved prismatic microarchitecture. These outer layers consist of calcite, and in Naticopsis wortheni this layer still retains the original color pattern (Pl. 6).

Stehli (1956) reported that the outer layer of Straparolus (Amphiscapha) consists of calcite, as did Yochelson et al. (1967). The outer calcitic layer in Straparollus (Euomphalus) sp. is a feature of the suborder Macluritina to which it belongs (Knight et al., 1960, p. I184). Furthermore, the outer calcite layers found in Naticopsis wortheni and Trachydomia whitei are in agreement with the features of their suborder Neritopsina. It is noteworthy that Neritopsina gastropods have an outer layer which commonly shows preserved color patterns (Knight et al., 1960, p. I275).

The badly altered specimen of the gastropod Bellerophon (Bellerophon) sp. has a quartz-replaced outer layer. According to Yochelson et al. (1967, p. D77), however, the outer layer of Bellerophon (Pharkidonotus) sp. originally consisted of aragonite.

The Mg and Sr contents of each of the gastropods with a preserved outer calcitic layer are shown in Table V.

The wide range in these Mg contents seems to be most likely correlated with the nature of the sealing agent. The specimen of Naticopsis wortheni, for example, was asphalt-impregnated when found. It has the original color pattern preserved in the outer layer, and it has the lowest Mg concentration. On the other hand, the specimen of Straparollus (Euomphalus) with the highest Mg concentration was not

TABLE V

MG AND SR CONTENTS IN GASTROPOD SKELETAL CALCITES

FROM THE BUCKHORN ASPHALT QUARRY

Specimen	Sealing Agent	No. of Analyses	mol % $MgCO_3$	$(Sr/Ca)\times10^{-3}$ (atom)
S. (*Euomphalus*) sp.	C	1	3.58±0.11	1.98±0.26
S. (*Euomphalus*) sp.	sAsp	1	3.45±0.10	1.30±0.20
S. *wortheni*	Asp	1	0.43±0.07	1.41±0.22
T. *whitei*	mAsp	1	1.68±0.07	<1.0

Explanation

Asp - Asphalt   sAsp - Some asphalt

mAsp - Mostly asphalt   C - Calcite

asphalt-impregnated when taken from the outcrop. Thus, in spite of the greater than 3 mol % $MgCO_3$ in the calcites of the Straparollus (Euomphalus) sp. specimens, they appear to have the most altered Mg contents. Such a result is surprising, as one usually finds just the opposite.

As for the Sr contents in the outer layers of the same gastropod specimens, there is no apparent correlation in the amount of Sr versus the degree of asphalt impregnation. The usage of this data is hampered by the large errors associated in measuring such low concentrations of Sr by means of the electron microprobe.

Kulp, Turekian, and Boyd (1952, p. 707 and 712) have reported a Sr/Ca = 0.12 for Bellerophon crassus, a Desmoinesian age gastropod, and a Sr/Ca = 0.10 for Worthenia cf. tabulata, a Missourian age gastropod. These values are not useful, however, for there is no mentioning as to which shell layer or mineralogy each of the values correspond to.

The outer layers in the two specimens of Chaenocardia ovata consist of well preserved prismatic microarchitecture. These prismatic layers are calcitic. Stehli (1956) also reported an outer calcitic layer for Chaenocardia ovata.

Both analyzed bivalve specimens were asphalt-impregnated and the range in Mg concentration for the calcitic outer layer is 2.61 ± 0.08 to 3.24 ± 0.10 (Fig. 14), and the range in Sr/Ca ratios is from below the detection limit of the electron microprobe to 1.03 ± 0.16 (Fig. 15). Although it can be concluded that the outer layer was originally calcite, the Mg and Sr contents may have been originally different.

Detailed analyses of the microarchitecture of the various ostracode tests were not obtainable due to the fact that the specimens were used for microprobe studies rather than thin-sectioned. Each of the types, whether from the quarry or not, consists of a single-layer carapace which is calcitic.

The Mg and Sr contents in the various specimens are summarized in Table VI.

All the quarry specimens were asphalt-impregnated, and these all have higher Mg and lower Sr contents than the nonasphalt-impregnated specimens, except in the case of Cavellina sp. In the quarry specimen of Cavellina, the Mg content is lower and the Sr content is higher than in the nonasphalt-impregnated specimen.

It is clear that the nonasphalt-impregnated specimens of Hypotetragona sp., Proparaparchites sp., and Bairdia spp. have more altered Mg and Sr contents relative to the respective quarry forms. In the case of Cavellina sp., however, the two types of specimens have the same degree of preservation. The lowest Mg content of a quarry ostracode, excluding Cavellina sp., is higher than the maximum Mg content in any nonasphalt-impregnated specimen. Unlike the Mg concentrations, however, the Sr/Ca ratios for nonasphalt-impregnated specimens, excluding Cavellina sp., fall within the range for the quarry specimens. Thus, the Sr/Ca ratios for the quarry specimens, appear to be more altered than are the Mg contents.

Several large asphalt-impregnated fragments of the primary spines of the echinoid Archaeocidaris megastyla ? found in the quarry have porous to massive stereoms consisting of interlocking lamellae and trabecula. These spines consist of mixtures of calcite and dolomite,

TABLE VI

MG AND SR CONTENTS IN OSTRACODE SKELETAL CALCITES

FROM THE BUCKHORN ASPHALT QUARRY AND VICINITY

		Stratigraphic Location	No. of Analyses	mol % $MgCO_3$	$(Sr/Ca)\times10^{-3}$ (atom)
Hypotetragona sp.		Quarry	2	3.35 ± 0.10	<1.0
		DB-IV-2&3	2	1.22 ± 0.07	0.98 ± 0.15
Proparaparchites sp.		Quarry	1	3.04 ± 0.09	1.26 ± 0.19
Bairdia spp.	Sp.A.	Quarry	1	2.25 ± 0.07	1.03 ± 0.16
	Sp.B.	DB-IV-1	2	1.41 ± 0.07	1.36 ± 0.20
Cavellina sp.		Quarry	2	2.03 ± 0.08	2.78 ± 0.34
		DB-III	1	2.10 ± 0.08	1.82 ± 0.24

with trace amounts of SiO_2. Each of the nonasphalt-impregnated specimens from outside of the quarry is massive with most of the former stereom microstructure obliterated. These spines also consist of mixtures of calcite and dolomite with trace amounts of SiO_2. The medulla of all the spines consist of minute crystals of replacement calcite.

One of the quarry specimens (i.e., Specimen 2, see Appendix II), which has a porous to massive stereom, contains 3.00 ± 0.50 mol % $MgCO_3$ (Fig. 14), as determined by means of x-ray diffraction in a bulk analysis of the spine fragment. In addition, approximately 15 weight percent of dolomite was detected along with a minor amount of SiO_2. An aliquot of the same spine contains, on the average, 12.00 ± 0.12 mol % $MgCO_3$, as calculated from electron microprobe data. It is apparent that during the electron microprobe analysis, both calcite with low magnesium contents and dolomite were simultaneously analyzed. A material balance of Mg exists between the x-ray and electron microprobe analyses, as shown in Appendix II. The dolomite is uniformly scattered throughout the spine, as evidenced by the mottled appearance of the polished surface when stained with alizarin red-S. Also, the electron microprobe analyses are similar in terms of Mg content, except for one spot.

Another porous spine from the quarry (i.e., Specimen 1, see Appendix II) also contains 3.00 ± 0.50 mol % $MgCO_3$ (Fig. 14), as determined by means of x-ray diffraction analysis. In addition, there is a trace amount of dolomite and a trace of SiO_2. An aliquot of the same spine contains, on the average, 6.57 ± 0.13 mol % $MgCO_3$, as calculated from electron microprobe data. As with the other spine, the finely disseminated dolomite was analyzed simultaneously with the calcite during the electron microprobe analyses.

The approximately 3 mol % $MgCO_3$ in these quarry echinoid calcites falls within the range of Mg content in Archaeocidaris sp. spines of Pennsylvanian age reported by Weber and Raup (1968, p. 39). They reported a range in Mg for five specimens as from 2.8 to 5.3 mol % $MgCO_3$.

The Sr/Ca ratios for these quarry spines range between 1.42 ± 0.20 and 2.33 ± 0.31. There may be, however, some effect on these electron microprobe-determined Sr contents due to the dolomite and SiO_2 interferences. Perhaps the most representative specimen is Specimen 1, which contains only a trace of contaminants, 3 mol % $MgCO_3$, and an average Sr/Ca ratio of 1.42 ± 0.20. This Sr/Ca ratio is plotted in Figure 15.

One of the spines from outside of the quarry (i.e., Specimen 4, see Appendix II), consists of calcite, with Mg contents below the detection limit as determined by x-ray diffraction analysis, 4 to 5 weight percent dolomite, and a small amount of SiO_2. Based on electron microprobe data, there is an average 2.37 ± 0.10 mol % $MgCO_3$ in the spine. The beam integrated Mg contents of both calcite and dolomite. The Mg contents obtained from the electron microprobe and x-ray diffraction analyses are in agreement, as shown in the Appendix II. The electron microprobe determined Sr contents in these nonasphalt-impregnated spines are probably not representative due to the dolomite and SiO_2 interferences.

The medulla of both the quarry and nonasphalt-impregnated spines consist of replacement calcite with Mg and Sr contents, in most cases, below the detection limit of the electron microprobe. One quarry specimen (i.e., Specimen 2, see Appendix II) contains 1.90 ± 0.08 mol % $MgCO_3$. Calcitic cements in the quarry asphaltic units have similar Mg and Sr contents. The Mg contents range from 1.19 ± 0.06 to 1.61 ± 0.07, and the Sr contents are below the detection limit of the electron microprobe.

Nature of Diagenetic Alterations of Skeletal Calcites

Although obvious replacement calcite was not detected in any of the skeletal calcites in the asphalt quarry, it has been shown that wide ranges occur in the Mg contents of the gastropod and ostracode skeletal calcites.

The outer calcitic layers in the asphalt-impregnated gastropods contain more Mg than do corresponding layers in poorly to nonasphalt-impregnated specimens (i.e., from unit 11). In the walls of the ostracode tests, the asphalt-impregnated specimens of three genera have more Mg and less Sr than the corresponding congeneric nonasphalt-impregnated specimens from DB-IV. Unit 11 and DB-IV beds are more cemented than the asphaltic quarry beds. In unit 11, furthermore, there has also been dolomitization, silicification, and replacement calcite formation. Unit 11 and the DB-IV beds, therefore, have been chemically affected by percolating ground waters.

The skeletal calcite in Anthracospirifer opimus apparently has lower Mg and Sr contents relative to similar age specimens analyzed by others. The reason for this is undoubtedly related to the fact that the specimen occurred on an asphalt-depleted rock surface.

It is apparent, therefore, that the asphalt-impregnated gastropod and ostracode skeletal calcites are less altered than in corresponding less asphalt-impregnated or nonasphalt-impregnated specimens. The process of alteration, in most cases, probably involved partial dissolution of the original calcite and precipitation of replacement calcite. The process of dolomite formation in the seemingly microstructurally well preserved quarry echinoid spines may have occurred in a manner similar to that in the Falmouth formation of Jamaica, as proposed by Land and Epstein (1970, p. 196). In the Falmouth formation this dolomitization has occurred by "redistribution of available Mg in the Mg-calcite (red algae) clasts, accompanying some incongruent dissolution and loss of Mg commonly at the rim of the clasts". This process is not completely understood, as stated by Land and Epstein (1970), but it is clear that there is c-axis for c-axis replacement of the Mg-calcite by either calcite or dolomite. Such a replacement process results in preservation of most of the original microstructure. Based on Land's (1967) investigations into the nature of stabilization of Mg-calcites by dissolution, Land (1970) was able to offer the following reaction to possibly explain a similar Mg redistribution in the Middle Pleistocene Belmont formation of Bermuda.

$$\text{Mg-Calcite} + Ca^{2+} \rightarrow \text{Calcite (replacement product)} + Mg^{2+}(aq)$$

If the Mg in the dolomite, as well as in the calcite, in each quarry spine originally came from a high-Mg calcite, then it would mean that there had to be a closed system, as might have been provided by the sealing nature of the asphalt. Furthermore, it would then be possible to calculate the amount of original Mg-calcite, providing there was no $MgCO_3$ lost prior to sealing by oil. Such a calculation, shown below, has been made for one of the echinoid spines (i.e., Specimen 2, see Appendix II) from the middle of unit 9. Based on x-ray diffraction studies, there is 15 wt % dolomite associated with 85 wt % of calcite (errors unknown, see Appendix I) which contains 3.0 ± 0.5 mol % $MgCO_3$. The reaction is based on the one proposed by Land (1970).

$(CaMg)CO_3$ Original Reactant	→	$CaMg(CO_3)_2$ Dolomite	+	$(Ca_{0.97}Mg_{0.03})CO_3$ Calcite
100 wt %	→	15 wt %	+	85 wt %
		$\frac{15\ \text{wt}\ \%}{184.4\ \text{GFW}}$		$\frac{85\ \text{wt}\ \%}{99.6\ \text{GFW}}$
		0.08 moles	+	0.85±0.001 moles

moles needed of original reactant $(CaMg)CO_3$

to account for 0.08 moles $CaCO_3$ in dolomite	0.08
to account for 0.08 moles $MgCO_3$ in dolomite	0.08
to account for 0.825 moles $CaCO_3$ in calcite	0.825±0.005
to account for 0.025 moles $MgCO_3$ in calcite	0.025±0.005
Total	1.000 moles

moles of $MgCO_3$ in original reactant = (0.08+0.025±0.005) = 0.105±0.005

mol % of MgCO in original reactant:

$$\frac{0.105\pm0.005}{1.00} \times 100 \cong 10.5\pm0.5 \text{ mol \% } MgCO_3$$

If no Mg was lost prior to oil sealing of the spine, the calcite could have contained as much as 10.5 mol % $MgCO_3$. Such a value will be compared to the Mg contents in Recent echinoid spines in Part VIII of this report.

The dolomite in the quarry echinoid spines may have been due to dolomitizing solutions. Such solutions, possibly enriched with migrating biogenic Mg, apparently caused the formation of dolomite layers within the corallites of colonies of *Chaetetes* aff. *favosus* in the only slightly asphaltic unit 11. Furthermore, such solutions were probably responsible for the formation of minute dolomite rhombs in units 11, 12 and, to a lesser degree, in unit 13.

A third explanation of the dolomite in the spines is exsolution of Mg from Mg-calcite. Graf and Goldsmith (1956) investigated this phenomenon and concluded that at earth surface conditions it would be an infinitely slow process. Land (1967, p. 916), furthermore, mentioned that such a process is "...not certainly known to have occurred during natural diagenesis". Thus, it seems that an exsolution process to account for the spine dolomite is a more remote possibility.

The reason for the lesser amount of dolomite and presence of Mg-free calcites in the DB-IV section spines relative to the quarry spines may possibly be due to diagenetic events which affected the DB-IV section spines, but did not affect the quarry spines because of the oil impregnation.

VIII. COMPARISON OF THE MG AND SR CONTENTS OF SKELETAL CARBONATES FROM THE BUCKHORN ASPHALT QUARRY WITH THOSE IN RELATED RECENT FORMS

Skeletal Aragonites

Unfortunately, the inner aragonitic crossed lamellar layers of the quarry gastropods show varying degrees of alteration. The *Trachydomia whitei* specimen, however, shows the least amount of alteration, as the aragonite content of the inner layer exceeds the amount of replacement calcite. The Sr/Ca ratio for the shell layer in this specimen (Fig. 12) would plot within the lower part of the range in Sr/Ca ratios for Recent gastropod aragonitic shell layers, as reported by Thompson and Chow (1955) (Fig. 16). Odum (1957) and Lowenstam (1963b), however, reported higher Sr/Ca ratios in Recent gastropod aragonites (Fig. 16).

Lowenstam's (1963b) reported Sr/Ca ratio of 5.9 for the aragonite layer in *Euphemites* sp. from the Buckhorn asphalt quarry represents a Sr/Ca ratio for an unaltered aragonite. This ratio is much higher than the range in ratios for Recent forms. This trend in Sr/Ca ratios in gastropods has been investigated by Lowenstam (1963b). He concluded that "...the increase in Sr/Ca ratios in the gastropod shells with increase in geologic age...reflects biochemical evolutionary changes of increased discrimination by the gastropod against Sr to Ca from the late Paleozoic to the present." (Lowenstam, 1963b, p. 114).

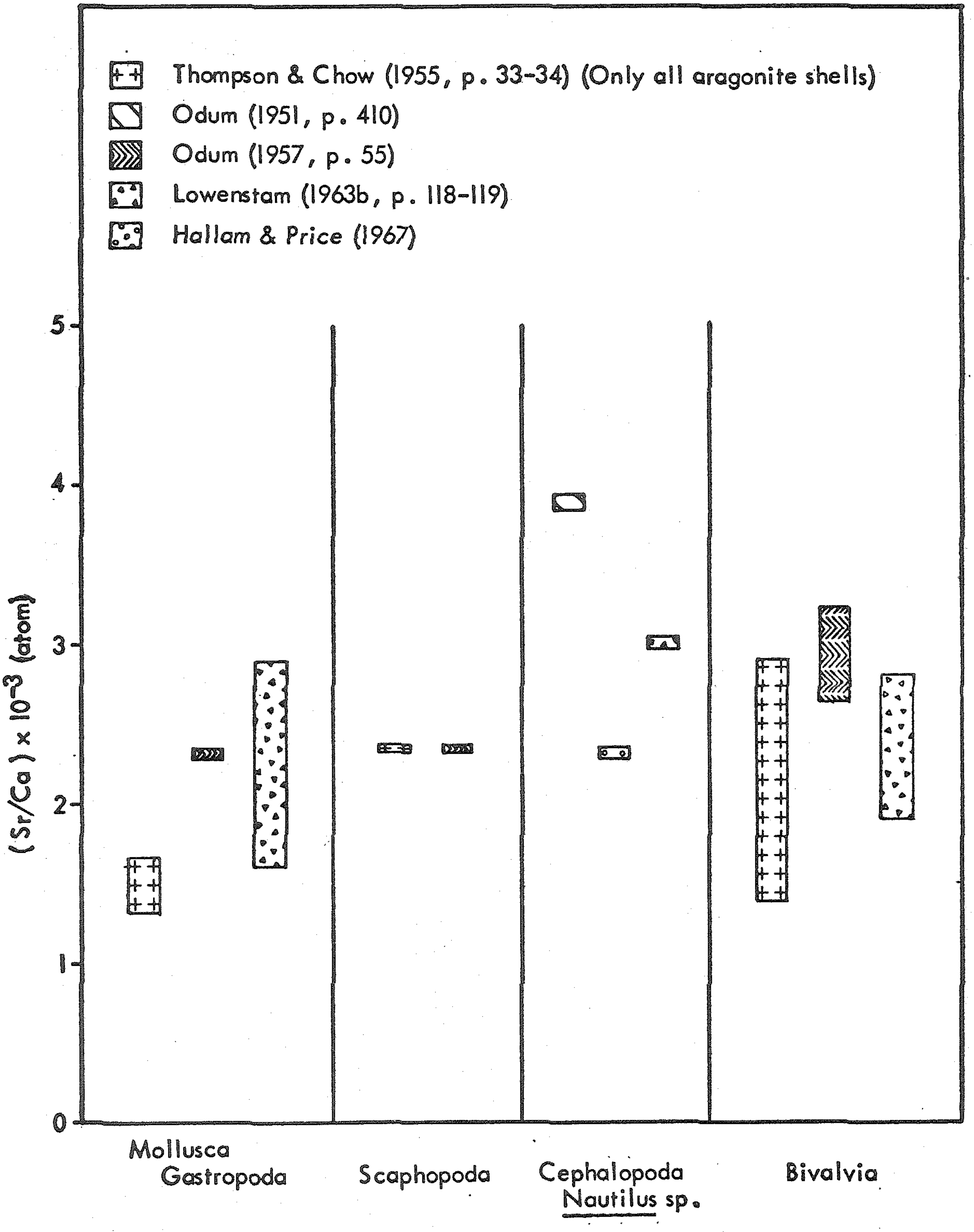


Fig. 16. (Sr/Ca) x 10^{-3} atom ratio in Recent aragonitic skeletons.

The Mg content in the partly altered aragonite in Trachydomia whitei (Fig. 13) is much higher than those reported by Chave (1954) and by Lowenstam (1963a) for Recent gastropod aragonites (see Fig. 17).

The only Recent form of a cephalopod with an external aragonitic shell is the coiled nautiloid Nautilus sp. The Sr/Ca ratio (Fig. 12) in the shell wall of the quarry specimen of Metacoceras cornutum is similar to the Sr/Ca ratios in the shell walls of Nautilus sp. reported by Hallam and Price (1967) and Lowenstam (1963b) (Fig. 16). Odum's (1951) Sr/Ca ratio for Nautilus sp. is somewhat higher (Fig. 16). The Mg content of the shell wall of Metacoceras cornutum is below the detection limit of the electron microprobe (Fig. 13), as are the values reported for Nautilus sp. by Clarke and Wheeler (1922) and Chave (1954) (Fig. 17).

The aragonitic inner layers of the two specimens of Chaenocardia ovata from the quarry have been partly replaced by calcite. The specimen which has the least amount of replacement calcite with the aragonite has a Sr/Ca ratio (Fig. 12) which would plot in the lower part of the range of Sr/Ca ratios reported by Thompson and Chow (1955) (Fig. 16. Odum (1957) and Lowenstam (1963b), however, reported somewhat higher Sr/Ca ratio ranges for Recent bivalve aragonitic layers (Fig. 16). The Mg content in the Chaenocardia ovata specimen with the least amount of replacement calcite is below the detection limit of the electron microprobe (Fig. 13), as are most of the Mg contents reported for Recent bivalve aragonites by Chave (1954) and Lowenstam (1963a and 1964) (Fig. 17).

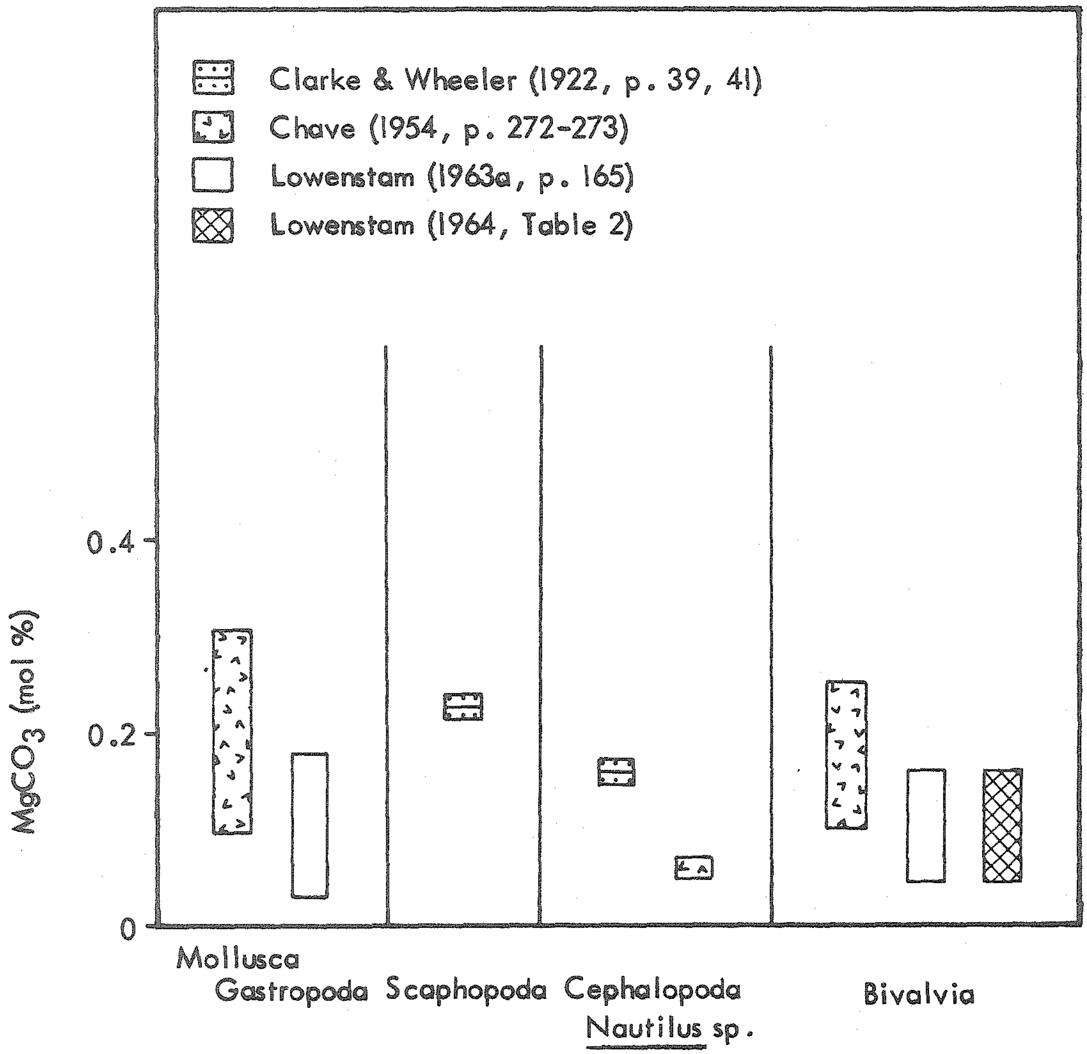


Fig. 17. $MgCO_3$ (mol percent) in Recent aragonitic skeletons.

Skeletal Calcites

The Mg contents in the quarry specimens of the foraminifera Globivalulina sp. and Wedekinellina ? sp. are about 3 mol % $MgCO_3$. These values of 3 mol % for these Pennsylvanian foraminifera would plot within the lower part of the range of concentration of Mg in Recent foraminifera (see Fig. 18). If these values are the original ones, these fossil foraminifera might possibly be included within the calcitic-low Mg (0-5 mol %) group for Recent forms, as determined by Blackmon and Todd (1959). This group includes all planktonic and some benthic forms. According to Blackmon and Todd (1959, p. 1), both high and low Mg content foraminifera types occur in identical environmental conditions. Unfortunately, no definite conclusions can be made as to the paleotemperatures which the quarry foraminifera experienced, as the Mg contents of foraminifera shells do not necessarily reflect the ambient temperature at the time of deposition of the shell carbonate.

The Sr content of the Globivalulina sp. test is below the detection limit of the electron microprobe (Fig. 15). In the fusulinid Wedekinellina ? sp., however, the Sr/Ca ratios (Fig. 15) are only about one-half of those reported by Odum (1957) and only about one-third of those reported by Thompson and Chow (1955) for Recent foraminifera Sr/Ca ratios (Fig. 19).

The data on the Mg content of Chaetetes sp. stated in this report represents the first information on the mineralogy and Mg and Sr contents of a Pennsylvanian age presumed tabulate coral. As mentioned before, Hartman and Goreau (1970), however, suggested that Chaetetes sp.

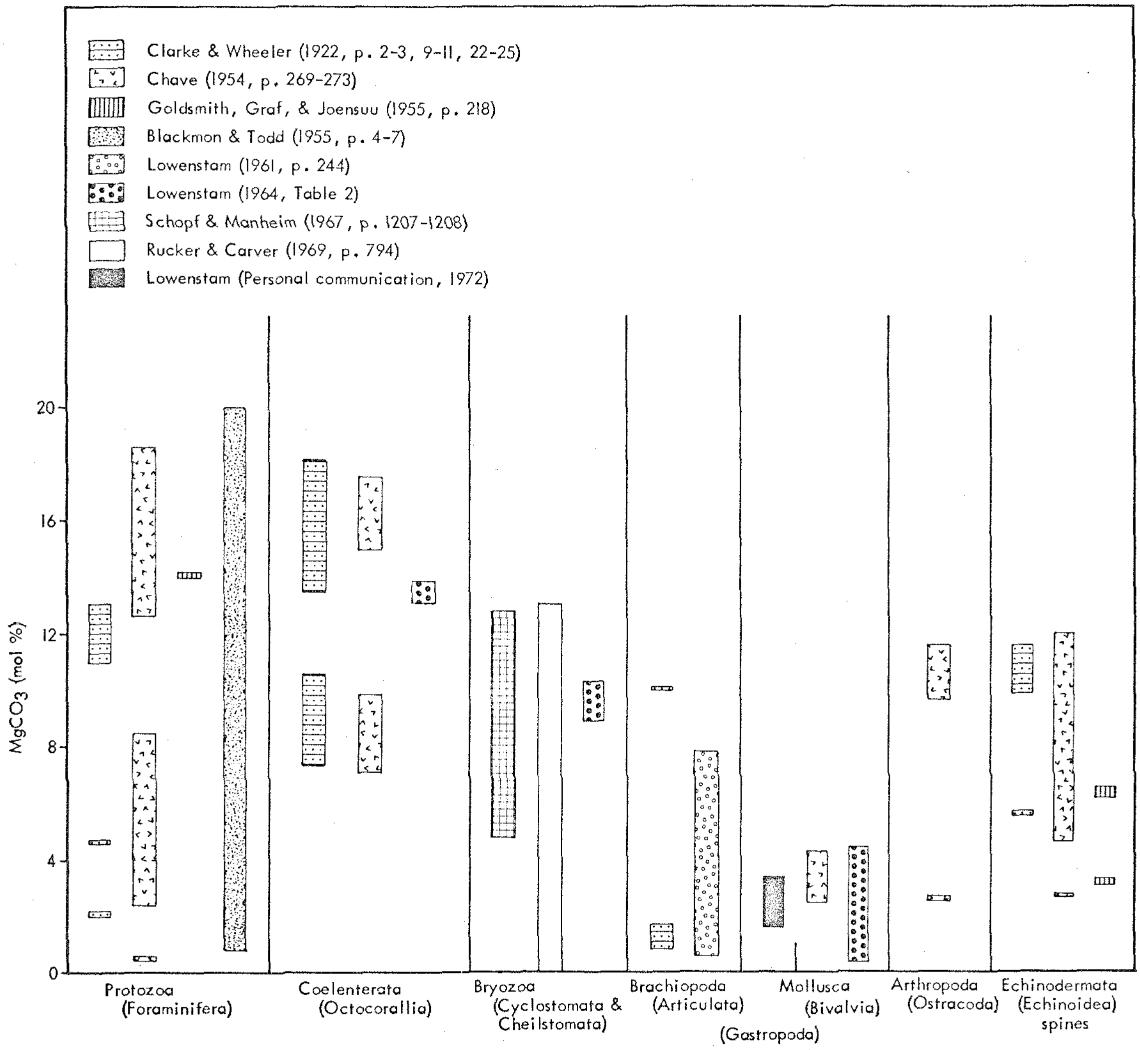


Fig. 18. $MgCO_3$ (mol percent) in Recent calcitic skeletons.

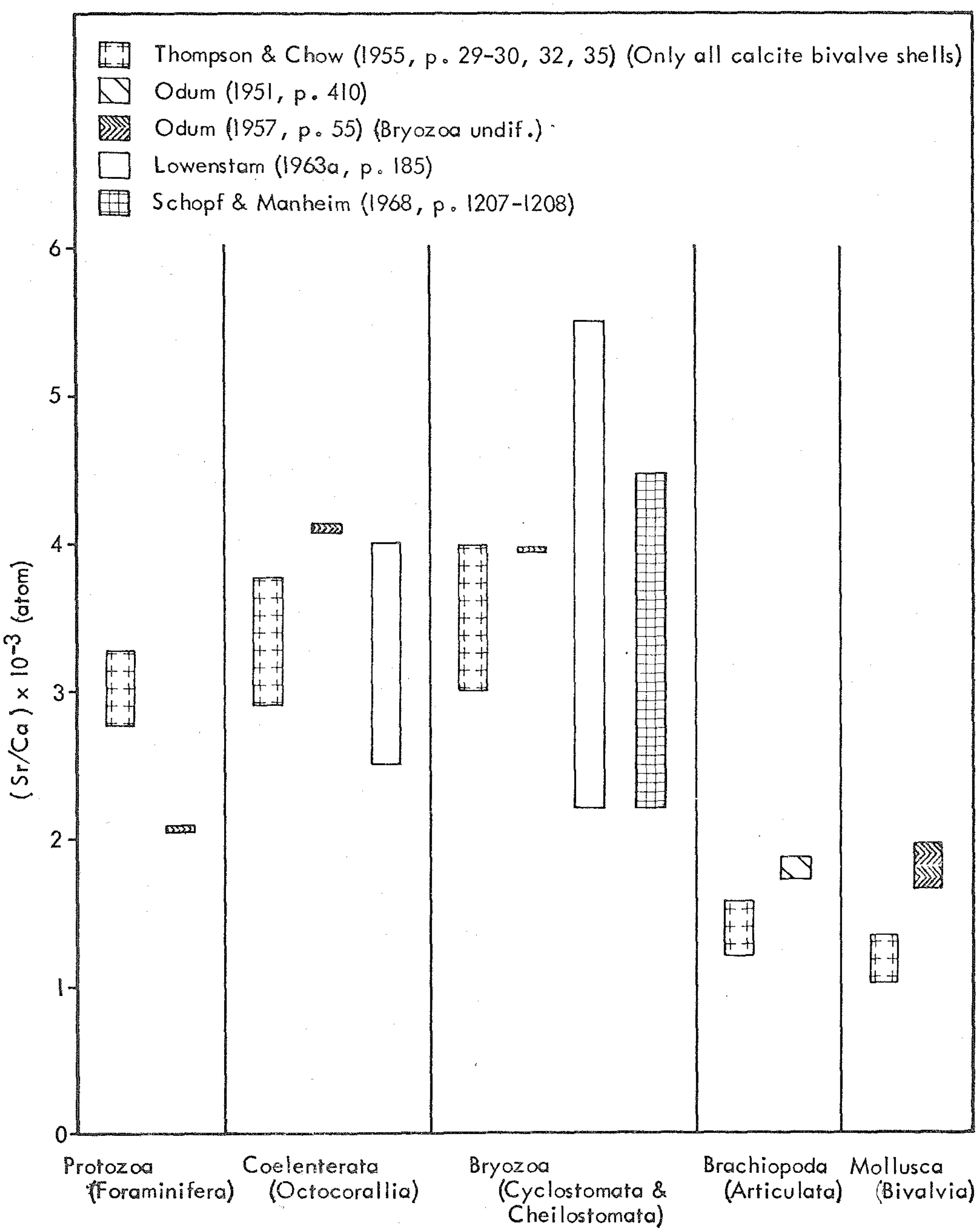


Fig. 19. (Sr/Ca $\times 10^{-3}$ atom ratio in Recent calcitic skeletons.

may be a coralline sponge. The mineralogy and Mg and Sr contents of Chaetetes sp., therefore, will be compared to that of Recent Octocorallia and Sclerospongia.

The Mg content of the most asphalt-impregnated specimen of Chaetetes cf. favosus is about 5 mol % $MgCO_3$ and represents the highest Mg content of any fossil studied from the quarry. Recent calcitic Octocorallia have a wide range in Mg content, as shown in Figure 18. The Chaetetes cf. favosus Mg content is just below the lower limit of the range of Recent calcitic octocorals, as determined by Clarke and Wheeler (1922) and Chave (1954) (Fig. 18). It has been shown by Chave (1954, p. 276), that there is a distinct positive correlation of the amount of $MgCO_3$ with temperature in the calcitic spicules of Recent Octocorallia. It is possible that the low Mg content in Chaetetes cf. favosus, relative to Recent octocorals, is due to low paleotemperatures, but it seems more likely that diagenetic effects have somewhat lowered the Mg concentration. The Sr/Ca ratio in Chaetetes cf. favosus (Fig. 15) is significantly lower than the ranges in Sr/Ca ratios in Recent octocorals reported by Thompson and Chow (1955), Odum (1957), and Lowenstam (1963a) (Fig. 19).

According to Lowenstam (1973, Personal communication), the Sclerospongia can consist of both the aragonite and opaline spicules, as reported by Hartman and Goreau (1970), or of both hi-Mg calcite and opaline spicules. No data are available at this time as to the Mg and Sr contents of the hi-Mg calcite spicules.

When compared to bryozoans of similar geologic age, the quarry specimens of Penniretepora ? sp. and Streblotrypa ? sp., have lower Mg and Sr contents (Figs. 18 and 19). The quarry forms are significantly lower in Mg contents (Fig. 14) relative to the ranges in Recent cyclostomata and cheliostomata, as reported by Schopf and Manheim (1967) and Lowenstam (1964), but would plot within the range reported by Rucker and Carver (1969) (Fig. 18). The Sr contents in the quarry forms (Fig. 15) are also lower relative to those in the ranges in Recent forms as reported by Thompson and Chow (1955), Odum (1957), Lowenstam (1963a), and Schopf and Manheim (1967) (Fig. 19).

The quarry specimen of Anthracospirifer opimus most likely has altered Mg and Sr contents possibly since it was derived from a weathered rock surface. The Mg content (Fig. 14) falls within the range of Mg for Recent brachiopoda, as reported by Clarke and Wheeler (1922) and Lowenstam (1961) (Fig. 18). The Sr content in the quarry specimen (Fig. 15) would plot near the lower limit of the range in Sr/Ca ratios in Recent articulates, as reported by Thompson and Chow (1955), but not within the range reported by Odum (1951) (Fig. 19).

In the outer calcitic layer of Naticopsis wortheni, the original color pattern is preserved and the Mg content (Fig. 14) is significantly lower than the range of Mg contents reported for calcitic layers of Recent gastropods, as reported by Lowenstam (Personal communication, 1972) (Fig. 18). The author is unaware of any published data on the Sr/Ca ratios for calcitic layers of Recent gastropods.

Although the Mg and Sr contents of the outer calcitic layers in the quarry bivalve Chaenocardia ovata may be somewhat altered, the range of the Mg contents (Fig. 14) would fall well within the ranges reported for Recent forms by Chave (1954) and Lowenstam (1964) (Fig. 18). The Sr/Ca ratios for the quarry specimens (Fig. 15) would fall within the lower limit of the Sr/Ca ratio range in Recent forms, as reported by Thompson and Chow (1955), but not within the range of Odum (1957) (Fig. 19).

The asphalt-impregnated tests of the ostracodes Hypotetragona sp., Proparaparchites sp., and Bairdia sp. A all have about 3 mol % $MgCO_3$. This Mg content would fall within the lower limit of the wide range of values for Recent ostracodes, as recorded by Chave (1954) (Fig. 18). Chave (1954, p. 280) also observed a positive correlation between temperature and amount of Mg in the calcite shells of "...mixed ostracod species, selected out of bottom sediments from various parts of North America...". Perhaps the relatively low Mg contents in the quarry ostracodes are due to low paleotemperatures, but as in the case with the Chaetetes sp. specimens, subtle diagenetic effects have most likely lowered the Mg values somewhat. The author is unaware of any published data on the Sr concentrations in Recent ostracode tests.

As noted before, the Mg contents of the quarry echinoid spines may have been altered. The present occurrence of about 3 mol % $MgCO_3$ in the calcitic parts of the spines is similar to the lower Mg concentrations reported for Recent echinoid spines by Chave (1954) and Goldsmith et al., (1955). The calcites occur in association with dolomite in the quarry specimens. In each spine the Mg, which now resides in the calcite and dolomite, may have originally occurred in the form of high-Mg calcite. If this closed system model of in situ formation of low-Mg calcite and dolomite, by a process of incongruent dissolution and reprecipitation, is the case for the quarry spines, then the calculation discussed earlier as to determining the original amount of Mg in one of these spines provides a maximum of about 10 mol % $MgCO_3$. This calculation is also dependent upon no prior loss of Mg before the dissolution and reprecipitation process. Such a concentration is similar to the maximum amounts of Mg reported for Recent echinoid spines by Clarke and Wheeler (1922) and Chave (1954). Specifically, Chave (1954, p. 270) reported spines of _Trypneuites_ sp., from Florida waters, as containing as much as 11.9 mol % $MgCO_3$. Clarke and Wheeler (1922, p. 24) reported as much as 11.5 mol % $MgCO_3$ in the large spines of _Heterocentrotus_ from the southern Pacific Ocean.

Both Clarke and Wheeler (1922, p. 25) and Chave (1954) observed a positive correlation between temperature and the amount of Mg in the calcitic echinoid tests. Chave (1954, p. 277) also showed a similar correlation for echinoid spines. Pilkey and Hower (1960) determined that in _Dendraster excentricus_, the common Pacific Coast sand dollar, the Mg content appears to be directly related to temperature and salinity. They also concluded that such trends are "...not continuous in a linear manner with warmer water echinoid species of the same environmental type." (Pilkey and Hower, 1960, p. 203).

Recently, Sumich and McCauley (1972) have studied the Mg concentrations in the Recent echinoid, _Allocentrotus fragilis_ (Jackson), which occurs along the Pacific Coast of North America. They concluded that the Mg concentrations in the calcitic test plates of this sea urchin are age-dependent and not temperature-dependent. In contrast to this study, Davies *et al.* (1972) showed that, based on gross chemical data, the Mg concentrations of laboratory grown spine regenerates of the Atlantic Coast sea urchin, *Arbacia punctulata*, are directly related to the growth rate, which is temperature dependent. Most likely, this lack of agreement in such studies is due to the fact that the various investigators are analyzing vastly different skeletal parts.

IX. CONCLUSIONS

(1) The limestone pebble and cobble conglomerates (i.e., units 14 and 15) capping the Buckhorn asphalt quarry are part of the Ada formation.

(2) Beds correlative with the Buckhorn asphalt quarry beds crop out in the upper parts of the DB-IV section and Thompson Ranch sections. These strata are all part of the same channel deposit and have been correlated with the upper part (i.e., DB-IV-4) of Waddell's (1966a, 1966b) DB-IV fusulinid biozone.

(3) Similar channel deposits occur in slightly older beds in the area, as an identical situation to the above exists between the Stock Pond and the DB-III sections.

(4) These channel beds are fragmental foraminiferal to foraminifera-molluscan grainstones which were formed in shallow, turbulent water conditions in a near coastal marine environment. Underlying calcareous sponge spicule-echinoderm-brachiopod-fusulinid mudstones and wackestones were deposited in slightly deeper, less turbulent waters.

(5) Foraminifera occur in most of the quarry beds associated with previously unreported *Chaetetes* aff. *favosus* colonies, bryozoan remains, ostracodes, and echinoid spines.

(6) Most of the Buckhorn asphalt quarry and the asphaltic Stock Pond strata are very weakly cemented and show evidences of compaction, as opposed to the well-cemented uncompacted underlying strata in each area.

a) Early entrapment of oil in the highly porous and permeable channel grainstones stopped further cementation and permitted later compaction due to tectonic deformation.

b) The oil impregnation was Pennsylvanian in age and most likely occurred after deposition of the quarry strata of early middle Desmoinesian age and before the deposition of the overlying nonasphaltic Ada formation conglomerates of middle Virgilian age.

(7) Due to the early sealing of the quarry beds by oil, the microarchitecture and mineralogy of various skeletal carbonates have been preserved in some cases.

a) Carbonate skeletons originally composed of aragonite include: *Plagioglypta* ? sp.

"Orthoceras" unicamera

Pseudorthoceras knoxense

Metacoceras cornutum

Domatoceras sp.

Pseudoparalegoceras sp.

Wellerites mohri ?

b) Skeletons with an original outer calcite layer (prismatic) and inner (crossed lamellar layer) aragonite layer occur in:

Naticopsis wortheni

Trachydomia whitei

Straparollus (*Euomphalus*) sp.

Chaenocardia ovata

c) Carbonate skeletons originally composed of all calcite include: *Globivalulina* sp.

Wedekinellina ? sp.

Penniretopora ? sp.

Streblotrypa ? sp.

Anthracospirifer opimus

Hypotetragona sp.

Proparaparchites sp.

Bairdia spp.

Cavellina sp.

d) Carbonate skeletons originally composed of Mg-calcite are inferred to have occurred in:

Chaetetes cf. *favosus*

Archaeocidaris megastyla ? (spines)

e) These Pennsylvanian age skeletal aragonites and calcites are similar in terms of mineralogy and morphology to those in related Recent species of the same taxonomic group.

(8) Diagenetic effects were detected in skeletal carbonates

a) Skeletal aragonites

1) The amount of replacement calcite increases with decreasing asphalt content of the stratigraphic unit in which the shells were deposited.

2) The replacement calcite (usually intermixed with the aragonite) probably formed by a process of dissolution of the original skeletal aragonite and precipitation of the calcite. Such a process causes

increasing obliteration of shell microarchitecture with increasing alteration.

3) In the altered specimens, the Sr contents decrease and the Mg contents increase with decreasing aragonite content.

b) Skeletal calcites

1) Apparently altered specimens have lower Mg and Sr contents relative to forms of similar geologic age, as best illustrated by the cryptostome bryozoans and possibly *Anthracospirifer opimus*.

2) Asphalt-impregnated specimens contain, in nearly every instance, more Mg and usually less Sr than corresponding nonasphaltic specimens.

3) The low-Mg calcite and dolomite in the *Archaeocidaris megastyla* ? spines may have formed by a closed system redistribution of the Mg from originally high-Mg calcites. Alternatively, the dolomite may have been related to dolomitizing ground waters which caused secondary dolomite layering on the corallite walls of *Chaetetes* aff. *favosus*.

(9) Data obtained on the Mg and Sr concentrations of the best preserved specimens for samples of species from different phyla and classes indicate the following:

a) Skeletal aragonites

1) The Sr/Ca ratio for the aragonitic shell walls of

the coiled nautiloid Metacoceras cornutum is similar to that for the shell walls in the Recent Nautilus sp.

2) The shell wall and septal aragonites of "Orthoceras" unicamera and Pseudorthoceras knoxense have lower Sr contents relative to the associated cameral and endosiphuncular deposits. These large Sr differences are apparently due to the "vital effect" of the organisms.

3) The Mg contents in the aragonitic shell layers of the quarry cephalopods are below the detection limit of the electron microprobe.

4) The Sr/Ca ratio in the aragonitic crossed-lamellar inner layer of Chaenocardia ovata is within or slightly below the range of Sr/Ca ratios for Recent forms, depending upon which published data it is compared to.

b) Skeletal calcites

1) The Mg contents in the calcites of the foraminifera, bivalves, and ostracodes fall within the range of Mg contents in related Recent forms.

2) The calcitic corallite walls in Chaetetes cf. favosus contain about 5 mol % $MgCO_3$, and this represents the highest Mg content of any fossil studied from the quarry.

3) The outer calcitic layer in Naticopsis wortheni still retains the original color pattern and has lower Mg

contents relative to Recent gastropods.

4) The present-day low Mg contents in the echinoid spine calcites are the same as in spines of similar geologic age.

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APPENDIX I

Sample Preparations and Chemical Techniques

Extraction of asphalt

A commercial 1000 ml capacity Soxyhlet extractor was used in the removal of asphalt from the quarry rock. The solvent used was U.S.P. grade CH_2Cl_2, which is dichloromethane or methylene chloride, which is an inflammable medium toxicity chlorinated hydrocarbon. The boiling point of dichloromethane is 40°C and some vaporization does take place at room temperature. In order to allow rapid vaporization, a heating mantle is needed.

Several small pieces of asphalt can be accommodated at the same time in the extractor thimble. The maximum amount of material is roughly one pound. The process of complete extraction requires about 96 hours, but many of the rather large samples were left for 120 hours. Fischer ceramic boiling stones, which are non-volatile, were used as to prevent superheating of the solvent.

The samples were air-dried for 24 hours before separating the rock matrix around the fossils or before making thin sections. After the extraction of the asphalt, the rock asphalt easily crumbled upon picking with a needle. Many of the samples were crumbled and passed through a series of sieve screens in order to pick out the microfossils.

Chemical analyses were made on biogenic carbonate standards in order to insure that there was no chemical effect from the solvent. Elemental analyses of aliquots of these standards were made by means of an electron microprobe (see below) both before and after immersion in the solvent and asphalt for 120 hours in the extractor. There were no noticeable differences between the two groups of analyses.

Methods of Analyses

Electron microprobe:

Quantitative analyses for Ca, Mg, Al, Si, P, Mn, Fe, and Sr in the biogenic carbonate minerals were made with a MAC-5-SA3 electron microprobe interfaced with a PDP-8/L computer. Standard operating conditions were an accelerating potential of 15 kV with beam current integration and pulse height selection, a sample current of 0.020 μa, and a beam spot diameter of 40μ to 50μ. The sample current and beam spot diameter were chosen after skeletal aragonite and calcite stability tests were conducted for various sample currents (0.010 μa to 0.035 μa) and various beam spot diameters (8μ to 50μ). The primary standards used in the probe analyses are simple well characterized carbonates, silicates, and phosphates.

Although CO_2 cannot be measured directly, such values were derived by assuming carbonate stoichiometry of CO_2 with Ca, Mg, Sr, Mn, and Fe. In addition, the measured values of these different elements were corrected for CO_2 interferences using the general reduction technique of Bence and Albee (1968). Analytical data were normalized based upon these cations.

Secondary standards supplied by L. Land were used in determining the precision and counting error of the electron probe analysis. These standards include Mg-calcite and strontium-bearing aragonites, for which the various minor element concentrations have been determined by wet chemical techniques. These minor element contents are also sim lar to those in the analyzed fossils.

According to L. Land, the secondary standard E-4 contains 5.9 ± 0.1 mol % $MgCO_3$ based on wet chemical techniques. Repeated electron probe analyses yield 5.7 ± 0.2 (1σ) mol % $MgCO_3$ for the same sample. Secondary standard, Caltech Spec. Lab. #1058, contains 0.75 ± 0.1 wt % Sr based on emission spectrograph results, and 0.76 wt % Sr (error not given) based on wet chemical techniques. Electron microprobe analyses yield 0.80 ± 0.06 (1σ) wt % Sr.

Repeated analysis of these secondary standards and selected typical fossil carbonates allows the calculation of standard deviations for the analyzed elements. These standard deviations are calculated primarily from counting statistics. Standard deviations would typically be $\leq$ 3% for elements whose concentration is greater than about 3 mol % expressed as the element in carbonate form, 6% for elements whose concentration is about 1 mol % in carbonate form (i.e., which is equivalent to a $(Sr/Ca)\times10^{-3}$ ratio of approximately 10), and $\geq$ 15% for elements less than 1 mol % but more than the detection limit of the microprobe. This detection limit is approximately 0.1 weight percent of the oxide of the element in question, which is equivalent to approximately 0.4 mol % $MgCO_3$ and a $(Sr/Ca)\times10^{-3}$ ratio of approximately 1.0.

Infrared techniques:

Mineralogical identifications were performed on a Perkin-Elmer Model 137 Infracord spectrophotometer. Spectra were obtained for most of the samples, and these were compared to the spectra of simple well characterized carbonate minerals.

The Perkin-Elmer Model 137 Infracord spectrophotometer required 1500 μg of material to yield sufficient intensity for identification. The relatively large sample required by this technique does not permit the identification of the mineralogy of single microfossils. The Perkin-Elmer Model 180 Recorder Console spectrophotometer, however, required much less sample material and allows identification of the mineralogy of individual microfossils. For example, a single foraminifera weighing approximately 18 μg was analyzed and contained calcite.

The samples used for the infrared studies were mixed with KBr and mechanically pressed into transparent pellets. Percentages by weight of various mixtures of calcite and aragonite were determined by comparing ratios of sample peaks against those of standard peaks. The main vibrational frequency used in the identification of 1) calcite is the v_4 (E') bending mode of vibration at 712 cm^{-1}; 2) aragonite are the v_y bending modes of vibration at 699 cm^{-1} and 712 cm^{-1}; dolomite is the v_y bending mode of vibration at 728 cm^{-1}. For a discussion of the symmetry of the v_y(E') vibration modes, see Nakamoto (1963, p. 90-92).

X-ray diffraction technique:

The qualitative and quantitative mineralogical analyses were made by means of a General Electric diffractometer. Powdered samples were mixed with a small amount of fluorite as an internal standard, then mounted on glass slides and exposed to 45 kV and 33 μa x-ray radiation with copper as the target element and nickel as the filter element. The identification of the carbonate mineral phases was based on the principal $CuK\alpha_1$ d-spacings of these minerals. For calcite, with (104) cleavage rhomb indices, the d-spacing used was 3.04 Å (2θ, 26.4°); for aragonite 3.40 Å (2θ, 26.24°); for dolomite with (104) cleavage rhomb indices, 2.88 Å (2θ, 30.99°); and for impure silica 3.38 Å (2θ, 26.37°).

The ratio of calcite and dolomite in a sample was determined by comparing the relative intensities of these peaks and plotting them on the percent dolomitization of calcite curve of Tennant and Berger (1957, p. 26). These authors did not discuss the errors involved in such a technique. The ratio of aragonite and calcite was determined by comparing the relative intensities of the 26.2° 2θ peak of aragonite with the 29.42° 2θ peak of calcite and plotting them on the weight percent aragonite curve of Lowenstam (1954, p. 288).

The amount $MgCO_3$ in solid solution in calcite was quantitatively determined for some of the samples. This determination is based on the changes in the d-spacing of the 3.04 Å peak for calcite. This relationship has been well established by Chave (1952), Goldsmith *et al.* (1955), Goldsmith and Graf (1958), and Gross (1961). The unpublished graph showing the relationship between Δd (Å) and mol % $MgCO_3$ in calcite by Gross at Caltech was used in this present report. According to Gross (1961, p. 190), the results obtained by this method are reproducible to within ± 0.50 mol % $MgCO_3$

Chemical staining techniques:

Each of the probe polished sections of the samples was chemically stained in order to ascertain the mineralogy, or to confirm the mineralogy if otherwise analyzed by infrared or x-ray techniques. The staining procedure is part of one outlined by Friedman (1959, p. 89).

The procedure results in the differentiation of calcite from aragonite in a sample. After the presence of one or both of these minerals is ascertained by a positive reaction to alizarin red S stain, aragonite can be recognized by a positive reaction to Feigl's solution, a specific stain for this mineral. Dolomite could not be reliably determined by any staining suggested by Friedman.

APPENDIX II

Faunal Descriptions and Chemical Data

The following is a faunal list of the various fossil types which were chemically analyzed. These fossils represent the more common to abundant asphalt quarry faunal elements which are identifiable. Where possible, the same or closely similar forms from outside the quarry were also analyzed in order to determine the effects of alteration. Each fossil type will be discussed in terms of general description, skeletal morphology or observed microarchitecture of shell layers, stratigraphic position, mineralogy, and quantitative chemical composition. The compositions are expressed in terms of weight percents. The $(Sr/Ca)\times10^{-3}$ (atom) and mol % $MgCO_3$ values are also given. X-ray diffractometer-determined and/or infrared spectrometer-determined mineralogy, and electron beam scan data on the spatial distribution of Mg or Sr in various shell layers are also included.

FORAMINIFERA:

Globivalulina sp.
Wedekinellina ? sp.

COELENTERATA ?:

Chaetetes aff. *favosus* Moore and Jeffords
Chaetetes cf. *favosus* Moore and Jeffords

BRYOZOA:

Penniretepora ? sp.
Streblotrypa ? sp.

BRACHIOPODA:

Anthracospirifer opimus (Hall)

GASTROPODA:

Bellerophon (*Bellerophon*) sp.
Straparollus (*Euomphalus*) sp.
Naticopsis wortheni Knight
Trachydomia whitei Knight

SCAPHOPODA:

Plagioglypta ? sp.

ORTHOCONE NAUTILOIDEA:

"*Orthoceras*" *unicamera* Smith
Pseudorthoceras knoxense (McChesney)

COILED NAUTILOIDEA:

Metacoceras cornutum Girty
Domatoceras sp.

AMMONOIDEA:

Pseudoparalegoceras sp.
Wellerites mohri ? Plummer and Scott

BIVALVIA:

Chaenocardia ovata Meek and Worthen

OSTRACODA:

Hypotetragona sp.
Proparaparchites sp.
Bairdia spp.
Cavellina sp.

ECHINODERMATA:

Archaeocidaris megastyla ? Shumard and Swallow

Phylum Protozoa (Protista)

Order Foraminifera

Superfamily Endothyracea

Family Biseriamminidae

Specimen: *Globivalulina* sp. Schubert, 1921

Genotype: Schubert, R. J., 1921, Palaont. Zeitschr., v. 3, p. 129-188.

Description: Subglobular, biserial, each chamber overlapping preceding chambers, aperture on ventral side in a broad depression. Diameter 0.25 mm; thickness 0.12 mm.

Skeletal morphology: Single layer

Stratigraphic position: Unit 13, middle part, channel sample area

Discussion: Asphalt-impregnated specimen

Chemical data:

Chemical staining: Calcite

Infrared spectrophotometer: Calcite

Electron microprobe:

wt %	wall
CaO	53.02
MgO	1.20
SrO	0.01
MnO	0.14
FeO	0.41
P_2O_5	0.19
SiO_2	0.06
Al_2O_3	0.09
CO_2	43.26
TOTAL	98.38
$(Sr/Ca)\times10^{-3}$	0.08
mol % $MgCO_3$	3.02

Superfamily Fusulinacea

Family Fusulinidae

Specimen: <u>Wedekinellina</u> ? sp. Dunbar and Henbest, 1933

Genotype: Dunbar and Henbest, 1933, <u>in</u> Cushman Lab. Foram. Research, Spec. Publ. 4.

Description: Minute, ellipsoidal to highly inflated fusiform, unfluted septa, broad tunnel, low and asymmetrical chomata. The first two volutions are irregularly coiled.

Skeletal morphology: In all the examined specimens, only the first one or two volutions are present as the others have been worn away. The tunnel and chomata are clearly visible in these badly abraded specimens.

Stratigraphic positions: 1, Unit 13, middle part, channel sample area
2, Unit 11, channel sample area
3, Unit 9, middle part, channel sample area

Discussion: 1, Asphalt-impregnated specimen
2, Walls not impregnated with asphalt, although chambers were
3, Asphalt-impregnated specimen

Chemical data:

Chemical staining: 1, 2, 3 Calcite

Electron microprobe:

wt %	1a wall	1b wall	avg.	2a wall	2b wall	avg.	3 wall
CaO	53.69	53.68		52.41	52.41		52.68
MgO	1.26	1.19		1.46	1.29		1.14
SrO	0.09	0.06		0.11	0.10		0.11
MnO	0.07	0.09		0.14	0.16		0.06
FeO	0.08	0.25		0.34	0.95		0.18
P_2O_5	0.09	0.05		0.15	0.10		0.05
SiO_2	0.01	0.01		0.01	0.02		0.09
Al_2O_3	Tr	0.00		0.01	0.04		0.01
CO_2	43.64	43.66		43.07	43.27		42.78
TOTAL	98.93	98.99		97.70	98.34		97.10
$(Sr/Ca)\times10^{-3}$	0.93	0.62	0.78	1.12	1.03	1.10	1.14
mol % $MgCO_3$	3.15	2.98	3.07	3.71	3.26	3.49	2.91

Phylum Coelenterata ?

Class Anthozoa

Order Tabulata ?

Family Chaetetidae

Specimen: *Chaetetes* aff. *favosus* Moore and Jeffords, 1945

Type Species: Moore, R. C., and Jeffords, R. M., 1944, Univ. Texas Publ. No. 4401, p. 193-194.

Description: Small corallum in growth position and rounded at the top, height 200 mm, length 550 mm, width 250 mm; irregularly polygonal corallites is greater in one direction than another; maximum longest diameter 0.29 mm on the average, with variation of longest diameter from 0.20 mm to 0.45. Wall thickness is more uniform with 0.06 mm on the average. In places, there is a faint beaded appearance to the wa ls. No pseudosepta were observed. Fission is present but uncommon. There is a wide spacing of the flat tabulae, and where they occur, there can be as many as 5 per mm. Most occur near the middle and basal parts of the corallum. Most tabulae are complete, but incomplete ones are present. Except for the lack of abundant incomplete tabulae, this specimen agrees well with the main characteristics of the species.

Skeletal morphology: Some of the corallites and tabulae are rimmed by a thin transparent dolomite layer (0.02 mm thick on the average). The brown dense corallite wall and tabulae are readily discernible, both physically and optically. In places, there is partial filling of corallites with blebs of clear transparent calcite, but most of the corallites are unfilled once the asphalt is removed.

Stratigraphic position: Unit 11, 4 inches above unit 10, approximately 30' northeast of channel sample area.

Discussion: Several transverse and longitudinal probe sections were prepared. The samples are from the middle of the corallum near one margin. The corallum was shiny black due to asphalt impregnation.

Chemical data:

Chemical staining: Corallite walls and tabulae: Calcite
Rim material: Dolomite
Clear blebs: Calcite

X-ray diffractometer:
Quantitative: Bulk corallum analysis - Calcite, 2.5 mol % $MgCO_3$; and dolomite

Chaetetes aff. favosus (Continued)

Infrared spectrophotometer:

Corallite walls: Calcite
Rim material: Dolomite
Clear blebs: Calcite

Electron beam scan:

Inhomogeneous distribution of Mg in corallite wall; extremely Mg-rich transparent layer

Electron microprobe:

wt %	1a wall	1b wall		1c Clear Rim	1d Clear Rim	
CaO	51.54	55.36		42.80	36.39	
MgO	2.32	1.96		10.53	13.74	
SrO	0.04	0.01		0.03	0.05	
MnO	0.07	0.17		0.01	0.01	
FeO	0.13	0.18		0.05	0.08	
P_2O_5	0.08	0.09		0.08	0.07	
SiO_2	0.02	0.02		0.03	0.05	
Al_2O_3	0.08	0.31		0.11	0.19	
CO_2	43.11	45.80		45.13	43.64	
TOTAL	97.39	103.90		98.77	94.22	
			avg.			avg.
$(Sr/Ca)\times10^{-3}$	0.37	0.05	0.21	0.43	0.78	0.61
mol % $MgCO_3$	5.87	4.68	5.28	25.47	34.37	29.92

Remarks: A maximum value of only 34 mol % $MgCO_3$ was determined by microprobe analyses for the dolomite rim material. This is undoubtedly due to the fact that during the probe analysis of the 30-50μ thick rim, part of the 40μ beam spot might have been on part of a corallite wall or on epoxy, thereby resulting in lower concentrations. The opposite is undoubtedly true for the analyses of the corallite walls (i.e., 1a and 1b). These analyses resulted in an average of 5.28 mol % $MgCO_3$, but only 2.5 mol % $MgCO_3$ could be detected by means of quantitative x-ray diffractometer techniques. During the microprobe analyses of the walls, therefore, the beam must have been on part of the rim material, thereby resulting in higher concentrations.

Specimen: Chaetetes cf. favosus

Description: Small fragment of corallum, length 1.25 mm, consisting of a transverse section of 13 corallites. A few of the corallites are 6-sided polygons, but most are irregular. Several have 2 to 3 beads on each polygon wall, and a few other corallites are surrounded by spines. The larger corallites are 0.30 mm in diameter. No pseudosepta were observed. Wall thickness is about 0.06 mm and is very uniform. As no tabulae were present, an exact species assignment could not be made. The observable features, however, are closely similar to C. favosus.

Skeletal morphology: There is no rimming of the beaded corallite walls with any transparent carbonate material. The preservation of the corallite spines is exceptional in that such features were not seen in the Chaetetes aff. favosus specimens.

Stratigraphic position: Unit 13, middle part, channel sample area.

Discussion: A probe section was made of one-half of the asphalt-impregnated fragment.

Chemical data:

Chemical staining: Calcite

Electron microprobe:

wt %	1a wall	1b wall	
CaO	51.17	52.34	
MgO	2.00	1.85	
SrO	0.23	0.10	
MnO	0.10	0.07	
FeO	0.09	0.24	
P_2O_5	0.11	0.08	
SiO_2	0.04	0.04	
Al_2O_3	Tr	0.00	
CO_2	42.55	43.33	
TOTAL	96.29	98.05	avg.
$(Sr/Ca)\times10^{-3}$	2.41	1.07	1.74
mol % $MgCO_3$	5.13	4.66	4.90

Phylum Bryozoa

Order Cryptostomata

Family Acanthocladiidae

Specimen: Penniretepora ? sp. d'Orbigny, 1849

Genotype: d'Orbigny, A. P., 1942-52, p. 1-394.

Description: Two rows of cylindrically shaped zooecia with round apertures only on front side of dilicate stem. Randomly distributed pustules on back side. The sample consists of a single fragment, length 1.5 mm, width 0.5 mm.

Skeletal morphology: Dense calcareous coenosteum, skeletal micro-architecture could not be readily obtained as the only fragment found was made into a polished section rather than a thin section.

Stratigraphic position: Unit 13, middle part, channel sample area.

Discussion: Asphalt-impregnated specimen.

Chemical data:

Chemical staining: Calcite

Electron microprobe:

wt %	wall
CaO	53.56
MgO	1.09
SrO	0.09
MnO	0.02
FeO	0.23
P_2O_5	0.09
SiO_2	0.16
Al_2O_3	0.00
CO_2	43.42
TOTAL	98.66
$(Sr/Ca)\times10^{-3}$	0.95
mol % $MgCO_3$	2.75

Family Rhabdomesidae

Specimen: Streblotrypa ? sp. Vine, 1885

Genotype: Vine, G. R., 1881-85, Br. Assoc. Adv. Sci., Rept. 54th mtg., 1885, p. 97-219.

Description: Oval apertures in longitudinal rows with several mesopores between each pair of apertures. The sample consists of a single fragment, length 4 mm, width 0.5 mm.

Skeletal morphology: Dense calcareous coenosteum, skeletal microarchitecture could not be readily obtained as the only fragment found was made into a polished section rather than a thin section.

Stratigraphic position: Unit 13, middle part, channel sample area.

Discussion: Alphalt-impregnated specimen.

Chemical data:

Chemical staining: Calcite

Electron microprobe:

wt %	1a wall	1b wall	1c wall	
CaO	53.37	52.43	54.46	
MgO	1.08	1.82	1.06	
SrO	0.08	0.08	0.09	
MnO	0.18	0.03	0.01	
FeO	0.19	0.27	0.19	
P_2O_5	0.16	0.13	0.17	
SiO_2	0.02	0.02	0.02	
Al_2O_3	0.00	0.00	0.01	
CO_2	43.33	43.34	44.06	
TOTAL	98.41	98.12	100.07	avg.
$(Sr/Ca)\times10^{-3}$	0.83	0.81	0.89	0.84
mol % $MgCO_3$	2.73	4.57	2.60	3.30

Phylum Brachiopoda
Class Articulata
Order Spiriferida
Family Spiriferidae

Specimen: Anthracospirifer opimus Hall, 1858

Type Species: Hall, James, 1858, Geol. Iowa, v. 1, pt. 2, p. 711.

Description: Biconvex, rounded cardinal extremities, lateral plications prominent and simple, none bifurcating, fold and culcus narrow with several plications, hinge line and shell width approximately the same. Most of the specimens consist of disarticulated single valves or occur as steinkern impressions of single valves.

Microarchitecture: Prismatic

Stratigraphic position: Unit 7, 2" below top, northeastern end of quarry.

Discussion: Specimen consists of pedicle valve with white pearly luster exterior and occurred on asphalt-depleted rock surface. Only a few Anthracospirifer opimus occur in the asphaltic unit 7, and most occur in the poorly asphalt-impregnated upper part of unit 11.

Chemical data:

Chemical staining: Calcite

Infrared spectrophotometer: Calcite

Electron microprobe:

wt %	wall	wall	
CaO	53.57	54.23	
MgO	0.33	0.31	
SrO	0.10	0.12	
MnO	0.06	0.00	
FeO	0.01	0.00	
P_2O_5	0.06	0.08	
SiO_2	0.01	0.02	
Al_2O_3	0.01	0.00	
CO_2	42.49	42.95	
TOTAL	96.64	97.71	
			avg.
$(Sr/Ca)\times10^{-3}$	1.05	1.23	1.14
mol % $MgCO_3$	0.86	0.79	0.83

Phylum Mollusca

Class Gastropoda

Order Archaeogastropoda

Family Bellerophontidae

Specimen: Bellerophon (Bellerophon) sp. Montfort, 1808

Genotype: Montfort, 1808, Tome 1, Coquilles univalves cloisonées. Paris.

Description: Planispiral, isostrophic, median selenizone, rounded whorls, growth lines on surface. The only complete specimen has been compressed and it is difficult to determine whether the umbilicus is narrow or absent.

Microarchitecture: Thin outer foliated? layer; thicker inner crossed-lamellar? layer.

Stratigraphic position: From float near base of unit 11, channel sample area.

Discussion: Mature specimen, height 7½ mm, width 12 mm, asphalt coated.

Chemical data:

Chemical staining: Outer - Quartz; Inner - Calcite + aragonite

Infrared spectrophotometer: Inner - mostly Aragonite; some Calcite.

Electron microprobe:

wt%	Outer	Inner
CaO	0.49	33.05
MgO	Tr	0.00
SrO	0.00	0.38
MnO	0.00	0.04
FeO	0.00	0.00
P_2O_5	0.02	0.03
SiO_2	97.61	0.12
Al_2O_3	0.00	0.00
CO_2	0.39	26.23
TOTAL	98.51	59.85*
$(Sr/Ca)\times10^{-3}$	0	6.15
mol % $MgCO_3$	—	0

Remarks: *Due to surface damage of the aragonite under the microprobe beam, the microprobe results do not sum to 100%.

Specimen: Straparollus (Euomphalus) sp. Sowerby, 1814

Genotype: Sowerby, J., 1812, v. 1, London.

Description: Discoidal, slightly elevated spine, outer-upper edges of whorls are raised and angular, fine growth lines on outer surfaces.

Microarchitecture: Thin outer prismatic layer; thicker inner crossed lamellar layer.

Stratigraphic positions: 1, Unit 11, 0" to 4" above top of unit 10, about 65' northeast of channel sample area.

2, Unit 7, about 130' southwest of channel sample area.

Discussion: 1, Broken specimen - early mature, 4 whorls, slight asphalt impregnation.

2, Mature - 5½ whorls, not asphalt-impregnated.

Chemical data:

Chemical staining:

	Outer	Inner
1,	Calcite	Aragonite + calcite
2,	Calcite	Calcite + aragonite

Infrared spectrophotometer: Inner

2, Mostly Calcite, some aragonite

Electron microprobe:

wt %	1a Outer	1b Inner	1c Inner		2a Outer	2b Inner
CaO	53.48	37.14	40.41		52.86	53.62
MgO	1.43	0.00	0.02		1.36	0.89
SrO	0.20	0.27	0.38		0.13	0.06
MnO	0.00	0.01	0.00		0.05	0.08
FeO	0.05	0.02	Tr		0.00	0.28
P_2O_5	0.05	0.06	0.04		0.08	0.03
SiO_2	0.03	0.01	0.03		0.03	0.03
Al_2O_3	0.00	0.00	0.00		0.02	0.00
CO_2	43.65	29.28	31.91		43.05	43.30
TOTAL	98.89	66.78*	72.79*		97.58	98.29
$(Sr/Ca)\times 10^{-3}$	1.98	3.92	5.13	avg. 4.53	1.30	0.63
mol % $MgCO_3$	3.58	0	0.08	0.04	3.45	2.25

Remarks: *Due to surface damage of the aragonite under the microprobe beam, microprobe results do not sum to 100%. The aragonites which have altered to calcite (i.e., analysis 2b) do, however, sum to nearly 100%.

Family Neritopsidae

Subfamily Naticopsinae

Specimen: Naticopsis wortheni Knight, 1933

Type Species: Knight, J. B., 1933, St. Louis, Missouri, Pennsylvania outlier, Jour. Paleo., v. 7, no. 4, p. 359-392, pl. 43, figs. 3a-k.

Description: Naticiform, low spine, and large body whorl in adult forms, fine growth lines, nucleus small, smooth, simple and dextral; color pattern consists of light-chestnut and white revolving bands, with a thin white band next to the suture, followed by a chestnut band, a broad white band, another chestnut band broader than the first, another broad white band, a chestnut band, and a thin circum-umbilical white band. The identification was based on several specimens ranging in size from juvenile to ephebic forms. All the specimens display the same prominent color banding. Heretofore, the color banding of this species was only known from juvenile species.

Microarchitecture: Thin outer prismatic layer, thick inner crossed lamellar layer.

Stratigraphic positions: 1, From a boulder excavated from near the middle of unit 9, near channel sample area.

2, From a talus slope debris boulder along the southern margin of the quarry approximately 50 feet southwest of the channel sample area.

Discussion:

Age	No. of whorls	Height (mm)	Width (mm)
1, Late stage juvenile	3½	6	6½
2, Ephebic	-	11	12

[All specimens were asphalt-impregnated, but the boulders from which the specimens were taken have weathered surfaces.]

Chemical data:

Chemical staining:	Outer layer	Inner layer
	1, Calcite	Calcite + aragonite
	2, Calcite	Calcite + aragonite

X-ray diffractometer:

Qualitative: 2, Bulk sample - Calcite with approximately 2.5 mol % $MgCO_3$, some aragonite?

Naticopsis wortheni (continued)

Infrared spectrophotometer: Outer Inner

1, - Approximately equal amounts of calcite and aragonite.

Electron beam scan: 2, More Mg in outer layer relative to inner layer.

Electron microprobe:

wt %	1a Inner	1b Inner		2a Outer
CaO	53.44	52.79		54.00
MgO	0.81	1.00		0.17
SrO	0.05	0.15		0.14
MnO	0.02	0.04		0.00
FeO	0.00	0.05		0.35
P_2O_5	0.03	0.06		0.10
SiO_2	0.01	0.03		0.02
Al_2O_3	0.00	Tr		0.10
CO_2	42.85	42.64		42.83
TOTAL	97.21	96.76		97.71
			avg.	
$(Sr/Ca)\times10^{-3}$	0.45	1.48	0.97	1.41
mol % $MgCO_3$	2.06	2.56	2.31	0.43

Remarks: Although the inner layers contain some aragonite, as determined from staining and infrared techniques, the microprobe analyzed spots are for calcite areas. Such a conclusion is based on the fact that the analyses sum to nearly 100%, which is atypical of aragonites in other gastropods from the quarry.

Subfamily Neritopinae

Specimen: *Trachydomia whitei* Knight, 1933

Type Species: Knight, 1933, Jour. Paleo., v. 7, no. 4, p. 386-387, pl. 46, figs. 2a-d.

Description: Globular, medium size gastropods, with surface covered by fine growth lines and small quincunxially arranged pustules; the uppermost row consisting of coarser, more prominent pustules. The subsutural band is wide and shallow. Color of specimens after removal of asphalt is chestnut brown.

Microarchitecture: Thin outer prismatic layer, thick inner crossed lamellar layer.

Stratigraphic positions: 1, Unit 11, 0" to 3" above unit 10, about 62' northeast of channel sample area.

2, Unit 9, $9\frac{1}{2}$' to $10\frac{1}{2}$' interval; near channel sample area.

3, As 1.

Discussion:

Age	No. of whorls	Height (mm)	Width (mm)	Remarks
1, Juvenile	$4\frac{1}{2}$	6	5	Mostly asphalt-impregnated
2, Juvenile	4	4	6	Asphalt-impregnated
3, Juvenile	$3\frac{1}{4}$	7	7	Fair asphalt coating

Chemical data:

Chemical staining:

	Outer	Inner
1,	Calcite	Aragonite + calcite
2,	Calcite	Aragonite + calcite
3,	Absent	Aragonite + calcite

Infrared spectrophotometer:

2, Inner: Mostly aragonite

Trachydomia whitei (Continued)

Electron microprobe:

wt %	1a Outer	1b Inner	1c Inner		2a Inner	2b Inner	3 Inner
CaO	54.99	35.05	34.25		41.74	52.71	38.56
MgO	0.70	0.00	0.00		0.74	0.72	0.02
SrO	0.05	0.32	0.27		0.37	0.14	0.15
MnO	0.70	0.00	0.02		0.09	0.08	0.00
FeO	1.37	0.00	0.00		0.19	0.14	0.03
P_2O_5	0.09	0.04	0.04		0.05	0.07	0.11
SiO_2	0.01	0.03	Tr		0.48	0.01	0.10
Al_2O_3	0.02	0.14	0.00		0.10	0.01	0.02
CO_2	45.21	27.64	27.01		33.90	42.34	30.37
TOTAL	103.14	63.22*	61.59*		77.61*	96.22	69.36*
$(Sr/Ca)\times10^{-3}$	0.54	4.87	4.28	avg. 4.56	4.75	1.39	2.08
mol % $MgCO_3$	1.68	0	0		2.39	1.85	0.08

Remarks: *Due to surface damage of the aragonite under the microprobe beam, the microprobe analyses do not sum to 100%. The fact that analysis 2b of the inner layer of Trachydomia sums to 96% is due to the fact that the inner layer of this particular specimen consists of both calcite and aragonite, as determined by infrared techniques. This particular point, therefore, is an analysis of an altered calcite area.

Class Scaphopoda

Family Dentaliidae

Specimen: *Plagioglypta* ? sp. Pilsbry and Sharp, 1897-98

Genotype: Pilsbry, H. A., and Sharp, B., 1897-98, *in* Tryon, G. W., Manual of Conchology, v. 17, 280 p., 39 pl.

Description: Tapering shell, circular in cross section, without longitudinal sculpture, with close and fine obliquely encircling growth lines with regularly space, slightly grooved areas. The sample consists of a fragment 1 mm long and 0.5 mm wide.

Skeletal morphology: Shell consists of a single layer of aragonite which has parallel extinction under crossed nicols.

Stratigraphic position: Unit 13, middle part, channel sample area.

Discussion: Asphalt-impregnated specimen.

Chemical Data:

Chemical staining: Aragonite

Electron microprobe:

wt %	Wall
CaO	47.31
MgO	0.03
SrO	0.34
MnO	0.06
FeO	0.04
P_2O_5	0.05
SiO_2	0.04
Al_2O_3	0.02
CO_2	37.37
TOTAL	85.26
$(Sr/Ca)\times10^{-3}$	3.86
mol % $MgCO_3$	0.10

Remarks: The probe analysis is of poor quality due to surface damage of the aragonite under the microprobe beam.

Class Cephalopoda

Order Orthocerida

Family Orthoceratidae

Specimen: "Orthoceras" unicamera Smith, 1938

Type species: Smith, 1938, Univ. Chicago Lib., 40 p., 66 figs.

Description: Straight, slowly expanding phragmacone with nearly parallel sides; the distance between the evenly spaced septa is approximately equal to the diameter of the conch; centrally located orthochoanitic siphuncle. The surface ornamentation consists of fine transverse lirae on the thin fragile outer wall. As with Pseudothoceras knoxense, the specimens of "Orthoceras" unicamera are mostly fragmental with only the more mature parts of the phragmacone abundant. The cameral deposits are more calcareous and not as intergrown with organic material as in the specimens of Pseudothoceras knoxense. The dorsal cleft does not run the full length of each chamber. Specimens of "O" unicamera correspond to quarry specimens identified as Michelinoceras directum by Unklesbay, 1962.

Microarchitecture: The outer wall which bears transverse lirae on the exterior surface consists of three thin nacreous layers. As in Pseudorthoceras knoxense, the middle layer is the thickest and the innermost layer is the thinnest. The septa are nacreous. In places the calcareous cameral deposits are intergrown with organic material in a mammillary fashion.

Stratigraphic position: Unit 9, upper 2', few feet southwest of channel sample area.

Discussion: Partial phragmacone of adult specimen, asphalt-impregnated.

Chemical data:

Chemical staining:
- Walls - Aragonite
- Septa - Aragonite
- Cameral deposits - Aragonite

Infrared spectrophotometer:
- Walls - Aragonite
- Septa - Aragonite
- Cameral & Endosiphuncular deposits - Aragonite

"*Orthoceras*" *unicamera* (Continued)

Electron microprobe:

wt %	Outer Wall	Middle Wall	Inner Wall		Septum	Septum		Cameral	Endosiphuncular
CaO	51.75	51.81	51.53		53.39	53.72		54.34	54.53
MgO	0.00	0.00	0.01		0.01	Tr		0.03	0.05
SrO	0.13	0.08	0.10		0.17	0.15		0.59	0.66
MnO	0.00	0.00	0.05		0.04	0.00		0.10	0.05
FeO	0.00	0.04	Tr		0.00	0.00		0.00	0.00
P_2O_5	0.08	0.07	0.08		0.00	0.07		0.08	0.13
SiO_2	0.02	0.02	0.03		0.00	0.02		0.05	Tr
Al_2O_3	0.02	0.00	Tr		0.00	0.01		0.02	Tr
CO_2	40.67	40.71	40.52		41.98	42.23		42.99	43.15
TOTAL	92.67	92.73	92.32		95.59	96.20		98.20	98.57
$(Sr/Ca)\times10^{-3}$	1.36	0.85	1.06	avg. 1.09	1.76	1.53	avg. 1.65	5.82	6.50
mol % $MgCO_3$	0	0	0.02	0.01	0.02	0.01	0.01	0.08	0.12

Family Pseudorthoceratidae

Specimen: Pseudorthoceras knoxense McChesney, 1860

Type Species: McChesney, 1860, p. 69, Chicago.

Description: Smooth phragmacone which expands gradually toward the adoral end and which has slight exogastric curvature in first few apical chambers; circular cross section with siphuncle usually subcentral, evenly spaced moderately convex apicad septa. Although orthocones are quite abundant in the quarry fauna, most of the specimens are fragmental and represent only the more mature parts of the shells; hence, the siphuncle segments are usually the subspherical variety. Banded thick cameral deposits consisting of mural, apiseptal, and hyposeptal deposits, are well developed and are intergrown with organic matrices in the well preserved specimens. The dorsal cleft runs the full length of each chamber.

Microarchitecture: The outer wall of the unornamented phragmacone consists of three thin nacreous layers. The middle layer is the thickest, and the innermost layer is the thinnest. The thin septa are also nacreous. Cameral deposits have a radial-fibrous fabric which is mammillary in the central parts of the septa. The admixed and intergrown organic material gives the cameral deposits a yellow-brown color. In some specimens, patches of diagenetically formed calcite are accompanied by partial to complete loss of the original growth banding in the cameral deposits. In the completely calcitized specimens, as in the specimen from the DB-IV section, there is nearly complete obliteration of all internal structure.

Stratigraphic positions: 1, Unit 9, 9½' to 10½' interval, about 10' southwest of channel sample area.

2, Unit 11, 2" to 4" interval near top of unit 10, about 65' northeast of channel sample area.

3, DB-IV section, middle part of DB-IV-2 & 3.

Discussion: 1, Partial phragmacone of adult specimen, asphalt-impregnated.

2, Partial phragmacone of adult specimen, slight asphalt content.

3, Only a few septa of an immature specimen, not asphalt-impregnated.

Pseudorthoceras knoxense (Continued)

Chemical data:

Chemical staining:	Walls	Septa	Cameral Deposits	Endosiphuncular Deposits
	1, Aragonite	Aragonite	Aragonite	Aragonite
	2, Absent	Absent	Calcite + aragonite?	Calcite + aragonite?
Infrared spectrophotometer	3, Absent	Absent	Calcite	-
	Cameral deposits 2, Most calcite, some aragonite			

Electron microprobe:

wt %	1a Wall	1b Cameral	1c Cameral		1d Endosiphuncular	2a Cameral	2b Cameral		3a Cameral
CaO	54.38	54.70	54.19		55.25	54.99	54.03		55.38
MgO	0.00	0.04	0.05		0.02	0.22	0.54		0.80
SrO	0.13	0.70	0.75		0.72	0.33	0.21		0.13
MnO	0.09	0.06	0.00		0.04	0.00	0.03		0.00
FeO	0.01	0.00	0.00		0.00	0.04	0.06		0.13
P_2O_5	0.08	0.05	0.06		0.05	0.13	0.05		0.07
SiO_2	0.00	0.03	0.03		0.01	0.03	0.02		0.03
Al_2O_3	0.00	0.00	0.05		0.00	0.02	0.00		0.04
CO_2	42.79	43.30	42.90		43.71	43.56	43.14		44.46
Total	97.48	98.88	98.03		99.80	99.32	98.06		101.04
								avg.	
(Sr/Ca$\times 10^{-3}$	1.33	6.84	7.46	7.15	7.01	3.21	2.06	2.64	1.26
mol % $MgCO_3$	0	0.11	0.12	0.12	0.05	0.55	1.38	0.97	1.95

Order Nautilida

Family Tainoceratidae

Specimen: Metacoceras cornutum Girty, 1911

Type Species: Girty, 1911, New York Acad. Sci., Annals, v. 21, p. 145-146.

Description: The identification was based on a single large fragment of the wall part of a mature conch. All other specimens are also fragmental. The large fragment is nautiliconic and has nodes on the ventrolateral shoulders. The exterior surface is also missing.

Microarchitecture: The inner part of the wall of the conch consists of a thick nacreous deposit with the organic matrices still intact.

Stratigraphic position: Unit 9, upper 2 feet, about 45' northeast of channel sample area.

Discussion: Sample consists of large fragment of wall, asphalt-impregnated.

Chemical data:

Chemical staining: Aragonite

Infrared spectrophotometer: Aragonite

Electron microprobe:

wt %	Wall	Wall	
CaO	53.57	53.86	
MgO	0.01	0.00	
SrO	0.20	0.30	
MnO	0.04	0.06	
FeO	0.00	0.00	
P_2O_5	0.02	0.06	
SiO_2	0.02	0.04	
Al_2O_3	0.00	0.00	
CO_2	42.16	42.43	
Total	96.02	96.75	
			avg.
$(Sr/Ca)\times10^{-3}$	1.98	3.05	2.52
mol % $MgCO_3$	0.02	0	0.01

Family Grypoceratidae

Specimen: <u>Domatoceras</u> sp. Hyatt, 1891

Genotype: Hyatt, 1891, Texas Geol. Survey, Ann. Rept. 2, p. 327-356.

Description: The identification is based on a single specimen in which the conch has been filled with sediment with a corresponding flattening of the septa. In addition, the outer surface of the test is not present; hence, possible growth line ornamentation cannot be observed. The specimen is nautiliconic and the umbilical shoulder bears a row of nodes. The sutures form broad shallow lateral lobes.

Microarchitecture: The inner part of the conch wall and the septa are nacreous.

Stratigraphic position: Unit 9, 9½' to 10½' interval, about 10' southwest of the channel sample area.

Discussion: Most of the inner part of the conch wall has the nacreous luster, but in places the shell wall is chalky. Asphalt-impregnated specimen.

Chemical data:

Chemical staining: Aragonite + calcite

Infrared spectrophotometer: Approximately equal amounts of calcite and aragonite.

Electron microprobe:

wt %	Wall	Wall	
CaO	52.89	52.70	
MgO	0.00	0.00	
SrO	0.14	0.18	
MnO	0.00	0.00	
FeO	0.00	0.01	
P_2O_5	0.05	0.03	
SiO_2	0.01	0.03	
Al_2O_3	0.00	0.00	
CO_2	41.57	41.44	
Total	94.66	94.39	
			avg.
$(Sr/Ca)\times10^{-3}$	1.42	1.85	1.64
mol % $MgCO_3$	0	0	0

Order Ammonoidea

Superfamily Goniatitaceae

Family Neoicoceratidae

Specimen: Pseudoparalegoceras sp. Miller, 1934

Genotype: Miller, 1934, Jour. Paleo., v. 8, p. 18-20

Description: The identification is based on one large whole specimen on which the outermost wall material could not be recovered. Most of the sutures are also not well exposed, but they are better exposed on this one specimen than on the other 5 complete or incomplete specimens. The specimen has a maximum diameter of 160 mm and the umbilicus has a diameter of 45 mm. The exact number of colutions is indeterminate, but there are at least 6. The only part of the suture pattern which is discernible consists of a high, rounded U-shape first lateral saddle; a broad acuminate first lateral lobe; and a U-shape second lateral saddle. The nature of the ventral lobe and the suture pattern adjacent to the umbilical shoulder cannot be determined. The acuminate first lateral lobe is the most distinctive feature of this subdiscoidal ammoniticone.

Microarchitecture: The conch walls and septa are nacreous.

Stratigraphic positions: 1, Unit 9, upper 2 feet, about 80' northeast of the channel sample area.

2, From large boulder from the lower part of unit 9, in vicinity of the channel sample area.

Discussion: 1, Sample of a septum from a large fragment of a conch, asphalt-impregnated.

2, About one-half complete conch, asphalt-impregnated; material mostly chalky after removal of asphalt.

Chemical data:

Chemical staining: 1, Calcite + aragonite

X-ray diffraction:
Qualitative: 2, Calcite, some aragonite

Infrared spectrophotometer: 1, Approximately equal amounts of calcite and aragonite.

<u>Pseudoparalegoceras</u> sp. (Continued)

Electron microprobe:

wt %	1a	1b	
CaO	53.16	52.54	
MgO		0.01	
SrO	0. 5	0.22	
MnO	0.01	0.00	
FeO	0.00	0.00	
P_2O_5	0.06	0.08	
SiO_2	0.02	0.09	
Al_2O_3	0.00	0.00	
CO_2	41.83	41.33	
Total	95.33	94.07	
			avg.
$(Sr/Ca)\times10^{-3}$	2.49	2.23	2.36
mol % $MgCO_3$	-	0.02	0.01

Family Schistoceratidae

Specimen: *Wellerites mohri* ? Plummer and Scott, 1937

Genotype: Plummer and Scott, 1937, Texas Univ. Bull. 3701

Description: The identification is based on a small fragment of the conch on which most of the outermost layers have not been preserved. The fragment is typical of a discoidal and ammoniticonic test. The sutures in the ventral and umbilical areas are not present in this fragment. The three lateral lobes which are visible are all narrow, deep, and strongly pointed. The three visible saddles are rounded, asymmetrical, and broad.

Microarchitecture: Nacreous inner layer and septa.

Stratigraphic position: Unit 9, upper 2 feet, about 10' southwest of channel sample area.

Discussion: Sample of inner wall from small fragment of the conch, asphalt-impregnated.

Chemical data:

Chemical staining: Calcite + aragonite

Electron microprobe:

wt %	1a	1b	
CaO	52.88	52.93	
MgO	0.01	0.02	
SrO	0.21	0.16	
MnO	0.00	0.02	
FeO	0.00	0.00	
P_2O_5	0.07	0.06	
SiO_2	0.03	0.03	
Al_2O_3	0.00	0.00	
CO_2	41.59	41.64	
Total	94.79	94.86	
			avg.
$(Sr/Ca)\times10^{-3}$	2.12	1.63	1.88
mol % $MgCO_3$	0.02	0.06	0.04

Class Bivalvia
Order Pterioida
Superfamily Pectinacea
Family Aviculopectinidae

Specimen: Chaenocardia ovata Meek and Worthen, 1869

Type species: Meek and Worthen, 1869, Acad. Nat. Sci. Phil. Proc., p. 137-172.

Description: Prosocline, medium size mytiliform-like, wide postero-dorsal margin, wedge-shaped byssal sinus on right valve but poorly developed on left valve, faint crenulated radial ornamentation in addition to weakly developed growth lines. Most specimens consist of disarticulated single valves.

Microarchitecture: Thin outer prismatic layer; thick inner crossed lamellar layer.

Stratigraphic positions: 1, Unit 9, upper 2 feet, about 45' northeast of the channel sample area.

2, Unit 9, 9½' to 10½' interval, 10' southwest of the channel sample area.

Discussion:

Age	Length (mm)	Width (mm)	Valve	Remarks
1, Juvenile	19	16	-	Asphalt-impregnated
2, Adult	33	24	Right	Asphalt-impregnated

Chemical data:

Chemical staining:

	Outer	Inner
1,	Calcite	Aragonite + calcite
2,	Calcite	Aragonite + calcite

X-ray diffraction:

Qualitative:

	Outer	Inner
2,	Calcite	Aragonite + calcite

Chaenocardia ovata (Continued)

Electron microprobe:

wt%	1a Outer	1c Inner	1d Inner		2a Outer	2b Inner
CaO	51.87	53.53	54.17		53.38	54.73
MgO	1.25	0.02	Tr		1.03	0.02
SrO	0.10	0.14	0.12		0.06	0.17
MnO	Tr	0.05	0.00		0.02	0.04
FeO	0.01	0.00	0.03		0.01	0.00
P_2O_5	0.04	0.08	0.05		0.04	0.07
SiO_2	Tr	0.00	Tr		0.04	0.02
Al_2O_3	0.00	0.00	0.00		0.01	0.00
CO_2	42.12	42.12	42.58		43.06	43.06
Total	95.39	95.94	96.95		97.65	98.11
				avg.		
$(Sr/Ca)\times10^{-3}$	1.03	1.42	1.23	1.33	0.60	1.63
mol % $MgCO_3$	3.24	0.04	Tr	0.02	2.61	0.05

Phylum Arthropoda

Class Crustacea

Subclass Ostracoda

Order Palaeocopida

Family Geisinidae

Specimen: Hypotetragona sp. Morey, 1935

Genotype: Morey, 1935, Jour. Paleo., v. 9, no. 4, p. 326, pl. 28, fig. 1.

Description: Subquadrate, bisulcate, with anterior sulcus shallow; straight incised hinge line; right valve overlaps left valve to cardinal angles; no posterodorsal spine. Kloedenillid sexual dimorphism observed in various specimens. The female carapace is wedge-shape with the greatest width in the posterior; whereas, the male carapace is elongate-ovate with the greatest width in the medial area.

Skeletal morphology: Single-layer carapace

Stratigraphic positions: 1, Unit 11, o" to 4" above top of unit 10, about 45' northeast of the channel sample area.

2, DB-IV section, middle part of DB-IV-2 & 3.

Discussion: 1, Male specimen, asphalt-impregnated, length 0.7 mm, height 0.3 mm.

2, Female specimen, nonasphaltic, length 0.8 mm, height 0.4 mm.

Chemical data:

Chemical staining: 1, Calcite 2, Calcite

Electron microprobe:

wt %	1a	1b	avg.	2a	2b	avg.
CaO	52.59	53.03		53.31	53.87	
MgO	1.34	1.31		0.52	0.44	
SrO	0.08	0.03		0.09	0.10	
MnO	0.16	0.12		0.05	0.13	
FeO	0.18	0.19		0.28	0.45	
P_2O_5	0.10	0.14		0.05	0.07	
SiO_2	0.02	0.00		0.04	0.03	
Al_2O_3	0.00	Tr		0.09	0.14	
CO_2	42.98	43.25		42.64	43.16	
Total	97.45	98.07		97.07	98.39	
$(Sr/Ca)\times10^{-3}$	0.81	0.32	0.56	0.91	1.05	0.98
mol % $MgCO_3$	3.40	3.30	3.35	1.32	1.12	1.22

Family Paraparchitidae

Specimen: <u>Proparaparchites</u> sp. Cooper, 1941

Genotype: Cooper, 1941, Ill. State Geol. Survey Rept. Inv. No. 77, 101 p., 14 pl.

Description: Subrectangular, smooth, unilobate, nonsulcate, straight incised hinge line; left valve overlaps right valve along free margin; no pronounced forward swing, both ends similarly rounded.

Skeletal morphology: Single-layer carapace

Stratigraphic position: Unit 11, lower 1 inch, channel sample area.

Discussion: Asphalt-impregnated specimen

Chemical data:

Chemical staining: Calcite

Electron microprobe:

wt %

CaO	53.01
MgO	1.20
SrO	0.12
MnO	0.06
FeO	0.13
P_2O_5	0.06
SiO_2	0.02
Al_2O_3	0.00
CO_2	43.09
Total	97.69
$(Sr/Ca)\times10^{-3}$	1.26
mol % $MgCO_3$	3.04

Order Podocopida

Family Bairdiidae

Specimens: Bairdia spp. McCoy, 1844

Genotype: M'Coy, 1844, p. 164. Ireland

Description: Typical bairdiid morphology with the broadly arched dorsum, generally pronounced mid-height extremities with the anterior end higher and more rounded than the acuminate posterior region; left valve larger and overlapping the right valve around most of the carapace. Two species were recognized. Species A has a straight hinge area and a sharply rounded anterior extremity. Species B has a gently arcuate hinge area and both extremities are acuminate.

Skeletal morphology: Single-layer carapace.

Stratigraphic position: Species A, Unit 13, middle part, channel sample area.

Species B, DB-IV section, lower part of DB-IV-1.

Discussion: Sp. A, asphalt-impregnated specimen

Sp. B, nonasphalt-impregnated specimens

Chemical data:

Chemical staining: Sp. A. - Calcite
Sp. B. - Calcite

Electron microprobe:

wt %	sp. A	sp. B (a)	sp. B (b)	
CaO	52.70	53.40	52.44	
MgO	0.88	0.54	0.56	
SrO	0.10	0.17	0.10	
MnO	0.29	0.06	0.16	
FeO	0.39	0.46	0.72	
P_2O_5	0.08	0.07	0.08	
SiO_2	0.05	0.03	0.06	
Al_2O_3	0.00	0.10	0.29	
CO_2	42.77	42.89	42.33	
Total	97.24	97.72	96.74	avg.
$(Sr/Ca)\times10^{-3}$	1.03	1.74	0.98	1.36
mol % $MgCO_3$	2.25	1.38	1.44	1.41

Suborder Metacopina

?Family Cavellinidae

Specimen: Cavellina sp. Coryell, 1928

Genotype: Coryell, 1928, Jour. Paleo., v. 2, no. 2, p. 89-90, pl. 11.

Description: Ovate, smooth, moderately arched dorsum, ends rounded, right valve larger than left valve, and right valve overlaps left valve around margin of entire carapace. Shallow muscle-scar pit in area just posterior of central part of carapace.

Skeletal morphology: Single-layer carapace

Stratigraphic positions: 1, Unit 13, middle part, channel sample area.

2, DB-III section, 14' to 15' interval

Discussion: 1, Asphalt-impregnated specimen

2, Nonasphalt-impregnated specimen

Chemical data:

Chemical staining: 1, Calcite

2, Calcite

Electron microprobe:

wt %	1a	1b		2a
CaO	53.29	53.54		52.75
MgO	0.78	0.82		0.82
SrO	0.31	0.24		0.18
MnO	0.10	0.10		0.22
FeO	0.00	0.11		0.34
P_2O_5	0.06	0.08		0.05
SiO_2	0.02	0.03		0.02
Al_2O_3	0.00	0.00		0.00
CO_2	42.86	43.14		42.71
Total	97.42	98.06	avg.	97.09
$(Sr/Ca)\times10^{-3}$	3.11	2.44	2.78	1.82
mol % $MgCO_3$	1.99	2.07	2.03	2.10

Phylum Echinodermata

Class Echinoidea

Order Cidaroida

Family Archaeocidaridae

Specimen: Archaeocidaris megastyla ? Shumard

Type species: Shumard and Swallow, 1858, Trans. St. Louis Acad. Sci., v. 1, p. 225.

Description: Specimens consist of broken primary spines which are robust and rounded-triangular in section. There are three low ridges which are armed with somewhat widely, but regularly-spaced worn short spinules. On most specimens spinules along any one ridge are about 1 cm apart. Several spines are nearly 1 inch in length. Most of the specimens are broken fragments of the shaft area, but many basal parts of spines were found in the DB-IV section. These basal parts include the base, collar region, and neck area of the spines. Only one inter-ambulacral plate was found, and it is from unit 9 of the asphalt quarry. It is badly worn, but a circular scrobicular area, boss, platform, non-crenulated parapet, and tubercle are readily discernible. The central perforation on the tubercle is about half the diameter of the tubercle. Except for the rounded-triangular cross section, the specimens closely resemble A. megastyla.

Microarchitecture: A grading spectrum of preservation of microarchitecture exists in the analyzed specimens. The stereom, consisting of lamellae and trabeculae, is well preserved in the few asphaltized specimens from the quarry. The medulla, as are the pores in the stereom, in these specimens, is filled with secondary calcite. Due to the mechanical abrasion during transport, the outer thin to absent cortex layer has been worn off on these otherwise well-preserved specimens. A slightly weathered spine from the quarry has nearly 75% obliteration of the original microarchitecture due to secondary replacement by calcite. Only the outer stereom area is preserved. The spines and bases from the DB-IV section have essentially total obliteration of the microarchitecture. Each structure now consists of a seemingly single blocky, nonporous crystal. Only the former medulla area is not part of the single crystal, as it is composed of tiny crystals of secondary calcite.

Archaeocidaris megastyla ? (Continued)

Stratigraphic positions:

Specimens:
1, Unit 9, middle part, about 10' southwest of channel sample area.
2, As with 1
3, Float, probably from unit 9
4, DB-IV section, lower part of DB-IV-2 & 3.
5, As with 4.
6, As with 4.
7, As with 4.

Discussion:

Specimens:	Area	Nature	Remarks
1,	Shaft (3cm long)	Porous	Asphalt-impregnated
2,	Shaft	Massive to porous	Asphalt-impregnated
3,	Shaft	Weathered	Poor
4,	Shaft	Massive	Nonasphalt-impregnated
5,	Shaft	Massive	Nonasphalt-impregnated
6,	Neck & Shaft	Massive	Nonasphalt-impregnated
7,	Collar	Massive	Nonasphalt-impregnated

Chemical data:

Chemical staining: Calcite with uniformly scattered dolomite areas for all specimens

X-ray diffractometer:

Quantitative:

1, (3 mol % $MgCO_3$) Calcite, trace dolomite, trace SiO_2.
2, (3 mol % $MgCO_3$) Calcite, 15 wt % dolomite, trace SiO_2.
4, (0.0 mol % $MgCO_3$) Calcite, 4-5 wt % dolomite, SiO_2.

Infrared spectrophotometer:

Qualitative:

1, Calcite, trace dolomite, SiO_2
2, Calcite, SiO_2, trace dolomite ?
3, Calcite, dolomite ?
4, Calcite, trace dolomite
5, Calcite, dolomite, SiO_2
6, Calcite, dolomite, SiO_2
7, Calcite, dolomite, SiO_2

Archaeocidaris megastyla ? (Continued)

Electron microprobe:

wt %	1a Stereom	1b Stereom	1c Stereom	1d Stereom	1e Stereom	1f Stereom	1g Stereom	1h Stereom	avg.
CaO	50.52	48.69	50.06	53.50	53.91	53.85	53.77	50.81	
MgO	3.11	3.12	3.54	2.74	2.26	1.80	3.47	1.05	
SrO	0.15	0.14	0.21	0.10	0.15	0.08	0.17	0.09	
MnO	0.09	0.07	0.00	0.08	0.02	0.05	0.06	0.01	
FeO	0.10	0.00	0.00	0.11	0.00	0.07	0.00	0.00	
P_2O_5	0.06	0.07	0.05	0.09	0.05	0.04	0.05	0.06	
SiO_2	2.49	4.52	0.98	0.03	0.14	0.40	0.37	3.09	
Al_2O_3	0.83	0.30	0.16	0.21	0.43	0.00	0.14	0.05	
CO_2	42.23	41.72	43.24	45.14	44.86	44.33	46.09	41.06	
Total	100.58	98.63	98.24	102.00	101.82	100.62	104.12	96.22	
$(Sr/Ca)\times10^{-3}$	1.66	1.60	2.23	1.04	1.46	0.83	1.66	0.91	1.42
mol % $MgCO_3$	7.86	8.17	8.93	6.64	5.51	4.42	8.22	2.80	6.57

wt %	2a Stereom	2b Stereom	2c Stereom	avg.	2d Medulla	3a Stereom	3b Stereom	avg.
CaO	49.20	49.31	51.12		56.61	53.95	52.84	
MgO	5.66	3.50	5.63		0.79	1.15	0.63	
SrO	0.18	0.11	0.15		0.01	0.24	0.22	
MnO	0.00	0.00	0.03		0.07	0.21	0.21	
FeO	0.02	0.33	0.03		0.09	0.03	0.21	
P_2O_5	0.07	0.12	0.07		0.06	0.05	0.06	
SiO_2	0.04	0.06	0.02		0.01	0.03	0.02	
Al_2O_3	0.09	0.00	0.04		0.02	0.00	0.00	
CO_2	44.88	42.76	46.36		45.39	43.84	42.50	
Total	100.14	96.19	103.45		103.10	99.50	96.69	
$(Sr/Ca\times10^{-3}$	1.97	1.19	1.63	1.60	0.10	2.44	2.21	2.33
mol % $MgCO_3$	13.77	8.93	13.25	12.00	1.90	2.87	1.61	2.24

Archaeocidaris megastyla ? (Continued)

Electron microprobe:

wt %	4a Stereom	4b Stereom	4c Stereom	avg.	5a Stereom	5b Stereom	5c Stereom	avg.	5d Medulla
CaO	53.88	54.31	53.79		51.91	52.34	52.38		56.00
MgO	0.73	0.61	1.51		1.30	1.29	1.46		0.09
SrO	0.21	0.24	0.30		0.15	0.26	0.21		0.03
MnO	0.05	0.06	0.00		0.05	0.04	0.03		0.00
FeO	0.00	0.00	0.00		0.16	0.01	0.04		0.28
P_2O_5	0.03	0.05	0.06		0.10	0.04	0.09		0.03
SiO_2	0.02	0.02	0.03		1.22	0.41	0.88		0.03
Al_2O_3	0.17	0.08	0.09		0.31	0.06	0.21		0.00
CO_2	43.20	43.42	43.99		42.34	42.63	42.83		44.24
Total	98.29	98.79	99.77		97.54	97.08	98.13		100.70
$(Sr/Ca)\times10^{-3}$	2.10	2.42	2.98	2.50	1.52	2.73	2.13	2.13	0.32
mol % $MgCO_3$	1.84	1.52	3.75	2.37	3.36	3.30	3.73	3.47	0.23

wt %	6 Neck & Shaft Stereom	7a Collar Stereom	7b Collar Stereom	avg.
CaO	54.50	53.93	54.64	
MgO	1.44	1.09	1.21	
SrO	0.25	0.29	0.25	
MnO	0.00	0.00	0.05	
FeO	0.00	0.00	0.05	
P_2O_5	0.08	0.08	0.01	
SiO_2	0.03	0.01	0.05	
Al_2O_3	0.11	0.25	0.14	
CO_2	44.45	42.64	44.37	
Total	100.86	99.29	100.77	
$(Sr/Ca)\times10^{-3}$	2.50	2.90	2.47	2.68
mol % $MgCO_3$	3.54	2.73	2.99	2.86

Archaeocidaris megastyla ? (Continued)

Material balance calculations between x-ray diffractometer and electron microprobe data:

a) Specimen 2:

X-ray data						Electron microprobe data	
wt % dolomite	(wt % MgO in dolomite)	+	wt % calcite	(wt % MgO in calcite)	=	wt % MgO	average for electron microprobe data
0.15	(21.8)	+	0.85	(1.2±0.2)	=	4.9±0.1	
3.3		+	1.00 ± 0.2		≅	4.9±0.1	
			4.3 ± 0.2		≅	4.9±0.1	

Note: The fact that there is not exact material balance is undoubtedly due to not knowing the error associated with the amounts of dolomite and calcite, as Tennant and Berger (1957) did not publish the error data.

b) Specimen 4:

X-ray data						Electron microprobe data	
wt % dolomite	(wt % MgO in dolomite)	+	wt % calcite	(wt % MgO in calcite)	=	wt % MgO	average for electron microprobe data
0.045	(21.8)	+	0.95	(0.0±0.5)	≅	0.95±0.03	
1.0		±	0.5		≅	0.95±0.03	

Calcite Cement in Quarry Units:

Stratigraphic positions:

1, Unit 9, middle part, channel sample interval.
2, Unit 13, middle part, channel sample interval.

Chemical data:

Chemical staining: 1, Calcite
2, Calcite

Electron microprobe:

wt %	1a	1b		2
CaO	56.59	53.91		55.76
MgO	0.29	1.00		0.49
SrO	0.14	0.03		0.06
MnO	0.16	0.15		0.47
FeO	0.20	0.22		1.00
P_2O_5	0.04	0.09		0.02
SiO_2	0.02	0.03		0.02
Al_2O_3	Tr	0.12		0.00
CO_2	45.00	42.64		45.23
Total	102.44	99.29		103.05
			avg.	
$(Sr/Ca)\times10^{-3}$	1.37	0.34	0.86	0.57
mol % $MgCO_3$	0.71	2.50	1.61	1.19