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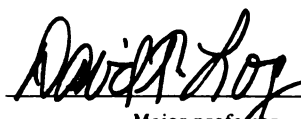
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AN APPLIED TEST OF THE ZONAL MODEL FOR
THE DIAGENESIS OF ARGILLACEOUS
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presented by

Gregory Scott Giles

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**CARBONATE CONCRETIONS OF THE ANTRIM SHALE:
AN APPLIED TEST OF THE ZONAL MODEL FOR
THE DIAGENESIS OF ARGILLACEOUS
MARINE SEDIMENTS**

By

Gregory Scott Giles

A THESIS

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ABSTRACT

CARBONATE CONCRETIONS OF THE ANTRIM SHALE: AN APPLIED TEST OF THE ZONAL MODEL FOR THE DIAGENESIS OF ARGILLACEOUS MARINE SEDIMENTS

By

Gregory Scott Giles

Semi-spherical, 80 to 100 cm. diameter authigenic calcite concretions from the Antrim Shale (Upper Devonian, Michigan Basin) were analyzed to determine their composition and origin. Concretion insoluble residues range from 4.5 to 10% and consist of illite, kaolinite, pyrite, chalcedony radiolarians and tasmanites. Calcite increases in Mg, Sr, and Mn concentration and decreases in Fe and Na concentration from concretion center outward. Calcite ^{13}C (-3.5 to -12.5 PDB) gets lighter and ^{18}O (-4.8 to -8.2 PDB) gets heavier from concretion center outward. An increase in pyrite concentration, change in pyrite ^{34}S , and decrease in calcite Fe concentration from concretion center outward suggests concretion formation in the sulphate reduction zone. When compared to the diagenetic zonal model proposed by C. D. Curtis, concretion characteristics do not match those listed for any of the model's diagenetic zones. Study results suggest that concretion formation is complex and can not be explained by the values listed in the zonal model.

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CHAPTER 1 INTRODUCTION

Authigenic carbonate concretions frequently occur in organic-rich marine shales. Curtis (1977, 1978) proposed a zonal sequence model for the burial diagenesis of argillaceous, organic-rich marine sediments. The diagenetic model proposed by Curtis (1977, 1978) is based on the assumption that, provided sufficient burial depth, organic-rich marine muds will pass successively through six distinct, depth related diagenetic zones (sulphate reduction zone, methanogenic zone, etc.).

Each diagenetic zone is defined by a zone specific organic degradation process (biotic or abiotic) that produces carbon dioxide. According to Curtis (1977) the carbon dioxide will dissolve in the surrounding pore waters and increase pore water bicarbonate levels. The increase in pore water bicarbonate may be sufficient to cause carbonate supersaturation and induce the precipitation of authigenic carbonate cement.

According to the zonal model, the physical and chemical composition of the carbonate cement that may precipitate will change with burial depth to reflect that of the diagenetic zone in which the carbonate precipitates.

For each diagenetic zone, the zonal model lists the sediment porosity, the mineralogy of the carbonate that may precipitate, and the carbon isotopic composition of the bicarbonate produced. According to Curtis (1978), the percentage of carbonate cement that occurs in the host rock

(cementation porosity) should be similar to the sediment porosity listed for the zone in which the carbonate precipitated, and the pore water carbon isotopic composition listed for each zone should be similar to that of the carbonate that may precipitate in that zone.

By proposing specific physical, isotopic and mineralogical compositions for the authigenic carbonates of each diagenetic zone, Curtis (1978) made the composition of the carbonate precipitate of each diagenetic zone unique to that zone. The unique carbonate compositions listed in the zonal model may enable the diagenetic zone in which an authigenic carbonate concretion precipitated (concretion origin) to be determined. If the values listed in the zonal model are representative of the diagenetic carbonate cements that precipitate during burial, the origin of a carbonate concretion from an organic-rich marine shale may be determined by analyzing the concretion for the parameters used by the zonal model and then comparing the concretion values to those listed for the six diagenetic zones.

NATURE OF PROBLEM

Studies of authigenic dolomite concretions by Curtis et al. (1986), Pearson (1985), and Wardlaw (1981) found that the concretions possessed an outer margin enriched in pyrite. According to the zonal model, authigenic dolomite should not precipitate above the methanogenic zone. Because the methanogenic zone is proposed to underlie the sulphate

reduction zone, the majority of pyrite formation should have occurred prior to dolomite precipitation.

While it can be argued that the amount of pyrite within a dolomite concretion should increase from concretion center outward due to dolomite precipitation in sediments of increased compaction (decreased porosity), the high concentrations of pyrite found at the outer margins of the dolomite concretions can not be explained by the sediment compaction argument.

Curtis et al. (1986) and Wardlaw (1981) found dolomite carbon isotopic values as light as -12 and -10.5 PDB (Pee Dee Belemnite carbon isotopic standard) respectively, and cementation porosities (proportion of carbonate cement in the host rock) as high as 90%. According to the zonal model, the uppermost dolomite cement that may precipitate (methanogenic zone) should have a carbon isotopic composition of approximately +15 PDB and a cementation porosity of approximately 30%.

The following concretion studies have used the zonal model to determine the origin of authigenic carbonate concretions: Campos and Hallam, 1979; Wada, 1980; Coleman and Raiswell, 1981; Tasse and Hesse, 1984; and Pearson, 1985. The above studies did not analyze the concretions for all the parameters used by the zonal model. Therefore, the above studies could not evaluate the concretions against all the parameters used by the zonal model to define the different diagenetic zones.

Because the zonal model is used by carbonate concretion studies to determine the origin of the carbonate concretions and the results of Curtis et al. (1986) and Wardlaw (1981) indicate that the values listed by the zonal model are not representative of some dolomite concretions, a study is needed to determine if the compositions of authigenic carbonate concretions can be matched to zonal model values for a specific diagenetic zone.

PURPOSE

While authigenic carbonate concretions are known to occur in several U.S. locations (Antrim Shale, Michigan; Hamilton Group, New York; Ohio Shale, Ohio; Pierrie Shale, South Dakota; Holz Shale, California; Shelikof Formation, Alaska) little work has been done on them. The purpose of this study is to determine the composition and origin of authigenic carbonate concretions from the Antrim Shale (Upper Devonian, Michigan Basin). Additionally, the physical and chemical compositions of the concretions will be interpreted in terms of the carbonate compositional values listed by the zonal model in an attempt to test the zonal model's ability to determine the diagenetic zone of concretion formation.

The above tasks will be accomplished by analyzing several authigenic carbonate concretions from the Antrim Shale for the compositional parameters used by the zonal model. This study will build on and attempt to confirm the

Antrim Shale carbonate concretion findings by Wardlaw (1981).

The working hypothesis of this study is that if the values listed by the zonal model are representative of authigenic carbonate concretions, then the compositions of the Antrim's concretions should be similar to the values listed for one of the diagenetic zones.

THE ZONAL MODEL

A zonal sequence model for the diagenesis of argillaceous, organic-rich marine sediments has been proposed by Curtis (1977, 1978) (Figure 1). The model was formulated on the basis of fragmentary evidence collected from numerous studies of both ancient and recent sediments (Curtis, 1978).

According to the zonal model, given sufficient burial depth, six depth related diagenetic zones may be recognized within the burial sequence of argillaceous, organic-rich marine sediments. Upon deposition, the sediment should reside in zone-1. With increasing depth of burial, the marine sediment should progressively pass from zone-1 to zone-6 (Figure 1).

Each diagenetic zone is defined by a specific organic degradation process which produce carbon dioxide which dissolves in the surrounding pore waters. According to the zonal model, the carbon dioxide is generated by biotic processes in zones 1 through 3 and abiotic processes in zones 4 through 6. At the pH of normal seawater the majority

ZONE	PROCESS DESCRIPTION	ZONE BASE DEPTH (m)	TEMP. ΔT °C	PERCENT AVERAGE POROSITY	13/C PDB CARBONATE	CARBONATES PRECIPITATED
1	BACTERIAL OXIDATION	.10	0	80	-25	NONE
2	BACTERIAL SULPHATE REDUCTION	10	0.3	75	-25	CALCITE LOW FE, MN PYRITE
3	BACTERIAL FERMENTATION	1000	30	30	+15	FERROAN CALCITE
4	DECARBOXYLATION	2500	75	15	-20?	FERROAN DOLOMITE OR SIDERITE
5	LIQUID HYDROCARBON GENERATION	4000	120	10	VARIABLE: MAY INCLUDE CARBON FROM PRIMARY OR EARLY DIAGENETIC CARBONATES	CACITE DOLOMITE FERROAN DOLOMITE SIDERITE DEPENDING UPON INSTABILITY OF EARLIER CARBONATES
6	GAS GRAPHITE METAMORPHISM	> 4000	120+	<10		

Figure 1. The zonal model (from Curtis, 1978).

of the carbon dioxide is converted to bicarbonate. According to Curtis (1978) the increase in pore water bicarbonate concentration may be sufficient to cause carbonate supersaturation and induce the precipitation of authigenic carbonate cements.

The precipitation of authigenic carbonate during the burial diagenesis of organic-rich sediments is supported by the studies of Abal-el Malek (1963), Berner (1968), Berner (1970) and Gardner (1973). The above studies found that the degradation of organic material may alter the surrounding pore water composition to that more favorable for the precipitation of authigenic carbonate.

The study by Lippman (1955) found that the precipitation of micritic carbonate cement within sediment pore spaces displaced pore water without significantly modifying pore geometry. Lippman (1955) hypothesized that the amount of carbonate cement within a host rock could be equated to the sediment porosity at the time of carbonate precipitation. Support for Lippman's hypothesis was shown by the study of Oertel and Curtis (1972) which found that detrital clay minerals within a siderite concretion showed progressively greater degrees of orientation (compaction) parallel to bedding from the concretion center outward. Based on the studies by Lippman (1955) and Oertel and Curtis (1972), Curtis (1977, 1978) proposed that the proportion of carbonate cement within the host rock should be similar to

the sediment porosity at the time and depth of carbonate precipitation.

The zonal model lists a single value for the sediment porosity of each diagenetic zone (Figure 1). The sediment porosity values listed in figure 1 are based on the depth/porosity data generated by Dickinson (1953), Ham (1966) and Preiss (1968). By equating the proportion (volume or weight percent) of carbonate cement with sediment porosity, Curtis allows the burial depth and diagenetic zone of carbonate precipitation to be determined.

According to Curtis (1978) the carbon isotopic composition of the carbonate that may precipitate in a diagenetic zone should be similar to that of the carbon dioxide produced in that diagenetic zone. The zonal model lists a specific carbon isotopic value for the carbon dioxide produced in zones 1 through 4 and proposes variable carbon isotopic compositions for the carbon dioxide produced in zones 5 and 6 (Figure 1).

According to Curtis (1977, 1978) the mineralogy of the carbonate that may precipitate in a specific diagenetic zone will be a function of the pore water composition of that diagenetic zone. The zonal model lists specific mineralogies for the carbonate(s) which may precipitate in each diagenetic zone (Figure 1).

The bacterial oxidation zone (zone 1) represents the uppermost diagenetic zone of the zonal model and is the only zone where dissolved (free) oxygen exists within sedimentary

pore water. This zone is commonly referred to as the aerobic zone. The presence and degree of bioturbation within a shale is frequently used to determine if the precursor sediments were deposited in an aerobic sedimentary environment.

Sediments in this zone may have porosities of 80% or greater (Preiss, 1968). In this zone, dissolved oxygen and aerobic bacteria oxidize organic material to produce carbon dioxide. This process may be represented by the following reaction:



The aerobic zone usually includes the entire water column and will extend into the sediment to a depth at which free oxygen exists (Irwin, 1977). When the water column is stagnant, stratified or contains a high organic input, the aerobic/anaerobic boundary may occur within the water column.

The depth to which zone 1 extends is affected by the nature of the sediment, the degree of bioturbation, the consumption rate of dissolved oxygen, and the sedimentation rate (Curtis, 1977). In slowly deposited pelagic sediments the aerobic zone may extend to a depth of at least 1 meter (Berner, 1978). In rapidly deposited sediments, the sediment will rapidly pass into the anaerobic zone.

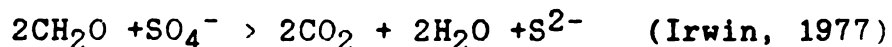
The soluble reaction products produced in the aerobic zone will diffuse back into the overlying depositional waters and not accumulate in the surrounding pore water (Curtis, 1978). Therefore, according to the zonal model authigenic carbonate should not precipitate in this zone.

Once the sedimentary pore-waters have become anoxic, and there is sulphate and reactive organic matter available, sulphate reduction commences (zone 2) and will continue until sulphate levels decrease or no more oxidizable organic matter is available (Goldhaber and Kaplan, 1975; Berner, 1964, 1983).

According to Berner (1985) over 90% of all medium to fine grained sediments buried in the marine environment become anoxic within a few centimeters of the sediment-water interface. Because ocean water contains higher levels of sulphate than dissolved oxygen, sulphate should diffuse deeper into the sediments than oxygen. If the water column is stagnant, stratified or has a high organic input, the upper limit of the sulphate reduction zone may occur within the overlying water column.

According to the zonal model, the sediment porosity of the sulphate reduction zone should be approximately 75%. Therefore, according to Curtis (1978), carbonates precipitating in the sulphate reduction zone should contain approximately 25% host sediment.

Sulphate reducing bacteria derive energy from the anaerobic oxidation of simple organic molecules by using aqueous sulphate as an electron acceptor. Sulphate reduction may be represented by the following reaction:



During sulphate reduction the organic matter is degraded forming CO_2 and H_2 as by-products of the oxidation.

The CO_2 is excreted and the H_2 is then passed through the cell wall where it is oxidized. The free electrons generated during the oxidation of H_2 pass back into the cell via vectorial electron transport and are utilized in a second reaction, the reduction of sulphate to sulphide (Odom and Peck, 1981). The protons produced by H_2 oxidation and the previously formed sulphide are both excreted and combine to form aqueous hydrogen sulphide. The free oxygen generated by the reduction of sulphate to sulphide combines with protons within the cell to form water which is excreted.

Because the carbon dioxide produced by sulphate reducing bacteria is converted to bicarbonate and the accompanying H_2S dissociates to HS^- , the process of sulphate reduction adds to both pore water alkalinity and acidity.

According to the zonal model low-Fe calcite should be the only carbonate to precipitate in this zone. The low-Fe designation of the zone-2 calcite is based on the studies by Curtis (1967) and Berner (1970) which found that the precipitation of pyrite in the sulphate reduction zone lowers the level of pore water iron. The formation of hydrogen sulphide and the occurrence of pyrite are commonly used as indicators of sulphate reduction (Berner, 1970, 1983).

The study by Kaplan and Rittenburg (1964) found that sulphate reducing bacteria preferentially metabolize isotopically light carbon. Therefore, the carbon dioxide produced in this zone should be enriched in isotopically

light carbon. The study by Presely and Kaplan (1968) found that pore water within the sulphate reduction zone increased in light carbon with increasing depth. The study by Presely and Kaplan (1968) found that the change in pore water isotopic composition could be modelled by adding carbon dioxide with an isotopic composition of -22 PDB. Based on the results of the above studies Curtis (1978) assigned a carbon isotopic value of -25 PDB to the carbon dioxide produced in the sulphate reduction zone.

Sulphate reducing bacteria have a preference for isotopically light sulphur and as a result, produce isotopically light sulphide. The preferential uptake of light sulphate by sulphate reducing bacteria causes the remaining sulphate reservoir to become progressively enriched in isotopically heavy sulphate. The rate of sulphate reduction and pore water sulphate concentration affect the isotopic composition of the sulphide produced and subsequently the pyrite precipitated (Faure, 1977). The degree of isotopic fractionation is inversely proportional to the rate of sulphate reduction (Postgate, 1979). If the size of the sulphate reservoir is limited, its isotopic composition will change as a result of the preferential reduction of isotopically light sulphate (Faure, 1977). The highest rate of sulphate reduction usually occurs near the sediment/water interface and decreases with depth. The decrease in sulphate reduction rate with depth is usually

due to decreasing levels of reducible sulphate and degradable organic material (Birnbaum and Wireman, 1984).

According to the zonal model, the methanogenic zone (zone 3) underlies the sulphate reduction zone (Figure 1). In this zone, methanogenic bacteria produce carbon dioxide and methane from the fermentation of organic material. The breakdown of organic matter by methanogenic bacteria may be represented by the following reaction:



Unlike sulphate reducing bacteria, methanogenic bacteria are not dependent upon the availability of an externally derived electron acceptor, but are limited by the availability of metabolizable organic material (Curtis, 1978). The methanogenic zone begins as soon as pore water sulphate levels decrease to a level where sulphate reduction ceases (Irwin, 1977). Like the overlying sulphate reduction zone, the methanogenic zone represents an anaerobic environment. The lower boundary of the methanogenic zone has been suggested to occur at temperatures around 30°C or when metabolizable organic material becomes exhausted (Curtis, 1978).

Studies have shown that when sulphate reducing bacteria and methanogenic bacteria are exposed to similar organic material, sulphate reducing bacteria outcompete methanogenic bacteria for the organic substrate (Thauer, 1982). Based on the above finding, methanogenic bacteria should not become active until most pore-water sulphate has been depleted and

supports the separation of sulphate reduction and methanogenesis into separate diagenetic zones.

The cessation of pyrite precipitation should allow pore water Fe concentrations to increase and allow more Fe to be incorporated into the carbonate phase. According to the zonal model, Fe-rich carbonates such as siderite, ferroan calcite and ferroan dolomite may precipitate in the methanogenic zone.

Methanogenic bacteria preferentially fractionate light carbon into the methane phase which enables biogenic methane to be isotopically distinguishable from methane derived from abiotic processes that occur during deeper burial. As a result of the above fractionation, it is commonly believed that the accompanying carbon dioxide should be isotopically heavy (Irwin et al., 1977; Curtis, 1978)

The study by Nissenbaum et al. (1972) found methanogenic zone carbon dioxide with a carbon isotopic composition of approximately +17 PDB. This value is significantly heavier than that found for sulphate reduction zone carbon dioxide and suggests that the two zones can be distinguished on the basis of pore water carbon isotopic composition. The study by Claypool et al. (1973) like that of Nissenbaum (1972) found isotopically heavy carbon dioxide in the methanogenic zone.

Based on the known fractionation of methanogenic bacteria and the pore water studies of Nissenbaum (1972) and Claypool (1973), Curtis (1978) proposed that carbon dioxide

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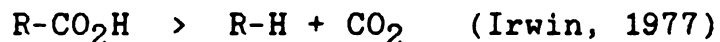
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produced in the methanogenic zone should have a carbon isotopic composition of approximately +15 PDB.

According to the zonal model, sediments within the methanogenic zone should have a porosity of approximately 30%. Therefore, according to Curtis (1978), carbonates precipitating in the methanogenic zone should contain approximately 70% host sediment.

Below the methanogenic zone lies the decarboxylation zone. Unlike the overlying methanogenic and sulphate reduction zones, decarboxylation is an abiotic process. In this zone carbon dioxide is generated by elimination reactions similar to the following:



Because decarboxylation is a temperature sensitive abiotic reaction it should not begin until a burial depth is reached at which the pore water temperatures rise high enough to trigger the reaction. The boundaries of this zone are not clearly defined and are dependent on sediment composition, burial rate and geothermal gradient (Tissot, 1978). The rate of CO₂ generation in this zone presumably increases with rising temperatures, reaches a maximum, and then decreases as the amount of metabolizable organic substrate decreases (Curtis, 1977).

The carbon isotopic composition of decarboxylation zone carbon dioxide should be light, reverting back to that of the organic material being degraded. Because the organic material at this depth has already been partially degraded

in the overlying zones, the organic material should be somewhat depleted in light carbon (Curtis, 1978). According to the zonal model carbon dioxide produced in the decarboxylation zone should have a carbon isotopic composition of approximately -20 PDB.

According to the zonal model the mineralogy of the carbonates that may precipitate in this zone is similar to that of the overlying methanogenic zone. According to the zonal model, sediment in the decarboxylation zone should have a porosity of approximately 15%. Therefore, according to Curtis (1978) carbonates precipitating in the decarboxylation zone should contain approximately 85% host sediment.

The kerogen modification study by Laplante (1974) and the experimental kerogen maturation study by Tissot et al. (1974) suggest that carbon dioxide should continue to be generated at depth in association with the zone of liquid hydrocarbon formation (zone-5) and the zone of graphite formation (zone-6).

According to the zonal model, sediment porosity in zone-5 should be approximately 10% and less than 10% for zone-6. Therefore, according to Curtis (1978), carbonate precipitating in the above zones should contain approximately 90% or more of host sediment respectively.

Zones 5 and 6 are less likely than the overlying zones to be influenced by carbon dioxide generated by the degradation of organic material, but the continued

precipitation of diagenetic carbonate must be anticipated in these zones as a consequence of the organic processes operating in these zones (Curtis, 1977). According to the zonal model, carbonates of variable carbon isotopic composition and mineralogy may precipitate in zones 5 and 6.

ANTRIM SHALE

The Antrim Shale is an Upper Devonian, organic-rich, pyritic, uraniferous, black marine shale that underlies most of the Michigan Basin (Bennett, 1978). The Antrim Shale was first listed in the geological literature by state geologist Douglas Houghton in 1838 (Rep. Inv. 22, 1979). The Antrim was given its present name in 1901 by A. C. Lane who named it after the northern Michigan county that contains the type section. Prior to 1901 the Antrim was referred to as the Huron Shale and the St. Clair Shale. The Antrim is in part correlative with and stratigraphically equivalent to the Ohio, New Albany, Chattanooga, Maple Hill, Mountain Glen, Kettle Point and Sweetland Creek Shales (Conant and Swanson, 1961).

The Antrim Shale is the lower member of a larger sequence of shales which are underlain by the Squaw Bay Limestone and overlain by the Marshall Sandstone. The Squaw Bay Limestone is a ten foot thick bed of brown limestone which is classified as the upper member of the Middle and Upper Devonian Traverse Group (Kelly and Smith, 1947). The paleontology of Traverse Group limestones is well known and Upper Devonian cephalopods have been identified in the Squaw

Bay Limestone. The nature of the Squaw Bay/Antrim contact is not known because the base of the Antrim has not been identified in outcrop (Rep. Inv. 22, 1979).

In western Michigan, the Antrim is overlain by the gray to gray-green Ellsworth Shale which grades upwards into the gray to blue-gray Coldwater Shale. In eastern Michigan the Antrim is overlain by the bluish gray Bedford Shale which grades upward into the Berea Sandstone; a fine grained quartz sandstone that becomes finer basinward (Asseez, 1969). The Bedford/Berea sequence is generally restricted to eastern Michigan, but tongues of the Bedford have been found to extend westward into the Ellsworth Shale (Asseez, 1969).

The Antrim Shale ranges in thickness from over 600 feet near the center of the Michigan Basin to approximately 100 feet near the basin margin (Bennett, 1978). Outcrops of the Antrim are located mainly in the northern part of the southern peninsula and occur in Antrim, Charlevoix, Emmet, Cheboygan and Alpena counties. The Antrim also outcrops in Oakland county in southeastern Michigan (Newcombe, 1928).

The Antrim is thought to have been deposited in an epicontinental sea which was bounded by a clastic delta to the east and a carbonate platform to the west (Routsula, 1981). The high organic content, high authigenic silica content and a lack of bioturbation and carbonate material suggest that the majority of the Antrim was deposited in a low energy environment.

Mineralogically the Antrim is composed of the following: 50-60% quartz, 20-35% illite, 5-10% kaolinite, 0-5% chlorite, 0-5% pyrite and up to 13% organics (Ruotsula, 1981). The majority of Antrim quartz is microcrystalline in habit and appears to be authigenic in nature (This Study). According to Hathon (1979), the abundance, microcrystalline habit, and light oxygen isotopic composition of Antrim quartz suggests that radiolarian tests may be the source of Antrim quartz.

The majority of the Antrim is composed of a black shale which is largely void of bioturbation and carbonate clastic material. Towards its base, the Antrim becomes calcareous and contains several limestone beds. These calcareous zones and the adjacent black shales are bioturbated (This Study). The calcareous zones are fossiliferous and typically contain brachiopods, bryozoans, crynoids, and conodonts (Bennett, 1978).

The organic matter within the Antrim is composed of both terrestrial and marine material. Most of the Antrim's organic matter consists of marine algae (Levanthel, 1978), such as Tasmanites, and Foerstia (Matthews, 1983). Most accumulations of tasmanite are marine in origin and are associated with near shore environments of ancient shallow seas (Cane, 1976). Foerstia has been detected in other midcontinent organic-rich shales and is used for stratigraphic correlation (Matthews, 1983). The terrestrial

material consists of Devonian land plant debris, principally the tree-like material of *Callixylon* (McGregor, 1954).

Authigenic carbonate concretions are found only in the lower section of the Antrim Shale. Carbonate concretions similar to those in the Antrim have been reported in the lower portion of the Kettle Point Shale (Antrim equivalent) (Daily, 1900) and the nearby Ohio Shale (Clifton, 1957; Foreman, 1959). Concretion bearing strata of the lower Antrim are exposed in the northeastern and northwestern areas of Michigan's Lower Peninsula and Kettle Point Ontario; suggesting a widespread occurrence of the Antrim's concretions (Figure 2).

The northwestern Lower Peninsula and Kettle Point exposures occur along the Great Lakes shorelines. Due to an inability to collect unweathered samples from these exposures, all the concretions sampled by this study were collected from the Paxton Shale Quarry. The Paxton quarry is located approximately 35 kilometers west of Alpena Michigan (Figure 2). With approximately 15 meters of stratigraphic exposure, the Paxton quarry represents the largest known exposure of concretion bearing Antrim strata.

This study separates the Antrim exposure at the quarry into 3 units (Figure 3). Units 1 and 3 consist of black, organic rich, fissile shales. These shales are free of clastic carbonate material, free of bioturbation, and contain both pyrite rimmed carbonate concretions and individual pyrite concretions.

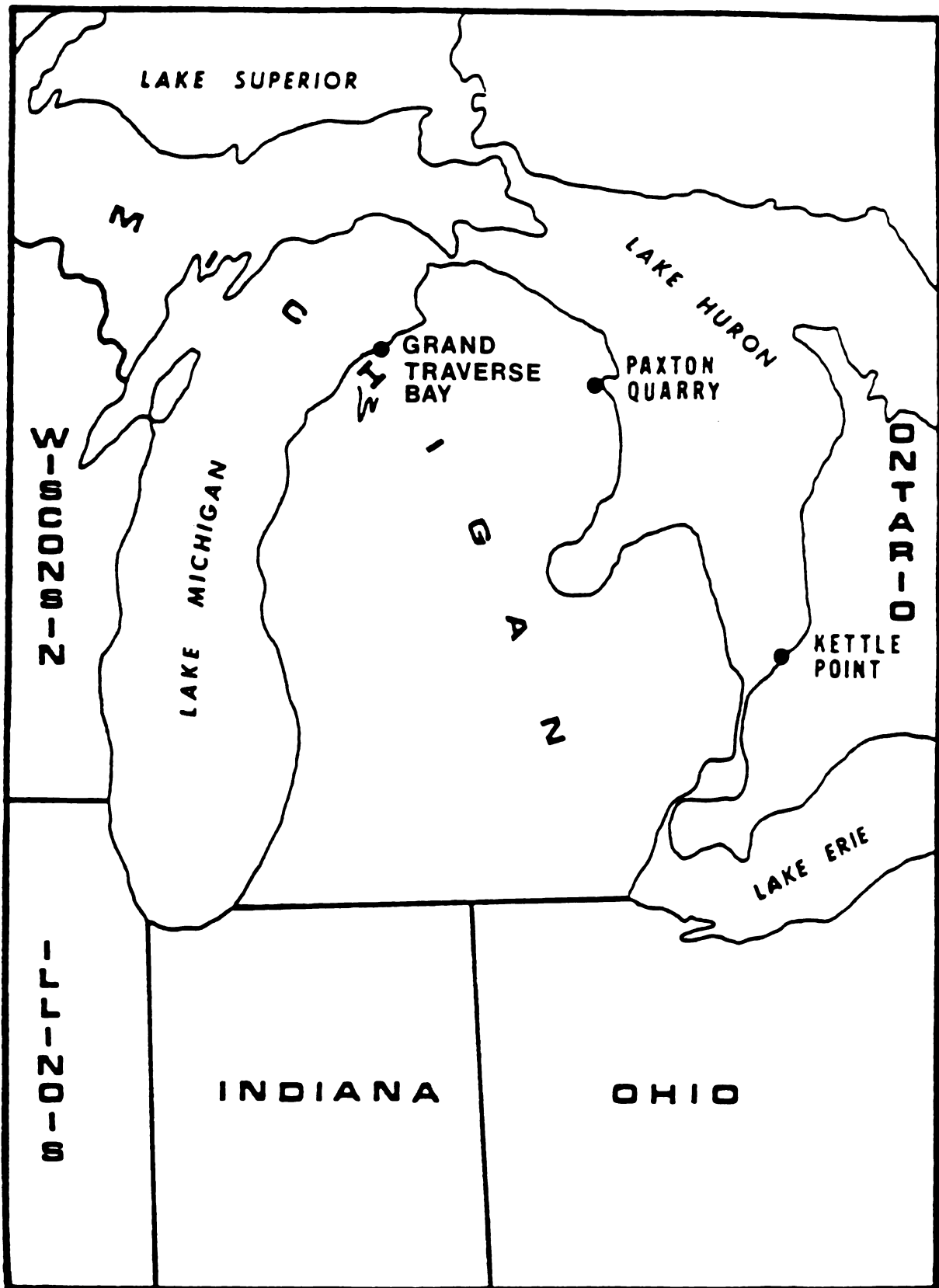


Figure 2. Antrim Shale outcrop locations of concretion bearing strata.

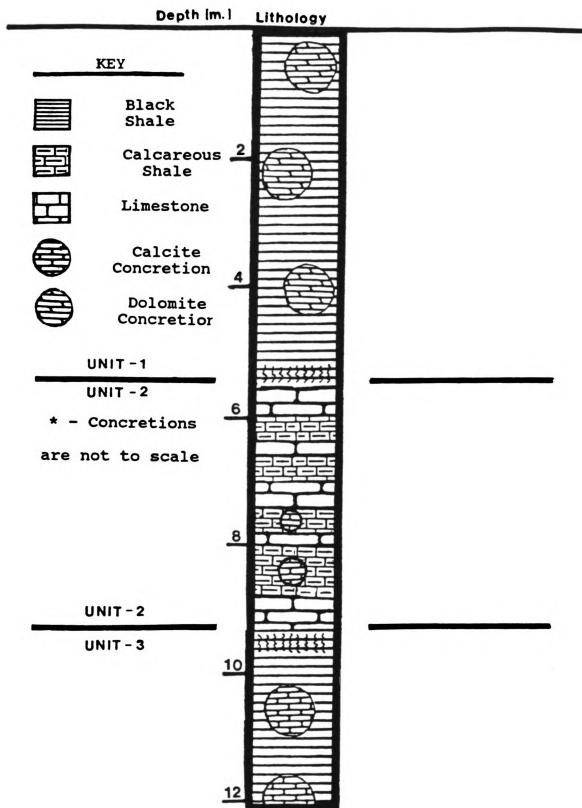


Figure 3. Stratigraphy of the Paxton Shale Quarry lower quarry pit.

Unit-2 consists of a series of interbedded, fine grained, gray-green, calcareous shales and limestones. The limestones are mottled, nodular (concretionary), fossiliferous and heavily bioturbated. At least two of the gray-green calcareous shales contain elliptical, gray-green, concretions that do not have pyrite rims.

The Paxton quarry contains an upper and a lower quarry pit. The lower quarry pit exposes strata of Unit-3, Unit-2, and between one and four meters of Unit-1. The upper quarry pit only exposes strata of Unit-1. The concretions sampled by the studies of Hathon (1979) and Wardlaw (1981) were collected from the upper quarry pit, whereas the concretions sampled in this study were collected from the lower quarry pit. Figure 4 shows a typical exposure of the lower quarry pit, strata of Unit-3, Unit-2, and the base of Unit-1 can be seen.



Figure 4. Typical Antrim Shale exposure at the Paxton Shale Quarry, lower quarry pit. Scale bar = approximately 3 meters.

CHAPTER 2 PREVIOUS CONCRETION WORK

PREVIOUS ANTRIM SHALE CONCRETION WORK

Concretion bearing strata of the Antrim Shale outcrop along the Lake Huron shoreline in Ontario Canada (Figure 2). Daily (1900) studied the concretions at this outcrop and found the concretions to be up to one meter in diameter, spherical in shape, and composed of calcite. Concretion crystals were found to be arranged in a radial fashion and contain little insoluble residue. No organic fossil material was found at the concretion centers.

According to Daily (1900), the shale beds adjacent to the concretions appear to drape over the concretions and the joints within the shale do not cut through the concretions. Based on the above observations, Daily (1900) concluded the following: (1) the concretions formed in place; (2) concretion growth displaced the surrounding shale; and (3) the concretions post date the period of shale joint development.

The largest known outcrop of concretion bearing Antrim strata occurs at the Paxton Shale Quarry (Figure 2). Hathon (1979) analyzed a carbonate concretion from the Paxton quarry while conducting a study on the isotopic composition of Antrim quartz. The concretion analyzed by Hathon (1979) was spherical in shape, approximately 30 cm. in diameter and possessed an outer margin enriched in pyrite. The concretion was found to be composed of ferroan dolomite. The dolomite carbon isotopic composition was found to range from -12.2 to

-10.1 PDB and the oxygen isotopic composition was found to range from -7.54 to -6.28 PDB. Concretion dolomite was found to increase in heavy carbon and increases in light oxygen from concretion center outward.

Wardlaw (1981) analyzed two spherical concretions from the Paxton quarry that appear to be similar to the concretion analyzed by Hathon (1979). The concretions analyzed by Wardlaw (1981) had vertical diameters of 30 and 32 cm. respectively, possessed outer margins enriched in pyrite, and were found to be composed of ferroan dolomite. Dolomite carbon isotopic composition was found to range from approximately -12 to -10 PDB and increase in heavy carbon from concretion center outward. Dolomite oxygen isotopic composition showed little variation and was found to range from -9.29 to -9.10 PDB.

Wardlaw analyzed concretion dolomite for Ca, Mg, Na, Sr, K, Fe, and Zn. No discernible trace element trends were found within the concretions. The carbonate trace element data generated by Wardlaw suggest that either: (1) the ferroan dolomite concretions did not record any changes in pore water chemistry that may have occurred during concretion growth; (2) the changes in pore water composition that occurred during concretion growth are very complex and not readily identifiable as trends; or (3) there was no trend in pore water chemistry during growth of the concretions.

Wardlaw measured the amount of organic carbon across the concretions (approximately 0.30 to 0.85%) and found no trend. Concretion cementation porosities were found to range from approximately 48 to 90%. While the cementation porosities found in concretion #7 showed no discernable trend from concretion center outward, a decrease in cementation porosity from concretion center outward was found in concretion #3.

According to Wardlaw, the isotopic composition of the concretions do not reveal any information on the state of the sedimentary environment associated with concretion precipitation, the time of concretion growth or the temperature or salinity of the pore waters associated with concretion growth.

Wardlaw proposes that the carbon isotopic values represent a mixture of either sulphate reduction zone and methanogenic zone carbon, or methanogenic zone and decarboxylation zone carbon. Wardlaw attributes the light oxygen isotopic values to a lighter Devonian seawater or concretion formation in a nearshore brackish environment. Wardlaw suggests that the consistency in oxygen isotopic value represents concretion formation in an open system.

Wardlaw concluded that while the stable isotopic composition suggests precipitation at deep depth, the physical characteristics of the concretions suggest precipitation at shallower depth. Wardlaw proposes that the

concretion precipitated within the top 10 meters of the sediment.

According to Wardlaw, the increase in heavy carbon from concretion center outward, combined with an outer rim of iron sulphide, make concretion compositions inconsistent with the values listed by zonal model.

Coniglio and Cameron (1990) studied authigenic carbonate concretions from the black shales of the Kettle Point Formation (Antrim equivalent - Ontario, Canada). The concretions of the above study were collected from an outcrop along the Lake Huron shoreline (Figure 2). This is the same outcrop sampled by the study by Daily (1900).

Coniglio and Cameron (1990) sampled portions of four concretions from the rubble at the base of the Lake Huron shoreline. The concretions sampled were spherical to elliptical in shape, 40 to 60 cm. in size, and were found to consist of ferroan calcite with lesser amounts of ferroan dolomite and pyrite. The concretions were found to be composed of a mosaic of pseudospar crystals up to 5 mm. in size. The outer half of the concretions were found to be composed of calcite crystals acicular to fibrous in shape. The acicular crystals are parallel to each other and radial to the concretion centers.

The carbon isotopic composition of concretion calcite was found to range from -13 to -4 PDB. The oxygen isotopic composition of the concretions was found to range from -7 to -4 PDB. The concretions were found to increase in heavy

carbon and light oxygen from concretion center outward. The increase in heavy carbon was attributed to methanogenesis in the surrounding sediments. The increase in light oxygen was attributed to an increase in temperature associated with increasing burial depth.

Concretion cementation porosities were found to be approximately 65 to 70% for the pseudospar at the center of the concretion and approximately 80 to 85% for the acicular crystals near the concretion edge. The occurrence of lower amounts of insoluble residue near the concretion edge suggests that concretion growth modified the fabric of the host sediment.

Pyrite concentrations were found to increase at the concretion edge. The only carbonate trace element measured by Coniglio and Cameron (1990) was Fe. The outer region of the concretions were found to contain higher calcite Fe concentrations than the inner region.

Coniglio and Cameron (1990) concluded that disseminated ferroan dolomite and pyrite precipitated in the top of the sulphate reduction zone, and with continued sulphate reduction, ferroan calcite precipitated to form the concretions.

PREVIOUS CARBONATE CONCRETION WORK

Early studies on carbonate concretions from marine shales focused on their field occurrence, structure (Daily, 1900; Tarr and Twenhofel, 1932; Weeks, 1953) and chemistry (Strakhov, 1960). The study by Daily, (1900) was one of the

Table 1. Summary of carbonate concretion research.

Morphology

sheet - 6,9,12,14,16,21,22,23

nodule - 2,3,4,5,7,10,13,14,18,19,20,21,22,23,24,25,26

Relative Age

diagenetic precompaction - 5,7,12,14,15,18,20,,22,23,24,25,26

diagenetic compaction - 17,20,21,22,23

epigenetic - 3

Mineralogy

calcite - 1,4,5,7,10,11,13,14,15,16,17,19,20,21,23,24,25,26

dolomite - 5,12,15,16,17,18,20,21,22,23,25

siderite - 6,8,9,12,14,15,16,20,22,25

Chemical Determinations

Ca - 1,2,3,7,8,9,10,11,18,22,23,24,25

Mg - 1,7,8,9,10,11,15,16,17,18,22,23,24,25

Fe - 1,3,7,8,9,11,14,18,22,23,24,25,26

Mn - 3,8,10,16,18,22,23,24,25

Sr - 4,7,10,11,18

Isotopes

Carbon - 2,4,6,7,9,12,13,14,15,16,17,18,21,22,25,26

Oxygen - 4,7,12,13,16,17,18,19,21,22,25,26

Sulphur - 18,20,25

- 1 Hallam, A. (1967)
- 2 Galimov, E. M. and Girin, Y. P. (1968)
- 3 Girin, Y. P. (1970)
- 4 Hoefs, J. (1970)
- 5 Raiswell, R. (1971)
- 6 Curtis, C. D., Petrowski, C. and Oertel, G. (1972)
- 7 Sass, E. and Kolodny, Y. (1972)
- 8 Pearson, M. J. (1974)
- 9 Curtis, C. D., Pearson, M. J. and Somogyi, V.A. (1975)
- 10 Raiswell, R. (1976)
- 11 Dickson, J. A. and Barber, C. (1976)
- 12 Irwin, H. and Curtis, C. D. (1977)
- 13 Hudson, J.D. (1978)
- 14 Pearson, M.J. (1979)
- 15 Hein, J. R., O'Neil, J. R. and Jones, M. G. (1979)
- 16 Irwin, H. (1980)
- 17 Wada, H., et al. (1980)
- 18 Wardlaw M. (1981)
- 19 Colman, M. L. and Raiswell, R. (1981)
- 20 Matsumoto, R. and Iijima, A. (1981)
- 21 Gautier, D.L. (1982)
- 22 Tasse, N. and Hesse, R. (1984)
- 23 Pearson, M. J. (1985)
- 24 Boles, J. R., Landis, C. A. and Dale, P. (1985)
- 25 Curtis, C. D., Colman, M. L. and Love, L. G. (1986)
- 26 Coniglio, M. and Cameron, J. (1990)

Figure 5. Studies reviewed to construct table 1.

first to perform a chemical analysis of a carbonate concretion. An early diagenetic origin for authigenic carbonate concretions was proposed by Tarr and Twenhofel (1932) and reiterated by Weeks (1957)

Table 1 summarizes much of the carbonate concretion work that has been conducted over the last 25 years. The studies reviewed to construct table 1 are listed in figure 5. The study numbers listed in table 1 are correlatable with the numbers listed in figure 5.

Authigenic carbonates in marine shales may occur as sheets (horizons) but nodules (concretions) predominate. Authigenic carbonate concretions range in size from approximately 2 cm. in Miocene age deep sea sediments (Wada, 1980) to approximately 2 m. in diameter (Boles, 1985; This Study). Concretion shape ranges from sperical to elliptical with semi-spherical being the most common. Carbonate concretions usually have longer horizontal axis than vertical axis. There is a preference for concretions to develop along specific horizons (Weeks, 1957; Raiswell, 1971; Irwin, 1980). Authigenic carbonate concretions have been found at depths as shallow as 6 meters (Wada, 1980), and have been estimated to have formed at depths as great as 3 kilometers (Matsumoto and Iijima, 1981)

The study by Galimov and Girin (1968) concluded that concretions grow from their center outwards. Support for radial concretion growth is provided by Oertel and Curtis (1972) which found that clay particles within a siderite

concretion exhibited progressively increasing degrees of orientation parallel to host rock bedding from concretion center outward. Support for radial concretion growth is also supported by Raiswell (1971) which found a decrease in concretion carbonate content from concretion center outward.

MINERALOGY

Based on a review of previous concretion work (Table 1), the principal concretion forming authigenic carbonates are calcite > dolomite > siderite. Rhodochrosite has been found by some concretion studies (Tasse and Hesse, 1984) but occurs infrequently.

While concretions of different mineralogy frequently occur within the same formation, concretions along the same stratigraphic horizon are usually of similar mineralogy. Occasionally concretions are found that exhibit a change in mineralogy from concretion center outward. The study by Galimov and Girin (1968), and Gautier (1982) found siderite concretions with calcite centers. Pyrite is a common constituent of authigenic carbonate concretions and has been used to indicate that concretion precipitation occurred in marine sediments.

TRACE ELEMENT COMPOSITION

The calcite concretion study by Boles et al. (1985) found a decrease in calcite Fe, Mn and Mg concentration and an increase in calcite Ca concentration from concretion center outward. In contrast to the above the study, Coniglio and Cameron (1990) found an increase in calcite Fe from

concretion center outward. Like the study by Boles et al. (1985), the study by Girin (1970) found a decrease in Mn concentration from concretion center outward. In contrast to the study by Boles et al. (1985), the study by Girin (1970) found an increase in calcite Fe and Mg concentration and a decrease in calcite Ca concentration from concretion center outward.

The dolomite concretion studies by Irwin (1980) and Curtis (1986) found an increase in dolomite Fe and a decrease in dolomite Mg from concretion center outward. The dolomite concretion study by Wardlaw (1981) found no discernable trend in carbonate Ca, Mg, Sr, Fe, or Na across the concretions.

The siderite concretion studies by Curtis (1975) and Curtis et al. (1986) found a decrease in siderite Fe and Mn concentration and an increase in siderite Mg concentration from concretion center outward. No discernable trend in siderite Ca concentration across the concretions was found by the above studies.

The limited number of studies that have conducted multiple sampling of individual concretions for carbonate trace element composition prohibit making any generalities on trace element concentrations trends across carbonate concretions.

OXYGEN ISOTOPIC COMPOSITION

Table 2 summarizes the oxygen isotopic composition of the common concretion forming carbonate mineralogies.

Table 2. Summary of the isotopic compositions found for the common concretion forming carbonates, and associated concretion pyrite.

Author	Date	Calcite			Dolomite		Siderite		
		13/C	18/O	34/S	13/C	18/O	13/C	18/O	34/S
Coleman & Raiswell	1981	-15.44 / -12.90	-9.90 / -2.35	-24.28 / -2.56					
Compos & Hallam	1979	-13.79 / +8.26	-12.61 / -1.77						
Coniglio & Cameron	1990	-13. / -4.	-7. / -4.						
Curtis Pearson Somogy	1975						+1.41 / +7.50		
Curtis Colman Love	1986	-21.49	-8.91		-10.48 / -8.67	-4.61 / -3.87	-3.09 / +10.35	-8.94 / -5.35	
Galimov & Girin	1968	-2.27 / -0.96					-1.13 / -0.56		
Gautier	1982	-20.73 / -20.27	-2.67 / -1.72				-19.52 / +10.38	-7.45 / +0.14	-32.08 / +16.40
This Study		-12.37 / -3.74	-7.6 / -4.78	-9.8 / -0.7					
Hathon	1979				-12.2 / -10.1	-7.54 / -6.28			
Hein O'Neil Jones	1979	-21.09 / -7.16							

* - No sulphide analyses were found for dolomite.

Table 2. Continued

Author	Date	Calcite			Dolomite		Siderite		
		13/C	18/O	34/S	13/C	18/O	13/C	18/O	34/S
Hennessey & Knauth	1984				-10.2 / +10.8	-2.98 / +3.14			
Hudson	1978	-14.09 / -3.91	-4.62 / -1.18						
Irwin Curtis Coleman	1977	-15.74 / -14.57	-2.91 / -0.17		-6.38 / +9.28	-6.46 / -1.64			
Irwin	1980				-2.73 / +9.56	-4.46 / -1.56			
Pearson	1979	-8.02					-3.81 / +7.27		
Sass & Kolodny	1972	-15.1 / -6.6	-9.4 / -1.5						
Tasse & Hesse	1984				-11.0 / -6.2	-9.6 / -7.7	-7.5 / -7.0	-9.0 / -4.4	
Wada	1980	-42.9 / -0.2	+3.9 / +6.2		-14.3 / +13.5	+4.3 / +5.9			
Wardlaw	1981				-12.0 / -10.2	-9.29 / -9.10			

* - No sulphide analyses were found for dolomite.

Authigenic calcite oxygen isotopic compositions were found to range from -12.6 (Compos and Hallam, 1979) to +6.2 PDB (Wada et al., 1984). The range of oxygen values found for calcite is greater than that found for either dolomite or siderite. The study by Wada et al. (1984) found only positive (heavy) calcite oxygen isotopic values and is the only study that found positive calcite oxygen values.

The variation in calcite oxygen isotopic composition within a single concretion can be small (0.95 mills, Gautier, 1982) or large (7.55 mills, Coleman and Raiswell, 1981). The variation in calcite oxygen isotopic composition within a single concretion is usually smaller than the variation between different calcite concretions from the same formation. The study by Coleman and Raiswell (1981) analyzed two calcite concretions from the same formation and found oxygen isotopic ranges of -8.94 to -9.9 and -2.26 to -4.77 PDB respectively. The study by Sass and Kolodney (1972) analyzed two calcite concretions from the same formation and found oxygen isotopic ranges of -7.2 to -9.4 and -1.5 to -3.0 PDB respectively.

Where multiple sampling was conducted on calcite concretions, an increase in light oxygen from concretion center outward was usually found (Sass and Kolodny, 1972; Irwin, 1980; Colman and Raiswell, 1981). When calcite and dolomite concretions occur in the same formation (Curtis, 1972; Curtis, et al. 1986) or when calcite and dolomite

occur within the same concretion (Gautier, 1982), lighter oxygen was found in the calcite phase.

Authigenic dolomite oxygen isotopic values range from +5.9 (Wada, 1980) to -9.6 PDB (Tasse and Hesse, 1984). Positive dolomite oxygen isotopic values were found by Wada (1980), and Tasse and Hesse (1984) but occur infrequently. The study by Wada (1980) found only positive dolomite oxygen isotopic values and is the only study to do so. Where multiple samples were collected from a dolomite concretion, little variation in isotopic composition is usually found.

Oxygen isotopic values for authigenic siderite concretions were found to range from -9.0 (Tasse and Hesse, 1984) to +0.14 PDB (Gautier, 1982). Multiple sampling of siderite concretions was performed by Curtis et al. (1986) and Gautier (1982). Both studies found an increase in light oxygen from concretion center outward. Gautier (1982) found an oxygen isotopic range of -7.45 to +0.14 PDB between siderite concretions from the same formation, but variation within a single concretion was commonly around 1 mill.

The increase in light oxygen from concretion center outward found in most concretions supports the work of Sayles and Manheim (1975), which found that sedimentary pore waters become isotopically lighter with increasing burial depth.

CARBON ISOTOPIC COMPOSITION

Table 2 summarizes the carbon isotopic values found for the common concretion forming carbonate mineralogies. Carbon

isotopic values found for authigenic calcite range from -42.9 (Wada, 1980) to +8.26 PDB (Compos and Hallam, 1979). The study by Compos and Hallam (1979) is the only study in which positive calcite carbon isotopic values were found.

Of the studies in which multiple sampling of an individual concretion was conducted, the studies by Galimov and Girin (1968), and Coleman and Raiswell (1981) found an increase in heavy carbon of approximately 2 mill between concretion center and edge. The study by Coniglio and Cameron (1990) found an increase in heavy carbon of approximately 3.6 to 7.3 mills from concretion center to edge. In contrast to the above studies, the study by Sass and Kolodny (1972) found an increase up to 6.2 mill in light carbon from concretion center outward.

Dolomite carbon isotopic values have been found to range from -14.3 to +13.5 PDB (Wada, 1980). Most dolomite concretion studies find both positive and negative carbon isotopic values. Of the studies in which multiple sampling of a concretion was conducted, the studies by Hathon (1979) and Wardlaw (1981) found an increase in heavy carbon from concretion center to edge of approximately 2 mill.

The dolomite concretion studies by Irwin (1980), and Irwin et al. (1977) found an increase in light carbon from concretion center to edge. These studies found carbon isotopic variations within individual concretions of approximately 12 mill and 1.5 to 10 mills respectively. The study by Irwin (1980) concluded that the heavy carbon at the

center of the concretions (+9.56) was due to the influence of primary clastic calcite found at the concretion centers.

Siderite concretion carbon isotopic values range from -19.5 to +10.4 PDB (Gautier, 1982). Most siderite concretion studies find both positive and negative carbon isotopic values. The studies by Galimov and Girin (1968) and Tasse and Hesse (1984) found only negative siderite carbon isotopic values, and found little isotopic variation. The siderite concretion studies by Gautier (1982), Curtis et al. (1975), and Curtis et al. (1986) found an increase in light carbon from concretion center to edge.

There are two principal arguments with respect to the interpretation of concretion carbonate elemental and isotopic data. The study by Galimov and Girin (1968) concluded that trends in carbonate composition across a concretion reflect (record) the diagenetic changes occurring in the surrounding host sediment. In contrast, The studies of Sass and Kolodny (1972), and Raiswell (1976) concluded that concretions precipitate in localized microenvironments of carbonate supersaturation created by microbial metabolic processes, and do not reflect the diagenetic changes occurring in the surrounding host sediment.

CEMENTATION POROSITY

It is generally accepted that authigenic carbonate concretions form by the precipitation of a carbonate cement within sedimentary pore spaces. Sediment porosity at the location of carbonate precipitation (concretion growth) is

commonly referred to as cementation porosity. Cementation porosity is usually found by determining the weight or volume percent of carbonate cement within the concretion. Table 3 summarizes the concretion cementation porosities found for the common concretion forming carbonate mineralogies.

Calcite cementation porosities were found to range from 63% (Hudson, 1978) to 96% (Curtis et al., 1986). Calcite cementation porosities of 80% or greater were found by all studies where calcite cementation porosities were determined. When concretions from the same formation but different mineralogy are compared, the calcite concretions were found to possess higher cementation porosities (Gautier, 1982; Pearson, 1979; Curtis et al., 1986).

Boles et al. (1985) and Coniglio and Cameron (1990) found an increase in calcite concretion cementation porosity from concretion center outward. The study by Boles et al. (1985) attributed the increase in cementation porosity to the replacement of detrital minerals. The study by Coniglio and Cameron (1990) attributed the increase to the displacement of the surrounding sediment by the precipitation of acicular calcite.

Dolomite cementation porosities range from 17% (Raiswell, 1971) to 95% (Henessy and Knauth, 1984). Dolomite cementation porosities of 70% or greater were found in all studies where dolomite cementation porosities were determined. Wardlaw (1981) determined the cementation

Table 3. Summary of the cementation porosities found for the common concretion forming cabonates.

Author		High	Low
CALCITE			
Raiswell (1971)		89	78
Raiswell (1976)		87	73
Hudson (1978)		95	63
Pearson (1979)		80	80
Coleman & Raiswell (1981)		87	74
Gautier (1982)		83	82
Curtis (1986)		96	96
This Study		95	90
DOLOMITE			
Raiswell (1971)		73	17
Curtis et al. (1972)		87	57
Wardlaw (1981)		90	48
Henessy & Knauth (1984)		95	39
Curtis et al. (1986)		90	90
SIDERITE			
Curtis et al. (1975)	wt.%	81	45
	vol.%	73	34
Pearson (1979)		74	24
Gautier (1982)		87	57
Curtis (1986)		85	20

porosities across two dolomite concretions and found both to have higher cementation porosities in the outer half of the concretion than in the inner half.

Siderite cementation porosities were found to range from 20% (Curtis et al. (1986) to 87% (Gautier, 1982). Siderite cementation porosities of 74% or greater were found by all studies where siderite cementation porosities were determined.

Concretion cementation porosity (percentage of carbonate cement) commonly decreases from concretion center outward, and should due to concretion growth into sediments of progressively increased compaction (less porosity) In contrast to the above argument, several of the concretion studies listed in table 3 found higher cementation porosities in the outer half of the concretion than at the concretion center and suggests that the percentage of concretion carbonate should not be equated to sediment porosity. Based on the cementation porosities listed in table 3, calcite concretions usually have higher cementation porosities than dolomite or siderite.

CHAPTER 3 PROCEDURES AND METHODS

SAMPLING

Four large semi-spherical concretions with vertical axial diameters between approximately 80 and 110 centimeters were chosen for sampling. Large concretions were chosen for sampling with the rationale that they may have formed over a longer period of time and therefore possessed a greater probability of recording changes in pore water chemistry. In an effort to obtain concretions that possessed minimal environmental exposure, whole, uncracked concretions that had recently been exposed by quarrying activities were chosen for sampling. Therefore, the above concretions were collected from Unit-3 of the lower quarry pit where quarrying activities were ongoing. Figure 6 is a picture of concretion #1. This concretion is typical of the four Unit-3 concretions sampled.

Ten centimeter diameter cores were removed from the vertical axis of all four concretions (VC-series). Additionally, one concretion (concretion #2) had a 10 centimeter diameter core removed from its horizontal axis (HC-series). While the full diameter of the concretion was recovered for concretion cores HC2, VC3 and VC4, one edge of the concretion was not recovered for cores VC1 and VC2.

The concretion cores were extracted from the concretions with a water-cooled drill. One side of each core was then removed to make thin-sections. The resulting flat faced cores were then sampled by removing 2.5 cm. diameter



Figure 6. Concretion #1 of this study. This concretion is typical of the other Unit-3 concretions sampled by this study.

plugs along the length of the cores with a water cooled drill.

The Unit-1 concretion previously collected from the Paxton quarry and analyzed by Hathon (1979) was sampled by this study for comparison purposes (Figure 7). One sample was collected for isotopic analysis and two samples were collected for determination of cementation porosity.

Detailed stratigraphic work conducted by this study at the Paxton quarry revealed that authigenic carbonate concretions occur throughout the entire stratigraphic column exposed at the quarry. In addition to the four concretions sampled from the black shales of Unit-3 and the Unit-1 concretion previously collected by Hathon (1979), this study collected three from the calcareous rocks of Unit-2. The Unit-2 samples were collected for comparison to the carbonates in the surrounding black shales. The samples collected from Unit-2 will only be analyzed for carbonate isotopic composition.

Samples were cleaned with distilled water in an ultrasonic cleaner. After cleaning, the samples were powdered in a titanium ball mill and split into aliquots for porosity, carbonate chemistry and isotopic analysis.

Figure 8 gives descriptions of the samples analyzed by this study. Figure 9 shows the the sampling nomenclature used by this study for the concretions from the black shales. Figure 10 shows the relationship between the samples



Figure 7. The Unit-1 ferroan dolomite concretion sampled by Hathon (1979) and this study.

Sample	Sample Type	Sample Description
UNIT-1		
Hathon Dolomite	Single	Dolomite concretion from Unit-1, brown carbonate, 28cm. diameter, pyrite rim.
UNIT-2		
Limestone Stringer	Single	Stringer limestone from the top of Unit-2, mottled, gray-green carbonate, fossiliferous.
Limestone Concretion	Single	Calcite concretion from the middle of Unit-2, mottled, gray-green carbonate, fossiliferous, no pyrite rim, 15cm. diameter.
Fossil Concretion	Single	Calcite concretion from the base of Unit-2, contains crynoid event layer, light brown carbonate, no pyrite rim, 33cm. diameter.
UNIT-3		
Study Concretions	Core Sets	Calcite concretions from Unit-3, brown carbonate, non-fossiliferous, pyrite rims, up to 115cm. diameter.

Figure 8. Descriptions of the Paxton Shale Quarry carbonates sampled by this study.

Concretion Sampled	Sample Type	Sample Name	Comments
1	Vertical Axis Core	VC1 Series	87.6 (cm) core One edge missing
2	Vertical Axis Core	VC2 Series	94.6 (cm) core One edge missing
2	Horizontal Axis Core	HC2 Series	109.8 (cm) core Full core
3	Vertical Axis Core	VC3 Series	81.3 (cm) core Full core
4	Vertical Axis Core	VC4 Series	87.6 (cm) core Full core
Hathon	Single	Hathon	28.0 (cm) dia.

Figure 9. Sampling scheme and nomenclature used by this study for the carbonate concretions from the black shales of the Paxton quarry.

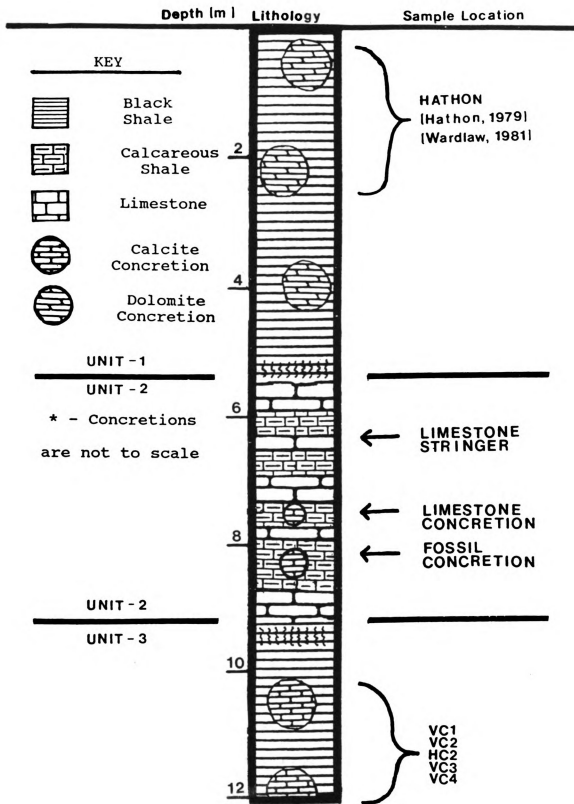


Figure 10. Stratigraphic relationship between the samples collected from the Paxton quarry.

analyzed by this study and their stratigraphic location at the Paxton quarry.

ANALYSES

Cementation porosities were measured by dissolving 20 grams of powdered sample in a 1N sodium acetate solution, buffered to a pH of 4.5 with acetic acid. This procedure was used to minimize dissolution or damage to the clays that might occur if stronger acids were used to dissolve the carbonate matrix. After mixing the sample and the sodium acetate solution, the sample and solution were heated in a water bath to approximately 43°C to facilitate the dissolution of the dolomite that was observed in some concretion thin sections. The remaining insoluble residue was then filtered, dried and weighed.

All isotopic analyses were performed by the Department of Physics at the University of Calgary. Carbon and oxygen isotopic values were determined by reacting powdered samples with 100% phosphoric acid at 25°C using the method of McCrea (1950).

Because of cost and laboratory constraints, only a few concretion samples could be analyzed for sulphate and sulphide composition. Instead of analyzing one or two samples from each concretion core, multiple sampling of one half of concretion core VC4 was performed. Sulphate and sulphide concentrations and isotopic compositions for concretion core VC4 were determined by the Kiba method (Ueda and Sakai, 1983). In accordance with the Kiba method, rock powders were

decomposed at 280°C under vacuum with phosphoric acid containing Sn^{2+} as a reducing agent. Sulphate and sulphide are collected in liquid nitrogen traps as SO_2 and H_2S respectively and separated by successive vacuum distillation. Sulphide H_2S is then converted to SO_2 by reaction with Cu_2O . All other sulphide isotopic values were determined by the standardized vanadium pentoxide method.

Unlike pyrite, iron monosulphide will dissolve in strong acids. Relative concentrations of monosulphide were determined for concretion cores VC2 and HC2 by transferring iron monosulphide sulphur to H_2S and then precipitating the H_2S sulphur as cadmium sulphide. Four grams of powdered sample were dissolved in 6N HCL. The carbon dioxide and hydrogen sulphide produced were carried (bubbled) through a sealed test tube containing distilled water and into a solution of cadmium acetate by a nitrogen carrier gas. Upon contact with the cadmium acetate, the hydrogen sulphide sulphur is precipitated as cadmium sulphide. The cadmium sulphide was then filtered, dried and weighed.

Trace element chemistry of the concretion carbonate was measured by atomic absorption spectrometry following the technique by Barber (1974). Ten grams of powdered sample were dissolved in 100 ml. of a 25% acetic acid solution. After dissolution, the solution was centrifuged, decanted, and the supernatant filtered. The solution was then brought up to the original volume with distilled water to offset evaporative loss of the original solution.

Elemental subsamples were then prepared according to the techniques of U.S.G.S. (1979). These samples were analyzed on a Perkin-Elmer 560 Atomic Absorption Spectrophotometer using single and multi-element hollow cathode tubes and a single 4-inch single slot burner head. The standards used to calibrate the spectrophotometer were prepared using the same reagents and dilution water used to prepare the samples.

Concretion carbonate was X-rayed by mounting powdered sample on a glass thin-section slide that had been grooved with a diamond tipped engraver. The carbonate was X-rayed on a Rigaku Gigerflex diffraction machine using Cu K-alpha radiation.

Concretion clays were extracted from powdered samples by dissolution in 1N sodium acetate solution. Organic matter, pyrite and iron oxides were then removed following the techniques of Mortland (1984). Subsequent to mounting the clays on porous plates, the clays were magnesium saturated and glycerol solvated. The clays were X-rayed on a Rigaku Gigerflex diffraction machine using Cu K-alpha radiation.

Concretion oil samples were analyzed by gas chromatography by the Department of Atmospheric and Oceanic Science at the University of Michigan.

CHAPTER 4 STUDY RESULTS

THE CONCRETIONS AND THEIR SURROUNDINGS

The authigenic carbonate concretions represent the only visible carbonate material within the black shales.

Concretion occurrence is commonly associated with non-continuous thin layers of friable, rust brown, silt size, chalcedony (Figure 11). While the largest concretions in the black shales usually occur in association with the friable layers, the smallest concretions found in the black shales (between 10 and 20 cm. in diameter) may occur independently of them.

The shale surrounding the concretions is fissile in nature and shows no sign of bioturbation. The shale beds appear to drape over the top of the concretions forming differentially compacted shale wedges at the concretion's sides (Figure 12). Therefore, significant post concretion compaction appears to have occurred in the surrounding shales. The appearance of slickensides on the shales in contact with the concretions support post concretion compaction of the surrounding shale.

The concretions sampled from the black shales of units 1 and 3 are semi-spherical in shape and have outer margins (rims) enriched in pyrite. The sulphide rims on the four large Unit-3 concretions sampled by this study are approximately 0.66 cm. in thickness. Smaller Unit-3 concretions (between 10 and 20 cm. in diameter) have sulphide rims approximately twice as thick as the larger



Figure 11. Rust brown, friable, silica rich- horizon typical of that commonly associated with concretion occurrence (arrows point to the bed of interest). The depression in the quarry wall represents the former location of a concretion. Scale bar = approximately 1 meter.



Figure 12. Shale beds associated with concretion occurrence thin over the top of the concretions and thicken at the concretion's sides. The shale wedge that occurs at the sides of the concretions (between arrows) is formed by differential compaction around the concretion. Scale bar = approximately 2 meters.

Unit-3 concretions. The difference in sulphide layer thickness between the large and small concretions suggests that there may be a correlation between concretion size and sulphide rim thickness.

While septarian cavities were found in some Unit-2 concretions, and a zone of carbonate vugs was found in the Unit-1 concretion previously sampled by Hathon (1979) (Figure 7), neither septarian cavities nor vugs were found in any of the Unit-3 concretion cores. While a possible nucleating source was found at the center of two broken concretions at the quarry and the concretion sampled by Hathon (1979) (Figure 7), no nucleating source was found in any of the Unit-3 concretion cores.

Small scale bedding can be seen in the concretion cores and is accentuated by thin beds rich in radiolarian tests or chalcedony. Variable concentrations of organic material and clay within the concretion cores give the cores a striped appearance when wet. Concretion carbonate is brown in color and darkens from concretion center outward. During thin section preparation, hydrogen sulphide and petroleum-like odors were produced. The intensity of the odors increased from concretion center outward.

Concretion size and frequency of occurrence at the Paxton exposure appears to change with composition of the host rock. Concretions in the black shales of units 1 and 3 are predominantly large (greater than one meter in diameter) and usually do not occur in close proximity to one another.

The carbonate concretions of units 1 and 3 rarely occur as twins (Figure 13).

At the top of Unit-3 the shales are bioturbated and contain what appear to be multi-nucleated concretions (Figure 14). These multi-nucleated concretions may have started off as a group of individual concretions that, with time, coalesced into a single large concretionary mass.

In contrast to the large brown concretions of units 1 and 3, peanut size, gray-green concretions abound in the thin limestone beds of Unit-2 (Figure 15). Larger, gray-green concretions (up to 33 cm. in diameter) occur in Unit-2 but appear to be restricted to the calcareous shale layers (Figure 16). None of the concretions in Unit-2 contain outer margins enriched in pyrite. Based on the above observation, it appears that concretion size decreases and concretion abundance increases with increasing carbonate content of the host sediment.

CONCRETION PETROGRAPHY AND CONSTITUENTS

The calcite crystals in the Unit-1 concretions range in size from 0.2 to over 4 mm. Crystals at the concretion edge represent some of the largest in the concretions and contain large amounts of pyrite (Figure 17).

The amount of host sediment incorporated in the concretion calcite (clay, organic matter, etc.) varies significantly between different beds in the concretion. Calcite crystals in beds containing higher amounts of host sediment are usually smaller than those in beds containing



Figure 13. Unit-3 concretion twin. Note the concentric banding within the concretion. Scale bar = approximately 1 meter.



Figure 14. Multinucleated concretion from the top of Unit-3.



Figure 15. Nodular limestone from Unit-2.



Figure 16. Grey-green concretions within the calcareous shales of Unit-2. Arrows point to the concretion bearing horizon. Scale bar = approximately 1 meter.

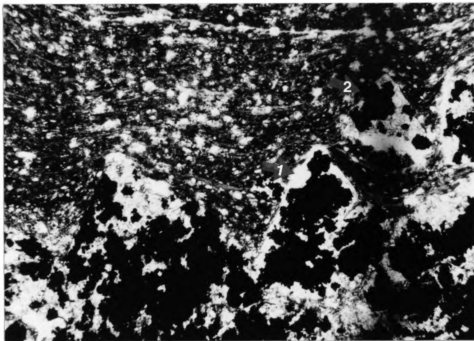


Figure 17. Calcite crystals (1) at concretion edges contain large pyrite crystals (2) that appear to occur only within the boundaries of the of the calcite crystals. Scale bar is parallel to bedding. Thin section with crossed polars. Scale bar = approximately 2mm.

lower amounts. Host sediment is commonly displaced into crystal/crystal boundaries. Triple-point junctions, which occur at the intersection of three calcite crystals, usually contain the the highest amount host sediment (Figure 18). Stylolites were observed in the concretions but are rare. The stylolites can be recognized by the high level of host sediment that occurs in them.

Recognizable constituents in the concretions include dolomite, pyrite, gypsum, chalcedony, radiolarian tests, wood fragments and planktonic spores (tasmanites). Figure 19 shows an uncrushed radiolarian and tasminite collected from near the edge of concretion core VC3.

Dolomite only occurs in the inner half of the concretions and occurs as random groups of small, sediment free, euhedral rhombs. It is unknown whether the dolomite precipitated in the host sediment prior to concretion formation, or is secondary. The study by Coniglio and Cameron (1990) found dolomite rhombs in the concretions and proposed that the dolomite precipitated prior to concretion formation.

Gypsum crystals occur sparsely throughout the inner half of the concretions as groups of randomly oriented, small, euhedral crystals. Calcite-filled gypsum molds occur more frequently and are commonly found near the gypsum crystals (Figure 20). The gypsum molds occur individually and are usually larger than the gypsum crystals.

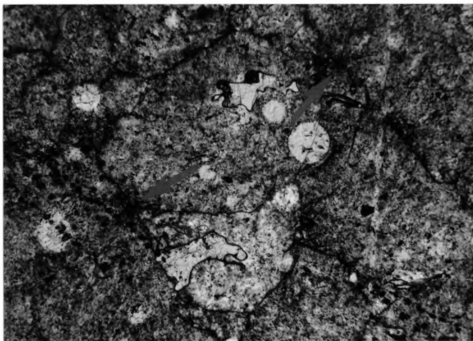


Figure 18. Host sediment within the concretions is commonly partitioned into crystal boundaries. The highest concentrations of sediment frequently occurs at the junction of 3 crystals (see arrows). Thin section with crossed polars. Scale bar = approximately 1mm.

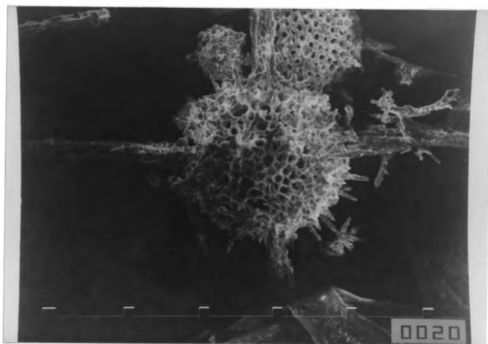


Figure 19. Well preserved radiolarian (upper picture) and tasmanite spore case (lower picture) from the edge of concretion #3. Scanning electron microscope pictures. Scale bar = approximately 0.5mm.

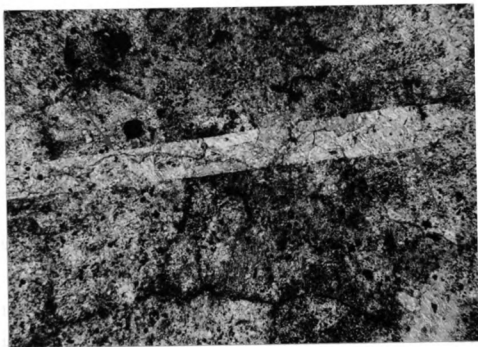


Figure 20. Calcite filled mold of a gypsum crystal (see arrows). Thin section with crossed polars. Scale bar = approximately 2mm.

As mentioned previously in Chapter 3, sulphate and sulphide analyses were limited to one half of concretion core VC4. Figure 21 shows the change in sulphate (gypsum?) concentration across one half of concretion core VC4. The highest concentration of sulphate (approximately 750 ppm) was found at the concretion center. Adjacent to the concretion center, sulphate concentration drops rapidly to what appears to be a base line value. The sulphate concentration rises in the intermediate region of the concretion, falls back to the proposed base line concentration and then rises again near the concretion edge. The increase in sulphate concentration in the intermediate region of the concretion is correlatable with an increase in sulphate ^{34}S , an increase in pyrite ^{34}S and increase in carbonate ^{18}O content.

Figure 22 shows the change in sulphate isotopic composition across one half of concretion core VC4. With the exception of an increase in sulphate ^{34}S in the intermediate region of the concretion, sulphate increases in light sulphur ^{32}S from concretion center outward. Because modern day studies have found pore water sulphate to become progressively depleted in ^{32}S with increasing burial depth (Kaplan, 1983), the increase in sulphate ^{32}S from concretion center outward is not understood.

Euhedral pyrite crystals occur throughout the concretions and increase in abundance from concretion center outward; culminating in an outer layer (rim) composed

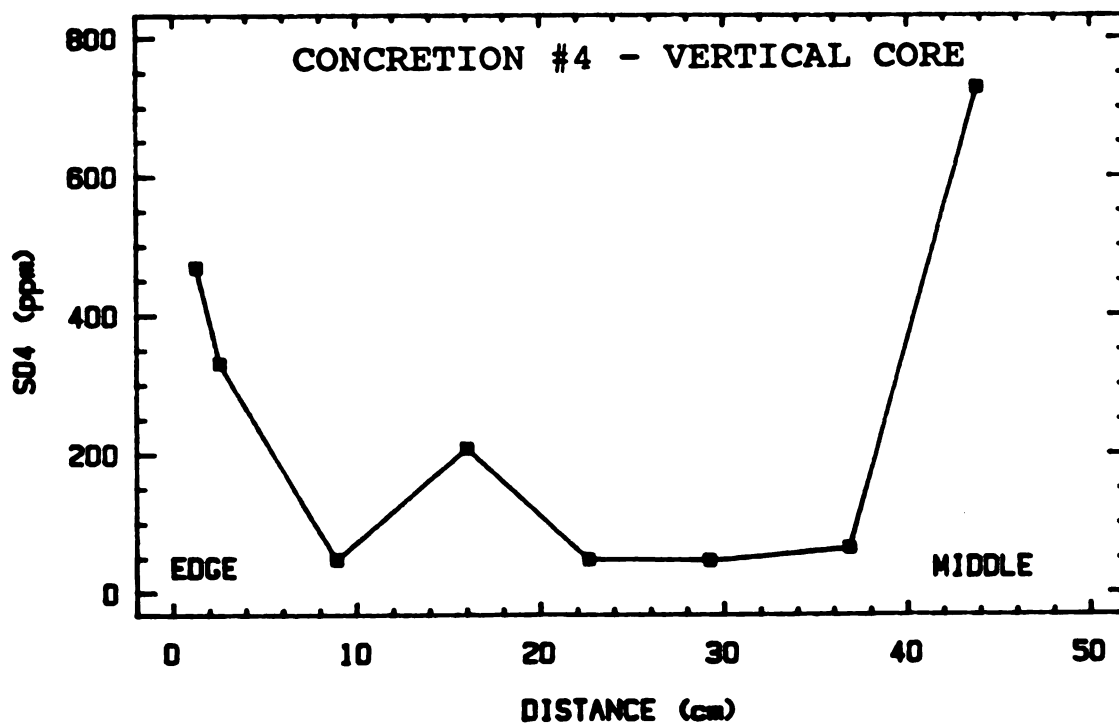
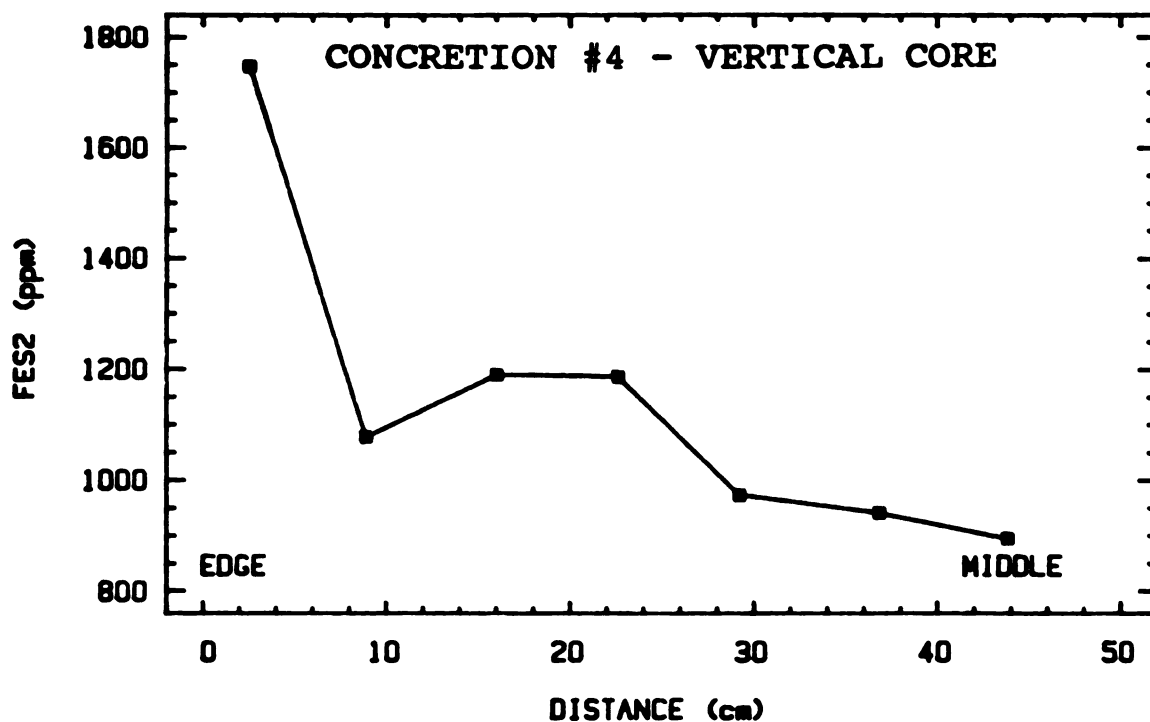


Figure 21. Trends in sulphide and sulphate concentration from concretion center outward (concretion #4).

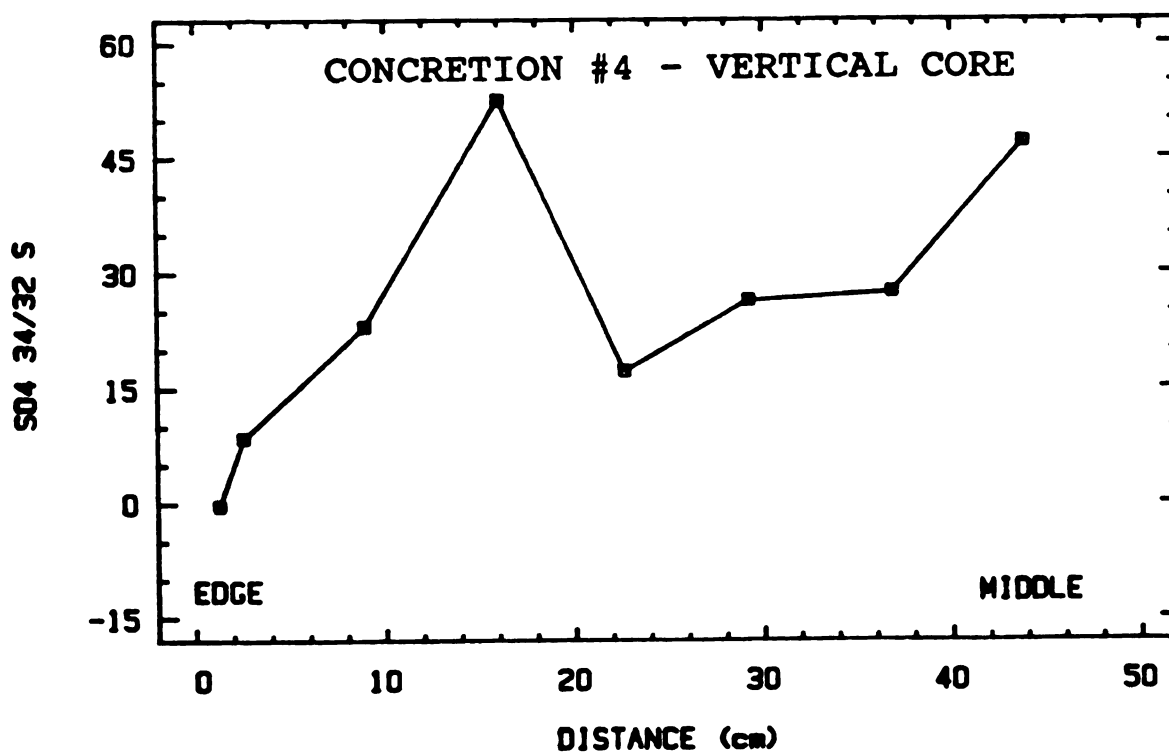
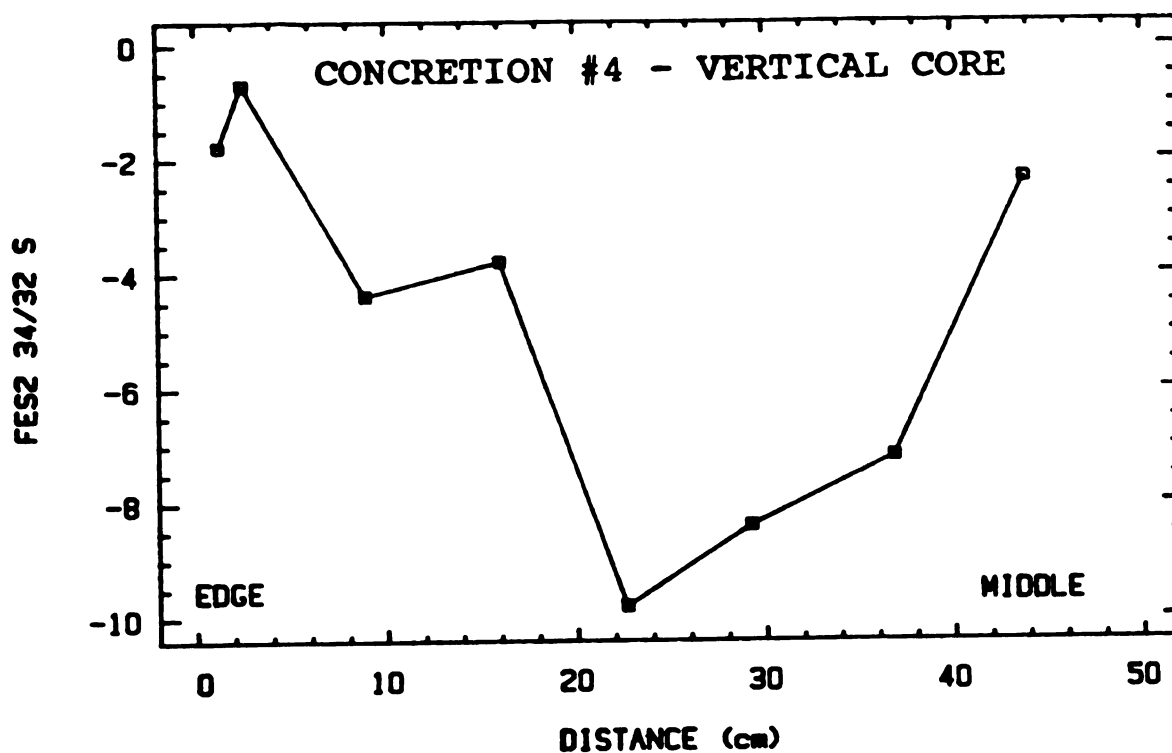


Figure 22. Trends in sulphide and sulphate sulphur isotopic composition from concretion center outward (concretion #4). Isotopic values are relative to the Canyon Diablo Troilite (CDT) isotopic standard.

principally of pyrite (Figure 23). Figure 21 shows the change in pyrite concentration across one half of concretion core VC4. The increase in pyrite concentration shown in figure 21 supports the increase in pyrite concentration observed in thin section. Large pyrite crystals occur at concretion edges and appear to be restricted in shape by the boundary of the surrounding calcite crystal (Figure 17). Localized accumulations of pyrite are associated with masses of chalcedony and with microfossil structures.

Figure 22 shows the change in pyrite sulphur isotopic composition across one half of concretion core VC4. Concretion pyrite was found to increase in light sulphur from the concretion center to the intermediate region and then decrease in light sulphur to the concretion edge. Because concretion pyrite increases in light sulphur in the inner half of the concretion and decreases in light sulphur in the outer half, the sulphide isotopic data suggests that more than one process is affecting the isotopic composition of concretion pyrite.

The amount of acid soluble iron monosulphide across concretion cores VC2 and HC2 was determined by converting the iron monosulphide to cadmium sulphide and then measuring the amount of cadmium sulphide that precipitated. Figure 24 shows the amount of cadmium sulphide produced from samples of concretion #2. The cadmium sulphide data plotted in figure 24 suggests qualitatively that the amount of iron monosulphide increases from concretion center outward. The

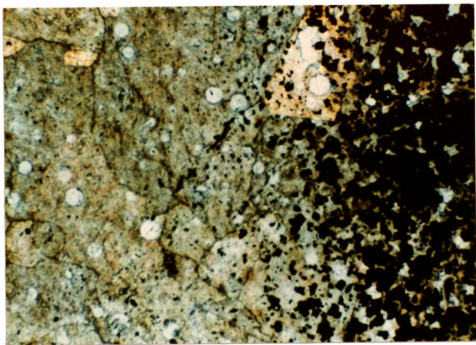


Figure 23. Increase in pyrite concentration that occurs at the edge of the concretions. Concretion edge is to the right of the picture. Thin section with crossed polars. Scale bar = approximately 4mm.

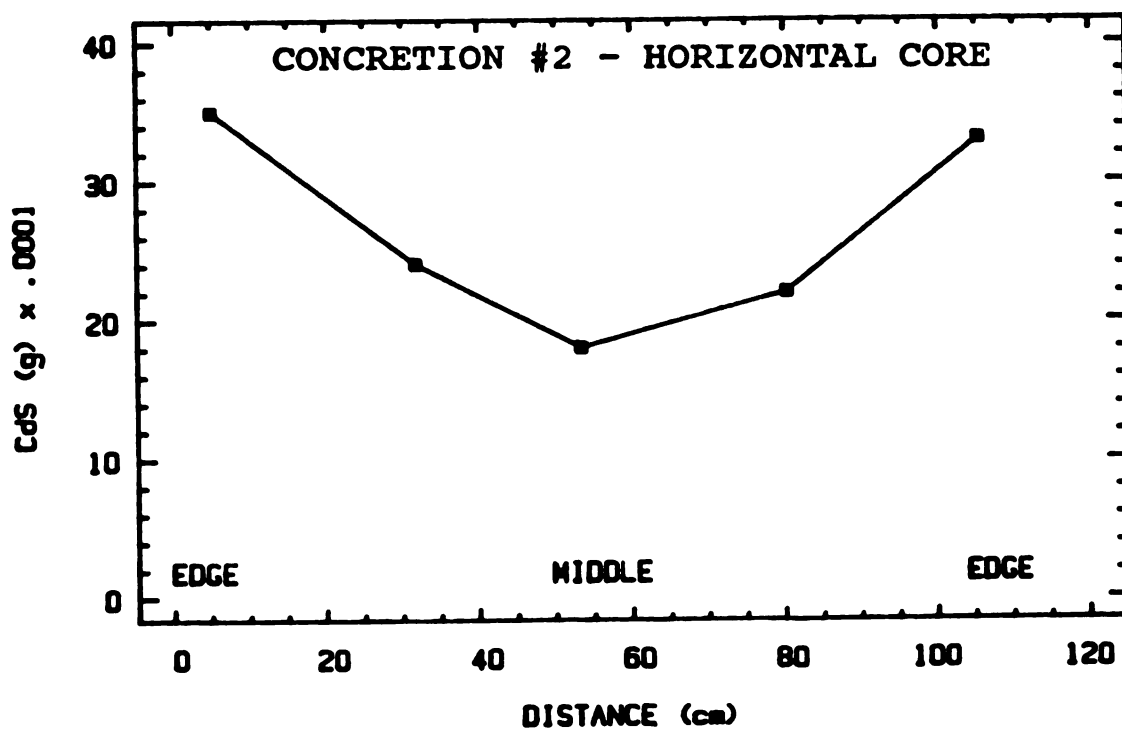
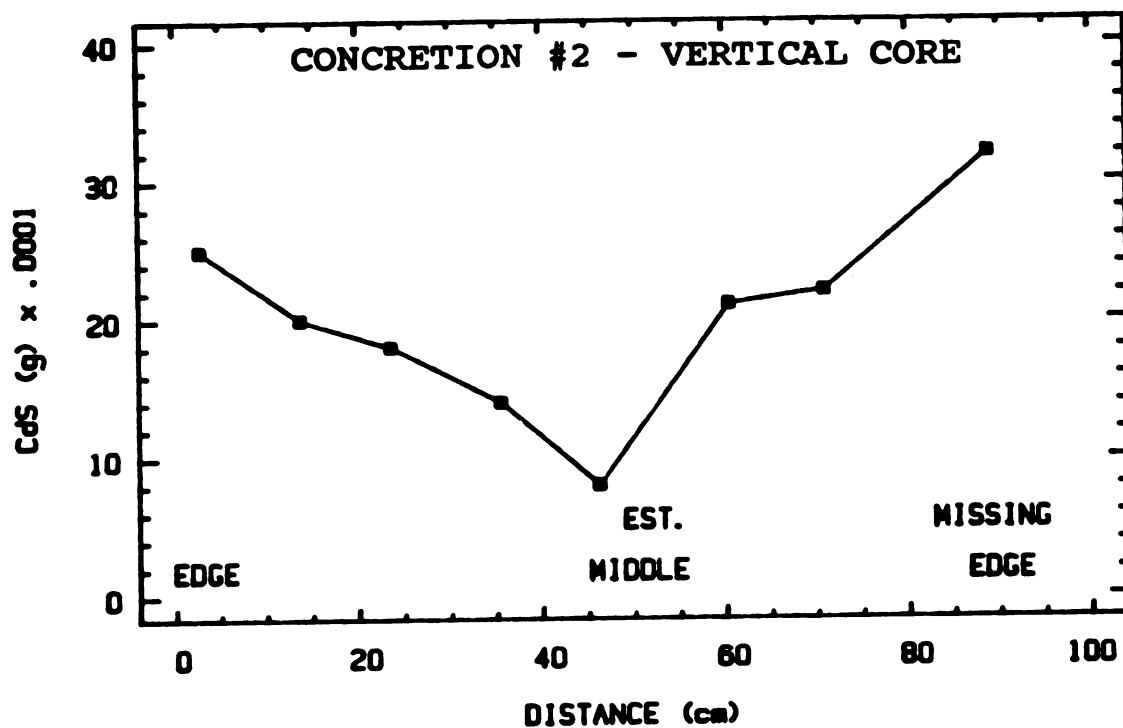


Figure 24. Trends in relative monosulphide concentration, as a cadmium sulphide precipitate, across concretion #2.

data in figure 24 is based on the assumption that a sample containing more iron monosulphide will produce more cadmium sulphide.

Radiolarians, or molds thereof, occur throughout the concretions and may exist in great numbers in some beds. The degree of radiolarian preservation increases from concretion center outward. At the concretion center, all radiolarian tests have been dissolved; leaving circular voids filled with clean calcite cement (Figure 25). Radiolarians tests in the intermediate region of the concretion also show signs of dissolution. In the intermediate region of the concretions small masses of chalcedony frequently occupy the voids left by individual radiolarian tests (Figure 26) and larger masses of chalcedony occur parallel to bedding (Figure 27). The masses of chalcedony parallel to bedding preferentially occur within beds containing lower concentrations of host material.

In the outer region of the concretions, radiolarian preservation improves greatly. Radiolarians near the concretion edge are uncrushed and show no signs of dissolution (Figure 28). No detrital (clastic) quartz was identified in approximately 200 concretion thin sections.

CONCRETION CLAYS

X-ray analysis of concretion clays indicate the presence of illite and lesser amounts of kaolinite (Mortland, 1985). Unlike the study by Ruotsula (1981) no chlorite was found. Therefore, concretion clay composition

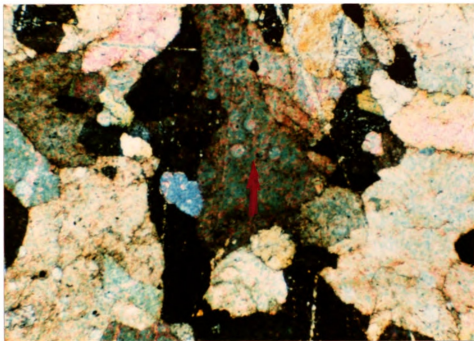


Figure 25. Calcite filled molds of radiolarian tests typical of those commonly found at concretion centers. Arrow points to three calcite filled molds. Thin section with crossed polars. Scale bar = approximately 2mm.

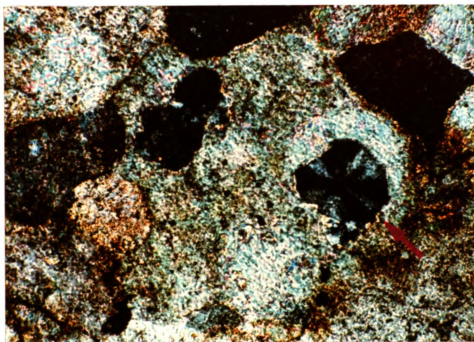


Figure 26. Radiolarian mold partially filled with chalcedonic silica, typical of those observed in the intermediate regions of the concretions. Thin section with crossed polars. Arrow points to the chalcedonic mass of interest. Scale bar = approximately 1mm.

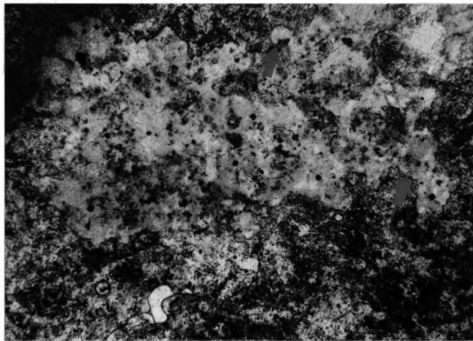


Figure 27. Mass of chalcedonic silica parallel to bedding, typical of that found in the intermediate regions of the concretions. Thin section with crossed polars. Arrows point to chalcedonic filled molds of radiolarians. Scale bar = approximately 1mm.

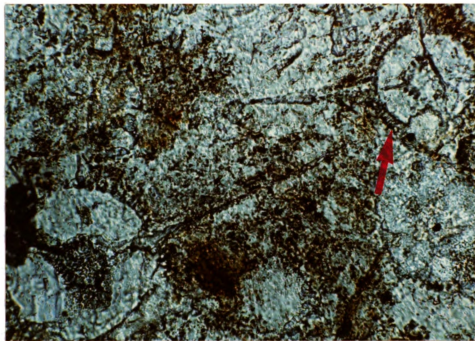


Figure 28. Well preserved radiolarian tests typical of those observed at concretion edges. Thin section with crossed polars. Scale bar = approximately 2mm.

suggests that the concretions formed prior to the formation of Antrim chlorite. A typical concretion clay X-ray is shown in Appendix A.

CONCRETION OIL

While analysis of Antrim shale organic matter from the Paxton quarry suggests that the shale at the quarry is too immature to have produced liquid hydrocarbons (Hathon, 1979), a viscous oil was found in two gray-green concretions from the interface between units 1 and 2. The oil was found to only occur in septarian cavities of the gray-green concretions, and adheres to the crystals lining the cavity.

While no carbonate samples were collected from the oil bearing concretions, an oil sample was collected for analysis. Analysis of the concretion oil by gas chromatography shows the oil to have a chromatographic signature similar to that of oils that have been heavily biodegraded (personal communication, Philip Meyers, 1986). The chromatogram of the oil is shown in Appendix B.

While liquid hydrocarbons were not reported in any of the concretion studies listed in figure 5, liquid hydrocarbons have been found in quartz geodes from the Mississippian age carbonates of Illinois and Indiana. This study hypothesizes that the oil found in the Antrim concretions and quartz geodes may represent an accumulation of organic material that has been degraded by microbial processes associated with concretion/geode formation.

CEMENTATION POROSITY

Cementation porosity measurements were originally planned for all five concretion cores. Because little variation in cementation porosity was found in cores VC1 and VC3, no cementation porosity measurements were performed on concretion cores VC2, HC2 and VC4.

Figure 29 shows the cementation porosity profiles found for concretion cores VC1 and VC3. Cementation porosities measurements were found to be high and range from approximately 90 to 95%. While cementation porosities were to have been determined for all five cores, cementation porosities were not determined for cores VC2, VC4 and HC2 because of the similarity in the values found in cores VC1 and VC3. An increase in cementation porosity from the concretion center into the intermediate region was found in both concretion cores. Consequently, concretion center cementation porosities represent some of the lowest values found.

CARBONATE COMPOSITION

TRACE ELEMENT COMPOSITION

All five concretion cores were found to be composed calcite. This mineralogy was not expected and is different from the ferroan dolomite found by Hathon (1979) and Wardlaw (1981) for Paxton quarry concretions.

The concretions were found to be composed of calcite by the following results: (1) unpowdered samples exposed to dilute HCl reacted rapidly; (2) thin sections exposed to

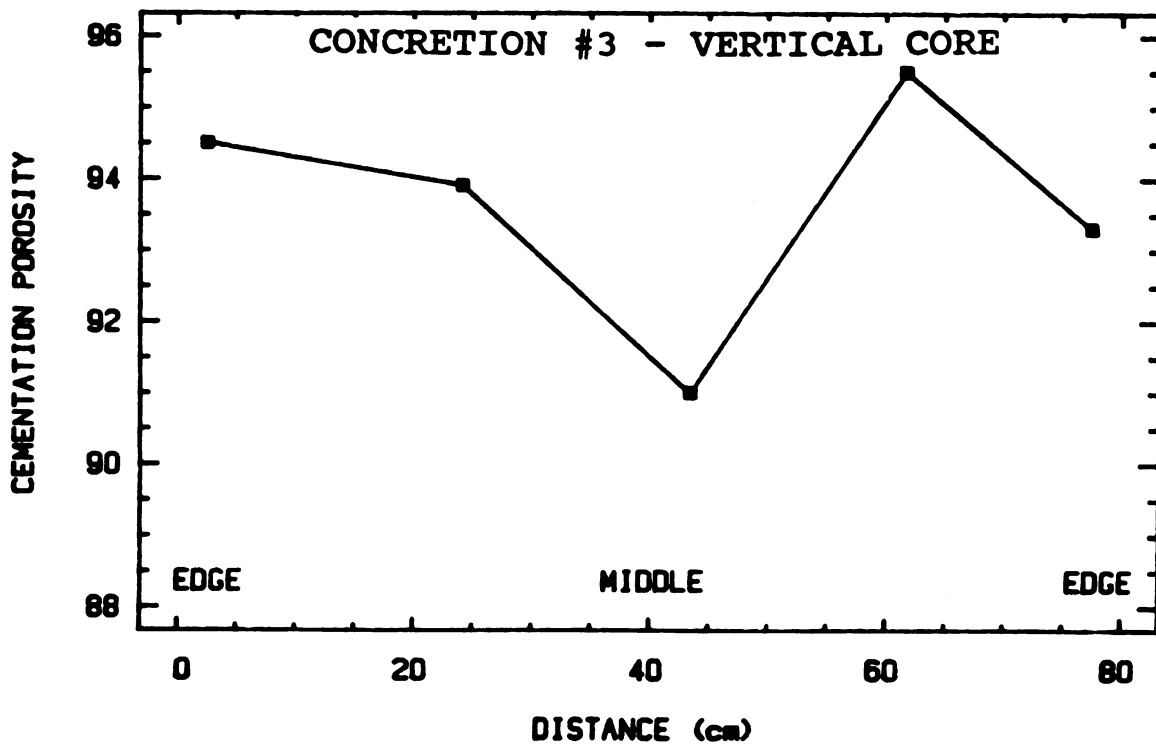
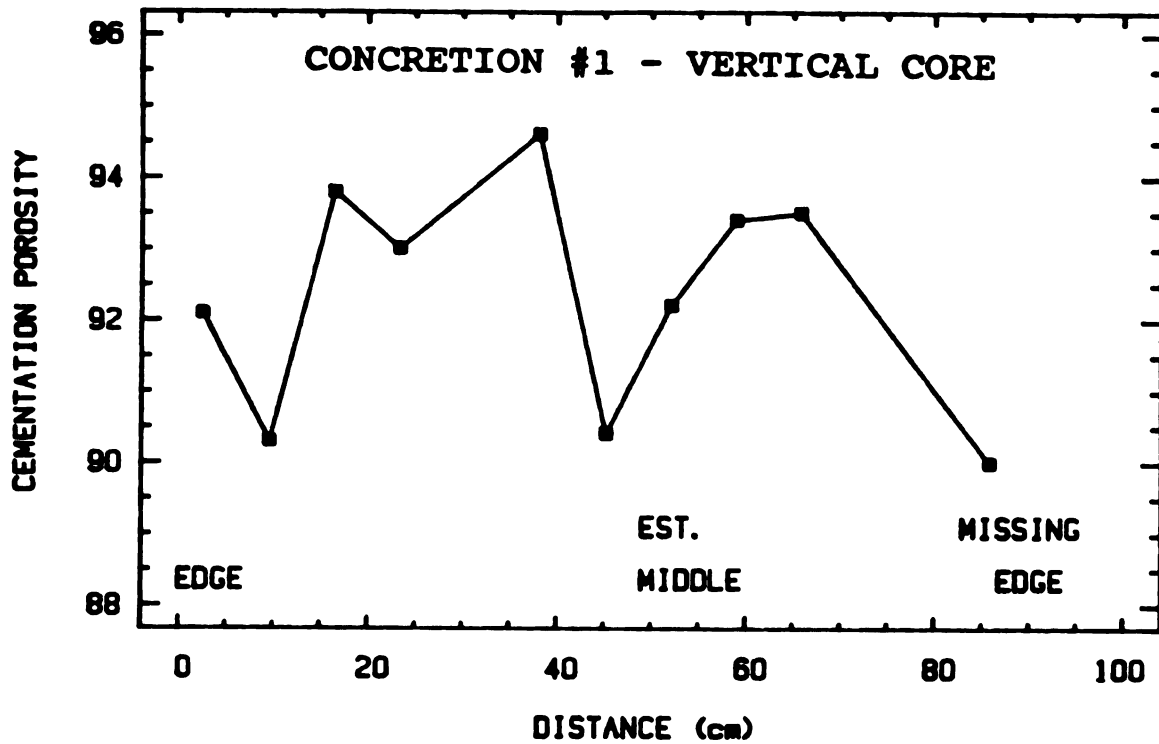


Figure 29. Trends in cementation porosity across concretions #1 and #3.

alizerian-red stain turned red; and (3) X-ray analysis of powdered concretion samples using Cu K-alpha radiation showed a strong reflection at approximately 29.4° . According to the Cu K-alpha X-ray diffraction patterns of Chen (1977) a strong reflection peak at approximately 29.5° is characteristic of calcite. Appendix C shows a typical Unit-3 concretion carbonate X-ray.

Concretion calcite was analyzed for the following elements: Mg, Sr, Mn, Fe, Na and K. Potassium concentrations were found to range from 8 to 30 ppm. Because no discernable trend was observed in the calcite K concentration profile, the K concentrations were not plotted. Figures 30 through 34 show the carbonate trace element profiles across the concretions. Due to the procedure in which the concretions were cored, one concretion edge was not recovered for concretion cores VC1 and VC2 and is appropriately noted on the profiles.

Concretion carbonate was found to increase in Mg, Sr and Mn from concretion center outward. In contrast, concretion carbonate was found to decrease in Fe and Na from concretion center outward. The carbonate trace element concentration profiles for a specific trace element are similar in trend and magnitude between different concretions.

While Mg, Sr, and Mn concentrations are higher at concretion edges than concretion centers, the concentration of the above elements frequently decreases in the

intermediate region. Because a decrease in the above trace elements occurs in the intermediate region of each concretion, the decrease is not thought to be due random variation in the data but more likely a process associated with concretion formation or a change in pore water chemistry of the surrounding sediments.

Magnesium concentrations were found to range from approximately 350 to 1200 ppm and are shown on figure 30. The concretions all show lower Mg concentrations at their centers than their respective edges. The concretions decrease in Mg concentration in the intermediate region for all the concretion cores except one half of concretion core HC2. Why a Mg decrease was not found in the above core is not known.

An increase in Mg concentration was not found at the end of one half of core VC1 and is thought to be due to the fact that a concretion edge was not recovered for this core. The largest range in Mg concentration was found in core VC3. Concretion core VC3 also had the highest Mg concentration found at a concretion center.

Strontium concentrations were found to range from approximately 17 to 30 ppm and are shown on figure 31. Strontium concentrations at the concretion edges are always higher than their respective concretion centers. Strontium concentrations were also found to decrease in the intermediate region of the concretions.

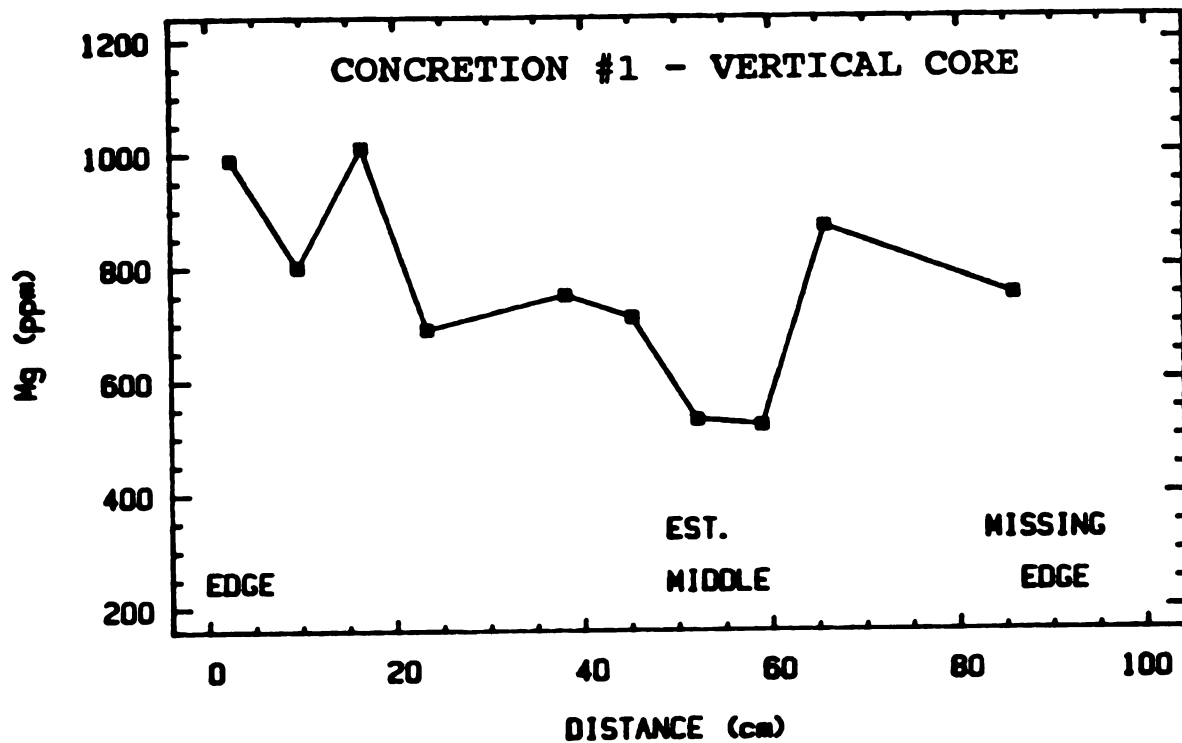


Figure 30. Trends in carbonate Mg concentration across the concretions. The values along the horizontal axis represent distances into the concretions. The zero value represents the concretion edge.

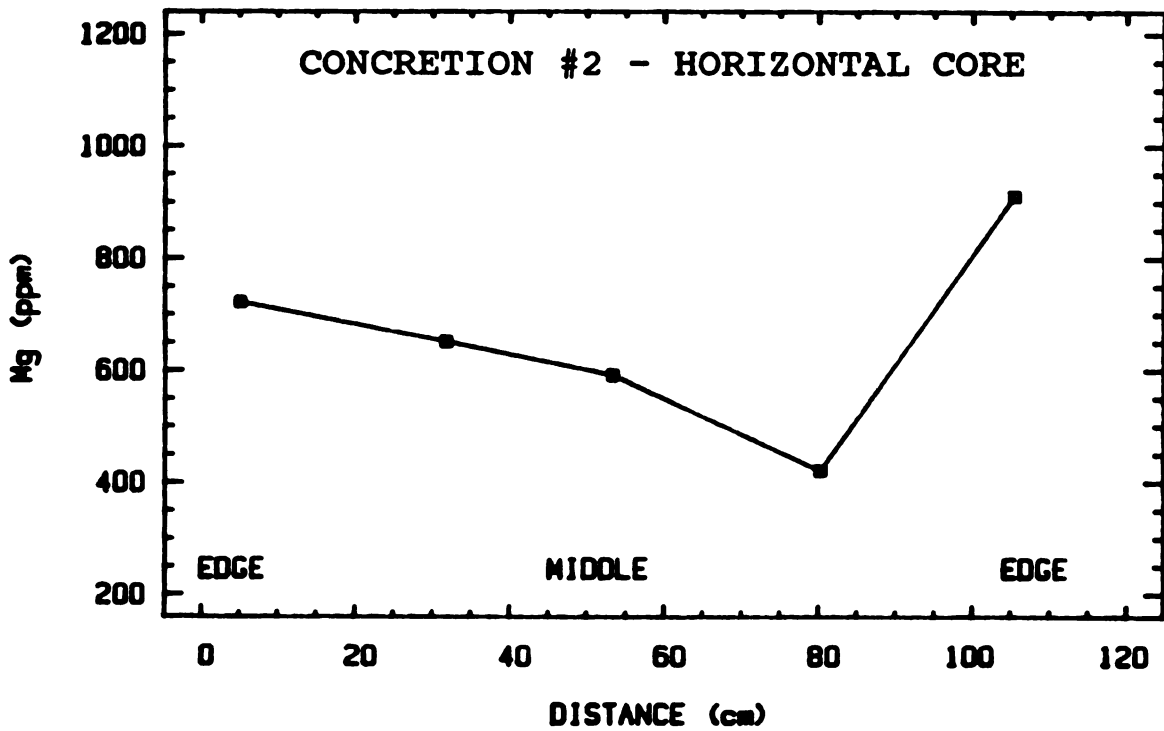
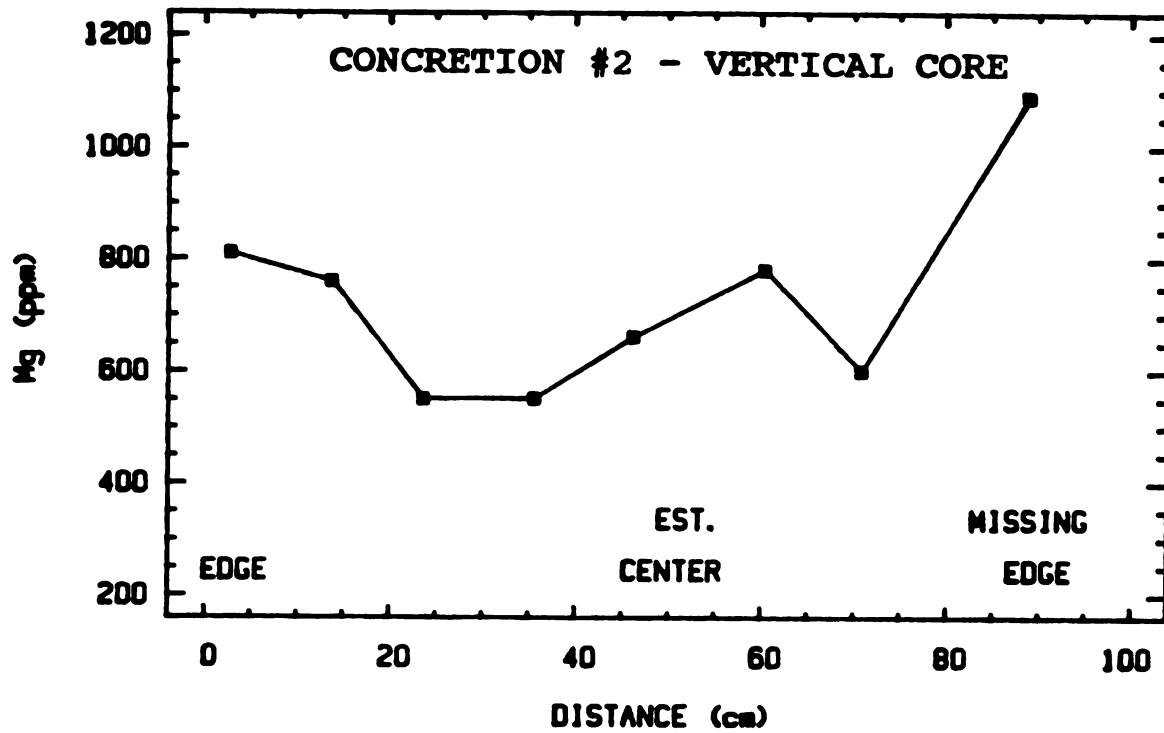


Figure 30. Continued

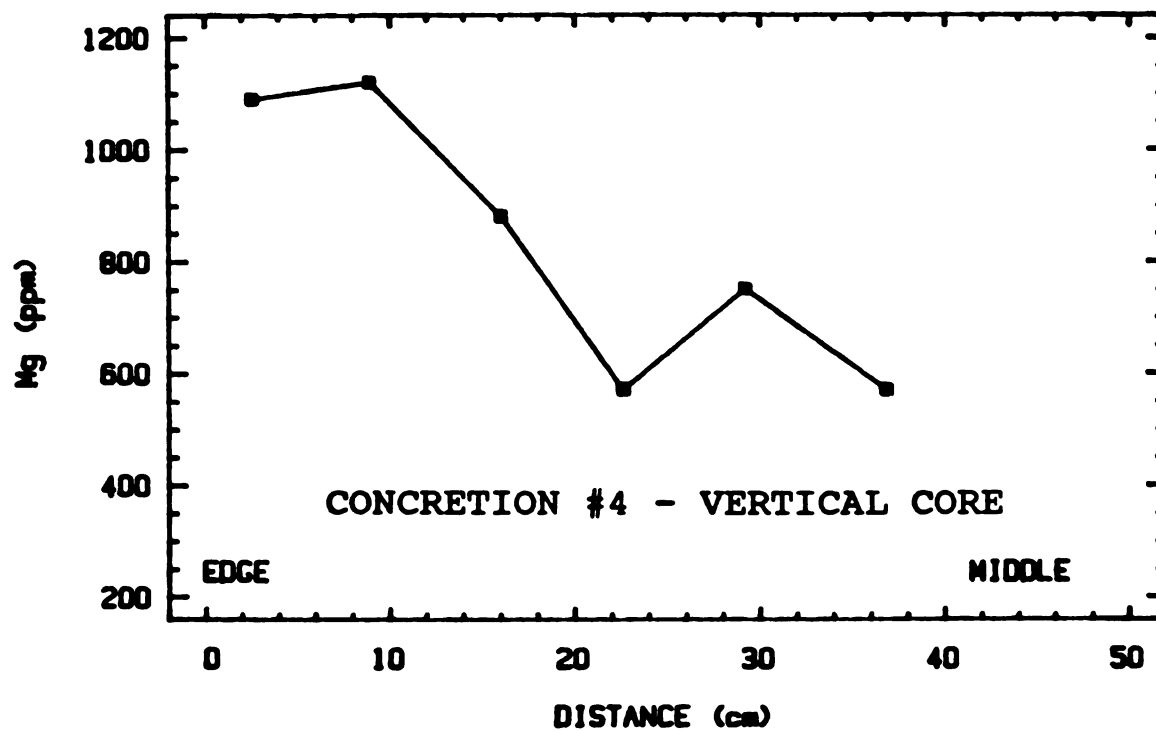
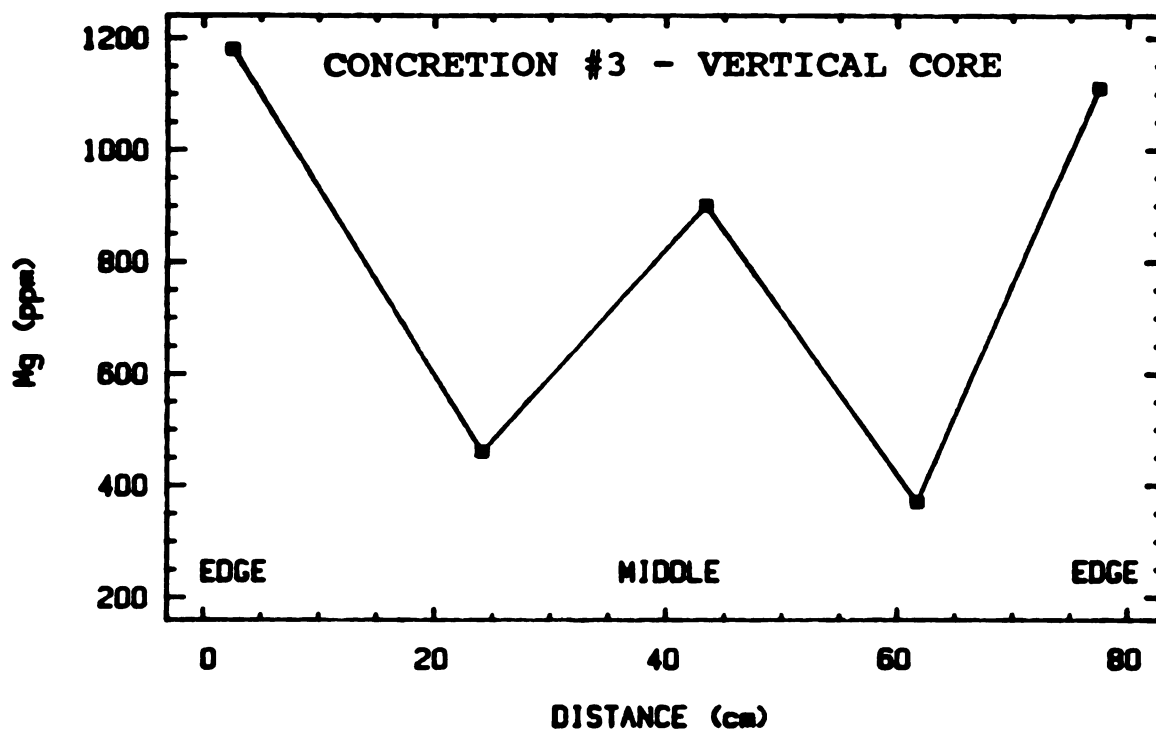


Figure 30. Continued

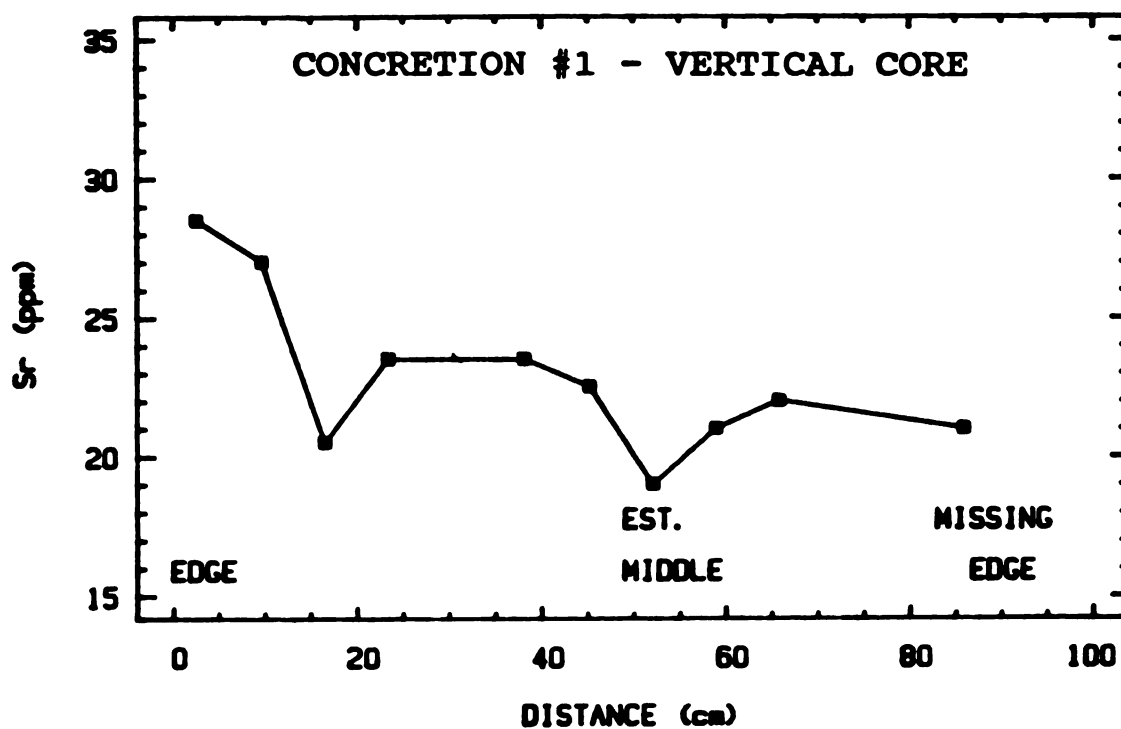


Figure 31. Trends in carbonate Sr concentration across the concretions. The values along the horizontal axis represent distances into the concretions. The zero value represents the concretion edge.

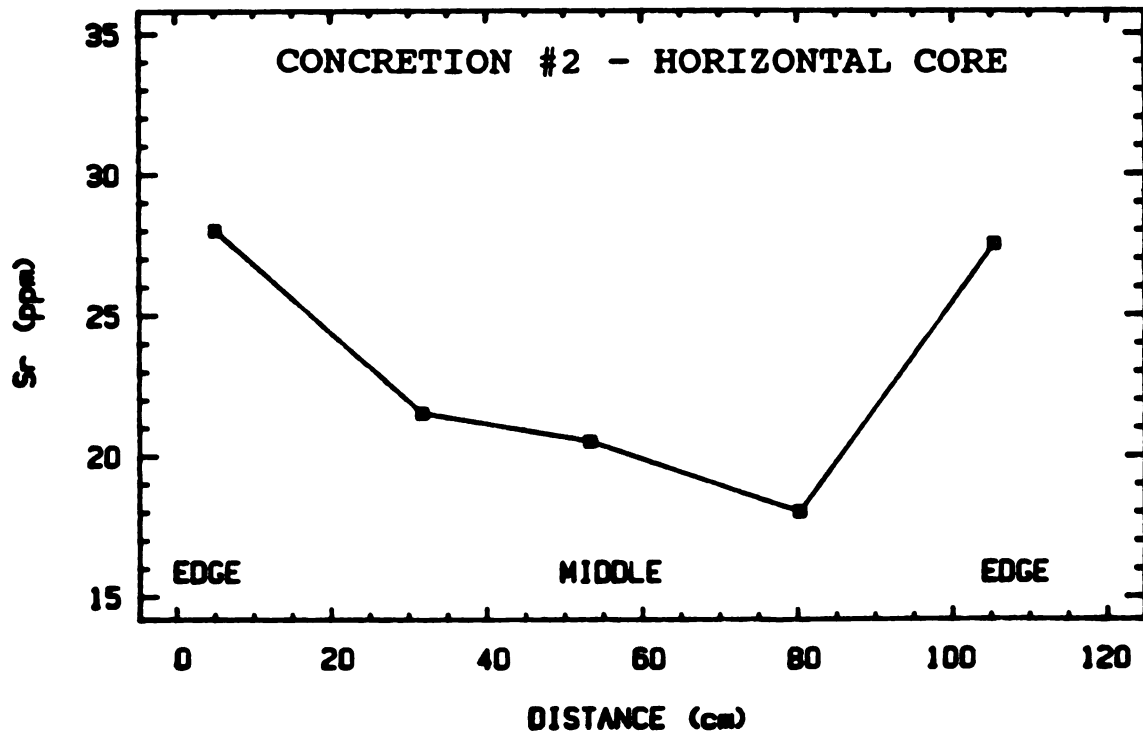
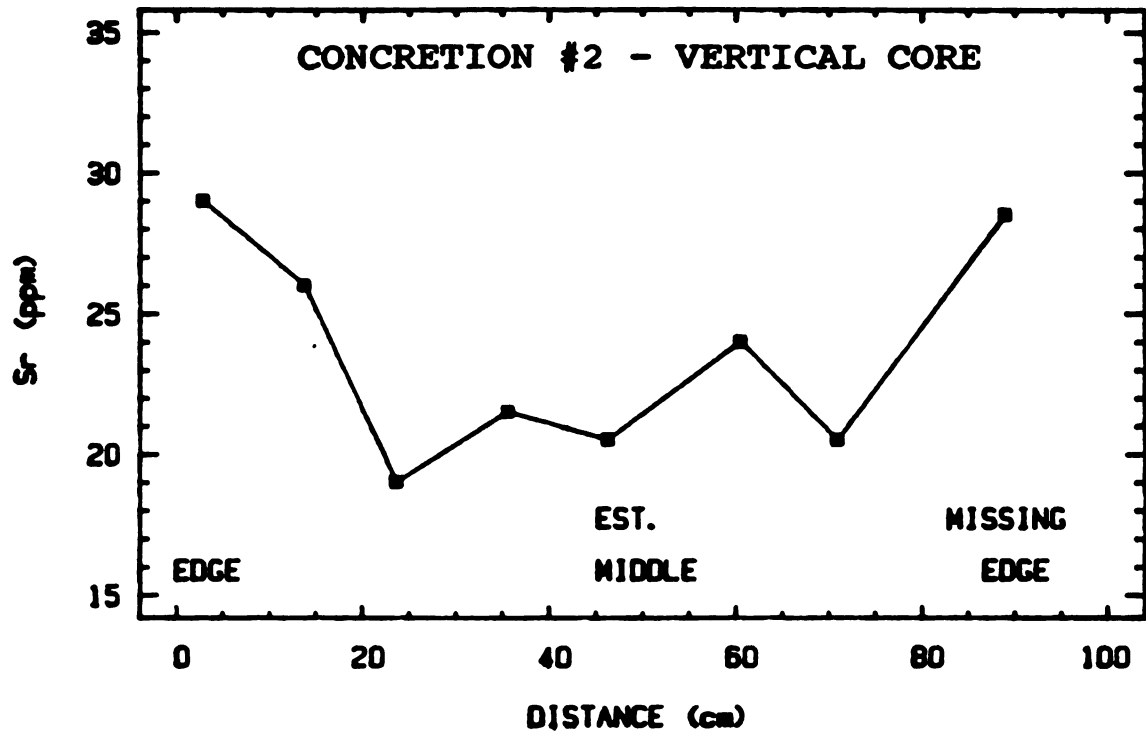


Figure 31. Continued

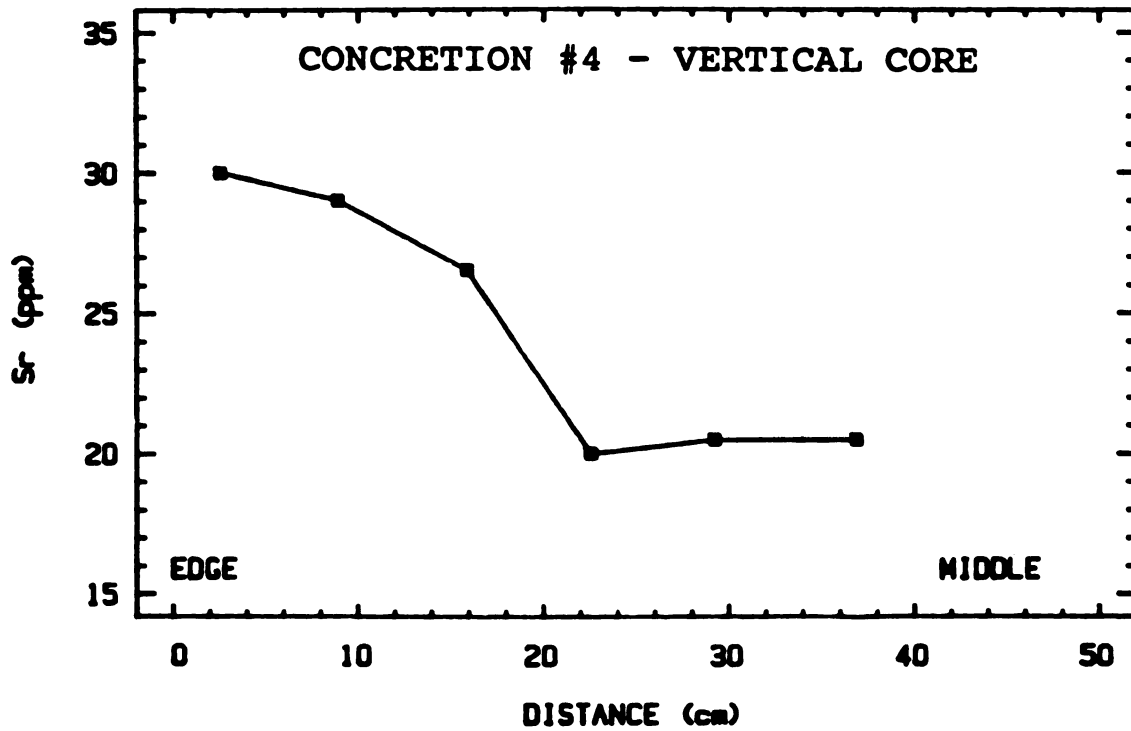
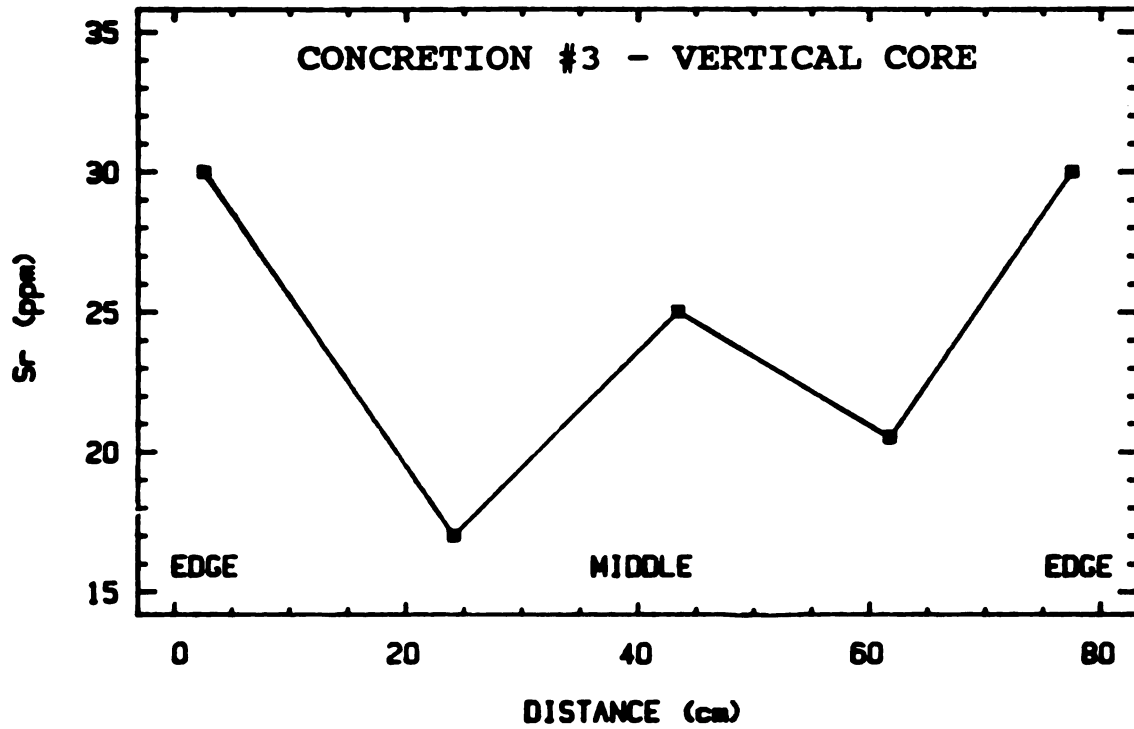


Figure 31. Continued

The trends in Sr concentration across the concretions are similar to those found for concretion Mg. In similarity to carbonate Mg, concretion core VC3 was found to have the largest range in Sr concentration and the highest Sr concentration for a concretion center.

Iron concentrations were found to range from 20 to 140 ppm and are shown in figure 32. Concretion Fe was found to decrease from the concretion center outward for all the concretions. The rate of Fe decrease in the concretions is usually highest in the outer half of the concretion. The rate of Fe decrease was highest in core HC2, the only core taken parallel to bedding. The concentration of Fe found at the concretion edge is similar for all the concretion cores.

Manganese concentrations were found to range from approximately 70 to 106 ppm and are shown in figure 33. In similarity to the trends found for Mg and Sr, Mn concentrations usually decrease in the intermediate region of the concretion and then increase near the concretion edge. Mn concentrations at concretion edges are higher than the respective concretion centers. The decrease in Mn concentration in the intermediate region of the concretion appears to occur closer to the concretion edge than the decreases in Mg and Sr.

The Mn concentrations at the center of concretion cores VC2 and HC2 are significantly different. The high Mn concentration found at the center of concretion core HC2 may be biased due to the sampling location. Three of the

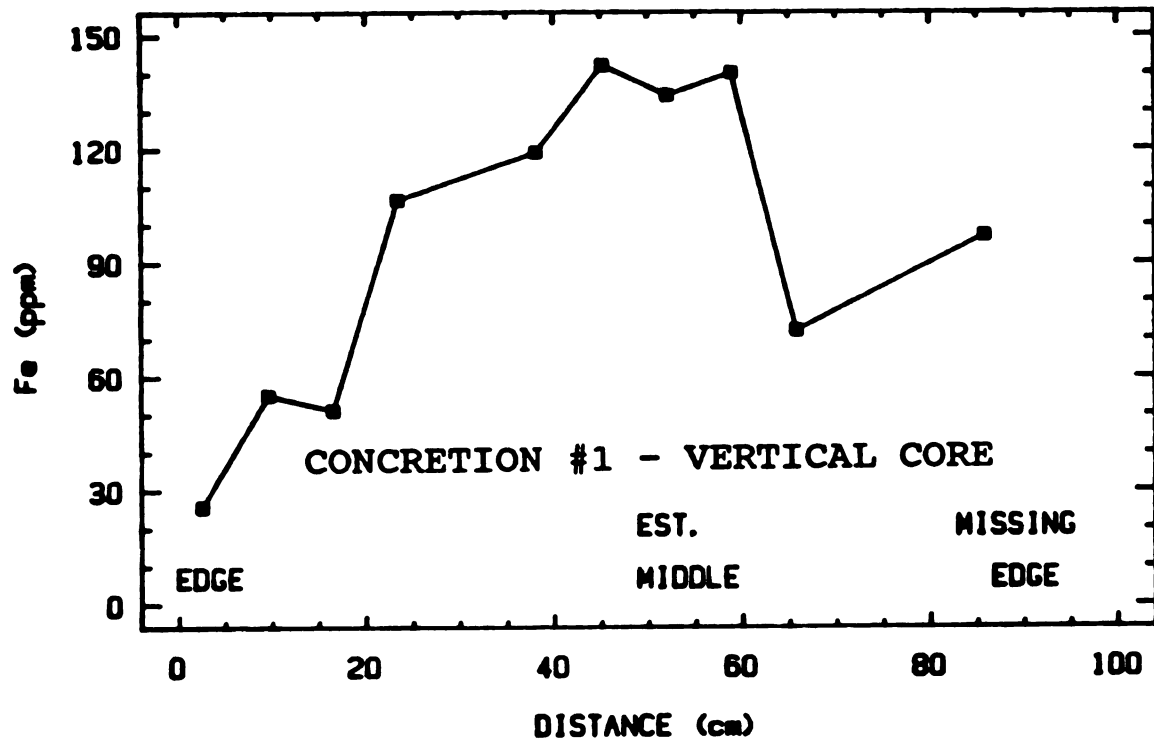


Figure 32. Trends in carbonate Fe concentration across the concretions. The values along the horizontal axis represent distances into the concretions. The zero value represents the concretion edge.

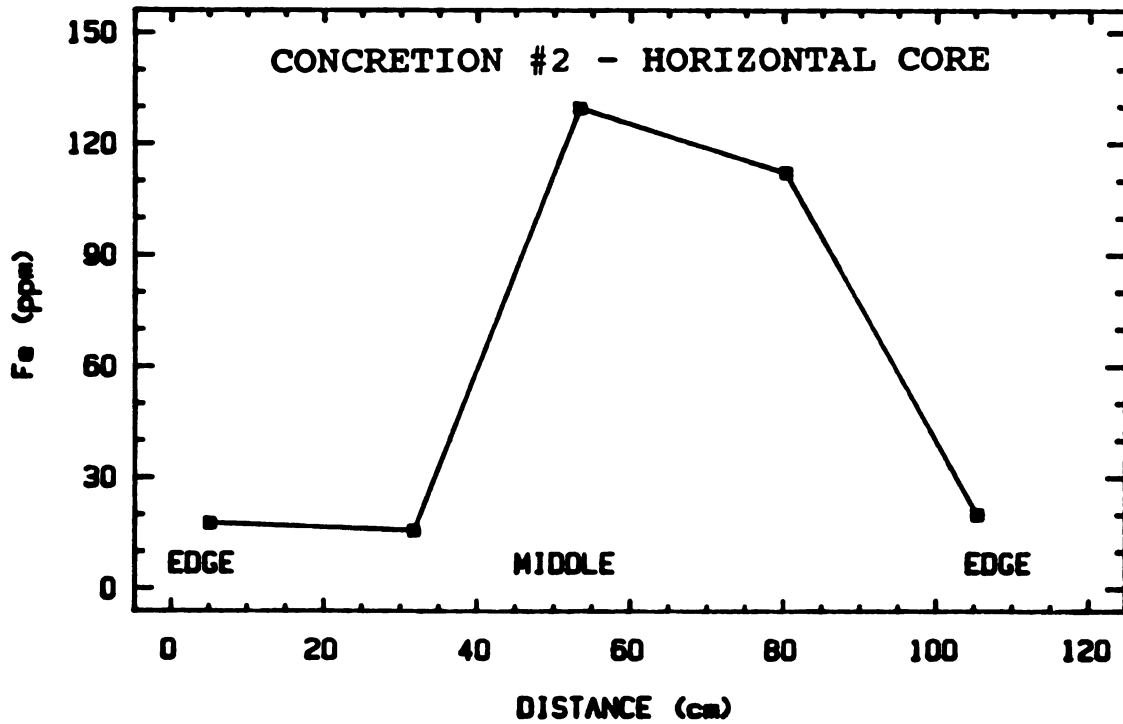
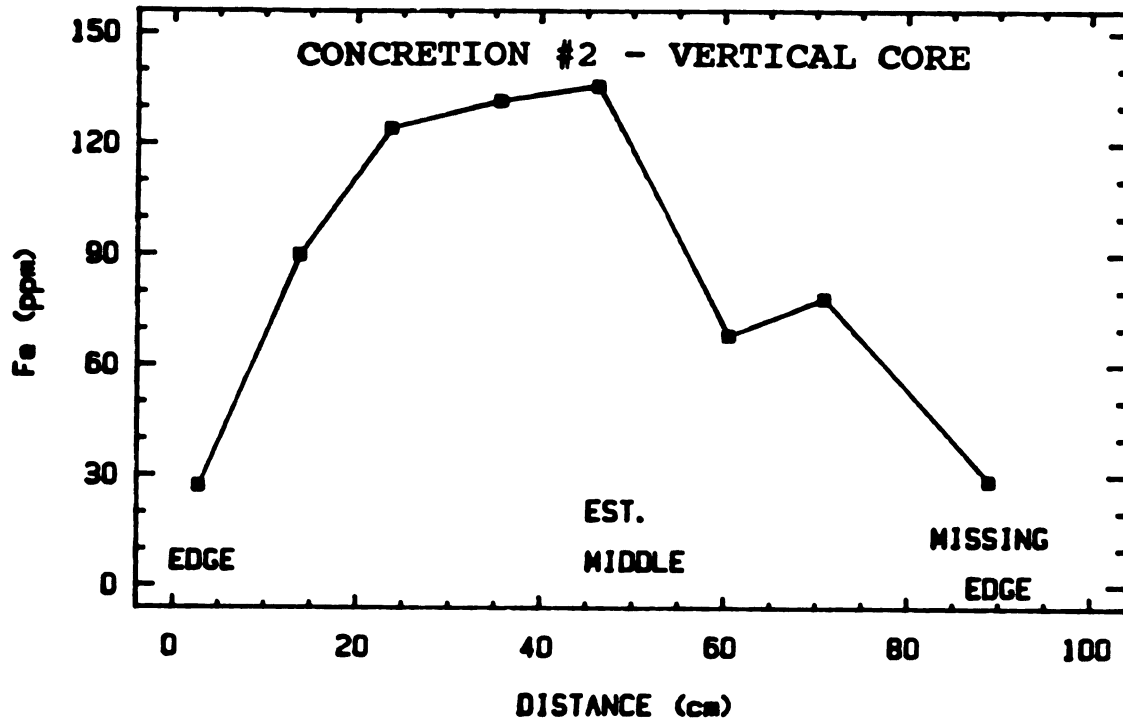


Figure 32. Continued

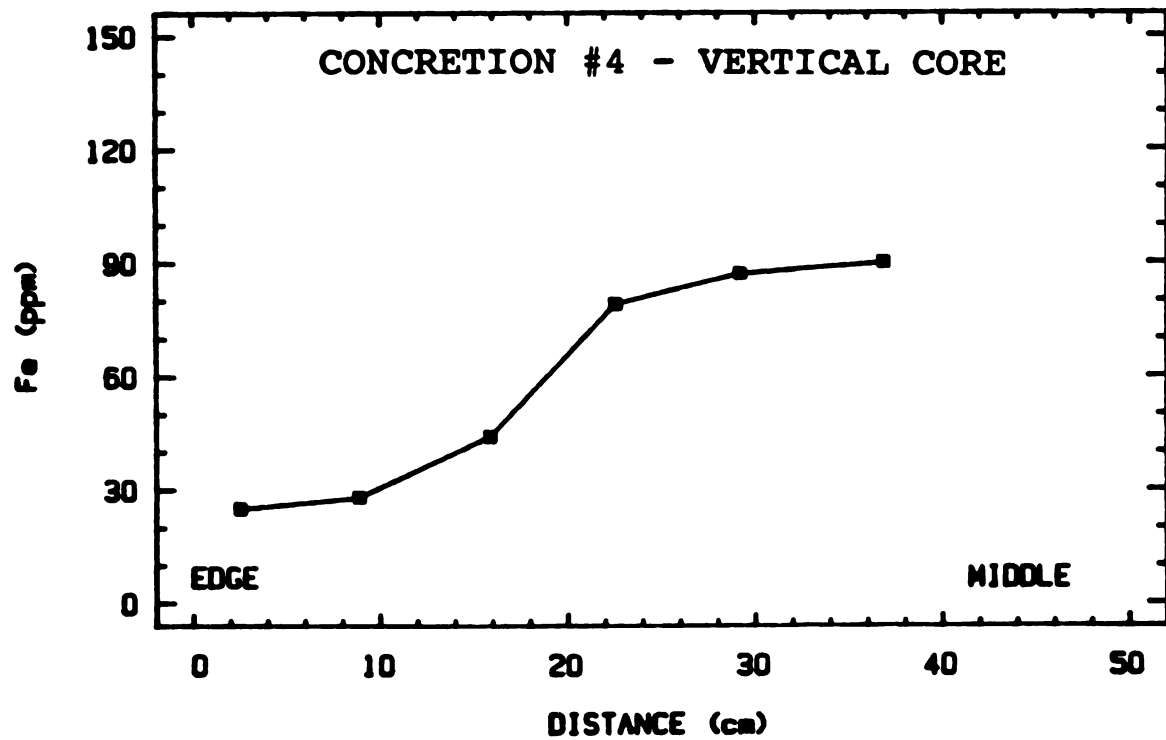
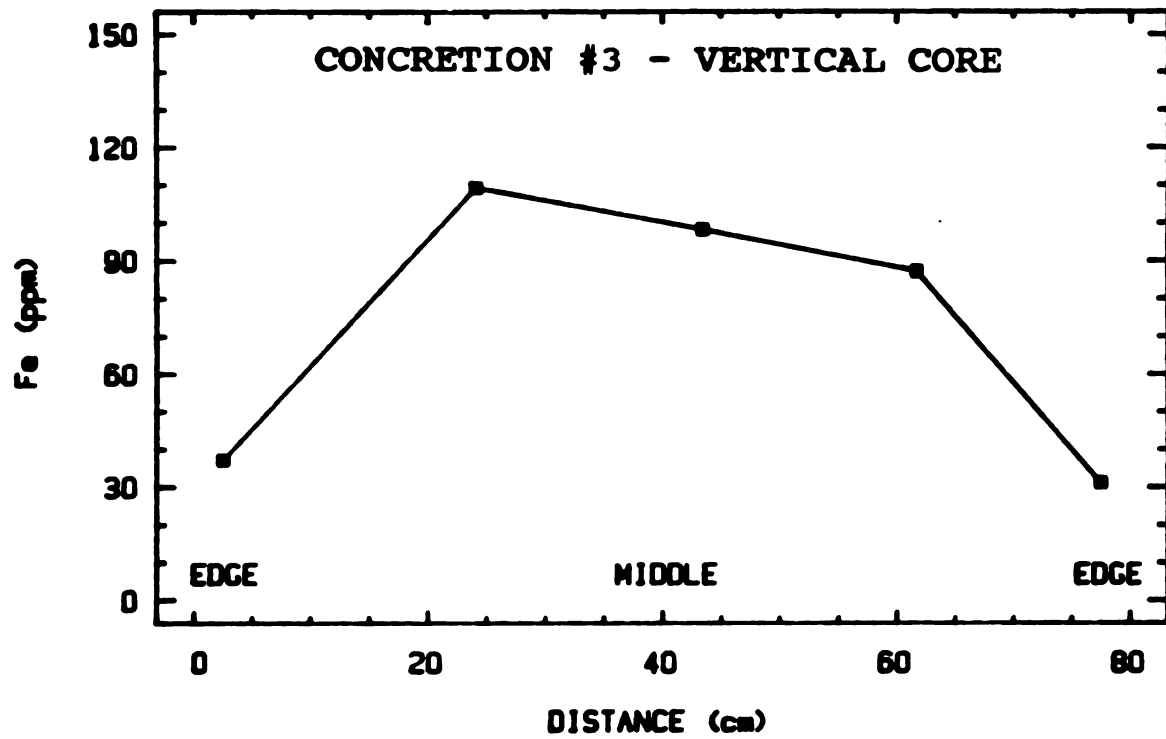


Figure 32. Continued

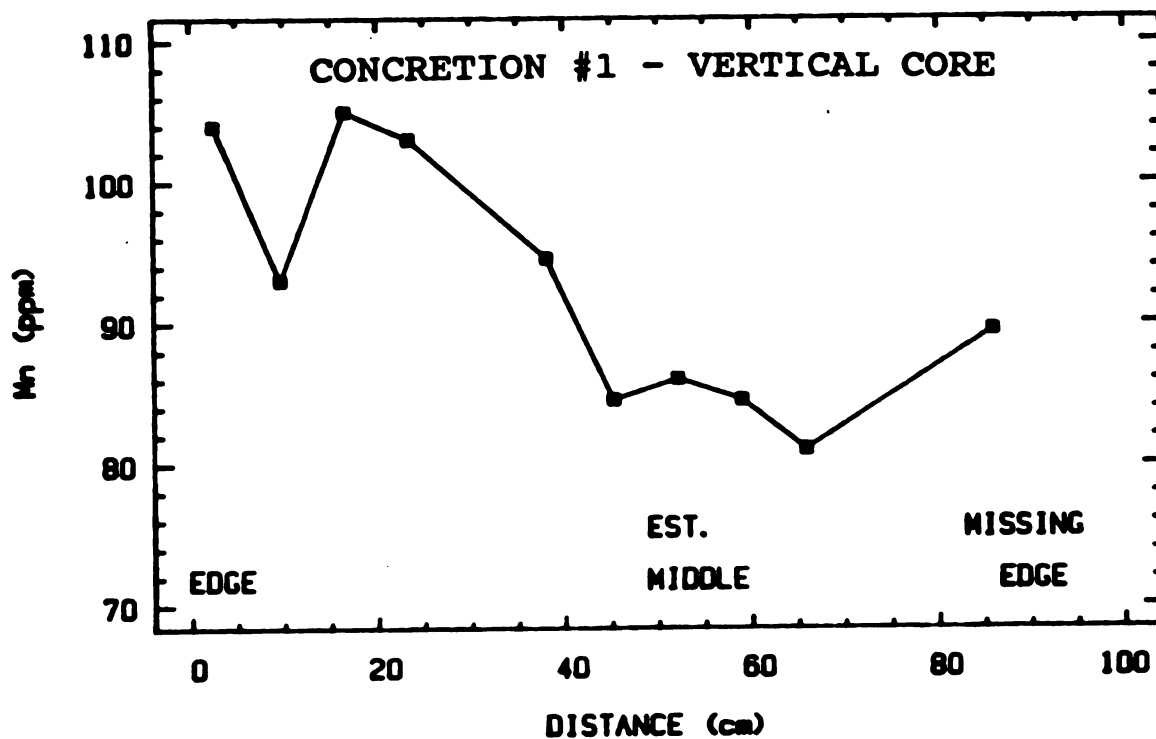


Figure 33. Trends in carbonate Mn concentration across the concretions. The values along the horizontal axis represent distances into the concretions. The zero value represents the concretion edge.

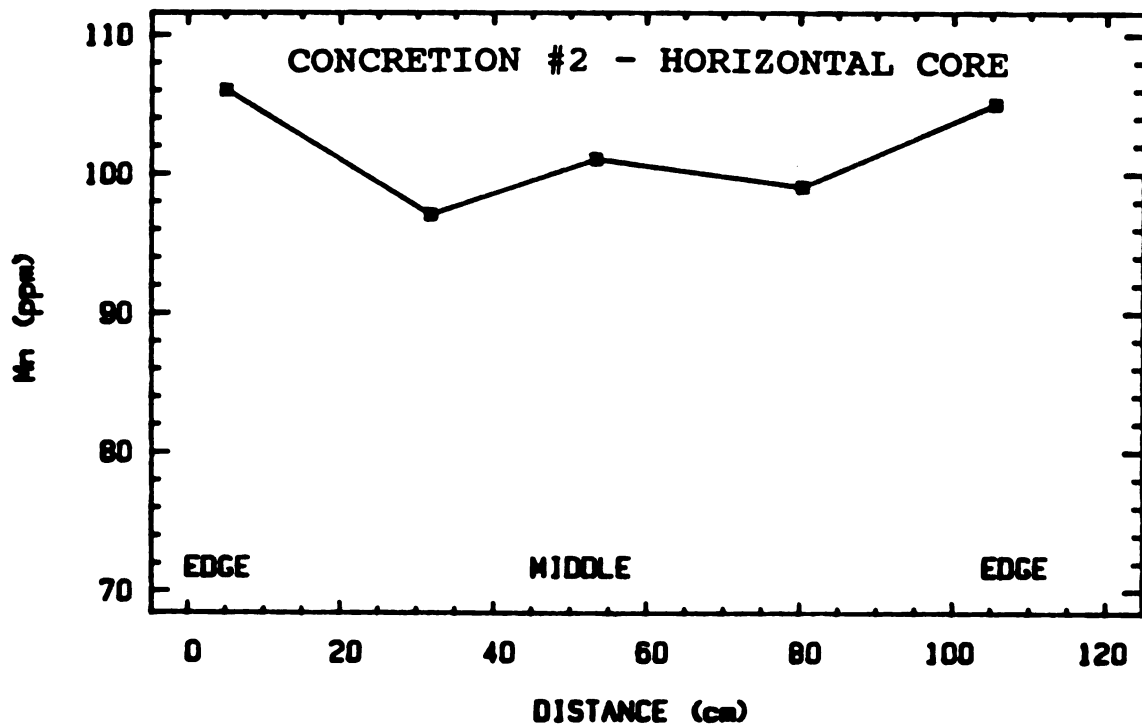
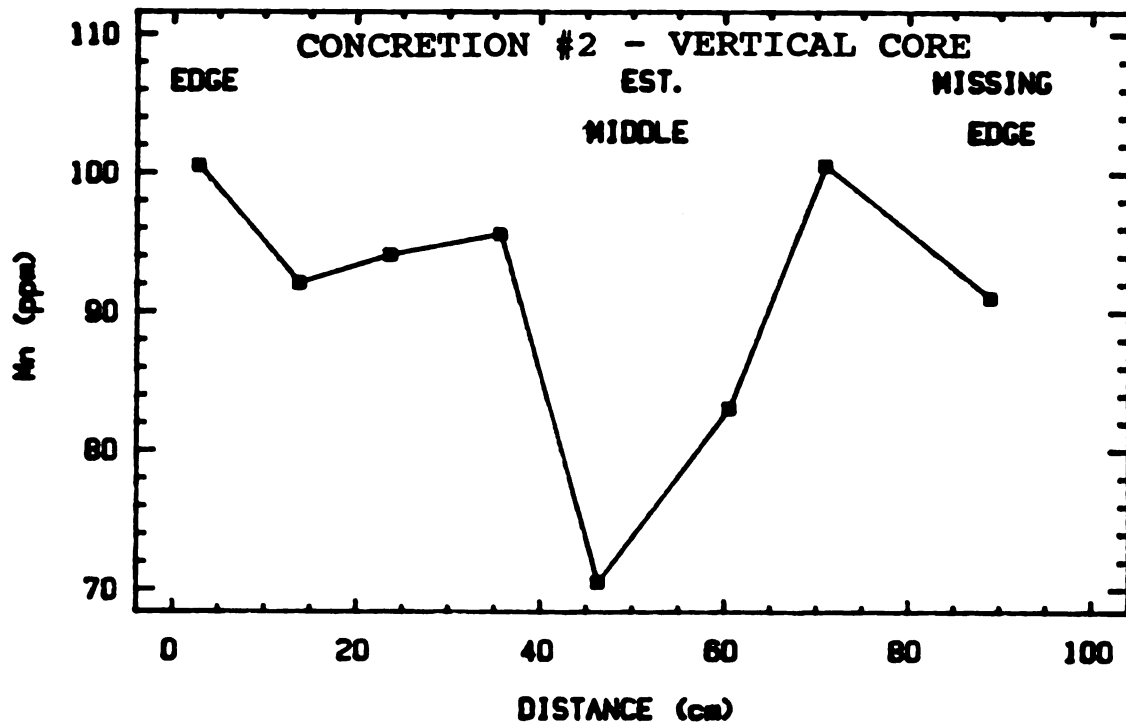


Figure 33. Continued

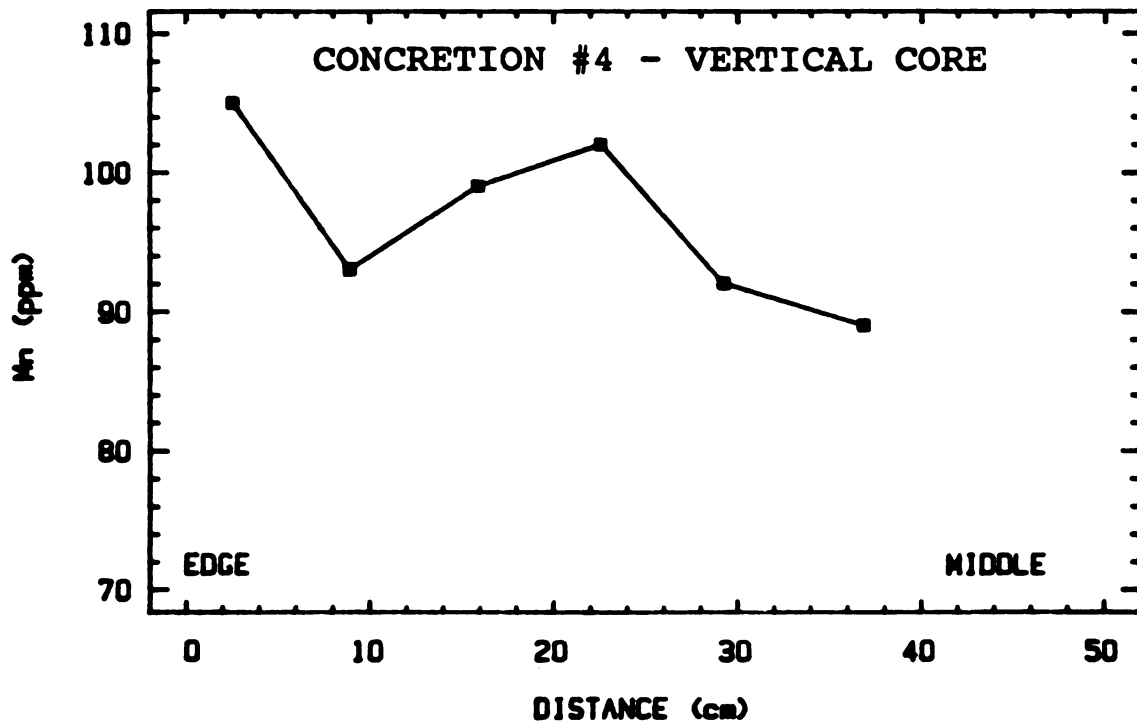
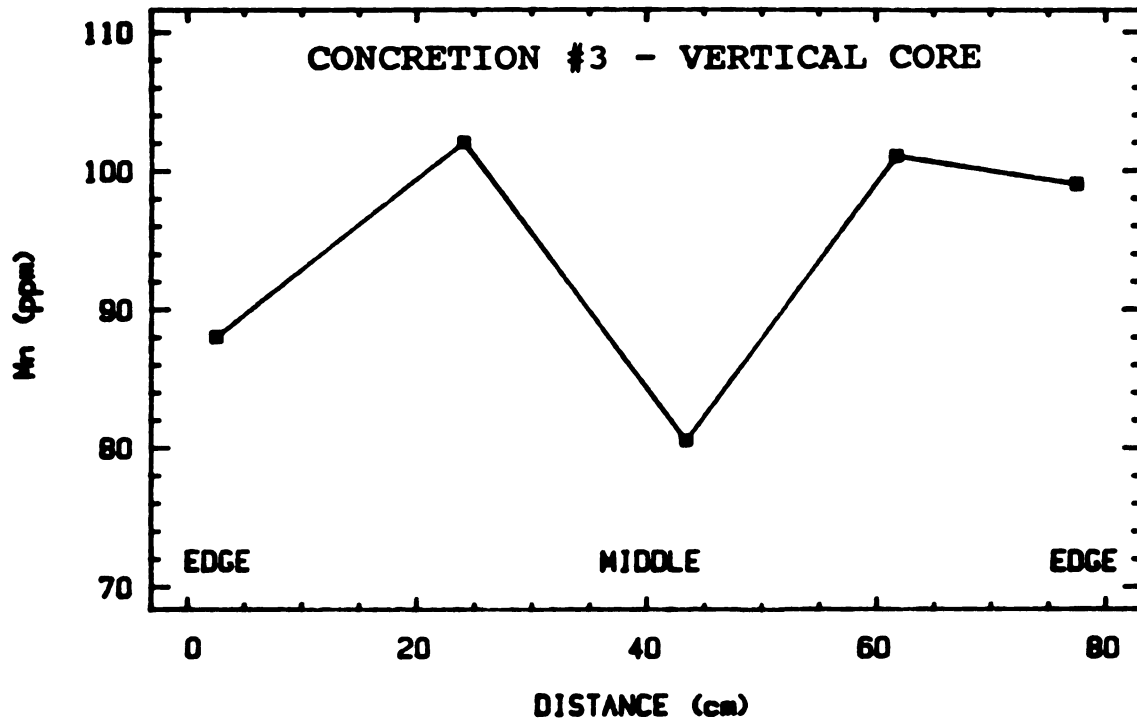


Figure 33. Continued

concretion cores show a sharp increase in Mn adjacent to the concretion center. Because Concretion core HC2 only intersected half of core VC2, it appears that core HC2 missed the center of the concretion by approximately five centimeters. Therefore, values listed for the middle of core HC2 may represent a value approximately 5 cm. away from the concretion center.

Sodium concentrations were found to range from approximately 26 to 57 ppm and are shown in figure 34. Concretion center concentrations are commonly higher than their respective edge concentrations. Concretion cores VC1, VC2, and VC4 show an increase in Na concentration in the intermediate region of the concretion. No increase in Na concentration was found in concretion cores HC2 and VC3.

The trends in calcite Na concentration show more variability between the concretions than the other trace elements measured. Concretion core VC1 shows the largest range in Na concentrations and is the only core that shows a sharp decrease in Na concentration near the concretion center. In contrast to core VC1, cores HC2 and VC3 show little variation across the concretion (a gradual decrease from concretion center outward).

CARBON ISOTOPIC COMPOSITION

Carbon isotopic profiles for the concretions are shown in figure 35. Carbon isotopic values were found to range from -12.5 PDB in core VC3 to -3.7 PDB in core VC2. Values for concretion centers range from approximately -8 to -9.5

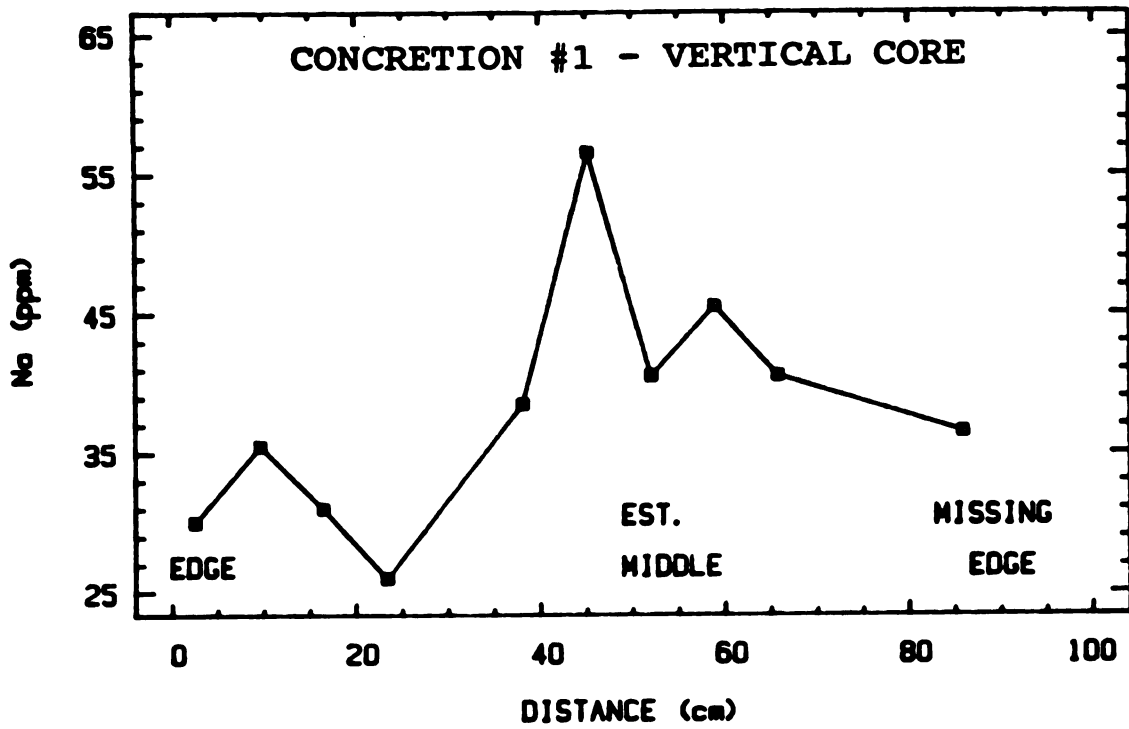


Figure 34. Trend in carbonate Na concetration across the concretions. The values along the horizontal axis represent distances into the concretion. The zero value represents the concretion edge.

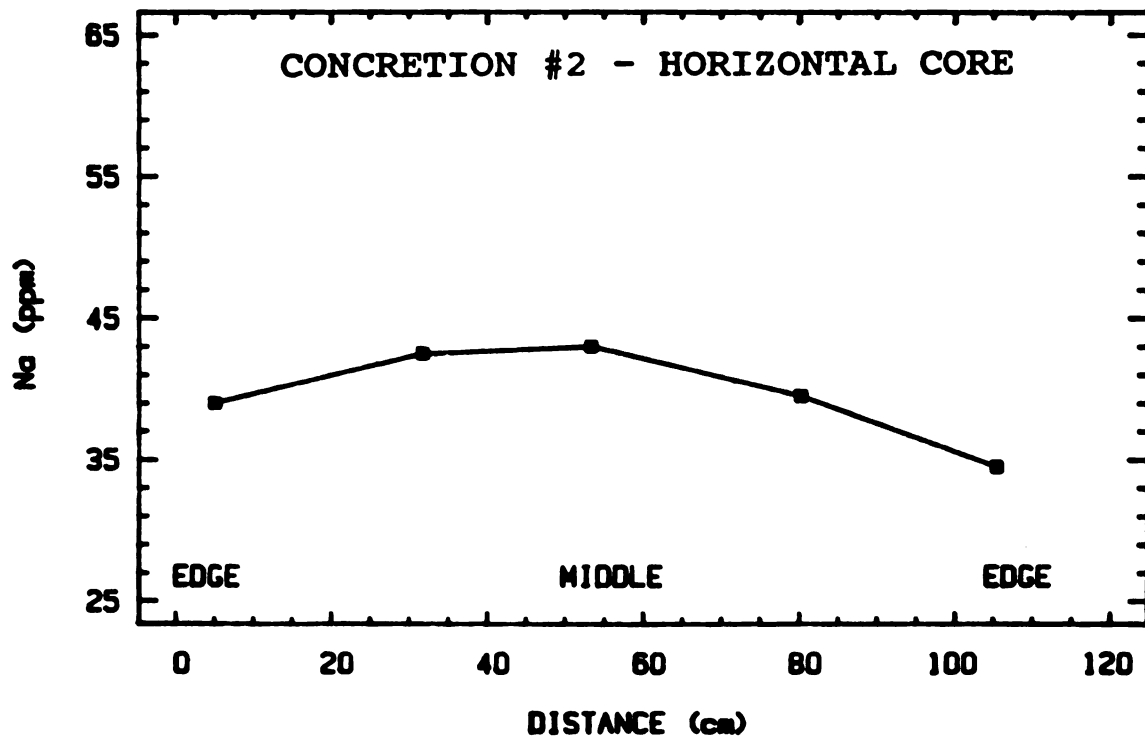
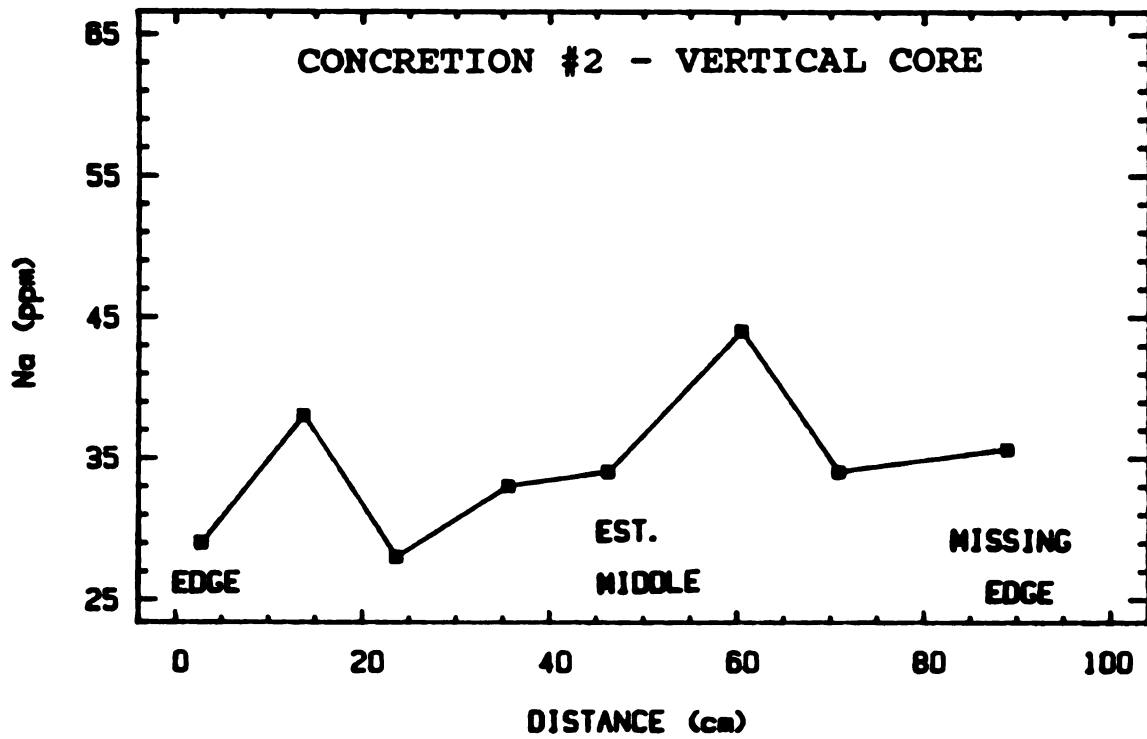


Figure 34. Continued

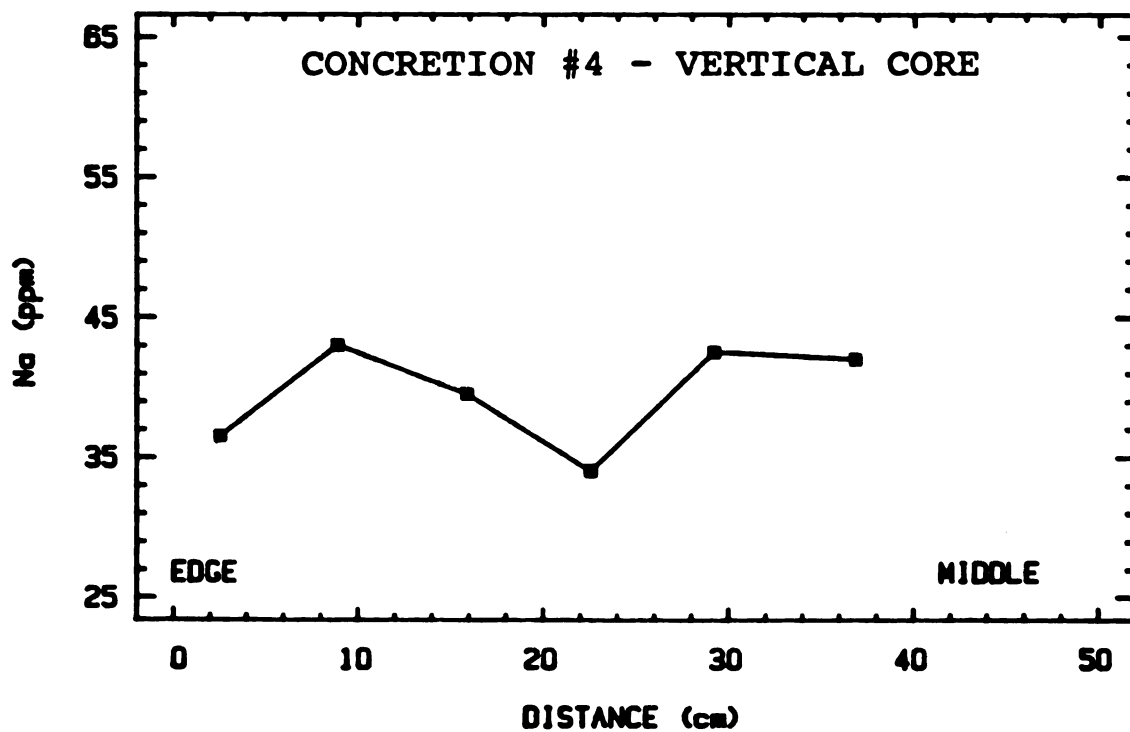
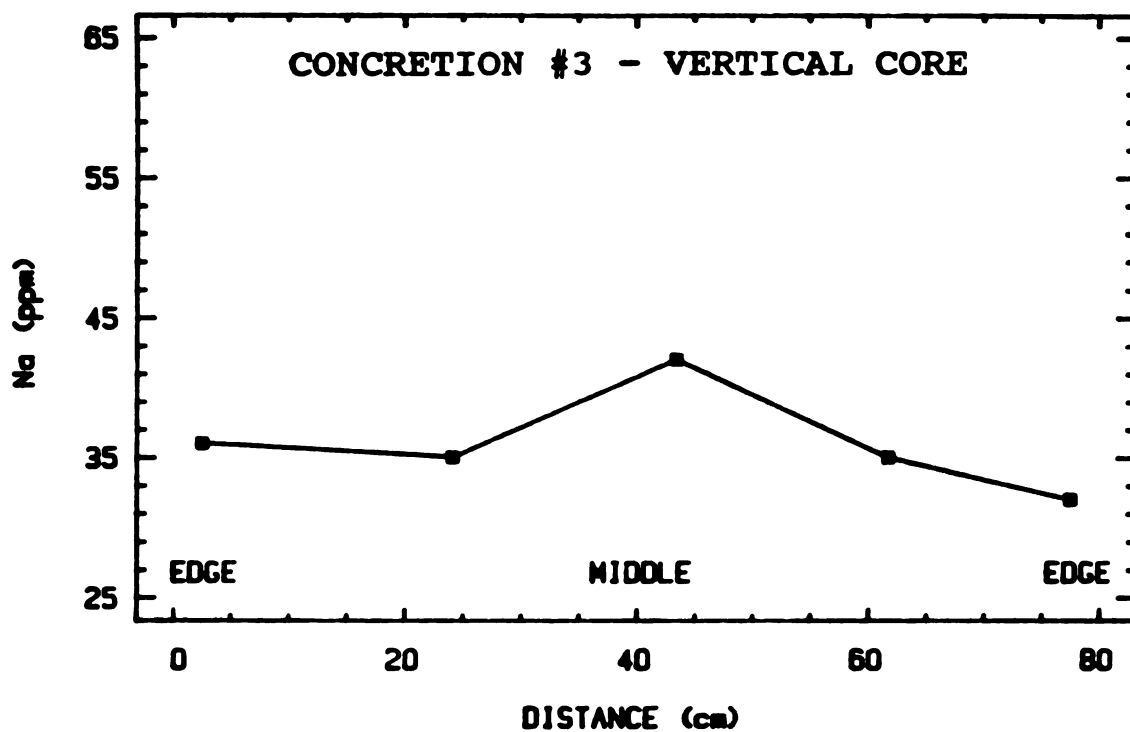


Figure 34. Continued

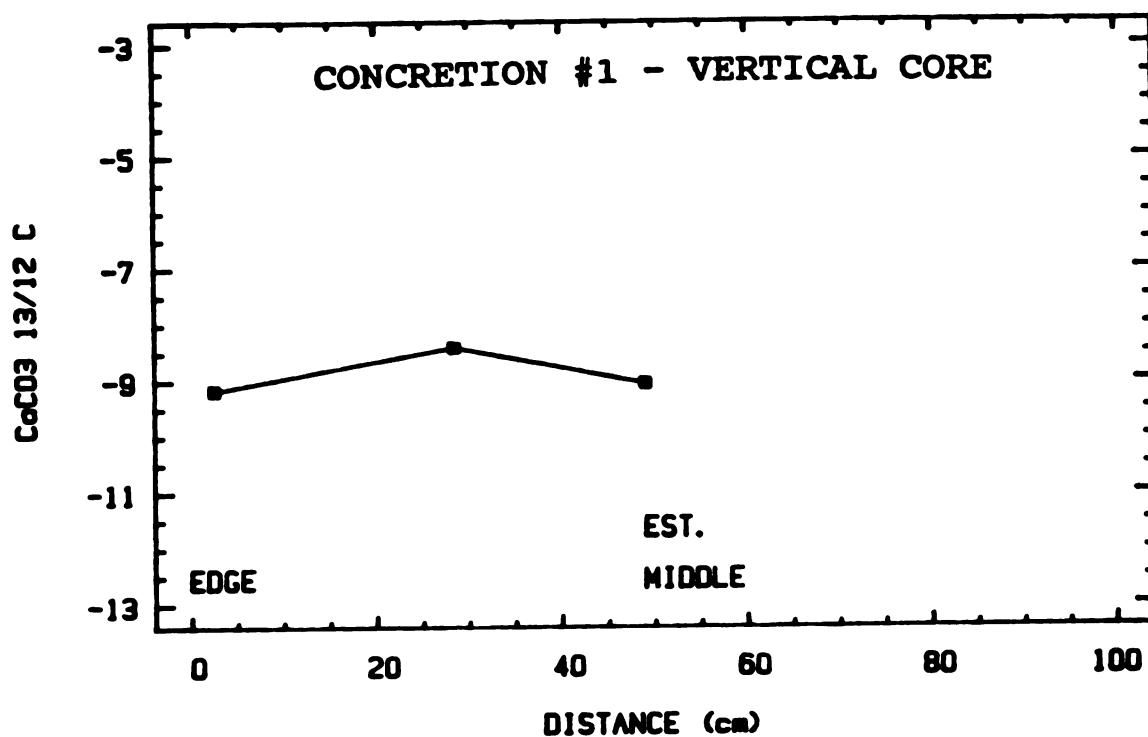


Figure 35. Trends in carbonate carbon isotopic composition across the concretions. The values along the horizontal axis represent distances into the concretions. The zero value represents the concretion edge.

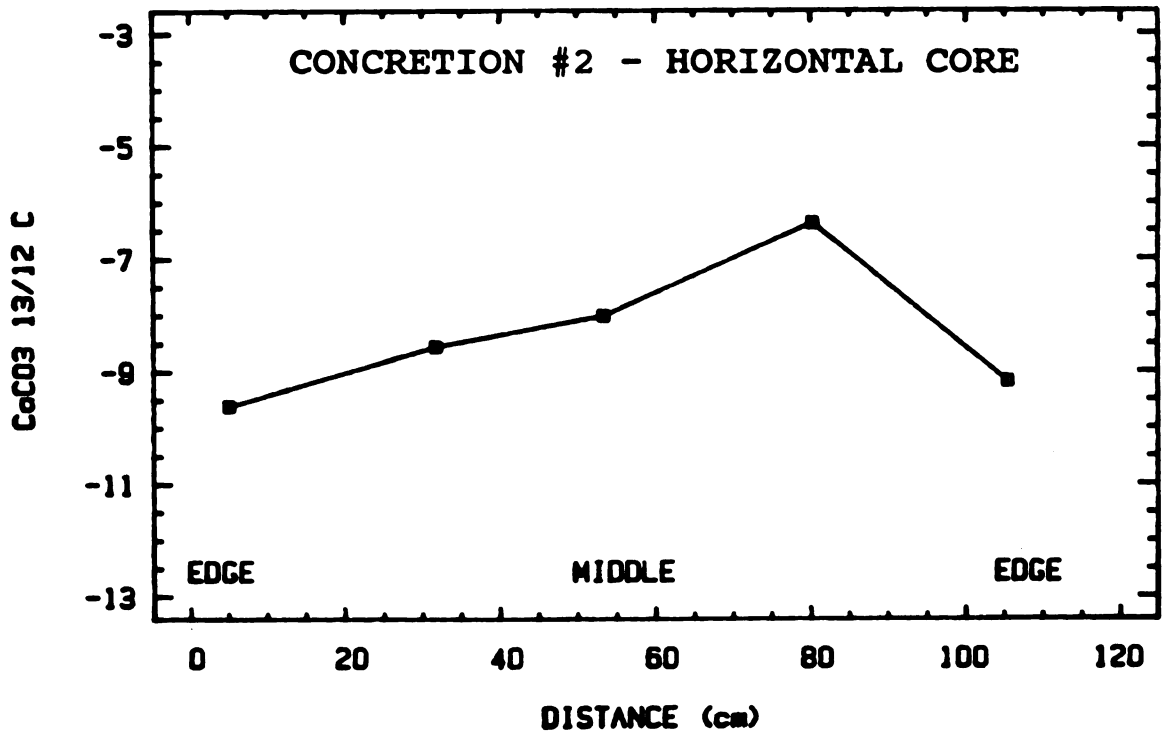
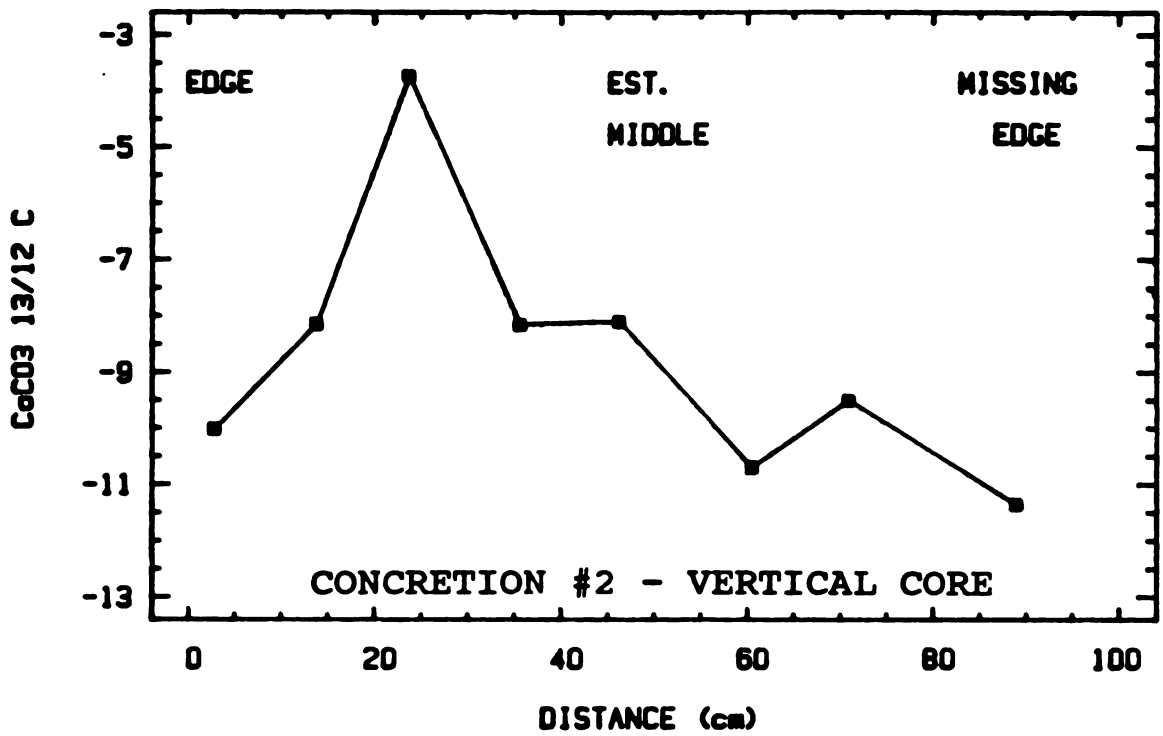


Figure 35. Continued

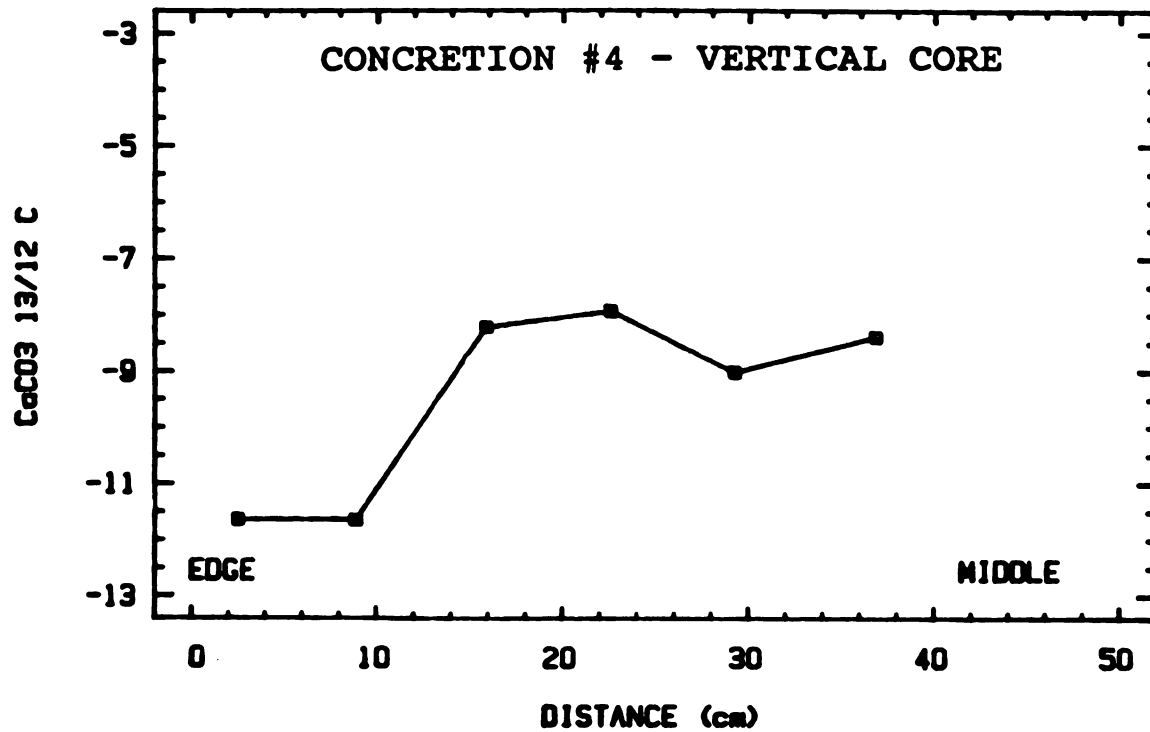
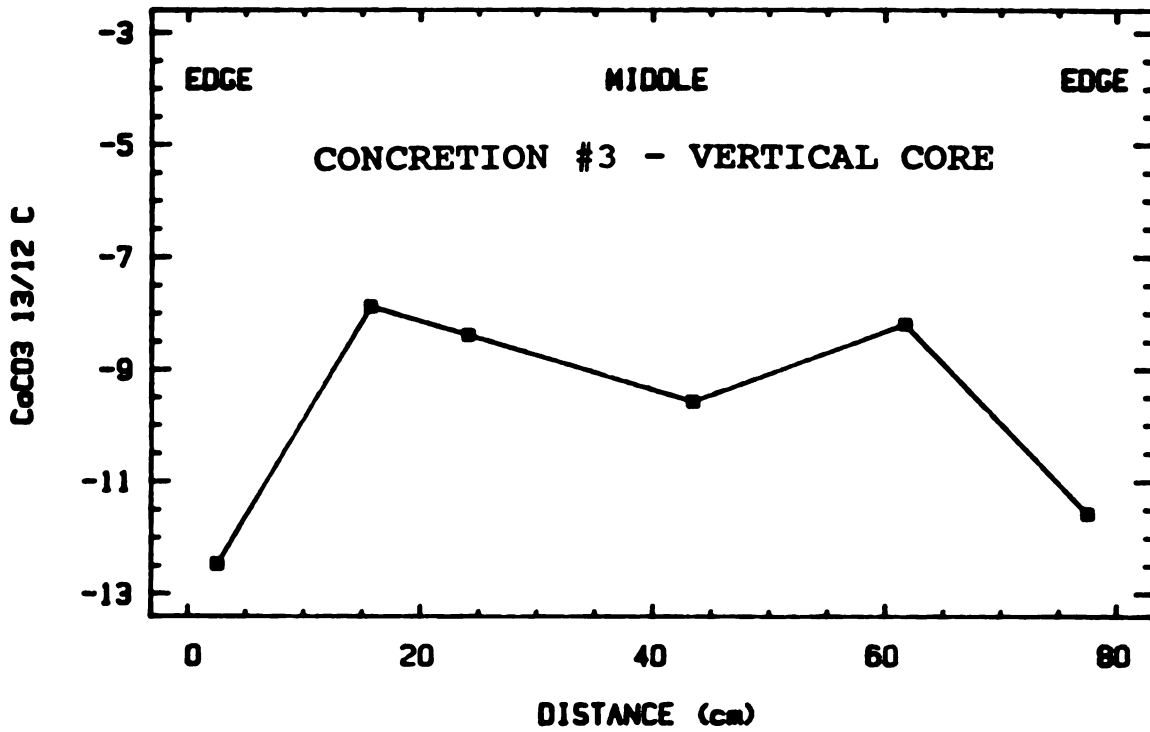


Figure 35. Continued

PDB. Carbon isotopic values of concretion edges range from -9.18 in VC1 to -12.48 PDB in VC3 and are lighter than the corresponding concretion centers. Differences between concretion center and edge values range from approximately -0.11 in VC1 to -3.26 PDB in VC4. While the data suggest that the overall trend is for the concretions to become isotopically lighter from concretion center outward, all the concretion cores, except one half of core HC2, show a decrease in heavy carbon in the intermediate region of the concretions.

The carbon isotopic value found for the Hathon dolomite concretion and the samples collected from the calcareous rocks of Unit-2 are shown in table 4. The carbon isotopic value found for the Hathon dolomite concretion is similar to the heaviest value found by the previous Antrim concretion studies by Hathon (1979) and Wardlaw (1981).

The concretions sampled from the calcareous shales of Unit-2 are enriched in heavy carbon relative to the Unit-3 and Unit-1 concretions and suggests that a lower amount of organic carbon was incorporated into the Unit-2 concretions. The Unit-2 limestone sample analyzed by this study was found to have a carbon isotopic composition near 0.0 PDB and suggests that the limestone is composed almost entirely of oceanic carbon and is not diagenetic in origin.

OXYGEN ISOTOPIC COMPOSITION

Oxygen isotopic values for concretion carbonate range from -7.63 in core HC2 to -4.75 PDB in core HC2 (Figure 36).

Table 4. Carbonate and pyrite isotopic compositions from the three stratigraphic units at the Paxton Shale Quarry. Data from this study only.

Sample Name	^{13}C PDB	^{18}O PDB	^{34}S CDT
UNIT-1			
Hathon Dolomite	-10.64	-8.16	+3.56
UNIT-2			
Limestone Stringer	-0.17	-5.67	-20.57
Limestone Concretion	-2.02	-6.58	-7.34
Fossil Concretion	-5.68	-6.63	+27.05
UNIT-3			
(1) Unit-3 Concretions	-3.74 -12.48	-4.78 -8.26	(2) -0.7 -9.8

PDB = Pee Dee Belemnite - oxygen and carbon isotopic standard

CDT = Canyon Diablo Troilite - sulphur isotopic standard

(1) range of values from all Unit-3 concretion data, heavy/light

(2) sulphide data is from one concretion only

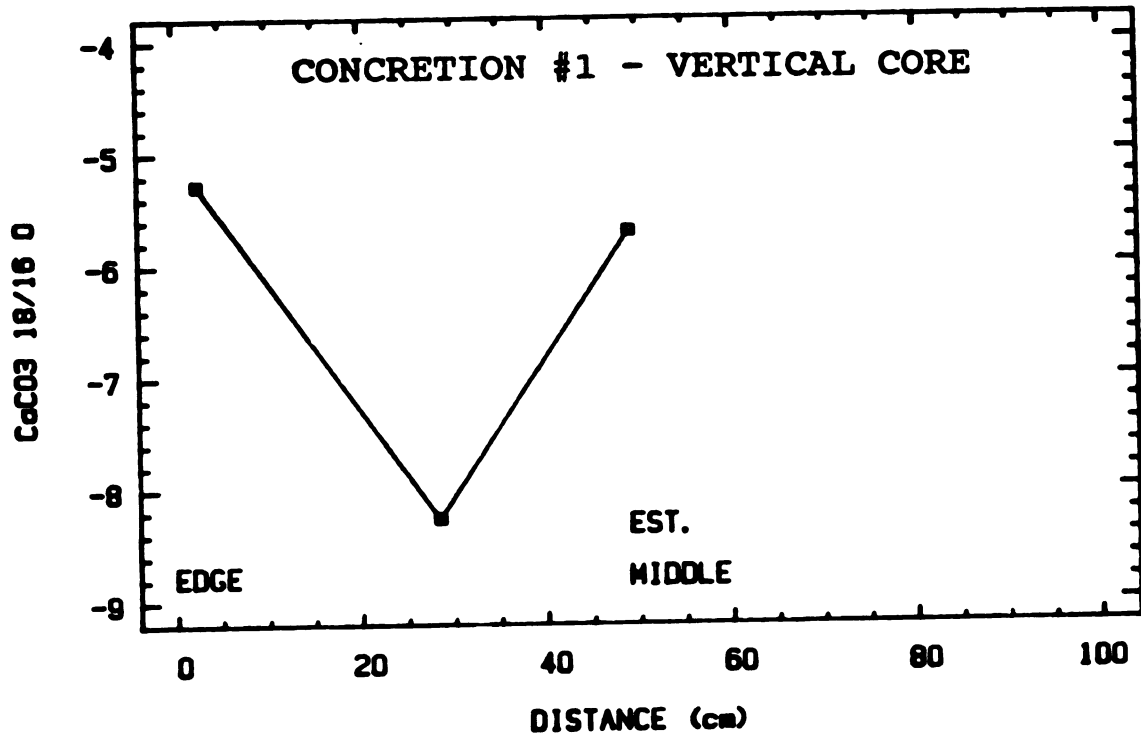


Figure 36. Trends in carbonate oxygen isotopic composition across the concretions. The values along the horizontal axis represent distances into the concretions. The zero value represents the concretion edge.

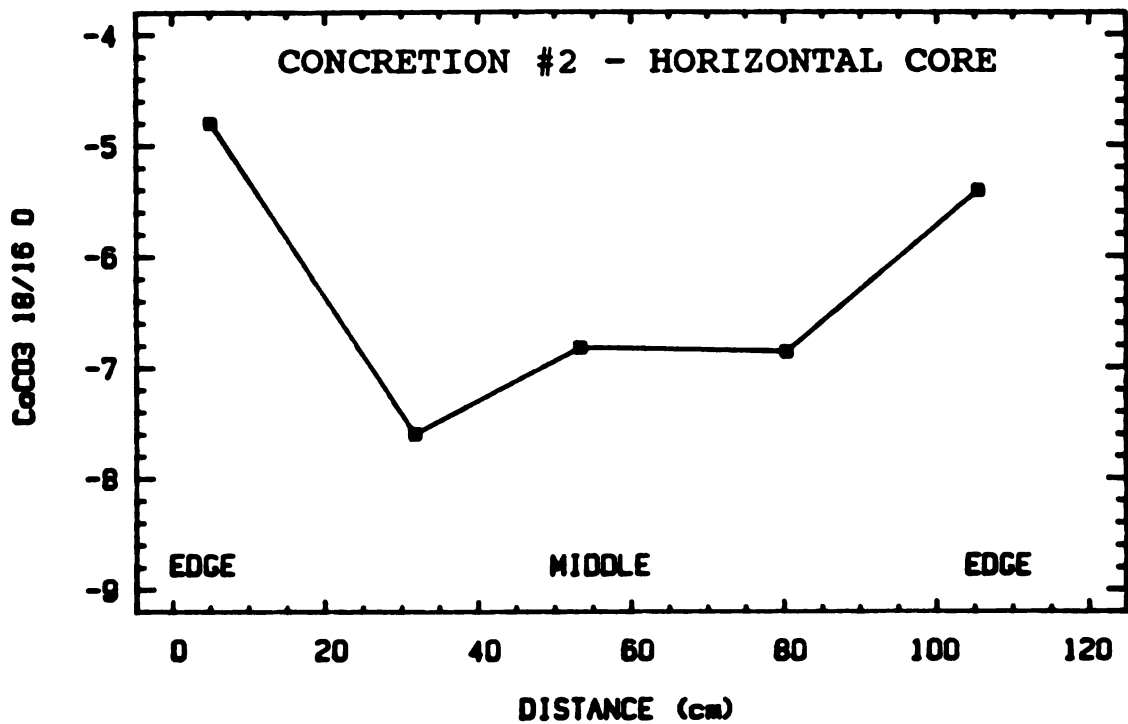
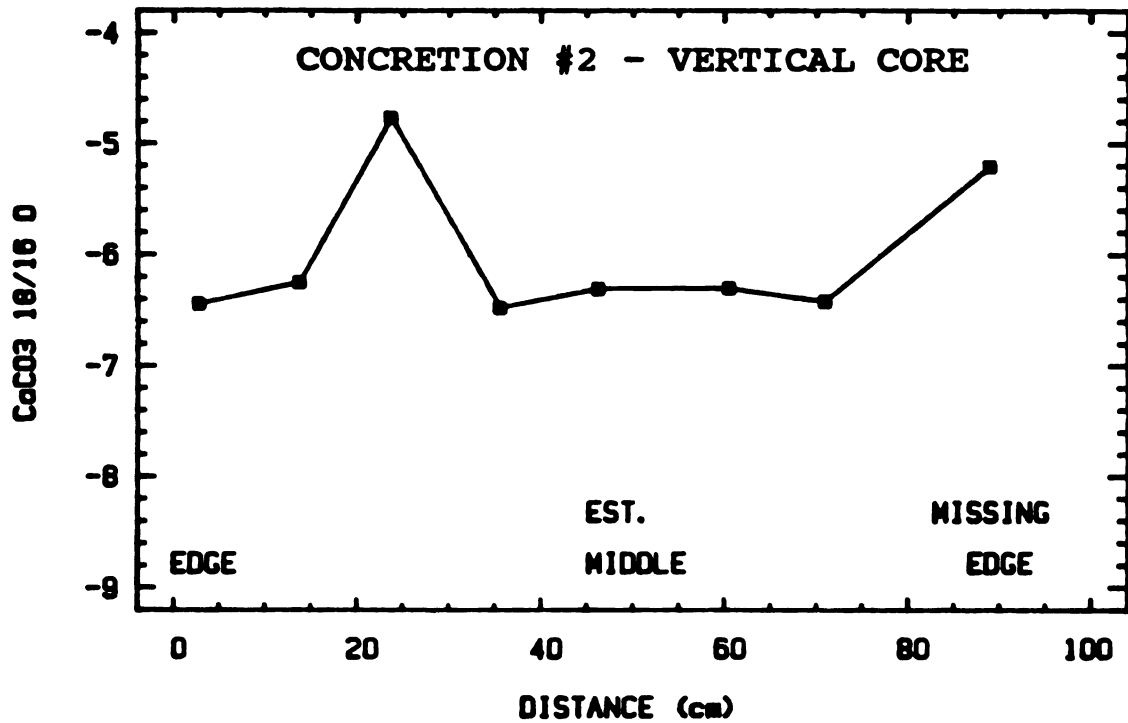


Figure 36. Continued

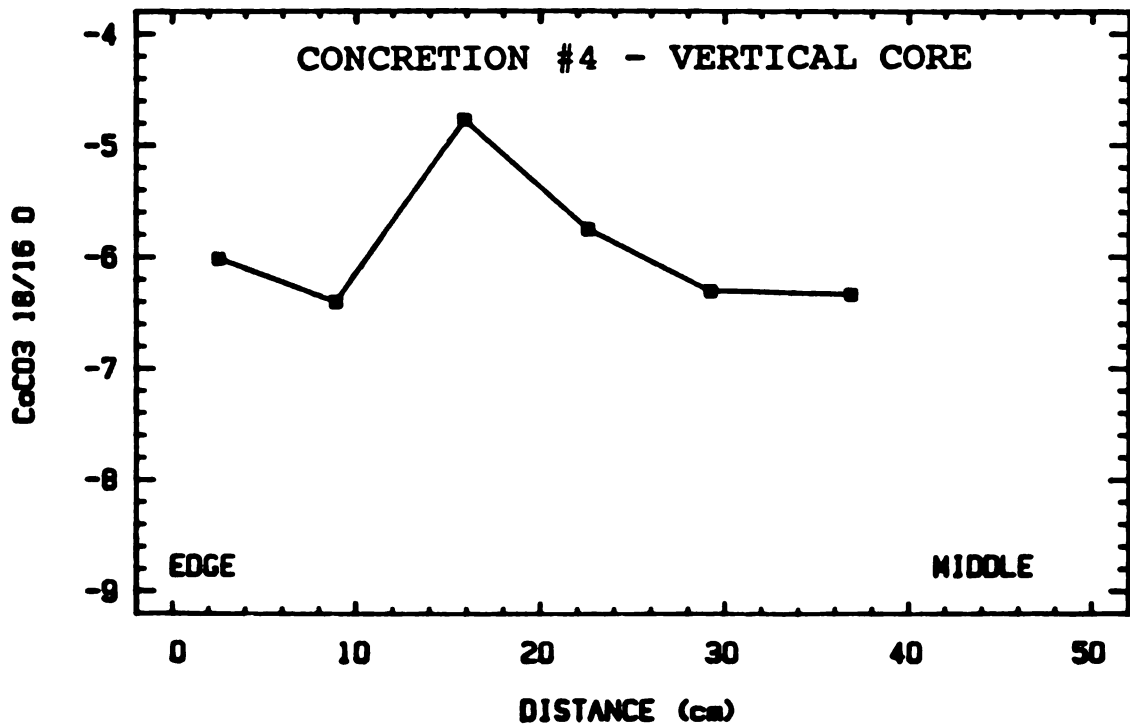
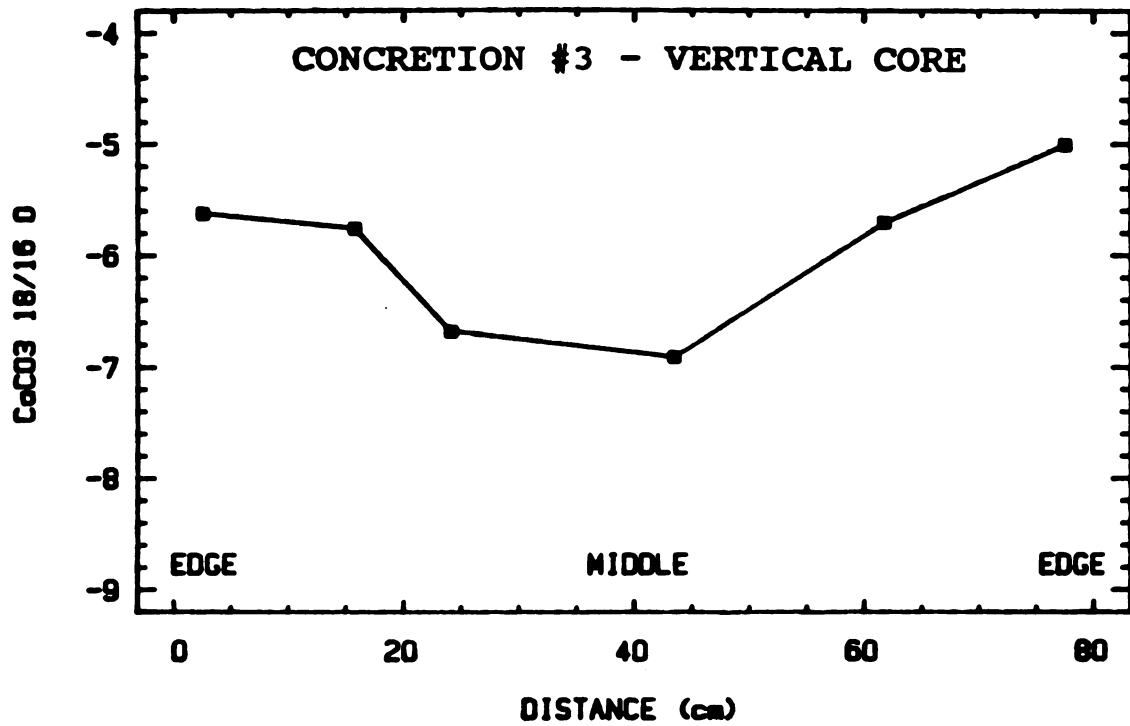


Figure 36. Continued

The oxygen isotopic data can be separated into three different patterns.

1) Concretion core VC1 shows an increase in light oxygen in the inner half of the concretion followed by an increase in heavy carbon in the outer half. The increase in heavy oxygen in the outer half of the concretion is similar to that found in core HC2. The increase in heavy oxygen in the inner half of the concretion is more pronounced in this core because core VC1 has the lightest concretion center value.

2) Concretion cores HC2 and VC2 decrease in light oxygen from concretion center outward.

3) Concretion cores VC2 and VC4 decrease in light oxygen in the intermediate region of the concretion and then increase in light oxygen toward the concretion edge so that concretion edge values are similar to concretion center values. The similarity between concretion center and edge values for cores VC2 and VC4 suggests that the increase in heavy oxygen may have been due to a transitory increase in heavy pore water oxygen.

The oxygen isotopic composition found for the Hathon dolomite concretion and the samples collected from the calcareous rocks of Unit-2 are shown in table 4. The oxygen isotopic value found for the Hathon dolomite concretion is similar to the values found by Hathon (1979). The value found for the Hathon dolomite concretion is similar to the lightest value found for the Unit-3 calcite concretions.

The oxygen isotopic values found for the two Unit-2 concretions are similar to those found for the centers of the Unit-3 concretions. The oxygen isotopic value found for the "Limestone Stringer" sample is heavier than that found for the Unit-2 concretions and the centers of the Unit-3 concretions, but lighter than some of the values found in the outer half of some Unit-3 concretions.

CHAPTER 5 INTERPRETATION AND COMPARISON OF DATA

INTERPRETATION OF DATA

CONCRETION OCCURRENCE

Because the concretions occur as separate entities and represent the majority of the carbonate in the black shales, it appears that concretion formation was triggered by the development of localized microenvironments having a pore water chemistry different from that of the surrounding sediments. Because concretion size decreases and abundance increases with increasing carbonate content of the host rock, it appears that concretion nucleation is affected by the carbonate content of the sediment.

The strong correlation between concretion occurrence and the stratigraphic location of thin, friable layers rich in chalcedony suggests that concretion nucleation was facilitated by the nature of the sediment in the friable layers. The large size and semi-spherical shape of the concretions suggest that they precipitated before the sediments could develop significant differences between vertical and horizontal permeabilities.

CONCRETION CONSTITUENTS

This study proposes that the liquid hydrocarbons found by this study may have formed by the diagenetic processes associated with concretion formation. The following arguments support the formation of liquid hydrocarbons in association with concretion formation:

- 1) liquid hydrocarbons were only found in concretion septarian cavities;
- 2) the Unit-3 concretions sampled by this study were found to change in color from brown to black, and increase in petroliferous odor, from concretion center outward;
- 3) the chromatographic signature of the concretion oil sampled by this study is reportedly similar to that of oils that have undergone extensive microbial degradation;
- 4) liquid hydrocarbons have been found inside quartz geodes from Mississippian age rocks from Illinois and Indiana; and
- 5) the study by Hathon (1979) concluded that the black shales at the Paxton quarry are not mature enough to have produced liquid hydrocarbons.

Excluding concretion clay, no clastic inorganic material was identified in concretion thin sections. The high concentration of radiolarians and tasmanites in the concretions suggests that the bulk of the sediment incorporated into the concretions is pelagic in nature. Therefore, the composition of the sediment incorporated into the concretions suggests that the concretions precipitated in sediments deposited outside the range of terrestrial influences.

Because the best preserved radiolarians occur at the concretion edges, the radiolarian tests within the surrounding host sediment must have been intact and well preserved throughout the entire period of concretion formation. Therefore, it appears that the chemical

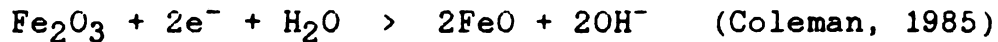
conditions associated with concretion nucleation and early growth caused the local dissolution of radiolarian tests.

The solubility of silica below a pH of 9 is low and for all practical purposes pH independent. Above a pH of 9 silica solubility increases and becomes pH dependent (Aston, 1983, Krumbein, 1983). The following is a hypothesized scenario to explain the change in radiolarian preservation:

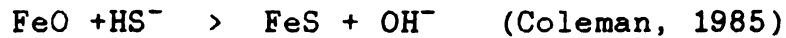
- 1) A microenvironment with an elevated pore water pH develops. The microenvironment becomes supersaturated with respect to calcite and concretion nucleation occurs. Concurrently, the elevated pore water pH causes the dissolution of nearby radiolarians.
- 2) As burial depth of the microenvironment increases, the microenvironment becomes increasingly closed and the pore water levels of hydrogen sulphide increase. The rising concentration of hydrogen sulphide causes the pore water pH to decline. The decrease in pore water pH lowers the silica solubility and induces the precipitation of chalcedony in the intermediate region of the concretion.
- 3) At the edge of the concretion the accumulation of hydrogen sulphide drops the pH of the microenvironment to the point where radiolarian dissolution is negligible. Concretion growth stops as the level of calcite supersaturation drops and a layer of iron sulphide precipitates around the concretion.

Three processes may occur during early diagenesis that may cause an increase in pore water pH:

(1) the production of OH^- associated with the reduction of trivalent Fe and Mn



(2) the production of iron monosulphide



(3) the production of ammonia and ammine compounds by the biodegradation of organic matter (Berner, 1968, 1969). The solubilization of silica by bacterial action has been demonstrated by several studies (Aston, 1983). If concretion growth occurred in the sulphate reduction zone, all of the above processes could have been in operation.

Because iron monosulphide is not usually found (preserved) in ancient sediments, the increase in iron monosulphide from concretion center is not understood. Because iron monosulphide is only stable at high concentrations of HS^- , the increase in iron monosulphide concentration may represent increasing concentrations of HS^- at the concretion growth front as the microenvironment became increasingly closed. Additionally, the precipitation of concretion calcite may have trapped some of the iron monosulphide before it could be converted into pyrite.

With increasing depth and time in the sulphate reduction zone, sediments should contain higher concentrations of pyrite. The increase in pyrite concentration from concretion center outward suggests that concretion growth occurred in the sulphate reduction zone. Concretion growth in this zone is supported by the decrease

in calcite Fe from concretion center outward, and the high concentration of pyrite at the concretion edge.

Below the sulphate reduction zone, the concentration of pyrite per unit of sediment should increase with depth due to progressive compaction of the sediment. Therefore, the increase in pyrite concentration from concretion center outward found in concretion core VC4 may be due to the propagation of the concretion into sediment of progressively increased compaction. The low amount of host sediment found throughout the concretions and the anomalously high concentration of pyrite at the concretion edges argue against the compactional argument.

The study by Raiswell (1976) hypothesized that pyrite may precipitate as a direct result of, and in conjunction with, concretion formation. The concentration of iron sulphide at the concretion edge is significantly higher than that in the surrounding host sediment. Therefore, the concretions of this study support the hypothesis of Raiswell (1976).

The study by Coleman and Raiswell (1981) found a sulphide isotopic trend in a calcite concretion similar to that found by this study. The above study attributed the isotopic trend to changing proportions of early formed isotopically light framboidal pyrite and later formed isotopically heavier euhedral pyrite. This study hypothesizes that the pyrite isotopic trend may be due to a combination of changing sulphate reduction rates and a change in the

isotopic composition of the pore water sulphate reservoir. Near the concretion center high sulphate levels fueled high sulphate reduction rates leading to low isotopic fractionation. With continued concretion growth, sulphate levels decreased, sulphate reduction rates decreased, and subsequently sulphate isotopic fractionation increased. In the outer half of the concretion sulphate reduction rates remained low but the sulphate reservoir became increasingly enriched in heavy sulphur, leading to the production of heavier sulphide.

Because pyrite isotopic compositions were found to systematically change across concretion core VC4, the pyrite isotopic data suggest that concretion growth occurred in the sulphate reduction zone and grew in a closed system. While the concretions in the calcareous rocks of Unit-2 appear to contain higher concentrations of pyrite than the surrounding host rock, none of the concretions in Unit-2 were found to have outer margins enriched in pyrite. Because carbonate concretions were found to occur throughout the Paxton quarry exposure, it would appear that the nature of the host sediment determines if an outer margin of pyrite formed. Higher levels of pyrite would be expected in the black shales because the higher levels of organic matter and reducible iron would facilitate the reduction of iron and the precipitation of pyrite respectively.

The profiles of sulphate concentration and isotopic composition for one half of core VC4 are shown in figures 21

and 22. Previous work on concretion sulphate analysis could not be found, and the data found by this study is not understood. A possible interpretations of the sulphate profiles are listed below.

- 1) The high sulphate concentrations found at the concretion center and intermediate region correlate with the heaviest sulphate values and may be due to clusters of gypsum crystals found in the inner half of the concretion.
- 2) Because the heaviest sulphate values found are significantly heavier than than the +22 to +27 CDT found in Upper-Devonian evaporites (Claypool et al., 1980), the heavy sulphate values suggest that significant sulphate isotopic fractionation had occurred prior to concretion nucleation.
- 3) Four samples in the intermediate region of the concretion were found to have low sulphate concentrations (approximately 50 ppm) and isotopic compositions (approximately +17 to +27 CDT, Faure, 1977) similar to those of Upper-Devonian evaporites. The similarity and magnitude of the above values suggest that they may represent some type of baseline value.
- 4) The increase in sulphate concentration found at the concretion edge may be due to weathering of the pyrite rim. The fact that the sulphate at the concretion edge represents the lightest sulphate found, and has an isotopic composition similar to the pyrite at the concretion edge, supports the proposed origin.

CEMENTATION POROSITY

The radial arrangement and acicular habit of the carbonate crystals in some of the concretions at the Paxton quarry suggest that the concretions precipitated from center outward. Concretion growth from center outward is supported by the increase in pyrite concentration and decrease in calcite Fe concentration from the concretion center outward. If concretion nucleation was associated with a microenvironment of elevated pore water pH, the increase in radiolarian preservation from concretion center outward also supports concretion growth from center outward.

If the concretions grew from center outward, cementation porosities should decrease from concretion center outward due to propagation of the concretion into increasingly compacted host sediment. Concretion studies commonly find a decrease in cementation porosity from concretion center outward. The cementation porosities found by this study do not decrease from concretion center outward. Cementation porosity values were found to increase (less insoluble residue) in the intermediate region of the concretion (Figure 29)

Several factors could affect the cementation porosities found by this study.

- 1) Because the cementation porosities were calculated by determining the weight of carbonate removed by dissolution, the cementation porosities could be affected by the different densities of the material within the concretion. While the density of the carbonate being removed is

approximately 2.7, the density of the associated pyrite is significantly higher and the density of the associated organic matter is significantly lower.

2) The sediment displacement observed in concretion thin section probably increased the cementation porosity on the scale of individual crystals (small scale) but the affect of the sediment displacement on a larger scale is unknown.

3) The dissolution of host sediment and its subsequent replacement by calcite may increase the cementation porosity.

4) The precipitation of non-carbonate minerals in association with concretion growth (chalcedony, pyrite, etc.) may lower the cementation porosity.

Near the concretion edge, no gypsum crystals, gypsum molds or chalcedony was found. Additionally, no dissolution of the radiolarians was found. Therefore, the only factors listed above that may affect cementation porosities are sediment displacement and pyrite formation. While pyrite should lower the cementation porosity, the values found at the concretion edges are similar to or slightly higher than that found at the respective concretion center. Therefore, the displacement of host sediment may have a significant affect on cementation porosities.

While the cementation porosities found by this study can not be equated to sediment porosities, the magnitude and consistancy of the values suggest that the concretions precipitated in sediments with high porosities, and that a

significant change in host sediment porosity did not occur during concretion growth.

TRACE ELEMENT COMPOSITION

The concentration range and magnitude of each trace element is similar between different concretions. The similarity in the trace element concentration profiles suggest that either the concretions recorded similar small scale changes in the microenvironments associated with concretion formation, or the concretions recorded large scale changes that occurred throughout the unit. It is possible that the concretion profiles represent a mixture of the micro and macro environments.

If the concretions precipitated in a closed system, the manner in which a trace element is incorporated into the calcite may be dependent upon the partition coefficient for that element. A partition coefficient greater than one will partition the trace element into the carbonate, and a partition coefficient less than one will partition the trace element into the pore water. Therefore, a partition coefficient other than one should create a trace element concentration trend across the concretion. Magnesium, Sr, and Na have partition coefficients less than one, whereas Fe and Mn have partition coefficients greater than one.

The trace element concentrations found in the concretions are different than the equilibrium trace element concentrations listed by Veizer (1983). The Mg, Sr and Na concentrations found by this study are lower than those

listed by Veizer (1983) and the Fe and Mn concentrations are higher. Because the equilibrium concentrations listed by Veizer (1983) are for near-surface oceanic carbonates, the difference between the values found by this study and those listed by Veizer (1983) may be due to the nature of the host sediment or the chemistry of the surrounding environment.

Because partition coefficients are affected by changes in temperature and precipitation rate, the use of partition coefficients assumes the system is at complete equilibrium. Because the concretions are thought to have precipitated as authigenic cements in localized microenvironments of calcite supersaturation, the precipitation rate may have been affected by the calcite saturation level.

While Mg and Sr concentrations increase from concretion center to edge, a decrease in Mg and Sr concentration occurs in the intermediate region of the concretions. Because the decrease in Mg and Sr is correlatable between different concretions, is weakly correlatable with changes in carbon and oxygen isotopic composition, and is contrary to the overall trend for the trace elements, the decrease appears to be due to a change that occurred in the unit and not a perturbation in the data.

The decrease in carbonate Fe from concretion center outward is thought to be due to the removal of pore water Fe by the precipitation of pyrite. The high concentration of carbonate Mn may be due to a mobilization of Mn in

association with the the dissolution of the radiolarian tests. Iron and Mn oxides are known to precipitate on the tests of siliceous microfossils as they fall to the sea bottom. A correlation between increases in dissolved silica and increases in Mn concentration has been interpreted by Gieskes (1981) as the release of adsorbed Mn during the dissolution of siliceous tests.

The difficulty in correlating the trace element profiles between concretions may be due to any of the following factors: 1) the trend across the concretion is complex in nature; 2) the different number of samples collected from the concretions (sampling density); 3) the possibility that the concretions were of different sizes when the proposed pore water flushing event occurred; and 4) the rate of calcite precipitation may have varied during concretion growth.

CARBON ISOTOPIC COMPOSITION

It is likely, that the concretion center values represent the isotopic composition of the pore waters associated with concretion nucleation. The magnitude of the concretion center values suggest that diagenetic processes had already modified (enriched in isotopically light carbon) the pore water isotopic composition. The similarity of concretion center carbon isotopic values suggests that the concretions nucleated in similar diagenetic environments (zones), and therefore similar burial depths.

While the overall trend of the concretions is to become isotopically lighter from concretion center to edge, all the concretion cores, except one half of core HC2, show an increase in heavy carbon in the intermediate region of the concretion. It is not known why the increase in heavy carbon was not found in one half of core HC2. The increase in heavy carbon in the intermediate region of the concretion can be weakly correlated to changes in the Mg and Sr concentration trends and an increase in heavy oxygen.

Because the increase in heavy carbon was found in all four of the concretions, is correlatable with other calcite chemistry changes, and is followed by an increase in light carbon at the concretion edge, it is likely that the increase in heavy carbon represents a transitory change that occurred in the sedimentary waters and not a result of the processes associated with concretion formation. The change in the carbon isotopic composition across the concretions supports concretion growth in a closed system.

When the carbon isotopic compositions of the the Unit-3 concretions are compared to the samples collected from the calcareous rocks of Unit-2, the Unit-3 concretions are enriched in light carbon, suggesting a higher input of light organic carbon.

OXYGEN ISOTOPIC COMPOSITION

When compared to the oxygen isotopic composition of modern day seawater and modern day carbonates, the oxygen isotopic values found by this study are significantly

enriched in isotopically light oxygen. A review of the oxygen isotopic data listed in table 2 shows that carbonate enrichment with isotopically light oxygen is frequently found.

At present there is no generally accepted explanation for the enrichment of the concretions with isotopically light oxygen. Proposed sources of light oxygen in the diagenetic environment include closed system diagenesis of volcanically derived phyllosilicates (Lawrence et al., 1976), meteoric flushing (Coleman and Raiswell, 1981), unusually warm temperatures (Brand and Veiser, 1980), and isotopically light Paleozoic pore waters (Popp et al., 1981).

While the oxygen values found by this study seem light in comparison to modern day carbonates, they appear to be in accordance with other carbonate oxygen isotopic values of their age. A study of mid-continent Devonian limestones by Popp, Anderson and Sandberg (1986) found values ranging from -3 to -7 PDB with the majority between -4 and -7 PDB. A study by Popp et al. (1981) proposed that Mid-Devonian seawater had an oxygen isotopic composition of approximately -5 PDB. The Unit-2 sample named "Limestone Stringer" (Figures 8 and 10) was found to be composed principally of oceanic carbon. This sample was found to have an oxygen isotopic value of -5.67 PDB (Table 4) and supports the value proposed by Popp et al. (1981).

The classical calcite paleotemperature method proposed by Epstein et al. (1953) assumed that the seawater oxygen isotopic composition was the same as modern day seawater (close to zero PDB). Shackleton and Kennett (1975) concluded that pre-glacial seawater should have had an oxygen isotopic composition of approximately -1.2 PDB because less isotopically light water was bound up in glacial ice. The equation proposed by Shackleton and Kennett (1975) is listed below:

$$T^{\circ}\text{C} = 16.9 - 4.38 (*\text{C} - *\text{W}) + 0.10 (*\text{C} - *\text{W})^2$$

T = temperature at which the calcite nucleated

*C = oxygen isotopic composition of the carbonate

*W = oxygen isotopic composition of the water

If a value of -5 PDB is used for the overlying seawater, and a value of -6.5 PDB is used for the concretion centers, a concretion nucleation temperature of approximately 23.7°C is calculated using the above formula. Using the estimated seawater temperature and geothermal gradient used by Hudson (1978) (13°C and 30°C/Km respectively) a burial depth of approximately 350 m. is generated. Viewed as an approximation, the above depth does not seem unreasonable.

Using a seawater oxygen isotopic composition of 0.0 PDB and a concretion center value of -6.5 PDB, a concretion nucleation temperature of approximately 50°C and a nucleation burial depth of approximately 1230 m. is found. This temperature approaches that proposed for the maximum

burial temperature of the surrounding shales and is in conflict with an early diagenetic origin for the concretions.

Figure 37 shows a plot of carbonate oxygen isotopic composition versus geologic time. The diagram in figure 37 is from Viezer and Hoefs (1976). The data and regression line plotted in figure 37 suggests that carbonates increase in light oxygen with increasing age. The range of oxygen isotopic values found for the Unit-3 concretions is shown in figure 37 by a vertical bracket. The isotopic range covered by the bracket does not significantly deviate from the regression line plotted for the other data. An estimated average concretion center value is plotted on figure 37. This value plots close to the proposed regression line and is shown by the symbol X.

The similarity between the oxygen isotopic compositions of the concretions sampled from the calcareous shales (Unit-2) and the Unit-3 concretion centers suggests that the Unit-3 concretions nucleated at a similar burial temperature (depth) as the Unit-2 concretions.

This study found an increase in heavy oxygen in the intermediate region and/or near the concretion edge. Because most concretion studies (including previous Antrim concretion studies) find the heaviest oxygen near the concretion center, the increase in heavy oxygen is not thought to be due to the processes associated with

Figure 37. Comparison of the oxygen isotopic values found by this study and the changes in carbonate oxygen isotopic composition with geologic time. Data points and regression line are from Veiser (1976). The range of oxygen values found by this study are shown by the vertical bracket. Concretion center average is marked with the symbol X.

concretion formation. The source of the heavy oxygen is unknown.

Concretion cores VC2 and VC4 show the oxygen isotopic composition at the concretion edge returning to a value similar to that found at the respective concretion center. This pattern suggests that the increase in heavy oxygen is not tied to a process associated with concretion formation. Because the increase in heavy oxygen in cores VC2 and VC4 appears to be transitory, is correlatable with increases in heavy carbon and changes in the Mg and Sr concentration trends, the increase in heavy oxygen may be due to a hydrologic process such as pore water flushing. If sedimentary pore waters increased in isotopically light oxygen with increasing burial depth, the similarity between some concretion center and edge values suggest that concretion growth did not take place over a wide range of burial depth.

COMPARISON WITH PREVIOUS ANTRIM CONCRETION WORK

While the concretions analyzed by Hathon (1979) and Wardlaw (1981) were collected from the same locality as the concretions of this study, the concretions of the aforementioned studies were collected from the black shales of Unit-1, and not the black shales of Unit-3 (Figure 10). While the concretions collected by Coniglio and Cameron (1990) are reported as being from the Kettle Point Formation (Canadian name), the location of the outcrop sampled is consistent with a locality where the Antrim should outcrop

in Canada. The exact stratigraphic relationship between the concretions studied by Coniglio and Cameron (1990) and those of this study is not known.

The concretions analyzed by the above studies have the following similarities to the concretions of this study:

- 1) are semi-spherical to elliptical shape;
- 2) have an outer margin enriched in iron sulphide;
- 3) have large carbonate crystals (ie., non-micritic);
- 4) show displacement of host material within the concretion due to crystal growth;
- 5) contain uncrushed microfossils.

The concretions of the previous Antrim studies are approximately one half to one third as large as the Unit-3 concretions sampled by this study. The concretions of this study differ texturally from those of the previous studies. While, the concretions of the previous studies contain an outer zone of long acicular crystals that are radial to the concretion center, the concretions of this study are composed of a mosaic of equant to elliptical shaped spar from concretion center to edge.

TRACE ELEMENT COMPOSITION

The concretions of the previous Antrim studies differ in mineralogy from the concretions of this study. In contrast to the low-iron calcite (approx. 18 to 142 ppm Fe) found by this study, the concretions of Hathon (1979) and Wardlaw (1981) (approx. 18,260 to 81,810 ppm Fe) were found to be composed of ferroan dolomite, and the concretions of

Coniglio and Cameron (1990) (approx. 1920 to 6500 ppm Fe) were found to be composed of ferroan calcite. While higher iron concentrations in the dolomite would be expected due to the difference in lattice spacing caused by incorporation of Mg in the carbonate structure, the magnitude of the Fe concentration difference suggests that the concretions of this study precipitated in an environment containing lower pore water Fe concentrations.

The trace element concentrations found by Wardlaw (1981) are higher than those found by this study. The study by Coniglio and Cameron (1990) only reported calcite Fe concentrations and as noted above, the calcite Fe concentration was found to be significantly higher than that found by this study.

In contrast to the findings of this study, Wardlaw (1981) found no discernable trends in carbonate trace element concentration across the concretions. This study hypothesizes that the differences between the trace element concentration profiles found by Wardlaw (1981) and those found by this study may be due to one of the following: 1) the chemistry of the pore waters associated with dolomite concretions formation did not change during growth of the dolomite concretions; or 2) authigenic calcites are more sensitive to recording pore water changes than authigenic dolomites.

The trend in concretion Fe concentration appears to vary in Antrim concretions. While this study found a

decrease in Fe from concretion center outward, the study by Wardlaw (1981) found no discernable change in Fe concentration from center outward and the study by Coniglio and Cameron (1990) found an increase in Fe concentration from center outward.

CEMENTATION POROSITIES

The cementation porosities found by Wardlaw (1981) range from approximately 48 to 90%. The cementation porosities found by this study for the dolomite concretion previously sampled by Hathon (1979) are similar to those found by Wardlaw (1981). The cementation porosities found by Coniglio and Cameron (1990) range from approximately 65 to 85%. The above values are lower than those found for the Unit-3 concretions. The cementation porosity data suggest that the Unit-3 concretions of this study contain more carbonate material than the concretions of Hathon (1979), Wardlaw (1981) and Coniglio and Cameron (1990).

Like the findings of this study, the studies by Wardlaw (1981) and Coniglio and Cameron (1990) found higher cementation porosities in the outer half of the concretion than near the respective concretion center. The cementation porosities found by this study for the dolomite concretion previously sampled by Hathon (1979) were also found to be higher in the outer half of the concretion. Table 5 summarizes the cementation porosities found for the dolomite concretions of Unit-1.

Table 5. Summary of the cementation porosities found for the Unit-1 dolomite concretions from the Paxton Quarry.

Study	Sample	Location	Cementation Porosity
This Study	Hathon Concretion	Inner Half	75.6
		Outer Half	89.8
Wardlaw (1981)	#3 Horizontal Core	Center-1	81
		2	73
		3	60
		4	64
		5	50
		Edge-6	5
	#3 Vertical Core	Edge-1	65
		2	71
		3	56
		4	50
		Center-5	81
		6	57
		7	50
		8	46
		9	62
		Edge-10	ND
	#7 Horizontal Core	Center-1	67
		2	80
		3	70
		4	60
		5	69
		6	69
	#7 Vertical Core	Edge-7	71
		Edge-1	66
		2	63
		3	ND
		4	81
		Center-5	67
		6	69
		7	73
		8	66
		9	74
		Edge-10	90

ND - Not Determined

The fact that Antrim concretions do not decrease in cementation porosity from concretion center outward suggests that the processes associated with the growth of Antrim concretions modify the porosity of the surrounding host sediment. Therefore, the cementation porosities found for Antrim concretions are probably higher than the actual sediment porosity at the time of carbonate precipitation.

CARBON ISOTOPIC COMPOSITION

The carbon isotopic values found by Coniglio and Cameron (1990) are similar in magnitude and range to that found by this study. The carbon isotopic values found by Hathon (1979) and Wardlaw (1981) are similar in magnitude but smaller in range than that found by this study. The smaller isotopic range found for the Unit-1 concretions may be due to their smaller size (shorter growth period?) or less variation in the isotopic composition of the surrounding pore waters during concretion growth.

Two differences can be seen in the carbon isotopic compositions found by this study and those found by the previous Antrim studies: 1) the concretion centers of this study are isotopically heavier than the concretion centers of the previous studies; and 2) in contrast to the findings of this study, the concretions of the previous studies decrease in isotopically light carbon from concretion center to edge. Table 6 summarizes the carbon isotopic values found for the dolomite concretions of Unit-1.

Table 6. Summary of the isotopic compositions found for the Unit-1 dolomite concretions from the Paxton Quarry.

Study	Sample Location	Sample Type	^{13}C PDB	^{18}O PDB
Hathon (1979)	Unit-1	Inner	-11.3	-6.28
		Middle	-12.2	-6.86
		Outer	-10.1	-7.54
Wardlaw (1981)	Unit-1	Center-1	-11.8	-9.29
		2	-12.0	-9.29
		3	-11.7	-9.29
		4	-11.3	-9.29
		Edge-5	-10.7	-9.10
This Study	Unit-1 (Hathon)	Outer Edge	-10.6	-8.16

PDB = Pee Dee Belemnite - carbon and oxygen isotopic standard

Because the concretions of this study increase in isotopically light carbon from concretion center to edge, and the concretions of the previous Antrim studies decrease in isotopically light carbon from concretion center to edge, the carbon isotopic data suggests that the concretions of this study precipitated in a different diagenetic environment (zone?) than the concretions of the previous Antrim studies.

OXYGEN ISOTOPIC COMPOSITION

In similarity to the oxygen isotopic values found by this study, previous Antrim concretion studies found carbonate oxygen isotopic values significantly lighter than those found in modern day seawater.

The oxygen isotopic values found by Hathon (1979) are similar to the lightest values found by this study, but in contrast to the findings of this study, increase in isotopically light oxygen from concretion center outward. The oxygen isotopic values found by Wardlaw (1981) are approximately 2 to 4 mill lighter than the concretions of this study and show little variation. The oxygen isotopic values found by Coniglio and Cameron (1990) are similar in range and magnitude to the values found by this study, but in contrast to the findings of this study, increase in isotopically light oxygen from concretion center outward.

Deep Sea Drilling Project (DSDP) data show that sedimentary pore waters may become systematically lighter, by up to 3 mill, to a depth of 300 m. (Lawrence et al.,

1976). Based on the findings of Lawrence et al. (1976), the increase in light oxygen from concretion center outward found by Hathon (1979) and Coniglio and Cameron (1990) may be due to an increase in pore water light oxygen with increasing burial depth. If the oxygen isotopic data of Wardlaw (1981) is correct, the findings of Lawrence et al. (1976) would suggest that the concretions studied by Wardlaw (1981) precipitated at a greater burial depth (i.e., warmer temperatures) than the other Antrim concretions.

With four different Antrim concretion studies finding three different oxygen isotopic trends (no variation, isotopically lighter from center outward and isotopically heavier from center outward), interpretation of the data is difficult. Table 6 summarizes the oxygen isotopic values found for the dolomite concretions of Unit-1 and shows their lighter oxygen values. Because an increase in isotopically heavy oxygen from concretion center outward is only found in the concretions of this study, this study proposes that the increase in isotopically heavy oxygen is not due to the processes associated with concretion formation.

In summary, the physical and chemical differences between the concretions of this study and those of previous Antrim concretion studies show that the composition of Antrim Shale concretions is complex.

COMPARISON WITH OTHER CONCRETION STUDIES

The concretions of this study represent some of the largest calcite concretions that have been studied. Calcite

concretions of comparable size have been studied by Clifton (1957), Raiswell (1976), Coleman and Raiswell (1981) and Boles et al. (1983).

The Unit-3 concretions of this study (Figure 10) contain outer margins heavily enriched in iron sulphide. Calcite concretions with outer margins enriched in iron sulphide have also been found by Raiswell (1976), Hudson (1978), Pearson (1979), Colman and Raiswell (1981), and Curtis et al. (1986). Dolomite concretions with outer margins enriched in iron sulphide have been found by Hathon (1979), Pearson (1979), Wardlaw (1981) and Curtis (1986).

This study measured the change in pyrite isotopic composition across one half of concretion core VC4. Pyrite in the inner half of the concretion was found to increase in light sulphur from concretion center to the intermediate region and decrease in light sulphur from the intermediate region to the concretion edge. The study by Coleman and Raiswell (1981) measured the pyrite isotopic composition across two calcite concretions. One concretion was found to have similar isotopic values and trends to that found by this study. The other calcite concretion was found to be isotopically lighter and decreased in light sulphur from concretion center to edge.

The study by Raiswell (1981) attributes the change in pyrite isotopic composition across the concretion to changing proportions of early formed framboidal pyrite and later formed euhedral pyrite. This study hypothesizes that

the change in pyrite isotopic composition is due to changes in the isotopic composition of the pore water sulphate reservoir and the rate of sulphate reduction.

The concretions in the black shales of units 1 and 3 (Figure 10) appear to preferentially occur along thin friable horizons that are rich in chalcedony. The study by Weeks (1957) found concretions to preferentially occur along specific horizons. The studies by Raiswell (1971), and Tasse and Hesse (1984) found that concretions preferentially occur along horizons with permeabilities higher than that of the surrounding host rock.

Well preserved radiolarian tests were found in the outer half of the concretions but not in the host shales. The studies by Blome and Albert (1985) and Hennessy and Knauth (1985) also found siliceous microfossils in the concretions but not in the surrounding shales.

The cementation porosity values found by this study are similar to the highest calcite and dolomite cementation porosities listed in table 3, and higher than all the siderite concretion values listed in table 3. In similarity to the Antrim concretion studies by Wardlaw (1981) and Coniglio and Cameron (1990), the host sediment within the concretions of this study appear to have been displaced by the precipitation of large carbonate crystals. Because the concretions of some studies are composed of micritic carbonate, the cementation porosities found for Antrim

concretions may not be comparable to the cementation porosities found by other studies.

The carbon isotopic values found by this study are similar to those found for the calcite concretions of Sass and Kolodny (1972), Hudson (1978), Curtis et al. (1978), Colman and Raiswell (1981) and Coniglio and Cameron (1990); the dolomite concretions of Hathon (1979), Wardlaw (1981), Tasse and Hesse (1984) and Curtis et al. (1986); and the siderite concretions of Tasse and Hesse (1984) (Table 2). Therefore, the carbon isotopic compositions found by this study are within the range of values found for each of the three common concretion forming carbonates.

Like this study, the studies by Sass and Kolodny (1972) and Curtis et al. (1986) found an increase in light carbon from the concretion center to edge. While the carbon isotopic values found by Hudson (1978), Hathon (1979), Colman and Raiswell (1981), Wardlaw (1981) and Coniglio and Cameron (1990) are similar to those found by this study, the aforementioned studies found an increase in heavy carbon from concretion center outward; opposite the carbon isotopic trend found by this study.

The concretions of this study frequently increase in heavy oxygen from concretion center outward. While Curtis et al. (1986) found one dolomite concretion that increases in heavy oxygen from concretion center outward, normally concretions increase in light oxygen from the concretion center outward. An increase in isotopically light oxygen

from concretion center outward was found in the calcite concretion studies by Coleman and Raiswell (1981), and Coniglio and Caméron (1990), the dolomite concretion studies by Irwin (1977) and Hathon (1979); and the siderite concretion study by Gautier (1982). Therefore, the increase in heavy oxygen found by this study may not be due to the processes associated with concretion formation.

The concretions of this study were found to decrease in calcite Fe concentration from concretion center to edge. Of the three other calcite concretion studies in which one or more carbonate trace element concentrations were measured, the studies by Boles et al. (1985) and Galimov and Girin (1968), found a decrease in calcite Fe from concretion center outward and the study by Coniglio and Cameron (1990) found an increase in Fe from concretion center outward.

The concretions of this study were found to increase in calcite Mn concentration from concretion center outward. The calcite concretion studies by Boles et al. (1985) and Galimov and Girin (1968) found a decrease in Mn from concretion center outward. The difference in the Mn concentration profiles is not understood but may be related to the composition of the sediment in which the concretions precipitated.

While the concretions of this study are similar to other calcite concretions in occurrence, shape, carbon isotopic composition, and the occurrence of an outer margin rich in pyrite, the concretions of this study differ from

other calcite concretions in that they are composed of large grained carbonate spar, increase in heavy oxygen from concretion center outward and increase in Mn concentration from concretion center outward.

CHAPTER 6 EVALUATION OF THE ZONAL MODEL

COMPARISON OF STUDY RESULTS TO THE ZONAL MODEL

The study by Hathon (1979) tested organic material from the black shales of the Paxton Shale Quarry and concluded that the shales were not mature enough to have produced liquid hydrocarbons. This study hypothesizes that the liquid hydrocarbons found in the Unit-2 concretions were formed by the microbial degradation of organic material in association with concretion formation, and not by elevated temperatures associated with deep burial. Therefore, this study will only consider zonal model diagenetic zones 1 through 4 (Figure 1) with respect to the formation of the concretions.

The lack of bioturbation and clastic carbonate material in the black shales of Unit-3 suggest that the shales were deposited in an anoxic environment. Therefore, it is possible that the sulphate reduction zone (the uppermost zone in which the zonal model predicts that carbonate precipitation may occur) may have extended up to the sediment/water interface and included the high porosity sediments normally occupied by the aerobic zone. If the host shale was deposited under anoxic conditions concretion nucleation may have occurred in sediments with porosities higher than that for which the zonal model states that carbonate precipitation may first occur (Figure 1). The cementation porosities found by this study are higher than all the sediment porosities listed by the zonal model.

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The dissolution of radiolarian tests in the inner half of the concretion, the precipitation of chaledony, the precipitation of pyrite, and the displacement of host sediment within the concretion indicate that the processes associated with concretion formation modify the content and fabric of the host sediment incorporated into the concretions. The above arguments, combined with the fact that this study found higher cementation porosities in the outer half of the concretions than at the respective concretion centers, suggest that the cementation porosities found by this study can not be equated to sediment porosity at the time of concretion formation. Therefore, the cementation porosities found by this study can not be compared directly to the sediment porosity values listed by the zonal model.

With carbon isotopic values ranging from -3.7 to -12.4 PDB, the carbon isotopic values found by this study do not match any of the values listed by the zonal model (Figure 1). When compared to the zonal model, the magnitude of the carbon isotopic values found by this study are closest to that listed for carbonate precipitating in the decarboxylation zone. When assessed against the proposed burial depth of the decarboxylation zone, the low amount of insoluble residue found throughout the concretions suggests that concretion precipitation in the decarboxylation zone is unlikely.

Comparing the carbon isotopic values listed in the zonal model and the isotopic profiles found in the concretions, it could be argued that concretion growth started in the isotopically light pore waters of the sulphate reduction zone, increased in heavy carbon in the intermediate region due to growth in the methanogenic zone, and then increased in light carbon at the concretion edge due to growth in the decarboxylation zone. With respect to other aspects of the zonal model, the following points suggest that the above scenario is unlikely: 1) According to the zonal model, a significant decrease in sediment porosity occurs from the sulphate reduction zone to the decarboxylation zone. A significant increase in the amount of host sediment from concretion center outward was not found; 2) The high concentration of iron sulphide at the concretion edge is inconsistent with concretion growth below the sulphate reduction zone; and 3) According to the zonal model, the continuous decrease in carbonate Fe concentration from concretion center outward is inconsistent with concretion growth in the methanogenic zone or decarboxylation zone.

The concretions were found to increase in pyrite concentration and decrease in calcite Fe concentration from concretion center outward. According to the zonal model, the above combination should only occur in the sulphate reduction zone. Unfortunately, the carbon isotopic values found by this study are significantly heavier than the -25

PDB listed for the sulphate reduction zone (Figure 1). Additionally, according to the zonal model, calcite that precipitates in the sulphate reduction zone should be low in Fe and Mn. While concretion calcite Fe concentration was found to decrease from concretion center outward, concretion calcite Mn concentration was found to increase from concretion center outward.

In summary, while the concretions of this study were found to possess several of the sulphate reduction characteristics listed by the zonal model, when compared to the zonal model, the concretion compositions do not fully match the characteristics listed for any of the diagenetic zones.

ASSESSMENT OF THE ZONAL MODEL

The burial order in which the zonal model lists the diagenetic zones to occur is similar to that found in the modern day sedimentological study by Claypool and Kaplan (1973) and is representative of the model accepted for the decomposition of sedimentary organic matter in marine environments.

Several studies have shown that the order in which aerobic/anaerobic organic degradation reactions take place during burial is related to the free energy of the oxidant (Claypool and Kaplan, 1974; Froelich et al., 1979; and Berner, 1980). According to the above studies, diagenetic organic matter degradation reactions occur in such an order that the oxidant yielding the greatest free energy per mole

of organic matter will be consumed first (i.e., $O_2 > MnO_2 > HNO_2 > HNO_3^- > Fe_2O_3 > SO_4^{-2}$).

The study by Berner (1981) concluded that the assessment of mineral stability and the classification of diagenetic environments based on pH and Eh is impractical because of the small variation in pH observed in the sedimentary environment, and the difficulty in obtaining accurate field Eh measurements. In response to the above pH/Eh problem, Berner (1981) proposed a geochemical classification for diagenetic environments based on parameters that are known to vary and are easily measured; the presence or absence of dissolved oxygen (aerobic/anaerobic) and sulphide (non-sulphidic/sulphidic). The above parameters are used in the zonal model. Based on the material presented above, the burial order of the diagenetic zones listed in the zonal model appears to be adequately substantiated.

Black, organic-rich marine shales frequently show little or no bioturbation, suggesting that they were deposited under anoxic conditions. If the aerobic/anoxic boundary occurred at or above the sediment/water interface, no aerobic zone will occur in the sediments. Therefore, the zonal model may not accurately portray the depositional environment that it was constructed to describe.

CEMENTATION POROSITY

According to the zonal model, the uppermost zone in which authigenic calcite may precipitate is the sulphate

reduction zone. The sediment porosity listed for this zone is 75%. Like this study, the calcite concretion studies listed in table 3 found cementation porosities above 75%. According to the zonal model, the uppermost zone in which dolomite and siderite may precipitate is the methanogenic zone. The sediment porosity listed for the methanogenic zone is 30%. All the dolomite and siderite concretion studies listed in table 3 found cementation porosities above 30% (some significantly higher).

Because all the carbonate concretion studies listed in table 3 found cementation porosities higher than the sediment porosities listed for the uppermost zone in which that mineralogy is proposed to precipitate (Figure 1), some aspect of the zonal model appears to be incorrect. Hypothesized explanations for the higher cementation porosities include the following: 1) the precipitation of dolomite and siderite in the sulphate reduction zone; 2) the sediment porosities listed in the zonal model may wrong; and 3) the argument by Curtis (1978) that the amount of concretion carbonate can be equated to the sediment porosity at the time of carbonate precipitation may not be valid for authigenic carbonate concretions.

CARBON ISOTOPES

The majority of the concretion studies listed in table 2 found carbon isotopic compositions heavier than that listed for the sulphate reduction zone and decarboxylation zone, and lighter than the that listed for the methanogenic

zone. While the carbon isotopic values listed in the zonal model may be representative of the carbon dioxide generated by the organic degradation reaction operating in that diagenetic zone, the carbon isotopic values listed in the zonal model are not representative of the values found by most carbonate concretion studies.

Because the top of the sulphate reduction zone may be in close proximity to the sediment/water interface, the top of the sulphate reduction zone may contain a large volume of pore water with an isotopic composition similar to that of the overlying seawater. With increasing burial depth, the pore water within the sulphate reduction zone should become increasingly closed to communication with the overlying seawater, and decrease in volume due to sediment compaction. Concurrently, an influx of isotopically light carbon from the action of sulphate reducing bacteria is being added to the pore waters. Therefore, with increasing depth into the sulphate reduction zone, the proportion of isotopically light pore water carbon should increase. Based on the above arguments, this study hypothesizes that carbonates precipitating in the sulphate reduction zone may have a carbon isotopic value ranging from slightly lighter than the overlying seawater to that of the carbon dioxide produced by the sulphate reducing bacteria.

According to the zonal model the carbon isotopic composition of methanogenic zone carbonates should be approximately +15 PDB. Curtis (1978) chose this value based

on the results of the study by Nissenbaum et al. (1972). It is widely accepted that during the concurrent production of methane and carbon dioxide in the methanogenic zone, isotopically light carbon is preferentially fractionated into the methane phase. Based on this fractionation, it has been argued that the associated carbon dioxide should be isotopically heavy (Claypool and Kaplan 1974, Curtis 1978). Nissenbaum (1972) studied the methanogenic zone pore waters from a reducing fjord (Saanich Inlet, British Columbia) and found the carbon dioxide of the methanogenic zone to be isotopically heavy (up to +17.8 PDB).

Whiticar et al. (1986) conducted a literature review of the isotopic composition of carbon dioxide associated with methane production and found a wide range of isotopic values (Figure 38). Whiticar et al. (1986) found carbon dioxide values ranging from approximately -32 PDB (Claypool et al., 1973) to approximately +17 PDB (Nissenbaum et al., 1972). The literature review conducted by Whiticar et al. (1986) revealed that only a few studies found carbon isotopic values heavier than 0.0 PDB. Based on the study by Whiticar et al. (1986), it appears that Curtis (1978) chose an anomalous carbon dioxide composition to represent the isotopic composition of the methanogenic zone.

CARBONATE MINERALOGY

According to the zonal model authigenic dolomite should not precipitate above the methanogenic zone. The occurrence of dolomite concretions with outer margins enriched in iron

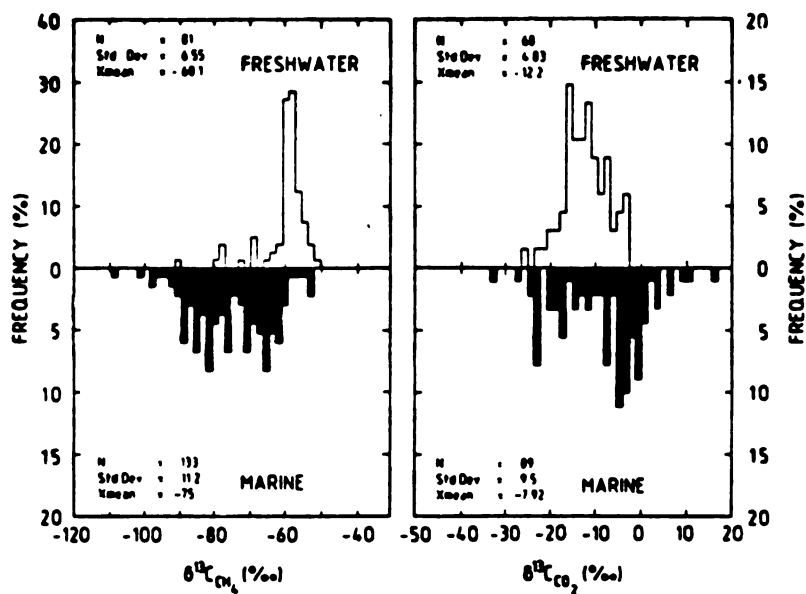


Figure 38. Histograms of methanogenic zone biogenic methane and carbon dioxide carbon isotopic composition. Sedimentary environments are defined as freshwater (open) and marine (shaded) (from Whiticar et al., 1986).

sulphide suggests that the restriction of dolomite precipitation from the sulphate reduction zone may be incorrect.

According to the zonal model, carbonate precipitating in the sulphate reduction zone should be low in Mn. The nature of the sediments that the zonal model was constructed to model (high concentrations of clay, organics and possibly pelagic microfossil tests) may contain high concentrations of Fe and Mn oxides. Unlike Fe, at elevated pH's (8 to 9) Mn should be incorporated into the carbonate phase and not the sulphide phase. Because of the anoxic conditions associated with the sulphate reduction zone and the ease with which trivalent Mn is reduced to divalent Mn, the low Mn designation for sulphate reduction calcite (Figure 1) zone may not be justified.

In summary, the differences between the values listed in the zonal model and those listed in tables 2 and 3 suggest that the diagenetic zone(s) in which a concretion formed can not be determined by comparing the concretion composition to the values listed in the zonal model

CHAPTER 7 FINDINGS AND CONCLUSIONS

FINDINGS

FINDINGS PERTAINING TO STUDY CONCRETIONS

- 1) Concretion occurrence appears to be stratigraphically controlled.
- 2) The concretions were found to be composed of a mosaic of calcite spar.
- 3) Unlike the concretions analyzed by previous Antrim studies, the concretions of this study were found to be composed of low-iron calcite.
- 4) Concretion calcite was found to increase in Mg, Sr and Mn, and decrease in Fe and Na from concretion center outward.
- 5) The isotopic composition of the concretion centers are similar.
- 6) Concretion edges are enriched in light carbon relative to concretion centers.
- 7) Unlike the concretions of previous Antrim studies, the concretions of this study frequently become enriched in heavy oxygen from concretion center outward.
- 8) Concretion cementation porosity values are similar to the highest values found by other calcite or dolomite concretion studies.
- 9) Like the results of previous Antrim concretion studies, higher cementation porosities were found in the outer half of the concretion than at the respective concretion center.

10) Radiolarian preservation increases from concretion center outward. While radiolarians at the concretion edge are fully intact, radiolarian presence at the center of the concretions can only be inferred by the presence of calcite filled radiolarian molds.

11) Concretion pyrite concentration increases from concretion center outward; culminating in an outer margin composed almost entirely of pyrite.

12) Concretion pyrite isotopic composition was found to change systematically from concretion center outward.

GENERAL FINDINGS

1) Three different types of carbonate concretions have now been identified at the the Paxton quarry: A) brown dolomite concretions with outer margins enriched in pyrite (Unit-1); B) brown calcite concretions with outer margins enriched in pyrite (Unit-3); and C) gray-green calcite concretions with no pyrite enrichment at the concretion margin (Unit-2). Each concretion type appears to dominate one of the three stratigraphic units proposed by this study (Figure 10).

2) Only concretions in the black shales contain outer margins enriched in pyrite.

3) At the Paxton quarry exposure, concretion size decreases and concretion abundance increases with increasing carbonate content of the host rock (i.e., limestones > calcareous shales > black shales).

4) At the Paxton quarry exposure, concretion carbonate appears to be enriched in heavy carbon with increasing carbonate content of the host rock.

CONCLUSIONS

CONCLUSIONS PERTAINING TO STUDY CONCRETIONS

- 1) The similarity in the physical and chemical compositions of the four Unit-3 concretions suggests that either they precipitated in similar diagenetic environments (zones) or that the processes associated with concretion formation cause the chemistry of the microenvironment associated with concretion growth to change (evolve) in a consistent manner.
- 2) The increase in radiolarian preservation from concretion center outward suggests that the chemistry of the microenvironment associated with concretion nucleation and early growth caused the dissolution of nearby radiolarian tests.
- 3) The large size and semi-spherical shape of the concretions suggests that concretion growth occurred in sediments possessing porosities high enough to allow unimpeded concretion growth to occur in all directions.
- 4) The low amount of insoluble residue within the concretions and the occurrence of slickensides on the shale surrounding the concretions suggests that significant post concretion compaction of the surrounding shale has occurred.
- 5) The decrease in calcite Fe, increase in isotopically light carbon, increase in pyrite concentration, and change in pyrite isotopic composition from concretion center

outward suggests that concretion growth occurred in the sulphate reduction zone.

6) Isotopic and trace element trends within the concretions suggest that the concretions formed in a closed system. A systematic change in pyrite isotopic composition across concretion core VC4 supports concretion growth in a closed system.

7) At the Paxton quarry exposure concretion nucleation appears to be facilitated by an increase in carbonate content of the host rock.

CONCLUSIONS PERTAINING TO THE ZONAL MODEL

- 1) The zonal model assigns physical and chemical compositional values to the authigenic carbonate cement of each diagenetic zone (Figure 1). The carbonate compositional values found by this study do not match those listed for any of the proposed diagenetic zones (Figure 1).
- 2) The sediment porosity and carbon isotopic values listed in the zonal model are not representative of those found by this study or most other concretion studies (Table 2).
- 3) The sulphate reduction zone carbon isotopic composition listed by the zonal model does not allow for any dilution or mixing of isotopically light carbon from sulphate reduction with isotopically heavier oceanic carbon.
- 4) A review of methanogenic zone carbon dioxide isotopic compositions by Whiticar et al. (1986) found that the majority of the methanogenic zone carbon dioxide values are isotopically lighter than the +15 PDB listed by the zonal

model. Therefore, the carbon isotopic value listed by the zonal model may be anomalous and not representative of methanogenic zone carbon dioxide.

5) According to Curtis (1977), the amount of carbonate cement in a concretion sample can be equated to the sediment porosity at the time of carbonate precipitation. The dissolution of host sediment material, the precipitation of non-carbonate authigenic minerals, and the displacement of host sediment by crystal growth suggest that concretion growth modified the original sedimentary fabric to an extent that the cementation porosities found by this study can not be equated to the sediment porosity at the time of carbonate precipitation. The fact that Wardlaw (1981), Coniglio and Cameron (1990) and this study all found higher cementation porosities in the outer half of the concretions than at the respective concretion centers suggests that the proportion of carbonate cement within Antrim concretions can not be equated to sediment porosity.

SUMMARY

Unlike the concretions of previous Antrim studies, the concretions of this study were found to be composed of low-iron calcite. The cementation porosities and carbon isotopic compositions found by this study are similar to those found by other calcite concretion studies. The semi-spherical shape of the concretions, the occurrence of slickensides on shale in contact with the concretion, the low amount of insoluble residue within the concretion, and the occurrence

of well preserved microfossils within the concretions suggest that the concretions formed prior to deep burial of the host sediment and that significant post concretion compaction of the host sediment has occurred.

Similar trends in calcite trace element concentration and carbon isotopic composition between different concretions suggest that either the microenvironments associated with concretion formation go through similar pore water chemistry changes during concretion formation or the concretions recorded large scale pore water changes that occurred throughout the surrounding sediments.

The decrease in calcite Fe concentration, increase in calcite light carbon, increase in pyrite concentration, and change in pyrite isotopic composition from concretion center outward suggest concretion formation occurred in the sulphate reduction zone. The concretion compositions found by this study, like that of previous Antrim dolomite concretion studies, do not match those listed for any of the diagenetic zones of the zonal model and suggest that the values listed in the zonal model can not be used to determine the origin of authigenic carbonate concretions.

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APPENDICES

APPENDIX A
CONCRETION CLAY X-RAY

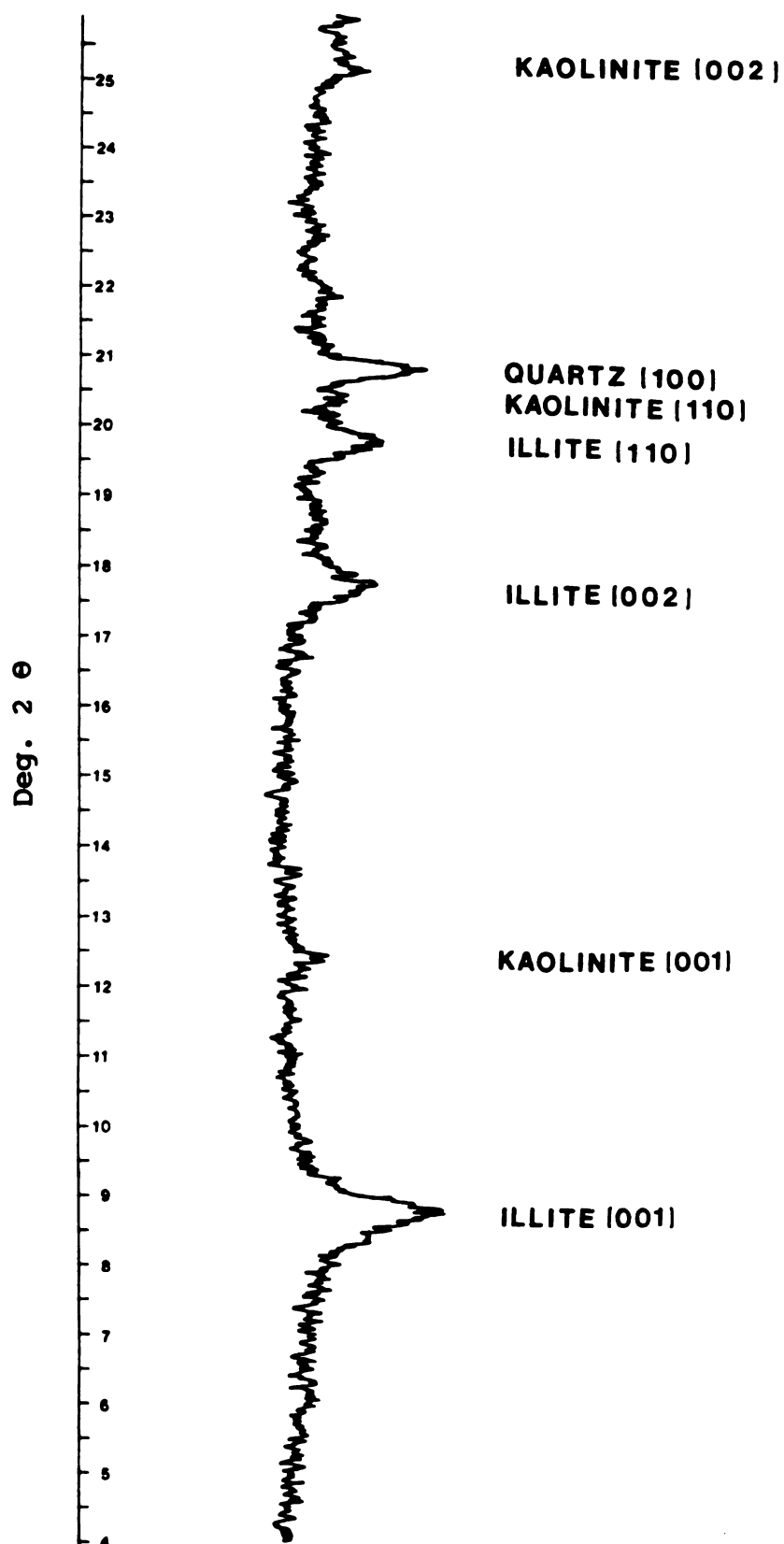


Figure 39. Typical concretion clay X-ray (Mg saturated, glycerol solvated).

APPENDIX B
CONCRETION OIL CHROMATOGRAPH

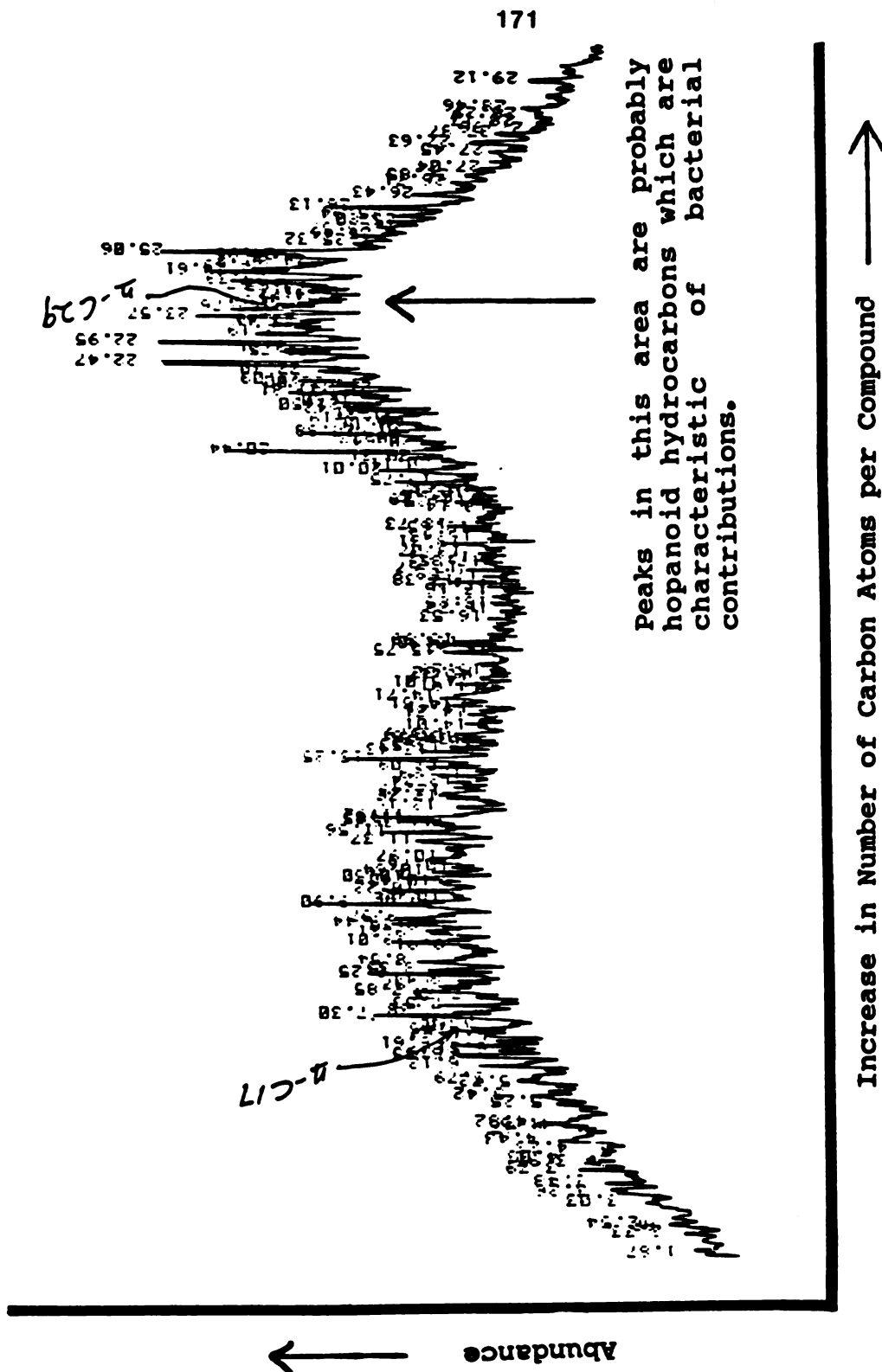


Figure 40. Chromatograph of a concretion oil sample collected from the Paxton Shale Quarry. Oil was collected from a concretion from the top of Unit-2.

APPENDIX C
CONCRETION CARBONATE X-RAY

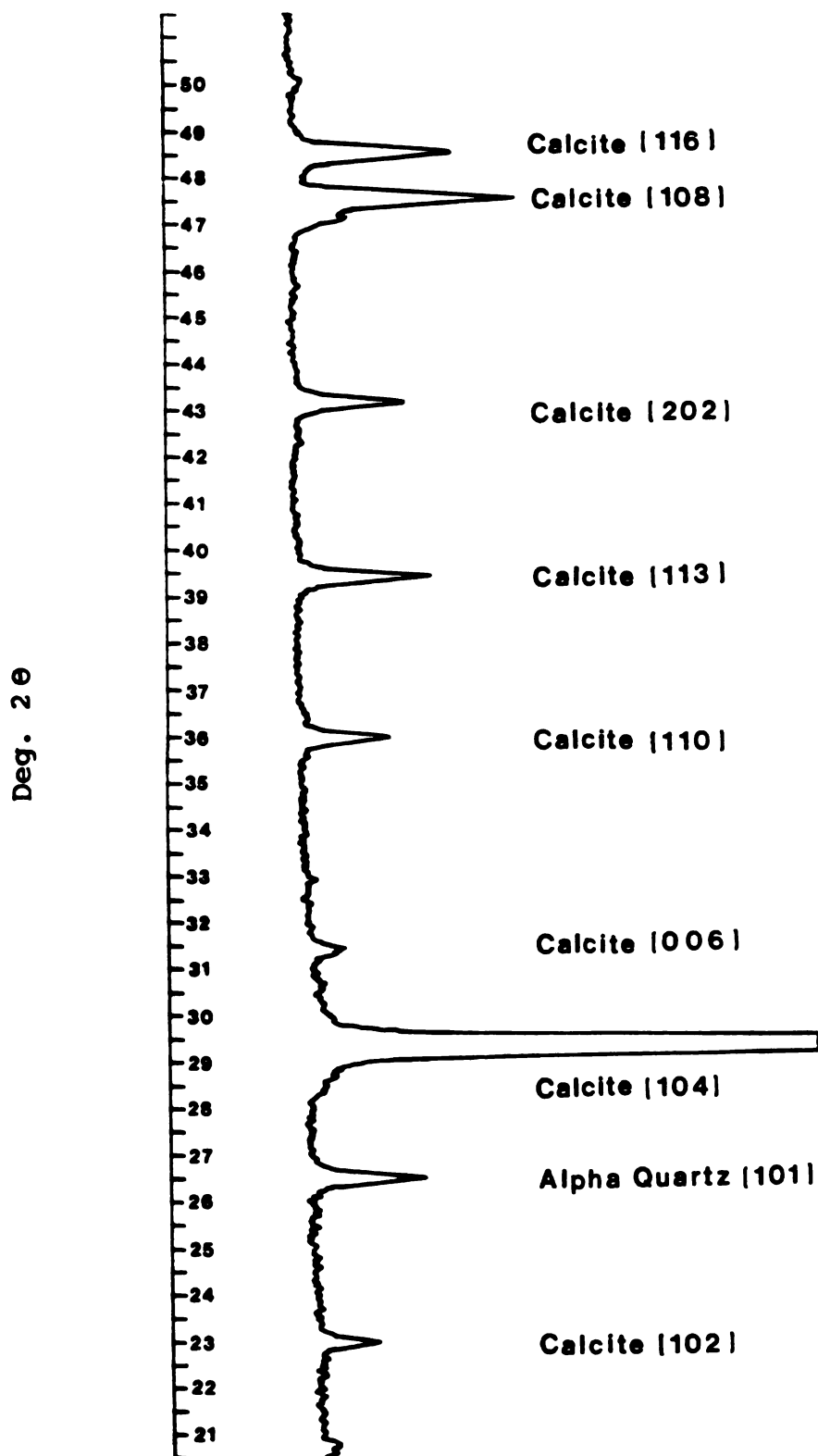


Figure 41. Typical concretion carbonate Cu K-alpha X-ray. The large 104 peak observed at approximately 29.5° suggests that the concretions are composed of calcite.

APPENDIX D
TABULATED DATA

TABULATED DATA

SAMPLE POSITION (cm)	CORE - VC1							
	MG	MN	FE	NA	SR	K	13/C	18/O
2.5	990	104	26	30	29	12	-9.18	-5.28
9.5	800	93	55	35	27	12	NA	NA
16.5	1010	105	51	31	21	12	NA	NA
23.5	690	103	107	26	23	14	NA	NA
27.3							-8.42	-8.26
38.1	750	95	119	39	23	14	NA	NA
45.0	710	85	142	57	23	8	NA	NA
48.9							-9.07	-5.71
52.0	530	86	134	41	19	12	NA	NA
59.0	520	85	140	45	21	9	NA	NA
65.8	870	81	72	41	22	8	NA	NA
85.7	750	89	97	37	21	17	NA	NA

SAMPLE POSITION (cm)	CORE - VC2							
	MG	MN	FE	NA	SR	K	13/C	18/O
88.9	1090	91	29	35	29	14	-11.37	-5.21
70.5	600	101	78	34	21	12	-9.51	-6.43
60.3	780	83	68	44	24	8	-10.71	-6.31
46.4	660	71	135	34	21	8	-8.11	-6.32
35.6	550	98	131	33	21	10	-8.17	-6.49
23.5	550	94	124	28	19	9	-3.74	-4.77
13.6	760	92	89	38	26	15	-8.16	-6.26
2.8	810	100	27	29	29	11	-10.03	-6.45

SAMPLE POSITION (cm)	CORE - HC2							
	MG	MN	FE	NA	SR	K	13/C	18/O
5.0	720	102	17	39	28	18	-9.62	-4.8
31.8	650	95	15	43	21	10	-8.56	-7.6
53.3	590	94	129	43	21	13	-8.02	-6.82
80.3	420	93	112	39	18	17	-6.38	-6.86
105.4	910	99	20	35	27	13	-9.18	-5.41

TABULATED DATA

SAMPLE POSITION (cm)	CORE - VC3							
	MG	MN	FE	NA	SR	K	13/C	18/O
2.5	1180	89	37	36	30	12	-12.48	-5.63
15.7							-7.89	-5.77
24.1	460	102	109	35	17	11	-8.4	-6.96
43.5	900	80	98	42	25	10	-9.59	-6.92
61.6	370	101	87	35	21	10	-8.2	-5.71
77.5	1110	99	31	32	30	8	-11.58	-5.01

SAMPLE POSITION (cm)	CORE - VC4							
	MG	MN	FE	NA	SR	K	13/C	18/O
2.5	1090	105	25	37	30	14	-11.65	-6.02
8.9	1120	93	28	43	29	14	-11.65	-6.41
15.9	880	100	44	39	27	12	-8.22	-4.78
22.5	570	102	79	34	20	11	-7.63	-5.76
29.2	750	92	87	43	21	30	-9.02	-6.31
36.8	570	89	90	42	21	11	-8.39	-6.34

TABULATED DATA

CORE	SAMPLE LOCATION (cm)	CEMENTATION POROSITY
VC1	2.5	92.1
"	9.5	90.3
"	16.5	93.8
"	23.5	93.0
"	38.1	94.6
"	45.0	90.4
"	52.0	92.2
"	59.1	93.4
"	65.8	93.5
"	85.7	90.0
VC3	2.5	94.5
"	24.1	93.9
"	43.5	91.0
"	61.6	95.5
"	77.5	93.3

CONCRETION CORE	SAMPLE LOCATION (cm)	WEIGHT CdS (g)
VC2	2.8	.0025
"	13.6	.0020
"	23.5	.0018
"	35.6	.0014
"	46.4	.0008
"	60.4	.0021
"	70.8	.0022
"	88.9	.0035
HC2	5.1	.0035
"	31.8	.0024
"	53.3	.0018
"	80.3	.0022
"	105.4	.0035

TABULATED DATA

Sulphate and sulphide analysis of core VC4

SAMPLE POSITION (cm)	SO ₄ ⁻²		H ₂ S	
	CONC. (ppm)	DEL 34/S	CONC. (ppm)	DEL 34/S
EDGE	468	- 0.4	59000	-1.8
2.5	330	+ 8.4	1747	-0.7
8.9	47	+22.9	1067	-4.4
15.8	208	+52.5	1189	-3.8
22.5	47	+17.1	1185	-9.8
29.2	46	+26.3	972	-8.4
36.8	64	+27.4	940	-7.2
CENTER	728	+47.0	894	-2.4