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The Origin and Geochemistry of Carbonate Concretions,
Antrim Shale(Devonian, Michigan Basin)

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# ORIGIN AND GEOCHEMISTRY OF CARBONATE CONCRETIONS ANTRIM SHALE (DEVONIAN, MICHIGAN BASIN)

by

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# ABSTRACT

Concretions may record diagenetic pore fluid reactions because they grow during sediment compaction. Diagenetic concretions from the Antrim Shale were studied to determine their origin, nature of growth and if they record pore fluid changes that occur during compaction. Detailed chemical, mineralogical and isotopic analyses revealed inconsistencies in interpretations of concretion origin and nature of growth that were not found in previous, less detailed, studies. The dolomite encased in pyrite, lack of chemical trends across the diameters, high porosity, uncrushed fossils and light $\delta^{18}O$ values were interpreted to indicate that the concretions were precompaction, not deeply buried, the carbon source was organic, the pore fluid was isotopically (oxygen) light and the system was open. The concretions originated as a result of bacterial activity and were early diagenetic; thus, they did not record and pore fluid changes that occurred during compaction.

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# ACKNOWLEDGEMENTS

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## PURPOSE

The purpose of this research is to determine the origin and nature of growth of the carbonate concretions in the Antrim Shale (Devonian, Michigan Basin). A working hypothesis for this research is that the trace element and stable isotope geochemistry of the concretions can be used to make interpretations about their origin and nature of growth. The approach is to study the bulk and three dimensional geochemistry and mineralogy of the concretions. Additionally, the geochemical study may shed some light on the chemical changes that occurred in the pore fluid and the surrounding sediment during compaction and lithification of the sediment in the basin.

## NATURE OF PROBLEM

During the evolution of a compacting sedimentary basin, chemical diagenetic processes occur that affect both the sediment and the pore water. Laboratory, theoretical and field studies have demonstrated these changes in modern systems. Laboratory squeezing studies of kaolinite and montmorillonite by Engelhardt and Gaida (1963), for example, show that the salinity of released pore water changes during compaction. They found decreasing salinity up to 800 atm compaction pressure followed by increased salinity up to 3200 atm of overburden pressure.

Samples from the Deep Sea Drilling Project also show that diagenetic processes occur that affect pore fluid chemistry in recent sediments. There are significant changes in specific ion concentrations with depth, and concomitant compaction and diagenesis, in some pore fluid samples from the DSDP. According to a summary by Sayles and Manheim (1975) Ca, Sr, and $HCO_3$ are generally enriched, while Mg and $SO_4$ are depleted in the pore fluid with increasing depth. Chemical changes in sediment during compaction have been reported also. In the samples studied the amount of illite increases with depth of burial at the expense of mixed layer illite-smectites. This is accompanied by increases in temperature and decreases in the sediment porosity (Perry, 1970; Hower, et al., 1976). Garrels and MacKenzie (1974) have used these results to interpret the chemical diagenetic history of rocks; however, this interpretation is as yet unequivocal.

An understanding of diagenetic processes in ancient rocks is important because these processes are in part responsible for the generation and migration of petroleum and the origin of low temperature ore deposits (e.g., the Mississippi Valley lead and zinc deposits).

The rationale for the present study is that concretions may provide a record of the chemical changes that occur in the pore waters of the sediment during burial and compaction. Concretions grow in various types of sedimentary rocks (Coleman and Raiswell, 1981; Sass and Kolodny, 1975; Tarr, 1920). Their origin is either syngenetic (formed at the time of deposition of the enclosing sediments), diagenetic (formed in the enclosing sediments while they are still soft and unconsolidated) or epigenetic (formed after consolidation of the enclosing sediments)(Raiswell, 1971). This study infers a diagenetic origin for the carbonate concretions in the Antrim.

Diagenetic concretions presumably grow during compaction, below the sediment-sea water interface (Raiswell, 1971). The precipitating carbonate material incorporates trace elements such as Na, Sr, Zn, Mn, and K, during growth. The concentration of the trace elements in the precipitated mineral will be a function of their concentration in the solution and their partitioning coefficient. If the concentration of a trace element in solution changes during concretion growth, then its concentration in the precipitating mineral should change accordingly. Thus the concretion may be a sort of chemical "tape recorder", recording chemical changes in the pore fluid that occured as the shale was compacted.

In order to determine if concretions are chemical "tape recorders", however, a better understanding of their origin and nature of growth is needed. This can be accomplished in part by detailed geochemical, petrographic and isotopic investigations of carbonate concretions found in black shales.

## ZONAL THEORY OF SHALE DIAGENESIS

With increasing burial depth, diagenetic reactions are known to occur that affect the sediment and the pore fluid. A sequence of diagenetic reaction zones in compacting marine mudstones was originally defined by Curtis (1978). Diagenetic concretions have been subsequently analyzed in light of these reaction zones (Coleman and Raiswell, 1981; Irwin, 1980; Curtis, 1978). In this study the Antrim concretions will be analyzed in order to determine if their origin and nature of growth can be predicted by the zonal theory.

According to Curtis (1978), Zone I is represented by a thin top layer of sediment that is well oxygenated by the depositional waters (Table 1). Bacterial oxidation of organic material takes place in this zone and diagenetic mineral precipitation does not occur because the ions diffuse into the overlying water. Below the sediment surface, in Zone II, reducing conditions are set up and bacterial sulfate reduction occurs. The source of the sulfate is the overlying water. Pyrite and iron-poor carbonates with isotopically light carbonate carbon, due to the sulfate reducing bacteria, are precipitated in this zone. Zone II merges into Zone III at the depth of approximately 10 m where $SO^{=}_4$ diffusion from the depositional waters into the sediment stops.

Bacterial fermentation of organic matter producing isotopically light methane and carbonate containing heavy carbon isotopes typifies Zone III. In this zone the ferrous material from unstable iron compounds precipitates as isotopically heavy, iron-rich carbonate mineral. The lower boundary of Zone III is inferred to be the lower limit of organic activity in the sediment.

In zone IV bicarbonate is produced by thermal decarboxylation and oxidized iron compounds continue to be reduced. These processes increase as temperature increases and stop when the reactants are used up. Isotopically light, iron-rich carbonates precipitate but their exact composition depends upon the composition of the original sediment.

There is not much organically derived bicarbonate in Zones V and VI, according to Curtis. Dissolution, reprecipitation or replacement occur in these zones involving unstable primary carbonates. The

| Zone | Process Description | Zone Base Depth (m) | T°C | Average Porosity | $\delta^{13}C_{PDB}$ ‰ Carbonate | Carbonates Precipitated | Other Minerals Precipitated | Mineral Modifications |
|---|---|---|---|---|---|---|---|---|
| I | Bacterial Oxidation | $10^{-2}$ | 0 | 80 | -25 | NONE: diffusion of solutes into overlying depositional waters | | Partial destruction of organic matter |
| II | Bacterial Sulphate Reduction | 10 | 0.3 | 75 | -25 | Calcite<br>Low Fe, Mn | Pyrite | Rapid destruction of soil colloids Fe, Mn, Al, Si |
| III | Bacterial Fermentation | $10^3$ | 30 | 30 | +15 | Ferroan Calcite<br>Ferroan Dolomite or Siderite | Amorphous Carbonate Apatites | Clay exchange reactions especially $Fe^{2+}/Mg^{2+}/Ca^{2+}$ |
| IV | Decarboxylation | $2.5 \times 10^3$ | 75 | 15 | -20? | | Kaolinite? | Montmorillonite<br>Mixed Layer Clays |
| V | Liquid Hydrocarbon Generation | $4 \times 10^3$ | 120 | 10 | Variable: May include carbon from primary or early diagenetic carbonates | Calcite<br>Dolomite<br>Ferroan Dolomite<br>Siderite<br>Depending upon instability of earlier carbonates | | Illite |
| VI | Gas<br>Graphite<br>Metamorphism | $> 4 \times 10^3$ | 120+ | <10 | | | | Mica Development<br>Chlorite<br>Biotite |

Table 1. Diagenetic zones within compacting marine mudstone sequences (from Curtis, 1978).

cation compositions are determined by silicate transformation in these zones.

Several processes are responsible for the carbon isotope distribution in carbonate minerals; 1) assimilation of dissolved primary carbonate; and the degradation of organic material by 2) bacterial fermentation, 3) sulfate reduction, and 4) decarboxylation (Coleman and Raiswell, 1981; Irwin, 1980).

Bacterial fermentation processes produce carbon dioxide with a $\delta^{13}C$ value of +15o/oo(PDB) and methane with values of -75o/oo (Irwin, 1980). Sulfate reduction produces carbon dioxide with $\delta^{13}C$ values of -10 to -25o/oo and carbonate precipitated due to assimilation of dissolved primary carbonate results in $\delta^{13}C$ values equal to 0o/oo (Irwin, 1980). Decarboxylation, the removal of a molecule of carbon dioxide from amino acids and proteins by bacterial action, produces $\delta^{13}C$ values of -20o/oo (Coleman and Raiswell, 1981).

Each process of carbon dioxide production occurs in a different burial depth zone (Curtis, 1978). The depth zones overlap; thus carbon dioxide production by two or more processes can occur simultaneously in certain zones in the sediment resulting in carbonate containing intermediate $^{13}C$ values (Irwin, 1980; Coleman and Raiswell, 1981).

## SUMMARY OF CONCRETION RESEARCH

Table 2 summarizes the current research on the nature and origin of carbonate concretions. (References are listed on Table 3; numbers

TABLE 2: SUMMARY OF THE RESEARCH ON CALCIUM CARBONATE CONCRETIONS

| Chemical Determinations[a] | Mineralogy[b] | Relative Age[c] | Morphology |
|---|---|---|---|
| 1,2,6,7,8,10,*<br>Ca | calcium carbonate<br>4,6,3,8,12,13,11,10 | diagenetic precompaction<br>4,9,6,13,* | 5,7,9,12<br>sheet |
| 6,7,8,10,12,*<br>Mg | | | 1,2,3,4,<br>nodule<br>6,8,11,13,* |
| 2,6,7,10,*<br>Fe | ferroan dolomite<br>4a,9,12,* | diagenetic compaction | |
| 2,7,8,12,*<br>Mn | | | |
| 3,6,8,10,*<br>Sr | siderite<br>5,7,9,12 | epigenetic<br>2 | |
| 12,10,*<br>Trace metals | | | |
| 1,3,5,6,12,13,7,9,11,*<br>C isotopes | | | |
| 3,6,9,11,12,13,*<br>O isotopes | | | |
| 13<br>S isotopes | | | |
| 2,5,6,7,9,12<br>mineralogy | | | |

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[a] chemical measurements made on concretions both bulk and trend analyses

[b] major mineralogy of concretion

[c] relative age of concretion growth with respect to surrounding sediment. Based on age classification for concretions by Tarr (1920)

*Contributions from this proposed research

TABLE 3: List of References used in constructing Table 2.

| KEY | REFERENCE |
|---|---|
| 1 | Galimov, E. M. and Girin, Y. P. (1968) |
| 2 | Girin, Y. P. (1970) |
| 3 | Hoefs, J. (1970) |
| 4 | Raiswell, R. (1971) |
| 5 | Curtis, C. D., Petrowski, C. and Oertel, G. (1972) |
| 6 | Sass, E. and Kolodny, Y. (1972) |
| 7 | Curtis, C. D., Pearson, M. J. and Somogyi, V. A. (1975) |
| 8 | Raiswell, R. (1976) |
| 9 | Irwin, H. and Curtis, C. D. (1977) |
| 10 | Dickson, J. A. and Barber, C. (1976) |
| 11 | Hudson, J. D. (1978) and Friedman, I. (1976) |
| 12 | Irwin, H. (1980) |
| 13a | Coleman, M. L. and Raiswell, R. (1980) |
| 13 | |
| 13b | Coleman, M. L. and Raiswell, R. (1981) |

used on Table 3 are also used in this section in order to facilitate referencing).

These studies have given some insights into the chemical nature of the associated pore waters during concretion growth, and can be summarized as interpretations on the nature of the pore water in terms of pH (1,2,6); Eh(2,6,7,9); bulk chemistry(1,2,3,7,9,11,12); isotopic chemistry(3,11,12,13); state of the system (i.e., open or closed)(3,13a); source of pore water (i.e., meteoric or marine)(3,11,12,13b); and source of dissolved ions (1,2,6,7,11,12). Interpretation of pH trends in concretions from center to edge have revealed a sequence of alkaline-acid-alkaline pore water conditions (1,2) and acid-alkaline conditions (6). Eh conditions were anoxic (2,6,7,9). Bulk chemical analyses reveal predominantly carbonate mineralogies including calcite, siderite and ferroan dolomite. Pyrite, marcasite, quartz and apatite are present in smaller quantities (1,2,3,7,9,11,12). Stable oxygen isotopic ratios indicated generally a freshening of the pore fluid during or after concretion growth, and stable carbon isotopic ratios indicated an organic source of carbonate carbon (3,11,12,13). The state of the system was open for some and closed for others (3,13a). The unaminously agreed upon source of pore fluid was seawater, but with later fresh water infiltration in some examples (3,11,12,13b). Various sources of dissolved ions were indicated by the studies: Ca--exchange sites of clays, calcite, seawater, feldspar; Mg--exchange sites of clays, organic matter, seawater, high Mg calcites; Mn--detrital oxides; Sr--primary carbonate, seawater; Fe--hydrated ferric oxides, clays; $CO_3$--organic matter;

$SO_4^{+}$—seawater (1,2,6,6,11,12). It is clear from these studies that chemical trends are found within carbonate concretions and that they may reflect the changing chemistry of the surrounding pore waters.

There is debate, however, as to the significance of these trends because effects other than changes in pore water composition during the formation of the concretions could cause chemical trends in the concretions. These include:

(1) Changes in the mineralogy of the concretion (Girin, 1970; Curtis et al., 1975; Irwin and Curtis, 1977). A change in mineralogy across the concretion could change the bulk chemistry and chemical trend analyses would not reflect original composition. However, a mineralogic change could possibly be used to interpret the pore fluid chemical changes.

(2) Recrystallization (Dickson and Barber, 1976). Although it would depend on the nature of recrystallization that had occurred, the bulk chemistry of the concretion including $\delta^{18}O$ and $\delta^{13}C$ might be unaffected. Trends in elements like Sr would need careful interpretation.

(3) Formation in a closed system (Coleman and Raiswell, 1979). If a concretion grew in a closed geochemical system, then the manner in which a component would be depleted from the pore solution would depend on its partitioning coefficient. A coefficient other than 1 would create a chemical trend across the concretion. This process would affect most trace components in the concretion forming minerals including $\delta^{18}O$ and $\delta^{13}C$. Since many partitioning coefficients

are known or can be estimated for carbonate minerals, predictions can be made as to what type of trends can be expected if the concretion formed in a closed system. If a variety of components are measured, each with a different partitioning coefficient, then it may be possible to determine whether the concretion formed in a closed or open geochemical system.

(4) Nature of concretion growth (Raiswell, 1976; Curtis et al., 1975). During this process the microbial action surrounding some concretions creates a unique local geochemical environment unrelated to the chemistry of the surrounding pore waters. This would affect the distribution of components such as $HCO_3$, S, Fe, C, etc.; however, most of the bulk distributions of the non-major mineral forming elements should be unaffected.

(5) Post lithification reequilibration with meteoric waters (Hoefs, 1970). Most researchers recognize that the chemistry of marine deposited carbonates can be affected during the chemical reequilibration of the concretion with meteoric waters. This is particularly true for oxygen isotopes.

In order to make meaningful interpretations from the chemistry of concretions the above effects must be considered. Unfortunately only a few investigators have done the relatively detailed work on the chemistry and mineralogy of the concretions necessary to address the problems (Raiswell, 1976, ; Coleman and Raiswell, 1979, 1981, 13; and Irwin, 1980).

However, a few conclusions on the nature of the geochemistry of the concretions that to characterize most of the past work. They are:

1. The source of C appears to be mainly degradation of organic matter (1,2,3,5,6,7,8,9,10,11,12,13). This conclusion is based on the light (negative) $\delta^{13}C$ values found in the concretions.

2. The $\delta^{13}C$ values (may) reflect the type of microbial activity and possibly the depth of the formation of the concretion (8,9,12,13b). In many of the carbonate concretions analyzed listed in Table 2, $\delta^{13}C$ values were found to change along the radius of the concretion. Since $\delta^{13}$ values do not appear to be affected by diagenetic reactions, the trends indicated across the concretion could indicate changes in the pore waters (chemical or biological) during the course of carbonate precipitation. Early interpretations were that the change from negative $\delta^{13}C$ values to positive values indicated a change in the source of C from organic (microbial activity) to inorganic (dissolved bicarbonate in seawater)(Galimov and Girin, 1970). More recent interpretations on the trends in $\delta^{13}C$ values are that the source of C remains organic matter, but the organic matter is degraded by different chemical processes operating at various depths during burial diagenesis (Coleman and Raiswell, 1981; Irwin, 1980). These different processes (sulfate reduction, fermentation, and thermally-induced decarboxylation) would each produce a unique $\delta^{13}C$ value.

3. The $\delta^{18}O$ values, when a trend is indicated usually become lighter from center to edge (3,9,11,12,13b). This change in $\delta^{18}O$ has been attributed to the influence of meteoric

water during the formation of the concretion, and growth of the concretion in a closed system. There is not enough data available to make a definitive statement as to which of these is more important. Although there is a strong indication that contact with meteoric waters during the growth of some concretions has influenced the $\delta^{18}O$ values (11,13b), measurement of independent chemical indicators for the source of the water is needed to support these conclusions.

4. The absolute $\delta^{18}O$ values of the concretions are lighter than what would be expected if the concretions precipitated form modern seawater (3,11,12,13b). The light values have been attributed to a high temperature of precipitation, the influence of meteoric water during concretion formation, an overall lighter $\delta^{18}O$ value of Devonian seawater, and local effects due to microbiological activity or the fractionation of the isotope as the carbonate minerals precipitate directly from the pore fluid. A geochemical analysis of a variety of concretions may help to eliminate some of these alternatives.

## PHYSICAL INTERPRETATIONS FROM PREVIOUS CONCRETION RESEARCH

From previous work several physical indicators of the nature of concretion growth have been used to interpret the time of concretion growth relative to shale compaction. For example, concretions that are covered with boring or encrusting organisms have been interpreted to have grown exposed at the sediment-seawater interface (Pantin, 1958), and represent paleoecologic hardgrounds. These are syngenetic concretions and thus have a precompaction origin.

The presence of uncrushed fossils at the center of concretions also indicates that concretion growth began before compaction of the sediment crushed the fossils (Weeks, 1953).

The nature of the sediment layers within and surrounding the concretions can be used to interpret the timing of concretion growth relative to compaction. According to Clifton (1957), horizontal bedding lines in a concretion indicate concretion growth after shale deposition but before shale compaction. Beds that curve around the concretion indicate that concretion growth occurred before sediment compaction (Raiswell, 1971).

The shape of a concretion is in part related to vertically continuing pressure, and therefore, the compactional history of a basin. During early pre-compaction growth concretion shape should be spherical, indicating that the rate of growth was equal in all directions (Pantin, 1958). As vertical compaction increases, lateral growth would exceed vertical growth and a flattened, oblate concretion would result (Clifton, 1957).

## DESCRIPTION OF THE ANTRIM SHALE AND ITS CONCRETIONS

The Antrim Shale was first recorded in the geological literature by state geologist Douglass Houghton in 1838 and 1841 respectively (Rep. Inv. 22, 1979). The formation was given its present name in 1901 by A. C. Lane who named it after the northern Michigan county that contains its type section. The unit was variously named before 1901 as the Huron Shale and the St. Clair Shale.

The Antrim Shale is dark brown to black, highly carbonaceous, pyritic, finely laminated, fissile and hard (Lane, 1902). The total organic carbon content, determined by the dry combustion method, ranges from 5 to 10 percent in the shale (Beers, 1945). Lenses of light gray shale or limestone are located at the base of the Antrim followed by uniform black beds in the middle and lighter beds at the top (Tarbell, 1941).

Fossils found in the shale include Paleoniscids, Lingula and other brachiopods, fossil wood, including Callixylon newberry, conodonts and several types of spores (LeMone, 1964; Winslow, 1962). The fossil spores of floating plants (Protosalvinia huronensis), disc-like objects with thick walls, are inferred to be a source of the carbonaceous material in the shale (Mozola, 1955). The spore cases are scattered throughout the carbonate concretions as well as through the shale.

The Antrim encompasses the Upper Devonian-Lower Mississippian boundary. It was initially classified as exclusively Devonian, however, Mississippian fossils were found in the upper part of the shale (Newcombe, 1933).

The Antrim Shale ranges from 100 to 450 feet in thickness in Michigan (Newcombe, 1928). It thins from east to west with the thickest part located in the Saginaw Bay region. Outcrops of the shale are located in the northern part of the southern peninsula, in Antrim, Charlevoix, Emmet, Cheboygan and Alpena counties. The Antrim also outcrops in Oakland county in southeastern Michigan (Newcombe, 1928).

The Squaw Bay Limestone, the upper member of the Middle and

Upper Devonian Traverse Group, underlies the Antrim (Kelly and Smith, 1947). The Squaw Bay Limestone is a 10 foot thick bed of brown crystalline limestone that contains Upper Devonian cephalopods. The nature of the Squaw Bay-Antrim contact is unknown because the base of the Antrim has not been identified in outcrop (Rep. Inv. 22, 1979).

Overlying the Antrim in eastern Michigan is the Mississippian Bedford Shale and in western Michigan the Upper Devonian Ellsworth Shale (Rep. Inv. 22, 1979). In western Michigan the upper two-thirds of the Antrim interfinger with the lower half of the Ellsworth (Tarbell, 1941). A facies relationship is inferred between the Antrim of eastern Michigan and the Ellsworth of western Michigan (Rep. Inv. 22, 1979).

The Antrim is stratigraphically equivalent to the Ohio, Sunbury, New Albany, Chattanooga, Maple Mill, Mountain Glen, Kettle Point, and Sweetland Creek Shales (Conant and Swanson, 1961). There are two major hypotheses regarding the environment of deposition of these black shales. According to Conant and Swanson (1961), the black shales were deposited in the mid-continent region by an epicontinental sea. Such a sea would have poor circulation creating anoxic conditions in both the bottom water and sediments (Heckel, 1977).

An alternative to the restricted-epicontinental sea environment is the shallow lagoon model (Merrill, 1975). According to this model, the sediment is deposited in shallow, plankton-covered lagoons. The migration of the lagoonal environment across the continent as the sea transgressed would account for the widespread nature of the Devonian black shales.

For the Antrim, reducing conditions are indicated by the presence of abundant pyrite framboids and vegetal material and a lack of fossils in the shale. However, the environment of deposition of the Antrim, epicontinental sea or shallow lagoon, is as yet an unresolved issue.

The area of study for this research is located at the Paxton Quarry near Alpena, Michigan (Figure 1). The occurrence of the concretions in the Antrim Shale is similar to what has been reported for the stragigraphically equivalent black shales of the Ohio Shale and the Kettle Point Formation, Ontario (Daly, 1900; Bownocker, 1911; Clifton, 1957; MacDonald, 1960); however, the occurrence of the carbonate concretions in the Antrim has not been reported in detail in the literature.

Two major types of concretions are common in the shale and are differentiated by mineralogy. Large iron carbonate concretions, roughly spherical in shape and ranging from eight inches to six feet in diameter, occur in the lower part of the formation. Smaller pyrite or marcasite concretions range in size from one to three inches in diameter, are shaped like flattened spheres and lie parallel to the bedding planes in the lower part of the shale.

Little work has been done on the geochemistry of the concretions from either the Antrim or its stratigraphic equivalents. Recently Hathon (1979) studied the origin of the quartz in the Antrim Shale. The Antrim has a uniquely large quartz content (50% quartz by weight in the less than 500 mesh size fraction).

Hathon (1979) measured the oxygen isotopes of the quartz and carbonate phases and the carbon isotopes of the carbonate phase of

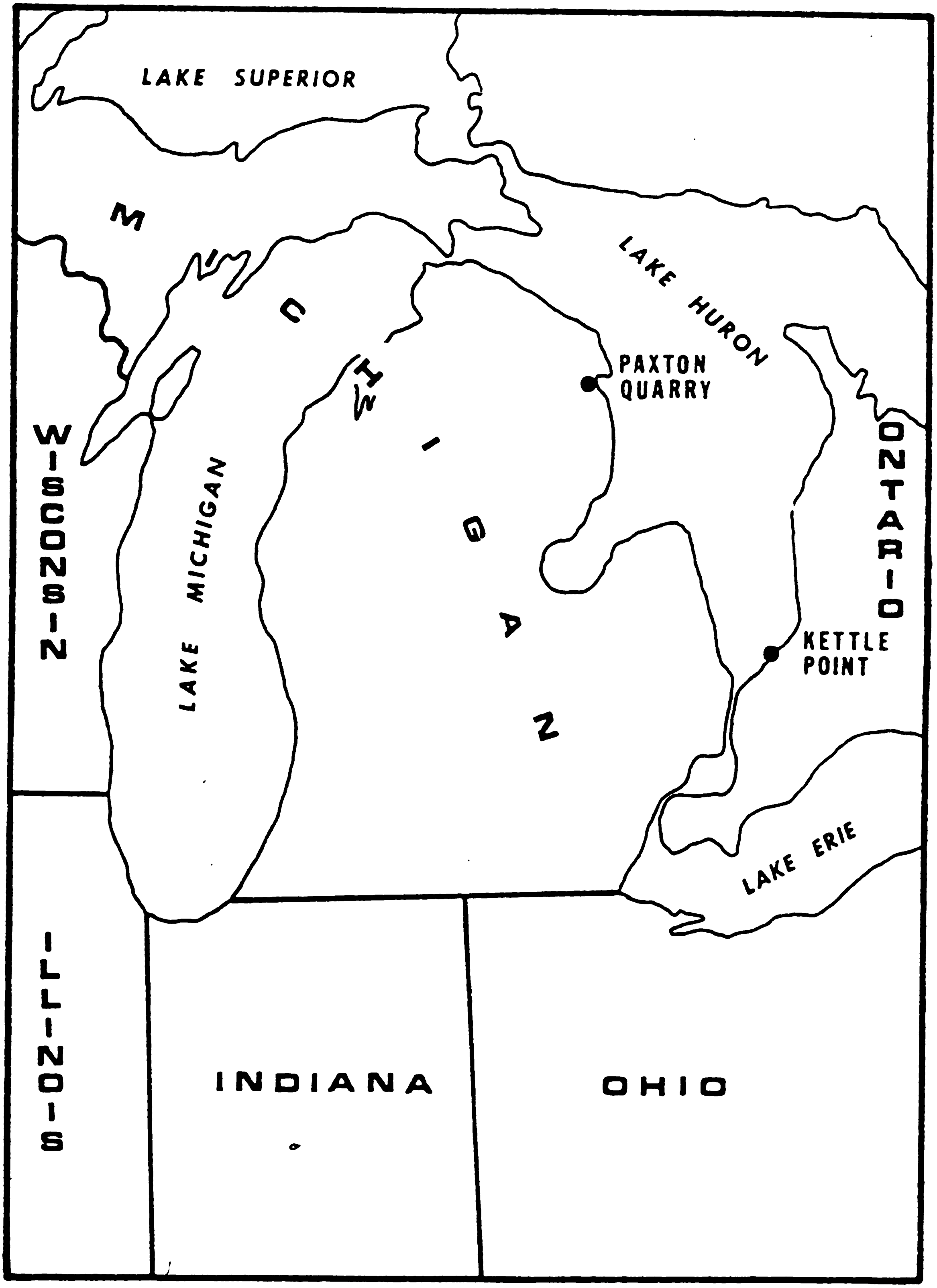


Figure 1. Location Map

the shale, including one concretion. The oxygen isotope values were highly variable in both the quartz and carbonate phases. This would suggest that post lithification isotopic reequilibration with meteoric waters had not taken place or had been of minor importance in determining the isotope values in the concretions. Hathon concluded that a gradual isotopic lightening of the pore fluids took place during the formation of the authigenic quartz and carbonate phases of the Antrim. This was also indicated in the lightening of the oxygen isotopes of the concretions from center to edge. His results, which will be discussed in detail in later sections, stimulated my interest to study the geochemistry of the Antrim concretions in more detail.

## RESEARCH GOALS

Black shales have frequently been reported to contain carbonate concretions (Irwin, 1980; Hudson, 1978; Curtis, et al., 1975; Raiswell, 1971; Hoefs, 1970; Girin, 1970; Tarr, 1920). These concretions are important because they form during shale diagenesis, at the same time that petroleum and low temperature ores are generated. Thus the presence and chemistry of carbonate concretions in black shales may indicate similar chemical and physical stages of diagenesis among the various host shales. The major questions addressed by this study, therefore, are:

I. Can the origin and evolution of the carbonate concretions in the Antrim Shale be interpreted in light of the "zonal theory of black shale diagenesis" proposed by Curtis (1978)?

II. Are the carbonate concretions in the Antrim Shale similar in terms of their geochemistry to similar concretions from Europe (Raiswell, 1971; Curtis, et al., 1975; Hudson, 1978; Irwin, 1980)? If so, does this suggest a commonality of origin and growth of carbonate concretions in black shales?

III. Can the Antrim concretions (and other carbonate concretions in black shales) be used to interpret changes in pore fluid chemistry during the diagenesis of black shale?

## METHODS

Both shale and concretions were studied by means of thin sections, atomic absorption, x-ray diffraction, and electron microprobe analysis. Components measured were mineral content, carbon and oxygen isotope values, and concentrations of Ca, Mg, Na, Sr, K, Fe, Mn, Pb, Cu, Zn and organic carbon.

### Collection

Concretions were collected from the Paxton Quarry, Alpena, Michigan (Figure 1). The Antrim is presumably 96 feet thick in the vicinity of the quarry; however, only a 50 foot section is exposed. The exposure in the quarry is about one half mile in length and concretions are exposed along the full length of the exposure. Only whole, unweathered, uncracked concretions composed of the iron carbonate were taken from the quarry. The sheer size and weight of the larger concretions prevented in situ collection, thereby making it necessary to take some of the smaller machine quarried concretions.

A total of nine concretions were collected and numbered randomly Close examination of the whole concretions in the lab revealed weathering and cracks in several of the nine concretions; however, two, #3 and #7, were uncracked and therefore, seemed relatively unaffected by weathering. Thus, these two concretions were used for the chemical analyses. In addition, randomly located shale samples were collected from the quarry floor for chemical analysis.

### Descriptions of Two Concretions Analyzed

I. Concretion #3 is roughly spherical. Its vertical diameter is 30 cm, somewhat smaller than its horizontal diameter of 38 cm (Figure 2). It is composed of iron carbonate (see mineralogy section) and encased in a 2 cm outer layer of iron sulfide. The crystals of both the iron carbonate and the iron sulfide radiate outward from the middle of the concretion. At its center the concretions contains very well preserved Devonian algae (Figure 3). The algae are preserved as a kelp-like structure roughly two cm wide and 10-13 cm long. The structure is filled with the iron carbonate in some areas and microcrystalline quartz in others. Solution cavities 1/2 to 1 cm in diameter, filled with coarse white calcite and dolomite crystals, are located 8-10 cm from the center of the concretion.

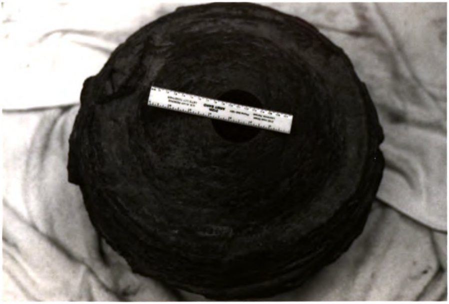


Figure 2. Concretion 3.

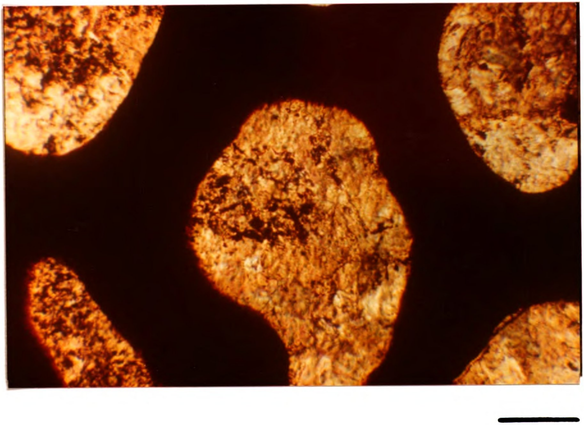


Figure 3. Devonian algal structure inside concretion 3. Scale bar = 0.1mm.

II. Concretion #7 is more irregular in shape than #3 and comprises two interpenetrating spheres (Figure 4). The vertical diameter is 32 cm and horizontal diameter is 35 to 40 cm. It is composed of iron carbonate crystals that radiate outward from the center with an outer layer of pyrite 1 cm wide. No fossils have been found in the center of the concretion. As in #3, solution cavities lined with coarse, white calcite or dolomite crystals are located 7.5-10 cm from the middle of the cores.

## Preparation Methods

Because the concretions were too large and heavy to saw apart, they were instead cored in two directions through their centers, vertically and horizontally relative to the bedding planes. A hand operated water-cooled corer was used. Distilled water was used as the coolant in order to avoid sample contamination as much as possible.

The cores were sawed in half lengthwise on a distilled water cooled saw and one half was polished with 600 mesh grit for macroscopic examination. The other half was again sawed in half lengthwise and one quarter was used for thin section preparation and the other subsampled and powdered for chemical and x-ray analysis. The subsample chips were cleaned in distilled water for 10 minutes in an ultrasonic cleaner, then each sample was powdered for 10 minutes (300 mesh) in a titanium ball mill.

Each powdered sample and thin section was assigned an alphanumeric code such as 3-v-1. The first digit denotes the concretion sampled. The v or h digit indicates which core in each

Figure 4. Concretion 7.

concretion, vertical or horizontal, the sample was taken from, and the second digit indicates the subsample location along the particular core. Each successive second digit assigned to the powdered samples from concretions #3 and #7 indicates a 1 to 2 cm increment from the center of the concretion.

### Thin Sections

Thin sections were prepared along the full length of the six cores for petrographic and microprobe analysis. Each thin section was polished and carbon coated for the microprobe analysis. After microprobing, the thin sections were etched and stained to aid in mineral identification utilizing the method of Bouma (1969).

The best results were obtained when the slides were first etched for 20 seconds in 10% cold HCl and then immersed in the staining solution for five minutes.

### Electron Microprobe Analysis

The mole percent of $CaCO_3$, $MgCO_3$ and $FeCO_3$ in the concretions was determined using electron microprobe analysis. Points spaced 1 cm apart along the full length of the cores were probed. To avoid burning holes in the thin sections, the probe was set at 10 KV and 1.5 MA. Five ten second readings were taken for each point and the results averaged to minimize instrumental error. The data was reduced to mole percent carbonates using a computer program by Bence and Albee (1967).

## Atomic Absorption

### Bulk Geochemistry

The bulk geochemistry of the subsamples was determined using atomic absorption analysis. The powdered samples were prepared using the fusion method of Perkin-Elmer (1980). Powdered rock (0.2 g) were mixed with 1 g of lithium metaborate and fused at 1000°C for 20 minutes. After fusion, the samples were dissolved in 50 ml of 10% cold HCl and diluted to 100ml. The samples were analyzed for Na, Zn, Mn, Sr, Pb and Cu.

### Carbonate Geochemistry

In order to determine the chemistry of the carbonate material in the concretions and the shale, 0.5 g of each sample was dissolved in 25% acetic acid solution by the method of Barber (1974). The samples were analyzed for Fe, Ca, Mg, Na, Zn, K and Sr. In order to bring the concentration of Mn down within the working range of the instrument, the sample solutions were diluted 10 times. Ca, Mg and Fe required dilution of 100 times.

The solution samples from the bulk chemistry and carbonate chemistry dissolutions were analyzed in an air-acetylene flame on a Perkin-Elmer Atomic Absorption Photospectrometer Model 306 using single and multi-element hollow cathode tubes and a 4-inch single slot burner head.

The standards used for each element were prepared with the same background solution as the unknown samples. The standards used with the fused samples were prepared with a blank lithium metaborate solution just as thse used with the dissolved samples were prepared with a 25% acetic acid solution. This was done in order to achieve maximum accuracy of measurement. Appropriate procedures were used to eliminate chemical and physical interference (Perkin-Elmer Methods Manual, 1980).

### Porosity

The volume of carbonate mineral in the concretions, represents the porosity of the sediment in which the concretions grew (Lippman, 1955). It was estimated by measuring the percent of the material dissolved in the 25% acetic acid dissolutions.

### X-ray Diffraction

Pellets of the powdered samples, some of the insoluble residue from the acetic acid dissolutions and powdered shale samples were x-rayed from 5° to 65° 2θ on a General Electric x-ray machine using Cu K-alpha radiation. The instrument was set at 50 KV and 10 MA and the best results were obtained at 500 CPS peak intensity.

The insoluble residue from the acetic acid dissolutions was x-rayed in order to determine if all the carbonate material was dissolved. Because the amount of insoluble residue left from the dissolutions was extremely small, only three samples could be x-rayed Of these three, one showed a small peak while the others showed only quartz peaks. Thus, the weight percent dissolved carbonate material discussed in a later section, are minimum values at best.

### Organic Carbon

The total organic carbon content of both the concentric zones in the concretions and the shale was determined using the titration method of Gaudette et al., (1974)(Appendix A).

### Carbon and Oxygen Isotopes

Stable carbon and oxygen isotope analyses were performed by Geochron Laboratories, Cambridge, Mass. Before sending the samples out for the analysis, the organic carbon was removed from the powdered samples. This was done by soaking 0.5 g of sample in 5.25% sodium hypochlorite solution (Chlorox) overnight (Barber, 1974). After soaking, the samples were filtered and washed and then dried in a cool oven.

## RESULTS AND INTERPRETATION

From the consideraton of the past work on concretions, four aspects of concretion growth have been defined from which interpretations on the nature and origin of concretions can be organized. These are (1) the state of the system during growth (i.e., open or closed), (2) how the data can be interpreted in terms of the zonal theory of shale diagenesis, (3) the time of concretion growth relative to shale compaction, and (4) the temperature and salinity of the local pore waters during growth. These aspects can be summarized as follows:

I. State of the system-- In the discussion of concretions the state of the system refers to the nature of the environment in which the concretion grew: whether it was open or closed to seawater circulation or diffusion. Raiswell (1971) used three indicators to determine whether the system in which the calcite concretions from the Upper Lias black shales of NE England precipitated was open or closed to seawater during growth: 1) porosity, 2) $Sr^{++}$, and 3) mineralogy. A high porosity, 80-90%, indicates an open system and a low porosity, 40%, indicates a closed system. $Sr^{++}$ concentrations of 1000-1500 ppm indicate an open system and $Sr^{++}$ concentrations of 600 ppm or less indicate a closed system according to Raiswell (1971). An open system is indicated by pyritiferous margins and a closed system by siderite concretions.

According to Raiswell (1971) the porosity of the sediment in which carbonate concretions grow can be determined by measuring the volume of the carbonate mineral in the concretions. The assumption is that as the concretions grow the carbonate precipitates in the open pore space in the sediment. Therefore, the percent carbonate that is in the concetions roughly represents the original pore space of the sediment. A problem with this type of interpretation clearly is that the crystals of carbonate could disrupt the sediment as they grow and thus the amount of carbonate would not be representative of the sediment pore space.

However, evidence that supports the hypotheses that the amount of carbonate in a concretion represents the original pore space of the sediment for Raiswell's (1971) concretions, is that the amount of carbonate in the centers of the concretions (80-90%) is near to or equal to the amount of pore space in uncompacted clays (Muller, 1967).

According to Raiswell (1971) pyritiferous margins on a concretion indicate tht the concretion was in contact with a steady supply of $SO_4^{=}$ that was in turn reduced and precipitated as the iron sulfide. The likely source of $SO_4^{=}$ is seawater (Berner, 1964); thus, pyritiferous margins on a concretion are evidence for an environment open to seawater circulation or diffusion through the sediment. If there was no source of seawater the reduced iron would precipitate as a carbonate mineral and the concretions would contain siderite instead of pyrite (Curtis, et al., 1975; Raiswell, 1971).

The amount of $Sr^{++}$ in calcite in a system open to seawater circulation, thus providing a source of $Sr^{++}$, is higher (1000-1500 ppm) than in a system closed to seawater (0-6000) (Raiswell, 1971). The use of $Sr^{++}$ content as evidence of an open or closed system may not be valid, however, for the Antrim concretions because they are composed of ferroan dolomite and the $Sr^{++}$ limits in ferroan dolomite have not been determined (Land, 1980).

Zonal Theory-- While it is difficult to prove the origin of carbonate concretions, it is possible to gain some insights by making interpretations of the data in terms of the zonal theory (Coleman and Raiswell, 1981; Irwin, 1980; Curtis, 1978). Results from this study will be compared to the model for the theory as discussed in the introduction. Three aspects of the theory will be studied (1) the nature of the reaction causing the local supersaturation of the carbonate (i.e. inorganic or organic), (2) the source for the carbon (fermentation), and (3) depth of burial.

Time of growth-- The time of concretion growth relative to compaction history can be determined by the ovservation of the physical nature of the concretions in the outcrops as discussed earlier in the summary of concretion research.

Temperature/Salinity-- The oxygen isotope ratio of carbonate material is a function of the temperature and the salinity of the precipitating pore solution (Craig, 1953). Thus the $\delta^{18}O$ values of the Antrim concretions can be used to make interpretations on the temperature and the salinity of the pore fluid.

Some trace elements in dolomite also may be indicative of the pore fluid salinity. The Na and K concentrations in dolomite have been used as indicators by Fritz and Katz (1972) and Land (1980). The use of trace elements to predict exact salinity of the pore fluid is as yet unreliable; however, trace elments have been used to make interpretations on pore fluid salinity (Land, 1980). Acccording to Fritz and Katz (1972) supratidal dolomites contain 200-900 ppm Na and 600-2000 ppm K. Early diagenetic dolomites contain 70-200 ppm Na and <1500 ppm K, while late diagenetic dolomites contain <150 ppm Na and <800 ppm K.

These aspects of the nature of concretion growth will now be interpreted in light of the data collected. Prior to interpretation, the results of each type of data collected are summarized.

## MINERALOGY

The carbonate concretions in the Antrim Shale are composed of ferroan dolomite with little change in mineralogy from the center to the edge of the concretions. The carbonate turns blue upon staining and does not react with HCl unless powdered, thus indicating dolomite. In thin section the crystals are long and slender, feathery-like in appearance, have curved edges and sweeping extinction, similar to what has been reported by Choquette (1971) (Figure 5).

Z-ray diffraction and microprobe analysis both confirmed the carbonate as ferroan dolomite. A typical x-ray pattern is shown in Appendix B. Quartz was the only other mineral indicated by a major peak. Brown (1961) established characteristic d spacings for common carbonate minerals and found that for dolomite d = 2.88 A. Irwin (1980) found that ferroan dolomite in concretions produced d spacings of 2.89-2.90 A. All of the Antrim concretion samples had peaks at 2.89 A.

According to Howie and Broadhurst (1958 ) dolomites with a MG:Fe ratio less than or equal to 4:1 should be classified as ankerite. Microprobe analysis revealed an average of 58% $CaCO_3$, 35% $MgCo_3$ and 8% $FeCO_3$ in the Antrim concretions. Because the Antrim concretions contain a higher ratio of Mg:Fe than 4:1 and d = 2.89 A when x-rayed, they are identified as ferroan dolomite rather than ankerite as previously identified by Hathon (1979).

Pyrite is also present in the concretions. It is scattered as rare euhedral crystals throughout the concretions and forms a 0.5 -

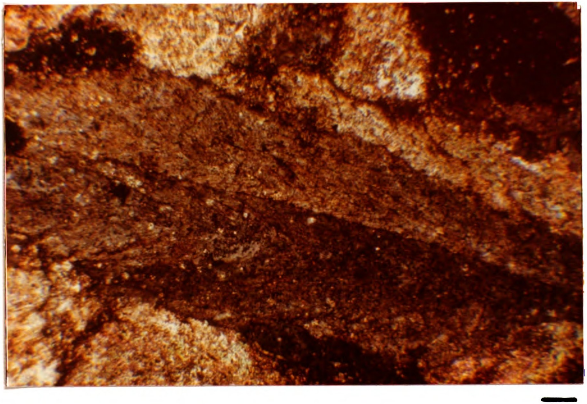


Figure 5. Photomicrograph of radial ferroan dolomite crystals in concretion 3. Scale bar = 0.1mm.

2 cm layer around the concretions.

Authigenic quartz fills many of the spores scattered throughout the concretion (Hathon, 1979). It also lines parts of the fossil algae in the center of concretion #3. A small number of detrital quartz grains are present in both of the analyzed concretions.

Calcite and dolomite, identified by staining, are present as white crystals lining the solution cavities in the concretions.

State of the system-- The pyritiferous concretion margins and the absence of siderite in both the Antrim concretions and the shale indicate an open system during concretion growth according to Raiswell (1971). Reduced iron precipitated with reduced sulfate to form pyrite, instead of with carbonate produced in the sediment by microorganic activity (Curtis, et al., 1975; Raiswell, 1971). This indicates a seawater source because sulfate is derived primarily from seawater.

Zonal theory-- According to Raiswell (1971) sulfate reduction takes place in the top 3 meters of the sediment through which there is a steady supply of $SO^{=}_4$ provided by the overlying water. The concretions studied by him are encased in pyrite and were thus interpreted by him to have formed in the upper 3 meters of the sediment. because the Antrim concretions are encased in pyrite, in light of Raiswell's interpretation, they accordingly should have formed in the upper 3 meters of sediment.

The carbonate mineralogy does not suggest that local reactions were organic or inorganic. The carbon source cannot be identified via the mineralogy. The presence of pyrite is indicative of sulfate reduction with the most likely mechanism being an organic reaction.

Time of growth-- The mineralogy of the Antrim concretions as studied does not provide any inference on the temperature or salinity of the pore fluids during concretion growth. Future work should be designed to interpret salinity based on Fe-S concentration by the method of Berner, _et al_., (1979).

## PHYSICAL SETTING

Field observations-- The carbonate concretions in the Antrim Shale are located in the lower part of the formation and are not limited to any particular horizon in the shale. The shale beds are compacted around the concretions, equally above and below (Figure 6). The shale beds can be traced through some of the concretions, near their outer edges. Most of the carbonate concretions are spherical or nearly spherical in shape (Figure 7). Some have slightly larger horizontal than vertical diameters.

Textural observations-- The centers of many of the carbonate concretions are composed of massive mudstone cemented with ferroan dolomites. Outward from the mudstone are the bladed ferroan dolomite crystals which are encased with pyrite. The body of the concretions extends a few inches outward from the pyrite and it is in this outer zone that the shale beds can be traced through the concretions. Some of the carbonate concretions do not contain the

Figure 6. Antrim Shale compacted around carbonate concretions, Kettle Point, Ontario.

Figure 7. Typical sphere-shaped carbonate concretion, Kettle Point, Ontario.

massively-textured center; rather, they contain only the bladed crystals. Others do not have the outer shale layers and are encased only in pyrite. Uncrushed Tasmanites, are scattered thoughout the concretions also (Hathon, 1979)(Fig. 8). The carbonate content of the Antrim concretions ranges from 50 to 90%. There is a trend to decreasing porosity from the center to the edge of #3 and no clear trend across #7. The porosity results are plotted on Figures 9 a,b,c,d.

State of the system-- The carbonate content of Antrim concretions indicates a porosity which can be classified as an open system according to Raiswell's (1971) criteria. The trend of decreasing porosity from the center to the edge of #3 is expected in a compacting clay.

Zonal theory-- The depth of burial indicated by the porosity of the Antrim concretions is a maximum of 10 m accrding to Curtis (1978) zones (Table 1). The absence of boring or encrusting organisms on the Antrim concretions can be interpreted to indicate that the concretions were buried and not exposed at the sediment-seawater interface during growth (Pantin, 1958), or were quickly buried or were formed at the surface on an anoxic bottom which excluded benthic organisms.

Time of growth-- The presence of uncrushed fossils at the center of # 3 and uncrushed Tasmanites throughout both analyzed concretions indicates that growth occurred before compaction of the shale (Weeks,

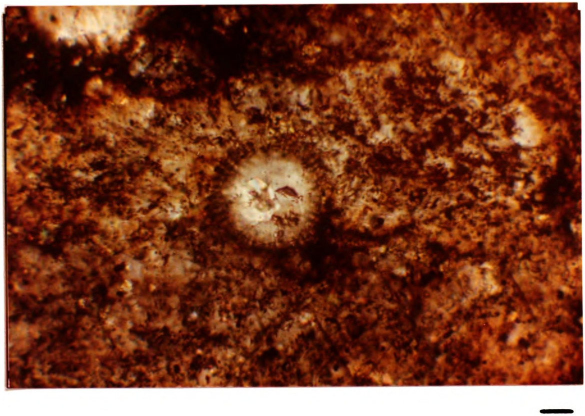


Figure 8. Uncrushed Tasmanites in concretion 3.
Scale bar = 0.1 mm.

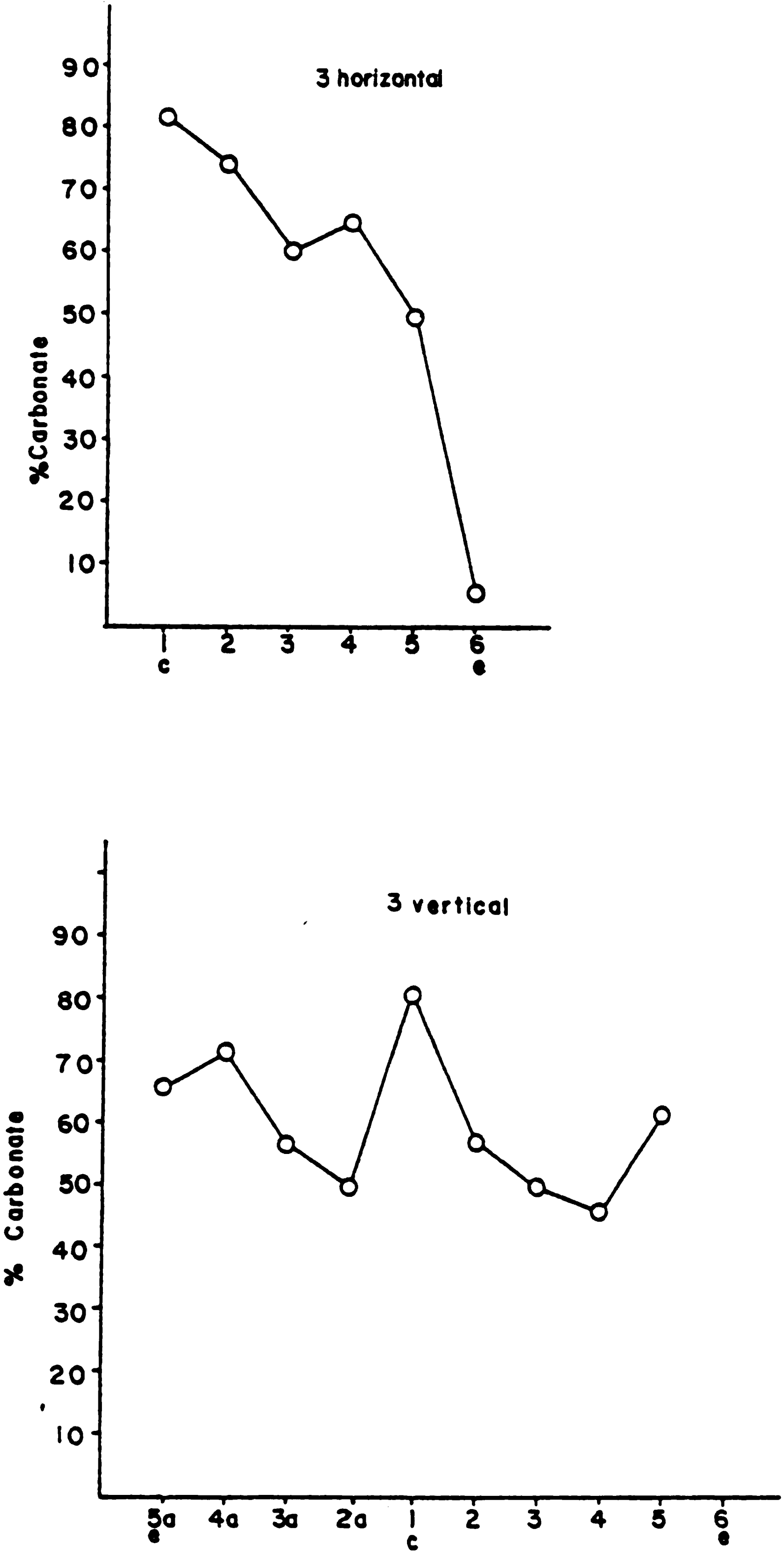


Figure 9a,b. Plot of percent carbonate in samples across concretions 3 and 7. (See text for explanation). Samples analyzed were approximately 3/4 inch apart across the concretions (c = concretion center; e = concretion edge).

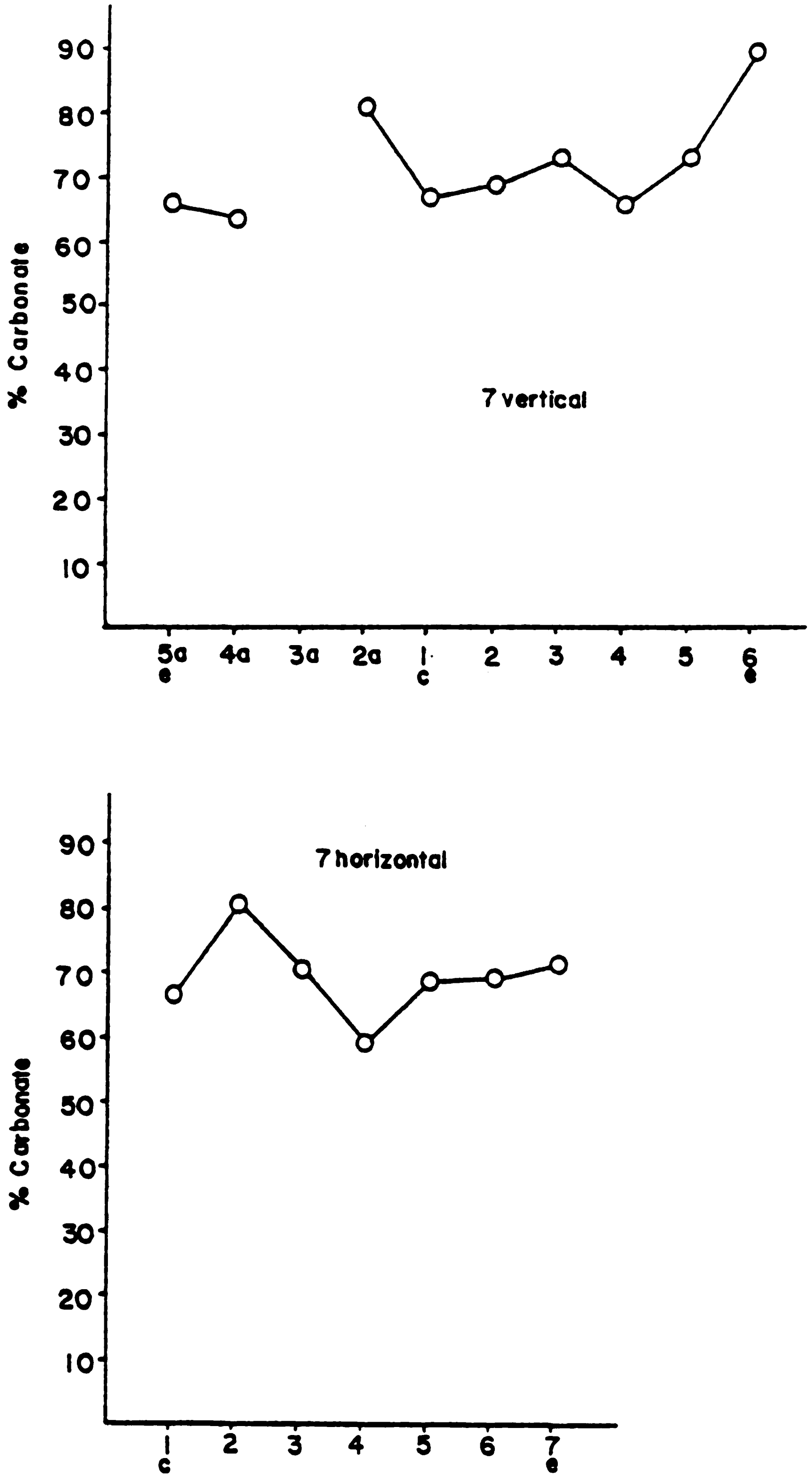


Figure 9c,d. Plot of total organic carbon content in samples across concretions 3 and 7.

1953). The nature of the shale beds around the Antrim concretions and the spherical shape of the concretions also indicates that growth took place before and during compaction of the shale.

## CHEMICAL TRENDS

The results of the atomic absorption analysis are listed in Table 4. The major element (Ca, Mg, Fe) and the 'trace' element (Sr, Zn, Cu, Pb, Na, K, Mn) concentrations vary somewhat but do not show any specific trends across concretions #3 and #7.

The total organic carbon content of the concretions ranges from 0.9% in #3 to 2.4% in #7 (Figure 10a,b,c,d) as compared to about 5% in the shale (Beers, 1945). There is no trend in the total organic carbon content across the concretions. The organic carbon value determined by Beers (1945) is inferred to be more representative of the Antrim Shale as a whole than the mx values because in the present study the sampling design is crude at best.

State of the system--The lack of chemical trends in the Antrim concretions can be interpreted as evidence of an open system during concretion growth. If a concretion grew in a closed system the manner in which a component would be depleted from the pore solution would depend on its partitioning coefficient. A coefficient other than one would create a chemical trend across the concretions. Thus trends in trace elments would be expected in a closed geochemical system. Because there are no trends in the trace element geochemistry across the Antrim concretions, it has been inferred that

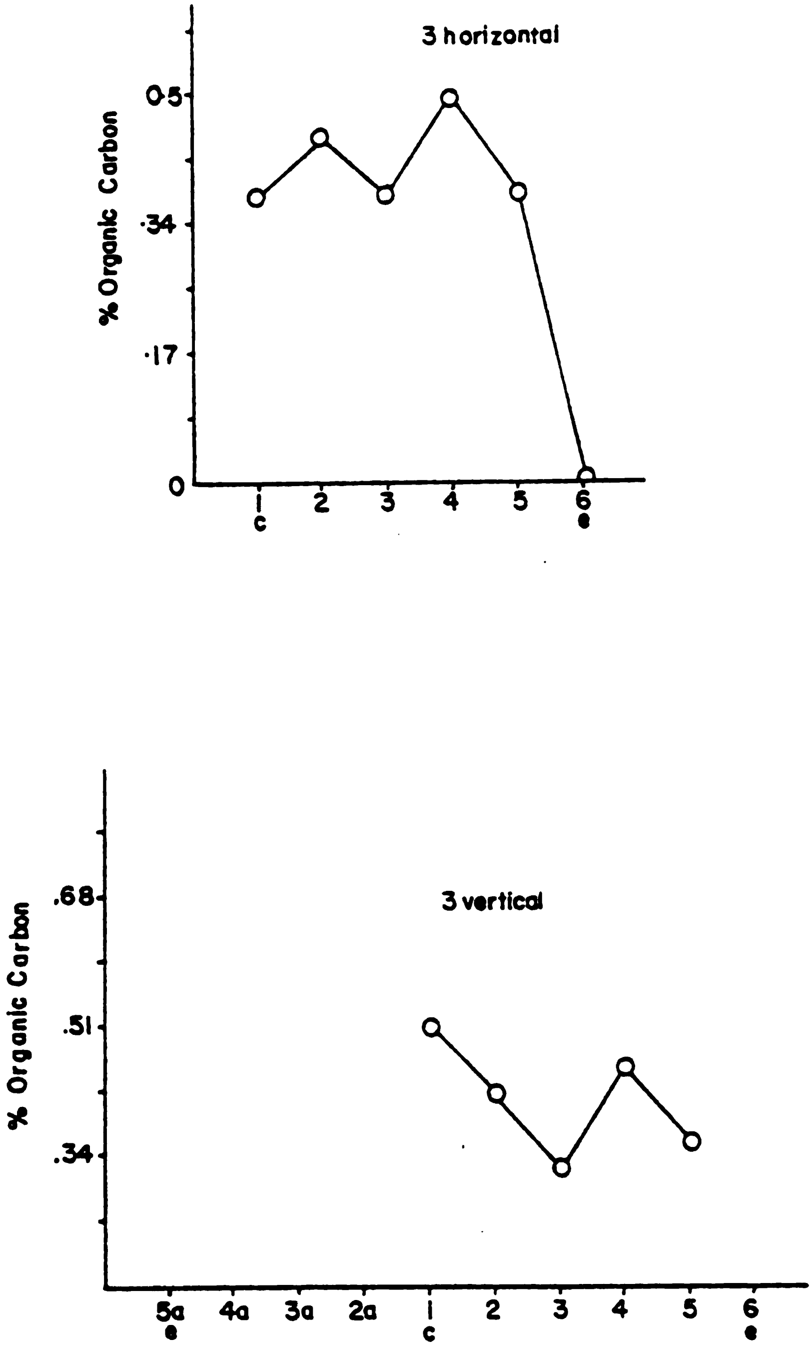
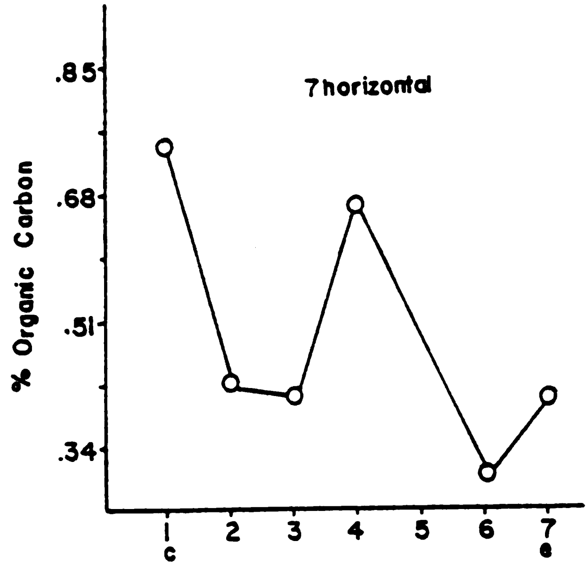


Figure 10a,b. Plot of total organic carbon content in samples across concretions 3 and 7.



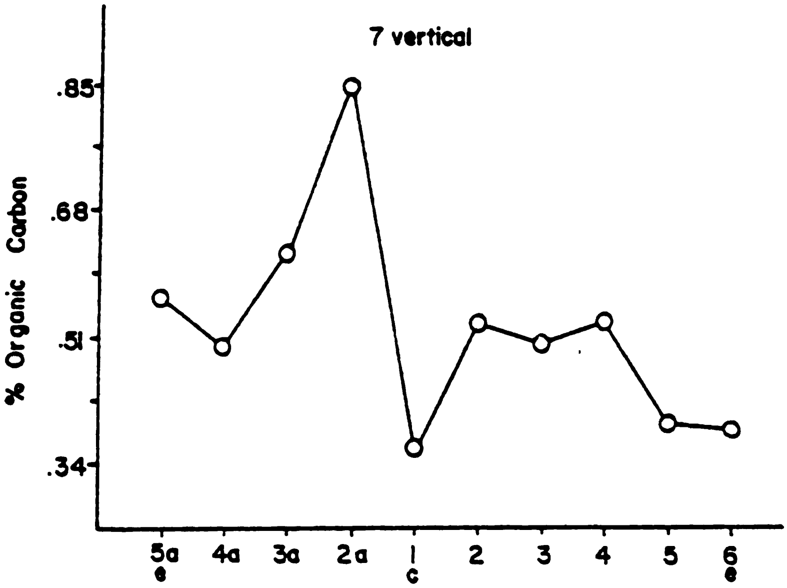


Figure 10c,d. Plot of total organic carbon content in samples across concretions 3 and 7.

TABLE 4: Carbonate Geochemisty (atomic absorption data).

| | | K | Sr | Zn | Mn | Mg | Fe | Ca | Na |
|---|---|---|---|---|---|---|---|---|---|
| 3 vertical | | | | | | | | | |
| edge | 5a | 356 | 146 | 17 | 6551 | 101395 | 43981 | 298985 | 462 |
| | 4a | 458 | 191 | 20 | 11054 | 94904 | 28252 | 304458 | 568 |
| | 3a | 493 | 272 | 109 | 9881 | 285214 | 39893 | 637536 | 537 |
| | 2a | 268 | 203 | 14 | 5635 | 113207 | 26439 | 303177 | 613 |
| center | 1 | 451 | 204 | 25 | 8878 | 84818 | 30309 | 316087 | 924 |
| | 2 | 211 | 174 | 9 | 5726 | 94712 | 22470 | 414767 | 427 |
| | 3 | 238 | 226 | 80 | 6342 | 127613 | 30460 | 335457 | 522 |
| | 4 | 140 | 165 | 11 | 4815 | 133350 | 22987 | 270444 | 395 |
| edge | 5 | 403 | 180 | 87 | 6039 | 87321 | 27784 | 303725 | 434 |
| 3 horizontal | | K | Sr | Zn | Mn | Mg | Fe | Ca | Na |
| center | 1 | 1014 | 179 | 14 | 5522 | 75546 | 26636 | 294051 | 598 |
| | 2 | 932 | 206 | 13 | 8200 | 87307 | 33355 | 204666 | 625 |
| | 3 | 893 | 186 | 12 | 9612 | 85179 | 28395 | 305944 | 430 |
| | 4 | 925 | 178 | 14 | 10156 | 96148 | 28041 | 308203 | 439 |
| | 5 | 1183 | 169 | 14 | 5645 | 90781 | 28024 | 297012 | 392 |
| edge (pyrite) | 6 | 4553 | 0 | 16 | 160 | 16821 | 81805 | 244649 | 1262 |
| Shale | | | | | | | | | |
| light | | 2603 | 0 | 218 | 1095 | 47,143 | 23175 | 116175 | 3079 |
| dark | | 11250 | 0 | 99 | 0 | 4941 | 0 | 0 | 7960 |
| 7 vertical | | | | | | | | | |
| | 6 | 283 | 293 | 11 | 5983 | 78634 | 22642 | 280723 | 353 |
| | 5 | 491 | 304 | 13 | 5351 | 91345 | 25785 | 303365 | 438 |
| | 4 | 647 | 316 | 14 | 6375 | 100458 | 27173 | 311790 | 653 |
| | 3 | 692 | 292 | 14 | 5358 | 95305 | 25105 | 300183 | 453 |
| | 2 | 617 | 289 | 13 | 6301 | 86149 | 23141 | 270196 | 417 |
| | 1 | 728 | 265 | 13 | 6301 | 86149 | 23141 | 270196 | 356 |
| | 2a | 750 | 178 | 9 | 5343 | 79175 | 18261 | 169749 | 356 |
| | 3a | 613 | 495 | 24 | 12390 | 182739 | 47425 | 509000 | 710 |
| | 4a | 777 | 282 | 14 | 4827 | 83676 | 27558 | 303970 | 586 |
| | 5a | 857 | 279 | 15 | 6378 | 93553 | 27918 | 309380 | 475 |
| 7 horizontal | | | | | | | | | |
| | 1 | 2154 | 266 | 14 | 6951 | 89850 | 29970 | 303413 | 626 |
| | 2 | 1229 | 269 | 15 | 8210 | 84783 | 18641 | 295549 | 449 |
| | 3 | 791 | 304 | 14 | 7790 | 94148 | 23455 | 281067 | 528 |
| | 4 | 1247 | 299 | 14 | 8278 | 102708 | 23639 | 267863 | 720 |
| | 5 | 1131 | 297 | 15 | 6744 | 93036 | 25943 | 277320 | 473 |
| | 6 | 524 | 303 | 17 | 7439 | 88444 | 25279 | 284152 | 617 |
| | 7 | 760 | 289 | 14 | 6406 | 81593 | 25476 | 267817 | 713 |

the concretions grew in an open system.

Zonal theory-- the trace element geochemistry of the concretions yields no information as to the time of growth of the concretions relative to compaction of the shale, the carbon source or the nature of the reactions.

Temperature/Salinity-- No information on the temperature of the pore fluid can be gained from the concretion geochemistry. However, according to Land and Hoops (1973) the Na and K content of a dolomite can represent the salinity of the most recent solution with which the dolomite has come in contact if no recrystallization or post-lithification reequilibration has occurred.

In thin sections there is no evidence of recrystallization in progress in the Antrim concretions; therefore, either none has taken place or the entire body of the concretion has been recrystallized leaving no trace of the original fabric. The oxygen isotope ratio in concretion #3 differs from those of the shale. This observation supports the hypothesis that no recrystallization or reequilibration with meteoric water has taken place in the Antrim concretions (Hathon, 1979). Thus the Na content of the Antrim concretions may be representative of the salinity of the pore fluid. According to Fritz and Katz (1972) the low concentration of Na and K in the Antrim concretions may indicate that the concretions formed in pore fluid of relatively low salinity. The lack of a monotonic gradient in sodium across the concretion can be interpreted as evidence that no change in pore fluid salinity occurred during concretion growth (Fig. 11,12,13,14).

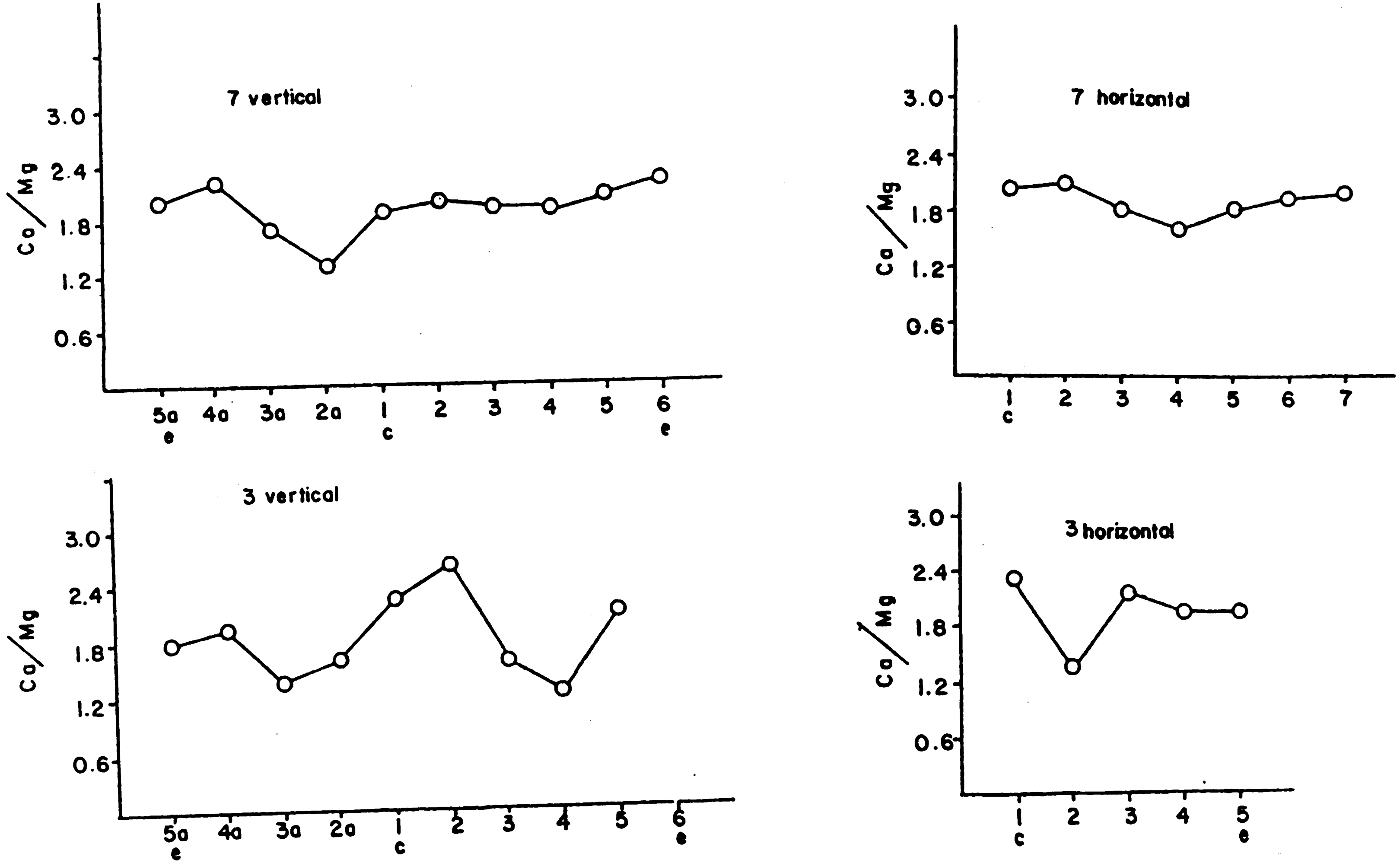


Figure 11a,b,c,d. Plot of Ca/Mg ratio in carbonate samples across concretions 3 and 7.

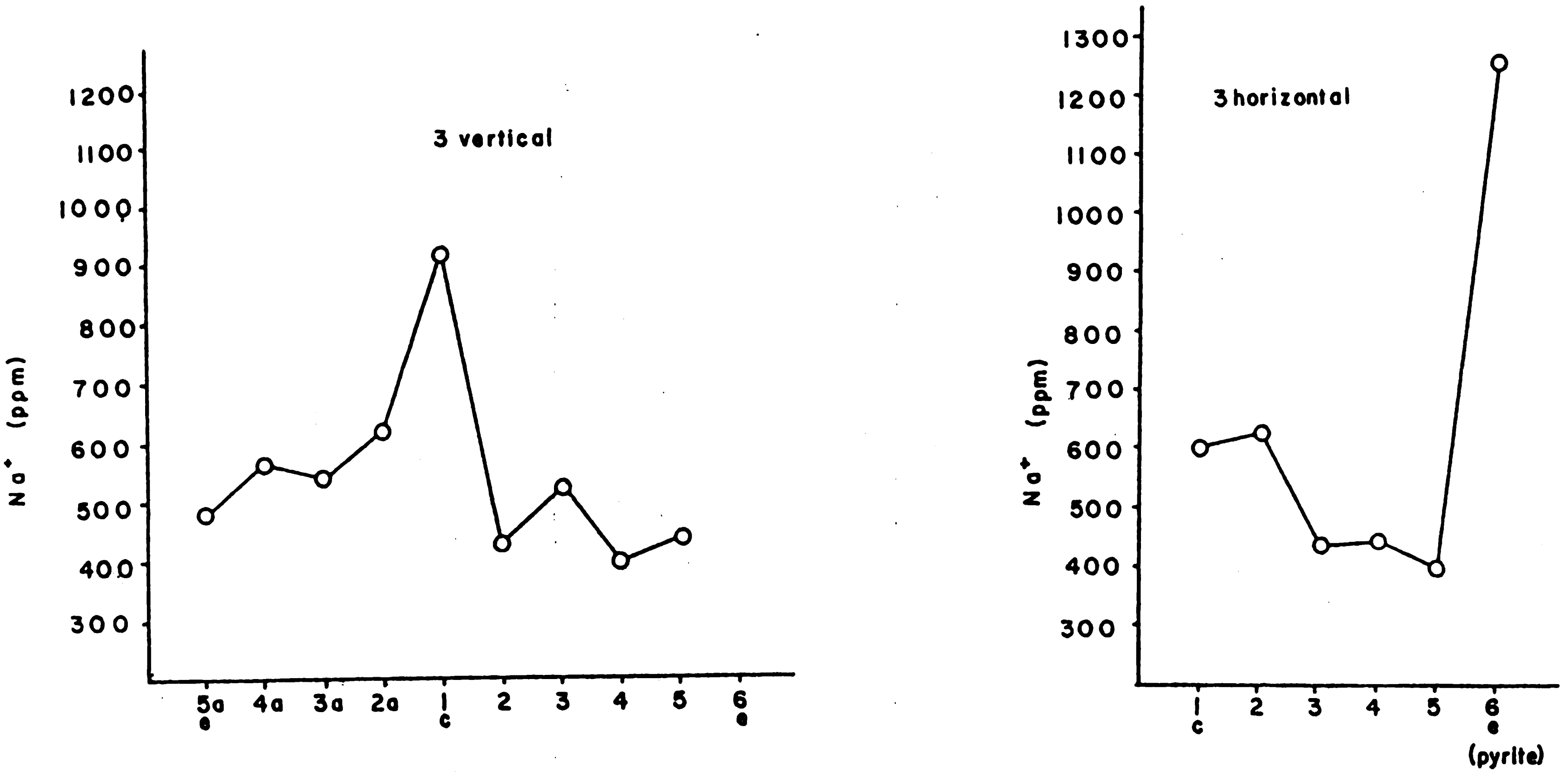


Figure 12a, b. Plot of sodium concentration in carbonate samples across concretions 3 and 7.

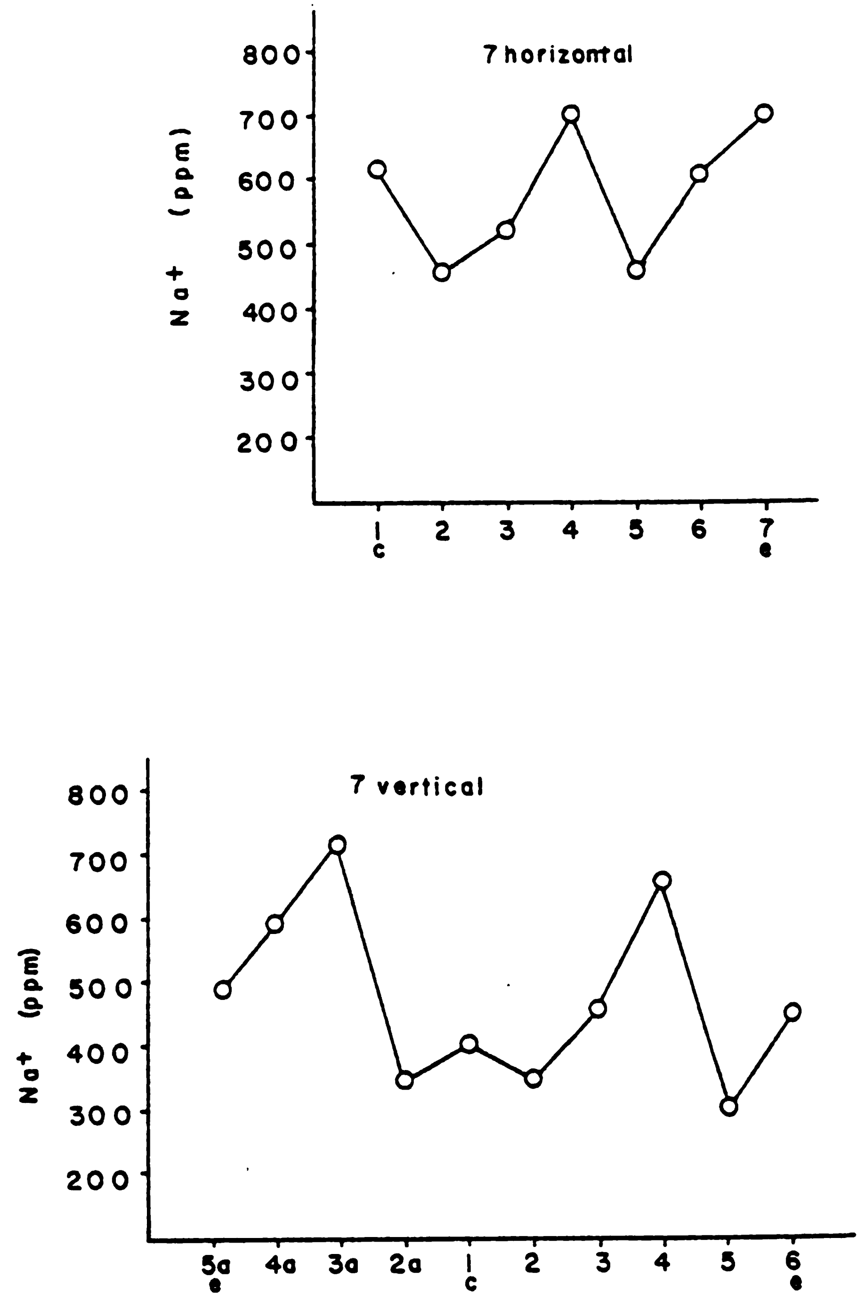


Figure 12c,d. Plot of Na concentration in carbonate samples across concretions 3 and 7.

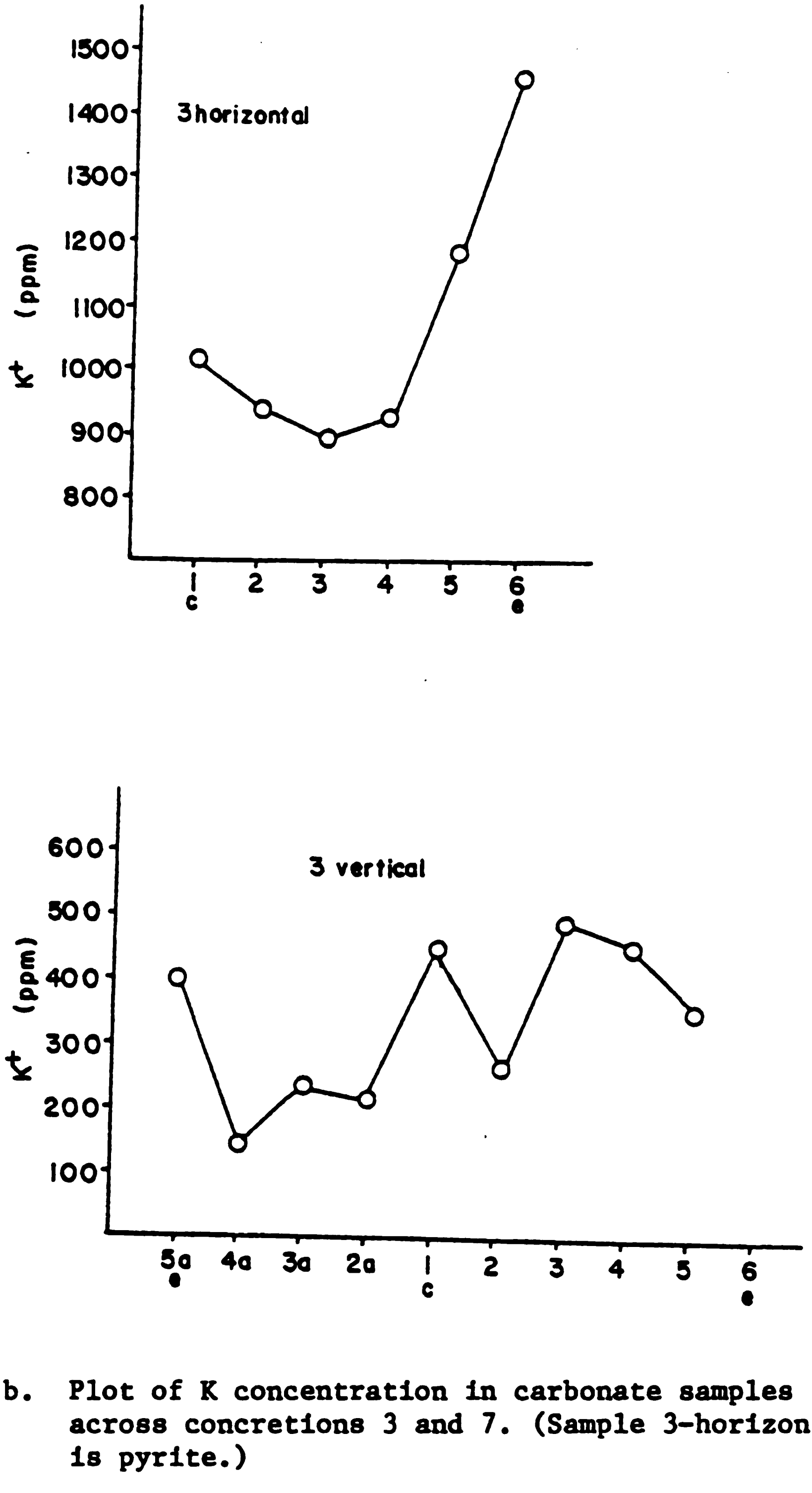


Figure 13a,b. Plot of K concentration in carbonate samples across concretions 3 and 7. (Sample 3-horizontal-6 is pyrite.)

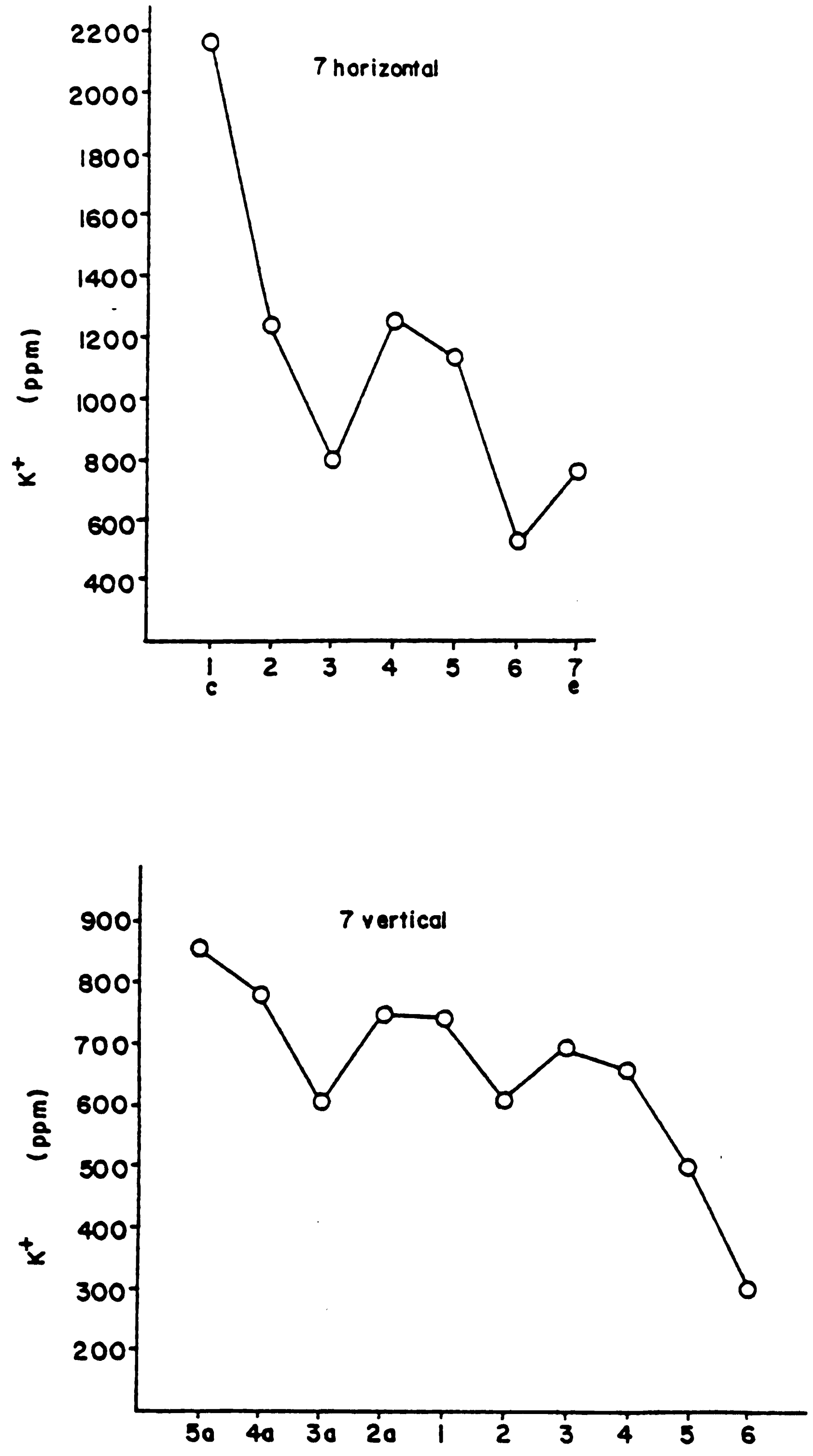


Figure 13c,d. Plot of K concentration in carbonate samples across concretions 3 and 7. (Sample 3-horizontal-6 is pyrite.)

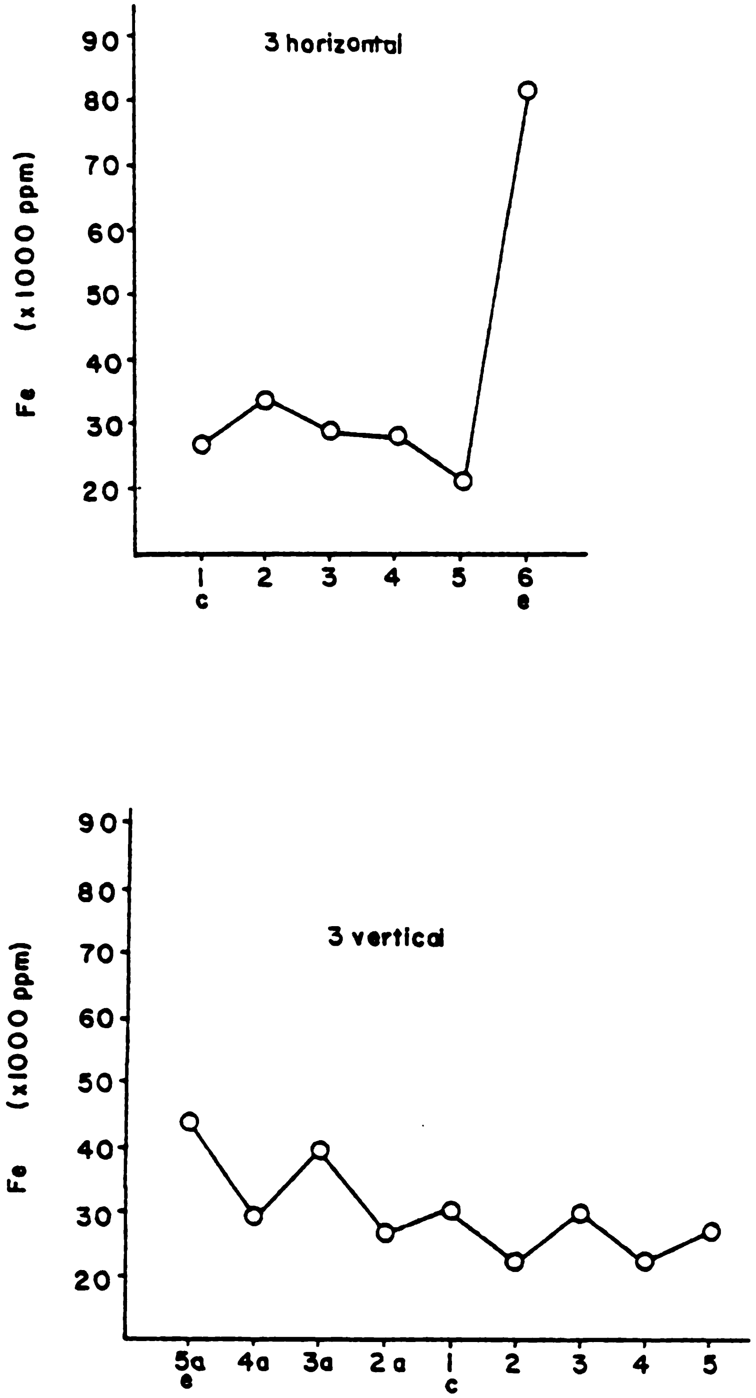


Figure 14a,b. Plot of Fe concentration in carbonate samples across concretions 3 and 7.

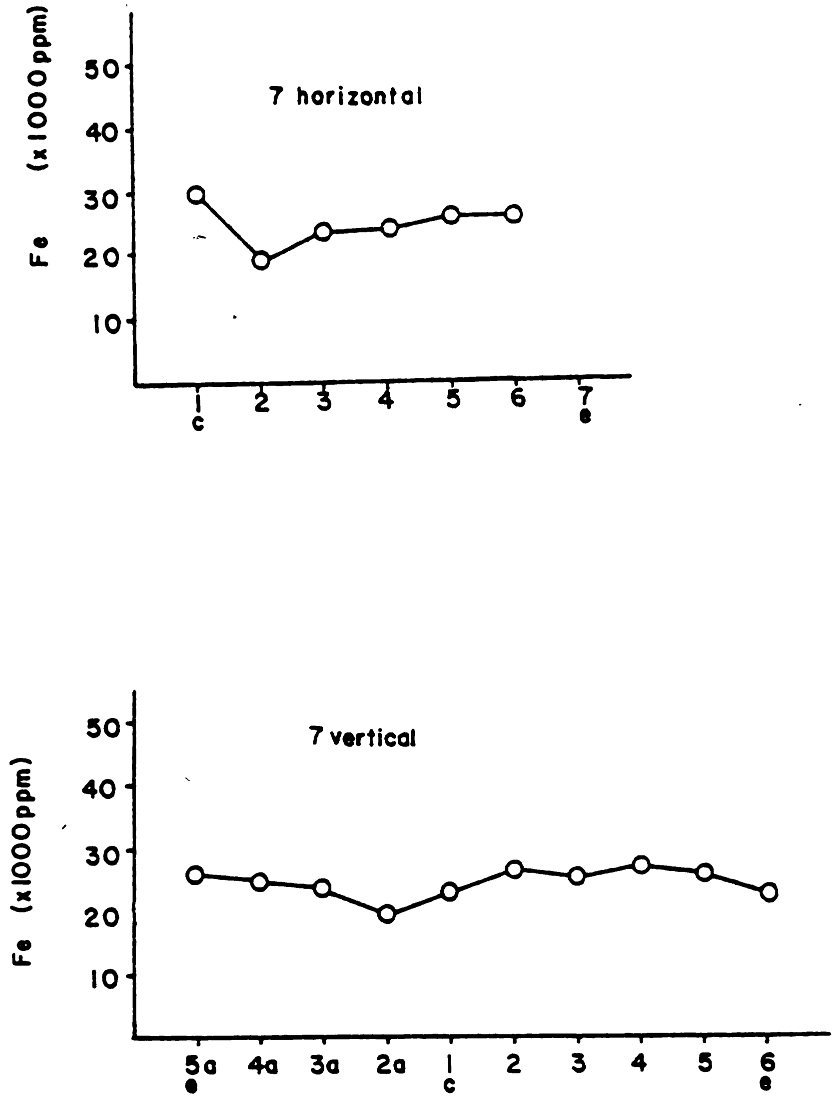


Figure 14c,d. Plot of Fe concentration in carbonate samples across concretions 3 and 7.

## OXYGEN ISOTOPES

The stable oxygen isotope ratios were determined for a group of samples traversing Antrim concretion #3 and for three samples across an Antrim carbonate concretion studied by Hathon (1979)(Table 5)(Fig. 15). There is no trend across concretion #3 except for a slightly heavier value at the edge of the concretion. There is a trend of lightening $\delta^{18}O$ values across the concretion studied by Hathon. THe Antrim Shale sample contains a somewhat lighter $\delta^{18}O$ value than concretion #3. The oxygen isotope values reveal no information on the time of growth of the concretions.

State of system-- The lack of a trend in the $\delta^{18}O$ values across the Antrim concretions can be interpreted as evidence that the system in which the concretions grew was open. If the system were closed, then an increase of lighter $\delta^{18}O$ values toward the edge of the concretion would be expected, because the $^{18}O$ will precipitate in the solid before the $^{16}O$, thus concentrating the $^{16}O$ in the pore solution and raising the $^{16}O/^{18}O$ ratio in the later-precipitated carbonate. If the system had been open to seawater, then no trend would be expected because there would be a constant source of $^{18}O$ to precipitate in the carbonate mineral.

Temperature/Salinity-- The oxygen isotope ratio of carbonate material is a function of the temperature and the salinity of the precipitating pore solution (Craig, 1953). Using the equation for dolomite-seawater fractionation by Matthews and Katz (1977):

TABLE 5: Carbon and Oxygen Isotope Values for Two Antrim Concretions

| #3 | | $\delta^{13}C(PDB)$ | $\delta^{18}O(SMOW)$ | $\delta^{18}O(PDB)$ |
|---|---|---|---|---|
| Center | 3-v-1 | -11.8 | +20.8 | -9.29 |
| | 3-v-2 | -12.0 | +20.8 | -9.29 |
| | 3-v-3 | -11.7 | +20.8 | -9.29 |
| | 3-v-4 | -11.3 | +20.8 | -9.29 |
| Edge | 3-v-5 | -10.2 | +20.0 | -9.10 |
| Shale | | -9.1 | +20.0 | -10.07 |
| Hathon (1979) | | | | |
| | inner | -11.3 | +23.9 | -6.28 |
| | middle | -12.2 | +23.3 | -6.86 |
| | outer | -10.1 | +22.6 | -2.54 |

$$PDB = \frac{-30.37 + SMOW}{1.03}$$

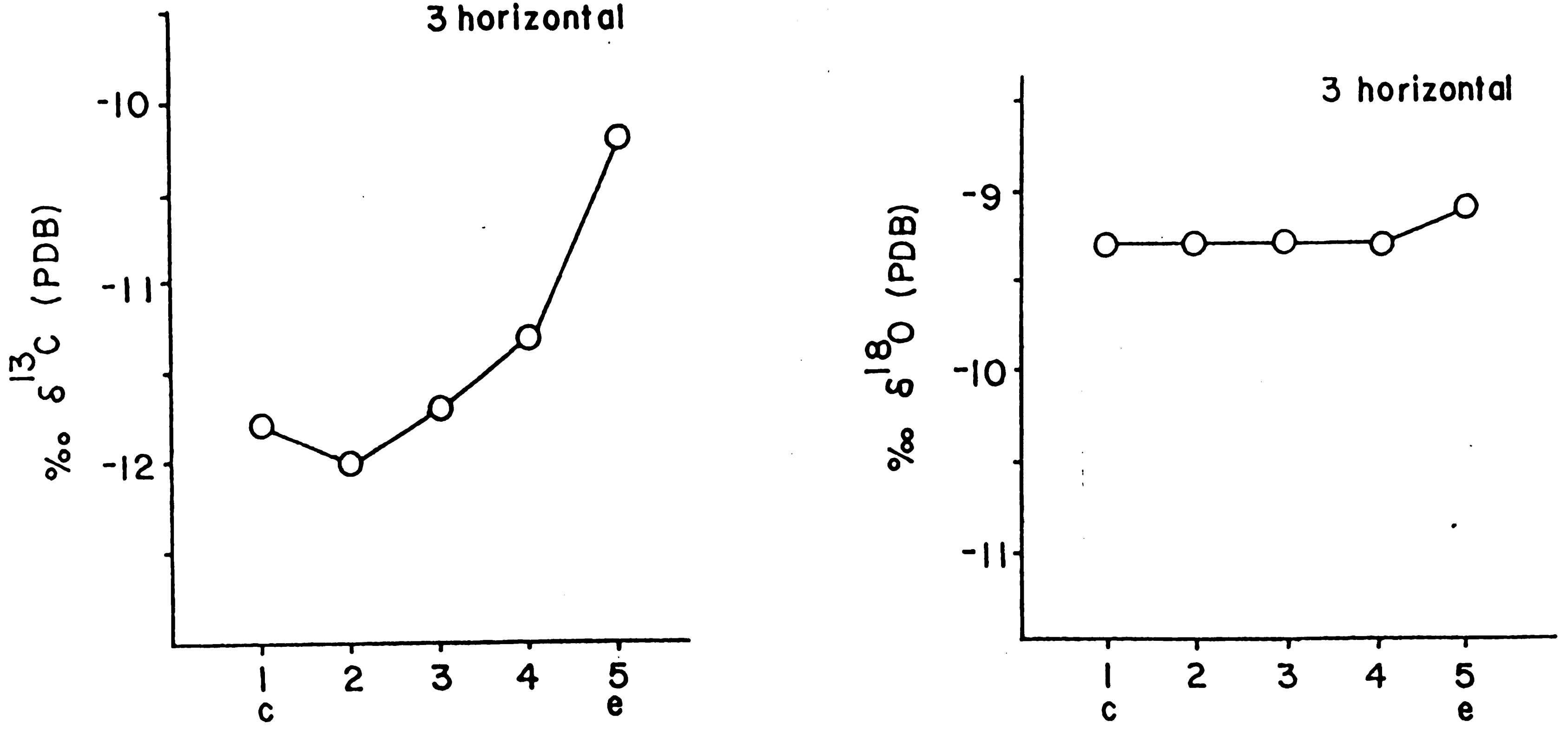


Figure 15a, b. Plot of stable carbon and oxygen isotopes across the horizontal core from concretion 3.

$$\ln \alpha = (3.06 \times 10^6 \times T^{-2} - 3.24)/1000,$$

and assuming that the $\delta^{18}O$ solution = 0o/oo, a temperature of approximately 83°C can be calculated from the $\delta^{18}O$ values of concretion #3.

The trend in $\delta^{18}O$ values can also be interpreted as evidence for a change in pore fluid salinity as the concretion grew. However, there are inconsistencies in the data because concretion #3 indicates an increase in salinity by its increase in heavier isotopes toward the concretion edge, whereas the concretion studied by Hathon (1979) indicates a lightening of the water by the increase of lighter isotopes toward the concretion edge. These inconsistencies will be discussed in a later section.

Zonal theory-- the $\delta^{18}O$ values of concretion #3 indicate a pore fluid temperature of 83°C. According to the zonal theory (Curtis, 1978; Table 1), 83°C would occur in the pore fluid at a burial depth of approximately 2500 meters.

## CARBON ISOTOPES

Stable carbon isotope ratios were determined for the same samples as the oxygen isotope ratios. The results are listed on Table 5 (Fig. 15). In both concretions analyzed, there is a gradual gradient in the $\delta^{13}C$ value across the concretions.

The carbon isotope values do not reveal any information on the state of the system, the time of growth or the temperature or salinity of the pore fluid.

Zonal theory-- The carbon isotopes can give information on the carbon source and the depth of burial of the concretions during growth. The $\delta^{13}$ values of the concretions are intermediate values, caused by a combination of either bacterial sulfate reduction ($\delta^{13}C$ = -25o/oo) and bacterial fermentation($\delta^{13}C$ = +15p/ppPDB), or bacterial fermentation and decarboxylation ($\delta^{13}C$ = -20o/ooPDB)(Curtis, 1978)(Table 1). According to Curtis (1978) the Antrim concretions can be interpreted to have grown either at a burial depth of approximately 10-100 meters between zone II and zone III or at a burial depth of 1000-2500 meters, between zone III and zone IV.

However, Coleman and Raiswell (1981) determined that the $\delta^{13}C$ value from carbonate concretions from Upper Lias black shale of northeastern England was the result of a mixture of three carbon sources: 1) bacterial fermentation, 2) sulfate reduction and 3) marine derived carbonate (skeletal or dissolved). They plotted the possible range of mixtures of these three sources that would result in a $\delta^{13}C$ value of -14o/ooPDB. If no fermentation occured, then 43% of the carbon must have come from a marine source in order to achieve the -14o/oo $\delta^{13}C$ value (Coleman and Raiswell, 1981). Because there was only a small amount of skeletal material in the shale, Coleman and Raiswell (1981) suggested that bacterial fermentation was a probable source of carbonate carbon in the concretions. The average $\delta^{13}C$ value of the Antrim concretions is approximately 11o/oo(PDB) and as there is little skeletal material in the shale, these interpretations can be applied to the Antrim concretions also (Fig. 16).

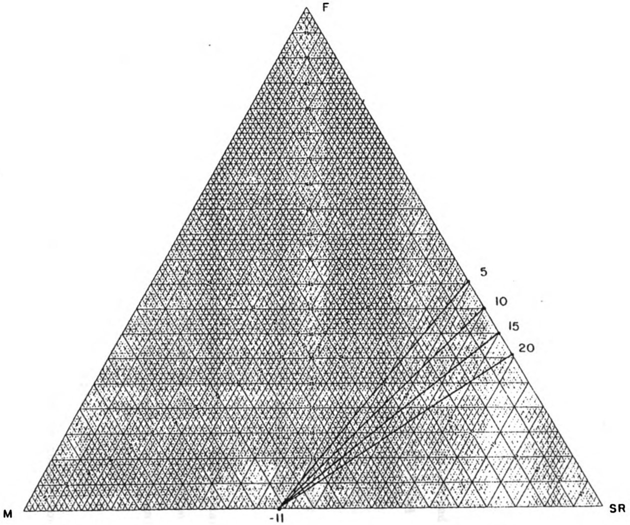


Figure 16. Mixtures of carbonate carbon from sulfate reduction(SR), bacterial fermentation(F) and marine origin(M) which give total $\delta^{13}C$ values of 11o/oo PDB.

Thus from the carbon isotope data alone, the Antrim concretions can be interpreted to have grown at either a shallow depth (10-100 m) as a result of sulfate reduction, bacterial fermentation and marine derived carbonate, or they could have grown at a deeper depth (1000-2500 m) as a result of bacterial fermentation and decarboxylation.

## DISCUSSION

The interpretations made from the geochemical data collected from the Antrim concretions have been tabulated on Figure 17 and are summarized below.

State of system-- The mineralogy, porosity and lack of monotonic gradients all indicate an open system during concretion growth.

Zonal theory-- The mineralogy and stable carbon isotope values can be interpreted to indicate sulfate reduction, bacterial fermentation and marine derived carbonate as sources of carbonate carbon in the Antrim concretions. However, the carbon isotope values can also be interpreted to indicate a combined carbonate carbon source of bacterial fermentation and decarboxylatin in the Antrim concretions.

The depth of burial is indicated to be shallow according to the mineralogy, physical characteristics and the carbonate carbon source of bacterial fermentation, sulfate reduction and marine derived carbonate. But the temperature indicated by the oxygen isotopes and the carbonate carbon source of bacterial

| Interpretation/ Type of Data | State of System | ZONAL THEORY | | | Time of Growth | Salinity | Temperature |
|---|---|---|---|---|---|---|---|
| | | Carbon Source | Burial Depth | Inorganic vs Organic | | | |
| MINERALOGY | OPEN | Presence of pyrite indicates sulfate reduction | pyrite<br>3 METERS<br>(Raiswell)<br>fedol<br>10 METERS<br>(Curtis) | organic activity | EARLY (pyrite) | | |
| PHYSICAL CHARACTERISTICS | Porosity OPEN | | Buried | Precompaction | | | |
| CHEMISTRY (TRENDS) | OPEN | | | | | No change during growth | |
| OXYGEN ISOTOPES | OPEN | | 83°C indicates 2500 m (Curtis, 1978) | | | Trend towards more saline in one conc. (#3) and a trend towards fresh in another conc. (Hathon's) | 83°C |
| CARBON ISOTOPES | | sulfate red.& bac.--><br>ferm. marine<br>or<br>bac. ferm. -------><br>decarboxylation | 10-1000m<br>1000-2500m | organic activity | | | |

Figure 17. Interpretations made from geochemical and physical data.

fermentation and decarboxylation can be interpreted to indicate a much deeper burial depth between 1000 and 2500 meters.

Time of growth-- The mineralogy and physical characteristics of the concretions in surface exposures indicate an early, precompaction time of growth.

Salinity-- The salinity of the pore fluid is not clearly indicated by the analyses performed on the Antrim concretions. A lack of a gradient in the sodium concentration may indicate that no salinity change occurred during concretion growth. The low concentrations of potassium and sodium in the concretions can be interpreted to indicate that the pore fluid salinity was low. The trends in the oxygen isotopes can be interpreted to indicate that a change in salinity did occur during concretion growth.

Temperature-- The oxygen isotope values indicate a pore fluid temperature of approximately 83°C. It is apparent that there are some inconsistencies in the data interpretation. These will be discussed below.

## COMPARISONS OF THE ANTRIM CONCRETIONS TO OTHER CARBONATE CONCRETIONS IN BLACK SHALES

Comparing the results of studies on carbonate concretions from various black shales may suggest a commonality in their origin and nature of growth. These comparisons can also be used to

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## COMPARISONS OF THE ANTRIM CONCRETIONS TO OTHER CARBONATE CONCRETIONS IN BLACK SHALES

Comparing the results of studies on carbonate concretions from various black shales may suggest a commonality in their origin and nature of growth. These comparisons can also be used to gain insights into the nature of black shale diagenesis. Earlier, four aspects that seem to characterize the nature of the geochemistry of concretions were summarized from past work. The results of this study on the concretions of the Antrim compare favorably to that summary in terms of bulk chemistry, of chemical trends from the center to the edge of the concretions and of their physical and geochemical relationship with their host shale. The following is a comparison of data:

Carbon isotopes--

| | |
|---|---|
| Irwin (1980) | edge: +2o/oo PDB; center; +9o/oo; edge: -2o/oo |
| Hudson (1978) | edge; -14.1o/oo; heavier toward edges |
| Galimov and Girin (1968) | edge: -96o/oo; center: -2.27o/oo |
| Hoefs (1970) | Cretaceous concretion: -3.3 to -43.2o/oo<br>Cretaceous shale: 0.9 to -5.3o/oo<br>Devonian concretion: 2.0 to -7.0o/oo<br>Devonian shale: -0.3 to -6.2o/oo |
| Curtis, <u>et al</u>. (1975) | edge: -2.0o/oo; center: 8.0o/oo; edge: -1.0o/oo |
| Sass and Kolodny (1975) | edge: -7.2o/oo; center: -7.6o/oo |
| Coleman and Raiswell (1981) | UA:edge: - 12o/oo; center: -13o/oo<br>UB:edge: - 13o/oo; center: -15o/oo |

Oxygen isotopes--

| | Coleman and Raiswell | | Hudson and Friedman | Irwin | Hoefs | Antrim #3 | Hathon (1979) |
|---|---|---|---|---|---|---|---|
| center | 2.3 | -8.9 | -0.7 | -1.56 | -9.0 | -9.2 | -6.4o/oo PDB |
| edge | -4.8 | -9.9 | -3.7 | -4.46 | -12.3 | -9.1 | -7.6 |

Porosity changes--

| | Coleman and Raiswell | Irwin | Hudson and Friedman | Curtis *et al.* | Antrim #3 | Antrim #7 |
|---|---|---|---|---|---|---|
| center | 77-87% | 80-95% | 78-95% | 73.2% | 81% | 81% |
| edge | | decrease | 63-76% | 10.2% | 60% | 69% |

Nature of system--

Irwin: closed

Hoefs: closed

Raiswell: open

Physical relationship with the surrounding shale--The Antrim concretions are similar to those studied by Raiswell (1971) in that in both cases the shale beds can be traced through the outer zones of the concretions and they bend around the concretions.

Black shale carbon isotopes--Similar to the Antrim, the concretions studied by Coleman and Raiswell (1981) and Hoefs (1970) contained carbon isotopes that were heavier than the values determined for the surrounding shales.

From the results of studies on carbonate concretions in black shales several conclusions as to the origin and nature of growth can be drawn:

1. The carbonate carbon source is a result of organic reactions in the shale.
2. The variable $\delta^{13}C$ values suggest different sources of

carbonate carbon among the concretions studied.

3. The porosity indicates early growth in uncompacted sediment.
4. The state of the system in which concretions grow can be open or closed.
5. The oxygen isotopes are lighter than what would be expected in carbonate precipitating from modern seawater.
6. The oxygen isotopes indicate a lightening of the pore fluid as concretion growth occurred.
7. The physical relationship between the shale and the concretions indicates early, precompaction concretion growth.
8. The oxygen isotopes of the shales are lighter than those of the concretions.
9. Pyrite was present throughout the concretions in one study (Hudson, 1976), and formed rims on concretions in another study (Coleman and Raiswell, 1981).

The data from the Antrim concretions and the previous studies can be interpreted to indicate that carbonate concretions in black shale are an early diagenetic phenomenon. They originate as a result of varying organic reactions in uncompacted sediment in a system open or closed to seawater, and as they grow the oxygen isotopes of the pore fluid are lightened.

## INCONSISTENCIES IN DATA INTERPRETATION

Zonal theory--For the Antrim, interpretations as to the source of carbon from carbon isotopes is difficult. Since the $\delta^{13}$ C values become heavier towards the edge (Table5, Figure15), in line with interpretations of $\delta^{13}C$ isotope trends in other concretions (Coleman and Raiswell, 1981; Hudson, 1976; Sass and Kolodny, 1975; Galimov and Girin, 1968), increasing contributions to the carbon pool are needed from either the process of bacterial fermentation or assimilation of primary marine carbonate material. However, sources of carbon from these processes may be inconsistent with the mineralogy of the concretion and the surrounding shale. Pyrite rims on the Antrim concretions indicate that sulfate reduction was a significant source of carbonate carbon in the concretions. However, the $\delta^{13}C$ values of carbonate formed as a result of sulfate reduction is -25o/oo PDB (Irwin, 1980) and the $\delta^{13}C$ values in the Antrim concretions average approximately -13o/oo. Thus, if sulfate reduction was the source of carbonate carbon, then the $\delta^{13}C$ values should be lighter and they should not become more positive toward the edge of the concretions. The $\delta^{13}C$ values should remain constant all the way across the concretions if sulfate reduction was the steady source, or the $\delta^{13}C$ value should become lighter if sulfate reduction was in increasing source of carbonate carbon in the concretions.

In order to achieve the absolute $\delta^{13}C$ values of the Antrim concretions there must have been another process besides sulfate reduction contributing carbonate carbon to bring the $\delta^{13}C$ value up from -25o/oo to -13o/oo. Both bacterial fermentation and the assimilation of primary marine carbonate could mix with sulfate reduction and cause the $\delta^{13}C$ values found in the Antrim concretions. Possible mixtures of these three sources to give a $\delta^{13}C$ value of -11o/oo, as in the Antrim concretions, are plotted on Figure 18. It is impossible to determine exactly how much carbonate carbon each process contributed to the Antrim concretions.

The association of pyrite with the ferroan dolomite is also inconsistent with the zonal theory. If sulfate reduction were the major source of carbonate carbon in the shale, as indicated by the pyrite and the $\delta^{13}C$ values, then the iron in the pore fluid should have been bonded with the reduced sulfur to form pyrite and not with the carbonate to form ferroan dolomite. The iron should not bond with the carbonate until the sulfur is depleted in the pore fluid. Thus, the Antrim concretions are mineralogically "inside out" with the ferroan dolomite on the inside and the pyrite forming rims on the concretions.

Temperature/Salinity--There are two inconsistencies in the interpretation of the oxygen isotope data: 1) the $\delta^{18}O$ values of the Antrim concretions are much lighter than would be expected of carbonate minerals precipitating form modern marine water, and 2) assuming normal seawater salinity and using the equation of Matthews and Katz (1977), the temperature of the pore fluid was calculated to be approximately 83°C. However, Hathon (1979) used vitronite reflectance and the burial depth of the Antrim Shale to determine a maximum temperature of 60°C for the Antrim Shale. Thus the temperature indicated by the oxygen isotopes is inconsistent with the independent data on the temperature of the pore fluids in the Antrim Shale.

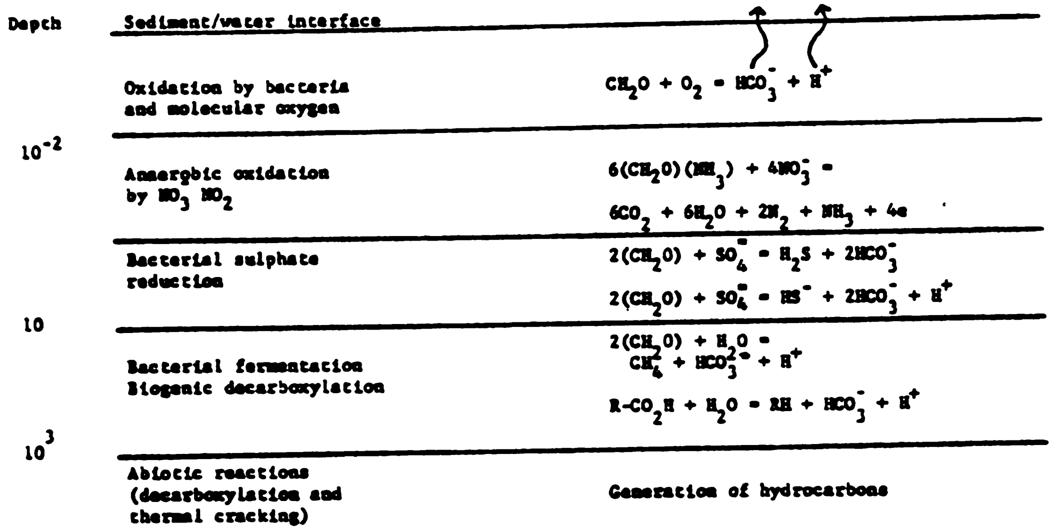


Figure 18. Expanded version of diagenetic zones within compacting marine mudstone sequences (Irwin, 1980).

## SPECULATIONS ON INCONSISTENCIES

A model of concretion growth is needed that accounts for the origin, the nature of growth and the inconsistencies in the data between the Antrim concretions and the zonal theory of black shale diagenesis. The physical characteristics and the pyrite rims on the Antrim concretions indicate early concretion growth at a shallow burial depth in the sediment. The stable carbon and oxygen isotope ratios can be interpreted to indicate later, more deeply buried conditions.

Oxygen isotope values--Any interpretation of the $\delta^{18}O$ values of the concretions must account for the trends in the $\delta^{18}O$ values and for the overall lightness of the $\delta^{18}O$ values of the Antrim concretions. There are several factors that can affect the isotope values, thus caution must be exercised when conclusions are drawn using the $\delta^{18}O$ values.

Speculations:

1. The experimental oxygen isotope values could be wrong. This speculation can be eliminated because the $\delta^{18}O$ values of concretion #3 are consistent with the values determined previously for an Antrim concretion (Hathon, 1979) and they are consistent with $\delta^{18}O$ values determined for carbonate concretions in other black shales (Coleman and Raiswell, 1981; Hoefs, 1970).
2. The trend of light oxygen isotopes towards the edges of the concretions has been attributed to an influx of meteoric water through the shales. The values may be primary (Hudson, 1976), so

that as the concretions grew, the $\delta^{18}O$ of the pore fluid changed, as suggested by Hathon (1979) for the Antrim. However, a meteoric influx is unlikely through sediment as impermeable as shale (Coleman and Raiswell, 1981). The $\delta^{18}O$ values also could be secondary, as a result of reequilibration with the meteoric water in the shale. This possibility can be eliminated for the Antrim because there is no evidence of recrystallization in the Antrim concretions (D. F. Sibley, 1981, pers. comm.).

3. The trend of light oxygen isotopes towards the edges of the concretions could be due to diagenetic reactions in the shale with depth as evidenced by samples from the Deep Sea Drilling Project (Sayles and Manheim, 1975). However, the mineralogy of the Antrim is different than the sediment from the DSDP which contains abundant volcanic material. Therefore, the diagenetic reactions caused by burial in the Antrim Shale probably would not be the same as those in the samples from the DSDP.

4. Local microenvironmental factors could effect the $\delta^{18}O$ values in the Antrim concretions. The precipitation of ferroan dolomite in a closed system could cause a gradient; however, the experimental data on the Antrim concretions has been interpreted to indicate that the system was open during concretion growth. Bacterial activity has been inferred to affect the local environment surrounding the concretions and thus affect the $\delta^{18}O$ values in the precipitated carbonate mineral (Coleman and Raiswell, 1981). There is no evidence as yet to eliminate this possibility.

5. The temperature of the pore fluid could have been 83°C, thus causing the light $\delta^{18}O$ values. This is unlikely because evidence

from the burial depth of the Antrim Shale and vitronite reflectance indicate a maximum temperature of 60°C for the shale. However, the Antrim is believed to be a source of natural gas in the Michigan Basin and unless the gas was generated biogenically, the temperature would need to have reached 150°C (J. H. Fisher, 1981, pers. comm.).

6. The Devonian seawater may have been isotopically lighter than modern seawater causing the overall lightness of the Antrim $\delta^{18}O$ values as suggested by K. C. Lohmann (1981, pers. comm.). The $\delta^{18}O$ values of the Antrim concretions indicate a $\delta^{18}O$ value of seawater of approximately -9.0o/oo PDB.

7. The overall light $\delta^{18}O$ values of the Antrim Shale and concretions may very likely indicate that the shale was deposited in a brackish to fresh water environment similar to the modern Florida coastline (D. T. Long, 1981, pers. comm.) instead of in a normal marine salinity environment.

Although various factors can affect the $\delta^{18}O$ values in the Antrim concretions, several can be eliminated using independent evidence. The possibilities that cannot be eliminated are local bacterial activity, the overall isotopic lightnes of the Devonian seawater and the possibility that the shale was deposited in a brackish water environment as opposed to a saline environment.

Zonal theory--It is difficult to formulate a geochemical model of concretion growth that accounts for the carbon source, the $\delta^{18}O$ values, the ferroan dolomite and the pyrite rims around the Antrim concretions. In the formulation of a model it can be assumed that either no recrystallization occurred or that recrystallization did occur in the Antrim concretions. There is no apparent evidence of recrystallization in the Antrim concretions (D. F. Sibley, 1981, pers. comm.); therefore, speculations assuming recrystallization are not discussed.

If no recrystallization occurred, then two possible models can be constructed. The first assumes that as the concretion grew, changes in the sediment and pore fluid surrounding the concretion caused changes in the concretion geochemistry according to the zonal theory of shale diagenesis (Curtis, 1978).

The zonal theory accounts for the characteristics of the Antrim concretions and the carbonate concretions in black shales in Europe studied prevously (Coleman and Raiswell, 1981; Irwin, 1980; Hudson, 1976) if concretion growth occurred at a shallow burial depth and during very early diagenesis of the shale. The physical characteristics of the Antrim concretions and the pyrite rims around the concretions are indicative of early diagenetic concretion growth at a shallow burial depth, according to the zonal theory. The presence of the pyrite strongly suggests that sulfate reduction played an important role in the concretion precipitation. The $\delta^{13}C$ vaues, however, indicate a mixture of carbon sources that can be interpreted to indicate a deeper burial depth than the physical characteristics imply according to the zonal theory. If the $\delta^{13}C$ values were controlled by sulfate reduction and primary primary marine-derived carbonate then the early diagenetic shallow burial model might be a good model for carbonate concretion growth. An expanded version of the zonal theory is depicted in Figure 18 (Irwin, 1980). This version details the shallow zones in the model of Curtis (1978; Table 1). According to the early diagenetic shallow burial model, concretion growth would begin in the anaerobic oxidation zone above the zone of bacterial sulfate reduction, and continue until further burial occurred causing sulfate reduction, pyrite precipitation and, thus, the end of concretion growth.

The second model, constructed by Coleman and Raiswell (1981), also assumes that no recrystallization occurred in the concretions. They suggested that the carbonate concretions in the Upper Lias black shale of northeastern England originated and grew due to sulfate reduction in the sediment. After growth the concretions were later infilled by carbonate derived from bacterial fermentation so that the concretions attained the heavier $\delta^{13}C$ values towards their edges. The assumption in this model is that the concretions retained some porosity that could be later infilled by heavier carbonate.

This model could help to explain the variations in $\delta^{18}O$ values found in the Antrim concretions. Each concretion might have experienced different amounts of infilling by later bacterial fermentation carbonate so that the early carbonate (with its unique oxygen isotope ratio) will be combined with the later carbonate (with its unique oxygen isotope ratio) in different proportions in each concretion, and will create the observed trends in each concretion. However, it is difficult to prove the assumption that the concretions retained pore space that could be later infilled with heavier carbonate.

Further study is needed. Carbon and oxygen isotopes are needed from a variety of carbonate concretions from the Antrim Shale. Samples to be analyzed should include portions of the massively textured and the bladed crystals in the concretions along with the samples of the surrounding shale. Paleosalinity analyses using the pyrite in the concretions and in the shale using the method of Berner (1979) would be useful in the determination of the original pore fluid salinity.

## CONCRETIONS AS CHEMICAL TAPE RECORDERS

Possible gradients across the concretions from the center to the outer edge include an increase or decrease in a specific ion concentration across the concretion or an increase or decrease in ionic ratios such as Ca:Mg across the concretion. Chemical trends could be due to changes in pore fluid composition during concretion growth.

Trends previously discussed are the increase in the $\delta^{13}C$ value, and the decreasing porosity and change in mineralogy from ferroan dolomite to pyrite across the concretions. These trends have been interpreted to show that the contribution of different sources of carbonate carbon changes, that the sediment porosity decreases and that an open system existed during concretion growth.

Because the Antrim concretions grew in an open system, any trends across them could be interpreted as changes in the chemical environment surrounding the concretions during concretion growth, as opposed to the effect of the partitioning coefficient of the particular component.

However, as discussed, the Antrim concretions analyzed, #3 and #7, do not contain any trends in carbonate geochemistry across their diameters. Thus, either no changes in pore fluid chemistry occurred during concretion growth, or changes in pore fluid chemistry were not recorded in the concretion geochemistry.

Physical evidence indicates that the concretions formed during the early diagenesis of the shale. Because the concretions were early diagenetic and grew in an open system, it is likely that no major changes in pore fluid chemistry occurred during concretion growth. Thus, although the concretions might have been able to record pore fluid changes in their geochemistry, no changes occurred for them to record as they grew. If the concretions were recrystallized after deep burial and compaction, anything they had recorded would have been wiped out by recrystallization.

## CONCLUSIONS

1. The carbonate concretions in the Antrim Shale are composed of ferroan dolomite and contain quartz and pyrite. The pyrite forms rims around the concretions, approximately 1 to 2 cm thick. The shale beds bend around the concretions, equally above and below, and the concretions are spherical or nearly spherical in shape. The weight percent of ferroan dolomite in the concretions ranges from 50-90% and decreases across the concretions from center to edge. There are no trends in the major or trace elements or the total organic content across the concretions. The oxygen isotope values of are approximately -9.1o/oo PDB and they do not vary systematically across the concretion. The carbon isotope values range from -10 to -13o/oo PDB, and they increase from the center to the edge of concretion #3.

2. The experimental data have been interpreted to indicate that the

concretions grew in a system open to seawater, and buried in the top 10 meters of the sediment. The carbonate contributing reactions were organic in nature. The concretions apparently grew before compaction occurred in the shale.

3. The geochemistry of the Antrim concretions is not consistent with the zonal thory of shale diagenesis. The carbon source is difficult to interpret from the carbon isotope values. The trend of increasingly positive $\delta^{13}C$ values towards the edge of concretion #3 is inconsistent with the pyrite rims on the concretion. The association of pyrite and ferroan dolomite is thermodynamically inconsistent. The $\delta^{18}O$ values of concretion #3 are lighter than what would be expected if the concretions precipitated from modern seawater.

The carbon isotope values can be explained the concretions formed at a very shallow burial depth in the sediment and gradually became buried until sulfate reduction caused pyrite precipitation. On the other hand, the $\delta^{13}C$ values could have been controlled by local microbiological activity.

The Devonian seawater could have been isotopically lighter than modern seawater producing the light $\delta^{18}O$ values in the concretions. Another possibility is that the Antrim Shale was not deposited in a marine environment, but in a brackish water, mangrove swamp-type or lagoonal environment.

4. The carbonate concretions in the Antrim Shale are similar in terms of their geochemistry to the concretions that have been studied in Europe. The concretions studied and the Antrim concretions have similar carbonate mineralogies; all were early diagenetic,

precompaction phenomena and they have similar trends in porosity and carbon and oxygen isotopes. The state of the system in which the concretions grew was not interpreted to be open, as interpreted in the Antrim concretions, in all cases, however. Although the other concretions studied also compared favorably to the zonal theory, they shared the same inconsistencies with the theory as the Antrim concretions.

5. The Antrim concretions were not used to interpret changes in pore fluid trace element chemistry during diagenesis of the shale because no trace element trends were present across the concretions. The concretions were used to interpret changes in the stable isotopic chemistry of the pore fluid during diagenesis of the shale.

# APPENDIX A

# APPENDIX A

Titration method for organic carbon (Gaudette, et al., 1974)

$$\% \text{ Organic Carbon} = 10(1-T/S)(0.336N)(0.003)(100/W)$$

T = Sample titration, ml ferrous solution
S = Standardization blank titration, ml ferrus solution
0.003 = 12/14,000 = meq weight of carbon
N = Normality of $K_2Cr_2O_7$
10 = Volume of $K_2Cr_2O_7$ in ml
W = weight of sediment sample in grams

Reagents:
85% $H_3PO_4$
Solid NaF
concentrated $H_2SO_4$

Standard 0.336N $K_2Cr_2O_7$ solution: Dissolve 49.4 g $K_2Cr_2O_7$ in water; dilute to 1 liter.

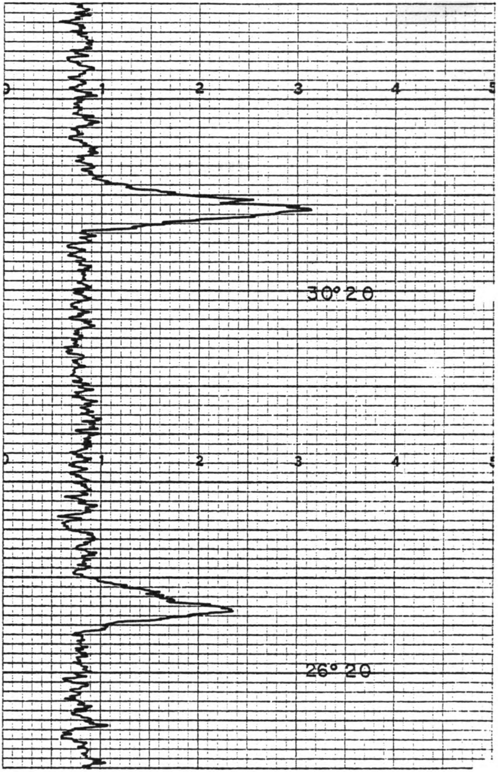
0.5 N Ferrous solution: Dissolve 196.1 g of $Fe(NH_4)(SO_4)_2 \cdot H_2O$ in 800 ml water containing 20 ml concentrated $H_2SO_4$; dilute to 1 liter.

Dipehylamine Indicator: Dissolve approximately 0.5 g of reagent grade diphenylamine in 20 ml of water and 100 ml of concentrated $H_2SO_4$

Procedure:

1. Place a 0.2 to 0.5g dried and sieved (10 mesh, ASTM) sediment sample in a 500 ml Eelenmeyer flask.
2. Exactly 10 ml of 0.336N $K_2Cr_2O_7$ solution is added by buret and mixed by swirling the flask.
3. Twenty ml of conc. $H_2SO_4$ are added (by buret) and are mixed for about 1 minute.
4. Allow mixture to stand for 30 minutes.
5. Run a standardization blank with each set of samples.
6. After 30 minutes, dilute the solution to 200 ml with distilled water.
7. Add 10 ml 85% $H_3PO_4$, 0.2 g NaF and 15 drops diphenylamine indicator to the flask.
8. Titrate solution with 0.5 N ferrous ammonium sulfate solution. The color will progress from an opaque green-brown to green upon the addition of approximately 10 ml of ferrous solution. The color will continue to change upon titration to a bluish-black grey; at this point the addition of 10-20 drops of ferrous solution will shift the color to a brilliant green giving a one-drop endpoint.

# APPENDIX B



Appendix B. X-ray diffraction pattern of dolomite (30.86$^{\circ}$2θ) and quartz (26.67$^{\circ}$2θ) in Antrim concretion 7.

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