

GENESIS OF CARBONATE CONCRETIONS

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IN  
THE UPPER LUDLOWVILLE, MIDDLE DEVONIAN  
OF  
ERIE COUNTY, NEW YORK

By  
FRANK WILLIAM JORDAN, B.A.

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AUTHOR: Frank William Jordan, B.A. (Rice University)

SUPERVISOR: Professor J. R. Beerbower

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SCOPE AND CONTENTS: (Abstract) Concretions in a zone about 4 m. below the Tichenor Limestone formed just below the sediment water interface. Their growth was initiated about an organic-rich fossil cluster and was probably completed before they were more than 5 to 8 m below the sediment surface. Chemical products of organic decay, notably bicarbonate ions and ammonia, diffused outward, raising the pH and precipitating calcite from connate waters already nearly saturated with respect to calcium carbonate.

These conclusions derive from the shape of the concretions, from their relation to the enclosing shales, and from their overall structure, particularly the position of pyritic fossil clusters. The relative volumes of soluble material (calcite) in the concretions are consistent with relative pore volumes through the upper 5 m. of recent, fine-grained, clayey sediments. The postulated genetic sequence agrees with recent work on carbonate diagenesis. Restriction of the concretions to discrete layers was most probably due to a widespread combination of high rates of organic productivity, high rates

of sedimentation, and low rates of water circulation, that lasted a short period of time and resulted in the rapid burial of much undecomposed organic material.

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## INTRODUCTION

### General

A concretion must represent some sort of localized chemical anomaly which brings about precipitation of a binding agent or cement that does not form in the surrounding sediments. In fine-grained, marine shales, where concretions are typically found in thin, widespread layers (for example, those observed in the Hamilton Group of Western N. Y., those reported from the Fox Hills Formation of South Dakota by Waage, those in the Ohio Shale discussed by Clifton, and numerous others), such chemical anomalies must have occurred for short periods of time over large areas. The problems to be investigated here are: a) the time of existence of these chemical anomalies relative to the deposition of the enclosing sediments, and b) the factors, chemical, biological and physical, governing their existence.

### Stratigraphy and Location

A concretionary zone near the top of the Wanakah Shale member of the Ludlowville Formation, Hamilton Group, was chosen for this project. This zone has a conspicuous, extensive outcrop in the bed of Cazenovia Creek, just west of the Northrup Road bridge at Spring Brook, in Erie County, New York, about 10 miles south-east of Buffalo. Here the

zone lies about 4 m below the Tichenor Limestone, the uppermost member of the Ludlowville. Other outcrops at approximately this stratigraphic level have been observed from the Lake Erie shore near Highland-on-the-Lake to a location near Darien Center - a distance of more than 30 miles. A stratigraphic section of the Hamilton Group of Western N.Y., reproduced from Buehler (1966), is shown in Fig. 1. Figs. 2 and 3 show the location of the general area and of the major outcrop studied.

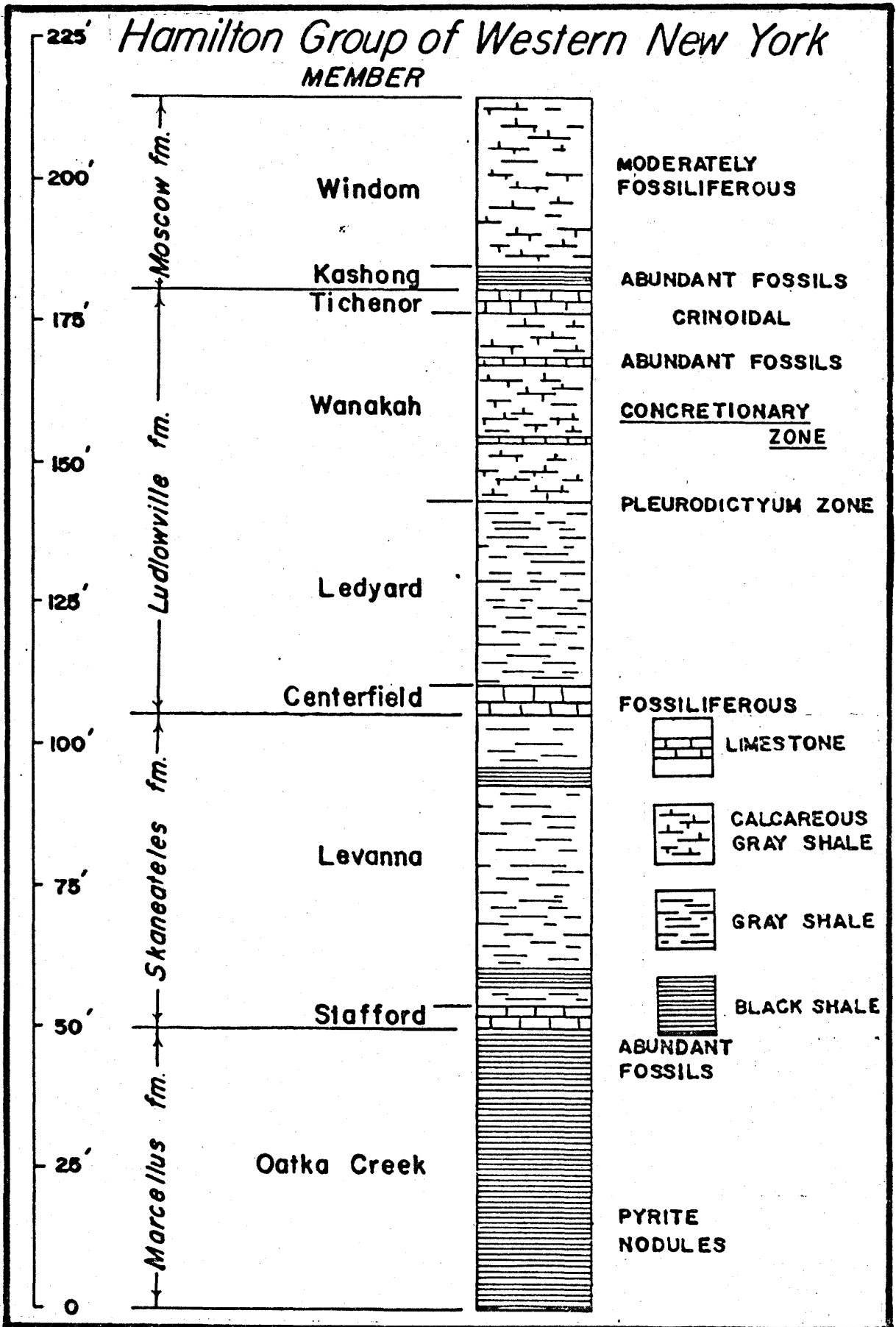


Fig. 1 Stratigraphic Section, adapted from Buehler, 1966.

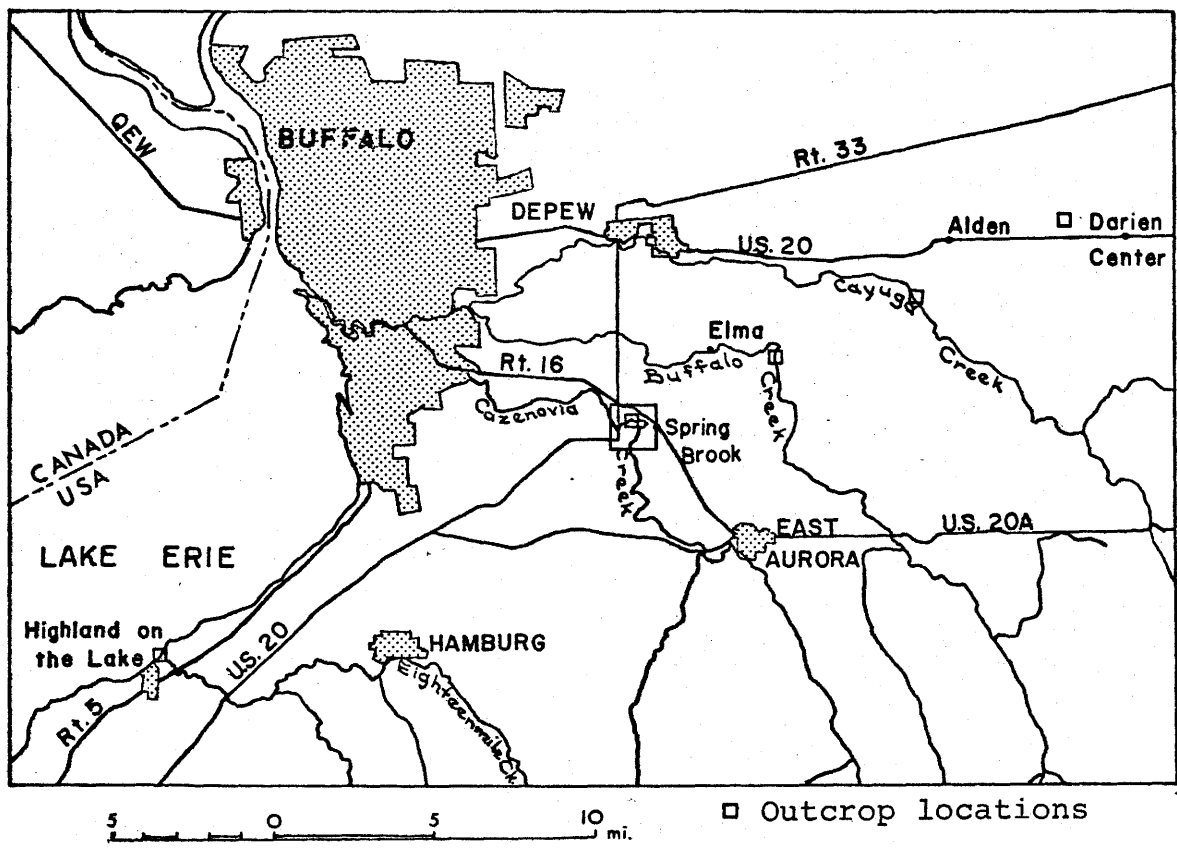


Fig. 2. Location map of outcrop areas.

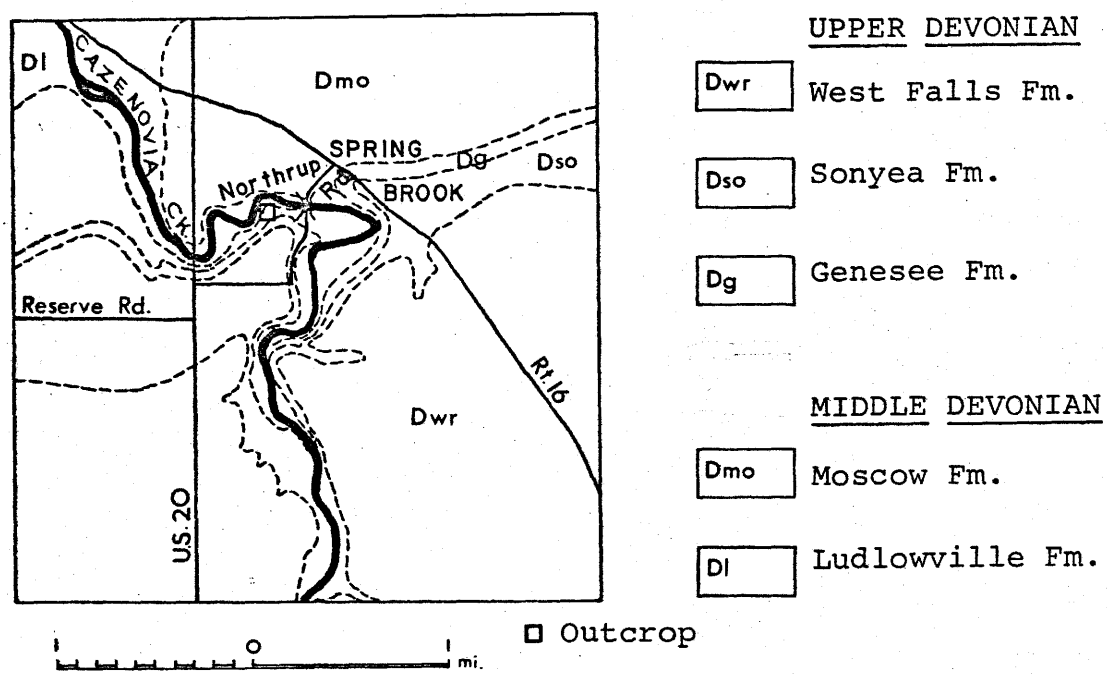


Fig. 3. Enlarged map of the major outcrop area, near Spring Brook, N.Y. showing surrounding bedrock geology.

## DESCRIPTION OF CONCRETIONS

The concretions in this zone vary in length from about 10 cm to somewhat more than 1m . Width is commonly about 2/3 the length, and thickness about 1/3 the length, ranging from a few centimeters to about 1/3 of a meter. Lengths of a half to one meter are most common. Shape in plan view is basically ovoid, with considerable deviation therefrom. The upper surfaces of the concentrations are flat to irregularly rounded. The lower surfaces are always rounded.

Each concretion includes part of a cluster of pyritized fossils, 1 to 2 cm thick and extending 10 to 20 cm or more beyond the lateral boundary of the concretion. Clusters of fossils also occur stratigraphically above and below the concretions for a few tens of centimeters, but these contain only scattered pyrite--less than a tenth as much as those in the concretions. Much of the pyrite is in the sediment immediately surrounding and within the fossils. The rest coats internal shell surfaces, internal structures such as brachiopod spiralia and cephalopod septa, and forms a layer on the sediment that infiltrated the shells. It also occurs as internal molds of some cephalopods, gastropods, and pelecypods, wherein the original shell material has been dissolved. Scattered

fossils in the same zone but not in the concretions or in the fossil clusters show the same type of pyritization.

Cracks that are wider at the top and more abundant toward the lateral boundaries of the concretions occur in their upper portions. These cracks have been filled with a dark-colored, sparry calcite, similar in appearance to spar calcite found in fossil cavities not otherwise occupied by pyrite or sediment. Frequently a lip of concretionary material, 5 to 10 cm thick, extends beyond the major portion of the concretions, as illustrated in Fig. 6. The fossil layer extends through this lip and beyond its boundaries. Where the lip exists, the above-mentioned cracks are most common near the margin of the main body of the concretion.

Within some of the concretions may be found a second system of cracks, somewhat similar in appearance to those found in septaria. These cracks are interconnected and approximately vertical, but never horizontal. Their separation in the vicinity of the fossil layer and their extent above and below this layer, while limited and fairly consistent across the width of the concretions, is largely dependent on concretion thickness. They terminate at the surface of a concretion only when this surface is coincident with one of the surfaces of the enclosed fossil bed.

In one portion of the Spring Brook outcrop the concretions described above are overlain by a larger type of

concretion, much more elongate and somewhat rounder in cross-section. They lack the spar-filled cracks and the distinct fossil layer of the former type, but do contain scattered fossils and some pyrite. Where the two types occur together, the lower grade directly into the upper, with no shale partings separating them; yet they are apparently the result of two separate stages of formation. The former type provides the basis of this study.

The long axes of all the concretions are essentially parallel and oriented approximately  $35^{\circ}$  east of North. This trend is consistent over the 30 miles of outcrop studied. Figs. 7 and 8 illustrate the parallelism, as well as the general appearance of the concretions in the Spring Brook outcrop.



—  
10 cm

Fig. 4 A. Upper surface of concretion "LC-E" in place in the shale. Brunton compass is oriented N35°E.



—  
10 cm

Fig. 4 B. Side view of the same concretion, removed from the shale and viewed upside-down. The N-E end is shown facing left.





10 cm

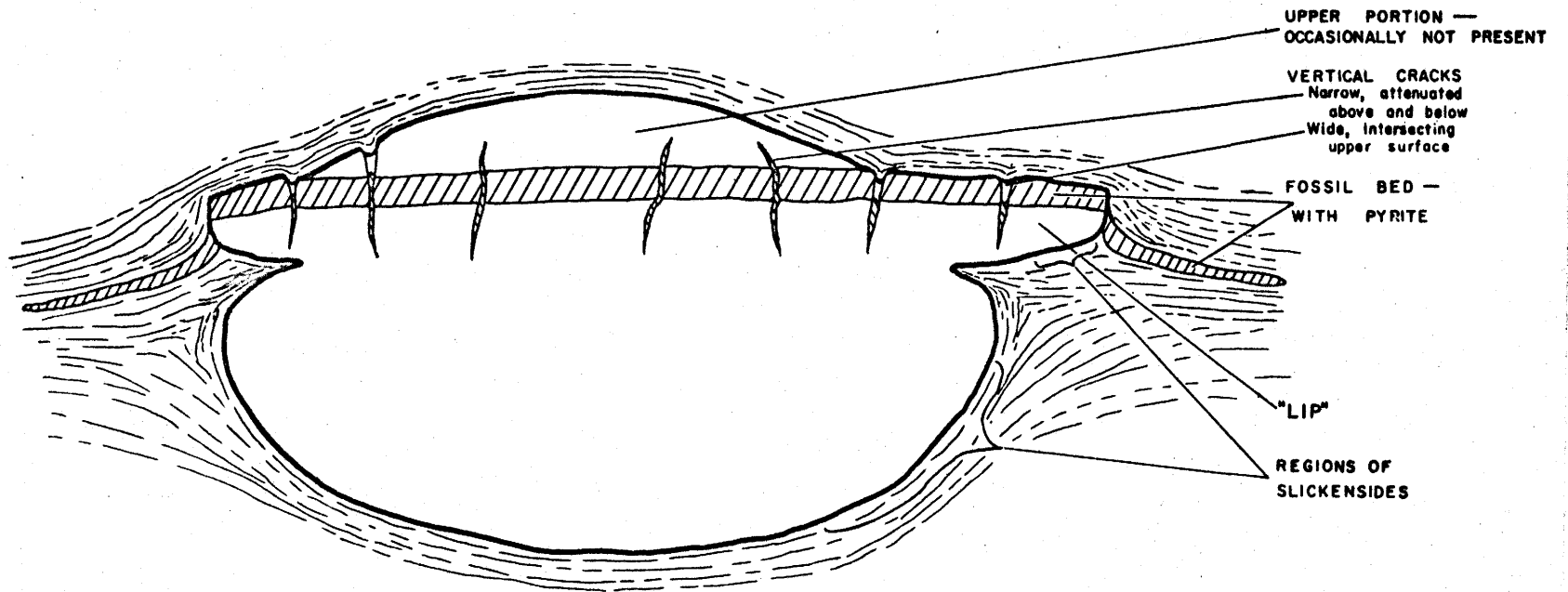
A



10 cm

B

Figs. 5 A&B Two examples of concretions found in the zone studied. In Fig. 5 A, the tape-measure is in feet and inches, the Brunton compass is oriented due north. In Fig. 5 B, the tape is in meters, showing 10 cm intervals, and the concretion is oriented so that left is  $N35^{\circ}E$ .



Typically 10 to 20 cm.

**GENERALIZED CONCRETION**  
 SHOWING DRAPE OF SURROUNDING SHALE

Fig. 6



Fig. 7. Cazenovia Creek, Spring Brook outcrop, facing roughly S-W, showing the general appearance of the outcrop and the elongate nature of the concretions.

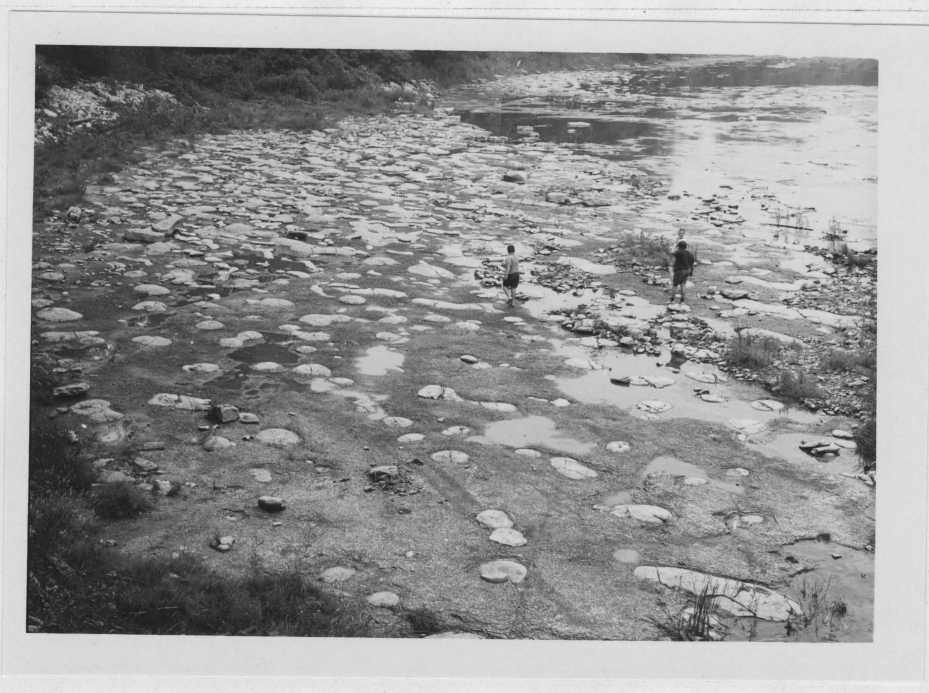


Fig. 8. Spring Brook outcrop facing roughly N-E.

## TIME OF FORMATION

### General

The problem of time can be approached from two related points of view: When did the concretions form? How long did the process take? Restating the combined questions in terms of the surrounding sediment: At what depth below the sediment-water interface did the initiation and termination of calcium carbonate precipitation take place? According to the literature the relative ages of concretions vary from syngenetic, that is, formed as the included sediments are deposited (eg. Tarr, Weeks) to metamorphic (eg. Barth, Ramberg). Formation after deposition but prior to consolidation (eg. Stopes & Watson, Daly) and formation after consolidation but prior to metamorphism or weathering (eg. Sheldon) are termed respectively early and late diagenetic. These examples were taken from Crimes, who presented an example of early diagenetic concretions and discussed the general subject of terminology and its development.

### Relative Compaction:

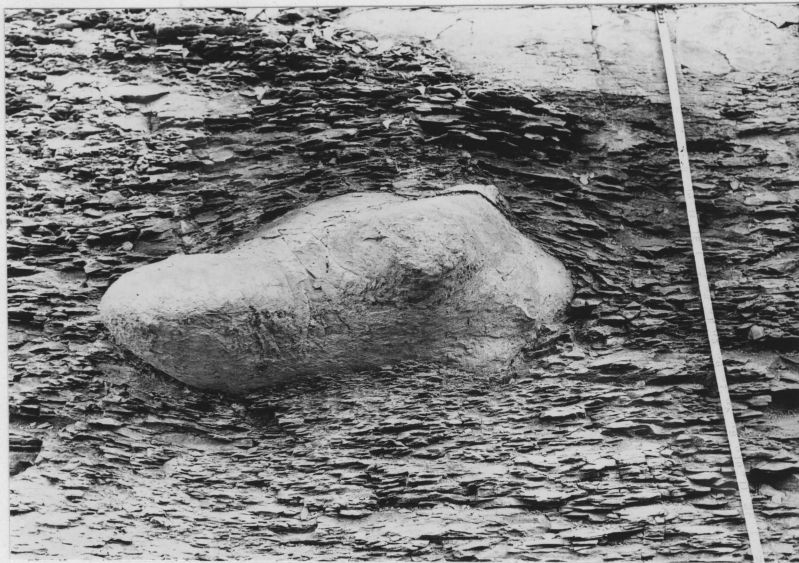
The drape of shale fissility around the concretions (Fig. 9) can have two opposing interpretations: a) Fissility was draped around pre-existing concretions. b) The shale

layers were forced apart by the growing concretions due to the exclusion of sediment particles by the growing calcite crystals. Evidence strongly indicates the former interpretation. First, original sediment is included in the concretions. Second, if the latter situation had obtained, some sediment and perhaps fossil material should have accumulated around the margins of calcite crystals during their growth. No evidence has been found, either microscopically or macroscopically, of such accumulations or of any segregation of original sediment from secondary calcite crystals. Third, slickensides around the lateral margins of the concretions indicate that the shale was compressed around the already-formed concretions. Therefore, the concretions must have formed prior to the majority of compaction, and original sediment must have been more or less uniformly included in the growing concretions and not pushed aside to any significant extent.

If the concretions did form late in the compaction process, any fossils found within them should show a degree of crushing and distortion similar to that of the fossils found in the surrounding shales. No particular evidence of distortion of concretionary fossils has been found, and much of the shell material still has a remarkably fresh appearance. This suggests that the concretions formed early enough to protect the enclosed fossils from extreme compressive forces,

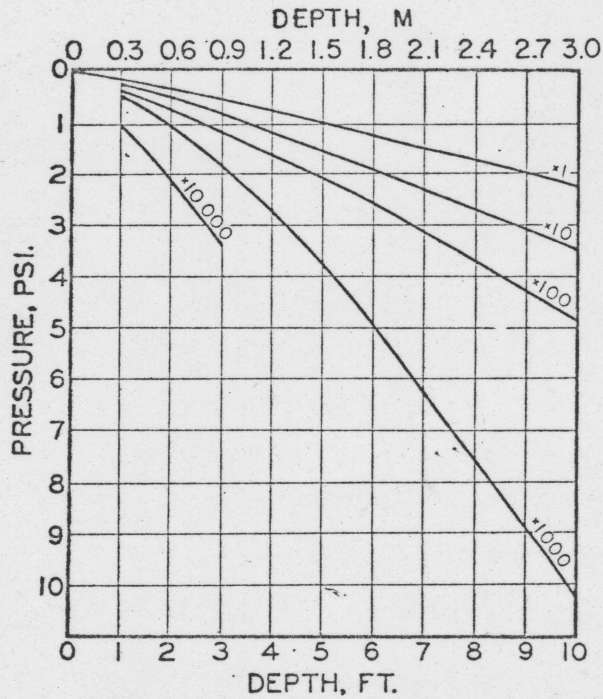
although such a conclusion is of questionable validity due to the difficulty of observing whole fossil specimens within a concretion. Outside the concretions but at the same level, the abundant specimens of the brachiopod Athyris spiriferoides are typically articulated and filled with calcareous sediment and/or spar calcite to give the same cross-sectional appearance as those specimens found in the concretions. These fairly large fossils (3 to 4 cm wide) can easily be extracted from the shale and, in contrast to shells having little or no internal carbonate, show no apparent distortion except at the very thin shell margins. If precipitation of calcite within them took place at the same time as the precipitation of concretionary calcite, then their lack of distortion strengthens the above argument for early concretionary formation.

An attempt to estimate, from fossil deformation, a maximum depth of burial at the time of formation would require, first, a working relationship between depth of burial and percent distortion. In the present case, a compactive pressure as low as one atmosphere might have been adequate to produce noticeable distortion in mature Athyris shells. According to the pressure-depth relationship for fine-grained sediments given by Weller (p. 287), calcite precipitation would thereby have taken place within about 15 m (50 feet) of the sediment-water interface (Fig. 10). A reasonable estimate, however, is still dependent on the recognition and measurement



10 cm

Fig. 9. A freshly weathered cliff face, showing shale drape about a concretion.



Graph showing approximate relations between pressure and depth. Figures of both scales should be multiplied by factor shown at end of segment of curve.

Fig. 10. From Weller, p. 287.

of distortion in Athyris shells, requiring, secondly, that one compare them with definitely undistorted shells, ideally with live ones. In practice, the least distorted specimens available are those that have been internally filled with calcite -- the very ones in question.

From the conclusion that original sediment was included in the concretions, it follows that the concretions record the degree of compaction (percent decrease in volume) of the shale at the time they were formed. Likewise, the shale should record the degree of its compaction at the time of final lithification. If the latter can be estimated and used in determining the former, and a relationship between degree of compaction and depth of burial can be obtained, then it should be possible to make a reasonable estimate of the depth of the concretions below the sediment-water interface at the time they formed. The thickness of sediment deposited above the concretionary zone can be estimated at 800 (Tesmer) to possibly 1,500 m (2,500 to 5,000 feet). Referring to the graph in Fig. 12 (Weller, p. 288) of unit compaction as a function of depth of burial, and assuming that lithification of the shale took place beneath the above-mentioned thickness of overburden, total compaction of the shale would be from 73 to 77%. Compaction at the time of concretionary formation relative to total compaction should be reflected in the ratio of the vertical distances between two marker beds in the shale and between the same two beds



where they pass through a concretion. The fossil layer, where present, was taken as one such bed. A suitable, second bed was never found, however, and the fossil layer was too thin and innately variable to use its upper and lower surfaces. Nevertheless, a level of equilibrium could be found in some concretions, usually near the widest part and typified by a lack of slickensides, wherein no movement relative to the shale seemed to have occurred. In other words, a bed through this level would show no offset or drape where it entered the shale. Measurements between this level and the fossil bed (see Fig. 11) indicate that the amount of compaction subsequent to concretionary formation was about 3

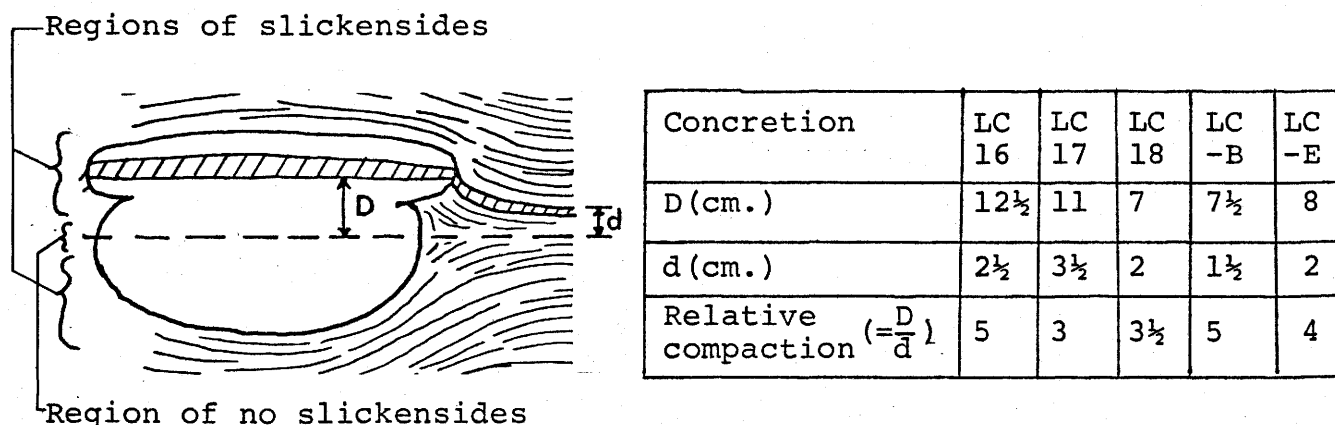


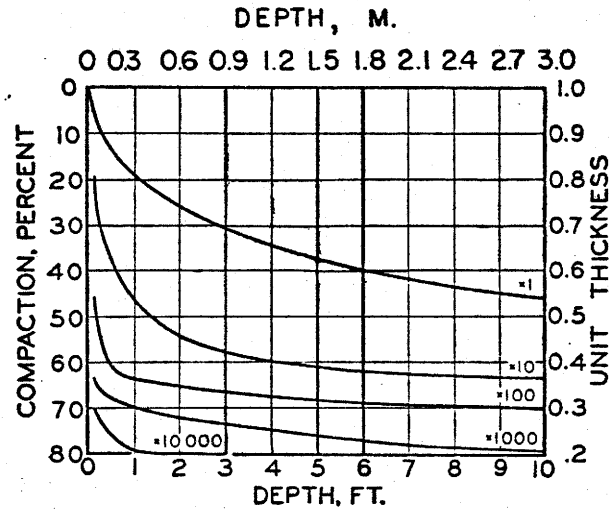
Figure 11

Diagram of a concretion and the surrounding shale, showing the determination of relative compaction as the ratio of D to d. D is the distance between the fossil layer within the concretion and a level at which there was no relative movement, during compaction, of the concretion with respect to the shale; d is the distance between the same level and the fossil bed outside the concretion.

to 5 times the amount up to the time of their formation. A relative compaction factor of 5 means that the sediment at the time of concretionary formation occupied 5 times the volume it presently does. The shale now occupies 23% of its original, depositional volume (77% total compaction); 5 times 0.23 is 1.15, indicating that the concretions formed when the sediment occupied 1.15 times its original volume. This impossible result can either be attributed to the inaccuracies of this rather approximate method, or it can be interpreted to mean that the Devonian sediment had a higher initial porosity than the 80% used in Weller's calculations. In either case, this result represents an upper limit that indicates the possibility of very early formation. The lower relative compaction estimate of 3 indicates concretionary formation at 69% of original volume (31% compaction), corresponding to a depth of about 1 meter (Fig. 12) below the sediment-water interface. The variation of these results very likely records, beyond the inaccuracies of this method, different times of concretionary formation.

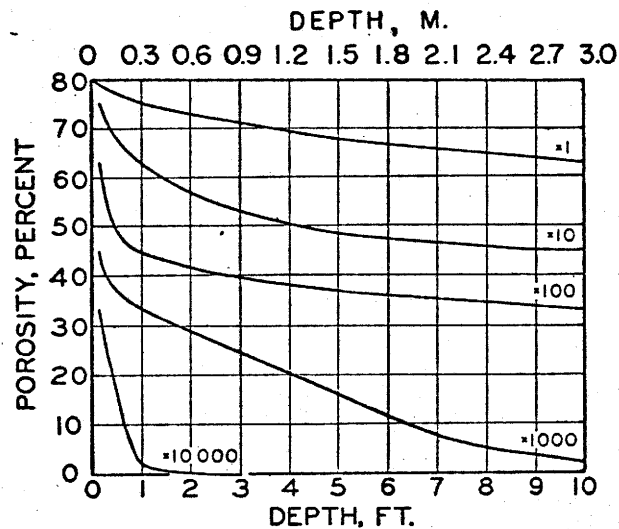
#### Measurement of Porosity

The porosity of a fine-grained sediment decreases with depth below the sediment-water interface due to compaction and the resultant squeezing out of pore fluids (Fig. 13, after Weller, p. 276). If calcite replaced all the



Graph showing approximate relations between per cent compaction or unit thickness and depth of burial.

Fig. 12. From Weller, p. 288.



Graph showing approximate relations between porosity and depth of burial. Curves are drawn to depth scale that increases by factor of 10 for each successively lower curve. To determine depth for any curve, multiply figures of lower scale by factor that appears at end of that curve.

Fig. 13. From Weller, p. 276.

water in the pore spaces, then percent porosity at the time of formation should be equal to the volume percent of secondary calcite in the concretions. Texture of the concretions in thin-section indicates that calcite precipitated between and around the sediment particles to fill most or all of the pore space. (The actual relationship between crystals of calcite and sediment particles cannot be optically resolved, even under high magnification - see photo-micrograph in Fig. 14. It is possible, though, that calcite nucleated around individual particles of sediment.) If the pore space was not all filled with calcite, then the porosity estimate derived from percent calcite will be lower than original porosity. A correction can be made for part of this error using present porosity of the rock .

Volume-percent calcite was taken from the weight loss of a sample after treatment in dilute (5%) HCl, as described in the Appendix. Insoluble secondary minerals such as pyrite and celestite would result in lower estimates of porosity, while dissolution of fossil material and exchange of  $H^+$  for heavier cations previously on the clays would give erroneously high results. Errors due to exchange reactions must be endured but are probably small; they would tend, however, to cancel errors due to incomplete filling of pore spaces by calcite. To minimize these effects, samples were chosen to be as nearly free as possible of fossil specimens

and secondary minerals other than calcite. Various locations within a concretion were sampled to determine areal variation and in particular to test the hypothesis that outer portions were formed at later times, when the porosity of the included sediments was lower. If this effect is observed - as an outwardly decreasing trend in calcite percentages - then the earliest-formed portion of the concretion should be marked by the highest calcite values.

Summarized results are presented on the cross-sectional view of a portion of a generalized concretion shown in Fig. 15, with the values of volume-percent calcite given in the appropriate sample locations. Referring to Weller's graph (Fig. 13), the highest calcite values, about 80%, are seen to correspond to the maximum porosity of a freshly deposited, fine-grained sediment. If the porosities of Weller's sediment and those of the Devonian sediment are similar, and if the previous line of reasoning and the various assumptions are all correct, then the concretions must have begun to form very shortly after the included sediment was deposited.

Considering, next, that porosities range downward to below 60%, it follows that formation of the concretions continued for some time. Reference to Fig. 13 indicates that they were on the order of 5 to 8 m below the sediment-water interface when the precipitation of concretionary calcite finally ceased. The distribution of porosities throughout an

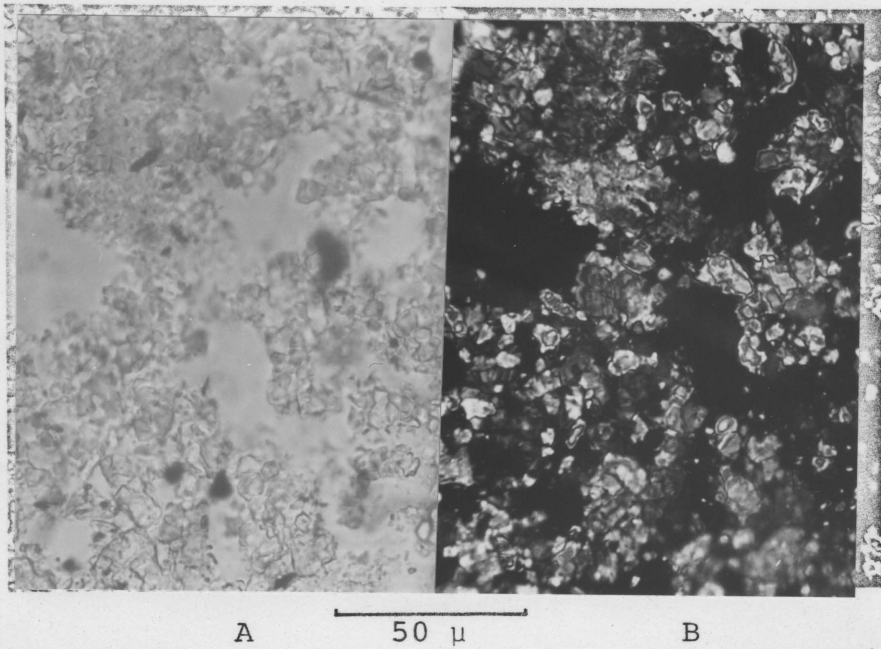


Fig. 14 A&B. Photomicrograph of a thin-section of concrectionary material, showing clusters of calcite crystals separated during preparation. Fig. 14 A - Plane-polarized light. Fig. 14 B - The same area under crossed Nicols.

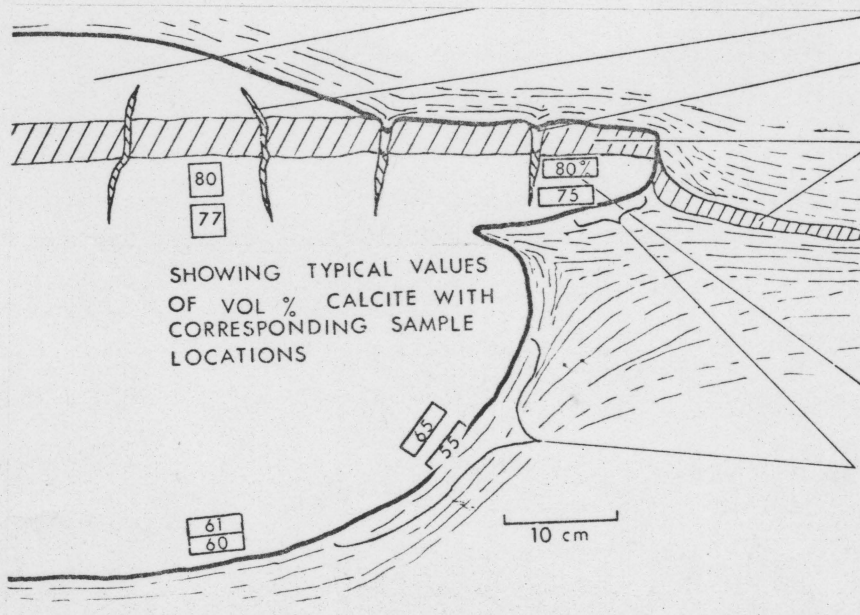


Fig. 15. A portion of the "Generalized Concretion" of Fig. 6, showing volume-percent calcite at various locations throughout the concretion. Data from concretion LC-E.

individual concretion suggests that portions immediately surrounding the fossil layer were the first to form and that succeeding growth proceeded downward therefrom. Further observation shows that the "lip" mentioned above formed quite early and quite rapidly and that the main body of the concretion formed more slowly, in what might be termed a second "stage" of growth. The thickness of the first stage over the width of the concretion was approximately the same as that of the lip where it occurs (about 5-10 cm). Several factors point to this condition of the first stage:

a) a consistency of calcite percentages across the concretion, b) a wedge of shaley material where the main portion of the concretion joins with the lip, and c) the termination of systems of cracks found within the concretion at a consistent level below (and above) the fossil layer throughout the width of the concretion. Formation of the first stage occurred while the concretion was within about 1/3 meter of the sediment-water interface.

The second stage, roughly centered on the first stage, grew downward and occasionally upward from it and was completed at a depth of no more than 8 meters below the sediment-water interface. One would expect this continuous, regular addition of calcium carbonate to result in a rather smoothly rounded form built around the original locus of precipitation. The observed form, however, though fairly smooth and rounded,

appears to be flattened on the lower surface and extended or bulged around the sides. This form is attributed to a vertical compression during compaction with resulting lateral bulging. The absence of cracks in the lower portion of the concretions suggests that this sort of distortion took place by means of plastic flow of concretionary material. Such plastic flow might have taken place while the concretions consisted of minute crystals of calcium carbonate that were not yet completely bound together. A wedge of uncalcified sediment was, in many concretions, caught between the lip and the bulge and very tightly compacted.

Of the two vertically oriented sets of spar-filled cracks in the first stage, one is readily accounted for: The first stage was usually above the bulk of the concretion and extended further laterally. As a consequence, compactive pressure was unevenly balanced from below and tended to force the edges downward, creating cracks that are widest at the top. Sediment was squeezed into the upper parts of these cracks (flow lines may still be seen in the sediment) and was later calcified (Fig. 17). The lower portions of the cracks contain spar calcite that merges into the micrite above. The existence of these cracks and their termination at a constant level, roughly the level of the lower surface of the lip, is taken as evidence that the first stage was fairly solid at a time when the second stage was still capable of plastic deformation.



This observation and the requirement that formation of a large part of the second stage antedate the cracks places their time of formation near completion of the host concretion.

The second set of cracks is also vertically oriented, spar-filled, and of the same downward extent. These, however, have a smaller separation -- seldom over a millimeter or two. They tend to be centered about the fossil layer and die out upward as well as downward, unless the upper surface of the concretion coincides with the upper surface of the fossil layer. The origin of this set is problematical, but two possibilities can be considered. First, the cracks could be due to shrinkage centered about the fossil layer. There is no immediately apparent reason, however for shrinkage to have occurred at this one level in the concretion and not throughout its entirety.\* Shrinkage cracks would form perpendicular to the direction of shrinkage, thus presumably parallel to all outer surfaces of the concretions, and in greatest number perpendicular to the long axis, the direction of maximum shrinkage. Horizontal cracks should also have formed except for compactive forces. Second, the concretions were thickest in the central region, resulting in maximum compactive pressure there. Pressure could have been partially equalized by outward spreading

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\* Berner (1968) suggests a possible reason for shrinkage, but it may not be applicable here, as will be discussed below.

of the entire concretion in response to vertical shortening of the central region. Spreading of a solid portion of the concretion could only take place through the formation of tension cracks oriented perpendicular to the direction of spreading. The predominant orientation of the observed cracks is parallel to long axes of the concretions, and thus perpendicular to the expected direction of maximum spreading. Near the extremities of the concretions, expectation and observation differ from the above. Here, lateral spread is expected to increase the circumference, resulting in cracks perpendicular to the edges, particularly near areas of increased curvature. Such cracks are, indeed, found, but they seldom extend very far into the concretion or all the way to the edge, pinching out instead in both directions. The confining pressure of the surrounding sediments might have been sufficient to bring about the small amount of flow necessary to prevent these cracks from reaching the very edge. This type of crack development supports the suggestion, already presented, that one portion of the concretion had already become fairly solid while the rest was yet capable of some plastic deformation.

According to the above scheme, the second set of cracks must have formed at about the same time as the first. In fact, they are often seen to merge, with no apparent evidence as to which came first. Finally, the minute calcite

grains became sufficiently bonded together to form concretions that could fully withstand compaction, which left its mark in the form of slickensides, and sledge hammers, wielded by enthusiastic geologists.

#### Time in Years

Thus far, time has been considered as a depth of burial below the sediment-water interface. The number of years required for this burial was a function of the sedimentation rate. In Fig. 16 A is shown the calculated relationship between time (in years) and the rate of sedimentation of uncompacted sediments for a concretion buried to 5 m. The mode of burial of the brachiopod Athyris spiriferoides found in the concretionary zone suggests that one millimeter per year might be a representative rate for the sediments in this horizon. This follows from the observation that many of the Athyris specimens in the shale adjacent to the concretions are found in what is taken as the life position, that is, the beak, or posterior end, projects downward into the shale, and the plane of commissure is inclined at a nearly vertical angle. To have maintained such an unstable position from the time of death through burial and preservation would require that a brachiopod be supported by the sediment at the time it died. That is, it would have been submerged within the sediment to a depth of about 1/3 its length of 2-1/2 to 3-1/2 cm. This suggests that the shell was supported by about one cm of sedi-

ment, which most likely built up around it by continual deposition of sediment while the brachiopod was still supported by a pedicle. It is doubtful that these organisms lived as long as 10 years (eg. Rudwick, or work mentioned by Williams and Rowell) so that a sedimentation rate of 1 cm/10 yr, or 1 mm/yr, derived in this manner can be taken as a probable minimum. This gives an age of 6,000 to 7,000 years for the formation of the concretions. Fig. 16 B shows age in years as a function of burial depth for a sedimentation rate of 1 mm/yr.

#### A Correction Factor

If the approximately 20% calcite in the shale surrounding the concretions was deposited in the pore spaces of the sediment at some time much later than the time of concretionary formation, then a compaction factor for the shale of about 1:4 is indicated. Appeal to Weller's graph of porosity vs. depth of burial (Fig. 13) indicates that such an event could have taken place beneath a 1200 meter (4000 foot) column of sediment. This figure for relative compaction is consistent with the 1:3 to 1:5 estimate derived from bedding drape around the concretions, 1:5 being a necessary maximum for any sediment of 80% original porosity or less. Eight hundred meters was presented above as a probable minimum for the thickness of sediment deposited above the Ludlowville Shale and 1,600 m as a more likely figure. The figure de-

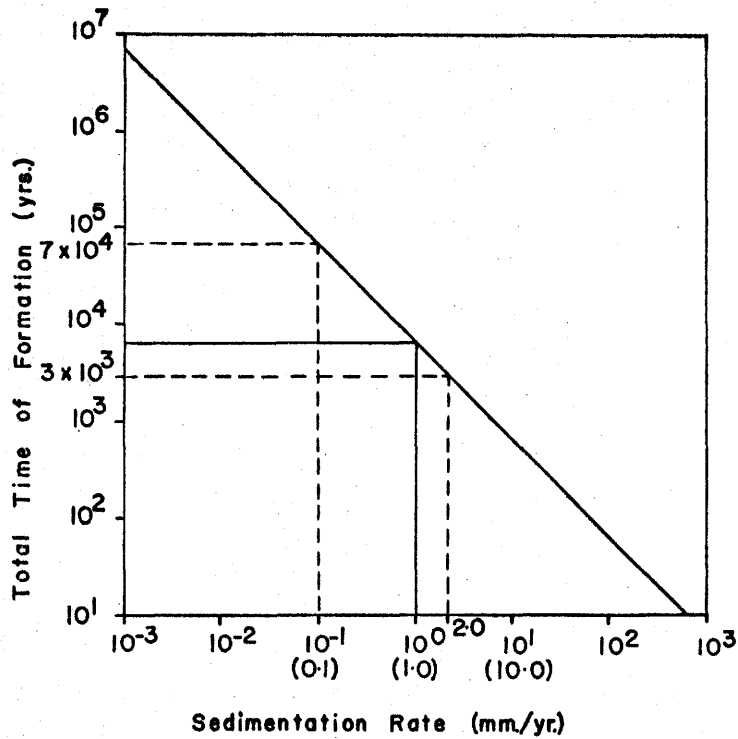


Fig. 16 A. Age in years as a function of sedimentation rate, for a concretion completely formed at a depth of burial 5 m.

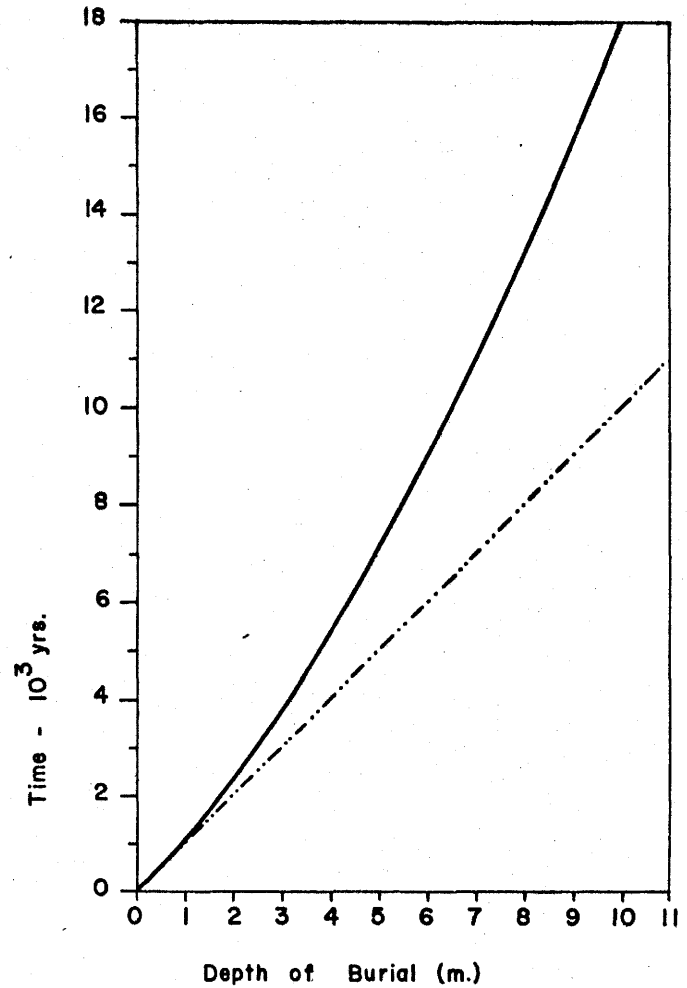


Fig. 16 B. Age in years as a function of burial depth for a sedimentation rate of 1 mm/yr. The straight line representing the hypothetical condition of no compaction is included for comparison.

rived here of 1200 m falls within this general range, suggesting that most or all of the  $\text{CaCO}_3$  in the shale could have been deposited after compaction as a secondary material.

At the other extreme, all of the  $\text{CaCO}_3$  presently in the shale, and perhaps even more, could possibly have existed in the sediment at the time of deposition. This would have represented 5% of the bulk composition of the sediment prior to compaction; it would lower the maximum values in the concretions of about 80% calcite to 75% and would lower values of 60% to 50%. Formation would then have taken place from a half meter to 10 or 15 m below the sediment-water interface, corresponding to a few hundred to 25,000 years, a factor of about 4 times longer than the previously derived estimate. Very probably the actual amount of original carbonate in the sediment was between these limits of 0 and 5%, indicating that the estimated time of formation is slightly low. The independent estimates of shale porosity, derived from the probable thickness of overburden, suggests a low value for original calcite percent. A parallel analysis could be undertaken on concretions in less calcareous or noncalcareous shales to eliminate this factor.

A second deviation could arise from grain size differences between the Devonian sediment and the sediment referred to in Weller's graphs. Weller points out that his data have been taken from studies of "a column of ordinary

mud and shale that has reached equilibrium". In this sense, the Devonian shale is very likely an "ordinary" or average shale. Weller further points out that the data he has taken from Skempton refer to clayey sediments with an average of 42% clay-sized material (less than 8 $\phi$ ). No grain-size analyses are available for the Ludlowville sediments, but a microscopic analysis of insoluble residues shows that a majority, 50-75%, is smaller than 8 $\phi$ , suggesting that any inaccuracies in the results caused by grain-size discrepancies are minor and of a quantitative, rather than a qualitative, nature.

## GENESIS

### Nucleation

The simplest answer to the problem of the formation of concretions is that of direct precipitation of calcite from a supersaturated solution onto some nucleating agent, with successive growth taking place through precipitation onto the latest-formed crystals. The unique controlling factor in such a case would be a nucleating agent, such as a fossil or a grain of pyrite. In the case of the Ludlowville concretions a more complex situation is indicated. Outside the concretions but at the same level many fossils and bits of pyrite lack concretionary deposits, while there is no single, distinct nucleating body found in any of the concretions in the horizon studied. If inorganic nucleation brought about formation, why are the concretions restricted primarily to clusters of pyritized fossils, why do the edges of the clusters extend well beyond the concretionary boundaries, and why has calcite precipitated inside some isolated fossils but not on their external surfaces? No answers to these questions, compatible with simple inorganic nucleation, have been found. Furthermore the shapes of the concretions indicate formation as a single unit, rather than as a coalescence of many small concretions,



each one nucleated about an individual fossil or bit of pyrite. This point is best illustrated by the small concretion illustrated in Fig. 18, wherein concretionary material seems to have precipitated about two specimens of Athyris spiriferoides as a whole rather than about each separately.

The preceding discussion is not intended to imply that precipitation of calcite from a supersaturated solution did not take place. It would seem, rather, that while nucleation did take place, it was not by itself the factor governing the formation of concretionary material. Nonetheless, precipitation was initiated in the region of the fossil layer, as shown by the time relationship discussed in the previous section, and each concretion in the horizon studied does contain a fossil bed.

Exposure to meteoric water appears to be a major factor in effecting the diagenesis of lime sediments to limestone, probably by flushing out dissolved magnesium. A recent discussion of this problem is given by Berner (1966), who points out that Recent lime sediments that have been exposed to meteoric waters show evidences of the first stages of recrystallization. Much older sediments, on the other hand, that have remained in contact with marine water, show much less alteration, if any. Furthermore, there is very little mention in the literature of limestone diagenesis that definitely did not involve exposure of the sediments to meteoric waters.



Fig. 17. Thin-section of a calcite-filled crack. The top of the crack is near the upper surface of the concretion. Sediment, squeezed in from above and then calcified, extends down past the pyritized fossil layer. (X2.5).



Fig. 18. Cut section of a "micro-concretion" formed about two spar-filled *Athyris* specimens. Shell material and spar calcite appear dark, pyrite is light, and the concretionary micrite is gray. The concretion is oriented as it was found, thus showing it to be one of the few concretions observed to have a greater accumulation of concretionary material above the fossils than below. (X1½).

It might thus be suspected that the concretions formed through some sort of interaction of meteoric water with the fossil clusters. This "fresh" water could have come either from uplift and subaerial exposure of the sediments, or by movement of ground water through the sediments under the influence of a substantial hydrostatic head on land. The evidence is strongly against either possibility, however. The concretionary zone lies within a sequence of fully marine shales and limestones that shows no evidence of subaerial exposure within a reasonable stratigraphic distance. Likewise, marine rocks of the Middle Devonian are found over such a large area surrounding the outcrop locations that land must have been too far away for meteoric water to have reached the region in question by moving through the sediment.

It follows that concretionary calcite must have precipitated from marine water trapped in the sediment. If the removal of magnesium is as important as has been suggested (eg. Berner, 1966, and Pytkowicz), it is possible that enough of this ion may have been removed by adsorption on the clay minerals or incorporated into the clay structure.

#### Petrologic Sequence Within the Fossil Clusters

The importance of the fossil layer in the formation of the concretions has already been mentioned. A fossil cluster is found in each concretion and apparently serves as the site of initial precipitation of calcite. Further

significance can be attached to the presence of pyrite, calcite and celestite in the fossil layers and to the replacement of molluscan shells by spar calcite. The significance of these materials follows from the order in which they formed. This order has been deduced from the physical relationships observed in the fossils in the concretions. Similar relationships are found in isolated Athyris spiriferoides outside the concretions; these give the same interpretation of time sequence.

Figure 19 shows a photograph of a specimen of the brachiopod Ambocoelia umbonata from one of the concretionary fossil layers. It shows the pedicle valve in a convex-up position, a layer of sediment beneath an area of clear spar calcite in the cavity formed by the shell, several pieces of shell material and perhaps part of the spiralia. Clumps of pyrite coat the shell surfaces and hang downward from the ceiling of the cavity; large amounts of pyrite have also accumulated on the upper surface of the sediment and are scattered throughout it. Pyrite distribution is independent of calcite grain boundaries, suggesting that it formed prior to calcite infilling. In fact, the pyrite appears to have formed in a solution-filled cavity, settling through the solution to accumulate on the sediment at the bottom. Some fossils outside the concretions -- principally articulated

Athyris -- show identical sediment-pyrite-calcite relationships, suggesting a response to similar or identical physical-chemical conditions. Generally these relationships are more easily observed in the relatively large Athyris than in fossils found in the concretions.

The gastropod fossil in Fig. 20 is a spar calcite cast of the original shell, which was most probably aragonite. Pyrite had formed an internal mold before the original shell material was dissolved. During dissolution the pyrite mold slowly settled until it rested against the sediment that originally enclosed the gastropod shell. Finally, calcite crystallized to form a distorted cast of the original shell. Thus, aragonite dissolution occurred prior to calcite precipitation but after the formation of pyrite. Other types of molluscs -- pelecypods, goniatites, and nautiloids -- show the same relationships. In the shale outside the concretions pyritic internal molds or impressions of these shells are found but no calcitic casts.

Some fossils, typically the Athyris, contain some celestite (strontium sulfate). The celestite is commonly bounded by calcite spar that shows typical crystal faces, indicating that the celestite formed in whatever voids remained after the formation of calcite.

The overall sequence of fossil preservation begins with burial in an environment characterized by a lack of

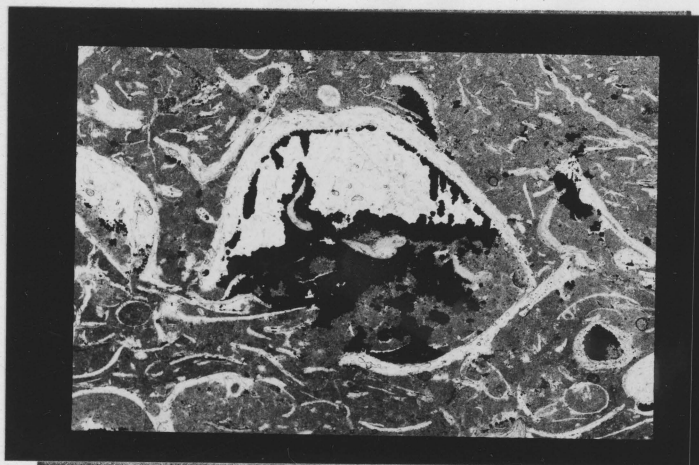


Fig. 19. Photomicrograph of an Ambocoelia umbonata specimen in a thin-section taken from the fossil layer of a concretion. The pedicle valve occurs convex-upward. Pyrite is opaque, and thus black; calcite, both as spar and as shell material, is clear, and thus white; concretionary micrite is gray. (X8).



Fig. 20. Photograph of a thin-section showing a gastropod shell in the fossil layer of a concretion. Spar calcite (white) now takes the place of the original shell material. Pyrite, again, is black and concretionary material dark gray. (X3).

physical disturbance, as indicated by the large number of fossils found in life position and by the lack of any features suggesting current action. Any observed physical disturbance can easily be attributed to the action of burrowing or scavenging organisms. Following burial came the formation of pyrite, dissolution of aragonite and precipitation of calcite in the remaining voids, all in a fairly short time. Finally, when calcite was no longer being precipitated, celestite formed in any voids that were incompletely filled by calcite.

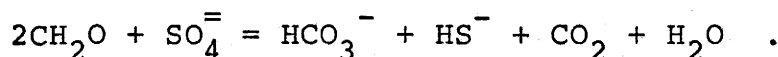
The precipitation of concretionary, micritic calcite and of void-filling, spar calcite must have occurred at about the same time in response to the same set of chemical conditions, both in the concretions and in Athyris found outside the concretions. This follows from the observation that spar and micrite are commonly found in contact within the concretions. In all likelihood the original boundary between soft sediment and a solution-filled cavity was not capable of separating the chemical systems on both sides of it to the extent that the calcite on either side (micrite and spar) would have formed at significantly different times. The Athyris in the surrounding shales illustrate a situation in which calcite-precipitating solutions were chemically isolated from the enclosing sediments. Calcite precipitated only within unbroken, articulated shells, suggesting a nearly closed chemical system with only enough chemical transfer for

internal mineralization. Occasionally these shells broke prior to mineralization, resulting in a build-up of concretionary deposits around the region of the break (Fig. 18). This supports the conclusions that articulated, unbroken shells formed effective chemical barriers and that the sediment-solution interface mentioned above was an ineffective chemical barrier. Furthermore, it demonstrates a connection between the precipitation of concretion-forming calcite and of spar calcite in fossils outside the concretions.

### Interpretation

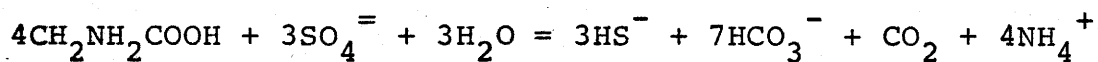
The first event after burial was the formation of considerable amounts of pyrite. This implies strongly reducing conditions and the formation of sulfides, most probably  $\text{HS}^-$ . A small percentage of the sulfide could have come from the decomposition of sulfur-bearing proteins, but most of it probably arose through the activity of sulfate-reducing bacteria. Berner (1966) suggests the following two generalized reactions for metabolism of carbohydrates and proteins by sulfate-reducing bacteria.

For carbohydrates, which may be represented as aggregates of  $\text{CH}_2\text{O}$  units:



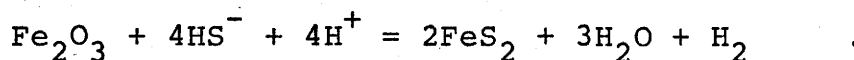
For proteins, represented by the simplest amino acid, glycine:





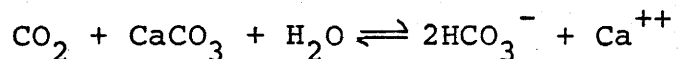
(Berner's reactions are given slightly differently, in that he included the  $\text{CaCO}_3$  equilibrium).

Iron in the sediment, probably existing as an oxide or hydrated oxide adsorbed on clay minerals, reacted with  $\text{HS}^-$  to form pyrite, as represented by the following reaction:

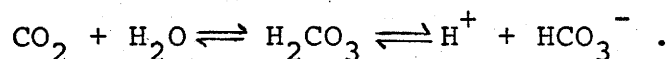


Since hydrogen sulfide is a weak acid, the presence of  $\text{HS}^-$  in a system will lower its pH; therefore, removal of much of this ion as a pyrite precipitate will result in a rise of pH.

Directly following the formation of pyrite came the dissolution of mollusc shells, presumably aragonite which, at near surface conditions, is thermodynamically unstable with respect to calcite. This suggests that the pH was still too low for the precipitation of  $\text{CaCO}_3$ , probably due to the initial production of excess  $\text{CO}_2$  from bacterial metabolism. The following reaction illustrates this dissolution of  $\text{CaCO}_3$  in the presence of  $\text{CO}_2$ :



The effectiveness of this reaction, however, depends on maintenance of a low pH by the dissociation of carbonic acid when  $\text{CO}_2$  is dissolved in water:



If the pH can be kept above about 7.5 (as by removal of  $H^+$  in the above reaction), there will be a build-up of bicarbonate from bacterial metabolism, and this, in turn, will drive the carbonate dissolution reaction to the left, precipitating  $CaCO_3$ . The metabolic reactions show the formation of at least one "molecule" of ammonia for every amino acid unit that is broken down, thus providing an effective means of raising the pH. Some amino acids contain substantially more nitrogen than the one atom involved in the peptide bond. Such nitrogen is not so readily released during decomposition and would provide a means of maintaining a high pH for longer periods of time.

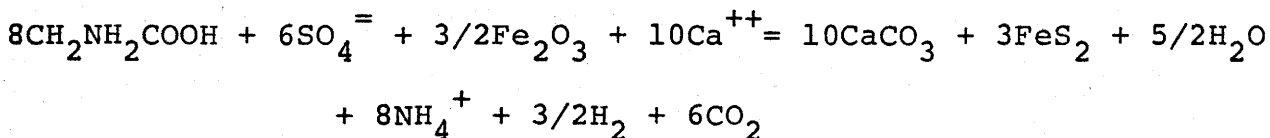
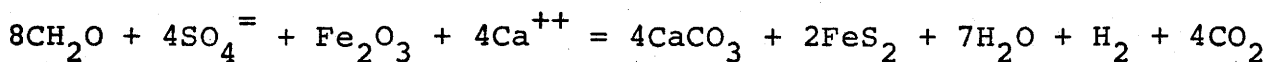
Berner (1968), in some experiments involving the decay of fish, has substantiated some of these conclusions and has suggested, at least in the case of fish-bearing concretions, an extra step in the formation of  $CaCO_3$ . Monitoring the decay of ground-up fish in sea water and in artificial salt solutions, Berner found an initial decrease of pH from 6.5 to 5.9, followed by a rise to about 8.5 at the end of the experiment. This is quite sufficient to permit the precipitation of calcite. Most of the increase in pH was accompanied by increasing concentrations of  $NH_3$  and total dissolved carbonate and decreasing concentrations of dissolved calcium and magnesium, presumably due to the formation of solid carbonates. Analysis, however, showed the presence of palmitates rather

than carbonates, due to the precipitation of  $\text{Ca}^{++}$  and  $\text{Mg}^{++}$  by the corresponding fatty acid. This soap of palmitic acid is far more stable thermodynamically than calcite, but since the organic part of the compound can be expected to break down over a long period of time to a compound less stable than calcite, calcite should eventually precipitate to replace the original calcium palmitate. This replacement would be accompanied by excessively low  $\text{C}^{13}/\text{C}^{12}$  ratios and a decrease in volume. The argument presented earlier in this thesis against a decrease in volume is tenuous at best, and carbon isotope ratios have not yet been measured. However, low ratios would be expected for any carbonates formed through the decomposition of organic matter, with or without a palmitate intermediate, making a test of this sort difficult to interpret. Moreover, the role of palmitates or other fatty acid derivatives is probably not so important in this case as in the case of fish-bearing concretions, since the invertebrates involved probably contained a lower percentage of fatty acids than do fish. The aspect of Berner's experiments that is more important to this problem is that of the production of ammonia and the associated pH increase.

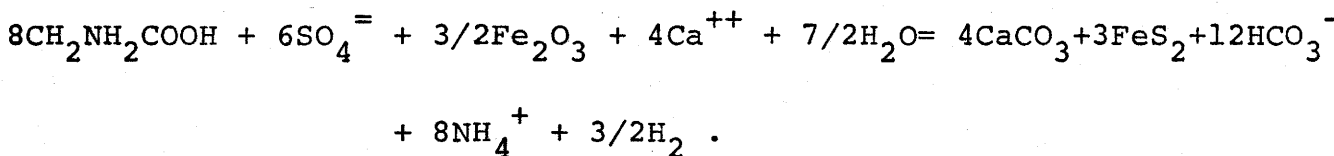
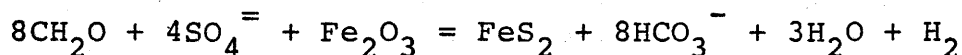
The reactions for the metabolism of carbohydrates and proteins by sulfate-reducing bacteria can now be rewritten to include the formation of pyrite and the precipitation of  $\text{CaCO}_3$ . They are presented in two forms, and in neither case

is  $H^+$  allowed as a reaction product:

a) Assuming the loss to the system of  $CO_2$  with the precipitation of all remaining  $HCO_3^-$ ,



and b) Assuming no loss of  $CO_2$ ,



Removal of  $CO_2$  from the system by diffusion would permit more rapid precipitation of  $CaCO_3$ .

The remaining problem is the source of  $Ca^{++}$ .

The two most probable sources are a) trapped connate water and b) dissolution of aragonite shells. It is improbable that either of these could have supplied adequate  $Ca^{++}$  within the fairly thin concretionary zone. Connate water moving upward through the zone might, however, have brought in sufficient calcium. This would account for the buildup of concretionary material below the fossil layer.

In a large column of sediment, compaction during the burial of a recently deposited layer results more in depression

of that layer below the level at which it was deposited than it does in elevation of the surface of continued deposition (cf. Weller). Burial of the concretionary layer to 8 m. would thus have displaced a column of water about 7 m long. The most likely direction for this water to move is upward. Weller points out that trapped and adsorbed water in a fine-grained, clayey sediment maintains hydraulic continuity with the overlying sea water down to the level at which porosity is about 35 to 37%. This suggests that slow, uniform, upward movement of water is possible, and, as the shortest escape path, upward movement seems much more likely than lateral movement. Therefore, a cylinder of water, 5 to 7 meters in vertical length and having the same plan-view shape as a given concretion, would have come into contact with that concretion during its growth. The calcium dissolved in that cylinder, or column, of water, augmented by the dissolution of aragonite, would have been available for the formation of that concretion. Undoubtedly some additional calcium diffused into the region of calcite precipitation in response to the resulting  $\text{Ca}^{++}$  concentration gradient.

Upward-moving water must also have brought bicarbonate into the region of growing concretions, and some of it must have been included in the concretions, especially during the later stage of formation. This would be expected to show up in a carbon isotope analysis as higher  $\text{C}^{13}/\text{C}^{12}$  ratios in

the outer portions of the concretions, since the carbon in shells is generally heavier than organic carbon.

The fossil clusters controlled the formation of the concretions but the extremities of the clusters are typically not included in the concretions. This is a result of diffusion and of the structure of the fossil clusters, thinnest toward the edges and thickening inward. Although excess bisulfide, bicarbonate, and ammonia was produced throughout the entire cluster, as indicated by the occurrence of pyrite everywhere in the cluster, less of these materials was produced near the edges than elsewhere because the clusters are thinnest there. Furthermore, near the edges these materials would have experienced a significant concentration gradient through nearly  $180^\circ$ , that is, outward as well as downward and upward, and would thus have diffused away from the clusters quite readily, resulting in concentrations below that necessary for the precipitation of calcite. Inward from the edges, where the clusters were thicker and the formation of metabolic products was correspondingly greater, concentration gradients were strong only in two directions, upward and downward, so that ammonia and bicarbonate were lost by diffusion much more slowly than they were near the cluster margins.

During the second stage of formation, the boundary of concentrations sufficient for calcite precipitation was still

more limited. Effective diffusion rates, dependent primarily on rates of formation of bicarbonate and ammonia were also dependent on the character of the sediment - the ability of these materials to diffuse through it. This in turn would have been modified by the rate of upward movement of connate water. The large size of the concretions indicates production of large amounts of bicarbonate and ammonia and high rates of diffusion of these products through the sediment. The preponderance of concretionary material below the fossil layer suggests that the vertical diffusion of ammonia and bicarbonate and the upward flow of water were generally fairly well balanced so that concentrations of bicarbonate, ammonia, and calcium were enhanced below the fossil layer and attenuated above it. Occasionally this situation did not hold and concentrations above the fossil layer built up, resulting in considerable accumulation of calcite there.

The factor typifying the concretionary horizon is the burial during sedimentation of large amounts of organic material, indicated by the extensive pyritization in this zone. Fossil clusters found immediately above and below this zone show minor pyritization at best, while in the concretionary horizon, even the extremities of fossil clusters, although lacking concretionary deposits, have been pyritized. It is difficult to imagine this pyrite as indicating a wide-spread

killing due to a foul bottom environment in the Devonian sea because of the great number of apparently healthy organisms it sustained, reflected in the many fossils now found in the shales (cf. Bray).<sup>\*</sup> On the other hand, wide-spread killing by a strong disturbance of the physical environment is also most unlikely. No evidence of strong current action has been found, either in the fossils or in the sediments. In fact, the sediments and the fossils give evidence of very quiet, though reasonably well oxygenated environment: no current bedding occurs in the shale, and many of the fossils are found in life position or nearly so. The only evident disturbance of the fossil material was most likely caused by vagile organisms.

Some evidence does indicate, however, that the rate of influx of terrigenous sediments may have reached a maximum at about the level of the concretions, resulting in the burial of a maximum amount of organic matter at this level. This rate could have been sufficiently high that large quantities of still undecomposed organic material were buried, yet just low enough to permit the existence of an extensive bottom fauna adapted to a high sedimentation rate. Such a condition could be expected, further, to extend over a fairly

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\* Waage suggests wide-spread killing as underlying the formation of concretionary layers in the Fox Hills Formation of South Dakota.



large area. The shales surrounding the concretions show the development of faunal communities adapted to a high sedimentation rate and to the soft muddy bottom that would result therefrom. The fossil clusters included in these concretions are one indication of such adaptations. According to Bray the clusters, typified by the small brachiopod Ambocoelia umbonata, represent a conditioning of the substrate such that once a cluster was initiated the shells of the earliest individuals provided a substrate more suitable than the sediment surface for succeeding generations. Development of clusters of this sort would thus be linked with especially soft substrate conditions offering little in the way of physical support. Soft substrates could develop under conditions of rapid influx of sediment and minor post-depositional reworking of the sediment. The clusters occur in abundance through about one meter of shale that includes the concretionary zone, indicating the existence of conditions favorable to their development, in this case probably abnormally high sedimentation rates, during the time of deposition of those sediments.

The Athyris in the Ludlowville also indicate that the concretionary zone represents a time of exceptionally high sedimentation rates. At this level a large number of these brachiopods are found in life position - beak down and commissure directed upward. Since the adult forms have a small pedicle, they were probably largely supported by the sediment at maturity. Below and above the concretionary zone,

decreasing percentages of articulated Athyris are found as well as very few specimens in life position. Furthermore, the faunal content of the shale changes noticeably above the concretionary zone, with a development of current-washed fossil accumulations and a culmination in the fairly clean Tichenor Limestone some 4 m above the concretions. Of particular importance, these changes indicate a decrease in the rate of accumulation of terrigenous material and an increase in the amount of disturbance of the sediments after deposition, possibly related to a decrease of depth. In turn, the former implies a slower rate of burial of organic material on the sea floor; the latter implies increased reworking of buried organic matter, leaving it more readily oxydized or utilized by scavengers. Both effects reduced the chances for the occurrence of conditions leading to concretion formation.

#### Summarized Historical Sequence

At one time during the deposition of the Wanakah Shale, conditions of low current action at the sea floor and a high sedimentation rate resulted in the burial of large quantities of undecomposed organic matter chiefly concentrated in fossil clusters and within articulated Athyris valves. Sulfate-reducing bacteria, in metabolizing this organic material, produced excesses of bisulfide, bicarbonate, and ammonia. The first of these precipitated in and around the fossils as pyrite; the latter two contributed to  $\text{CaCO}_3$  precipitation.

Initially, calcium carbonate was precipitated in and immediately surrounding the fossil layer (and within the Athyris); cavities were filled by spar, and minute crystals of calcite formed throughout the fine-grained sediment. It is possible that the first stage of precipitation - surrounding the fossil clusters for a thickness up to 5 or 10 cm - followed some sort of calcium soap phase, as suggested by Berner (1968). This stage may well have formed primarily from calcium and carbonate derived from the fossil cluster itself or from its immediate surroundings. The second stage formed beneath the central portion of the first stage, indicating that the formation of bicarbonate and ammonia at a rate sufficient for precipitation of calcite was by then restricted to the central or thickest portion of the fossil cluster. Calcium and bicarbonate in upward-moving connate water interacted with bicarbonate and ammonia diffusing downward from the cluster, precipitating calcite as very small ( $<10 \mu$ ) grains. These were not thoroughly bound together until much later and hence deformed under compactive pressure to form a flattened concretion. Permeability of this mass of unbound calcite grains could most probably have been adequate for the slow movement of connate water and diffusing ions through it. While the second stage was undergoing deformation, cracks were forming in the first stage. Fig. 21 illustrates the various phases in the development of a concretion. The rate of calcite formation

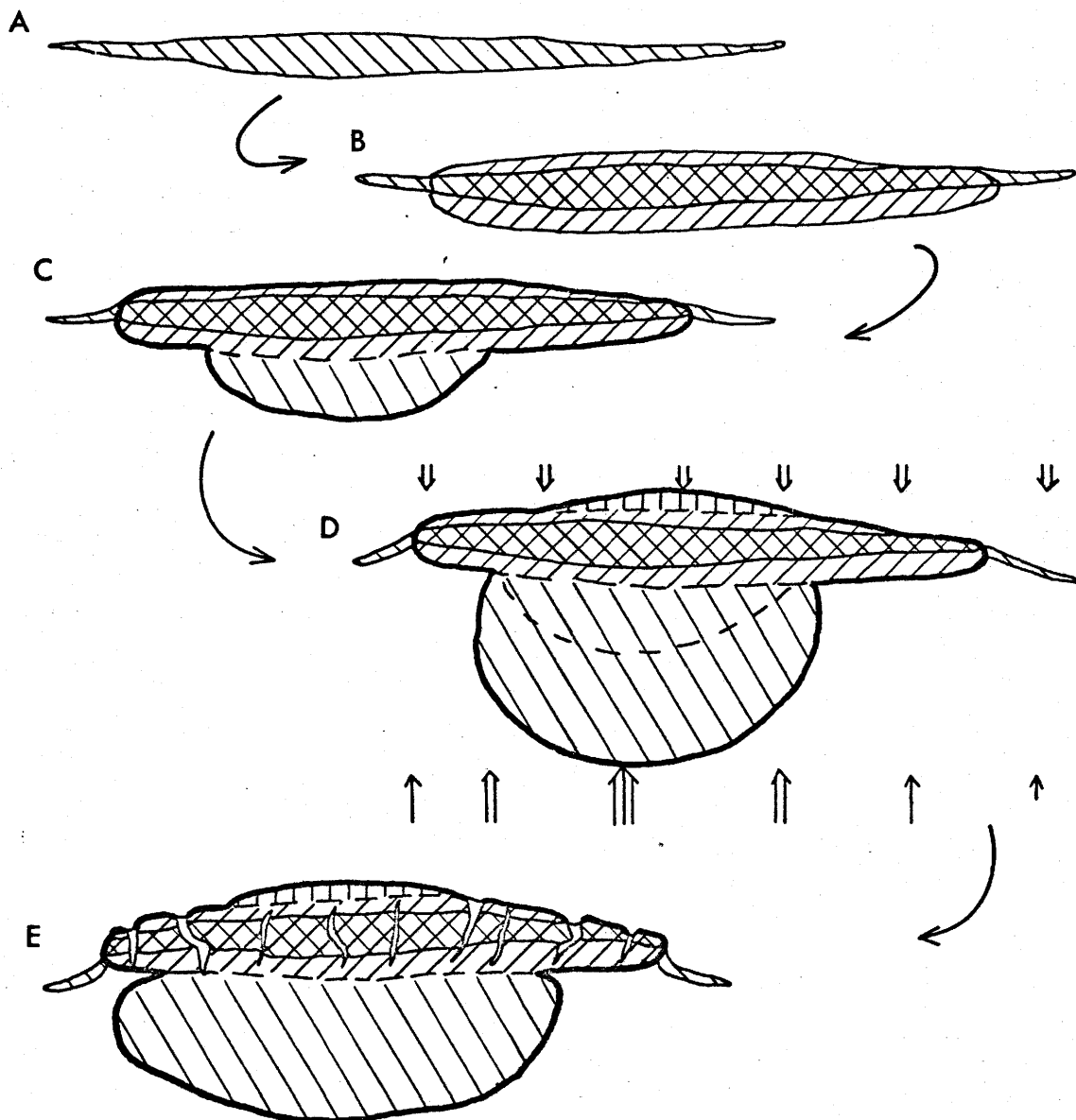


Fig. 21. Diagram illustrating the probable phases in the formation of a concretion.

- Phase A. Pyritization of a recently buried fossil cluster. Dissolution of aragonite.
- Phase B. First stage formation of  $\text{CaCO}_3$ .  $\text{Ca}^{++}$  probably of local origin.
- Phase C. Beginning of second stage precipitation of calcite, at a slower rate. Calcium supplied by upward-moving connate water and by diffusion.
- Phase D. First-stage calcite crystals becoming firmly bound. Compaction pressure becoming substantial.
- Phase E. Distortion of loosely-bound second stage. Depression of non-calcareous extremities of fossil cluster below the remainder of the cluster.

was high throughout the first stage and then dropped steadily to the completion of the concretions. This was probably a function both of the decreasing rate of production of metabolic products and of the decreasing rate of supply of connate water, and hence calcium, to the horizon with increased compaction. Finally, after the cessation of calcite precipitation, celestite formed in any remaining cavities in the sediment, especially in voids left by the incomplete filling of fossils by spar calcite. Although some of the strontium in this celestite may originally have existed in the buried sea water, most of it was probably released to the connate water during the dissolution of aragonitic shells.

#### Elongation and Parallelism

The concretions show no evidence that physical deformation has brought about their elongation, nor can their orientation be in any way related to local joint systems. Hence the factor that caused elongation must have been directly or indirectly connected with factors governing their formation and must have acted in a similar manner over a large area to produce the observed, widespread parallelism. The most readily apparent, direct cause would be an elongation of the accumulation of organic matter that initially led to formation of the concretions. Since this organic matter presumably came from the animals that are now represented by fossil clusters, an elongation should thus be observed in the

fossil clusters. Widespread factors such as gentle currents or sunlight might have acted on the animals to orient the direction of their spreading over the sea floor. No such preferred orientations have been observed in the fossil clusters, and any elongation observed in them is slight and not obviously related to the direction of orientation of the concretions. (A description of some fossil clusters slightly above the concretionary horizon is given by Bray.)

A more likely possibility is that movement of connate water included a horizontal as well as a vertical component, thus producing increased concretionary growth from one side of the fossil cluster as well as from the bottom. This is substantiated in part by the fact that some smaller concretions are asymmetric, being thicker on the N-W side than on the S-E. Among those that have deposits of calcite above the fossil layer the deposits are frequently found around the N-W margin of the concretion, encroaching upon the center, but are almost never found in the corresponding position on the S-E margin. The cause of such a unidirectional, lateral flow of connate waters is speculative; however, the orientation of the concretions, N35°E, is roughly parallel to the Appalachians, indicating that the precursor of this system in the Devonian may have had some effect on the flow of connate water or perhaps on some other, unrecognized factor. Although the problem of elongation must be related to the origin of the concretions its complete solution goes beyond the scope of this project.

## SUMMARY

Investigation of a horizon of carbonate concretions in the Middle Devonian Ludlowville Formation of western N.Y. resulted in the following answers to the questions of when and how they formed.

1. The concretions grew outward from fossil clusters shortly after pyritization of the clusters and were completely formed by the time they were buried beneath a probable five meters of sediment. At a sedimentation rate of 1 mm/yr of uncompacted sediment, this corresponds to about 7,000 years.
2. Growth took place in two stages with the precipitation of spar calcite in fossil cavities and of minute grains of calcite throughout the sediment. During the first stage, calcite was precipitated very closely around the flat fossil clusters at a fairly rapid rate. The second stage of formation took place primarily below the first stage; this portion was deformed due to compactive forces prior to complete binding of the calcite grains in it, resulting in tension cracks in the first stage and in a flattening of the concretions.

3. The following mechanism of formation is consistent with the determined sequence of events prior to and during formation.
  - a) A large quantity of organic matter was buried, concentrated mainly throughout the fossil cluster.
  - b) This material was utilized by sulfate-reducing bacteria, with the release of  $\text{NH}_3$  and  $\text{HCO}_3^-$  and of  $\text{HS}^-$ , which was quickly precipitated throughout the fossil layer as pyrite.
  - c) The pH of the system was raised, primarily through the influence of ammonia, to the level at which calcite could be precipitated (greater than about 7.5); saturation of the system with respect to calcite was exceeded by high concentrations of  $\text{HCO}_3^-$ , causing precipitation of calcite.
  - d) The necessary calcium was continually added to the system by diffusion and by the slow, upward movement of connate waters, enriched in  $\text{Ca}^{++}$  by the dissolution of aragonite shells and squeezed from lower sediments by compaction.
4. The concretions were restricted to a single horizon by a combination of low rates of water circulation, perhaps related to depth, and of high rates of sedimentation, such that especially large amounts of organic matter were



rapidly buried in a thin layer of sediment with a minimum of exposure to oxidizing conditions due to reworking.

5. The causes of elongation in the concretions acted over a large area, resulting in a parallelism of their long axes. This elongation is also oriented parallel to the Appalachians, indicating that the early stages of the formation of these mountains may have had some influence on the sediments, most probably by forcing a lateral component onto the upward movement of connate waters through the sediments.

## APPENDIX

### DETERMINATION OF VOLUME-PERCENT CALCITE

The hypotheses were developed that the concretions recorded the porosity of the surrounding sediments at the time of formation and that they formed during an extended period of time and thus should record highest porosities in the earliest-formed portions and lowest porosities in the latest-formed portions, after burial and compaction had resulted in reduction of the porosity of the surrounding sediments. Volume-percent of concretionary calcite was expected to approximate original porosity and thus a determination of volume-percent calcite at various places throughout the concretions should provide a test of these hypotheses, and if they proved valid, indicate which portions of the concretions were formed first and which last. Determination of volume-percent calcite in the shale was expected, further, to provide an independent check of previous estimates of relative compaction - total compaction of the shale relative to compaction at the time of concretion formation.

The concretion designated "LC-E" (Fig. 4) was chosen for this analysis because its large size (particularly

its thickness) was expected to provide a maximum of variability in the results. Two vertical slabs, one parallel to the long axis of the concretion and one perpendicular, were cut from the concretion as shown in Fig. 22A. Samples of up to 45 grams were taken from the slabs as shown in Fig. 22 B, to include duplicates of widely separated areas. These samples were originally intended for preliminary analysis to determine whether or not variations in volume-percent calcite throughout the concretion could be adequately measured using the method to be described, and if so, to indicate where further samples should be taken. Four samples of the surrounding shale were also included.

In the analysis, numbered 250 ml beakers were heated to about 105°C for several hours, allowed to cool to room temperature, and immediately weighed to 3 decimal places. The samples were then placed in the beakers and heated to about 105°C for more than 4 hours, following which, they were allowed to cool to room temperature and quickly weighed to 3 decimal places on the same balance, before too much moisture could be adsorbed on them. Volume of the samples was then determined by suspending them from the beam of an analytical balance by a fine thread and weighing them first dry and later immersed in water. The volume of water displaced was calculated by dividing the weight difference by the density of water, found in the Handbook of Chemistry

and Physics, at the measured temperature of weighing.

The samples were returned to their respective beakers, treated with about 200 ml of 5% HCl, and covered with a watch glass. After effervescence ceased, the acid was replenished by adding about 10 ml of concentrated HCl. When this treatment failed to produce further effervescence, the samples were allowed to stand for several weeks, with occasional addition of small amounts of acid. Excess acid was then carefully siphoned off using a glass tube connected to a vacuum aspirator through a water trap. Distilled water was added to the insoluble residues, which were then stirred vigorously and allowed to settle for a day or more, until clear. Wash water was carefully removed using the same aspirator apparatus, and the process was repeated 3 or 4 times.

The samples were done in two batches, the duplicates primarily forming the second batch. To reduce operator bias, the beaker numbers were unrelated to the sample numbers - making it essentially impossible to tell which sample was in each beaker, all beakers in a given batch were treated as nearly as possible the same, and order of treatment was largely haphazard. After being washed, the samples were dried at less than 100°C and then heated to 105-110°C for more than four hours. They were then cooled to room tempera-

ture and quickly weighed.

Since the samples were chosen to be as nearly free of fossil material as possible, weight loss after the above treatment was assumed to represent original weight of secondary (concretionary) calcite. Dividing by 2.711, the density of calcite (Handbook of Chemistry and Physics), this was converted to volume of calcite. Relative porosity is defined as pore space volume divided by total volume and multiplied by 100 to convert to percent. Volume loss was converted to volume-percent calcite by dividing by the initial volume of the sample and multiplying by 100, thus making the results comparable in form to relative porosities.

Initial weight, initial volume, density, weight loss, volume loss and volume-percent calcite (assumed to be the relative porosity of the sediment at the time of formation) are given in Fig. 23 for each sample. Samples treated in the first batch are given first, followed by those of the second batch.

Since the results substantiated the original hypotheses quite adequately and appeared reasonably reproducible, no further analyses were carried out at the time. Additional analyses would be useful in filling in the gaps in the already sampled concretion, and in substantiating the assumption that the conclusions garnered from these results can be at least qualitatively applied to other concretions of the same type. In particular, these conclusions include the

following:

- a) The part of the concretion immediately below the fossil layer was formed at maximum relative porosity.
- b) This porosity is essentially equal to porosities found at the surface of Recent, fine-grained, clayey sediments.
- c) Porosities in a layer just below the fossil cluster appear to be fairly consistent across the entire concretion for a thickness approximately equal to that of the lip.
- d) The porosities in the lower part of this layer are only slightly less than would be expected if the layer had been formed instantaneously, since the lower part of the layer would, at the time of formation, have been buried more deeply, in sediment of lower porosity, than would its upper part.
- e) The outer layers of the main portion of the concretion, below the layer mentioned above, were formed last - when sediment porosities were about equal to those 5 m below the sediment-water interface of similar Recent sediments. Samples taken from the very edge of the concretion suggested

a depth as low as 8 m, but this probably indicates the lack of a completely distinct concretionary boundary, so that some shale was included in the samples.

- f) Lithification of the surrounding shale could have taken place at sediment porosities as low as 20%, corresponding to a depth of about 1200 m. This would have occurred when a unit layer of sediment was compacted to  $\frac{1}{4}$  the thickness of that layer at the time of initial concretionary formation.
- g) No particular differences occur in samples taken from the two, perpendicularly oriented slabs.

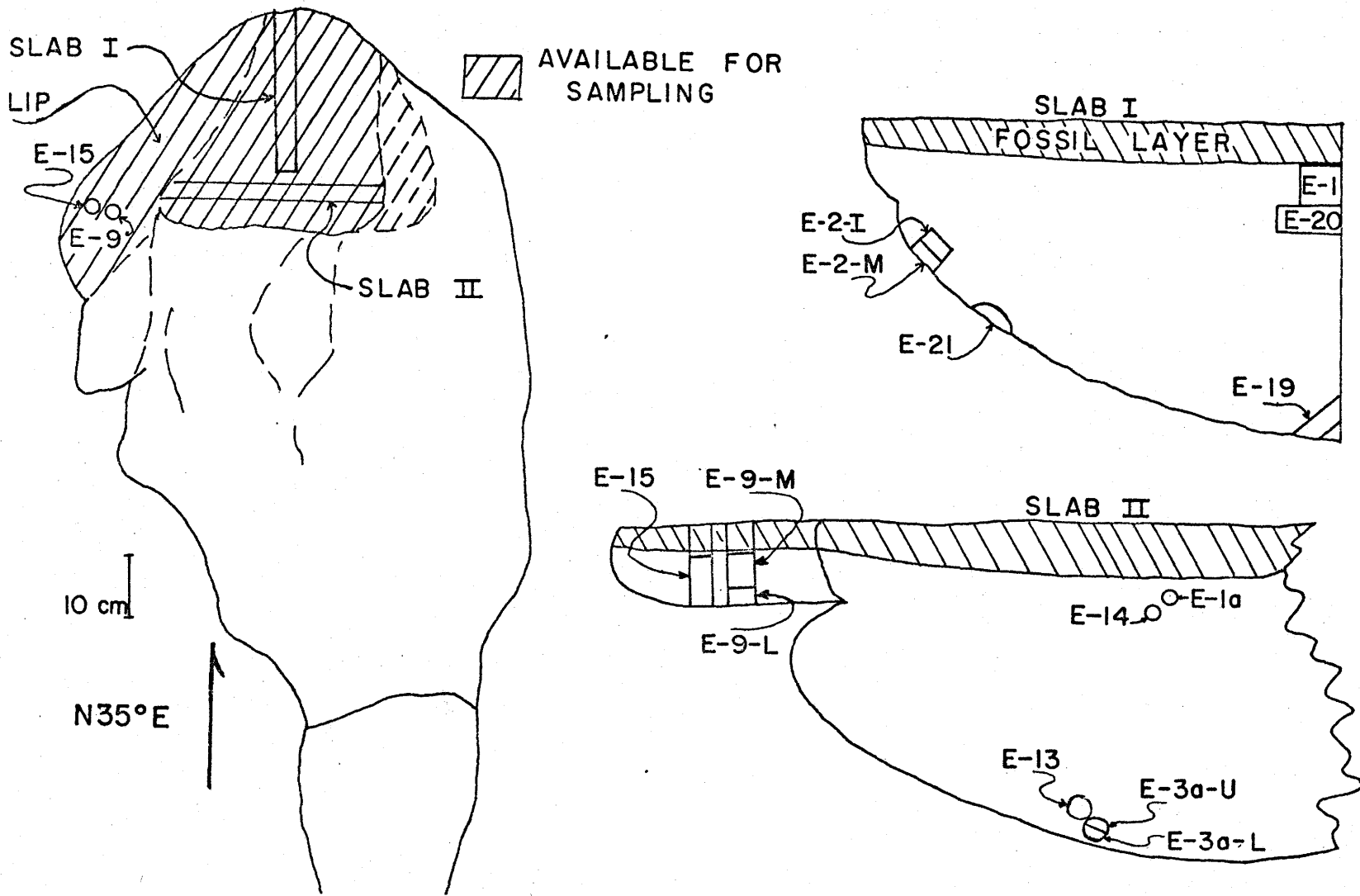


Fig. 22 A. Diagram of the upper surface of concretion "LC-E", showing the location of 2 slabs and 2 cores taken for sampling.

B. Cross-section of the perpendicularly cut slabs and of the cores, showing location of samples taken from them for volume-percent calcite analysis.



Sample	Weight (gm)	Volume (cc)	Density (gm/cc)	Weight Loss (gm)	Volume loss (cc)	Volume- percent calcite
E-1	17.859	6.614	2.70	14.094	5.199	78.6
E-1a	16.598	6.147	2.70	12.785	4.716	76.7
E-2-I	7.395	2.739	2.70	4.808	1.774	64.8
E-2-M	8.172	3.027	2.70	4.350	1.605	53.0
E-3a-L	9.341	3.485	2.68	5.601	2.066	59.3
E-3a-U	6.537	2.439	2.68	4.010	1.479	60.6
E-8-S	31.904	12.270	2.60	6.245	2.304	18.8
E-8a-S	9.086	3.481	2.61	2.259	0.833	23.9
E-9-L	2.143	.797	2.69	1.619	0.597	74.9
E-9-M	6.790	2.524	2.69	5.545	2.046	81.1
E-13	42.493	15.841	2.68	25.525	9.415	59.4
E-14	25.168	9.414	2.70	19.777	7.295	77.5
E-15	16.381	6.098	2.69	13.114	4.837	79.3
E-16S	25.707	9.847	2.61	5.623	2.074	21.1
E-17S	30.489	11.753	2.60	6.541	2.413	20.5
E-19	16.256	6.062	2.68	9.825	3.624	59.8
E-20	25.157	9.330	2.70	19.664	7.253	77.7
E-21	16.097	5.958	2.70	8.432	3.110	52.3

Fig. 23. Table showing volume-percent calcite data.  
Sample numbers with an "S" refer to shale samples.

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