Time Factors of Differentially Preserved Wood In Two Calcitic Concretions
In Pennsylvanian Black Shale from Indiana

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ABSTRACT

A large concretion in the black shale above Springfield Coal Member (No. V), Desmoinesian Series, Pennsylvanian, from the Blackfoot #5 mine, Pike County, Indiana, contains a piece of fossil wood with excellent preservation of cell structure. Both ends of the wood extending outward to the extremities of the ovoid concretion are replaced by a black calcareous rock in which there is no fossil wood structure. These end zones have sharp contacts with the concretion matrix and their dimensions correspond to those of the fossil wood plus associated calcite veins. These relations indicate that the concretion must have been well-established before the wood had suffered any structural disintegration through bacterial activity. The preservation of the central section of the wood was the result of early concretion formation, while the ends continued to rot away as they were open to the environment.

This is further evidence for the rapid early diagenetic origin of many concretions, particularly those associated with well-preserved fossils.

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sample and break open concretions wherever they occur. It is because of this persistent search that the authors have had the opportunity to describe and interpret these interesting specimens.

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INTRODUCTION

This paper describes two occurrences of fossil wood in concretions and discusses their bearing on the time of formation of the concretions in relation to degradation of the wood after incorporation in muddy sediments.

DESCRIPTION OF SPECIMENS

Specimen B540 (Field Museum collection)

This is a concretion from the black shale over Springfield Coal (No. V) collected in the Blackfoot #5 strip mine, Winslow quadrangle, Pike County, Indiana. It is a large ovoid concretion about 37 cm. long, 20 cm. wide, and 18 cm. thick. It was split along a fossil branch which lies a little off the median plane (fig. 1). This fossil wood shows a distinct fibrous texture, the result of the excellent preservation of cell structure contained within calcite (fig. 2). The wood is probably *Dadoxylon* Endicher 1847 (identified by J. R. Jennings, University of Michigan). Dark reddish-brown in color, the wood fragment is about 23 cm. long, 5.5 cm. wide, and 2.5 cm. thick, thus appearing notably flattened. However, the arrangement of the radial rays of the wood cells indicates that it is only a portion of a branch, and that the structure has only been minimally distorted. The two extremities of the branch within the concretion have sharp contacts with black zones about 6 - 7 cm. long, 7 cm. wide, and varying in thickness from less than 2 - 4 cm. at the surface of the concretion. These zones stand out in marked contrast to both the fossil wood and the mass of the concretion. The black material is not coalified wood; it bears some resemblance to the black shale adhering to the surface of the concretion, but it clearly shows cleavage surfaces of calcite and lacks the laminated structure so typical of the shale. Some smaller, coarser-grained aggregates of white calcite are also present. The black material appears to replace the wood which originally would have been present to the very margins of the concretion.

Pure white, coarsely crystalline calcite veins virtually surround and also penetrate the fossil wood, but do not extend into the black zone at each end of the wood (fig. 1).

The matrix of the concretion is typical of structureless, fine-grained carbonate concretions. There are streaks and patches of coarser, purer calcite. Finely disseminated pyrite occurs throughout, but it is particularly concentrated in two regions. Surrounding the fossil wood and calcite veins there is slightly more pyrite, and there is a prominent halo containing much pyrite in a band about 0.2 - 2.5 cm. inward from the surface of the concretion (fig. 1). The inner boundary of the halo is fairly sharp, but the outer boundary is diffuse. This halo stops just short of the black zone at each end of the concretion. A polished vertical section of the concretion shows a faint horizontal banding which represents bedding.

Microscopic Structure

The fossil wood exhibits excellent cell structure (fig. 3A). Reddish-brown organic residue outlines the cells and is contained within a mosaic of coarse-grained calcite. Optically continuous areas are irregular in shape, but are elongate parallel to the length of the wood cells. Over 96 per cent by weight of the fossil wood is carbonate; only 0.1 per cent remained after combustion of the residue, which is thus composed essentially of organic material and water. Fissures and cracks are filled with pure, coarse, anhedral calcite. The margin of the wood is interrupted and split apart by pyrite and calcite grains.

The boundary of the wood against the black end zones described above is sharp but ragged in outline (figs. 2, 3B), with the wood cells showing slight distortion and a breakdown of the structure at the immediate contact. The black material is composed of large (up to about 4.0 mm.) anhedral calcite, with inclusions of pyrite and streaky carbonaceous opaque material and sparse quartz grains. Patches and lenses of reddish-brown organic material are abundant, some of which are clearly disorganized wood cells. The carbonaceous and organic streaks are preferentially arranged in a parallel structure, although the orientation varies widely without an overall pattern from zone to zone in thin section. The contact of the material of the black end zones with the calcite veins is slightly gradational over a distance of less than 2.0 mm.

The matrix of the concretion is composed of fine-grained calcite (ca. 0.05 - 0.2 mm. grain size) and pyrite with disseminated fine

Fig. 1. Broken horizontal surface of concretion from black shale over Springfield Coal (No. V), Pike County, Indiana. Fossil wood, with well-preserved cell structure, lies along the center outlined by the white calcite veins. The black zones extending from the fossil wood to the concretion's exterior represent the extremities of the wood that were completely degraded after the concretion process was well advanced. Note the sharp boundaries with concretion matrix. Lighter colored areas in the concretion matrix are pyrite concentrations adjacent to the fossil wood and as a "halo" closer to the concretion surface.
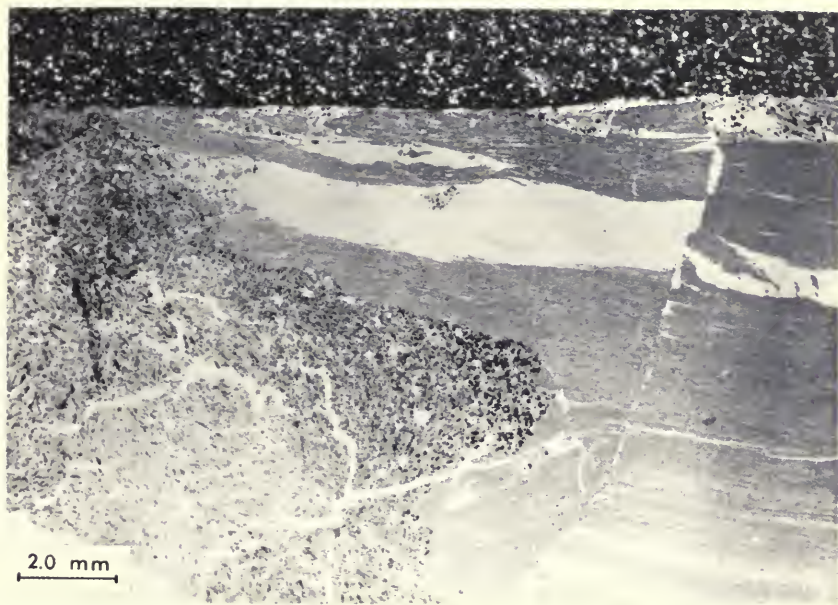
20.0 mm

FIG. 2. Photomicrograph of longitudinal thin section (#1476) from specimen in Figure 1 across the contacts between fossil wood (right), black degraded end zones (left), and concretion matrix (top). The opaque concentration in the concretion matrix is pyrite. Note the sharp contact between the permineralized fossil wood and the matrix of the end zones; the opaques in the latter are carbonaceous except near the contact. The contact between the calcite vein and the end zone material is slightly gradational.

clastic material. The wood or calcite veins and the black zones have sharp contacts with the concretion matrix (fig. 2). X-ray powder diffraction photographs show that the carbonate in the fossil wood and in the black material is calcite with little or no Mg or Fe.

Specimen B541 (Field Museum collection)

This is a concretion from the Mecca Quarry Shale Member, Linton Formation (Pennsylvanian), in Montgomery Creek, Wabash Township, Parke County, Indiana. Only a portion of the concretion is preserved. It contains fossil wood rather more broken up than in the previously-described specimen, with many coarse-grained pure calcite veins. The segment of wood with calcite veins is about 2 cm. across and 1.5 cm. thick. One extremity shows a nearly circular cross-section, about 2.5 cm. in width and 2.2 cm. thick, largely composed of a grey, mottled substance distinct from the concretion matrix. It is rich in calcite, with wood patches along one portion of the periphery and a very thin layer of wood cells outlining much of

the remainder of the near-circular section. This mottled substance appears to be a replacement, or perhaps partly a pith filling, of the original branch of wood. The concretion matrix is dense and fine-grained carbonate, with dark and light grey lensoid-shaped mottling and much finely-disseminated pyrite. It is typical of carbonate concretions found elsewhere in the black shales of Pennsylvanian age.

Microscopic Structure

A transverse section of the grey material that replaces the wood shows peripheral patches of fossil wood with the cell structure preserved as a reddish-brown residue embedded in calcite. The latter occurs as large (up to 1.3 mm), irregular, optically continuous grains. Fossil wood also is present as a thin layer, up to 0.23 mm. thick, between the concretion matrix and the replacement mass. In places, however, the wood layer is absent, and there is a thin calcite layer, 0.58 - 0.77 mm. thick, the margins of which are composed of small grains with coarser calcite within.

The replacement mass is composed of coarse, anhedral calcite, very variable in shape and size, but some grains are as much as 2.8 mm. long. Embedded in the calcite are abundant wisps and lenses of opaque material arranged in a parallel structure that partly follows the near-circular shape of the mass. The opaque wisps are associated with much indeterminate brown organic matter, also in streaks. The opaque substance is believed to be largely carbonaceous. There are larger patches of brown organic material that has little or no evidence of relict cell structure, and, in addition, there are sparse quartz grains and much finely disseminated dust clouding the calcite.

The concretion matrix is composed of very fine grained calcite, ca. 0.015 - 0.023 mm. across, with patches of even finer grained material, 0.002 - 0.005 mm. across. There are scattered abundant opaque particles approximately similar in grain size to the calcite. They are mainly carbonaceous, but there is also some finely disseminated pyrite. The latter is more abundant adjacent to the fossil wood. The calcite is, in part, stained brown by organic colloids.

DISCUSSION

The interpretations are based on Specimen B540, an entire concretion, but they are equally applicable to B541, a fragment of a
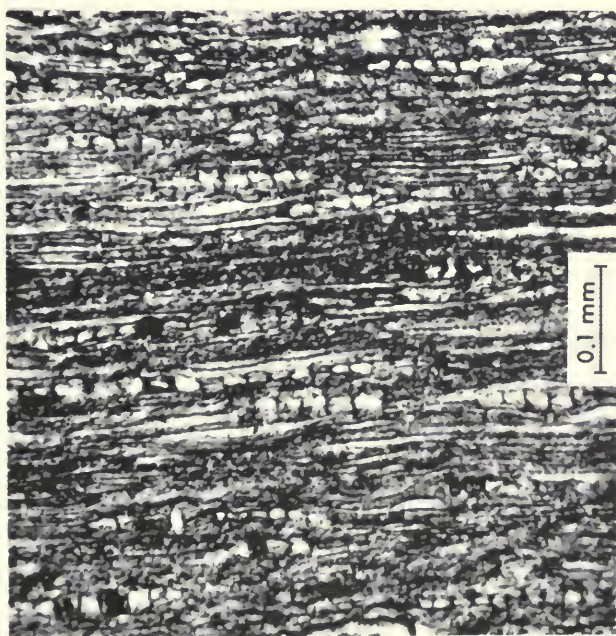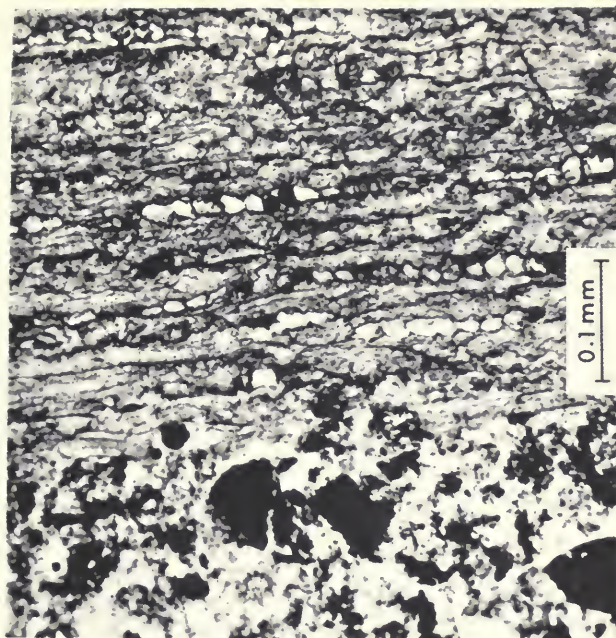
FIG. 3B. Enlargement of contact between well-preserved fossil wood (on right) and black degraded end zones (left); the large black objects are pyrite.

FIG. 3A. Enlargement of portion of the well-preserved fossil wood shown in Figure 2.

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concretion, the features of which are very similar to B540. The formation of the concretion mass around the wood indicates that the wood fragment was buried, probably rapidly, in an organic-rich mud.

The calcite veins are fillings of open spaces that formed in and around the wood after the concretion had been largely formed, since the contacts of the veins both with the wood and the concretion matrix are sharp. The open spaces must have developed after the concretion had reached a coherent state. They are interpreted as representing the isotropic shrinkage of the wood, resulting mainly from dehydration. The calcite veins amount to about one-third of the space originally occupied by the wood before shrinkage. The open spaces produced in this way must have preceded the calcite mineralization of the wood. It is possible that the calcite grew as the shrinkage cracks developed and that no actual open spaces were ever present. The vein fabric provides no evidence, although the bilateral symmetry in the thin vein between the concretion and the wood replacement in the smaller specimen, B541, does suggest filling of an open space.

In terms of time relationship the black zones at each end of the fossil wood are the most interesting features. These are considered to represent the ends of the wood which suffered decay after the surrounding mud had been at least partly filled in with calcite (or a carbonate precursor). In this respect it is probable that nucleation on the dispersed clay and carbonaceous particles took place synchronously throughout the mud mass, rather than by accretion of layers successively from within outward. This is analogous to the simultaneous nucleation of calcite on many different surfaces of layers or lenses of semi-consolidated mud; the continued growth of fibrous calcite and new nucleation produces the interfering complex cone-in-cone diagenetic concretionary structure (Woodland, 1964). The wood of the end zones was completely degraded and only some small patches with disorganized cell structure remain. The space resulting from this degradation was taken up by black mud surrounding the concretion. This is indicated by the prevalence of opaque carbonaceous lenses which are typical of the black sheety shales.

The composition of these black zones is quite different from that of the concretion matrix and the black shale. It contains a much greater proportion of shale material than the concretion but is also much richer in carbonate than the black shale, which has

little or none. This indicates that the mud contained much less water when it penetrated the end zones than in the earlier stage when the concretionary process began. Later, the pore spaces in the mud plug were filled with coarse calcite and pyrite. The coarser grain size relative to that in the concretion matrix is the result of a different fabric in this disturbed material at the time of nucleation.

The ingress of black mud into the two rotted end zones is indicated by one acid residue analysis of the black material. Some 53 per cent by weight is carbonate, and nearly 9 per cent is pyrite. Of the residue, there was a 5 per cent loss on combustion representing approximately the organic content and combined H_2O, leaving nearly 33 per cent as silicate residue representing the clastics of the original mud. On a carbonate-free basis, this amounts to about 70 per cent of silicate, 18 per cent pyrite, and 11 per cent organic content. This compares with one analysis of the concretion matrix from the zone between the inner and outer pyrite concentrations: 83 per cent carbonate, 12 per cent pyrite, 4 per cent silicates, and 1 per cent organics and combined water. On a carbonate-free basis this is 70 per cent sulfides, 23 per cent silicates, 7 per cent organics and combined water.

The relationship between the surrounding concretion matrix and the mud-filled rotted ends of the wood implies that the matrix had already acquired a coherence, so it did not collapse into the space resulting from the decay. The concretion matrix thus established remained distinct from the mud occupying the decayed ends of the wood. The required coherence may have been the result of the precipitation of calcium carbonate and monosulfide in the pore spaces and also perhaps the presence of organic molecules in the mud surrounding the wood. This precipitation may not have extended to the total thickness of the present concretion. In any case, the concretion process must have been well started before the decay had proceeded very far. The decay of the inner part of the wood was arrested before cell destruction, while decay of the ends could continue because the ends were essentially open to the environment (there is no concretion matrix external to the ends). In this respect it may be pointed out that Berner (1968a) reports the rapid (65 - 205 days) precipitation of calcium soaps from the rotting of fish and suggests that very early proto-concretions may be formed of such precipitates which could later be converted to calcium carbonate.

Sondheimer and others (1966) also describe the very early conversion of fish carcasses to concretions of calcium salts of fatty acids. An interesting effect reported on their Onondaga Lake, New York, concretions is that they contain more than 30 times the fatty acid content than an equivalent fish carcass. Thus, the rotting fish must have produced a micro-environment which attracted great concentrations of similar substances from the external environment to be precipitated along with those derived from the fish itself. Zangerl (1971) describes an experiment in which a fish was allowed to rot in a mud mix containing ferrous sulfate. A halo of denser material, presumably Fe, developed around the fish within nine days.

Rotting wood in the Indiana concretions would provide no fatty acids to form the soaps, but the increased alkalinity could promote early precipitation of calcium carbonate.

There is very little information pertaining to actual rates of concretion growth. Berner (1968b) calculates the time required for a spherical concretion to form, assuming the rate of diffusion to be the limiting factor. Under stagnant water conditions a concretion of 5 cm. radius could form in about 11,000 years and, with a ground water flow of 300 m/year, the same size concretion could form in about 2,000 years. Ehlin (1973), on the basis of radiocarbon dates obtained radially from the center to the periphery of a calcareous concretion from glacial varved clay, shows that a disc-shaped concretion with a radius of about 5 cm. and a maximum thickness of 1.5 cm. took about 2,000 years to form. He considers this result to be in agreement with Berner's (1968b) calculation.

Unfortunately, it is not possible to estimate the time interval involved between the onset of bacterial decay of wood and the destruction of its cell structure under the burial conditions of the organic-rich mud which ultimately formed the black shale. The carbonate of the concretion and particularly the concentration of pyrite provide evidence for bacterial activity on the wood. It is probable that such degradation would commence immediately after burial. The rate of decay is unknown. Experience with sunken or buried ships indicates that, while wood cells are degraded, the cell walls retain their shape and structure and the wood appears very similar to the original shape and size while waterlogged (e.g., Albright, 1966). Drying out without treatment usually results in considerable shrinkage and disintegration (Seborg and Inverarity,

1962). Wood from ships up to 3,000 years old has been found in this condition (Bass, 1967). Destruction of the organic substance so that only the resistant materials in the cell walls remain is probably a relatively quick process — a matter of a few years to a few tens of years.

Thus, the wood in the concretion may have retained its structural identity for several thousands of years. (Under the acid conditions of peat, wood is well-preserved for thousands of years, but a marine organic-rich mud environment cannot be compared with a peat bog.) The interval of time available for the concretion to have formed sufficiently to seal off the wood from complete disintegration may, therefore, be reasonable in relation to Berner's calculations and Ehlin's results. After the wood was sealed off from continued decay processes, the ends were subject to further degradation and complete destruction of structure before miner- alization was able to preserve any wood cells. Shrinkage of the central portion of the wood with preserved cell structure was not followed by ingress of mud from the ends into the open spaces. This suggests that the shrinkage took place after the ends, filled with mud, were stabilized by carbonate precipitation. Vein filling and permineralization of the shrunken wood were the last recognizable events, except that carbonate precipitation within the concretion may have continued longer.

Since over half (by weight) of the black end zones is carbonate, the mud had been only partly dewatered during the interval between burial and the time the wood disintegrated. If the vein space were then open, the mud surely would have seeped into it, unless the mud was already partly cemented by calcite. Alternative- ly, the vein spaces were never open spaces, that is, calcite was deposited simultaneously with shrinkage, and the state of the mud in the end zones at the time of vein formation would then be irrelevant. Some of the distortion of the wood cells reported earlier may also have been due to pressure of calcite crystallization in the shrinkage cracks. However, the actual inner contacts of the black zones adjacent to the concretion are either fossil wood or else the coarse calcite fabric of the vein appears continuous with that of the calcite of the black material. The latter suggests a continuous crystallization and thus probably a synchronous one.

The high pyrite content of the concretion matrix and its concentration into two bands may be related to the micro- geochemical environment established around the wood. The

presence of decaying organic matter creates a local anaeorbic environment in which sulfate-reducing bacteria produce a high concentration of hydrogen sulfide by reduction of sulfate ions in the pore water. The hydrogen sulfide co-precipitates with any ferrous ions available and forms an iron sulfide halo around the wood.
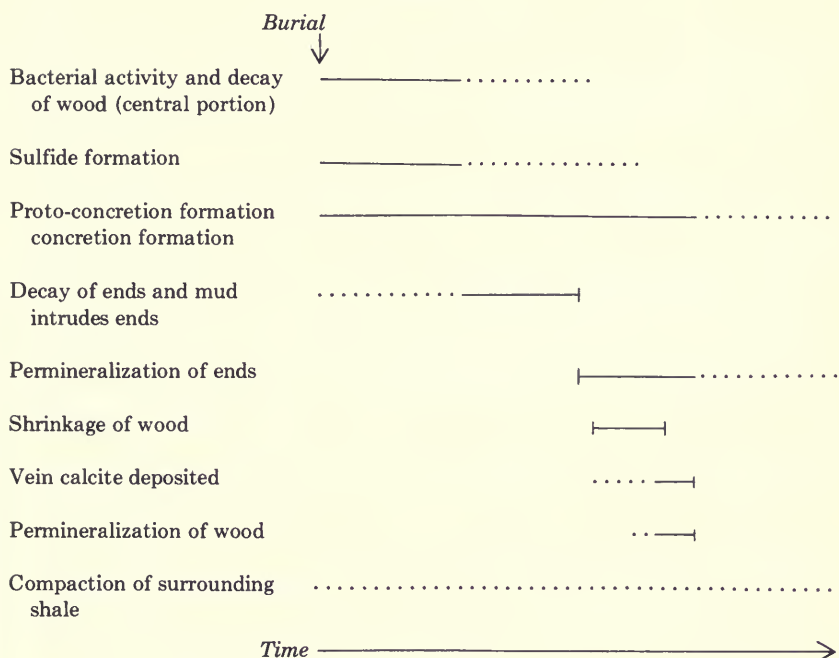
The concretionary system, as visualized, probably developed four concentration gradients that governed the precipitation of the iron sulfide: (1) As the sulfate is reduced by bacterial processes, the depleted area is replenished by diffusion of sulfate inward from the overlying sea water. (2) Hydrogen sulfide produced in excess of that necessary to precipitate initially available ferrous iron diffuses outward from the wood core. (3) Ammonia, methane, and other degradation products diffuse outward from the rotting wood core. (4) Ferrous iron solublized by organic degradation products (ferric iron in ferric hydroxides and silicates is reduced by ammonia, methane, etc. — Berner, 1969) diffuses inward toward the wood core.

If the diffusion of iron toward the wood core were slower than the outward diffusion of hydrogen sulfide, there would have been a region just outside the initially precipitated iron sulfide band in which the solubility product for iron sulfide was not exceeded. Farther out where the concentration of ferrous iron was greater, the solubility product for iron sulfide would have been exceeded, so a second sulfide band formed further out from the wood core. The initially deposited iron sulfide minerals were later transformed into pyrite, probably by reaction with elemental sulfur, during diagenesis (Berner, 1970). This explanation conforms to Berner's diffusion model with intermediate iron content of the sediments (Berner, 1969).

The pyrite concentrations formed in this way would seem to be dependent on several different factors: (1) the length of time in which the organic material was available as an energy source for the sulfate reducing bacteria, (2) the length of time communication between the sea water resevoir and the wood core was maintained, and (3) the amount of iron present in the sediments.

It is probable that the first two conditions limited the length of time during which the iron sulfide bands were forming. Since the sulfate-reducing bacteria rely on organic matter for an energy source, the production of sulfide must have ceased as the degradation of the organic matter did. This occurred before the cellular structure of the wood was destroyed. At the same time, the

TABLE 1

Burial
↓

Event	Timeline
Bacterial activity and decay of wood (central portion)	——————··········
Sulfide formation	——————···············
Proto-concretion formation concretion formation	———————————————···········
Decay of ends and mud intrudes ends	············ ————————┤
Permineralization of ends	┝————————···········
Shrinkage of wood	┝————┤
Vein calcite deposited	····· ———┤
Permineralization of wood	·· ———┤
Compaction of surrounding shale	···

Time ———————————————————→

pore space in the concretion was being filled with carbonate material, reducing communication between the overlying seawater and the wood core. Both of the processes indicate that the iron sulfide bands formed by the time the concretion was a coherent mass. This appears to have occurred over a geologically short time.

The above table summarizes the relative order and duration of events connected with the formation of the concretion, differential preservation of the wood, and precipitation of sulfides.

CONCLUSIONS

The relations between the well preserved fossil wood, the completely degraded ends of the wood, the surrounding concretion matrix, the pyrite, and the vein calcite all serve to show the dependence of the concretion forming process on the biochemical processes of decay of organic matter. This emphasizes that the concretion was formed during diagenesis and during a very short time span related, at least in part, to the duration of bacterial activity after burial of the wood.

REFERENCES

ALBRIGHT, A. B.
1966. The preservation of small water-logged wood specimens with polyethylene glycol. Curator, **9**, pp. 228-234.

BASS, G. F.
1967. Cape Gelidonya: a bronze age shipwreck. Amer. Phil. Soc., n.s., **57**, 177 pp.

BERNER, R. A.
1968a. Calcium carbonate concretions formed by the decomposition of organic matter. Science, **159**, pp. 195-197.
1968b. Rate of concretion growth. Geochim. Cosmochim. Acta, **32,** p. 477-483.
1969. Migration of iron and sulfur within anaerobic sediments during early diagenesis. Amer. Jour. Sci., **267,** pp. 19-42.
1970. Sedimentary pyrite formation. Amer. Jour. Sci., **268**, pp. 1-23.

EHLIN, P. O.
1973. Radiocarbon dating of a carbonate concretion. Geol. For. Forhand., **95**, pp. 398-399.

SEBORG, R. M. and R. B. INVERARITY
1962. Preservation of old water logged wood by treatment with polyethylene glycol. Science, **136**, pp. 649-650.

SONDHEIMER, E., W. A. DENCE, L. R. MATTICK, and S. R. SILVERMAN
1966. Composition of combustible concretions of the alewife, *Alosa pseudoharengus.* Science, **152**, pp. 221-223.

WOODLAND, B. G.
1964. The nature and origin of cone-in-cone structure. Fieldiana: Geology, **13**, pp. 187-305.

ZANGERL, R.
1971. On the geologic significance of perfectly preserved fossils. North Amer. Paleontol. Convention, Chicago, 1969, Proc. I, pp. 1207-1222.