

THE CARBONATE CONCRETIONS OF THE OHIO SHALE¹

H. EDWARD CLIFTON

106 North Market Street, Jefferson, Ohio

INTRODUCTION

Carbonate concretions comprise one of the characteristic features of the Ohio shale. The large spheroids are mentioned in the first geological literature of the state, and a number of theories as to their origin have been proposed. The Ohio shale also contains cone-in-cone structure and small discoid pyrite concretions, but the discussion in this paper is restricted to the carbonate spheroids.

LOCATION

The carbonate concretions are found only in the lower part of the Ohio shale. Located at several horizons, they are most frequent in the lower 50 feet of the formation (Stauffer *et al.*, 1911). Geographically, the concretions are found in a north-south band across central Ohio, wherever the lower part of the Ohio shale is exposed.

Kindle (1912) used the concretions as a stratigraphic marker. He proposed that the name Huron shale be applied to those beds of the Ohio shale in which concretions are found. The Ohio or Huron shale is present from Lake Huron to Kentucky.

CHARACTERISTICS

The carbonate Ohio shale concretions range from 1 to 10 feet in diameter. The smaller ones approach a spherical shape; the larger ones, flattened vertically, are ellipsoidal. The large concretions average 9 feet across and 6 feet in height. Many of these have a funnel-shaped depression in the top and bottom (fig. 1, 2). This depression, viewed in vertical cross section of broken, exposed concretions, creates the impression of double or twinned concretions (fig. 4). The larger concretions often have a ridge around the middle, composed of material different from the main body. The concretions are located along definite stratigraphic horizons. A group exposed at one locality tends to frequent the same horizon. The bedding of the shale arches equally above and below the concretion. This disturbance dies out a few feet on either side of the spheroid. Joints were found passing through some concretions, splitting them.

Cone-in-cone or similar structure typically appears in the outer edges of the concretion. The centers of some exhibit a septarian structure. Horizontal laminae are characteristic features of the main body of the concretion, the bands being one-half inch to several inches thick (fig. 3). The bands are alternating dark and light, the latter containing more chert. At the outer edges the bands curve toward the center plane. This banding is expressed as ridges on the outside of exposed concretions after differential weathering. Some concretions have a concentric ring of marcasite one-half inch thick around the outer edge.

COMPOSITION

The concretionary material typically consists of secondary crystals set in a very fine-grained matrix. The secondary material is usually calcite, dolomite,

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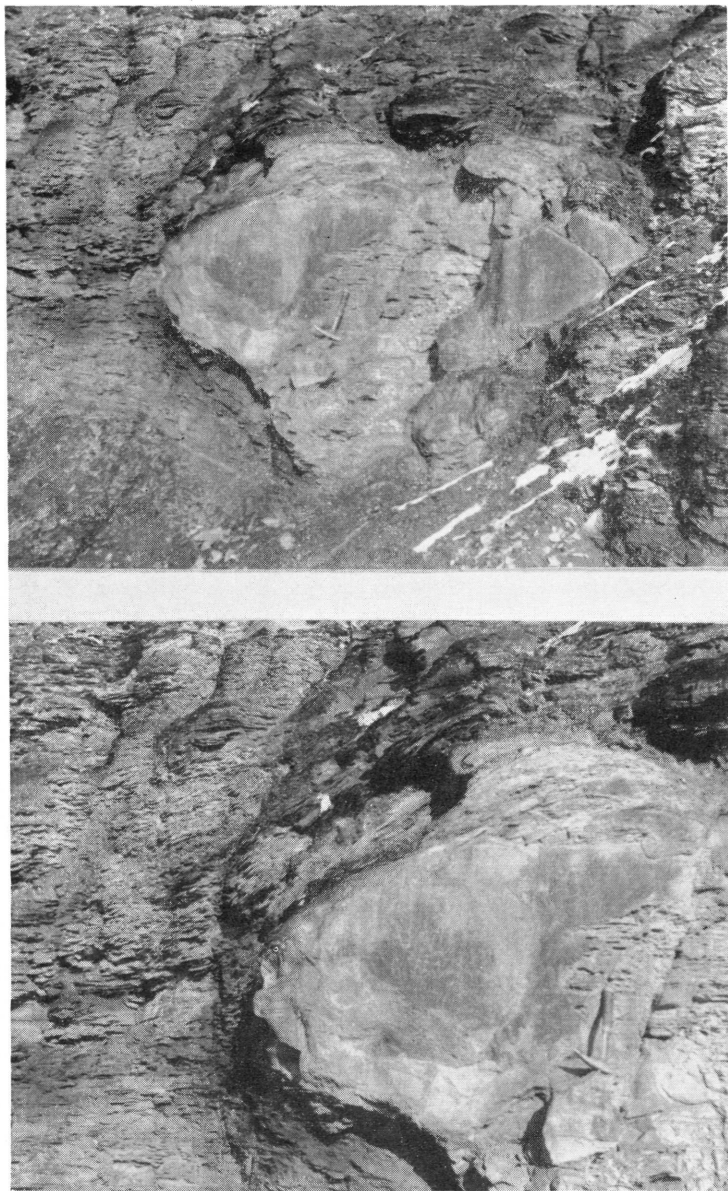


FIGURE 1. (Top) Typical Ohio shale concretion exposed in the quarry in southeast Delaware. Note zoning of concretion and the depression at the top and bottom. (Photo by R. L. Bates.)

FIGURE 2. (Bottom) Closer view of same concretion showing the deformation of the shale bedding. (Photo by R. L. Bates.)

pyrite and silica. The matrix is too finely divided to be identified, but probably contains carbonates, silica and organic matter.

The following chemical analysis of a concretion was made by Demorest for the Ohio Geological Survey (Westgate, 1926).

CO ₂	38.83 %
Ca O.....	27.29
MgO.....	13.80
SiO ₂	9.08
Fe ₂ O ₃	5.03
C (organic).....	2.25
Al ₂ O ₃	1.87
S.....	0.675
MnO ₂	0.50
Moisture at 105°C.....	0.20
TiO.....	0.12
P ₂ O ₅	trace
	<hr/>
	99.645%

The concretion centers contain varied crystal matter. Calcite, fluorite, barite, or celestite may comprise the nucleus of the concretion, although calcite is the most common (Westgate, 1926).

In the heart of larger concretions, the character of the material changes with distance from the center. The center is a soft, gray, porous material containing calcite veinlets. Here laminae are visible only as etched by differential weathering. The material becomes dense, hard, and black several feet from the center. The laminae here are well-defined alternating dark and light bands. These yield a fetid odor when struck, evidence of organic matter. The center material contains occasional rhombs or spherules of calcite or other carbonates. The dark, outer material is nearly all carbonate crystals, forming an interlocking mass. The crystals average 0.1 mm. in size. Detrital quartz fragments may be found throughout the concretion, and bands and patches of chert and chalcedony occur.

Replacement is an important factor in the history of concretions. Most of the crystalline matter is replaced material, and the matrix commonly exhibits large optically oriented patches, probably a product of coarse recrystallization. Plant tissue is often doubly replaced, first by carbonate and then by quartz. Many carbonate rhombs are zoned, indicating successive stages of replacement.

Fossil matter is common in the concretions. Plant spore cases about 0.25 mm. across are common. They consist of tasmanite, a brownish, resinous substance. Those in the center of the concretion are relatively undeformed; away from the center they are crushed between carbonate crystals or included in the crystal. Often those in the center are partially collapsed, probably from osmotic pressure. These spore cases are also abundant in the shale, where they have been flattened into plates.

Ostracods and unidentified spicules are often present in the concretion centers. Fossil wood, usually of an ancient pine, *Dadoxylon newberryi*, lies in the nucleus of some concretions. Well-preserved fish bones also have been found (Orton, 1878). Nearly all fossils are replaced by silica or carbonate.

The concretions have been designated as "ironstone" by several writers (Stauffer *et al.*, 1911). This probably results from pyrite and possibly siderite in the concretion. These weather to limonite, staining the shell of the concretion a typical yellow-brown. The concretions may be best classed as "carbonate" because of the predominance of calcite and dolomite.

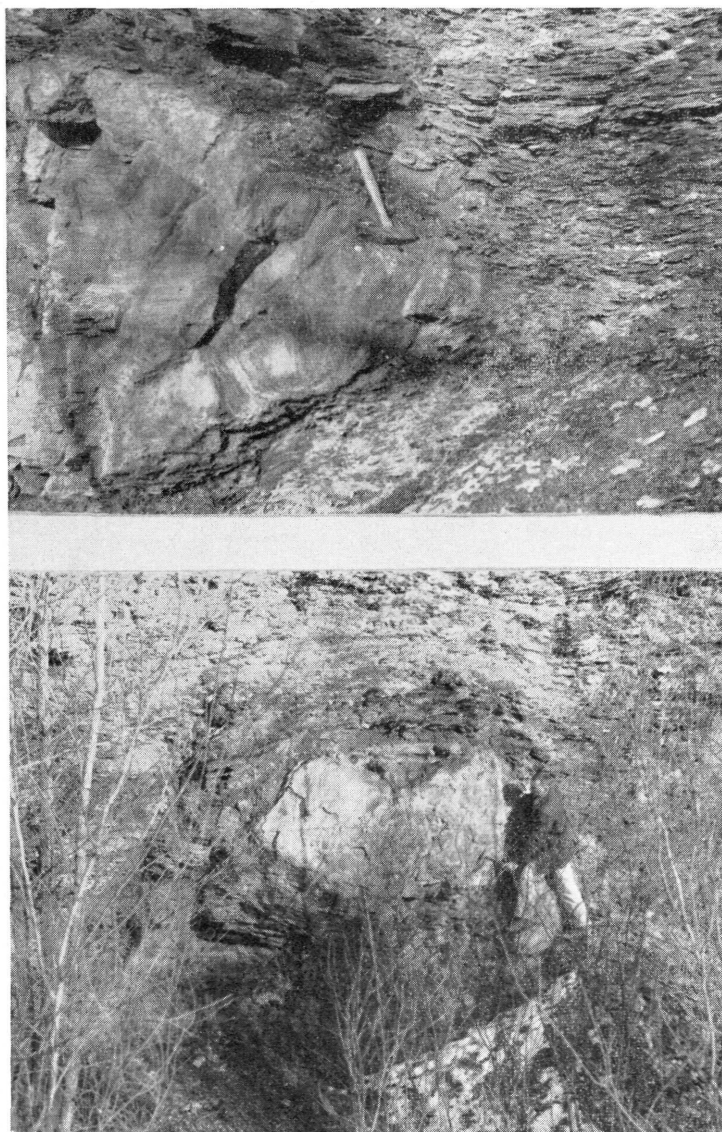


FIGURE 3. (Top) Delaware quarry concretion exhibiting horizontal laminae. (Photo by R. L. Bates.)

FIGURE 4. (Bottom) Concretion in Delaware quarry exhibiting pronounced depression on top and bottom. (Photo by R. L. Bates.)

PREVIOUS THEORIES OF ORIGIN

The origin of concretions is generally a geological puzzle, and the Ohio shale concretions are no exception. First reference to them was made by Newberry (1873). Describing concretions near Worthington, Ohio, he stated they were formed more or less syngenetically with the shale, and the curving of the shale above and below the concretion was caused by shrinkage and compaction of surrounding sediments.

Orton (1878) mentioned these concretions and noted the variety of minerals and fossils often enclosed in them. Orton apparently accepted Newberry's theory of syngenetic origin.

The next reference to the Ohio shale concretions was by Daly (1900), who described and discussed the origin of calcareous concretions at Kettle Point, Ontario. These concretions are in the lower part of the Huron shale (correlative with the Ohio shale). Daly noted that joints did not break the concretions, and the concretions had concentric structure and radial arrangement of crystals. Noting also that the shale arched under as well as over the concretions, he believed them to be epigenetic or secondary forms, the shale being deformed by the mechanical energy of crystallizing calcite. This crystallization was effected by the circulation of ground water within the shale. Daly supposed the joints to be produced by desiccation of the shale, and the concretions to be subsequent to the joints. Because the joints do not break the concretions and because of the radial arrangement of crystals, it is possible that the origin of the Kettle Point concretions is different from that in Franklin County.

In 1921, Richardson reported on experimentation with the deformation of bedding around concretions. On the basis of the experiments, Richardson determined that the conformity of stratification to concretions is caused by displacive growth and that the earliest possible date of formation of the concretion is later than the first compacting of the surrounding sediment. He also believed that the flattened ellipsoidal shape is confined to displacive concretions. He assumed vertical pressure, limiting growth in the vertical direction. His experiments, however, were made by using plastic clay to simulate the material surrounding the concretion. When subjected to vertical pressure, the plastic would flow around the concretion; there would be no shrinking due to de-watering of the sediment.

Although Richardson's experiments were not directed toward the Ohio shale concretions, his results apparently governed the thinking of Ohio geologists on this subject.

Stauffer *et al.*, (1911) mentioned the concretions in a discussion of the Ohio shale. He thought the concretions to be secondary because of the arching of the shale around them and their uniformity of composition.

Westgate (1926) discussed the concretions in detail and wrote that they were "clearly epigenetic." He believed they were related in some way to water circulation just above the impervious Olentangy shale. Why deposition occurred, what limited the size of the concretions, and why they are present only in the lower part of the formation, were questions he could not answer.

Although no further references on the Ohio shale concretions were found, several articles relating to concretions in shale were studied. These discussions favored syngenetic origin, in which the formation of the concretion occurred during or shortly after deposition of the enclosing sediments.

Tarr (1921) wrote that concretions in shale generally have a syngenetic origin. If epigenetic, they should crumple and distort the shale laterally. Tarr had never seen this lateral distortion.

According to those favoring a secondary origin, stratification lines in the concretions are an expression of the shale bedding prior to replacement or dis-

placement by concretionary growth. Tarr believed these lines were independent of the bedding, developing as the concretionary material accumulated. Well preserved, undeformed fossils within the concretions, and concretions of large volume, were also taken as evidence of a syngenetic origin. Both of these features are characteristic of the Ohio shale concretions.

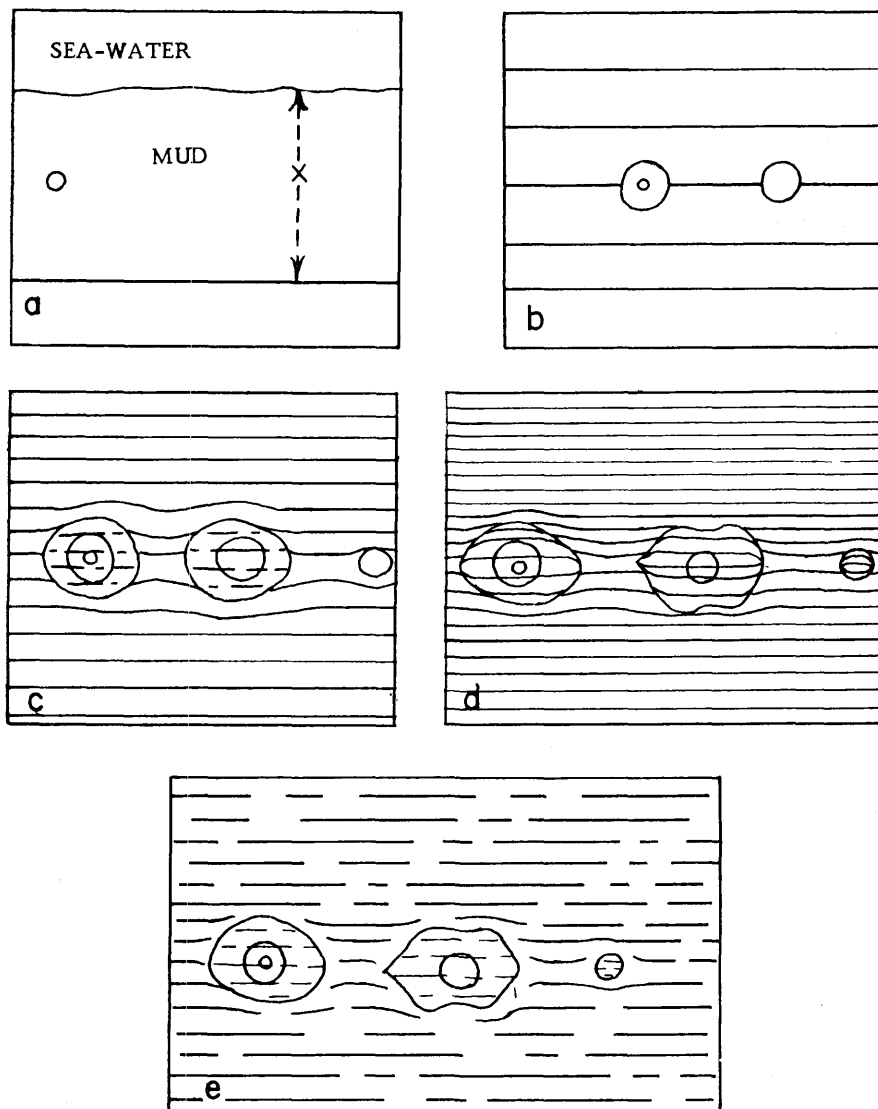


FIGURE 5. a. Sketch of muddy calcite forming in uncompacted mud. X is the original thickness of mud, successively compacted and shrunk in the following diagrams.

b. Concretion forming in partially compacted mud.

c. In more densely compacted mud, some concretions are still beginning to develop. Horizontal laminae of mud frozen in concretion.

d. Compaction of mud halts further concretion growth. Note laminae in edges of concretions curving toward center plane.

e. Ohio shale compacted and consolidated around the concretions. State of concretions today.

The probable inability of ground water to carry enough calcium carbonate through the impervious shale to form the concretion, and the fact that if formed by ground water in uniform shale the concretion would not occur in one bedding plane, were taken as evidence supporting the syngenetic theory.

A problem of the syngenetic theory is the calcium carbonate's forming a concretion rather than a bed. Tarr suggested that this may be due to slower precipitation of the carbonate in the forming of a concretion.

Twenhofel (1932) also discussed concretionary growth. He supported the syngenetic origin of concretions in shale with the same reasoning as Tarr.

It should be noted that both Tarr and Twenhofel used the term syngenetic to designate formation of the concretion during the accumulation of enclosing sediment. Epigenetic applied to growth after the material was buried. The authors favoring the epigenetic origin used the term to mean the formation of the concretion subsequent to the compaction and consolidation of the shale.

PENECONTEMPORANEOUS THEORY OF ORIGIN

Richardson (1921) designated three relative ages at which concretions might form: contemporaneous, penecontemporaneous, and subsequent. Contemporaneous concretions form at the same time and at about the same rate as the enclosing sediment; "contemporaneous" corresponds to "syngenetic" as used by Tarr (1921) and Twenhofel (1932). Penecontemporaneous is defined as formation more or less close to the surface of recently deposited material. Tarr would class such concretions as epigenetic. Subsequent concretions are those forming after deposition when the strata had largely consolidated. These would be classed as epigenetic by Westgate (1926).

The evidence suggests that the Ohio shale concretions are penecontemporaneous (fig. 5). They definitely are not subsequent forms, as they contain undeformed and unoriented spore cases. Spore cases in the shale are flattened and oriented parallel to the bedding. Furthermore, the evidence cited by Tarr to prove that concretions in shale are not subsequent is applicable to the Ohio shale concretions. It is unlikely the concretions are contemporaneous for it is doubtful that shale-forming mud could support a concretion at its surface, *i.e.*, at the water-mud interface.

Thus the formation of the concretions probably occurred during some stage of mud compaction. The water in this mud was strongly charged with minerals, as shown by the collapse of the spore cases due to osmotic pressure. The water in the spore cases diffused out of the cases into areas of higher mineral salt concentration. Crystallization of carbonates would begin around a nucleus, perhaps starting with the replacement of organic matter. From the nucleus, crystallization would move outward forming a crystal lattice. Replacement within this lattice by more carbonates, silica, fluorite, barite, and celestite occurred, forming large crystal masses. After the lattice had formed, the subsequent crystallization away from the center likely drew out water causing shrinkage and septarian structure to develop at the center.

During the early stages of formation of most concretions, compaction of mud probably had produced some orientation of particles. Horizontal laminae passing through the center of most concretions are evidence of this. The growth of the concretion continued outward "freezing" the mud and preserving the orientation as bands. The soft, porous, gray material of the inner part of the concretion was compacted less than the outer, dark, dense crystalline material. Water may have been drawn from the inner material to assist the formation and subsequent replacement in the outer section. This would undoubtedly alter the inside to some degree also.

Replacement continued also as rhombs and spherules of carbonates were formed, and the matrix was replaced by silica. Spore cases often served as the nuclei for the carbonate crystals, while the formation of crystals caught and crushed others.

New concretions formed after the mud was fairly well compacted. Less than two feet in diameter, these contain solid, dense, dark banded material throughout. This material is identical to the outer material of the larger concretions and may be assumed to have formed in the same way.

During the early growth of the concretion, the shape was probably spherical. As compaction increased the orientation of particles in the surrounding mud, the water circulation would tend to become more nearly parallel to the orientation.

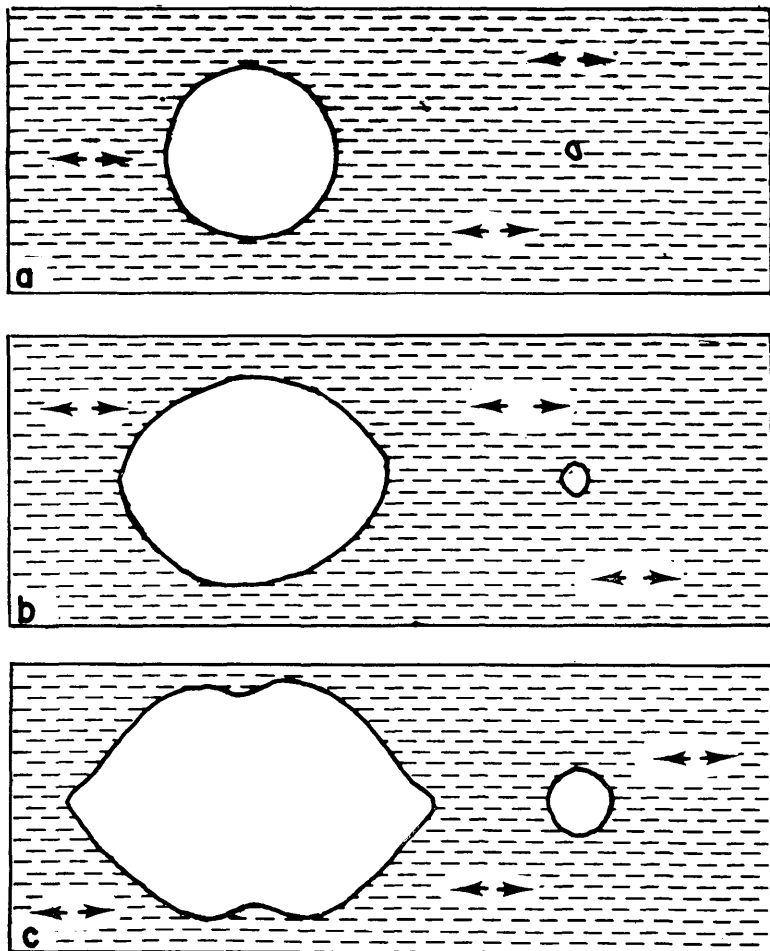


FIGURE 6. a. Systematic diagrams representing growth of two spherical concretions of different size. The view is a cross section. The water circulation is restricted to horizontal movement as shown by the arrows.

b. Additional crystallization is primarily lateral, for horizontally circulating water can not span the large surface area across the top and bottom. Less crystallization would occur here for mineral matter would crystallize on the sides. The small sphere grows equally in all directions.

c. Further crystallization builds up ridges around upper and lower surfaces of large concretions, leaving depressions at very top and bottom. Small concretions remain spherical.

This would give mineral material more access to the sides of the concretion than to the top and bottom. Lateral growth would, therefore, exceed vertical growth and a flattened form would result. This would not greatly affect the smaller concretions, for, with a smaller surface area, charged water could reach all the surface area by diffusion and capillary action. The larger concretions, with a large surface area across the top and bottom, would not receive as much mineral material in these points because it would tend to precipitate on the sides. The smaller the concretion, the more closely it approaches a sphere. In the larger concretions, water circulation would build up material in a ring at the top and bottom, leaving a depression at the very center, since the water reaching this point would have already lost its mineral matter and none would be deposited (fig. 6).

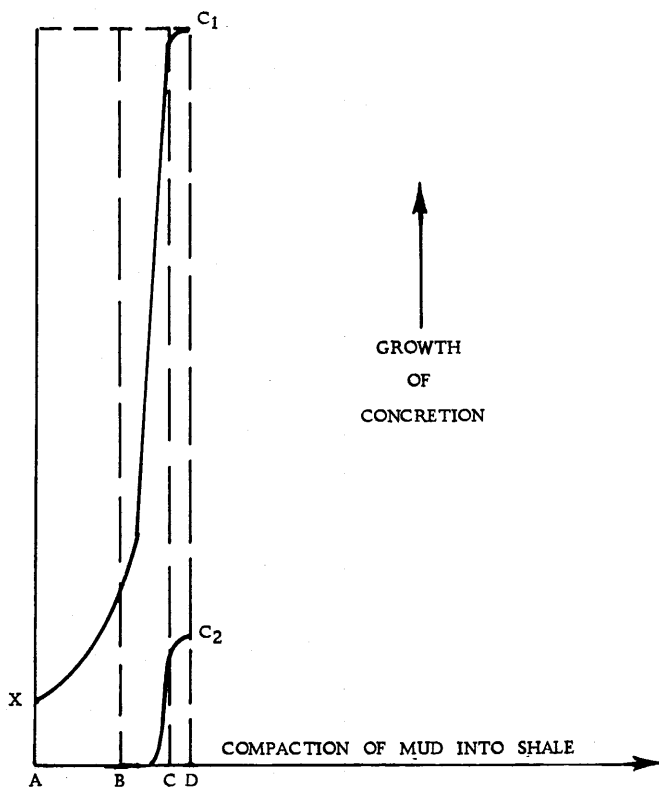


FIGURE 7. Possible range of formation with respect to the compaction of the mud. Curves C₁ and C₂ represent the limits of the range. Along coordinate A, the mud is soupy and uncompacted. The growth of any concretion (up to X) would be crystallization of muddy calcite. A to B on the compaction bar represents that period of compaction when the centers of large concretions were formed. B to C is when the concretion had its greatest growth. Here either the compaction was arrested or the rate of growth was optimum. C to D is the compaction that slowed and finally stopped the growth at D. From D on, the shale was arching over the concretions. C₁ is the curve for the large concretions with muddy calcite centers. C₂ represents small, uniform concretions.

The laminae curving toward the center plane at the edge of the concretion indicates compaction of the mud at the point where the concretion ceased to grow. This probably occurred because the water was squeezed out with compaction. Horizontal rather than convexly curved laminae indicate that the rate of growth

of the concretion did not correspond to the rate of mud compaction (fig. 7). Either the compaction of the mud was arrested, allowing the main part of the concretion to form while the bands remained uniform, or, more likely, the rate of growth was so much faster than the rate of compaction that the laminae are essentially horizontal. This infers that at a certain degree of compaction, conditions for crystal growth were optimum, perhaps with the greatest concentration of mineral salts. Compaction exceeding this optimum would squeeze off water and considerably slow and eventually stop the concretionary growth.

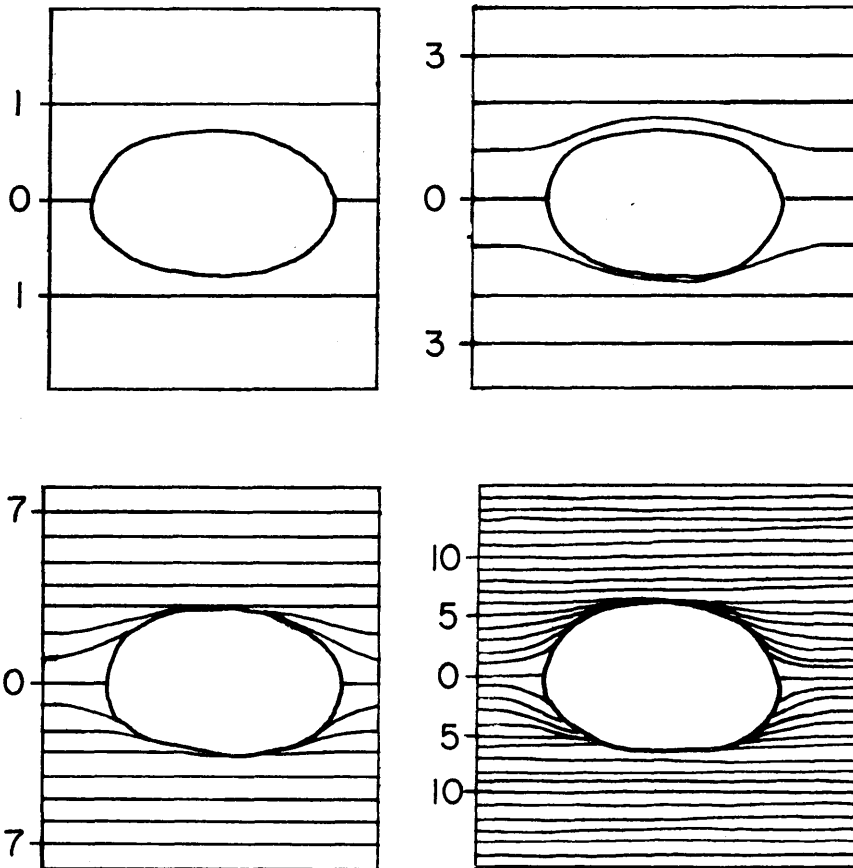


FIGURE 8. Systematic diagram showing compaction and shrinkage of a uniform medium around a solid body. Material reduced to one-eighth original thickness. As distance between lines approaches zero, an increasing number of lines are deformed over the solid body.

At any one time the difference between the compacted mud at the bottom of the concretion and that at the top would have been negligible. Because of the great thickness of sediments and the comparatively small area of the concretion zone, the concretion may be considered to have been formed in a uniform medium. Thus, when final compaction and shrinkage occurred, the mud was arched equally over the top and bottom (fig. 8). The compaction flattened and oriented the spore cases. The horizontal ring found around the middle of some concretions was formed after this, for it contains flattened and oriented spore cases. This material is not directly related to the main body of the concretion, for the ring weathers off exposed surfaces of the concretion, leaving a smooth curved face.

A small amount of growth due to replacement occurred at a later time. Rather than a sharply defined shale-concretion boundary, a gradual transition between the two exists. Some concretions have a small concentric ring of pyrite or marcasite around the outside, resulting from later replacement. Also cone-in-cone structure around the outer edge of some concretions is evidence of later growth. These areas contain no spore cases.

When the joints that cut the Ohio shale were formed, many concretions were broken. This exposure to ground water may have effected still later replacement within the concretion.

The reason for the concretion remains a problem. It may be as Tarr (1921) suggested, that slow precipitation of carbonates promoted concretionary structures instead of beds. Perhaps there was an exceptional amount of soluble material in the mud on the sea bottom. And an irrefutable answer may never be found.

SUMMARY

The Ohio shale concretions are large spheroids in the lower part of the formation. Consisting largely of calcite and dolomite, the concretions contain a great deal of replaced material, especially carbonates and silica. Fossil material is present throughout the concretions. Well preserved animal and plant remains comprise the nuclei of the concretions, and spore cases are present throughout.

Previous theories of origin favor a formation either subsequent to the solidification of the shale or during the deposition of the enclosing sediments. The evidence suggests it is more likely that the concretions formed after the deposition of the enclosing sediments but before complete compaction of the mud. Crystallization began around a nucleus and spread outward. Replacement and secondary growth of crystals were important processes during the development of the concretion. Horizontal banding in the concretion is an expression of the compaction of the mud, frozen by crystallization. Additional compaction, as recorded by laminae bending toward the center plane, squeezed out the water and halted further growth. At a much later time, ground water may have added marcasite rings or caused replacement of the shale near the concretion. Because water in the compacted mud would tend to circulate in horizontal planes, the larger concretions grow faster laterally, resulting in flattened ellipsoids. The small concretions were not affected by this, as the charged water could more easily reach all points on the surface. The arching of the shale above and below the concretion is due to the compaction and shrinkage of the mud around the solid object.

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