

FORMATION OF CONCRETIONS OCCURRING IN THE OHIO SHALES ALONG THE OLENTANGY RIVER.¹

In the Fall of 1968 a number of small concretions were collected. These had been liberated from the containing shale banks during highway excavation on the west side of the Olentangy River North of Columbus, Ohio. The concretions characteristically occur in the lower levels of the Ohio shale (approximately the lower fifty feet). The related geology has been described by Carman (1964); Clifton (1957); Stauffer, et al (1911); and Westgate (1926), and so will not be outlined here. Ranging in size from an inch or less in diameter up to several feet, the concretions occur in a multitude of shapes, they are generally spherical or oblate spheroidal. In cliff exposures, they resemble marbles pressed into a book, with pages curving under and over the insertion. They have been referred to as "shale balls," "fossilized cannonballs", "ironstone", and as "carbonate" concretions. Typically, they have an outer shell or iron sulfide (pyrite or marcasite) which readily weathers to iron oxide on exposure to the atmosphere, hence the second of these terms for the rust-colored balls found in creek bottoms. The term "carbonate" refers to the common occurrence of calcite and/or dolomite within the interior of shale balls. Clifton (1957) has reviewed the literature dealing with the structure and formation of these concretions. Rarely, organic matter is contained within the concretion, either plant or fish remains.

The origin of the concretions in Ohio shales has been of continued interest. In the origin suggested here, the following assumptions are made:

1. Concretion growth occurred only during the period of time when muds underlying prehistoric seas were still plastic, i.e. when incremental layers could be strained a considerable amount without fracture. The growth of concretions and the deposition of mud layers occurred more or less simultaneously.

2. Continued diameter growth occurred only during a period when aqueous solu-

tions flowed or diffused through surrounding mud layers from the sea bottom surface to the site of the developing concretion.

3. The starting "nucleus" was usually an organic casualty (animal or vegetable) which settled to the sea bottom, and may have been partially buried in soft mud. In the Devonian period (roughly 350-400 million years ago), marine vertebrates abounded, and amphibians and large tree-like plants appeared. The Ohio shale is of upper Devonian age.

Concretions occurred primarily through the interaction of animal or plant remains, colonies of sea bottom microorganisms, and diffusing sea water solutions. During the major part of size increase, it seems possible that more than one kind of bacteria were resident in the remains. The kinds and extents of such colonies were probably "tailored" in some sort of dynamic equilibrium to correspond to the nature of the organic deposit, and the changing nature of the local environment (rate of solution inflow, solution pH, oxygen content, nature of any additional nutrient from an external source, and so on) (Berner 1964, 1969; Napier, et al 1968; Peck, 1962).

The growth of small concretions, into larger concretions was terminated when the accumulation of iron sulfide ceased (marcasite or pyrite), due to the continued accumulation of mud layers over the site. The consequent generation of an oxygen-deficient environment, and the resultant site domination by sulfate-reducing bacteria probably sealed off the site from any exchange of fluid from the outside. Heavy sulfide shells are common on smaller concretions whereas large concretions appear to be either without surrounding sulfide cases, or at least with disproportionately thin surface sulfide layers. It has been suggested that the sulfur was a dominating factor in concretion formation (Peck, 1962).

The kind of reaction postulated for the production of iron sulfide, using sodium lactate as a stand-in for the organic component, may be: $\text{bacteria} + 2\text{C}_3\text{H}_5\text{O}_2\text{Na} + 3\text{MgSO}_4 \rightleftharpoons 3\text{MgCO}_3 + \text{Na}_2\text{CO}_3 + 2\text{CO}_2 + 2\text{H}_2\text{O} + 3\text{H}_2\text{S}$. The carbonate represents calcite or dolomite and ferrous iron in

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solution as $\text{Fe}(\text{SO}_4)$ is then converted to insoluble FeS_2 by reaction with the hydrogen sulfide made available by the reaction noted above. The amount of FeS_2 produced in most concretions calls for an inflow of supernatant sulfate solutions. Under more aerobic conditions, existing in the earlier stages of concretion development, sulfide or sulfur produced during fluctuating environmental conditions may have been removed by direct reaction with dissolved oxygen or oxygen compounds in solution. As the site became increasingly anaerobic, due to the increased thickness of overlying mud, incipient consolidation of overlying layers resulted in decreased permeability of oxygen. Sulfate-reducing bacteria then began to take over the action with the resultant accumulation of iron sulfides. Eventually, the shell of sulfides became impervious and cut off any material flow between the concretion and the overlying water. This would appear to explain why small and medium size concretions commonly have a sulfide outer surface when freshly broken out of a containing shale bed, and why very large concretions either have no sulfide shell, or per-

haps a disproportionately thin or a discontinuous shell. VINCENT D. BARTH. 139 Westview Ave., Columbus, Ohio 43214.

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