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BARITE CONCRETIONS FROM THE CLEVELAND SHALE IN NORTH-CENTRAL OHIO[1]

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Abstract. Concretions composed predominantly of barite occur in the Cleveland Shale of north-central Ohio. They have been traced about 8 km through discontinuous exposures along the Vermilion River in Erie and Lorain Counties. These septarian concretions are flattened in the plane of bedding and average 6 cm in length. The concretions contain a black matrix largely composed of fine crystalline barite, surrounded by a fine-grained pyrite rich shell. Septa composed predominantly of more coarsely crystalline barite are generally restricted to the matrix. Although the source of the barium is unknown, the stratigraphic restriction of the occurrence, the sedimentary character of the barite, and the upper Devonian age of the Cleveland Shale suggest that the occurrence may be related to events that formed important bedded barite deposits of mid-Paleozoic age in Arkansas, Nevada and California.

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An occurrence of septarian concretions along a northern portion of the Vermilion River in Ohio has been known for some time. These concretions were described by Herdendorf (1963) as being common in the shale bluffs and gravel bars of the major streams in the Vermilion (15 minute) Quadrangle, but the fact that they are composed primarily of barite has only recently been recognized. The purpose of this paper is to describe these concretions and their occurrence in detail.

METHODS

Mineralogical determinations were made by x-ray diffraction methods using a Debye-Scherrer camera. Thin sections were examined for study of internal structures and for assistance in the identification of the minerals. Samples of shale were analyzed for barium, and concretions were analyzed for strontium by atomic absorption spectrometry. Shales were fused with lithium metaborate and dissolved in a 5% nitric acid solution prior to analysis, and barite concretions were prepared for analysis by dissolving them in a solution of disodium EDTA.

RESULTS

Basic Geology. Exposed along the northern portion of the Vermilion River are the Cleveland and Bedford Shales. The Cleveland, the topmost member of the Ohio Shale, is composed chiefly of black, compact and fissile shales containing some layers of thin, argillaceous limestone. It is of Upper Devonian age. The Bedford Shale overlying it is Lower Mississippian (Willis 1912). In the Vermilion River area, it is a red shale, although at its base it is gray and intergradational with the black shales below it.

The barite concretions can be traced through discontinuous exposures for a distance of about 8 km in eastern Erie and western Lorain Counties. Seven locations where the concretions were found are shown in table 1. At sites 1 through 4 the concretions were found loose along the bank of the river. They were gray with weakly pronounced septa, with the exception of location 3, where they were brownish and the septa were strongly pronounced. A search of the wall rock at these locations did not reveal any in place occurrences, but these may have been obscured by debris from the cliffs above.

At sites 5 through 7 concretions were found in place, restricted to a narrow stratigraphic zone approximately 2 m thick and lying within the Cleveland

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TABLE 1
Localities for the concretions.

Location 1	Mill Hollow Bacon Woods Park, beginning along the north bank approximately 300 m west of the North Ridge Road bridge.
Location 2	Mill Hollow Bacon Woods Park, beginning along the south bank about 500 m east of the same bridge.
Location 3	Approximately 200 m north of the Garfield Road bridge, along the south and east banks.
Location 4	Approximately 1000 m south of the Route 113 bridge, along the west bank and a stream bar.
Location 5	Approximately 30 m north of Route 60 bridge, just south of the junction with Route 113; in place occurrence along the western bank. This site is most accessible from the north.
Location 6	Approximately 200 m south of the junction of the East Fork of the Vermilion with the Vermilion, along the East Fork. Concretions in place along southern walls.
Location 7	Directly west of the Vermilion Road bridge over a tributary, just south of the Gifford Road cutoff; concretions in place along southern bank. Not easily accessible.

Shale near its contact with the overlying Bedford Shale. This contact is generally obscure in the Vermilion area. The concretions were typically disc-shaped, flattened in the plane of bedding. Although the distribution of the concretions was highly variable, the spacing of centers of adjacent concretions would average one-half meter in a cliff exposure.

The concretions' length varied from 1.7 to 8.6 cm (see table 2). Weight varied from 4.28 to 240.01 g with an average of 59.55 g. When sectioned, the concretions displayed four general regions: an outer rind of gray-gold matrix; an inner, extensively fractured, gray to black matrix; a hard, outer septal material; and a softer, inner septal material. These septal fillings appear as white veinlets that markedly contrasted with the darker matrix. They thin rapidly toward the exterior, and pinch out within the outer shell. The veinlets average 2 mm in thickness and reach a maximum width of up to 6 mm near the concretion centers (see figs. 1 and 2).

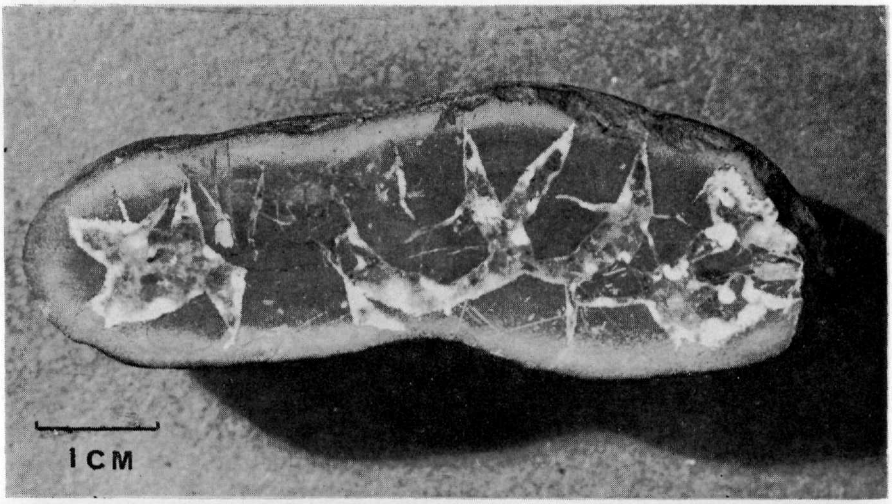
TABLE 2
Barite concretion physical data.

	Length (cm)	Weight (g)	Bulk Specific Gravity	
			Loose	In Place
Min.	1.7	4.28	2.64	3.80
Max.	8.6	240.01	4.55	4.90
Av.	4.3	59.55	3.91	4.12

The outer matrix is present only on concretions found in place, although loose concretions may contain traces of it. This outer rind averages 4 to 5 mm in thickness, and contains about an equal proportion of finely crystalline pyrite and barite. The inner matrix is composed largely of barite crystals less than 0.1 mm in size. Minor, small anhedral grains of pyrite occasionally are found. In addition, x-ray diffraction indicate trace amounts of quartz. The black color of the matrix is due to the presence of organic matter. When pulverized matrix was heated in a test tube over a bunsen flame (Twenhofel and Tyler 1941), dense, white fumes evolved and droplets of oil condensed on the walls of the tube. No definite visible traces of fossils could be observed, however, in any of the barite concretions.

Fracture systems found in the concretions are highly variable. Generally, fracture walls are lined with chalcedony, which displays colloform, oolitic and fibrous-radiating habits. The chalcedony is characterized by a muddy brown color under the petrographic microscope. The inner-septal material consists predominantly of white to gray, anhedral barite grains, 1–2 mm in diameter. Colorless, anhedral grains of yellowish-white, fluorescent calcite are present also. Although the septa are generally completely filled, euhedral crystals of barite and quartz occasionally line the walls of small vugs.

External differences between the in place and the loose concretions appear to be related to the retention or loss of the pyrite-rich rind. All concretions found in place display this rind in some form or another. Hypothetically, as the concretions are weathered from the shale bluffs, the rim is removed due to the



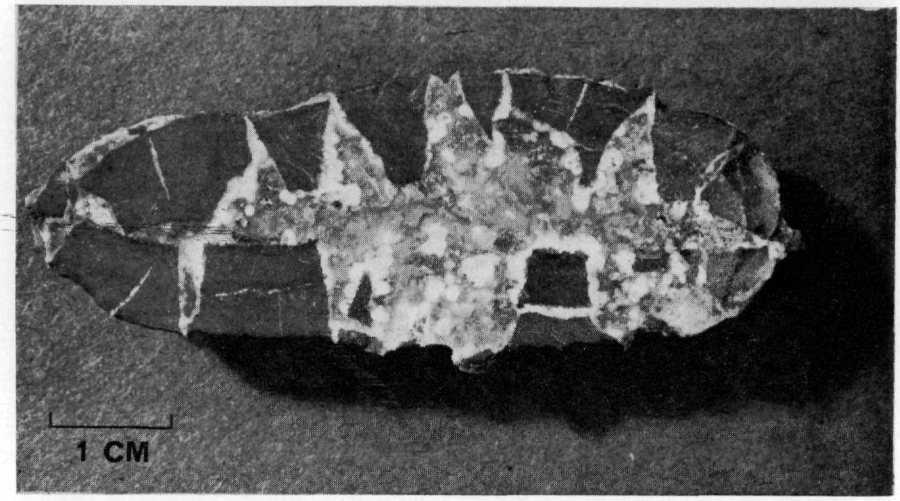


FIGURE 1. (Top) Interior of an in place concretion. The pyrite and barite rim enclose a matrix of fine-grained barite. Recrystallized barite is in the center and the fractures are lined with chalcedony. Note that the fractures terminate abruptly at the pyrite-barite rim.

FIGURE 2. (Bottom) The interior of a loose concretion showing the penetration of the fractures to the exterior.

relatively rapid oxidation of pyrite. The intricate septa fillings, because they contain minerals resistant to weathering, then stand out in relief. A complete gradation exists between the two extremes of no septa and prominent septa development (see fig. 3).

To test this "weathering" hypothesis in the laboratory, several concretions were placed in a bath of aqua regia, which was used because it oxidizes pyrite rapidly but does not affect barite (Dolezal *et al* 1968). Twelve hours' exposure to the acid was generally sufficient to remove the pyrite rind and expose the septa fillings. There were no apparent differences between naturally and artificially weathered specimens. A small difference in average bulk specific gravity between in place concretions (4.12) and loose concretions (3.91) would also be explained by this hypothesis.

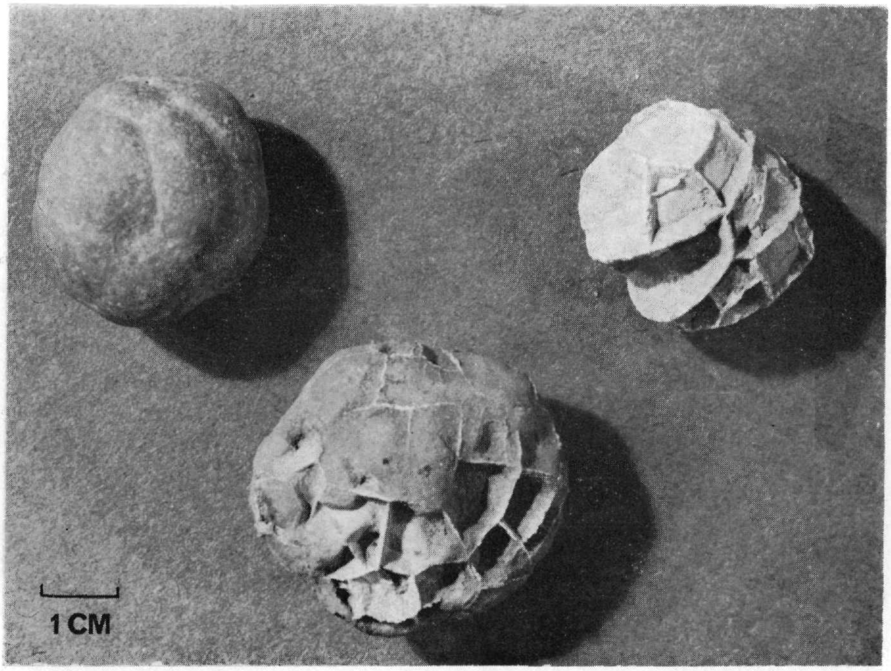


FIGURE 3. Representative examples of the three types of concretions: from left to right, in place with no septa visible, loose with most septa visible, loose with all septa visible.

A possible areal variation in the internal structure was noted: of the three locations where concretions were found in place, those found at site 5 had the best developed septal fractures. Often the entire central portion of the concretion consisted of coarse, anhedral crystals. Those from location 6 and 7, on the other hand, had only minor fractures and no significant development of more coarsely crystalline interiors. Since only a small number of concretions were collected at these three locations due to the difficulty of removing them from the shale wall, this may be only an apparent variation.

In order to determine if the shale containing concretions was barium-rich, shale samples were collected from location 5 at 5 one meter intervals; two above, two below, and one at the approximate center of the concretionary zone. Progressing downward, respective values determined were 221, 298, 634, 1437 and 659 ppm of barium, an average of 650 ppm. Worldwide mean barium content for all shales is reported by Wedepohl (1972) as 546 ppm. The Cleveland Shale thus does appear to have a slightly higher than average barium content near the concretionary zone, with definite stratigraphic control. As an additional test, two concretions were analyzed for strontium content, with a concretion from site 2 yielding 5962 ppm Sr and one from site 3 yielding 6055 ppm Sr. These strontium values fall within the reported range for bedded barite (up to 7000 ppm) as reported by Brobst (1973).

DISCUSSION

Concretionary forms of barite have been found a number of times, occasionally in the form of septaria (Samoilov 1917, Carpenter and Fagan 1969, Chuchrov and Yermilova 1970) more often as aggregates of oolites, or concretions displaying radial structure. Little agreement exists as to the genesis of these admittedly unusual occurrences. As barite is relatively insoluble in sea water, its transportation to and concentration at the depositional sites do indicate highly unusual conditions. Genesis is believed to occur where barium-rich hydrothermal fluids were introduced to the sediments during deposition (Revelle and Emery 1951, Carpenter & Fagan 1969) or where barium was transported via surface waters from a nearby land source (Haage and Krumbiegel 1968), or via a speculative biogeochemical process in which the concentrations were produced by amassing remains of a group of rhizopods known to concentrate barium within their body structures (Samoilov 1917, Wetzel 1970).

When considering the origin of these concretions, it is interesting to note theories concerning the origin of bedded barite deposits. The major deposits mined in the United States today are in Arkansas, Nevada and California, and consist of bedded, fetid, dark-gray to black, fine-grained barite. These deposits appear to be restricted to rocks of mid-Paleozoic age (Brobst 1973). Early workers with the Arkansas deposits believed they were replacement in origin (Scull 1958), although later workers leaned toward a sedimentary origin (Zimmerman and Amstutz 1964, Shawe, Poole and Brobst 1969, Zimmerman 1970). In a study comparing the Meggen deposits of West Germany with those of Arkansas, Zimmerman (1970) provided exhaustive evidence of the sedimentary features of both deposits and noted further that the sedimentary fabric found is indicative of formation under tidal flat or evaporite conditions; he further postulated the source for barium as sub-marine volcanic activity or an erosion of nearby land masses containing barite deposits. Workers with the Nevada deposits also leaned toward a sedimentary origin (Shawe, Poole and Brobst 1969, Rye, Shawe and Poole 1978).

The barite concretions found along the Vermilion River are suggestive of some aspects of bedded barite deposits. The Cleveland Shale is marine in origin, Upper Devonian in age. The shale was deposited in a reducing environment as indicated by the presence of abundant carbonaceous material and pyrite. Septa formation generally is considered to be a shrinkage phenomenon (Richardson 1919). The stratigraphic restriction and septarian character of the barite nodules themselves indicate they have a sedimentary origin as well, probably having formed during the diagenesis of the enclosing sediments. The precipitation of the barite of the matrix occurred under reducing conditions as indicated by its close association with both carbonaceous material and pyrite. The formation of the pyrite rich shell marked the close of the concretionary growth stage. The septa formed later and subsequently were filled, presumably during lithification of the sediments. But these two later developments have no bearing on the original formation of the barite itself.

Brobst (1973) speculated about whether or not the apparent restriction of bedded deposits to rocks of mid-Paleozoic age was coincidental. While the occurrence of barite concretions in the Vermilion River area does not constitute a deposit as such, their existence and the higher than average barium values for the enclosing shales prove that some type of concentrating process was operating in Ohio during Upper Devonian time. The lateral extent of the deposit could be somewhat greater than reported here since exposures in the area are generally quite poor. The mid-Paleozoic sedimentary barite association thus appears to extend into the north-central part of the United States. The exploration for economic deposits of bedded barite of this age in the Appalachia region also would seem justified.

The source of the barium for the Vermilion River deposits has not been determined. The nearest center of barite-bearing epigenetic mineralization occurs in northwestern Ohio along the flanks of the Findlay Arch. At present, however, there is no evidence linking those deposits with the Vermilion River barite.

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