

BITUMINOUS MATTER IN WARSAW GEODES

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In 1922 Van Tuyle¹ called attention to the geodes found in the Keokuk and lower Warsaw beds in this language: "Apart from Professor Brush's preliminary examination and description of a few select specimens submitted to him in 1865 by A. H. Worthen, then director of the Geological Survey of Illinois, no study of these remarkable geodes has ever been made, in spite of the fact that they bear a variety of metallic sulphides and promise to throw some light upon the origin of more important deposits of these materials in sedimentary rocks which show no signs of igneous influence." In addition to the sulphides, Van Tuyl later called attention to another very interesting phenomena connected with the geodes, namely the occurrence of a black bituminous matter. He wrote, "The geodes from the lower part of the Lower Warsaw at several localities near Niota, Illinois, are strikingly contrasted to those in other occurrences in that many of them are partly or completely filled with a black viscous bitumen. The fact that such bituminous geodes occur in a non-bituminous shale and may be found in close proximity to ordinary geodes which show no trace of bitumen, lends to this feature still greater interest. As a general rule, however, the regular hollow geodes which occur in the same layers with bituminous types show at least a black stain in their chalcedonic shells."

A few years ago Mr. Thayer Gruner, then a graduate student at Washington University, called the author's attention to the appearance of bituminous matter in what he described as "vugs" in the Alto formation a few miles south of Jonesboro, Illinois, specifically along the south line of the NW $\frac{1}{4}$ sec. 1, T. 13 S., R. 2 W., in the eroded bank of a small tributary of Dutch Creek. The vugs that Mr. Gruner described are crystal lined cavities found in the interior of siliceous concretions. These concretions could prob-

ably be called geodes, although we were not able to ascertain if they actually weathered out of the limestone and formed the familiar rounded pebbles or cobbles that most people usually think of when we use the term geode.

With these two occurrences of petroleum-like masses in geodes it appeared that there might be value in examining more precisely some of the chemical and physical properties of the bituminous matter and determining if there was any marked similarity between the bituminous matter found in these geodes and petroleum found elsewhere in the state. To this end about fifty petroleum-bearing geodes were collected from near Niota. The oil is usually a black tarry matter, so viscous that it will just about flow. We were able to collect enough of the material in this way for our determinations. However, we were able to collect only a few, eight or ten, of the geodes from the Alto formation and found bituminous matter to be, in these instances, merely a black mass lining parts of the geode cavity. It may be interesting to note in passing that small crystals of sphalerite were found in several of these bituminous-bearing geodes. In an attempt to obtain the bituminous matter we first distilled small amounts directly from the broken fragments of the geodes but were able to collect a few drops of viscous matter resembling a very soft paraffine, neither quite liquid nor quite solid. The color was dark but not black. Not obtaining a sufficiently large sample in this way, the balance of the geodes were broken up into small pieces, placed in a Soxhlet apparatus and extracted with carbon tetrachloride. The latter being distilled off, there remained a black, nearly solid mass of bituminous material which provided the samples for most but not all of the analyses performed.

For the purpose of comparison we obtained samples of petroleum from the Colmar-Plymouth oil field through the

¹"The Stratigraphy of the Mississippian Formations of Iowa," *Iowa Geological Survey, Annual Reports 1921-22, Vol. XXX.*

TABLE I.—PROPERTIES OF BITUMENS ANALYZED

	Crude oil from Colmar oil field	Topped residue from Colmar oil field	In geodes in Warsaw formation from near Niota, Ill.	In geodes in Alto formation from near Jonesboro
Carbon percent.....	82.68	85.58	82.83	86.4
Hydrogen percent.....	13.23	11.93	15.71	11.2
	95.91	97.51	98.54	97.6
Iodine number.....	21.0	21.0	29.0	50.0
Halogen content.....	trace	trace	trace	trace
Sulfur content.....	none	none	none	none
Specific gravity.....	0.867	0.902	0.785	0.895
Refractive index.....	1.4105	1.4100	1.425	1.534
Boiling point.....		110°C. 10 mm.	107°C. 7 mm.	109°C. 20 mm.
Solubility in carbon tetrachloride.....		sol.	sol.	sol.

courtesy of Mr. O. C. Ackman of the Ohio Oil Company. The oil here is found in the relatively shallow depth Hoing sand of Silurian age. This particular oil was selected because it was the nearest oil field to the Niota locality, being less than thirty miles away. We determined first the boiling point of the bitumen in the Warsaw geodes, and distilled the petroleum, rejecting all of the faction that boiled below the boiling point of the oil found in the geodes. The results shown in Table I were then obtained from the three bituminous residues.

From these results it becomes evident that there is marked similarity between the bitumen in the geodes from both Niota and Jonesboro and the topped oil from Colmar. They were paraffins of relatively high molecular weight. There are only negligible amounts of unsaturated hydrocarbons in all three. The geode oils show practically no halogen. The original sample of crude oil from Colmar contained a small amount of salt water. No traces of sulfur were found. The specific gravity is slightly high in all cases except for very high boiling point paraffin, (Hexadecane has a specific gravity of 0.775), but the refractive index and boiling points, (the latter taken under reduced pressure to avoid cracking as much as possible) correspond closely to those reported for paraffin hydrocarbons of high molecular weight.

In general the Alto geodes, appear to have lost more volatile material than the Warsaw ones. It seems reasonable to assume that the oils have at least similar sources and that they have been subjected to similar conditions affecting their formation, the Alto geodes having lost somewhat more of their volatile fraction.

The problem of migration of the oil into the geode is more difficult. Any assumption of original oil in the geode appears fantastic. We have found that the Warsaw formation where in contact with oil bearing geodes is quite saturated with petroleum in one locality, specifically along the south bank of Tyson creek about where it intersects the south edge of sec. 15, T. 7 N., R. 8 W., south of Niota, Illinois.

The chalcedony geode shell, and more particularly the shale layer immediately in contact with it are very impervious. Dr. Norris Johnston of the General Petroleum Corporation of California reports in a private communication that the air permeability of the geode walls run from 0.03 to 0.37 millidarcies, while that of a characteristic sample of Warsaw shale from the same horizon as the geodes was 0.54 millidarcies.

While the main part of the geode walls are highly impervious, in breaking some geodes there seem to be minute cracks or capillary tubes thru which the oil may have penetrated. There are sometimes seen fine black lines of oil extending from the center of some geodes to, or nearly to, the outer edge of the chalcedony shell. If oil was under considerable pressure in the rocks, it would probably find it easier to compress the gas contained within the geodes passing through the few capillary openings than to overcome the resistance of passage through the only very slightly pervious shale. We suspect the unusual imperviousness of the shale directly surrounding the geode is an important bit of evidence regarding the origin of the geodes themselves.

Conclusion: The bituminous matter in geodes found in the Warsaw formation

in the vicinity of Niota, Illinois, and in geodes found in the Alto formation a few miles south of Jonesboro, Illinois, is similar in some of its chemical and physical properties to petroleum found in the Hoing sand at Colmar, Illinois, except that the materials in the geodes have less of the more volatile hydrocar-

bons. The shale in contact with some bituminous bearing geodes is itself oil-bearing in at least one locality. The oil would find the shell of the geode in general difficult to penetrate, but there are capillary passages that would afford a passage to the interior of the geode.