Mineralization in the Harrodsburg Limestone

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Mineralization in sedimentary rocks, far from any known igneous activity, has been an interesting study in economic geology since such deposits were first discovered. Some of the more important lead and zinc deposits, as well as cadmium and other metals, are present in such environments. Deposits where the minerals are present in quantities great enough to make them of economic importance have been rather thoroughly investigated geologically, but in many areas there are smaller deposits which have not been the subject of much detailed study. The attention of the author was first called to the mineralization in the Harrodsburg limestone by Professor Ralph Esarey, of the Geology Department of Indiana University, and to Professor Esarey he wishes to acknowledge indebtedness for advice and many helpful suggestions, both in the field and in the laboratory. This paper represents a progress report on a study not yet completed. Mineral occurrences, relationships to the limestone, and paragenesis are described for only a limited area. At the present time the study has been extended to include all the Harrodsburg limestone in Indiana, and continued work may modify or completely change theories as herein postulated.

Much of the mineralization in these minor deposits occurs in geodes. These nodular masses of mineral matter occur in many places in the United States, but the most prolific and widespread horizon is in the Lower Warsaw Series of Indiana, Illinois, and Iowa. In this formation the geodes are perhaps the best developed and most abundant and contain the greatest variety of minerals of any place in the country.

In Indiana the Warsaw Series is represented by the Harrodsburg limestone. Perhaps the best exposure of this limestone in the immediate vicinity of Bloomington is in the quarry about one mile north of the city on State Road 37, where from 30 to 40 feet of the formation is exposed in a total formational thickness of from 60 to 90 feet. The floor of the quarry is not more than ten feet above the contact between the Harrodsburg and the Borden or Knobstone. It was from this quarry that most of the specimens were collected for study.

The Harrodsburg limestone is typically coarsely crystalline and contains great numbers of crinoids and bryozoans. In certain localities the formation becomes more shaly. This is especially true in the quarry north of Bloomington where the lower 15 to 20 feet of the 40 feet exposed is a greenish, shaly limestone, interfingering with more calcareous lenses. Toward the top of the section much of the argillaceous material disappears, and the formation assumes the light grey (often bluish), coarsely crystalline, very fossiliferous aspect of the typical limestone. In the zone of oxidation the color changes to a distinct buff or tan due to the presence of the hydrous oxide of iron. The line of

transition between the oxidized or weathered and the fresh limestone is very sharp in most places, there being practically no gradation.

Mineralization in the quarry is not confined to the geodes, some of the best occurrences of minerals being in drusy cavities, along joints, fractures, bedding planes, and stylolites, or disseminated in the limestone close to one of the avenues of lower resistance to mineralizing solutions.

The term "geode" comes from a Greek word meaning earthlike, because the usual form of the geode is spheroidal. Several definitions have been proposed, but none of them quite fills the requirements. Perhaps the best definition is one given by Van Tuyl:[1] "Geodes are rounded or nodular masses formed by the inward growth of mineral matter upon the walls of pre-existing cavities. They may be solid or hollow, depending on whether or not the process of filling has been carried to completion."

The definition, as stated, is too inclusive. Not all masses of mineral matter growing inward from the walls of pre-existing cavities can be classed as geodes. Many are cavities containing only a few crystals or having the walls only partially covered with mineral matter. The term geode should be restricted to those masses having a complete outer siliceous shell and the interior either wholly or partially filled. An amended definition, embodying the restrictions as stated above, follows: Geodes are rounded or nodular masses of mineral matter, having an outer siliceous shell and growing inward by the addition of mineral matter on the interior of the shell. They may contain one mineral or several and may be hollow or solid. Continued deposition tends to produce complete filling.

Typical geodes of the Harrodsburg limestone are practically limited to the lower ten or fifteen feet. They occur mainly in shaly facies; and, although generally small, are well-developed. One stratum about three feet above the floor of the quarry is almost one continuous geode, so closely are they spaced. These are about two inches in diameter and one inch thick, on the average, and are composed of crystalline quartz with subordinate amounts of calcite and rare occurrences of pyrite and sphalerite. This one horizon represents the only definite limitation of geodes to one particular stratum in the vertical section. Elsewhere, geodes are scattered indiscriminately, some areas being almost or totally barren and others having geodes in considerable abundance. The latter fact may be attributed to the greater permeability of one particular area to the percolating solutions.

Intermingled with the geodes and extending up to the top of the section are irregular cavities (druses) ranging in size from one-fourth inch to a foot or more in the longest dimension. Some of these apparently were initial cavities, that is, they were present when the limestone was deposited. An example of this type is the hollow space between the two halves of a brachiopod shell. Others, and by far the most common, appear to be due to differential solution by percolating waters above the water table and along stylolite seams, bedding planes, and joints and fractures. Some cavities, occurring in rather even textured, fresh limestone are difficult to explain either by the initial theory or by differential solution. These are located at some distance from any apparent

[1] Van Tuyl, F. M., 1921-1922. Iowa Geol. Sur. **30**: 305.

path for solutions. A possible explanation is that an initial cavity, affording an opportunity for percolating waters to become active, has been enlarged by the solvent action of these waters. An interesting feature of these mineralized cavities is the presence of a number of country rock inclusions within the later mineral matter. Inclusions of this type are not common and occur mainly in those cavities which have a preponderance of dolomite. The presence of inclusions would seem to indicate one of two things: either deposition has taken place on the outside of the initial layer of mineral matter, by replacement of the limestone, at the same time that deposition was taking place on the interior; or, in extremely irregular cavities, small masses of the limestone have been cut off from the rest and included between the crystals, with some replacement.

There are several types of mineralized cavities. One type, which occurs mainly in the geode zone and for a distance of about ten feet above it, is particularly filled with rhombohedral flesh-colored crystals of dolomite with smaller amounts of calcite and tabular crystals of gypsum, with or without quartz. A second type contains calcite with two generations of crystals; a third contains calcite and drusy quartz crystals; and a fourth contains quartz, calcite crystals, and later mammalary calcite and aragonite. The last three types are mainly above the geode zone, and the second is confined principally to the upper 15 feet of the section. Where the zone of weathering comes in contact with the second type, the calcite crystals are coated with limonite. In the limestone immediately adjacent to these cavities, especially those containing dolomite, glauconite, and pyrite, this occurs rather frequently. Sphalerite crystals are common, and millerite has been found in only two instances. Barite was found in one large cavity, with dolomite and calcite.

Along joints, fractures, bedding planes, and stylolites the chief minerals are glauconite, calcite, sphalerite, and pyrite, with little quartz. The minerals are not confined to the surface of the joint or fracture but may partially replace the limestone for a distance of from one to two inches in from the surface. Many fracture planes, which would otherwise go unnoticed, are made conspicuous by glauconite, which not only fills the actual break, but, in many cases, makes a gradational contact with the limestone on both sides. Irregular, vertical veins of calcite occur locally. Considerable limestone has been removed by solution along bedding planes, and a residue, in places one inch or more thick, of very glauconitic argillaceous material has been left. The chief mineral along such planes is pyrite, which is contained in the limestone adjacent to the plane as crystals up to one-fourth inch long. Chalcedony, showing Beekite rings, and calcite occur along stylolite seams. The black material present is mainly carbonaceous matter, with innumerable microscopic pyrite crystals imbedded in it.

It is apparent from a study of the minerals present that there has been a more or less definite order of deposition. This is especially true in the case of the earlier minerals, which are also those occurring most abundantly and consistently. In all cases where the three predominant minerals are present, the order is: quartz, dolomite, calcite. The order

of deposition of the minor minerals is more difficult to determine, since they are present in small amounts and are not all present in one locality. It seems probable that more than one period of deposition has occurred. Crystalline quartz, dolomite, calcite, sphalerite, and some pyrite belong to the first period. Mammalary calcite, aragonite, and more pyrite represent the second period. Glauconite probably belongs to the second period, but its relationships to the other minerals and its low solubility make this a matter of conjecture. Its deposition may have covered a longer period than that of any of the other minerals. Barite, gypsum, and limonite are the latest minerals, the last two having resulted from the alteration of calcite and pyrite. Some examples of the paragenesis of minerals are:

1. Geode: Quartz-dolomite.
2. Druse: Quartz-calcite-limonite.
3. Joint surface: (including one inch of country rock) Calcite-sphalerite-pyrite.
4. Irregular cavity: Quartz-dolomite-calcite- (pyrite inclusion) glauconite-pyrite.
5. Solid geode: Quartz-minute pyrite crystals.
6. Druse: Dolomite-calcite-gypsum.
7. Fracture plane: Glauconite-pyrite.

Several theories have been advanced to explain geodes. One states that a crinoid calyx may be replaced by silica.[2] Deposition begins between the plates which make up the calyx, and, as more silica is added, the plates are gradually forced apart and finally are engulfed in the silica. Bassler[3] says that many of the geodes can be traced directly or indirectly to a crinoidal origin, since there are large numbers of these organisms present in the rocks. He also says that the common brachiopod, *Athyris lamellosa*, may be next in importance. If conditions are right, almost any fossil can be replaced by silica. Some of the geodes of the lower Harrodsburg may have been formed by the replacement of fossils; but, for the most part, the lower beds in the section studied are shaly and not very fossiliferous. In no case was a geode found which had only partially replaced a fossil. Such replacement is common in the geodes of the upper part of the Borden formation.

Van Tuyl[4] ignores fossils in his theory for the formation of geodes in Iowa and Illinois. He states: "The origin of the geodes in the region studied is believed by the writer to be related to the calcareous concretions which originally must have been very abundant in the beds and which are still preserved in some localities. These nodules, being more soluble than the enclosing rocks, have been in large part removed, thus leaving cavities in which the geodes could be formed. * * * The removal of the calcareous nodules which, it is assumed, preceded the geodes, implies an interval of solvent action during which the beds were above ground-water level. The growth of geodes, on the other hand, undoubtedly took place below the ground-water level."

[2] Shaler, N. S., 1899. Geol. Soc. Amer. Bull. 10:253.
[3] Bassler, R. S., 1908. Proc. U. S. Nat. Mus. 35:133.
[4] Van Tuyl, F. M., *op. cit.* 344-346.

The writer does not wholly agree to any theory heretofore proposed, since insufficient evidence has been obtained to date on the Indiana geodes. Continued work may shed some light on this complex problem. In the vicinity of this study there are very few calcareous nodules left; so replacement must have been very complete, if such replacement has taken place. Fossils play an important part in the formation of geodes in the Upper Borden where over-silicification of brachiopods and corals is very apparent. The only fossils occurring abundantly in the lower part of the Harrodsburg in this quarry are crinoid stems; and these, while silicified, do not seem to have contributed in any way to the formation of the geodes. Also, crinoids occur only in the calcareous phases of the Lower Harrodsburg and are not present in the shaly members where the geodes occur.

The source of the minerals seems to be in the limestone itself. The Harrodsburg is overlain by the Salem limestone, which will average close to 96% pure calcium carbonate; and it is underlain by approximately 600 feet of intercalated shales and sandstones, comprising the Borden or Knobstone formation. It is highly improbable that either of these formations could have been the original source of the metallic minerals or that ascending thermal waters could be responsible, because of the widespread occurrence of the minerals. Apparently small amounts of the minor minerals were present in solution, either in the present combinations or in different ones in the Warsaw sea, and were precipitated out along with the lime. Water percolating through the limestone has taken the minerals into solution and redeposited them under favorable conditions. The composition of these solutions must have changed considerably or have been highly complex during the period of deposition, since part of the minerals are soluble in acidic and part in alkaline solutions. The composition also must have varied locally, because the same sequence of minerals is not present in all cases. Change in composition of the solutions probably was the chief factor controlling deposition, although the latest minerals, amorphous calcite and aragonite, and some encrusting chalcedony appear to have been deposited by evaporation.

Nothing can be said definitely as to the time of deposition, because there is nothing on which to base estimates. The process of taking into solution and redepositing obviously covered enormous periods of time and may still be going on in places where the limestone is below the water table. In the quarry studied, however, deposition seems to have been stopped for some time with corrosion of existing crystals and formation of secondary minerals, such as limonite, gypsum, and barite, the latest stage.