# ORIGIN OF PYRITE NODULES IN THE ST. PETER SANDSTONE, BUFFALO ROCK STATE PARK, ILLINOIS

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#### ABSTRACT

Pyrite nodules occur in the top of the Ordovician St. Peter Sandstone, directly beneath the unconformity with the overlying Pennsylvanian Colchester (No. 2) Coal at Buffalo Rock State Park. The pyrite formed as a result of the anoxic conditions produced by the Pennsylvanian coal swamp or by the coalification processes that would have expelled anoxic water into the permeable St. Peter substrate. The nodules are not present where units other than the coal overlie the St. Peter. The nodules are concentrations of pyrite that cement quartz grains in the sandstone and replace some of the earlier calcite and quartz cement. Localization of the nodules was controlled by bedding and cross-bedding planes and by irregular vertical joints. Many of the nodules are surrounded by bleached rims of gypsum cement and by very dark bands of limonite, both of which are the result of oxidation.

## INTRODUCTION

Nodules of pyrite occur in the exposed top of the Ordovician St. Peter Sandstone at Buffalo Rock State Park. The pyrite serves as a localized cement that binds the quartz grains of the sandstone. Although pyrite is abundant in Illinois coal beds and in associated organic-rich clays and shales, it is uncommon for it to be found in the clean, quartz sandstone of the St. Peter Formation. The purpose of this paper is to describe this unusual occurrence of the pyrite at Buffalo Rock and to offer an explanation for its presence.

A number of geologists have described the St. Peter Formation in the LaSalle area and/or in Illinois (Cady, 1919; Willman and Payne, 1942; Odum et al., 1962; Templeton and Willman, 1963; Reinertsen and Killey, 1971; and Willman et al., 1975). The only mention of pyrite in the St. Peter is by Willman and Payne (1942,

p.72), where they say that pyrite is locally present and is "abundant enough to form dark-colored streaks which accentuate the bedding-planes and to cement the sand grains into hard clusters." No further descriptions are given, nor are any geographic or stratigraphic locations.

Buffalo Rock State Park is located along the Illinois River about ten miles east of LaSalle and about five miles west of Ottawa, LaSalle County. Buffalo Rock itself is a large, steep-sided monolith of St. Peter sandstone, unconformably overlain by Pennsylvanian rocks, that rises 30-37 meters (100-120 feet) above the floodplain of the Illinois River. It was at one time an island in the river and its top is approximately at the same level as the tops of the bluffs on either side of the river. All but the east end of Buffalo Rock was strip mined for coal between 1950 and 1952. It is the stripping that exposed the surface of the St. Peter and the contained pyrite nodules. Surface reclamation is currently under way.

Structurally Buffalo Rock is situated approximately on the crest of the LaSalle anticline.

#### MATERIALS AND METHODS

Field examination of Buffalo Rock and adjacent areas was undertaken intermittently from the summer of 1987 to the fall of 1988. Collected samples were studied with a binocular microscope and thin sections were studied with a petrographic microscope. Mineral identifications were confirmed by X-ray diffraction (XRD), using a Siemens D-500 semi-automated diffractor. Specific gravity determinations were performed by weighing samples in air and in water, using a triple-beam balance.

## OBSERVATIONS AND DISCUSSION

The St. Peter Sandstone at Buffalo Rock is a very pure quartz arenite. The grains, of medium size, are well-sorted and well-rounded. Crystal overgrowths and pressure solution surfaces are sufficiently prevalent to close much of the original porosity, but not so common as to totally indurate the rock. Willman et al. (1975) describe the rock as locally cemented with silica, but generally lacking in calcite cement. Odum et al. (1962) comment that in the subsurface the St. Peter is tightly cemented by calcite and suggest that the absence of calcite cement near the surface is due to solution and removal by near-surface groundwater. Calcite cement is scattered throughout the thin-sections of rock I sampled from the stripped surface. Four pieces of sandstone were treated with dilute HC1 to determine calcite content. The results indicated a range of 8.76 to 10.38 weight percent calcite, with a mean of 9.71 percent (equal to a mean of 9.5 volume percent).

Pyrite nodules occur in the top of the St. Peter Sandstone immediately below the unconformity with the overlying Pennsylvanian rocks. They are most commonly found where the rocks above the St. Peter have been removed and the surface of the St. Peter is exposed. The nodules can be found at several such places along the north side of Buffalo Rock. A contour map of the most easily accessible site, located a short distance west of the western-most parking area at the State Park, is shown in Figure 1. The arrow on the map points to an exposure of the

unconformity, where the Colchester (No. 2) Coal overlies the St. Peter. The stippled area marks the stripped surface of the St. Peter where the pyrite nodules occur. The embayment in the contours is an abandoned quarry that served as a source of moulding sand. Additional sites are located (1) in a gully about 0.5km (0.3 miles) west of the above location and (2) above an abandoned quarry at the western end of Buffalo Bock.

The pyrite occurs in the upper one meter (3 feet) of the sandstone as nodules ranging in size from several centimeters to one meter in the longest dimension. Some of the nodules are elliptical, spheroidal or discoidal, but most are very irregular in shape. Many of the individual nodules are surrounded by a white, bleached rim, which itself is surrounded by a dark rusty-brown lineonite staining (Fig. 2), described in more detail later.

There are two main stratigraphic and structural controls that influence the location of the pyrite in the sandstone: (1) bedding and cross-bedding planes (Fig. 3), and (2) irregular vertical joints and fractures (Fig. 4). Many of the fractures form a crude polygonal pattern on the surface. In cliff faces the fractures can be seen to pinch out at depths estimated at approximately six to ten meters (20-33 feet). Sandstone filling the cracks is slightly more iron-stained than the rest of the sandstone. There is a suggestion that the pre-Colchester fractures were infilled with sand, which recemented during a period of exposure of the St. Peter.

The pyrite that comprises the nodules is in the form of localized cement in the sandstone. In most nodules the pyrite is massive and encloses quartz grains. Near the margins of the nodules, and in places where the pyrite is not so massive, some cubic crystals containing quartz grains are present (upper-left section of Figure 5a). Crystals of pyrite as large as 2mm were found.

Observations with both binocular and petrographic microscopes reveal a major contrast in sandstone texture between the nodules and the host rock. Within the host rock the quartz grains are vitreous and angular, with crystal overgrowths and calcite cement that lock the grains (Fig. 5a). There is little remaining porosity. Within the nodules the pyrite surrounds rounded grains having a dull luster and pitted surface (Fig. 5b). The change in texture is abrupt and occurs at the margins of the nodules. In some nodules that contain streaks of non-pyritized sandstone, the quartz grains have overgrowths where the pyrite is lacking. However, there are parts of the sandstone in which only minor amounts of pyrite are present, forming a thin layer on the outside of quartz overgrowths. This last observation indicates that the timing of pyritization was post-overgrowth.

The textural comparison described above strongly suggests that the pyrite was deposited by replacement, particularly by selective replacement of pre-existing calcite cement and quartz overgrowths, as well as by the filling of the small amount of remaining pore space. To a lesser extent it appears that parts of some of the original quartz grains may have been replaced also. Additional evidence of replacement is revealed in thin-section. This consists of: (1) pyrite truncating both calcite cement and cement produced by quartz overgrowths; and (2) minute embayments of pyrite into quartz grains; and (3) the fact that pyrite occupies more space than is available as porosity in the other parts of the rock.

In support of point 3 above, a specific gravity determination of a particularly well-cemented nodule yielded a value of 3.25. This indicates that 25.3 volume percent of the sample is pyrite, assuming the remainder to be quartz. It is apparent

in the thin sections that, where no pyrite is present, the rock porosity is considerably less than 25%. In addition, this amount of pyrite is much more than the 9.5% calcite present in the sandstone, indicating that some quartz must have been replaced, as well as the calcite.

Many of the pyrite nodules are surrounded by a rim or halo of white material adjacent to the pyrite. These rims are usually on the order of 3-10mm wide and they are often differentially weathered away. They are absent a few centimeters inside the rock, away from an exposed surface. The material that comprises the white rims surrounding the nodules is a soft cement that was identified by XRD as gypsum. The way gypsum surrounds rounded quartz grains is similar to the occurrence of the pyrite. The sandstone immediately surrounding the gypsum rims is stained dark rusty-brown with limonite, becoming lighter away from the nodules (Fig. 2, 3 and 4). The penetration of the limonite stain may be as little as 1mm into the rock. The stained sandstone has quartz overgrowths, with the boundary between the gypsum and limonite coinciding with the textural change. Thus, the gypsum most likely marks the original extent of the pyrite nodules. Both the gypsum and the limonite are the result of oxidation of the pyrite and can be explained by the equation:

 $190_2 + 8Ca^{+2} + 18H_2O + 4FeS_2 = 8 (CaSO_4 \cdot 2H_2O) + 4FeO \cdot OH$ . The source of the calcium could be from dissolved ions in groundwater or from the calcite cement within the rock.

A possible explanation why pyrite nodules are located in the top of the St. Peter can be found by looking at the local stratigraphy and structure, a schematic diagram of which is provided in Figure 6. The main structural feature of the area is the LaSalle Anticline, an asymmetric fold trending S20°E, with the west limb having the steeper dip. Folding was initiated during Ordovician time and continued episodically into post-Pennsylvanian time, with the axis continually shifting eastward (Cady, 1920; Clegg, 1965; and Nelson et al., 1988). During the Middle Ordovician the axis was near the city of LaSalle and during the deposition of the Colchester Coal it was at Buffalo Rock. A considerable amount of folding, uplift and erosion preceded deposition of Pennsylvanian sediments, producing a major unconformity.

The stratigraphic section in the central part of Buffalo Rock consists of the Ordovician St. Peter Sandstone overlain unconformably by the Colchester (No. 2) Coal at the base of the Pennsylvanian Carbondale Formation. Approximately 305 meters (1,000 feet) of section is missing at the unconformity here. The coal is 51cm (20 inches) thick and is overlain by the Francis Creek Shale. The coal thickens to the east and to the west, as this marks the axis of the LaSalle Anticline for that unit (Willman and Payne, 1942; Nelson et al., 1988). Also to the east and to the west, the Pennsylvanian rocks overlie strata younger than the St. Peter and the basal unit of the Pennsylvanian rocks is stratigraphically lower than the Colchester Coal (Fig. 6). According to Willman and Payne (1942) and Odum et al. (1962) underclay of the coal overlies the St. Peter at the west end of Buffalo Rock and to the cast and south of Buffalo Rock. However, the Colchester Coal directly overlies the St. Peter Sandstone at the abandoned quarry at the west end of Buffalo Rock. No underclay was observed there.

Outcrops west of Buffalo Rock, up to the west end of Starved Rock State Park, were field-checked in order to observe exposed surfaces of the St. Peter for pyrite

and to note the overlying units. In all cases the St. Peter was overlain by either the underclay of the Colchester Coal or by glacial drift. In no case was pyrite found where units other than the coal directly overlie the St. Peter. In other words, the presence of coal overlying the St. Peter appears to be intimately tied to the occurrence of pyrite.

The relationship between pyrite formation and reducing conditions has been well established in laboratory studies (Krumbein and Garrels, 1952) and such relationships noted petrographically and in the field are too numerous to cite individually. A discussion of some of these is given in Kirchner (1985). Pyrite formation most likely resulted from a reaction of iron ions in groundwater with hydrogen sulfide gas associated with decaying vegetation in the swamp or with the later coalification processes. At Buffalo Rock reducing conditions existed in the top of the St. Peter Sandstone where it served as the substrate for the Colchester Coal. Where the coal overlies the St. Peter, approximately the upper one half meter (1.5 feet) of the sandstone is medium to dark gray, colored by an abundance of organic matter. Plant roots and stagnant water extended down into it. In one place a large cast of a root was found in the sandstone. The anoxic conditions present here were certainly suitable for pyrite formation. This organic-rich zone is absent where the sandstone is overlain by units other than the coal.

It is also possible that the pyrite did not form during the period of the swamp's existence, but instead formed later during the coalification process. With compaction, gases and anoxic waters would have been squeezed out of the organic layer and down into the St. Peter. A thick shale above the coal would have restricted an upward flow. Such fluids not only could have been the agents for precipitation of pyrite in the sandstone, but most likely being acidic, could have easily facilitated the replacement of calcite cement by the pyrite.

Some consideration must be given to the possibility that the pyrite formed by groundwater interaction with the coal at some time later than the compaction of the coal, perhaps as late as the Pleistocene. In such a case, downward percolating water would have had to penetrate the Francis Creek Shale and the coal in order to reach the St. Peter Sandstone. Given the general impermeability of clay-based rocks, this seems the least likely explanation.

#### INTERPRETATIONS AND CONCLUSIONS

The pyrite occurs as concentrations of cement in the St. Peter Sandstone, occupying some primary intergranular porosity and, to a larger extent, replacing earlier quartz and calcite cement. The pyrite deposition was structurally controlled by permeability channels along bedding and cross-bedding planes and along joints.

The presence of the coal directly over the St. Peter was a critical association in the formation of the pyrite. To my knowledge, pyrite is not present in the St. Peter where overlain by units other than the coal. Either the swamp environment that existed during deposition of the coal or the later coalification processes provided the reducing conditions and hydrogen sulfide needed to form the pyrite. In the first case the pyrite would have originated by precipitation from anoxic groundwater that extended beneath the coal swamp into the St. Peter substrate. The organic-rich top of the St. Peter indicates that this condition existed. In the second case anoxic water would have been squeezed into the St. Peter during compaction of the

organic matter as a part of the coalification processes. It is not possible to tell which method resulted in the pyrite precipitation or if both were involved in the process.

Many of the pyrite nodules exposed on the surface are surrounded by white rims of gypsum cement, with outer zones of dark limonite. They are the result of pyrite oxidation, possibly since exposure due to stripping. These are not present for a depth of more than a few centimeters below the immediate surface, and in some cases not for more than a few millimeters.

### ACKNOWLEDGMENTS

I wish to thank Robert S. Nelson and Thomas K. Scaright for reviewing the initial manuscript and for their suggestions toward improvement of it. Will McCracken and an anonymous reviewer made constructive comments that led to the final version.

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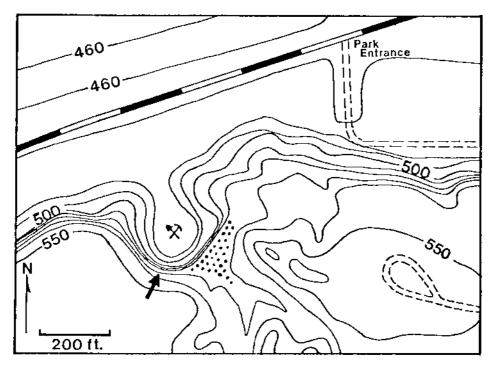
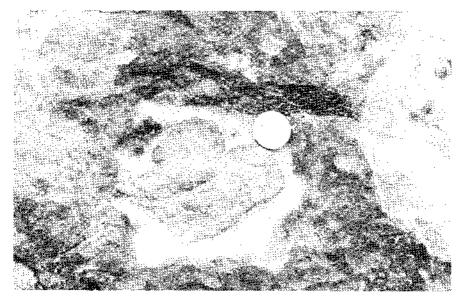


Figure 1. Topographic map of an outcrop of pyrite-bearing St. Peter Sandstone at Buffalo Rock State Park. Original base map is Starved Rock Quadrangle, 1:24,000.



 $\label{eq:constraint} Figure~2.~~Close-up~view~of~a~pyrite~nodule~surrounded~by~a~white~rim~of~gypsum-cemented~sandstone~and~by~limonite~staining.~Coin~is~21mm~~(0.8~inches)~in~diameter.$ 



Figure 3. Pyrite nodules (arrows) concentrated on a bedding-plane surface near the top of the St. Peter Sandstone. Hammer is 35cm (14 inches) long.

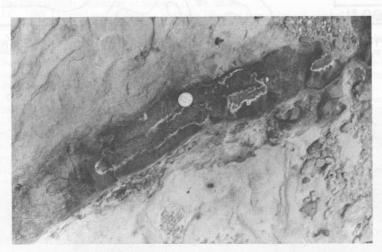
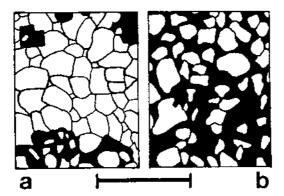
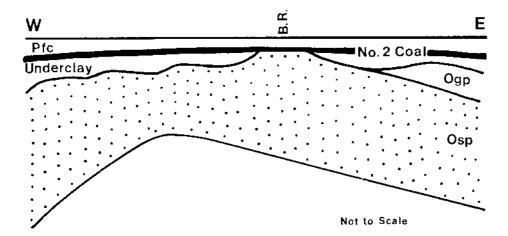


Figure 4. Bedding-plane view of a vertical joint along which elongate pyrite nodules occur. Nodules are surrounded by thin white rims and a band of dark brown limonite stain. Coin is 21mm (0.8 inches) in diameter.



Camera-lucida drawings comparing textures of thin sections of St. Peter Sandstone. Black areas are pyrite, white are quartz grains. Scale bar is 1mm.

- a. View of sandstone with little pyrite. Note the interlocking angular grains.b. Section of a pyrite nodule. Note the lack of overgrowths on the grains.



Schematic structural cross-section through the Buffalo Rock (B.R.) area. Osp: St. Peter Figure 6. Sandstone; Ogp. Galena-Platteville Group; Pfc: Francis Creek Shale.