X-RAY STUDY OF PYRITE OR MARCASITE CONCRETIONS IN THE ROCKS OF THE CLEVELAND, OHIO, QUADRANGLES

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INTRODUCTION

Concretions of iron sulfide from the Devono-Mississippian shales and sandstones in the vicinity of Cleveland, Ohio, have long been known. In some places, pyrite crystals could be identified easily, but in many localities nodular aggregates were found, which showed a massive compact or finely columnar radiated structure, that were not determinable by the usual methods. Similar acicular masses from other parts of the world generally have been designated as marcasite, presumably on the basis that an orthorhombic mineral might assume this habit more readily than an isometric crystal. An illustration is that of the "marcasite suns" which are disks with a radiating arrangement occurring in bituminous shales at Sparta, Randolph County, Illinois, which the present investigation proves to be pyrite. In July, 1931, when Bulletin 818 of the United States Geological Survey[1] was published, the occurrence of marcasite was mentioned more frequently than pyrite, especially in the shale formations. This did not conform to the few observations of the senior author of the present paper so that in October, 1931, additional specimens were collected, and an *x*-ray investigation was undertaken.

GEOLOGY OF THE REGION

The rocks which outcrop in the Cleveland district in ascending order are: Chagrin, Cleveland and Bedford shales, Berea and Sharpsville sandstones, Meadville shale and Sharon conglomerate. The last is considered to be the basal portion of the Pottsville, and therefore is of Pennsylvanian age, while the rocks from Meadville to Berea are Mississippian. The Chagrin is definitely Devonian while the Cleveland and Bedford shales are classified by the United States Geological Survey as either Devonian or Mississippian.

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[1] Geology and Mineral Resources of the Cleveland District, Ohio, H. P. Cushing, Frank Leverett and Frank R. Van Horn: *U. S. Geol. Survey, Bull.* **818,** Washington, 1931.

There are breaks below the Berea, Bedford, and Cleveland, some of which are regarded as unconformities. H. P. Cushing[2] was inclined to place the Devonian-Mississippian boundary between the Cleveland and Chagrin shales. The maximum thickness of all of these formations is about 1500 feet. Shales of Portage age, formerly called Huron, Olentangy shale, Delaware and Columbus limestones, which do not reach the surface in the vicinity of Cleveland, are at a maximum of 1000 feet below the Chagrin, but usually considerably less.

Methods of Distinguishing Pyrite from Marcasite

Pyrite and marcasite are generally distinguished by differences in crystal form, color, specific gravity, and manner in which they decompose under natural or artificial conditions. Most of these methods are not very satisfactory, and not usually applicable to concretionary masses, or to mixtures of the two minerals. In 1901, a chemical method of differentiation was devised by Stokes[3] and was called the "Stokes oxidation method" in the classic investigation of Allen, Crenshaw, Johnston, and Larsen[4] which recorded every method then known for the determination of pyrite and marcasite and for their preparation by artificial means. Since 1912 x-rays have been employed to distinguish these minerals. W. L. Bragg[5] has studied the crystal structure of pyrite while that of marcasite has been investigated by Frielinghaus,[6] Huggins,[7] and Buerger.[8] The most recent paper employing x-rays in the study of these sulfides is a very excellent contribution by Bannister[9] which describes chiefly the concretions from England, although two specimens from the United States were examined. One of these was a

[2] *Loc. cit.*, p. 39.

[3] On Pyrite and Marcasite, H. N. Stokes: *Bull.* **186,** *U. S. Geol. Survey*, 1901

[4] The Mineral Sulphides of Iron, E. T. Allen, J. L. Crenshaw, John Johnston, and Esper S. Larsen: *Am. Jour. Science*, vol. **XXXIII,** No. 195, pp. 169–236, 1912.

[5] The Analysis of Crystals by the *X*-Ray Spectrometer, W. L. Bragg: *Proc. Royal Soc. London*, (A) **89,** pp. 476–478, 1914.

[6] Röntgenographische Untersuchungen am Markasit, W. Frielinghaus: Dissert., Greifswald, **1926.**

[7] The Crystal Structures of Marcasite, Arsenopyrite, and Loellingite, M. L. Huggins: *Physical Review* (2), **19,** pp. 369–373, 1922.

[8] The Crystal Structure of Marcasite, M. J. Buerger: *Amer. Mineralogist*, vol. **16,** pp. 361–395, 1931.

[9] The Distinction of Pyrite from Marcasite in Nodular Growths, F. A. Bannister: *Mineralogical Mag.*, vol. **XXIII,** pp. 179–187, Sept., 1932.

marcasite "sun" from Sparta, Randolph County, Illinois, which was also investigated by the authors in February, 1932, and found by all to be pyrite and not marcasite. Bannister also used mineragraphic methods, studying the polished sections in polarized light as proposed by Schneiderhöhn and Ramdohr.[10] This is more rapid than x-ray methods and appears to distinguish definitely the two minerals but, unfortunately, the necessary equipment is not always available.

Occurrence and Habit of Iron Sulfide Concretions in the Cleveland District

Since October, 1931, fourteen occurrences of iron sulfide concretions have been examined. Of these, three were obtained from the Chagrin shale, ten from the Cleveland and one from the Bedford shale. There are three well-defined habits or types in which the iron sulfide is found. These are shown in Figure 1 and may be classified as follows: type 1, cubes with curved faces which sometimes occur individually but are more frequent as irregular aggregates. A sub-type was discovered in one locality in which the cube aggregates were not curved but roughened (Fig. 1, No. 1). This habit seems, therefore, to be uncommon; type 2, parallel growths or groups which consist of aggregates of curved cubes which are elongated in the direction of the trigonal axis (normal to the face of the octahedron), Fig. 1, Nos. 3–9. The most perfect is No. 8. This habit occurred in both the Chagrin and Cleveland shales, and even after more than casual inspection resembles the spear head twins of marcasite and they were assumed to be that mineral until the diffraction patterns revealed pyrite. These specimens have been shown to many mineralogists of the United States and Canada and with one exception all considered them to be marcasite. Consequently, this habit may be termed the *Pseudo-Spear Head* type, although the concretions are distinctly not pseudomorphous; type 3, the third habit is the most abundant and consists of small or large nodules which are sometimes massive compact but more usually exhibit a fibrous radiated structure (Fig. 1, No. 2). It is from concretions, sometimes containing pyrite, that many sharks and the large fish, Titanichthys and Dinichthys, have been obtained, and which have made the Cleveland shale world famous

[10] Lehrbuch der Erzmikroskopie, H. Schneiderhöhn and Paul Ramdohr, vol. 2, pp. 157, 192, *Berlin*, **1931**.

from a palaeontological standpoint. In the English concretions, Bannister[11] concludes that the radiating masses consist of tabular or blade-like aggregates which "are elongated along a cubic axis, and flattened parallel to a cube face." There is no evidence to indicate that this applies to the concretions in the Cleveland district but it may be possible.

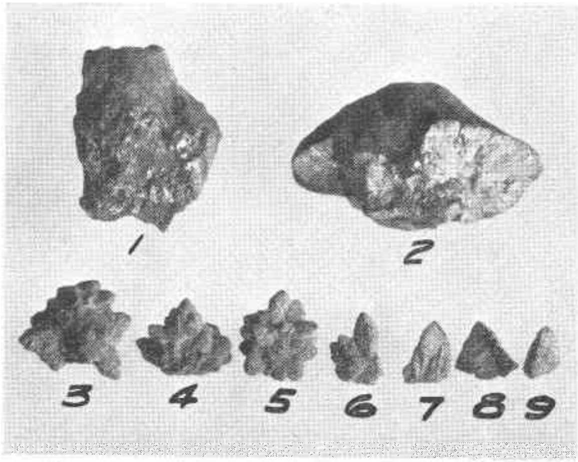

FIG. 1. No. 1. Pyrite cubes roughened but not curved (No. 1 sub-type), $4\frac{1}{2}\times 4$ cm., Bedford shale, near Olmstead Falls, Cuyahoga County, Ohio.

No. 2. Pyrite concretion showing radiating columnar structure (No. 3 type), 6×2 cm., Cleveland shale, Rocky River valley between "Little Cedar Point" and Olmstead Falls, Cuyahoga County, Ohio. (Figure 2, diffraction pattern No. 5.)

Nos. 3–9. Pyrite showing distorted cubes in parallel growths resembling spear head twins of marcasite, and termed "pseudo-spear heads" (No. 2 type), No. 3, $2\frac{1}{2}\times 2\frac{1}{2}$ cm.; No. 4, $2\times 2\frac{1}{2}$ cm.; No. 5, 2×2 cm.; No. 8, $1\frac{1}{2}\times 1\frac{1}{2}$ cm. Cleveland shale, Big Creek valley, near West 130th Street, Cleveland, Ohio (Figure 2, diffraction pattern No. 4).

X-Ray Technique and Preparation of Specimens

Diffraction patterns were made from samples prepared by powdering the minerals. Usually the minerals were brittle and could be powdered easily in a steel mortar to pass a 300 mesh screen. The photograms did not reveal any reflections corresponding to metallic iron, thus indicating that there was substantially no contamination of the samples by iron from the mortar. The

[11] *Loc. cit.*, pp. 184–185.

powder was placed in one part of a Pyrex glass capillary tube, 1 mm. outside diameter, then a separating cotton plug was inserted and a sodium chloride standard was placed in the other part. The capillary tube was sealed at the extremities and centered on a General Electric cassette containing a zirconium oxide filter.

Patterns were produced by the powder method on a General Electric apparatus equipped with a molybdenum target tube (K_α radiation), operating at 30,000 volts and 20 milliamperes. The exposure periods were 48 hours with Eastman diaphax films and the samples were rotated occasionally during this period. In measuring the positions of the diffraction lines, corrections were made

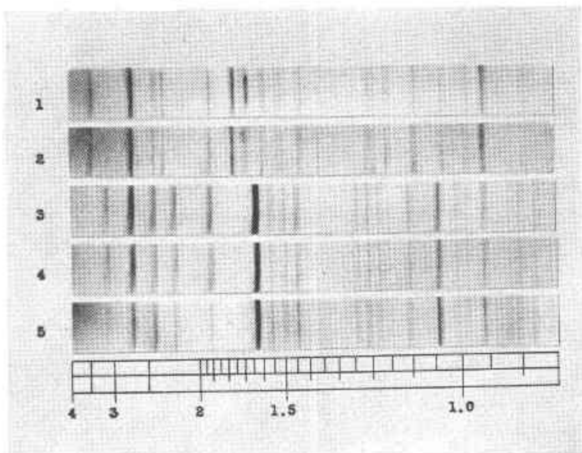

FIG. 2. Diffraction Patterns of Pyrite and Marcasite.

No. 1. Marcasite of greenish-yellow color having basal pinacoid and rounded prism which sometimes forms the aggregates called cockscomb pyrites. These crystals are associated with galena, and sphalerite on jasperoid, Joplin district, Missouri.

No. 2. Marcasite, spear head twins probably consisting of macro and brachydomes. Lower part of Olentangy shale (Middle Devonian), Delaware, Ohio.

No. 3. Pyrite with striated cube and pentagonal dodecahedron, Leadville, Colorado.

No. 4. Pyrite showing distorted cubes in parallel growths resembling spear heads and called here "pseudo spear heads" (No. 2 type), Cleveland shale, Big Creek valley, near West 130th Street, Cleveland, Ohio (same as Nos. 3–9, Fig. 1).

No. 5. Pyrite concretion showing radiating columnar structure (No. 3 type), Cleveland shale, Rocky River valley between "Little Cedar Point" and Olmstead Falls, Cuyahoga County, Ohio (same as Fig. 1, No. 2).

for any dimensional changes in the film by reference to the sodium chloride pattern, which was recorded on each photogram. The various reflections were rated as to intensity, five degrees of intensity being recognized.

Photograms were prepared from seven other massive or radiating concretions occurring in the Chagrin and Cleveland shales, and all gave the pyrite pattern. However, it is to be noted that Figure 2, No. 2 is the marcasite pattern obtained from the Olentangy shale of the middle Devonian, which is several hundred feet below the Chagrin, and over one hundred miles from the Cleveland Quadrangles.

Conditions of Formation of Pyrite and Marcasite

The conclusions of Allen, Crenshaw, Johnston and Larsen[12] were that marcasite forms under acid and fairly low temperature conditions, while pyrite originates in solutions containing no free acid and possessing a temperature that may be low but is generally high. Since the concretions in the Cleveland district were formed later than the enclosing rock, it is evident that different conditions prevailed during the deposition of pyrite than in the Olentangy shale at Delaware, Ohio. Allen *et. al.* state "that it is pretty generally believed that organic matter of certain shales acted as a precipitant of the pyrite they contain." These investigators tried to reduce ferrous sulfate with starch and glucose at 300°C. without success. They also discussed the probable action of hydrogen sulfide and the role of micro-organisms causing precipitation. Pyrite certainly is more abundant in the Cleveland shale which is characteristically black in color, containing carbon up to 11%, and petroleum up to twenty gallons per ton. One of the diffraction patterns was obtained from massive pyrite in a concretion which contained the large Devonian fish, Titanichthys, which indicates the association of organic matter, and possibly hydrogen sulfide and micro-organisms as well.

An analogous condition was observed by the senior author at Heidelberg, Germany, about 1896. A mouse was drowned in a Daniels cell containing ferrous sulfate, and when found, the surface, at least, was coated with iron sulfide exhibiting a light-brass yellow color and metallic luster. Since ferrous sulfate acts acidic, and the reaction occurred at a low temperature, we are inclined to

[12] *Loc. cit.*, pp. 190–192.

conclude that it was a "marcasite mouse," and that the reduction was presumably caused by hydrogen sulfide.

Summary and Acknowledgments

The results of crystallographic observations and x-ray analyses show that no marcasite has been found, as yet, in the iron sulfide concretions in the Chagrin, Cleveland, and Bedford shales of the Cleveland district. However, the Olentangy shale of the middle Devonian at Delaware, Ohio, which is several hundred feet below the formations referred to, does contain marcasite.

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