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ALTERNATING DEPOSITION OF PYRITE, MARCASITE AND POSSIBLY MELNIKOVITE

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INTRODUCTION

Numerous small deposits of pyrite or marcasite or both occur throughout central Missouri. They are especially common at the contact of the Mississippian and Pennsylvanian (where a marked unconformity exists), but are found also in sinkholes and along fault planes in the Ozarks and to the east of the St. Francis mountains in southeastern Missouri. Some deposits are of sufficient size to be worked on a small scale.

The material upon which the following notes are based was secured from a deposit about three miles southeast of Fredricktown, Madison county, Mo., in the southeastern part of the state. The deposit occurs in the Bonnetterre dolomite (Cambrian) and is evidently associated with a fault, though definite evidence of this is lacking. There are many prospect holes and pits in the vicinity, some of which were opened more than twenty years ago when a small amount of pyrite was mined and shipped. The Bonnetterre dolomite is probably thin for it rests upon rhyolite porphyry some 200 yards to the southwest, and the same porphyry outcrops 400-500 yards to the east.

Both marcasite and pyrite occur in the deposit, the former predominating quantitatively. The major part of the marcasite consists of radiating, plumose, and stalactitic aggregates. The sides and ends of all these forms are covered with crystals, some of which are 5 mm. across. Radiating rods of spear-head twins are quite common. Essentially all the crystal forms are either spear-head twins or coxcomb twins, the former showing a tendency to develop a pseudo-pyramidal form.

The pyrite consists of similar radiating and stalactitic aggregates, likewise terminating in crystal faces. The dominant form is the octahedron modified by the cube, but there are also a few

cubes modified by octahedrons. An octahedron with the solid angles truncated by a striated face was observed on a few specimens.

The interesting feature of this material is the occurrence of the pyrite and marcasite in alternating layers, varying from 1 mm. to 5 mm. in width. The layers are fibrous and radiating and often are terminated by crystal faces. Usually these layers are separated by a thin band of a black powder-like material. This is a sulphide, and probably was originally melnikovite, the amorphous black iron disulphide. The black mineral occurs between successive layers of pyrite about as frequently as between the pyrite and marcasite. It occurs very rarely between two layers of marcasite.

The last band or layer to be deposited, usually marcasite, may have a thickness up to several centimeters and is terminated with crystal faces. Any succeeding layer is not crystallographically similar, even though the mineral is the same. The pyrite layers frequently start with a very thin, dense band which soon becomes distinctly fibrous. This layer may form the inner wall of the stalactitic forms or the first layer after the black powder was deposited. The change from pyrite to the black powder or to marcasite was evidently rapid as crystal faces, if present on a layer, are very minute.

The black powder has tentatively been called melnikovite. It would be more correct to say it probably represents an original deposit of melnikovite, because the material, although a soft black powder, is not now magnetic. A careful study with a microscope revealed the presence of minute grains of pyrite all through the black powder, which in all probability is now extremely finely divided pyrite, as the amorphous melnikovite passes over into the crystalline pyrite in time. The change from pyrite to marcasite, or vice versa, was not dependent upon the presence of the black powder but took place independently. As will be shown below, the formation of the black band represents a rather special condition of the depositing solution.

There are many deposits of pyrite and marcasite in central Missouri in which either mineral may be deposited upon the other, but this is the only one where the writer has found them in alternating layers. The deposits we are discussing are of interest in showing how the character of the solutions may have varied sufficiently during the formation of a single deposit to permit the

deposition of any one of three different forms of a polymorphous substance as a layer on either of the other two.

CONDITIONS OF DEPOSITION

Some years ago, Stokes,¹ and then later, Allen, Crenshaw and Johnston,² investigated fully the conditions that control the formation of pyrite and marcasite. They found that they could be formed in the same deposit, never simultaneously, but always under slightly different conditions. There were two controlling factors, (1) the character of the solution, and (2) its temperature. Of these the major factor is the character of the solution, marcasite requiring an acid and pyrite a neutral or slightly acid solution.³ A complete change to an alkaline solution favors the deposition of the amorphous black disulphide, melnikovite.

The temperature of the solution, although important, is not as fundamental as the first. Pyrite certainly may be deposited from cold solutions, as is shown by its widespread occurrence in sedimentary rocks, and appears to be formed even better at temperatures well above 100°, as is indicated by its extremely common occurrence in high temperature deposits of all types. The conditions favoring the deposition of marcasite are very narrow as compared to those for pyrite. As shown by Allen, Crenshaw and Johnston, the optimum conditions for marcasite are 1.18% free H₂SO₄ at 100°. Decrease of acidity reduces its formation, and change of temperature in either direction does likewise. Decreasing the acidity to neutrality and raising the temperature favors the deposition of pyrite. Melnikovite evidently forms best at temperatures below 100° as is shown by its formation in the muds on the bottom of the Black Sea and probably on the ocean floor. It may form, however, at 100°C in alkaline solutions.

Pyrite may form in a slightly acid solution and therefore might be formed under conditions favorable for marcasite formation, so that the two might be deposited almost simultaneously, but with the pyrite greatly in excess.

The material studied shows no evidence of simultaneous deposition, but does show distinctive alternating periods of deposition of

¹ Stokes, H. N. "On Pyrite and Marcasite," *U. S. G. S. Bull.* 186 (1901).

² Allen, Crenshaw and Johnston. "The Mineral Sulphides of Iron." *Am. Jour. Sci.* (4) 33 169-236 (1912).

³ An editorial in the *Min. & Sci. Press*, vol. 107, p. 446 (1913), makes the statement that pyrite has been formed under surface conditions in an acid solution.

marcasite and pyrite, with a third member in the series appearing from time to time. Initial deposition in the material collected for study took place for the most part with marcasite, but in some instances pyrite was first. As the material was collected from dumps, the contact with the wall was not seen, hence it is not definitely known which was absolutely deposited first.

As the major part of the deposit is marcasite, it is evident that the temperature of the solution during deposition was near 100°C. The temperature may have exceeded or been less than this during the mineralization, but, in any case, the solution was fairly hot at all times.

Solutions having a temperature of 100° are certainly rising solutions, whether their source be meteoric or magmatic. As they passed through the Bonneterre dolomite in the last stages of their upward journey, unless their initial acidity was very high, they should have become neutralized to a certain degree. If neutralization took place, pyrite would be formed; whereas if the solution retained more or less free acid, marcasite would be deposited.

Assuming that marcasite was formed first from an acid solution, the acidity might be slowly reduced by the dolomite until conditions were favorable for the formation of pyrite. Its deposition would then continue until the character of the solution was changed again. If, after being reduced to neutrality, the solution was made alkaline in its passage through the dolomite (and probably accompanied by a downward temperature change) the amorphous black powder (melnikovite) would be deposited. The reverse change to neutrality would mean a layer of pyrite, or, a rapid change (by increased supplies from below) to marked acidity would cause marcasite to form; all these changes being possible at around 100°.

The fact that the black bands are more commonly interlayered with pyrite shows that the changes were probably brought about slowly, although there were times when the change was very rapid. The rare occurrences of black bands in the marcasite represent one of these rapid fluctuations from acidity to alkalinity and back again. The occasional wide bands of the black material with the pyrite, often as wide as the adjacent layers, indicate that the alkaline conditions lasted for some time.

Thus the successive layers and other alternating forms can readily be accounted for by change in the chemical character

of the depositing solution, for all might be deposited at the same temperature, or at least within a few degrees of each other. The material studied apparently gives striking support to the experimental work of the authors cited above, provided, of course, that the interpretation of the black powder as being originally melnikovite is correct.

The writer inclines to the view that the solutions are of magmatic origin. The cobalt-nickel-copper deposits of Fredricktown and Mine La Motte are only a few miles away. The former, which are within a mile of this deposit, contain enormous quantities of marcasite along with the other sulphides, and this deposit may well be connected with them in origin. In fact, this deposit has a structural position in the dolomite adjacent to two outcrops of igneous rocks, which are pre-Cambrian, that resembles to a marked degree the mode of occurrence at Fredricktown. It may be added that pyrite is abundant in the granites and granite-porphyrines of the St. Francis mountains to the west.

As far as could be determined from the literature, this is the first instance where the amorphous iron disulphide may have been deposited by hot solutions along with the other polymorphous forms of the iron disulphide, and this gives added interest to the deposit.

ADDITIONAL DATA ON THE PROPERTIES OF PUMPELLYITE, AND ITS OCCURRENCE IN THE REPUBLIC OF HAITI, WEST INDIES¹

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In 1921 during a geological reconnaissance in the Republic of Haiti, undertaken by the Haitian government in cooperation with the United States Geological Survey,² Dr. J. S. Brown and the writer collected a cobble of a peculiar amygdaloidal basalt from the bed of the Limbé River at Limbé in northern Haiti; the basalt was not greatly unlike many of the older basaltic rocks of this region, but the amygdules were very noticeable and abundant, most of them being lined with white albite and the central part filled with greenish-yellow iron rich epidote and a deep bluish-green min-

¹ Published by permission of the Director of the U. S. Geological Survey.

² Woodring, W. P., Brown, J. S., Burbank, W. S.; *Geology of the Republic of Haiti*: Dept. of Public Works, Rep. of Haiti, Port-au-Prince, 1924.