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DAHLITE PSEUDOMORPHS AFTER PYRITE CONCRETIONS  
FROM BIG HORN BASIN, WYOMING

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The occurrence of spherulitic phosphate concretions in the basal part of the Thermopolis formation (Upper Cretaceous) in the Big Horn Basin, Wyoming has been known for over fifty years. Fisher (1906) described these concretions as consisting mainly of "phosphate of lime" and having the structure of marcasite, the mineral he believed the phosphate had replaced. McConnell (1935) published a thorough petrographic description of these concretions. In his work he determined they are composed primarily of dahllite, the carbonate-hydroxyapatite. The suggestion was made that the forms might represent replacement, but he was unable to find relicts of a replaced material. The purpose of this note is to present evidence that indicates these masses are actually pseudomorphs of dahllite after pyrite. The specimens used in this study were collected by the senior writer in the summer of 1955 near Rainbow Canyon on the eastern edge of the Big Horn Basin.

The concretions are spherical in shape, frequently have a rough external surface, and average slightly over one inch in diameter. In cross section the specimens always exhibit a radial structure and show a rather consistent arrangement of their mineral constituents. At the center of all the concretions studied is an irregular mass of iron oxide which is often stellate in shape. This oxide was determined to be primarily goethite in all but one instance where hematite was found to be predominant. From the iron oxide center gray-brown dahllite extends to the surface of the spheres and constitutes the major portion of the spherulites. The concre-

tions frequently contain an external crust of earthy light-gray dahllite. Kaolinite is present in small cavities which are parallel to the general radiating structure. Pyrite, while occurring in all the specimens studied in detail, was present only in one specimen in sufficient quantities so as to be visible in the hand specimen. The pyrite in this specimen was in a radial form (Fig. 1).

Determinations of all mineral constituents of the concretions were verified by the powder  $x$ -ray diffraction method. Four patterns each of the dahllite crust, interior dahllite, interstitial clay, and iron oxide center

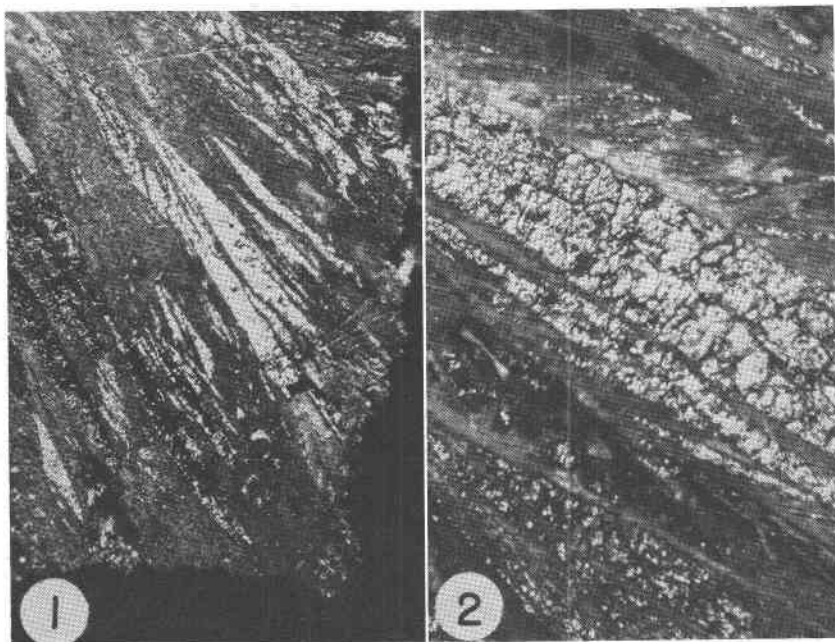


FIG. 1 (left). Photomicrograph of a polished cross section of spherulite showing the radial arrangement of pyrite (white) and dahllite (gray). Obliquely reflected light.  $\times 22$ .

FIG. 2 (right). Photomicrograph of a thin section showing the replacement of pyrite (white) by dahllite (gray). Notice isolated blebs of pyrite. Crossed nicols plus obliquely reflected light.  $\times 72$ .

were obtained from four different specimens. Interplaner spacings for the crusty and the interior phosphate indicate they are identical. However, a finer grain size in the crusty material is indicated by slightly more diffuse  $x$ -ray lines. A comparison of these interplaner spacings with those obtained by McConnell (1938) for dahllite reveals identical materials. Measurements of the clay patterns clearly show this material belongs in the kaolinite group, but a more precise categorization proved inconclu-

sive. Three of the iron oxide films revealed impure goethite, while the fourth showed hematite. A good pyrite pattern was obtained from one specimen.

Good evidence for the replacement origin of the phosphate was found in a study of thin sections of the specimen mentioned above which contains much pyrite visible to the unaided eye. These sections show many small veins of dahllite penetrating the radial pyrite. In some places the pyrite has been replaced to such an extent that it remains only as small blebs and elongate islands which are aligned more or less parallel to the radial structure of the spherulites. Some of these features are shown in Fig. 2. An examination of thin sections of several other specimens, with no pyrite visible to the naked eye, showed that relict pyrite is common in the form of these blebs and oriented elongate islands. The presence of iron oxide rims around some of these unreplaced pyrite areas suggests that oxidation was subsequent to phosphatization. Perhaps the larger areas of goethite and hematite present in the center of most specimens represent oxidized pyrite. Small specks of pyrite are frequently visible in these larger oxide areas.

The translucent brown goethite shows a fine fibrous structure in thin sections. These fibers show parallel extinction. Textural evidence indicates that part of the star-like goethite may represent crack-fillings in the concretions. Stellate cavities are known to the writers to occur in pyrite concretions from some localities. Opaque and red hematite, frequently in the form of hair-like veins and irregular blebs, is associated with the goethite in some specimens.

Thin sections show that dahllite varies in size from powdery masses to microscopic hexagonal prisms. The specimen containing much pyrite mentioned above consists of powdery dahllite. The clearly visible radial structure in this one is completely isotropic and is probably reminiscent of the former pyrite structure. Thin sections show that the radial appearance of the concretions is not due to a parallel alinement of dahllite fibers. In fact most specimens showed dahllite microlites both parallel and transverse to the pyrite fiber directions. The present radial appearance is most likely a result of controlled replacement by the former pyrite fibers. Small euhedral crystals of dahllite, exhibiting prisms and pinacoids, are commonly found in cavities in the specimens. All crystals and fibers proved to be length fast when tested with the gypsum test plate. Similar forms and characteristics of dahllite were previously described by McConnell (1935). Microscopic study also showed the presence of cavity fillings of kaolinite and quartz in parallel position to the original pyrite fibers. The general relationships indicate these were deposited in openings subsequent to the formation of dahllite. Other detrital-like quartz

grains, having no relationship to the spherulitic structure, were occasionally observed in the sections.

A striking identity was noted between the structure of these concretions and an unaltered pyrite concretion from a different locality which was sectioned for comparison. The writers feel this similarity, along with the evidence presented above concerning replacement, indicates that these dahllite spherulites are pseudomorphs after pyrite.

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THE MELTING OF CALCITE IN THE PRESENCE OF  
WATER AND CARBON DIOXIDE

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In the course of attempts to recrystallize calcite, it was found that the calcite could be melted at temperatures above about 900° C. in an atmosphere of water and carbon dioxide at a total pressure of 50 bars. The experiments were done in the following way. The specimen, of about 0.1 gm. weight, was wrapped in platinum foil and put in a pressure vessel, supplied by G. C. Kennedy, of approximately 1 cc. volume. A few drops of water were introduced and the pressure line was connected to a reservoir of carbon dioxide at 50 bars pressure. The pressure vessel was then put in a muffle furnace at the desired temperature. This produced an atmosphere in which the partial pressures of carbon dioxide and water totalled 50 bars but the proportions were not known. The same total pressure was maintained during the cooling of the pressure vessel.

The melting is best demonstrated with a cleavage rhomb of calcite. If this is heated under the above conditions at about 1000° C. for an hour, its original shape is lost and the material takes the shape of the enveloping platinum as if it were wetting the platinum (Fig. 1A). After cooling, a thin section of the specimen shows it to be polycrystalline, with a marked dendritic texture (Fig. 1B) which suggests that it has crystallized from a melt. An *x*-ray diffraction pattern shows no trace of CaO. Further evi-