A MINERALIZED SPHERULITIC LIMESTONE IN THE CHERTENHAM FIRECLAY*

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INTRODUCTION

The occurrence of a limestone in the Cheltenham fireclay of the St. Louis district is sufficiently unusual to merit a brief description. A spherulitic limestone in that situation should add to the interest, as adequate descriptions of spherulitic limestones are rare. This spherulitic limestone has two additional claims to distinction; it contains a sequence of five minerals including sphalerite, and the carbonate has been mistaken for diasporite and gibbsite.

Occurrence and Age of the Limestone

The limestone described in this paper occurs at the Prospect Hill Shale Pit of the Missouri Portland Cement Company, Riverview Drive, St. Louis. The limestone forms isolated nodules, or irregular masses, in the Cheltenham fireclay from three to five feet below a thin shaly coal, or a black fissile shale, that belongs to the Cherokee formation of Pennsylvanian age. The stratigraphic members exposed in this pit have been described by Knight, who mentions no limestone in the Cheltenham fireclay but makes the following statement:

"Locally, as at locality 8 (Prospect Hill Shale Pit) to the northeast, it (Cheltenham fireclay) contains large masses of the so-called diasporite of the clay miners. A hasty examination suggests that this is more probably gibbsite."

As diasporite and gibbsite add to the refractory character and economic value of a clay, the writer visited this locality in connection with his study of clays for the Missouri Geological Survey. He found no diasporite or gibbsite in the Cheltenham fireclay, but a gray limestone with spherulitic development which resembles somewhat diasporite clay with oolitic structure. Considering the possibility that the spherulitic limestone had been mistaken for diasporite clay, he interviewed the pit foreman and learned that a workman who was familiar with diasporite clay had identified the limestone masses as diasporite. This accounts for the erroneous report in the literature of diasporite in the Cheltenham fireclay.

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PETROLOGICAL AND MINERALOGICAL FEATURES

At the south end of the pit limestone nodules, two or three inches in diameter, underlie a shaly coal but are so weathered and coated with clay, iron oxides, and gypsum that it is difficult to determine their structure. About midway along the east side of the pit is an area of about ten feet square where the shale and clay have been removed exposing the limestone that forms the floor. The limestone is discontinuous and where the irregular masses are present they vary in thickness from five to eight inches. The center of each lens is massive and even grained, and in most of them the upper and lower two or three inches are composed of round particles having a maximum diameter of 2 mm. (Fig. 1). In thin section these round particles have a radial development (Fig. 2), but lack all traces of a concentric structure so that they are more properly termed spherulites than oölites.² In parallel light, between crossed nicols, the spherulites show the "spherulitic figure,"³ consisting of a dark cross with brushes parallel to the principal vibration directions of the nicols. The majority of the spherulites have a diameter of about 1.5 mm., and those near the top and bottom of each lens are coated with a thin film of clay which gradually decreases toward the central non-spherulitic portion.

The spherulites are composed of nearly pure calcite, and there is nothing present to suggest that they were deposited as some other mineral, such as aragonite, and later changed to calcite. The optical characteristics of the radial fibers are: \( \varepsilon = 1.495 \pm .005, \omega = 1.665 \pm .005 \), uniaxial, negative. These properties suggest that the mineral is calcite containing traces of iron or magnesium carbonate to increase slightly the refractive indices. Qualitative chemical tests showed the presence of small amounts of iron and magnesium, and a large amount of calcium, all present as carbonates. The spherulites dissolve in cold dilute HCl. All the data are in keeping with the idea that the spherulites are composed of calcite in which a small amount of iron and magnesium have isomorphously replaced some of the calcium.

Through the courtesy of Dr. H. A. Buehler, who⁴ has long been interested in the artificial formation of minerals, a chemical analysis of the spherulites was made in the laboratory of the Missouri Geological Survey with the following results:

² "Particles of dimensions similar to oölites and pisolithes but with radiate and not concentric structure are designated spherulites." Twenhofel, W. H., and others, Treatise on Sedimentation, p. 757, 1932.
The insoluble material was clay, coating the outside of the spherulites, which resisted all attempts to remove it.

The spherulites, and the granular limestone at the center of the lenses, contain angular quartz grains with a maximum diameter of .1 mm. Irregularly distributed grains of pyrite and dark veins of a brown carbonate, with rhombohedral cleavage, cut the limestone (Fig. 1). This mineral is probably ankerite as it is uniaxial, negative, with $e = 1.534 \pm .005$, also chemical tests indicated traces of iron and magnesium as well as calcium, present as carbonates. Likewise small veinlets of sphalerite traverse the limestone. Some of the sphalerite was isolated and examined optically, and the results verified the determination of this mineral. The sequence of deposition apparently was quartz, calcite, pyrite, ankerite, and sphalerite. Sphalerite in this association seems to be a clear case of deposition from cold water.
The origin of the spherulites may be briefly considered under four headings:

(1) The spherulites may be secondary and represent calcium carbonate leached from above and deposited around the central granular part of the limestone mass. If this were the case, it is difficult to understand how sufficient calcium carbonate found its way through the limestone lenses to form a thickness of spherulites on the under side nearly equal to that on the upper.

(2) An organic origin is not favored because of the absence of any organic structures, and because spherulites have been grown without the aid of organisms.

(3) Morse, Warren, and Donnay\(^5\) have produced artificial spherulites of many substances, including calcium carbonate, in gels. They regard mixing of the reacting solutions by diffusion and the absence of convection, as essential factors to the formation of spherulites. As the exterior of the spherulites near the top and bottom is coated with clay, which decreases in amount towards the center of the limestone, the possibility is suggested that finely divided clay acted as a colloidal medium through which calcium carbonate diffused to form the spherulites. But, as the spherulites closest to the central granular limestone are free from clay coatings, the presence of such clay material during deposition does not seem to be the determining prerequisite. Nor can the writer conceive of a condition whereby sufficient calcium carbonate could be stored in the under-and overlying clay to permit later additions of calcium carbonate to diffuse and form spherulites on the upper and under sides of the granular nucleus.

\(^5\) Loc. cit., p. 422, 1932.
(4) Johnson, Merwin, and Williamson have formed spherulites of calcium carbonate by slow precipitation from aqueous solutions in an alkaline medium. Although no difference in composition of the non-spherulitic part from that of the spherulitic could be established by chemical and optical tests, the writer favors the hypothesis that the spherulites were formed by precipitation from aqueous solutions. This probably took place under favorable conditions as regards composition, concentration, and rate of addition of the required solutions, and the optimum conditions were interrupted long enough to form the central non-spherulitic part, only to be resumed during the formation of the upper layer of the spherulites.