

THE OCCURRENCE AND ORIGIN OF CELESTITE AND FLUORITE AT CLAY CENTER, OHIO

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Celestite has been recorded from the Lower Helderberg rocks at a number of localities in the eastern United States, including Syracuse, Lockport, Jamesville, and Auburn in New York State (5) (10), Drummond and Maybee, Michigan (9), Put-in-Bay (8) and Clay Center, Ohio, and Mineral County, West Virginia (13).

The Put-in-Bay deposits are well known, because the caves at that locality have provided a number of large crystals, but the Clay Center occurrence is particularly interesting, not only because of the abundance of celestite, but also because of the associated minerals, especially fluorite.

These minerals are found at Clay Center in the Guelph member of the Niagara group. Higher strata have been eroded at this locality, but in other parts of Ottawa County, these uppermost Niagara beds (known in Ohio as the Cedarville-Springfield dolomite) are overlain unconformably by the last westerly remnants of the Salina.

The rock exposed in the quarry is a buff or brownish-yellow dolomite of granular texture and porous to cavernous structure, which forms evenly bedded strata having an individual thickness of several feet.

These beds are regarded as the probable equivalent of the Huntington dolomite of Indiana, the Guelph or Racine dolomite of Wisconsin, the Racine and Port Byron of Illinois, and the upper part of the Engadine dolomite of Michigan (3) (10) (12).

In thin section the rock is seen to consist almost entirely of pure dolomite grains, slightly clouded by argillaceous matter, with almost no calcite. Large detrital grains, mostly quartz, have been observed only in certain greenish-gray beds found sparingly in the lower level of the quarry.

Dolomitic grains bordering the frequent small solution cavities may have clear euhedral faces developed on their exposed sides, while the central portions of the grains are clouded as usual (Fig. 1). Calcite crystals with curved faces, due probably to a slightly magnesian character are occasionally found in the larger cavities.

The dolomite contains many fossils, usually preserved as casts

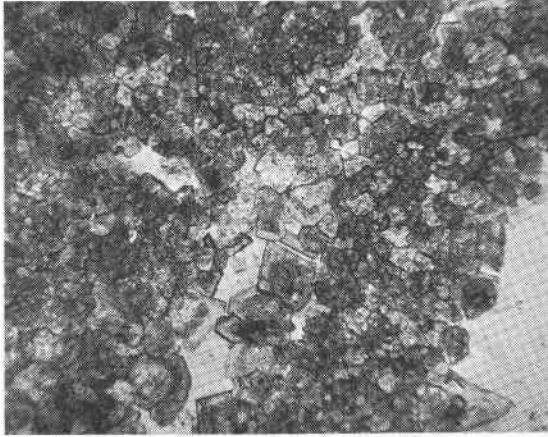


FIG. 1. Cedarville-Springfield dolomite from Clay Center, Ohio; coarse, cavernous phase, showing zoned development of crystal faces in cavities. Plane polarized light, $\times 27$.

only, which in part accounts for the cavernous structure of the rock. The corals are most frequently replaced by dolomite (Fig. 2). Practically no shells of mollusca or brachiopods replaced by this mineral were noticed.

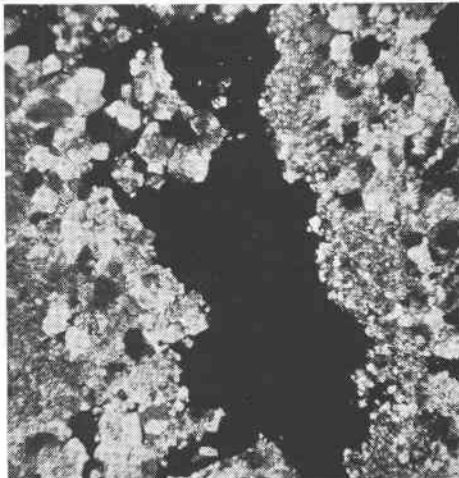


FIG. 2. Cedarville-Springfield dolomite, showing replacement along septae of a coral (*Diplophyllum caespitosum*). Crossed nicols, $\times 27$.

The northeastern part of the quarry shows evidence of a flat dome-like structure, which may be of depositional rather than tectonic origin. The known prevalence of coral reefs in the upper Niagara suggests that the former cause is the more probable (3).

Both regular jointing and evidences of faulting are absent.

MINERAL OCCURRENCES

Celestite. Celestite occurs mainly in roughly lenticular masses, from a few inches to several feet in breadth, with the longer dimensions commonly parallel to the bedding; and the celestite-bearing zones, which are rarely of any great horizontal extent, appear to occupy solution cavities.

The mineral occurs much more abundantly in the upper than the lower beds, and is at present particularly concentrated in the northeastern corner of the quarry, where the beds show a slight doming. Not only is more celestite present, and in larger crystals, but cavities, both filled and unfilled are larger and more numerous in this section. If the doming is the result of orogenic stresses, the resultant tension in the uppermost strata may have facilitated the development of solution cavities and replacement bodies at this location.

In the lower level the rock is less cavernous, and celestite is not so frequently found, but when present is observed to be in flat blade-like crystals, or in compact crystalline masses. Here also cavities are sometimes found filled with clay, which may contain celestite crystals. A border of white crystalline celestite may surround these pockets.

The crystals observed in the quarry range from pale blue to white and colorless. When first exposed, the larger ones are frequently bluish, sometimes quite deeply tinted, but after exposure to light and weather they become either white or colorless. Thin bladed crystals are by far the most abundant. Stout tabular ones are less common, but are occasionally observed in the larger vugs and pockets in the upper beds.

Spectroscopic analysis shows no metallic elements other than strontium in the Clay Center celestite.

Fluorite. Fluorite is much less abundant at Clay Center than celestite, and was observed by the writer in only two sections of the quarry. The mineral is found for a short distance along the southern end of the east wall, in the upper level. This is in the oldest part of

the quarry, and, since specimens are highly prized by collectors, most of the supply at this point has disappeared. The other deposit is found in a narrow zone along the bottom of the northern portion of the western wall of the lower level. These two occurrences do not seem to be connected, and, until further excavation is done, sufficient evidence is lacking to say that a fluorite zone is present, striking northwest-southeast.

The fluorite is found in irregular bodies, almost invariably associated with celestite, and in part replacing the dolomite. Vugs lined with fluorite crystals are common. Some of the large masses recently discovered in the lower level consist of massive brown fluorite interpenetrated by bladed white celestite.

A small quantity of purple fluorite can be observed in a vein-like mass of celestite near the top of the north end of the eastern quarry face, upper level. The mineral occurs in small anhedral grains disseminated sparingly through bladed celestite. All of the massive fluorite and most of the crystals found in the quarry are dark brown in color. Some of the crystallized material exhibits various lighter shades of brown and yellow, ranging to nearly colorless. The darker crystals are commonly zoned, with the centers always darker in hue than the outer portion. The faces of the cubes vary from less than one-eighth inch to one-half and rarely up to an inch and a half on edge.

Both the color and the striking photo-luminescence of the fluorite in this deposit seem due to included bituminous matter. Pure, colorless fluorite fluoresces with a white light under ultra-violet rays from a mercury vapor lamp. Hydrocarbons, such as crude oil, mineral oil, and petrolatum fluoresce with a deep yellow light. It is interesting to note that the intensity and hue of fluorescence of the Clay Center fluorite vary from whitish yellow towards a very strong clear yellow in direct proportion to the intensity of the brown color (under ordinary light). The fluorescence of this material is identical to that of fluorites containing petroleum inclusions (4). Under the recently developed argon glow lamp fluorescence of Clay Center fluorite varies from deep orange yellow for light brown or amber crystals, to strong greenish yellow for the dark brown massive material. Similar results have been obtained by E. M. Gunnell (4).

Phosphorescence is exhibited for about half a minute after exposure of the mineral to strong ultra-violet light. Heating or crush-

ing does not cause phosphorescence, though some other fluorites emit light after such treatment (4).

Upon heating to redness the brown fluorite changes to gray, while the yellow material becomes almost colorless. Heating for several hours at temperatures gradually increasing up to 500°F. does not cause any change in color. That the color change by heating is due to volatilization (and perhaps carbonization) of bituminous matter is, of course, not conclusive, since some metallic oxides might behave similarly. To further test for the presence of such oxides, a spectroscopic analysis of the dark brown fluorite was made. Strontium was found present in the order of 0.1 to 1.0 per cent, but all heavy metals were absent. The results of this analysis indicate that the brown coloration is due to included bituminous matter.

Calcite. Curved calcite crystals, colorless, or clear with a slight yellowish tint, are frequently found lining cavities in the dolomite. They vary from minute drusy individuals to those an inch or more in diameter. Spectroscopic analysis shows considerable strontium (around 1 per cent strontium) and magnesium (in the order of 1.0 to 5.0 per cent magnesia) replacing the calcium, which may account for the curved faces. Part of the curvature can be explained, however, by the development of scalenohedral faces on the acute rhombohedrons constituting the basic form. Slight etching somewhat obscures the interfacial angles.

Other Minerals. Minute drusy pyrite (marcasite?) crystals with remarkable iridescence (peacock blue, bronze red, greenish-yellow, purple, etc.) occur sparingly. They are found lining cavities in the dolomite, but can be observed only in the freshly quarried material, since they alter rapidly to limonite. The principal occurrence at present is in a zone in the eastern portion of the lower level.

Very rare and small masses of sphalerite have been found along the east wall of the quarry. The typical material is dark reddish brown in color, and is imperfectly crystallized. It appears to occupy former solution cavities in the dolomite, and partly replaces the rock.

A small pocket of snowy white gypsum has been reported from the lower level. At the time of the writer's visit, however, no occurrences of this mineral were observed. Small inclusions of anhydrite in bladed celestite have occasionally been noted in thin sections.

ORIGIN OF THE CEDARVILLE-SPRINGFIELD DOLOMITE

The abundance of coral and stromatoporoid remains in the Cedarville-Springfield dolomite indicates that this formation was deposited in a warm, clear, shallow sea, and also that in the deposition direct chemical precipitation was very slight or non-existent.

Dolomitization was the result of concentration of magnesium carbonate relative to calcium carbonate, and then of the union of the two carbonates to form the stable double salt, dolomite. The increase in magnesium carbonate may have been brought about by (a) leaching of the calcium carbonate, or by (b) replacement of the calcium carbonate by magnesium carbonate from the sea water. It seems probable that the former process was chiefly effective in the formation of the Cedarville-Springfield dolomite, though the latter process may also have contributed. The aragonitic hard parts of the organisms were most readily susceptible to either leaching or replacement, and hence may well have been more important in the dolomite production than the calcitic ones containing magnesium carbonate. Leaching of the calcium carbonate occurred after the elevation and exposure to the atmosphere of the Guelph sediments at the end of the Niagara epoch. Most of the cavernous structure of the rock may have been developed at that time.

ORIGIN OF THE CELESTITE

Celestite is known to be deposited by both magmatic and meteoric waters.

Deposits of the former type are usually found associated with igneous rocks or faulting, but since neither of these are present at Clay Center or in its vicinity, a magmatic source hardly seems likely.

Deposits of celestite as a primary constituent of sedimentary formations are not uncommon, and frequent associates are such minerals as gypsum, salt, and other salines: all of which are formed under semi-arid or arid conditions.

Occurrences of this type have been described from California (6, 11, 1) and Arizona (11). Celestite of sedimentary origin is also recorded from the Monroe formation of the Lower Helderberg (11). The deposits are frequently associated with dolomites or magnesian limestones.

The celestite may form a high percentage of the bed in which it occurs, or, as in the case of the Bass Island of the Monroe group in Michigan, and the Vermicular limestone of the same group in New York, the crystals are distributed through a fine-grained ground mass (8) (7). The sharp boundaries of the cavity walls left after the crystals were dissolved are considered by Kraus to indicate the slow formation of the crystals in unconsolidated sediments. They were therefore chemically precipitated. The lack of fossil remains in the authigenic celestite-bearing beds, in addition to the association of some with salt or gypsum all point to precipitation from water of high salinity.

Although celestite has been observed in slight amounts at least in all of the world's salt deposits (1), an unusually high concentration of it must have been present to yield deposits like some of those found in the southwest or even in the Bass Island beds. The cause of this concentration is not readily understood.

The solubility of celestite is moderately high, it being seven times more soluble than calcite in ordinary water. Solutions containing halides such as NaCl, MgCl₂, or CaCl₂ markedly increase the solubility. Celestite is less soluble than gypsum, hence when present may be the first formed of the saline residues.

The primary celestite present in any formation may through leaching by meteoric waters be carried into the lower beds of that formation, as at Put-in-Bay, Ohio, or into a lower lying formation before it is redeposited.

The widespread occurrence of celestite in the Bass Island formation has been pointed out and also the ease with which the mineral passes into solution, especially if halides are present. It is probable that the celestite at Clay Center was leached from the overlying Bass Island beds, and subsequently redeposited in the cavities in the Cedarville-Springfield dolomite, or also partly replacing the rock (Fig. 3). It is doubtful whether strontium-extracting organisms existed during Guelph times capable of depositing this element in the Cedarville-Springfield dolomite in the large quantities found at Clay Center. Since Clay Center is situated near the top of the Cincinnati Arch, it is probable that the Salina beds normally lying between the Niagara and Monroe groups were either absent or very thin, and that at this locality the Monroe rocks almost directly overlaid the Cedarville-Springfield dolomite.

It is of interest to note that Kraus has described a celestite occurrence near Maybee, Monroe County, Michigan (9), which is similar to that at Clay Center. In this case, the celestite occurs as crystalline masses in a porous dolomite, which is overlain by Bass Island beds rich in primary celestite.

ORIGIN OF THE FLUORITE

The reasons for not considering the Clay Center celestite to be of igneous origin apply also to the fluorite.

Fluorine is a minor constituent of most organisms, tending to be found in association with calcium phosphate (5). It is more promi-

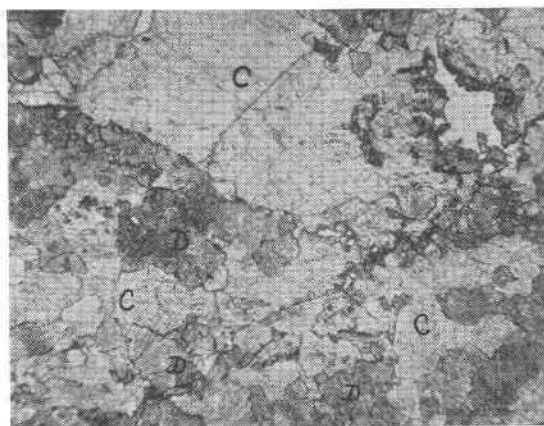


FIG. 3. Showing replacement of Cedarville-Springfield dolomite by celestite.
Plain light, $\times 27$. (C=celestite; D=dolomite.)

nent in marine than in fresh water forms, though most marine invertebrates contain only traces of this element (2). Oyster shells may contain as much as .012% fluorine, and Dana reports an average of 0.25% fluorides in corals (2). Limestones are especially apt to have a small fluorine content, and this element may be a much more common constituent of these rocks than it is ordinarily considered to be, since it is rarely determined quantitatively. In some the percentage of calcium fluoride is pronounced. Fluorite crystals occur in cavities in the Niagara group at Niagara Falls, Welland County, and elsewhere in southwestern Ontario (14). It is also found in the Lower Carboniferous limestone at St. Louis, Missouri.

Murray and Renard (5) have proposed the theory that the high fluorine content of fossil bones and teeth from deep sea deposits is due to slow double decomposition between the phosphatic bone material and fluorides in solution in the sea water. Carnot (5) found that bone fragments increase notably in fluorine content after immersion in weak sodium fluoride solutions. He believes that the tendency for such phosphatic calcareous remains to take up fluorine from solutions containing small amounts of fluorides accounts for the high fluorine content of fossil bones as compared with that of modern bones. Evidently the phosphates present in lime sediments are of importance in determining their ability to absorb fluorine from sea waters.

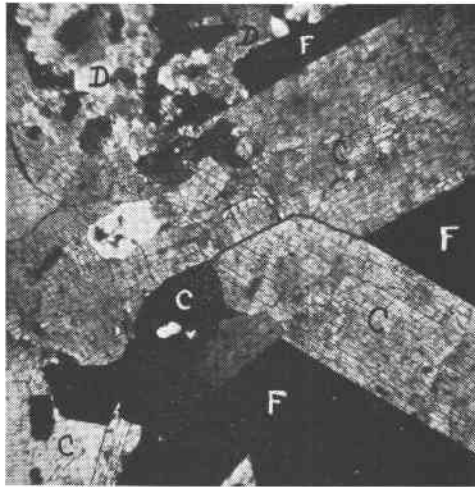


FIG. 4. Celestite and fluorite replacing Cedarville-Springfield dolomite. Crossed nicols, $\times 27$. (C=celestite; F=fluorite; D=dolomite.)

In spite of the prevalence of calcium fluoride in limestones and marine organisms, primary sedimentary deposits contain the mineral only in small quantities. The notable concentrations appear to be found almost entirely in areas where evidences of igneous activity have been observed. Primary sedimentary fluorites of even moderate purity have not been reported. Secondary concentration has been important in the formation of the richer deposits of sedimentary origin.

Calcium fluoride, although a relatively insoluble compound,

lends itself to concentration by meteoric waters. It is eight and one-third times less soluble in water at ordinary temperatures than celestite. As compared with calcite, fluorite is much less soluble in cold water, though it is more soluble than barite, which is thought to be sometimes concentrated by meteoric waters. Though the exact manner in which fluorite is dissolved, transported, and re-deposited by meteoric waters is not well understood, we have undoubted proof that this process does occur.

Fluorite is known to occur in considerable quantities along with the celestite in the Put-in-Bay dolomite of the Monroe series. The fluorite found at Clay Center may either have been derived from the overlying Bass Island, as was the celestite, or through concentration of fluorides present in the Niagara dolomite itself. The bodies at Clay Center are undoubtedly secondary, since they partly replace the walls of the cavities in which they occur.

Thin sections show the celestite to be definitely earlier than the fluorite, and extensively replacing the dolomite (Fig. 3). The former appears to have first been introduced along solution cavities, and then to have replaced the walls. Fluorite exhibits a weaker tendency towards replacement than the celestite. It appears filling interstices between celestite crystals (Fig. 4) or lining cavities more often than replacing the dolomite.

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A RAPID METHOD FOR THE DETERMINATION OF PLAGIOCLASE BY THE FEDOROV UNIVERSAL STAGE

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INTRODUCTION

A feldspar on the Fedorov universal stage, which has four axes of rotation, cannot be turned directly into the position for which the three principal optical directions coincide with the two horizontal and the vertical axes of the microscope respectively, that is into the position of proper orientation. In determining a feldspar, formerly, at least two optical symmetry planes must be located separately, and the optical orientation can be determined only after the completion of the stereographic projection. In 1929 R. C. Emmons¹ modified the Fedorov stage by adding an inner east-west horizontal axis between the inner vertical axis and the north-south axis. The position of orientation is then easily obtained by placing one optical symmetry plane vertical and parallel to the inner east-west (I. E-W) axis, and then tilting the section on the (N-S) axis to the position where the section remains at extinction on rotation about the outer east-west (O. E-W) axis. A method used in the author's laboratory overcomes the tedious procedures, and the position of orientation may be obtained directly on the old Fedorov stage.

POSITION OF ORIENTATION

The present method of operation may be explained by the aid of Figure 1. When the first optical symmetry plane is set in the

¹ Emmons, R. C., A modified universal stage: *Am. Mineral.*, vol. 14, No. 12, 1929; Plagioclase determination by the modified universal stage: *Am. Mineral.*, vol. 19, No. 6, 1934.