EXPERIMENTAL REPLACEMENT OF OOLITIC LIMESTONE BY FLUORITE

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In 1944, Dr. R. M. Grogan, then on the Illinois State Geological Survey staff, started an experiment designed to determine if fluorite could be formed by replacement of oolitic limestone in a non-acid environment at room temperatures. Four single-neck Erlenmeyer flasks containing limestone chips immersed in N/2 solution of sodium fluoride were prepared, sealed, and marked to be opened after a period of 3 to 6 months. For several reasons the experiment was forgotten but recently two flasks were opened and the limestone chips, now partially replaced by fluorite, examined.

The conversion of calcite to fluorite by the reaction of hydrofluoric acid solutions (Grayson, 1956) and the basic reaction of alkaline sodium fluoride solutions (Ames, 1961; Pasquali and Bisque, 1962) has been previously demonstrated. Grogan's experiments are of interest because of their long duration and because they afford an opportunity to observe the experimental replacement of the variety of limestone actually replaced by fluorite in bedding-replacement deposits in the Cave-in-Rock district, Hardin County, Illinois where important ore bodies occur in oolitic portions of the Ste. Genevieve Limestone. Favorable ore horizons occur at the top of the Ste. Genevieve and at the top of the lowermost member of the Ste. Genevieve and are overlain by relatively less permeable shale, sandstone, or sandy limestone stata. The ore-bodies are localized along minor fracture systems and it is postulated (Weller *et al.*, 1952, p. 127) that ore-forming solutions ascended along major faults in the area and spread outward and upward along intersecting minor fractures. It was assumed that the solutions were basic or near neutral in their reaction with limestone although previous writers referred or alluded to reactions involving hydrofluoric acid (Weller *et al.*, 1920; p. 275-281, Currier, 1944, p. 36-39).

THE EXPERIMENT

The experiment set up by Grogan was as follows: Four flasks were prepared, each containing oolitic limestone of the Ste. Genevieve Formation immersed in 200 cc. of N/2 sodium fluoride solution made with distilled water. Twenty grams of limestone chips, crushed to pass a 4-mesh sieve and be retained on an 8-mesh sieve, were immersed in each of two flasks. The average diameter of the chips was about 3 mm. Two pieces of limestone were similarly immersed in each of the two other flasks. These pieces ranged from 6 to 18 grams in weight and the piece subsequently studied had a maximum diameter of 27 mm. The 4 flasks were closed with rubber stoppers and sealed, air tight, with paraffin.

PRESENT STUDY

Two flasks were opened, one containing the coarse oolite pieces and the other containing smaller chips. The limestone was recovered and washed in distilled water. One of the coarse pieces was saved for analysis. The other, mounted in plastic, was used in the preparation of polished and etched surfaces. The smaller chips were embedded in plastic and thin-sections were prepared from them.

The liquid in both flasks contained a number of plate-like aggregates of tiny crystals that were recovered by filtration and subsequently studied by x-ray diffraction. The filtrate was evaporated to dryness and the crystallization products x-rayed to determine the mineral composition.

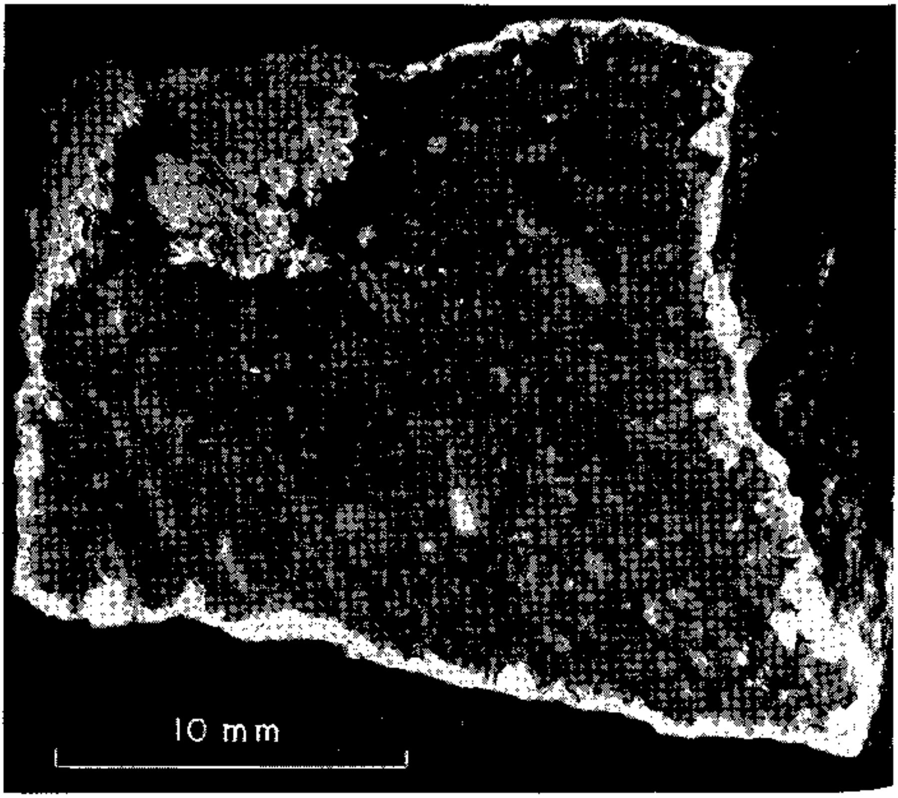

FIGURE 1.—Polished section of a large piece of oolite having a marginal replacement layer of fluorite. The preservation of the oolitic texture of the original rock is well shown in the upper left of the picture as is a sharp line between the oolite grains and the calcite matrix indicating selective replacement of the grains. Reflected light.

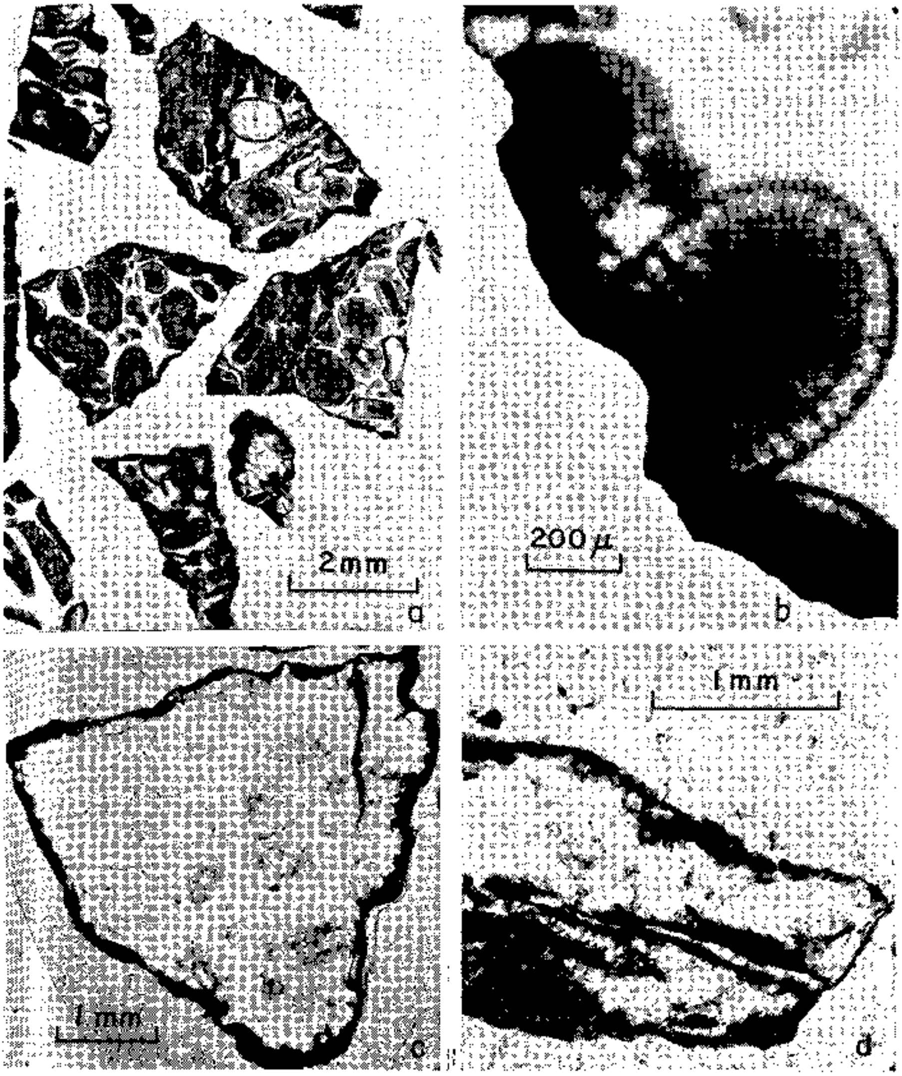

FIGURE 2.—Replacement layers of fluorite on small chips of oolitic limestone. (a) Thin section of small oolite chips having thin marginal deposits of fluorite that appear black. Transmitted light. (b) Much enlarged photograph of a thin section showing a replacement fluorite layer (black) coating an oolite rock fragment. Transmitted light. (c) Thin section that has been acid-treated to remove carbonates showing a surficial replacement layer of fluorite and replacement along a minute crack. Transmitted light. (d) Thin section that has been acid-treated to remove carbonates showing an oolite grain partly replaced by fluorite (dark gray). Transmitted light.

RESULTS

The limestone chips were replaced at their outer surfaces by a layer of microcrystalline, white fluorite that retained the original oolitic texture. The oolite grains and fossils were selectively replaced in preference to sparry calcite matrix (fig. 1). The thickness of the replacement layer is somewhat irregular being greatest where oolite grains and fossil debris occur at the outer surface of the limestone chip. The average thickness of the replacement layer formed on the coarse oolite chip studied was .29 mm. The extensive area of replacement in the upper left on Figure 1 is due to a surface irregularity rather than deep penetration into the center of the specimen.

The smaller chips were likewise replaced at their outer surfaces (fig. 2). Replacement advanced into the interior of some chips along minute cracks. The average thickness of the replacement layers was 0.11 mm; however, oolite grains occurring near the outer surface in some cases were almost completely converted to fluorite.

The aggregates filtered from the solution consisted principally of fluorite (CaF_2) and calcite ($CaCo_3$), with minor amounts of quartz (SiO_2) and dolomite ($CaMg(CO_3)_2$) as determined by x-ray diffraction.

Determinations of the pH of the solutions yielded values of 9.8 and 10.0, the higher value being for the solution from the experiment involving the smaller oolite chips. These values are in marked contrast to the approximate neutrality of the original solution and reflect the addition of CO_3^{--} ions. By evaporation, 4.8 grams of solid were recovered from the solution having pH of 9.8 and 4.1 grams from that having a pH of 10, but some solid was lost by an accidental boiling action at one point during the evaporation process. Villiaumite (NaF), sodium carbonate (Na_2CO_3), and thermonatrite ($Na_2CO_3.H_2O$) were identified by x-ray diffraction. A fourth phase, tentatively identified as trona ($3Na_2O.4CO_2.5H_2O$) and characterized by 10 Å basal spacing, was also present. Other hydrated forms of sodium carbonate are possibly present in lesser quantities.

DISCUSSION OF RESULTS

The design of the experiment does not allow much conjecture as to the mechanism of the calcite-fluorite replacement reaction. Reaction occurred along a replacement front that advanced from the outer surface toward the center of the chips. The replacement is one that involves minerals that contain a common cation and the reaction can be simply stated:

$$CaCO_3 + 2\,F^- \leftrightarrows CaF_2 + CO_3^{--}$$

This involves removal of the fluoride ion from solution and addition of the carbonate ion to the solution. Ames (1961, p. 738) states that Ca^{++} does not move from its lattice position, only the anions of the replaced solid move into solution. Pasquali and Bisque (1962) report that the common ion does move from its position and reaches equilibrium with Ca^{++} ions in the reaction solution.

The supply of fluoride ions in solution was not exhausted, but it is assumed that the replacement reaction had essentially, if not completely, stopped. The presence of calcite as a stable component of mineral aggregates in the ambient fluoride-bearing solution suggests that the reaction stopped for some reason other than any inability of fluoride ions to diffuse through the replacement layer of fluorite. It is thought that, as the CO_3^{--} concentration increased during fluorite replacements, the solution became increasingly basic according to the following hydrolytic reaction:

$$CO_3^{--} + H_2O \leftrightarrows HCO_3^{-} + OH^{-}$$

which, in turn, depressed the solubility of $CaCO_3$ relative to the solubility of CaF_2 and shifted the equilibrium

$$2F^{-} + CaCO_3 \leftrightarrows CaF_2 + CO_3^{--}$$

to the left.

The plate-like aggregates filtered out of the solution had the appearance of a precipitate. However, the mineralogical analysis—fluorite and calcite with minor quartz and dolomite — suggests partial replacement of slightly impure high calcium limestone. The presence of dolomite, not known to precipitate from aqueous solutions at room temperatures, seems to rule against precipitation. It is possible that this material flaked off or was abraded from the replacement layer.

The thickness of the replacement layer on the smaller chips is approximately one-third of that on the larger piece of limestone. Ames (1961) shows that the rate of fluoride removal from solution during replacement is directly proportional to calcite surface area. Therefore, because of the greater surface area the initial rate of replacement of the smaller chips was higher and equilibrium was reached after the formation of a thinner layer over the greater area. The total amount of fluorite formed on small chips was probably about equal to that formed on the larger pieces.

SUMMARY

The experimental replacement of oolitic limestone by fluorite is such that the original texture of the limestone is faithfully duplicated by microcrystalline fluorite. The reaction proceeds at room temperatures. The replacement is somewhat selective in that oolite grains and fossil debris are replaced at a faster rate than sparry calcite cement. The amount of surface area exposed to the replacing solution and the pH of the solution were major factors in determining the rate of replacement and the thickness of the replacement layer. It is thought that increased CO_3^{--} concentration and basic conditions, produced by hydrolysis, depressed calcite solubility so that calcite-fluorite-solution stability was attained.

ACKNOWLEDGMENTS

The writer is indebted to Josephus Thomas, Jr., who provided the x-ray data involved in this study and to a number of his colleagues for their comments and suggestions.

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Manuscript received April 24, 1963.